SECTION 16

Hydrocarbon Recovery

Gas processing covers a broad range of operations to prepare natural gas for market. Processes for removal of contaminants such as H_2S, CO_2 and water are covered extensively in other sections of the Data Book. This chapter will cover the processes involved in recovering light hydrocarbon liquids for sale. The equipment components included in the processes described are covered in other sections of the Data Book. This section will bring those components together in process configurations used for liquid production.

INTRODUCTION

The recovery of light hydrocarbon liquids from natural gas streams can range from simple dew point control to deep ethane extraction. The desired degree of liquid recovery has a profound effect on process selection, complexity, and cost of the processing facility.

The term NGL (natural gas liquids) is a general term which applies to liquids recovered from natural gas and as such refers to ethane and heavier products. The term LPG (liquefied petroleum gas) describes hydrocarbon mixtures in which the main components are propane, iso and normal butane, propene and butenes. Typically in natural gas production olefins are not present in LPG.

Typically, modern gas processing facilities produce a single ethane plus product (normally called Y-grade) which is often sent offsite for further fractionation and processing. Whether accomplished on-site or at another facility, the mixed product will be further fractionated to make products such as purity ethane, ethane-propane (EP), commercial propane, isobutane, normal butane, mixed butanes, butane-gasoline (BG), and gasoline (or stabilized condensate). The degree of fractionation which occurs is market and geographically dependent.

Early efforts in the 20th century for liquid recovery involved compression and cooling of the gas stream and stabilization of a gasoline product. The lean oil absorption process was developed in the 1920s to increase recovery of gasoline and produce products with increasing quantities of butane. These gasoline products were, and still are, sold on a Reid vapor pressure (RVP) specification. Vapor pressures such as 10, 12, 14, 20 or 26 psia are common specifications for gasoline products. In order to further increase production of liquids, refrigerated lean oil absorption was developed in the 1950s. By cooling the oil and the gas with refrigeration, propane product can be recovered. With the production of propane from lean oil plants, a market developed for LPG as a portable liquid fuel.

In lieu of using lean oil, refrigeration of the gas can be used for propane and heavier component recovery. The use of straight refrigeration typically results in a much more economical processing facility. The refrigeration of the gas can be accomplished with mechanical refrigeration, absorption refrigeration, expansion through a J-T valve, or a combination. In order to achieve still lower processing temperatures, cascade refrigeration, mixed refrigerants, and turboexpander technologies have been developed and applied. With these technologies, recoveries of liquids can be significantly increased to achieve deep ethane recoveries. Early ethane recovery facilities targeted about 50 % ethane recovery. As processes developed, ethane recovery efficiencies have increased to well over 90%.

In some instances heavy hydrocarbons are removed to control the hydrocarbon dew point of the gas and prevent liquid from condensing in pipeline transmission and fuel systems. In this case the liquids are a byproduct of the processing and if no market exists for the liquids, they may be used as fuel. Alternatively, the liquids may be stabilized and marketed as condensate.

GAS COMPOSITION

The gas composition has a major impact on the economics of NGL recovery and the process selection. In general, gas with a greater quantity of liquefiable hydrocarbons produces a greater quantity of products and hence greater revenues for the gas processing facility. Richer gas also entails larger refrigeration duties, larger heat exchange surfaces and higher capital cost for a given recovery efficiency. Leaner gases generally require more severe processing conditions (lower temperatures) to achieve high recovery efficiencies.

Gases are typically characterized by the gallons per thousand cubic feet of recoverable hydrocarbons in the gas. This is commonly expressed as “GPM.” GPM was traditionally meant to apply to propane and heavier components but is often used to include ethane. The GPM of a gas can be calculated as shown in Example 16-1.

The other major consideration in the evaluation of NGL recovery options is the specification of the residue sales gas. Sales specifications are usually concerned with a minimum Higher Heating Value (HHV) of the gas, but in some instances the maximum HHV can also be a consideration. The calculation of HHV is covered in Section 23 and in more detail in GPA Standard 2172, “Calculation of Gross Heating Value, Relative Density, and Compressibility Factor for Natural Gas Mixtures from Compositional Analysis.”

Removal of liquids results in gas “shrinkage” and reduction of the HHV. This shrinkage represents a loss of revenue for the gas sales which must be considered in the economics of an NGL recovery plant. In general, sales gas specifications set the minimum HHV at 950-1000 BTU/scf. Thus, if any components such as nitrogen or CO_2 are present in the gas, sufficient ethane and heavier components must remain in the gas to meet the heating value specification. If little nitrogen or CO_2 is present in the gas, the recovery level of the ethane and heavier components is then limited by markets, cost of recovery, and gas value. The calculation of HHV and shrinkage cost is illustrated in Example 16-1.

Example 16-1 — Find the GPM of the gas mixture in Figure 16-1. Find the HHV of the feed gas and the HHV of the residue gas with the following NGL recovery efficiencies: C_2 – 90%, C_3 – 98%, iC_4 /nC_4 – 99%, C_5+ – 100%. What is the shrinkage cost at $2/MMBTU?

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Solution Steps:

Solution is shown in Fig. 16-1.

From Fig. 23-2 obtain the gal/lb mole for each of the components. Multiply these values by the mole fraction of each component (mole%/100) and divide by 379.49 scf/mol to get gallons per standard cubic foot of gas. Then multiply this value by 1000 to get the GPM of each component. The total GPM from Fig. 16-1 is 3.117.

For the recoveries specified the net gal/day and residue composition can be found as shown in Fig. 16-1. In order to compute the HHV of the two streams, the HHVs of each component are found in Fig. 23-2. Multiplying the individual HHVs by the mole % gives a total HHV of 1115.01 for the feed gas and 971.24 for the residue gas.

The shrinkage volume can be found by the difference of the volume of the feed gas times the HHV and the volume of residue gas times its HHV. This volume is then multiplied by $2/MMBTU to get the shrinkage value of the NGLs.

$$\text{Shrinkage Value} = [(330 \bullet 1115.01) - (295.862 \bullet 971.24)] \bullet \$2/\text{MMBTU} = \$161{,}201/\text{day}$$

The value of the NGLs in $/gal versus the value of the components in the residue gas in $/gal or the "spread" between these values is the primary economic criteria for NGL recovery project evaluations. Fig. 16-2 provides a way to quickly estimate potential revenues possible for liquid recovery projects.

DEW POINT CONTROL

Retrograde condensation has long been known to occur at reservoir conditions. Recognition that it also occurs in typical

FIG. 16-1

Solution to Example 16-1

GPM CALCULATION

Component	Feed Gas Mole %	Gal/Mole	Available GPM	Available Gal/Day	Estimated Recovery %	Net Gal/Day	Residue Gas Mole %
N_2	1.000						1.115
CO_2	3.000						3.346
C_1	85.000						94.808
C_2	5.800	10.126	1.548	510840	90	459756	0.647
C_3	3.000	10.433	0.825	272250	98	266805	0.067
IC_4	0.700	12.386	0.228	75240	99	74488	0.008
NC_4	0.800	11.937	0.252	83160	99	82328	0.009
IC_5	0.300	13.860	0.110	36300	100	36300	0.000
NC_5	0.200	13.713	0.072	23760	100	23760	0.000
C_6+	0.200	15.566	0.082	27060	100	27060	0.000
Total	100.000		3.117	1028610		970497	100.000
MMSCFD	330.000						295.862

SHRINKAGE CALCULATION

Component	Feed Gas Mole%	Residue Gas Mole %	HHV BTU/scf	Feed Gas BTU/scf	Residue Gas BTU/scf
N_2	1.000	1.115	0.0	0.00	0.00
CO_2	3.000	3.346	0.0	0.00	0.00
C_1	85.000	94.808	1010.0	858.50	957.56
C_2	5.800	0.647	1769.6	102.64	11.45
C_3	3.000	0.067	2516.1	75.48	1.68
IC_4	0.700	0.008	3251.9	22.76	0.25
NC_4	0.800	0.009	3262.3	26.10	0.29
IC_5	0.300	0.000	4000.9	12.00	0.00
NC_5	0.200	0.000	4008.9	8.02	0.00
C_6+	0.200	0.000	4755.9	9.51	0.00
Total	100.000	100.000		1115.01	971.24
MMSCFD	330.000	295.862			

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processing conditions was an early result of computer calculations using equations of state to predict vapor-liquid behavior. The phenomenon is illustrated in Fig. 16-3 showing dew point calculations for a gas stream leaving a separator at 100°F and 1000 psia. These dew point curves show that as the pressure is reduced, liquid is formed. The heavier the hydrocarbon, the more the dew point temperature increases as the pressure is lowered. The cricondentherm of the dew point curve is primarily determined by the nature of the heaviest component in the gas rather than the total quantity of the heavy component in the feed gas.

When gas is transported in pipelines, consideration must be given to the control of the formation of hydrocarbon liquids in the pipeline system. Condensation of liquid is a problem in metering, pressure drop and safe operation. Condensation of liquid can also be a major problem with two-phase flow and liquid slugging.

To prevent the formation of liquids in the system, it is necessary to control the hydrocarbon dew point below the pipeline operating conditions. Since the pipeline operating conditions are usually fixed by design and environmental considerations, single-phase flow can only be assured by removal of the heavier hydrocarbons from the gas.

Low Temperature Separation

Several methods can be used to reduce the hydrocarbon dew point. If sufficient pressure is available, the removal can be accomplished by expansion refrigeration in an LTS (Low Tem-

FIG. 16-2

Shrinkage Value of NGL Components[1]

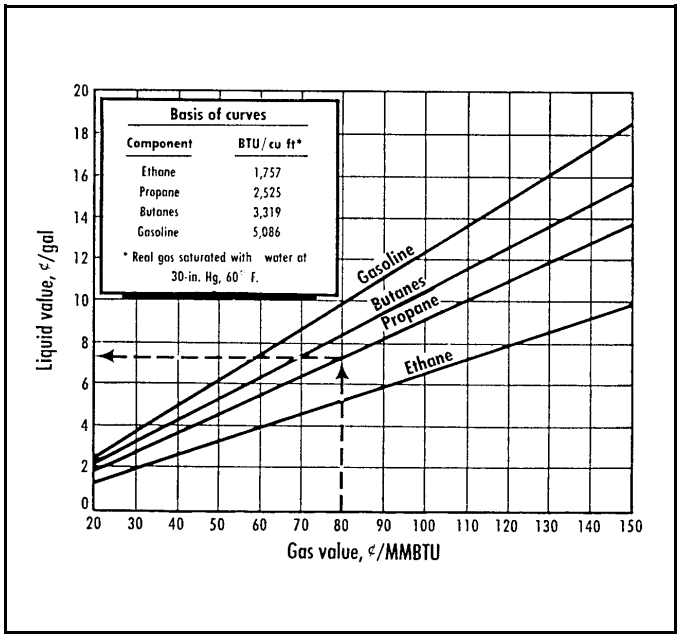
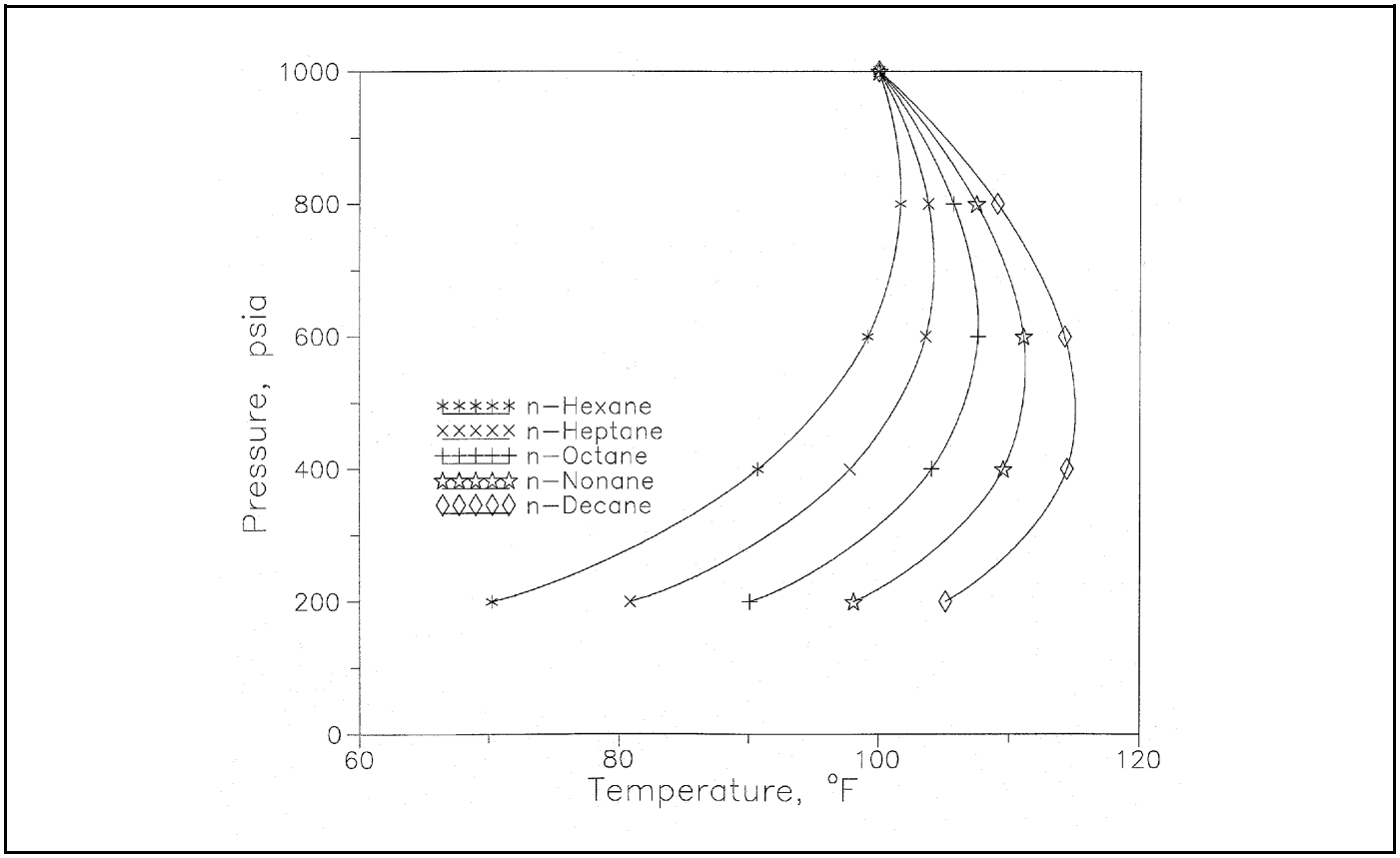


FIG. 16-3

Typical Low Pressure Retrograde Condensation Dew Point Curves[3]



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perature Separation) unit. The expansion refrigeration system uses the Joule-Thomson effect to reduce the gas temperature upon expansion. This temperature reduction results in not only hydrocarbon liquid condensation but also water condensation. The water is generally removed as hydrates in this process, melted and removed. Thus, the process can actually accomplish dew point control of both water and hydrocarbon in a single unit.

Fig. 16-4 shows one example of an LTS system. The high pressure gas may first go through a heater. This heater is often not needed, depending on the gas conditions. The gas then enters the heat exchanger coil in the bottom of the separator where the gas is cooled by exchange with the condensed liquid and hydrates. Any water or condensate produced at this point is removed in the high pressure separator (HPKO). The gas from the separator is then heat exchanged with the outlet product gas for further cooling. The temperature must be controlled at this point to prevent hydrate formation in the exchanger. The gas from this point passes through the pressure reducing valve where the Joule-Thomson expansion occurs. The hydrocarbon liquid and hydrates produced from this expansion fall to the bottom of the low temperature separator. The hydrates are melted and both the water and condensate are removed by level control. The gas leaving the separator has a hydrocarbon dew point equal to the temperature and pressure of the separator.

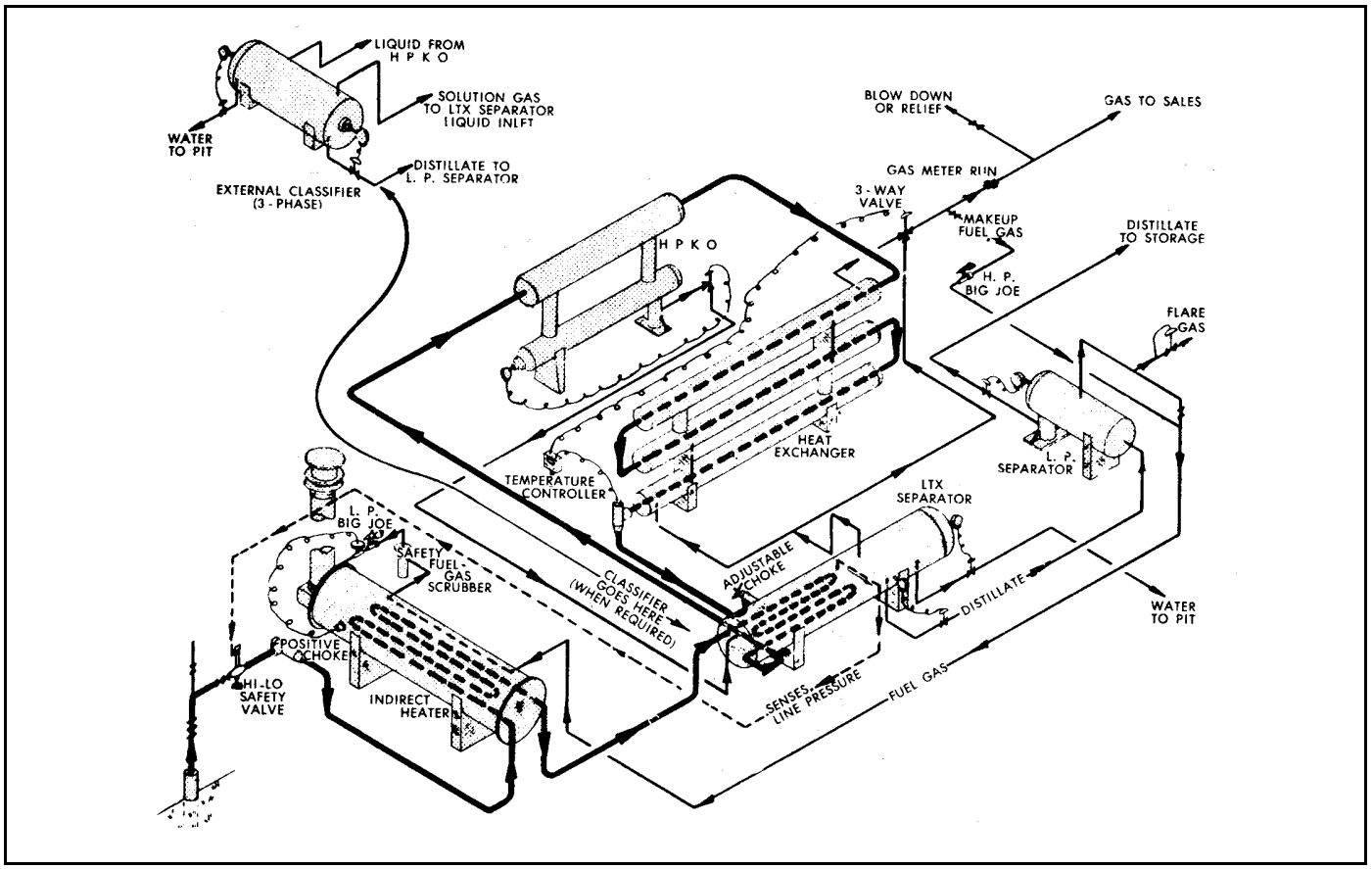
The hydrocarbon and water dew points achievable with this process are limited by the pressure differential available as well as the composition of the feed gas. The LTS system can only be used where sufficient pressure is available to perform the desired processing and separation. It is an attractive process step if sufficient liquid removal can be achieved at the available operating conditions. A further modification to this process is to add glycol injection to the high pressure gas to allow the achievement of lower water dew points when available pressure is limited. Fig. 16-5 shows an LTS system with glycol injection. The use of the glycol eliminates the need to heat the LTS liquid phase and helps to ensure that no hydrate formation will block the process equipment upstream of the LTS separator.

Refrigeration

Often excess pressure is not available to operate an LTS system. An alternative to the expansion refrigeration system is to utilize a mechanical refrigeration system to remove heavy hydrocarbon components and reduce the gas dew point. The schematic for a refrigeration dew point control unit is shown in Fig. 16-6. This process flow is essentially the same as that used for straight refrigeration NGL recovery. The gas pressure is generally maintained through the process allowing for equipment pressure drops. The gas is heat exchanged and then cooled by the refrigeration chiller to a specified temperature. Liquid is separated in the cold separator. The temperature of the separator is set to provide the desired dew point margin

FIG. 16-4

Low-Temperature Separation Unit[4]



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FIG. 16-5

Low-Temperature Separation System with Glycol Injection and Condensate Stabilization[4]

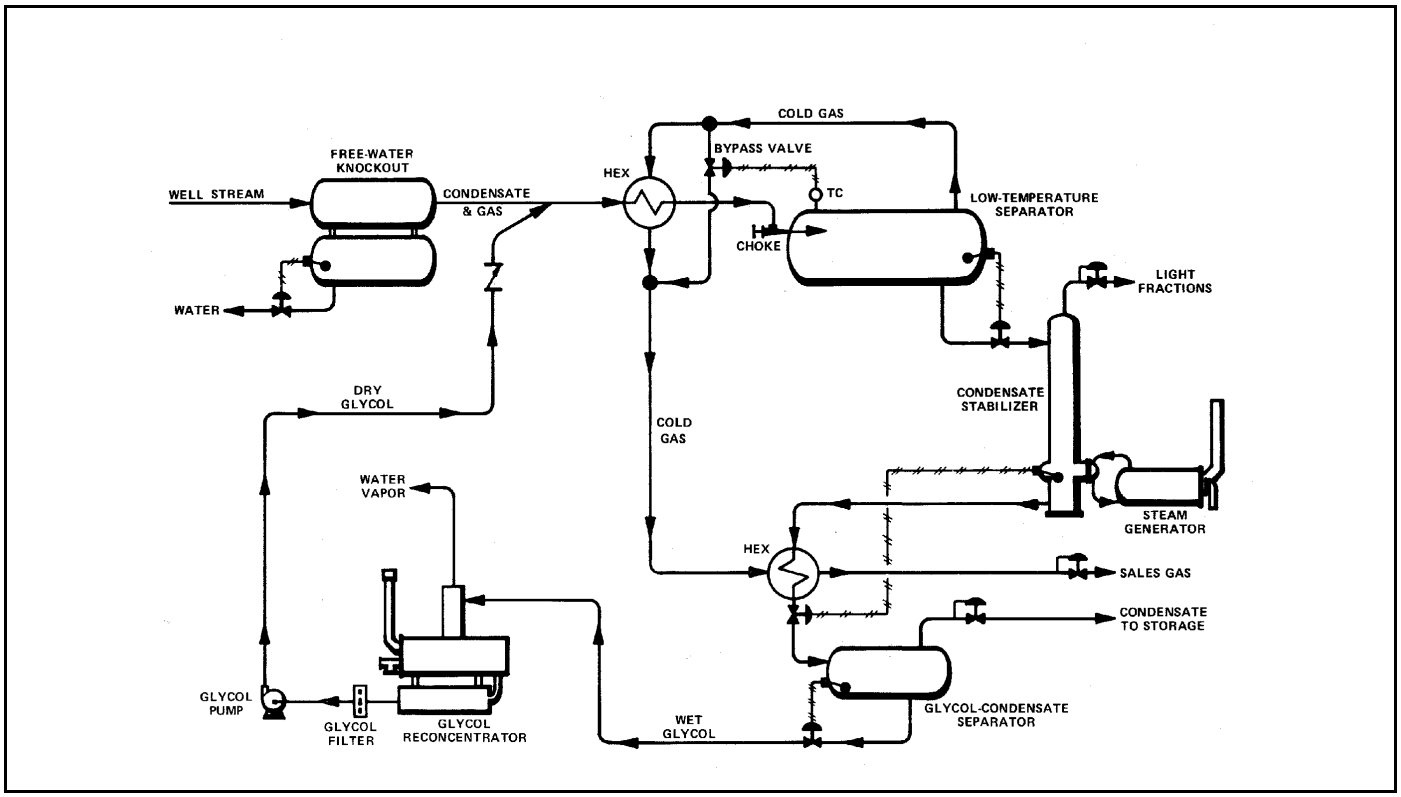
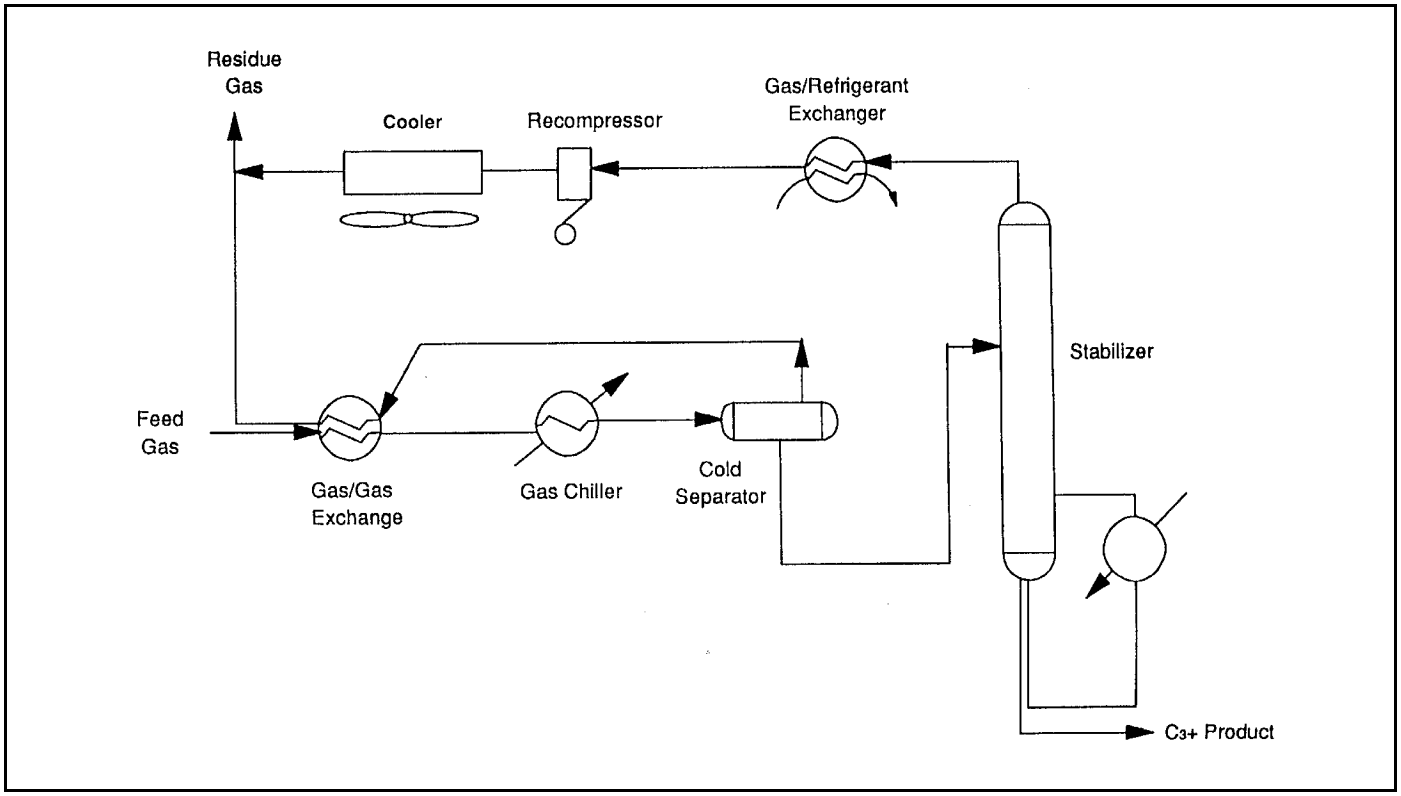


FIG. 16-6

Straight Refrigeration Process



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for sales gas operations. This temperature specification must take into account the gas which is recombined from the liquid stabilization step as well as potential variations in the feed gas pressure.

Provision must be made in this process for hydrate prevention. This can be accomplished by either dehydration upstream of the unit or by integrating the dehydration with the refrigeration unit. Use of glycol injection is usually the most cost effective means of controlling water dew points. The only drawback is that the refrigeration must be in operation to accomplish the dehydration. If it is desired to operate the dehydration at times independent of the refrigeration, then separate units are used.

Stabilization

One of the problems in using dew point control units of both expansion LTS and mechanical refrigeration systems is the disposition of the liquids removed. The liquids must be stabilized by flashing to lower pressure or by the use of a stabilization column. When the condensate is flashed to a lower pressure, light hydrocarbons are liberated which may be disposed of in a fuel gas system.

The stabilization column can produce a higher quality and better controlled product. The condensate stabilizer is usually a top feed column which runs at a reduced pressure from the cold separator and has a reboiler to produce a specified vapor pressure product. The overhead vapor is either sent to fuel as shown in Fig. 16-5 or recompressed and combined with the sales gas as shown in Fig. 16-6. The column contains either trays or packing to provide necessary mass transfer for stabilization of the liquid feed. After stabilization, the product is cooled and sent to storage.

Emerging Technologies

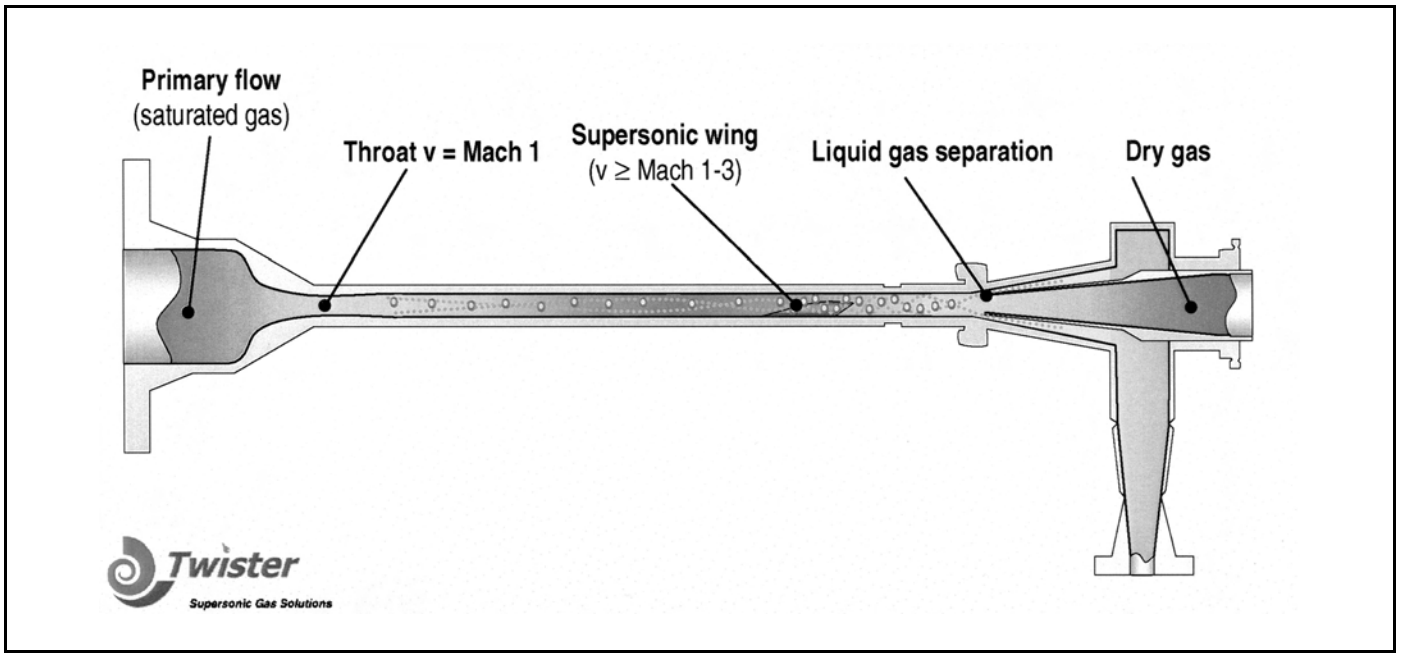
New process configurations are being brought to market to take advantage of gas expansion for liquid separation. Each of these processes use static equipment to achieve the desired separation and are focused on replacing Joule-Thomson expansion valves and/or turbo-expanders.

One of these processes is the Twister technology. This process (Figure 16-7) uses a supersonic nozzle in which the pressure is reduced and liquid is formed. The supersonic stream is then passed across vanes which swirl the stream. This centrifugal motion forces the liquid to the wall where it is drained from the apparatus. The vapor is then expanded in a diffuser nozzle and recovers 70-80% of the initial pressure. Tests have shown that this process has about 90% isentropic efficiency. This technology is focused on hydrocarbon dewpoint control and dehydration applications in both onshore and offshore locations.

Another process uses a vortex tube device to affect the separation. The vortex tube is based on the Ranque-Hilsch tubes developed in the 1940s. These tubes have been used as laboratory devices and small scale coolers. The working principle of these devices is the same. (Figure 16-8) A gas is injected tangentially through a nozzle into the center of the tube where it expands to a low pressure. The gas flows cyclonic to the far end of the tube. During this flow, two temperature zones are formed, a warm zone near the wall and a cooler zone near the center. At the end of the tube the center gas is deflected and returns along the tube through an orifice near the inlet nozzle. The tube is therefore capable of producing two gas streams at different temperatures. The cold gas is at a temperature below that achievable with an isenthalpic expansion. If the two outlet streams were to be mixed, the combined temperature would be equal to the temperature achieved by the isenthalpic expansion. Thus the vortex tube performs the same function as

FIG. 16-7

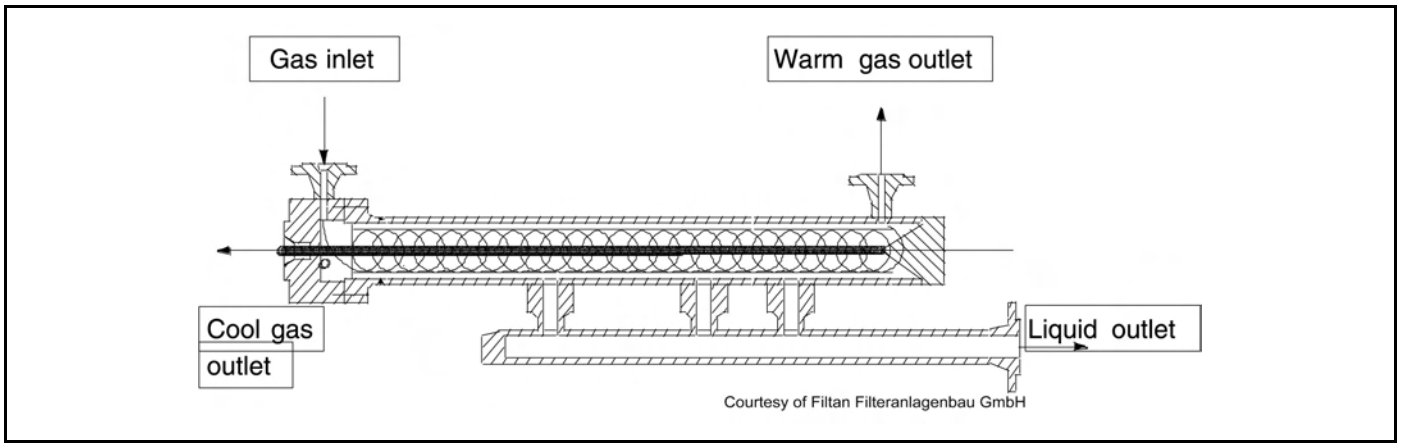
Concept of the Twister Process



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FIG. 16-8

Basic Design of a Vortex-Tube Device



Joule-Thomson valve but produces a lower outlet gas temperature for a portion of the stream. This apparatus could have application where gas pressure drop is available, dewpoint control is needed, and the warm and cool gas are recombined after liquid removal.

STRAIGHT REFRIGERATION

The straight refrigeration process is quite flexible in its application to NGL recovery. As outlined in the previous section, the process can simply be used for dew point control when modest liquid recovery is needed or desired. Alternatively, the process can be used for high propane recovery and, in the case of rich gases, for reasonable quantities of ethane recovery. The recovery level is a strong function of the feed gas pressure, gas composition and temperature level in the refrigeration chiller. Fig. 16-9 shows curves for estimating the recovery achievable as a function of temperature and gas richness for a given processing pressure. (GPM in this figure is propane plus.) Generally speaking, higher recovery efficiencies can be achieved with richer feed gas. The straight refrigeration process is typically used with a glycol injection system. This configuration is limited in the temperature of operation by the viscosity of the glycol at the lower temperatures. Also, refrigeration is typically provided by propane refrigeration which is limited to –44°F refrigerant at atmospheric pressure and thus a processing temperature of about –40°F. In order to go lower in processing temperature, upstream dehydration and alternative refrigeration systems must be considered.

Fig. 16-10 illustrates the ethane recovery efficiency which can be expected. As with propane recovery, for a given temperature level, higher extraction efficiency can be achieved with richer gas. However, ethane recovery of over 30% can be achieved from a gas as lean as 3 GPM (C_3+). Fig. 16-11 illustrates the effect of gas pressure on plant performance in propane plus recovery operation.

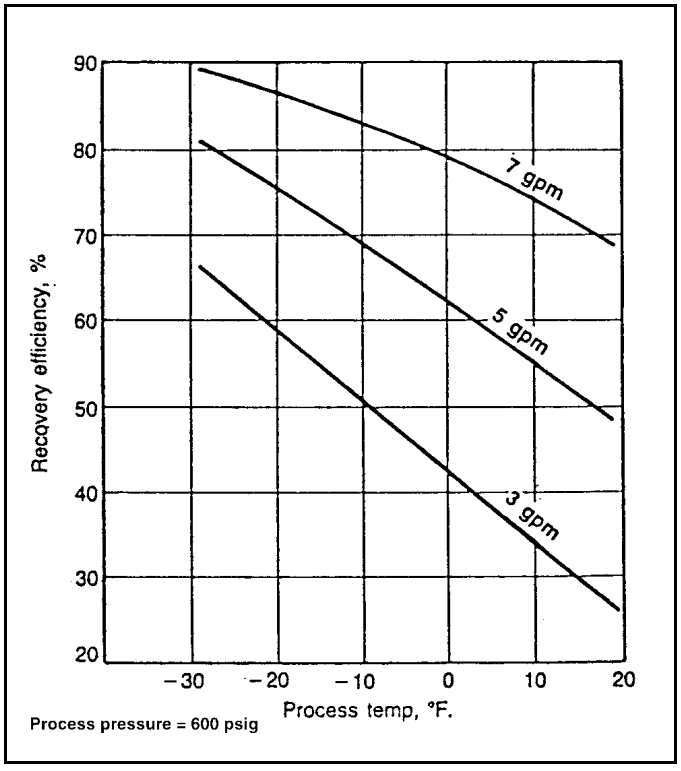
Refrigeration Process Alternatives

There are many variations in the straight refrigeration process. Fig. 16-12 illustrates four of the most common variations. In the first scheme the gas is cooled against the residue gas and the cold separator liquid before being chilled with refrigeration. This scheme uses a top-feed fractionator with the overhead being recompressed and recycled to the inlet. The use of the liquid /feed gas exchanger helps reduce the chiller load. In this case, the residue gas from the cold separator has a dew point of the cold separator operating conditions.

The second scheme also uses a top-feed fractionator, but the cold separator liquid is fed directly to the fractionator. This fractionator operates with a lower overhead temperature which justifies exchange with the refrigeration system. The overhead after being warmed is recompressed and blended with the residue gas from the cold separator. In this configuration the fractionator overhead usually raises the residue gas dew point somewhat. The cold separator temperature must be

FIG. 16-9

Recovery Efficiency, Propane Plus[5]



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set to ensure that the desired dew point specification of the combined stream is achieved.

The third process uses a refluxed fractionator. This type design usually has the highest liquid recovery efficiency, but has a higher cost due to the overhead system added. The fourth variation can be used where the cold separator liquid can be pumped and the stabilizer run at an elevated pressure. This eliminates the need for a recompressor.

Any one or a combination of the following conditions:

- Higher separator pressure
- Richer gas
- Recovery limited to propane-plus

will lead to higher recycle/recompressor rates. This results in more refrigeration horsepower, more recompressor horsepower, more fractionator heat, and larger equipment. These conditions favor the second and third schemes of Fig. 16-12.

Any one or a combination of the following conditions:

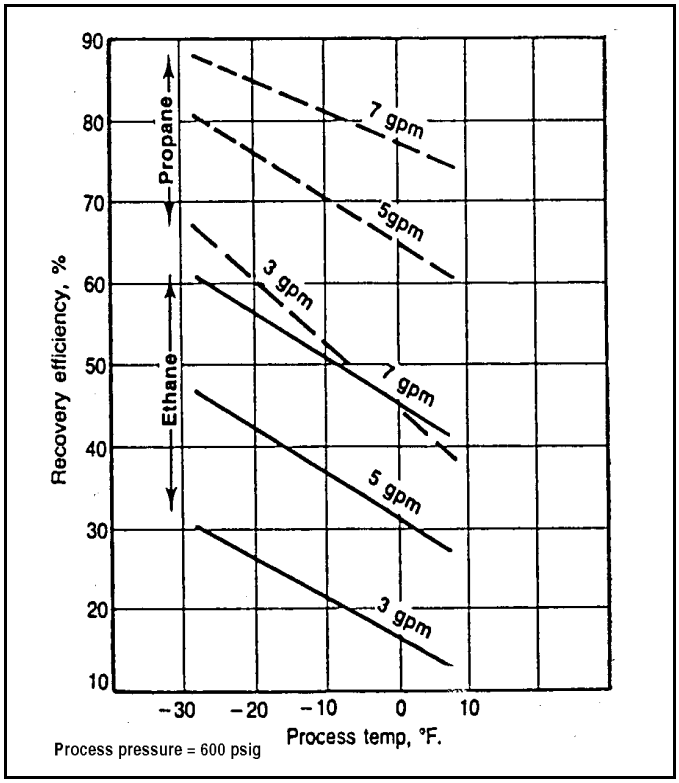
- Lower separator pressure (around 600 psig)
- Leaner gas (below 3 GPM C3+)
- Recovery includes ethane

will lead to lower recycle/recompressor rates. These conditions favor the first scheme in Fig. 16-12, or the fourth scheme if the separator pressure is not higher than 400-450 psig. Separator pressure below 400 psig, expecially with lean gas, will result in poor product recovery.

Regardless of the exact configuration employed, the capacity of the specific refrigeration system varies directly with refrigerant condensing temperature and evaporating temperature. Condensing temperature is set by the condensing medium available at the plant site, and the process chiller temperature is set by the refrigerant evaporating temperature. Refrigerant horsepower requirements vary with condensing and evaporating temperatures. Lower condenser temperature and higher evaporating temperature require lower horsepower per unit of refrigeration required. For a given refrigeration load, horsepower and condenser duties can be found in Section 14 for a variety of refrigerants.

FIG. 16-10

Recovery Efficiency, Ethane Plus[5]



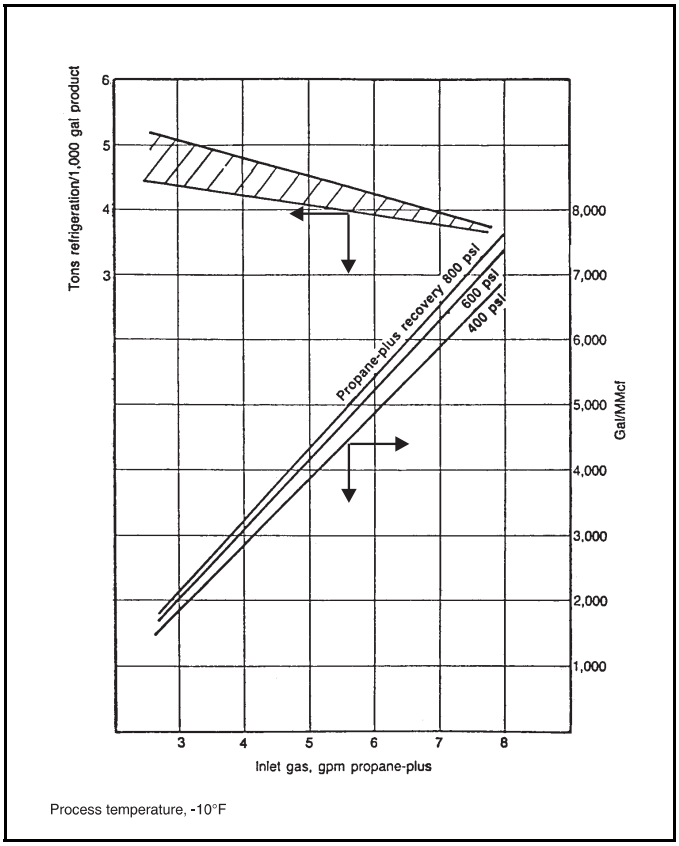
LEAN OIL ABSORPTION

Absorption is the physical process where a vapor molecule of a lighter hydrocarbon component will go into solution with a heavier hydrocarbon liquid (nonane, decane and heavier) and be separated from the gas stream. The process can be operated at ambient temperatures if only the heavier NGL products are desired. A refrigerated system enhances the recovery of lighter hydrocarbon products such as ethane and propane. The absorbing fluid (lean oil) is usually a mixture of paraffinic compounds having a molecular weight between 100 and 200.

Lean oil absorption processes have the advantage that the absorber can operate at essentially feed gas pressure with minimal loss of pressure in the gas stream which exits the process. Plants, whether ambient or refrigerated, are constructed of carbon steel. This type process was used from the early part of the 20th century and plants are still in use today. However, most lean oil plants have been shut down or replaced with more modern straight refrigeration or turboexpander process plants. The lean oil process requires large processing

FIG. 16-11

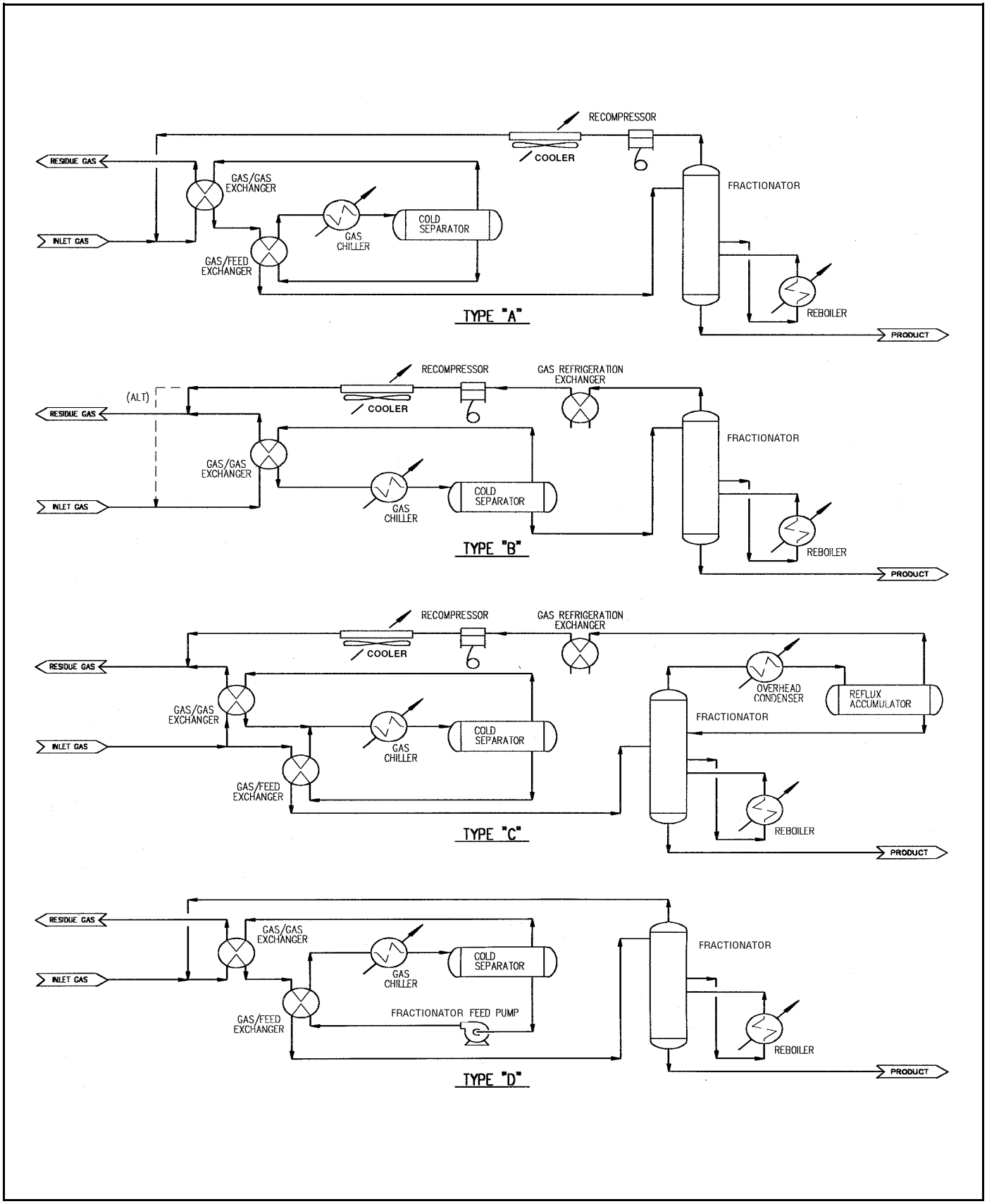
Effect of Gas Conditions on Propane Recovery[5]



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FIG. 16-12

Refrigeration Process Alternatives[6]



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equipment with excessive energy requirements. Lean oil absorption units are still used in many refinery operations.

Process Considerations

The desired composition of the lean oil is determined by the absorber pressure and temperature. The optimum molecular weight lean oil is the lowest weight oil which can be retained in the absorber with acceptable equilibrium losses to the residue gas. Lean oil absorption plants operating without refrigeration will require a higher molecular weight oil, usually in the 150-200 molecular weight range. Refrigerated lean oil absorption systems can operate with an absorbing medium as low as 100 molecular weight with proper design.

Since the absorption is on a molar basis, it is desired to contact the gas stream with the maximum number of moles of lean oil to maximize the recovery of products from the gas. However, the circulation rate is units of volume, e.g. cubic meters per hour. Therefore, a plant designed to circulate a heavier molecular weight oil can circulate more moles of oil with the same equipment if the molecular weight is lowered.

Many absorption oil recovery plants designed to originally operate at ambient temperatures have been modified to include a refrigeration system that allows both the lean oil and the gas to be chilled before entering the absorber. The reduced temperature increases the absorption and allows circulation of less oil of lower molecular weight because the vaporization rate into the residue gas is reduced. Oil is also lost with the NGL product. Oil losses with the product can be minimized by improving fractionation in the lean oil still. Many refrigerated lean oil absorption plants can recover enough heavy ends from the gas stream to offset oil losses from the absorber, thereby making its own absorption oil.

If the gas stream contains compounds that cause the absorption oil molecular weight to exceed design, a lean oil stripper can be used on a side stream of circulating lean oil to remove the heavy components. It is important to maintain the molecular weight of the absorption oil at the design value because the circulating equipment, heat exchangers, and distillation process are designed to utilize a particular molecular weight fluid.

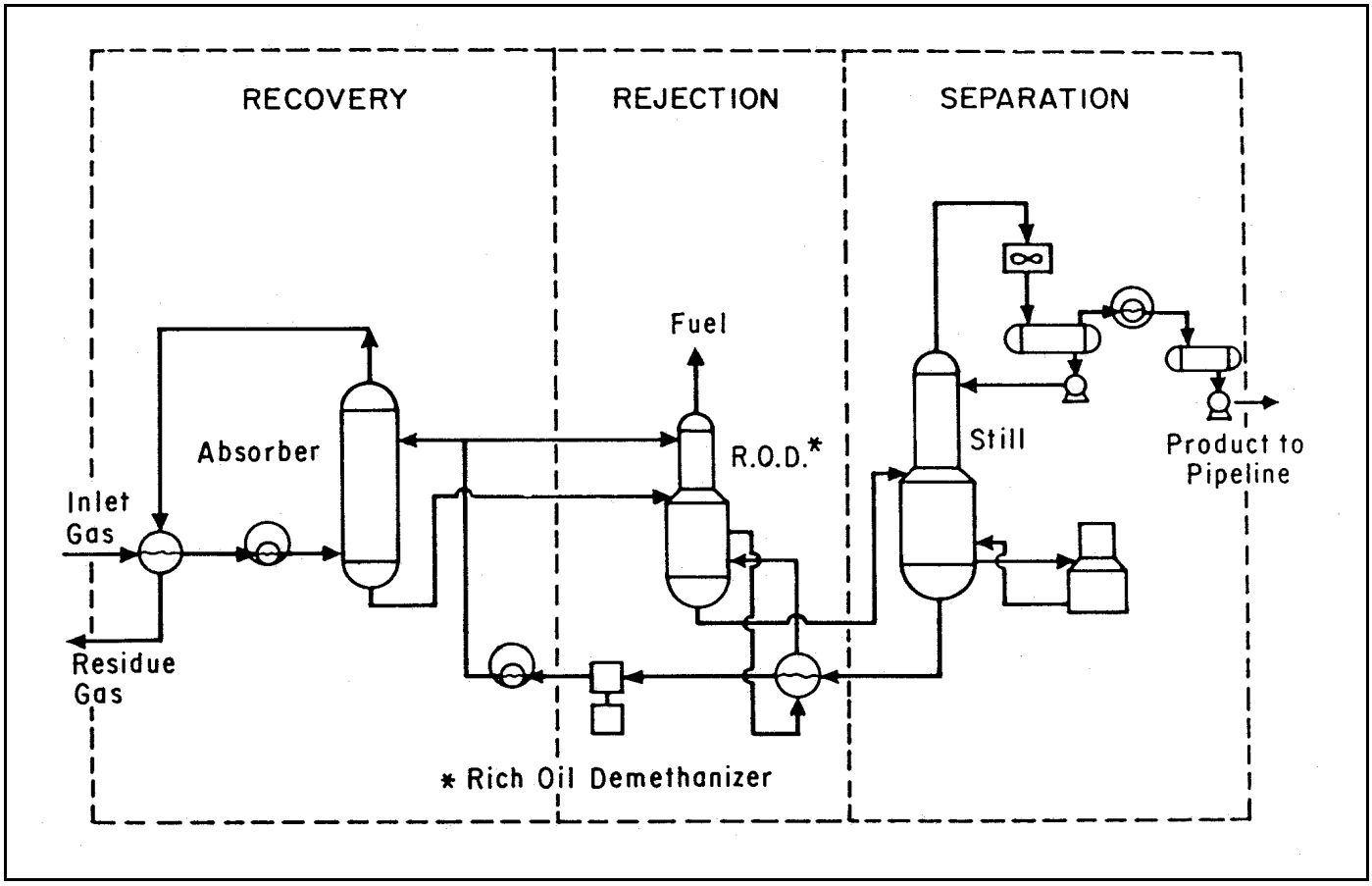
Refrigerated Lean Oil

Fig. 16-13 shows a typical refrigerated lean oil absorption process. The actual equipment configuration changes with different gas feeds and product recoveries.

Raw gas enters the plant inlet separator upstream of the main process where inlet liquids are separated. The gas then enters a series of heat exchangers where cold process gas and the refrigerant reduce the feed gas temperature. This reduction in temperature results in condensation of the heavier hydrocarbons in the inlet gas.

FIG. 16-13

Refrigerated Lean Oil Absorption[7]



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The gas is then fed to the bottom of the absorber where it flows upward countercurrent to the lean oil which is introduced at the top of the column. The lean oil has also been chilled to aid in NGL absorption. This column has trays or packing which increase the contact of the gas and lean oil. The lean oil physically absorbs the heavier hydrocarbons from the gas. The lighter components stay in the gas and leave the top of the absorber. The oil and absorbed hydrocarbons leave the bottom of the absorber as "rich oil."

The rich oil flows to the Rich Oil Demethanizer (ROD) where heat is applied to the rich oil stream to drive out the lighter hydrocarbons which were absorbed. Some of the cold lean oil is also fed to the top of the ROD to prevent loss of desirable NGLs from the rich oil.

The rich oil from the ROD is then fed to a fractionation tower or "still." The still is operated at a low pressure and the NGLs are released from the rich oil by the combination of pressure reduction and heat addition in the still. The operation of the still is critical to the overall plant operation as this is not only the point where the desired product is produced, but the lean oil quality from the bottom of the column is important in the absorption of NGLs in the absorber. The refrigeration required for the oil and gas chilling and the heat inputs to the ROD and still are the key parameters which must be controlled to operate a lean oil plant efficiently.

ETHANE RECOVERY

Dew Point control and mechanical refrigeration systems are intended for applications where moderate to high propane recoveries are desired. In order to achieve higher propane recoveries and ethane recovery, cryogenic temperatures are required. Generally, the natural gas processing industry considers cryogenic processing to be processes which operate below –50°F. Fig. 16-14 shows an estimate of the temperatures required to achieve 60 percent ethane recovery at various operating pressures; for an example feed gas. In order to achieve these temperatures, a combination of pressure expansion and chilling is used. There are three general methods which can be used to achieve the conditions necessary to attain high ethane recovery levels.

1. J-T Expansion
2. Turboexpander
3. Mechanical refrigeration

Each of these processes has been used successfully, with the turboexpander being the predominant process of choice for ethane recovery facilities.

One of the key parameters in the recovery of ethane and heavier products is the effect of the extraction on the BTU content of the residue gas. Fig. 16-15 is a generalized correlation of the ethane recovery limit to attain a 1000 BTU/cu ft HHV for various feed gas compositions. As can be seen from this chart, the quantity of inerts in the feed gas has an impact on the ethane recovery level which can be targeted in a plant design. Fig. 16-16 shows expected propane and butane recoveries which can be expected with increasing ethane recovery level. The propane recovery can vary quite a bit depending on the exact choice of the process configuration.

FIG. 16-14

Example of Pressure and Temperature to Recover 60 Percent Ethane[7]

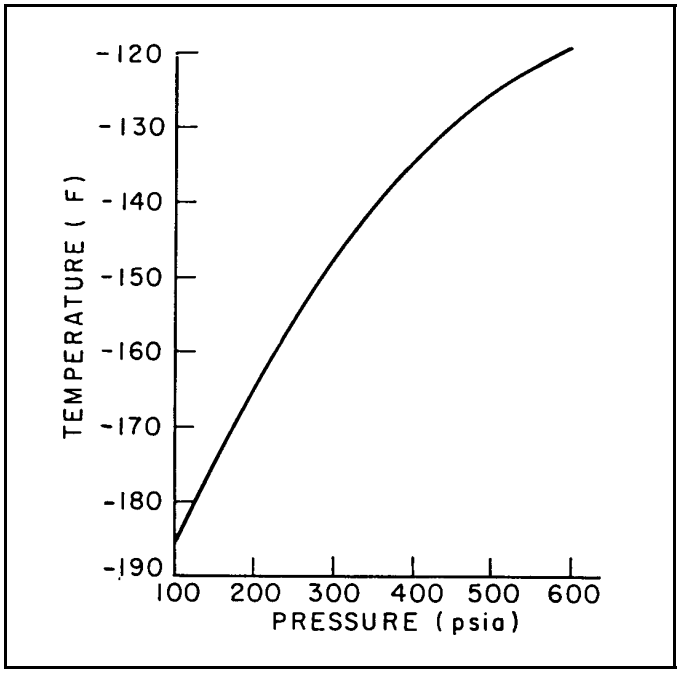
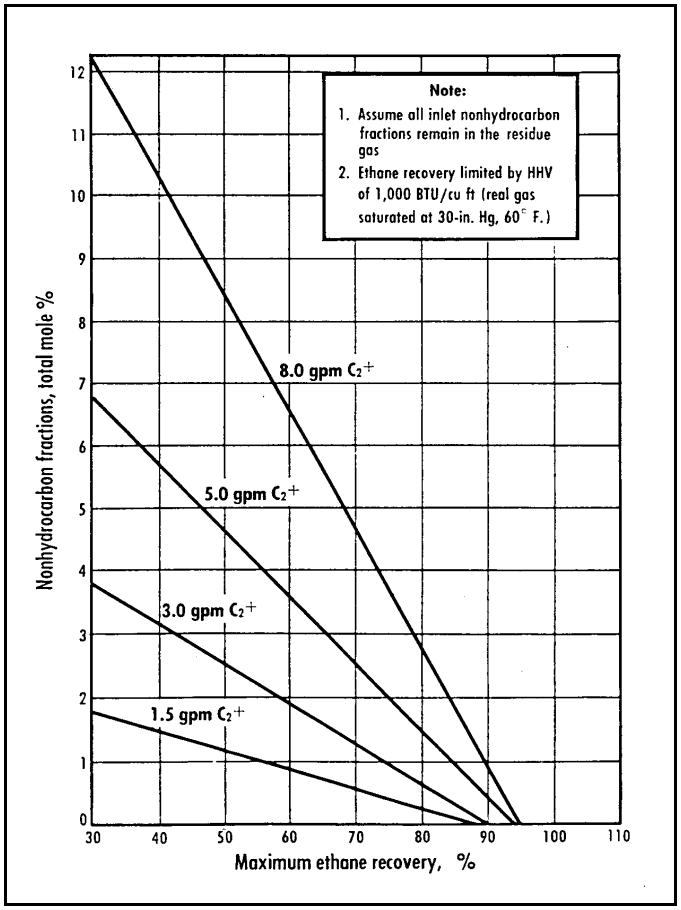


FIG. 16-15

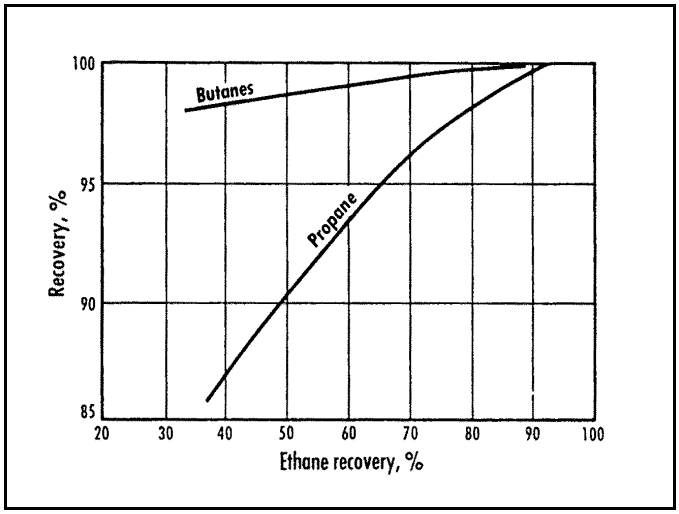
Maximum Ethane Recovery[1]



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FIG. 16-16

Relative Recovery Curves[1]



J-T EXPANSION

The use of the Joule-Thomson (J-T) effect to recover liquids is an attractive alternative in many applications. The general concept is to chill the gas by expanding the gas across a J-T valve. With appropriate heat exchange and large pressure differential across the J-T valve, cryogenic temperatures can be achieved resulting in high extraction efficiencies. The main difference between the J-T design and turboexpanders is that the gas expansion is adiabatic across the valve. In a turboexpander the expansion follows a more nearly isentropic path. Thus the J-T design tends to be less efficient per unit of energy expended than the turboexpander.

The J-T process does offer some advantages over the turboexpander and refrigeration processes in the following situations:

1. Low gas rates and modest ethane recovery.
2. The process can be designed with no rotating equipment.
3. Broad range of flows.
4. Simplicity of design and operation.

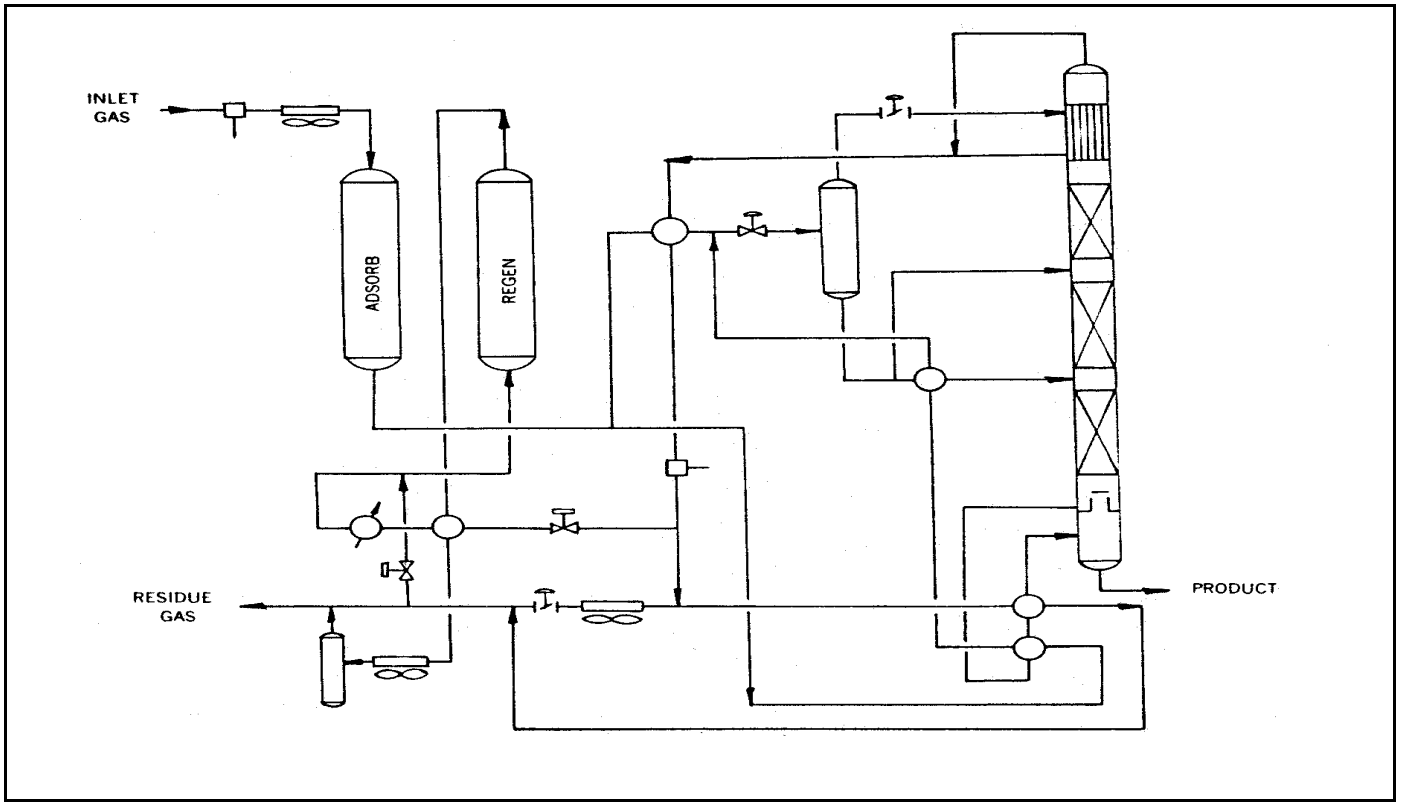
Process Flow

Fig. 16-17 illustrates the process arrangement for a J-T expansion process. In order to effectively use the J-T process, the gas must be at a high inlet pressure. Pressures over 1000 psia are typical in these facilities. If the gas pressure is too low, inlet compression is necessary or insufficient expansion chilling will be attained. The gas must first be dried to ensure that no water enters the cold portion of the process. Typically, molecular sieves or alumina are used for the drying. Methanol injection has been used in a few plants successfully but can be an operating problem.

After drying, the gas is cooled by heat exchange with the cold residue gas and also by heat exchange with the demethanizer

FIG. 16-17

J-T Expansion Process[8]



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exchangers and in some cases the liquid product from the cold separator. After chilling, the gas is expanded across the J-T valve and sent to the cold separator. The liquid from this separator is the feed to the demethanizer. Usually this tower is a cold, top feed design. However, in some designs such as shown in Fig. 16-17, a reflux arrangement is included for the ethane rejection operation. The cold liquid is demethanized to the proper specification in this tower. The cold overhead product from the demethanizer is exchanged with the feed and recompressed as necessary for residue sales.

The key to this process is the pressure driving force across the J-T valve and the quantity of heat exchange surface included in the plant heat exchangers. The process can operate over a wide range of feed gas conditions and produce specification product. The process is thus very simple to operate and is often operated as an unattended or partially attended facility.

Refrigerated J-T

In some cases the feed gas is not at high enough pressure or the gas is rich in liquefiable hydrocarbons. Then mechanical refrigeration can be added to the J-T process to enhance recovery efficiencies. Fig. 16-18 shows the J-T process with refrigeration added to aid in chilling the feed gas. Another process variation is shown in this figure. The gas in this design is expanded downstream of the cold separator. The location of the J-T valve is dependent on the gas pressure and composition involved. The advantage of refrigeration is that lower feed pressure can be used or, alternatively, the demethanizer can be operated at a higher pressure thus reducing residue compression.

The J-T process, whether refrigerated or non-refrigerated, offers a simple, flexible process for moderate ethane recovery. It is usually applied to smaller gas flows where some inefficiency can be tolerated for reduction in capital and operating costs.

TURBOEXPANDER PROCESSING

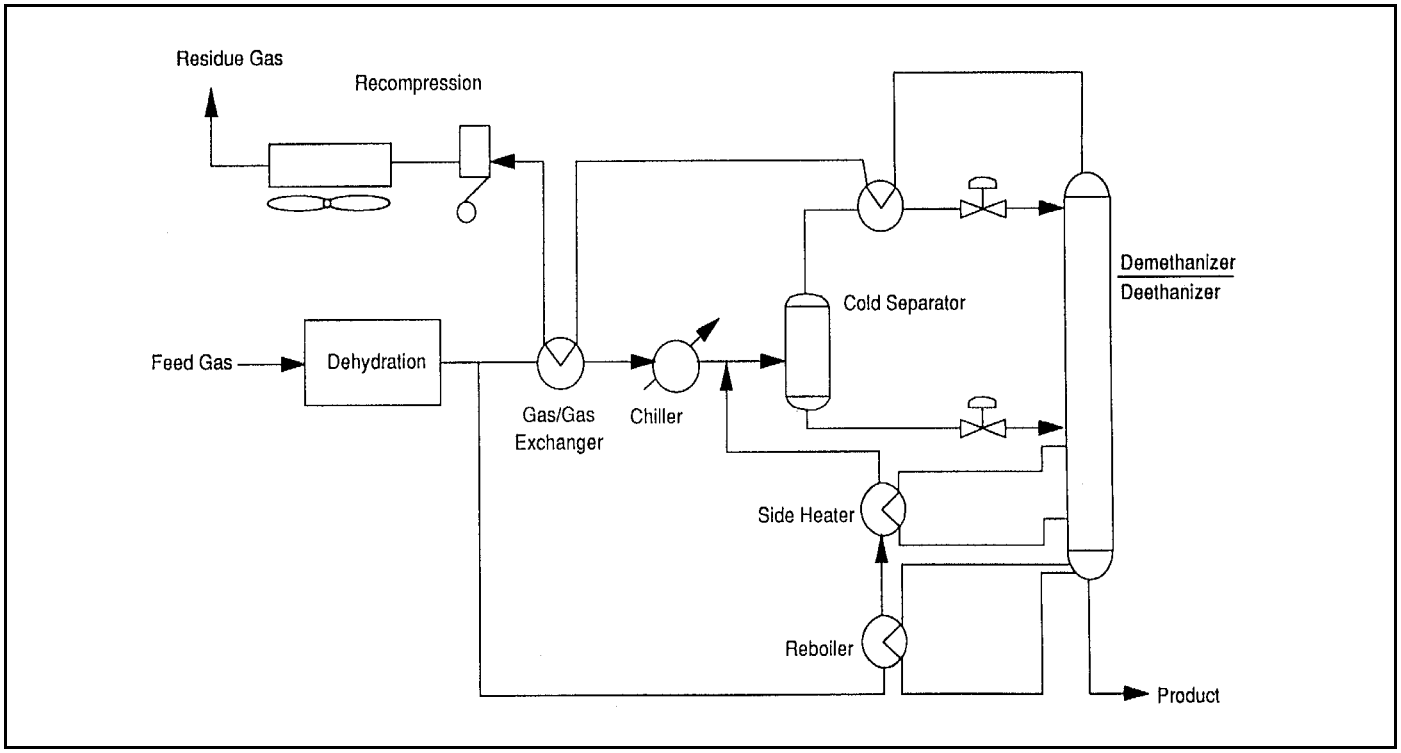
The process which dominates ethane recovery facility design is the turboexpander process. This process uses the feed gas pressure to produce needed refrigeration by expansion across a turbine (turboexpander). The turboexpander recovers useful work from this gas expansion. Typically the expander is linked to a centrifugal compressor to recompress the residue gas from the process. Because the expansion is near isentropic, the turboexpander lowers the gas temperature significantly more than expansion across a J-T valve. Details of the turboexpander equipment are in Section 13.

The process as originally conceived utilized a top feed, non-refluxed demethanizer. As higher and higher recovery levels have been desired, alternative designs have been developed. The focus of these designs is to produce reflux for the demethanizer to attain lower overhead temperatures and higher ethane recovery.

The turboexpander process has been applied to a wide range of process conditions and, in addition to ethane recovery projects, is often used as a process for high propane recovery. The process can be designed to switch from ethane recovery to ethane rejection operation with minimal operating changes.

FIG. 16-18

Refrigerated J-T Process



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Conventional Process

The original turboexpander process is shown in Fig. 16-19. Dry feed gas is first cooled against the residue gas and used for side heating of the demethanizer. Additionally, with richer gas feeds, mechanical refrigeration is often needed to supplement the gas chilling. The chilled gas is sent to the cold separator where the condensed liquid is separated, flashed and fed to the middle part of the demethanizer. The vapor flows through the turboexpander and feeds the top of the column. A J-T valve is installed in parallel with the expander. This valve can be used to handle excess gas flow beyond the design of the expander or can be used for the full flow if the expander is out of service.

In this configuration the ethane recovery is limited to about 80% or less. Also, the cold separator is operated at a low temperature to maximize recovery. Often the high pressure and low temperature conditions are near the critical point of the gas making the operation unstable. Another problem with this design is the presence of CO_2, which can solidify at operating temperatures found in this process. The critical design points are the expander outlet and the top few stages of the demethanizer. Chapter 13 discusses the CO_2 freezing problem and the methods of solid CO_2 formation prediction.

One alternative to the conventional design is the use of two expanders where the expansion occurs in two steps. While this design can help with approach to critical in the cold separator, it does little for solid formation conditions in the demethanizer column. This design has been used in a few plants but other modifications have been developed which relieve both the critical conditions and CO_2 freezing problems.

Residue Recycle

To increase the ethane recovery beyond the 80% achievable with the conventional design, a source of reflux must be developed for the demethanizer. One of the methods is to recycle a portion of the residue gas, after recompression, back to the top of the column. As shown in Fig. 16-20, the process flow is similar to the conventional design except that a portion of the residue is brought back through the inlet heat exchange. At this point the stream is totally condensed and is at the residue gas pipeline pressure. The stream is then flashed to the top of the demethanizer to provide reflux. The expander outlet stream is sent a few trays down in the tower rather than to the top of the column. The reflux provides more refrigeration to the system and allows very high ethane recovery to be realized. The recovery level is a function of the quantity of recycle in the design.

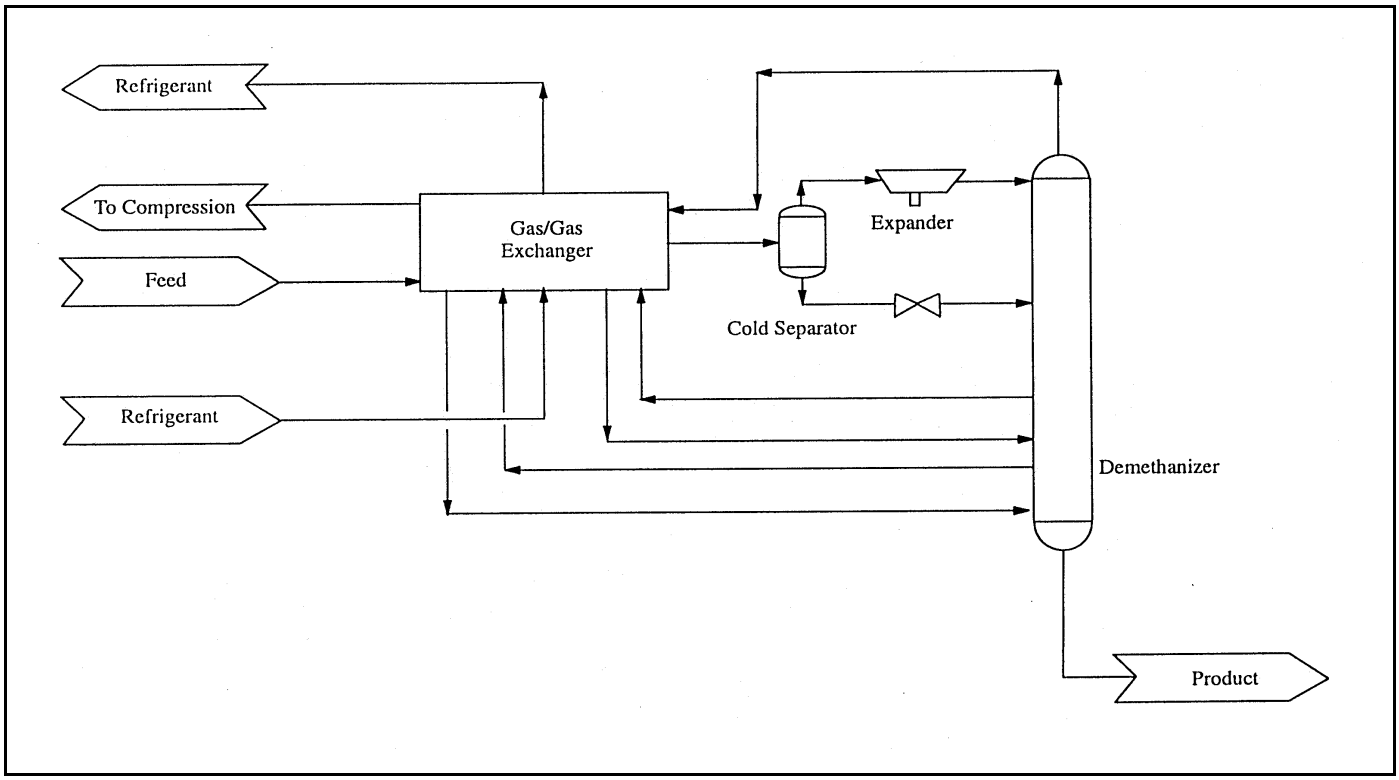
The residue recycle (RR) system has been used successfully in numerous facilities. It is CO_2 tolerant and the recovery can be adjusted by the quantity of recycle used. The RR process can be used for very high ethane recoveries limited only by the quantity of horsepower provided.

GSP Design

The Gas Subcooled Process (GSP) was developed to overcome the problems encountered with the conventional expander process. This process, shown in Fig. 16-21, alters the conventional process in several ways. A portion of the gas from the cold separator is sent to a heat exchanger where it is totally condensed with the overhead stream. This stream is then flashed to top of the demethanizer providing reflux to the demethanizer.

FIG. 16-19

Conventional Expander



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FIG. 16-20

Residue Recycle

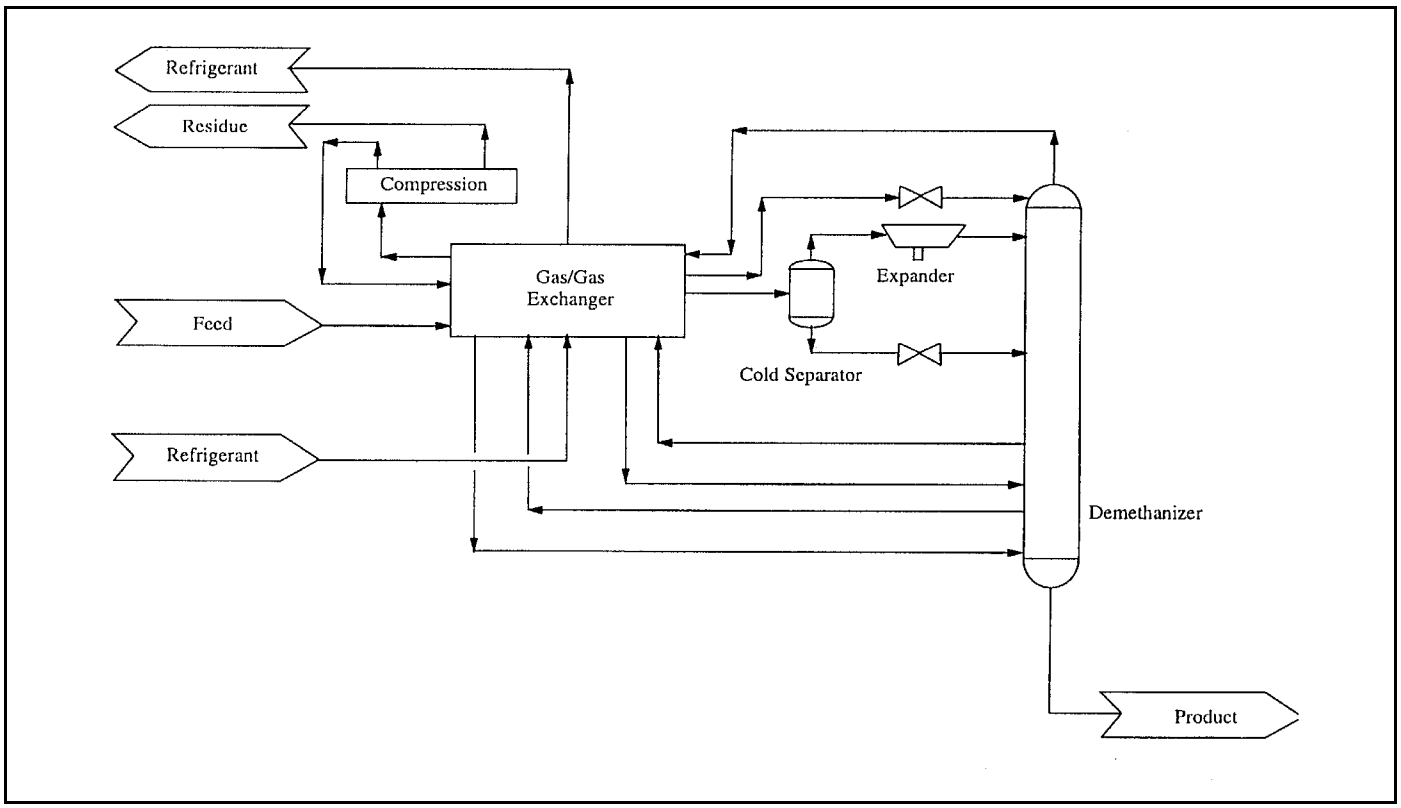
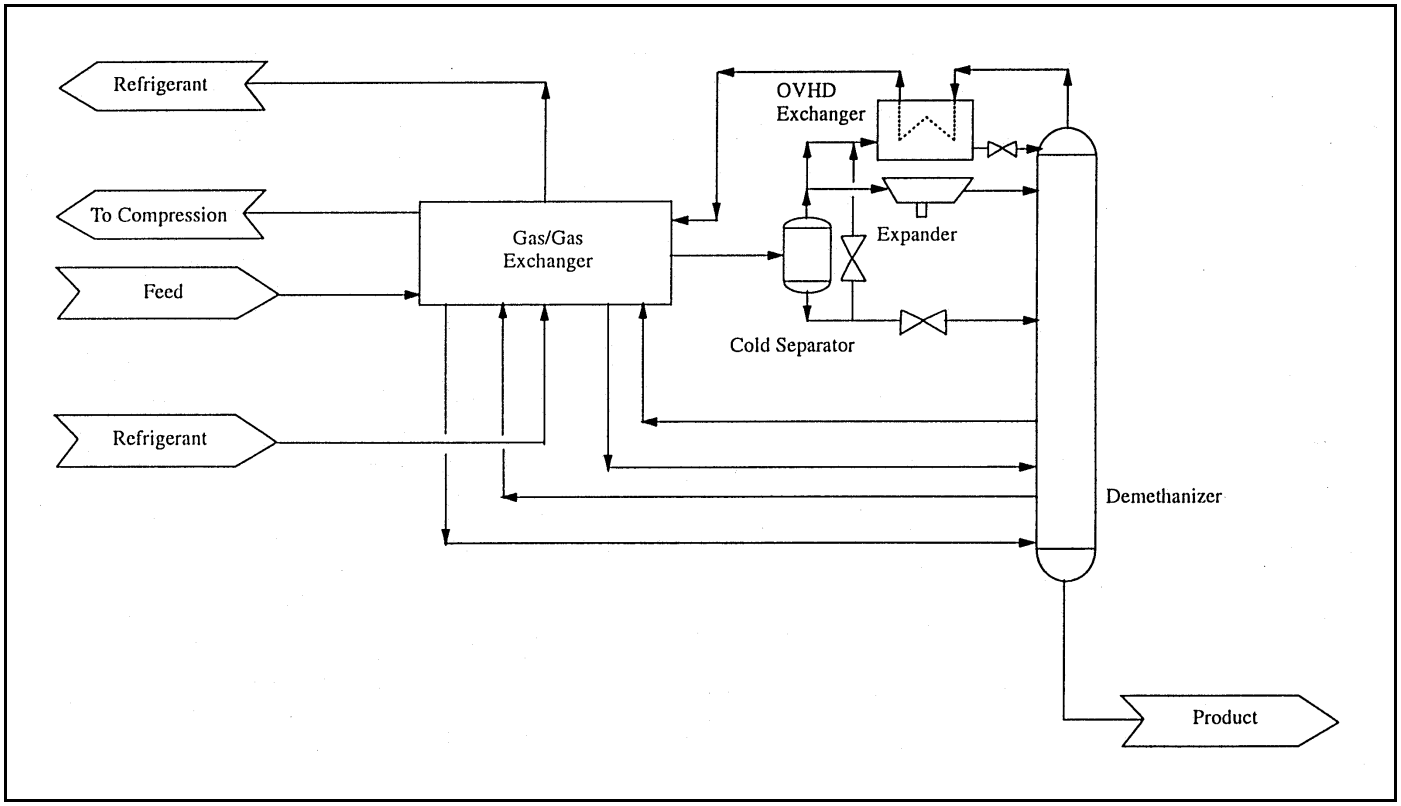


FIG. 16-21

Gas Subcooled Process



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As with the RR process, the expander feed is sent to the tower several stages below the top of the column. Because of this modification, the cold separator operates at much warmer conditions well away from the system critical. Additionally, the residue recompression is less than with the conventional expander process. The horsepower is typically lower than the RR process at recovery levels below 92%.

The GSP design has several modifications. One is to take a portion of the liquid from the cold separator along with the gas to the overhead exchanger. Generally, this can help to further reduce the horsepower required for recompression. Also, the process can be designed to just use a portion of the cold separator liquid for reflux. This modification is typically used for gases richer than 3 GPM. The GSP design is very CO_2 tolerant; many designs require no up front CO_2 removal to achieve high recovery. CO_2 levels are very composition and operating pressure dependent, but levels up to 2% can usually be tolerated with the GSP design.

A new process scheme has been developed to combine the GSP and RR processes into an integrated process scheme. This concept is based on applying the best features of each process to the integrated design. This combination can result in higher ethane recovery efficiency than can be achieved with GSP.

CRR Process

The Cold Residue Recycle (CRR) process is a modification of the GSP process to achieve higher ethane recovery levels. The process flow in Fig. 16-22 is similar to the GSP except that a compressor and condenser have been added to the overhead system to take a portion of the residue gas and provide additional reflux for the demethanizer. This process is attractive for extremely high ethane recovery. Recovery levels above 98% are achievable with this process. This process is also excellent for extremely high propane recovery while rejecting essentially all the ethane.

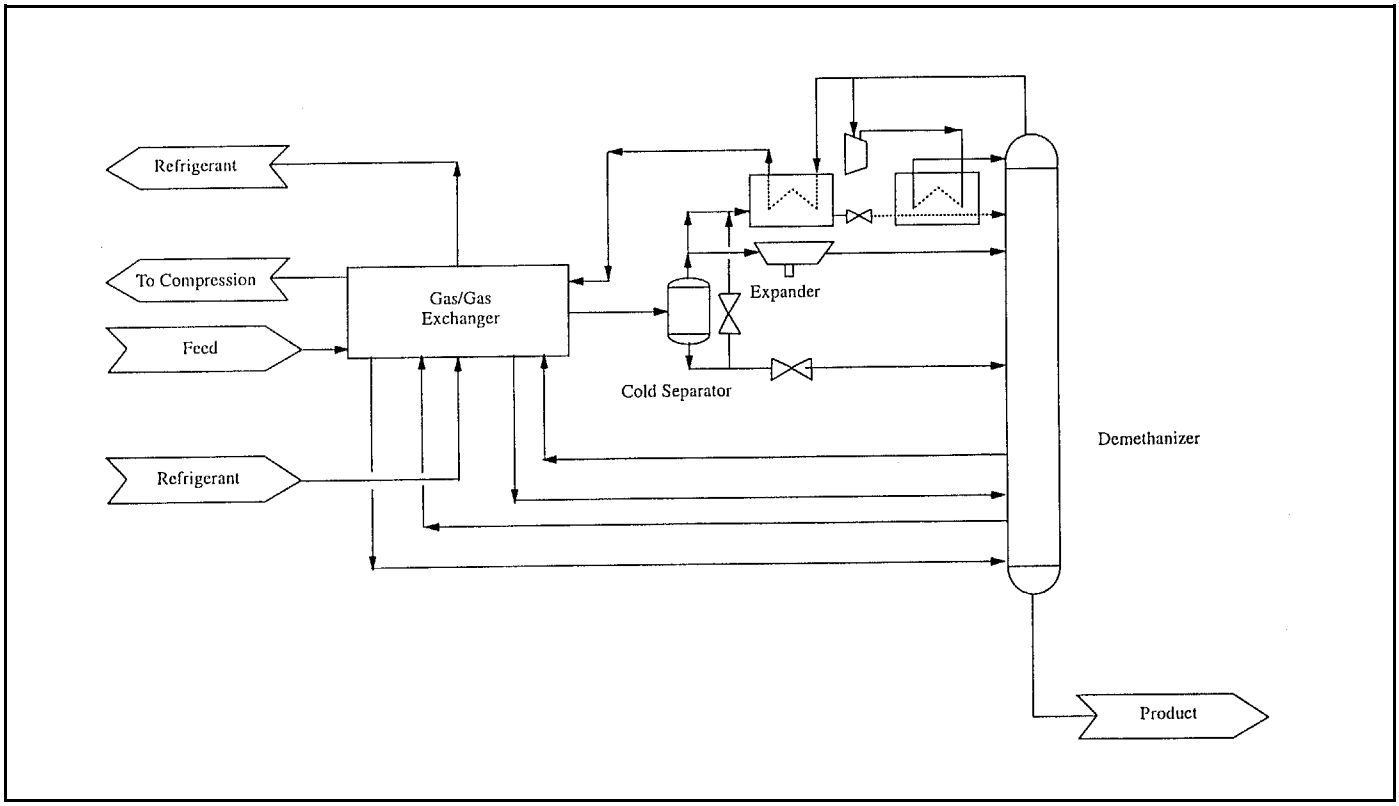
A comparison of the RR, GSP and CRR processes for one particular case is shown in Fig. 16-23. This comparison is typical for these processes. The RR design is the least efficient up to about 91%. Above this point the RR design can achieve higher ethane recovery than the GSP design. As can be seen, the RR process is quite sensitive to available power. The GSP design has a rather flat recovery curve and is a good choice for recoveries around 90+%. The CRR process has the highest recovery for the available residue recompressor power, but consideration must be given to the cost of the additional overhead system equipment and recycle compressor.

Enhanced NGL Recovery Process

Another improvement of the turboexpander-based NGL process is the IPSI Enhanced NGL Recovery Process. (Figure 19-24) This process utilizes a slip stream from or near the bottom of the distillation column (demethanizer) as a mixed refrigerant. The mixed refrigerant is totally or partially vaporized, providing refrigeration for inlet gas cooling otherwise normally accomplished using an external refrigeration system. The vapor generated from this "self-refrigeration" cycle is specifically tailored to enhance separation efficiency, then is recompressed and recycled back to the bottom of the tower where it serves as a stripping gas. The innovation not only reduces or eliminates the need for inlet gas cooling via external refrigeration, but also provides the following enhancements to the demethanizer operation:

FIG. 16-22

Cold Residue Recycle Process



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FIG. 16-23

Example % Ethane Recovery vs. Residue Compression Power

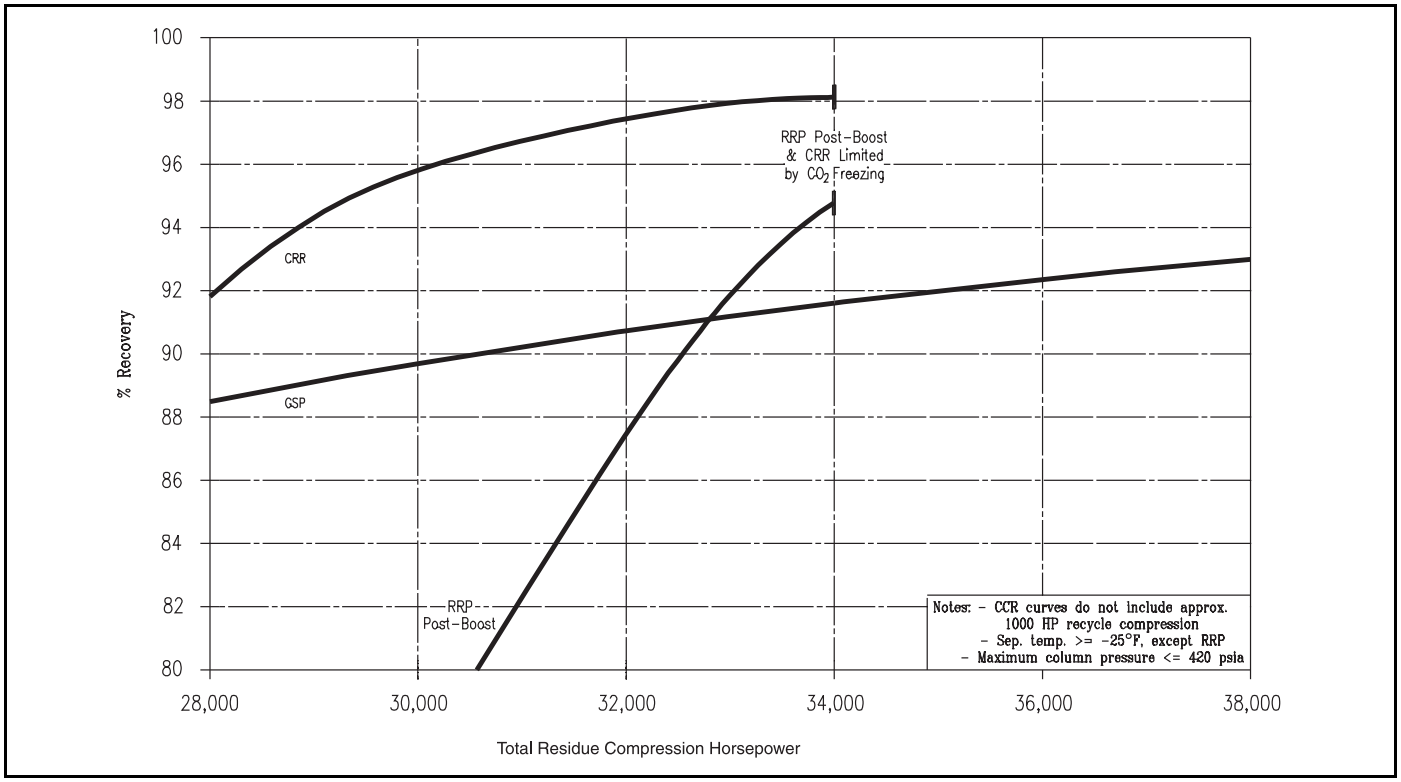
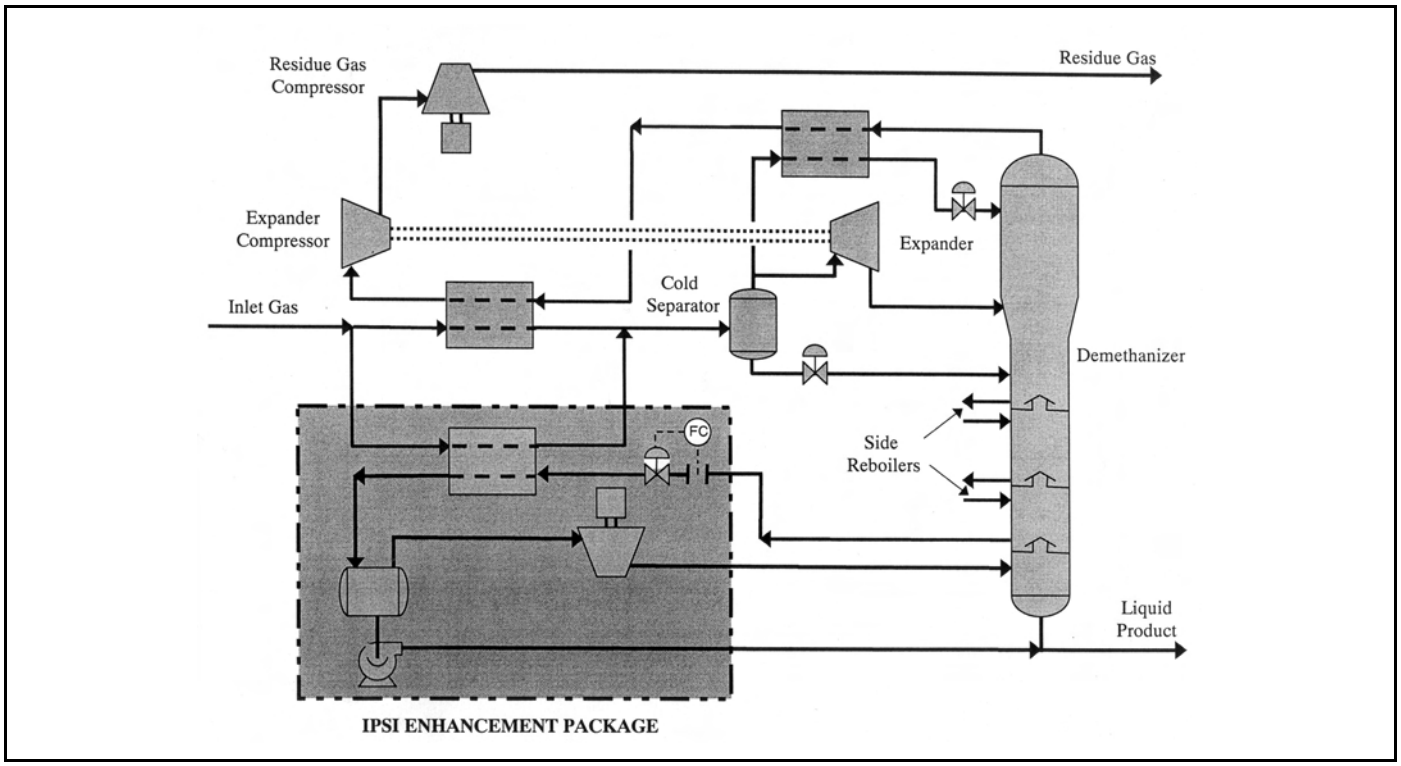


FIG. 16-24

IPSI Enhanced NGL Recovery Process



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- Lowers the temperature profile in the tower, thereby permitting better energy integration for inlet gas cooling via reboilers, resulting in reduced heating and refrigeration requirements.
- Reduces and/or eliminates the need for external reboiler heat, thereby saving fuel plus refrigeration.
- Enhances the relative volatility of the key components in the tower when operated at a typical pressure, thereby improving separation efficiency and NGL recovery; or alternatively allows increased tower pressure at a typical recovery efficiency, thereby reducing the residue gas compression requirements.

High Propane Recovery Processes

The processes shown in Figure 16-20, 21, and 22 are processes which can recover ethane in the presence of CO2. They can also be configured to reject ethane and recover a reasonable level of propane. The processes are equilibrium limited in the overhead reflux stream to achieve high propane recovery. Other process configurations have been developed which focus on high propane recovery. These are especially attractive in locations where ethane recovery is not contemplated.

One such process is the OverHead Recycle process (OHR) shown in Figure 16-25. This process configuration uses an absorber column and deethanizer column to achieve the desired separation. The overhead from the deethanizer is condensed and used to absorb propane from the expander outlet stream. This configuration provides more efficient recovery of propane but is not suitable for ethane recovery. This process can be reconfigured to the GSP if ethane recovery is desired.

The OHR process has been improved to make better use of the refrigeration available in the feed streams. The Improved Overhead Reflux (IOR) process shown in Figure 16-26 makes a few strategic changes from the OHR process. In this process the reflux for the deethanizer is produced in the absorber overhead system which produces reflux for both towers. The absorber bottoms is heated against the feed before being sent to the deethanizer. The use of the two columns results in a propane recovery of over 99% while the ethane recovery is set to produce the desired purity propane in the deethanizer bottoms. This basic IOR setup has been modified by combining the absorber and deethanizer into a single column with a side draw to produce reflux. If this process, dubbed the SCORE process, can be accommodated in the plant from a structural standpoint, there is potential for saving equipment from the IOR process.

MIXED REFRIGERANT PROCESS

The use of a mixed refrigerant process is an interesting alternative to the turboexpander process. Such processes have been used widely in LNG processing and to a lesser extent in NGL recovery. One of the characteristics of the process is that low temperatures can be achieved with significantly reduced inlet gas pressure. The chilling can be achieved totally with mechanical refrigeration or with a mixture of refrigeration and expansion. If inlet compression is contemplated for a turboexpander plant, then mixed refrigerant processing can be an economic alternative.

Fig. 16-27 shows one type of mixed refrigerant process. In this case the feed gas is chilled to cold separator temperature where the liquid is sent to the demethanizer as in an expander process. The overhead vapor is split and the majority sent through an expander to the upper part of the demethanizer. A portion of the gas is cooled further in the main heat exchanger and sent to the top of the demethanizer as reflux. Alternatively, the turboexpander can be eliminated and the total stream cooled in the main exchanger and fed to the demethanizer. The residue gas would be exchanged with the feed in the main heat exchanger. The refrigeration is provided by a single mixed refrigerant system designed to provide the necessary low temperature conditions. The refrigerant would typically be a methane, ethane, propane mixture with some heavier components as dictated by the design conditions. A critical aspect of the design is to maintain the desired refrigerant composition during plant operation.

FIG 16-25

OHR Process

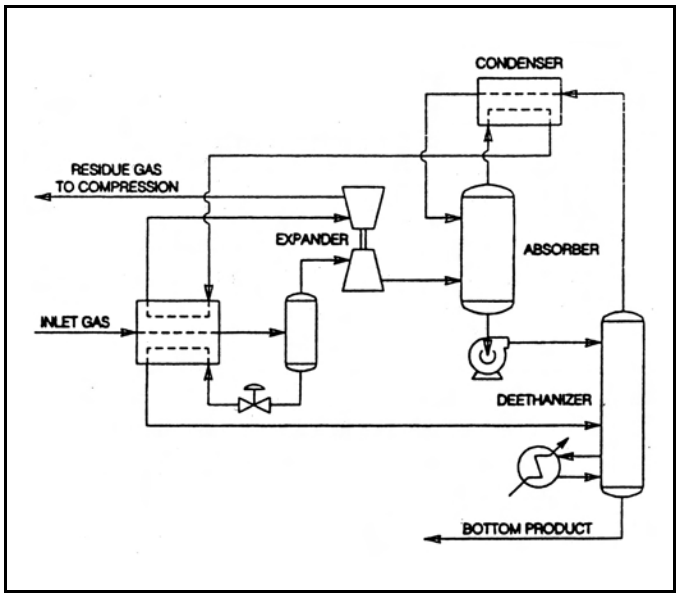
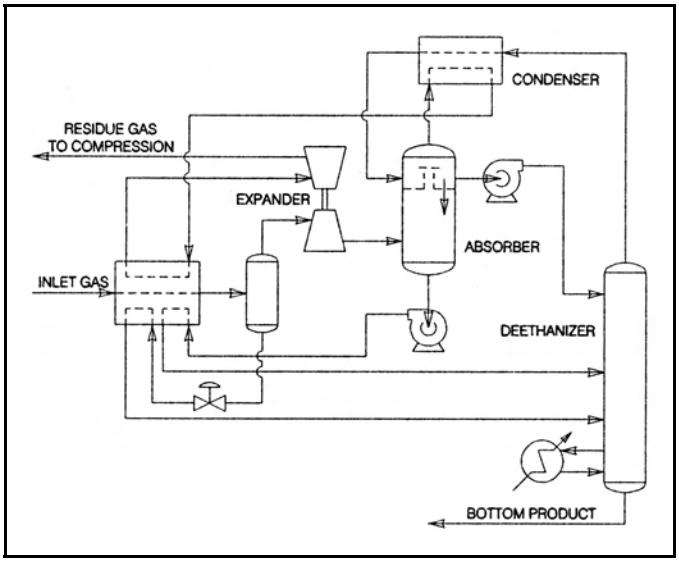


FIG. 16-26

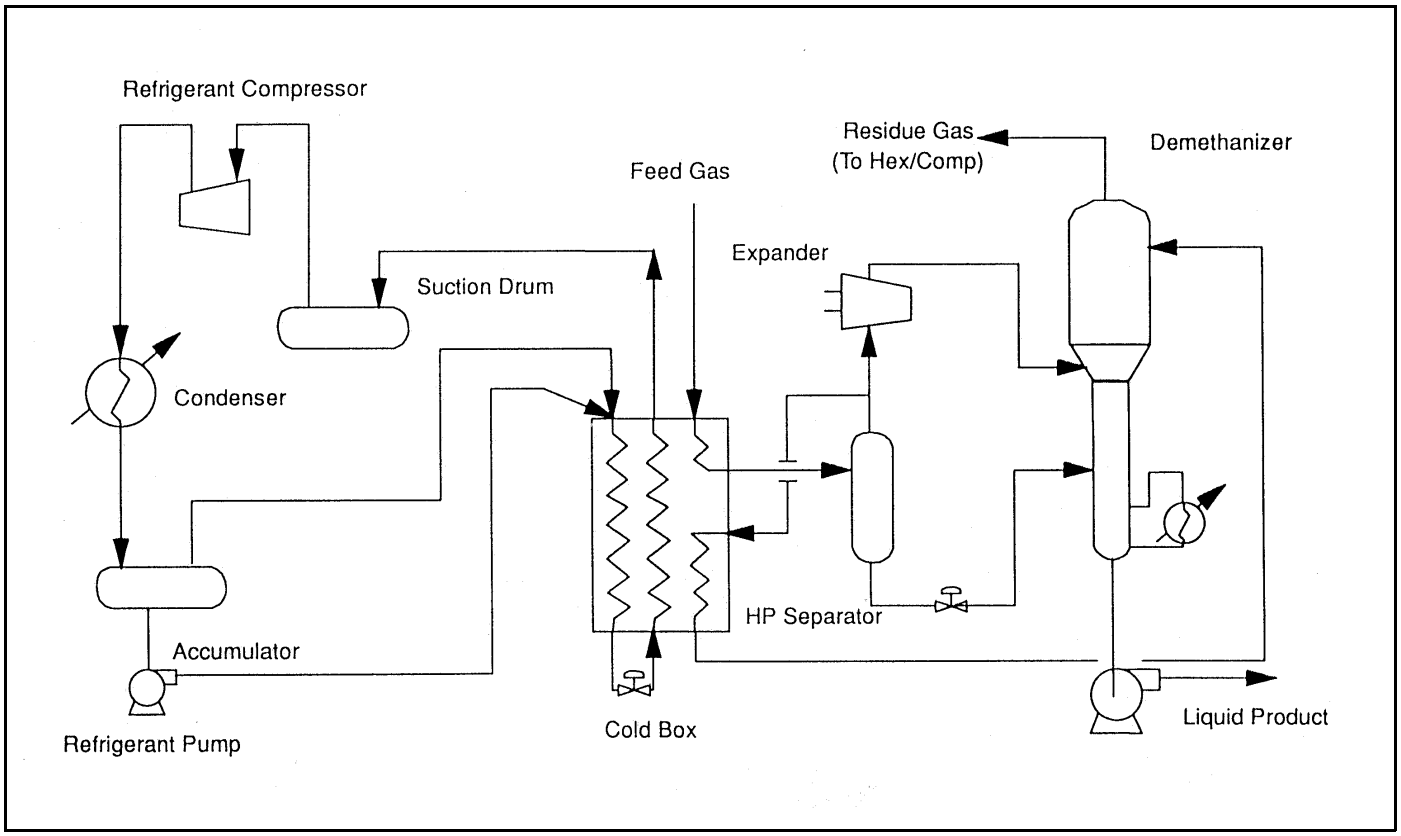
IOR Process



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FIG. 16-27

Mixed Refrigerant NGL Recovery Process



FRACTIONATION CONSIDERATIONS

In all NGL recovery processes, one of the final steps in the plant is the production of the desired liquid product by use of a fractionation column. This column produces the specification product as a bottom product with the overhead stream being recycled to the process or sent out of the plant as residue gas product. This mixed product then needs to be separated into usable products in a series of one or more fractionation columns. The number and arrangement of these columns is dependent on the desired product slate.

If the NGL stream is an ethane plus stream the first step is to separate the ethane from the propane and heavier components in a deethanizer. The propane is then separated from the butane and heavier components in a depropanizer. If further processing is desired the butane may be separated in a debutanizer and the butanes further separated in a butane splitter column. The butane splitter is only used when a differential value can be realized for the isobutane versus the mixed butane stream. A schematic of a four column fractionator is shown in Fig. 16-28. Section 19 in the Data Book covers the specifics of fractionation systems for NGL streams.

MERCURY REMOVAL

It is not unusual for gas streams to contain 1 to 10 micrograms/Nm3 (approx. 0.1 to 10 ppbv) of mercury. Some gas streams have been reported to have over 100 micrograms/m3 (approx. 10 ppbv). The mercury can attack aluminum in the plate fin heat exchangers used in most modern cryogenic plants. In order for the attack to occur, the mercury must be present as a free liquid. This situation cannot occur above –40F. Technically, mercury containing feedstocks can be handled without aluminum corrosion. Mercury containing equipment which is kept at low temperature can be decontaminated by carrying out a cold, then warm purge with bone dry gas. However, this is not a practical method to be assured that mercury attack does not occur.

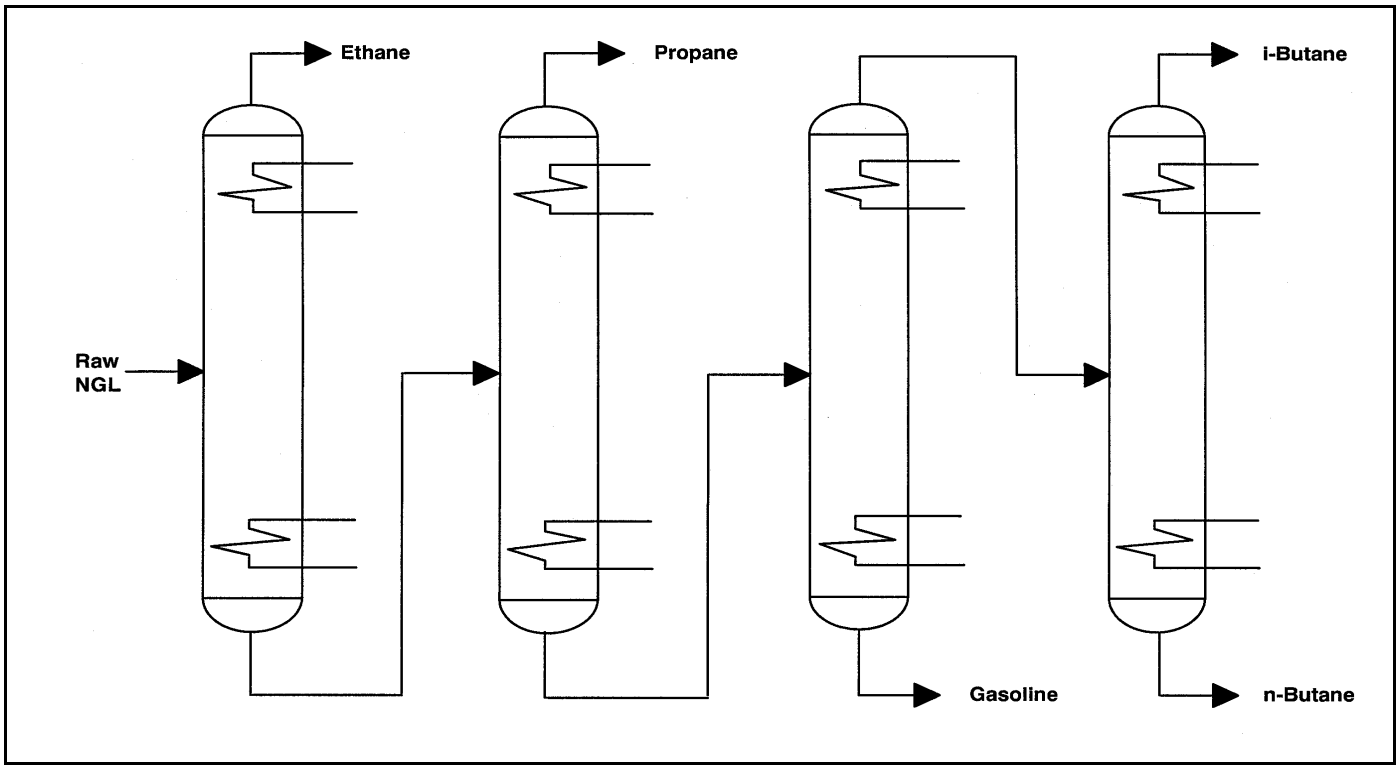
The mercury in the feed gas can be removed with a mercury removal bed. The bed uses a sulfur based trapping material which reacts with the mercury to form cinnabar (HgS) on the bed. The trapping material is carried on activated carbon, zeolite or alumina. The trapping bed is usually located downstream of the dehydration. In this location, the gas is free of entrained liquids and water. Locating the bed in other locations is very dependent on the material used as recommended by the vendor. Figure 16-29 shows an example mercury removal bed. The mercury beds are designed to remove the mercury to 0.001 micrograms/Nm3.

Each vendor has criteria for sizing beds for their material but some rules of thumb are that the bed should be sized for a superficial flow velocity of about 50 ft/min and a residence time of 10 seconds. With the rather small mass of mercury which is typically removed, the beds can last many years between change outs.

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FIG. 16-28

Four-column Fractionation System



LIQUEFIED NATURAL GAS PRODUCTION

The principal reason for liquefying natural gas is the 600-fold reduction in the volume which occurs with the vapor-to-liquid phase change. This volume reduction is important in the transportation and storage of the gas. In the liquid state, the gas can be transported in discrete quantities, can be economically stored in tanks for use as required, and can be transported long distances not feasible with gas pipelines.

Because methane is the primary component of natural gas, the production of Liquefied Natural Gas (LNG) involves the chilling of the entire natural gas feed stream to cryogenic temperatures sufficient to totally condense the gas stream. Common to all LNG liquefaction processes is the need to pretreat the gas to remove components, such as CO2 and water, which will solidify in the liquefaction step. The liquefaction unit also has to remove hydrocarbon components, such as benzene and cyclohexane, which can solidify.

Two types of LNG facilities have been developed: 1) large base load units for continuous LNG production to export markets, and 2) small peak shaving plants for gas distribution systems. The large scale based load units are typically designed with emphasis on process efficiency. In addition to the process units involved in the liquefaction step, base load LNG plants tend to be large complex facilities which involve product storage, loading and complete stand-alone utility systems.

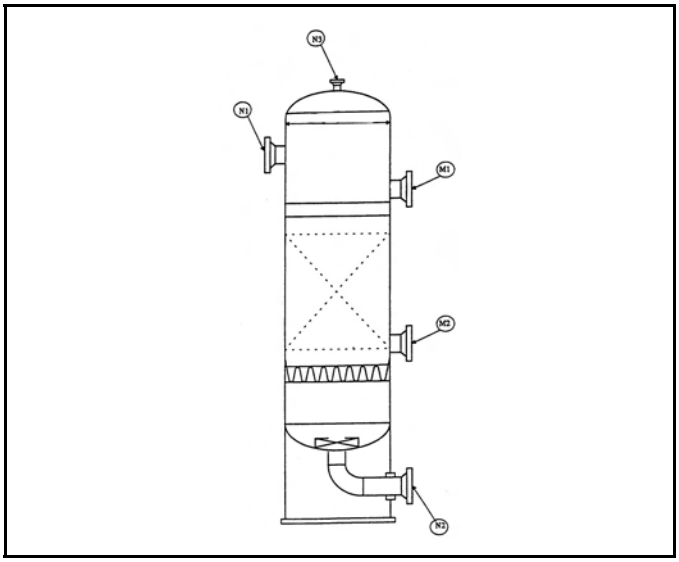
Peak shaving facilities differ from base load units in several aspects. Peak shaving plants are much smaller, operate only a portion of the year, and are often located near the point of use for the gas. The design emphasis is thus on capital cost minimization rather than thermodynamic efficiency.

In order to produce the low temperature necessary for liquefaction, mechanical refrigeration systems are utilized. Three types of liquefaction processes can be used to accomplish this refrigeration:

1. Cascade Refrigeration Process
2. Mixed Refrigerant Process
3. Precooled Mixed Refrigerant Process

FIG. 16-29

Mercury Removal Bed



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Each of these processes has been used for liquefaction facilities with the PreCooled process being the predominant technology in base load units. The Cascade and Mixed Refrigerant processes have both been used in a wide range of process sizes in both base load and peak shaving units with the Mixed Refrigerant process being the dominant technology in peak shaving units.

Cascade Refrigeration

The first LNG liquefaction units utilized the cascade refrigeration process. These facilities use the classical cascade cycle where three refrigeration systems are employed: propane, ethylene and methane. Two or three levels of evaporating pressures are used for each of the refrigerants with multistage compressors. Thus the refrigerants are supplied at eight or nine discrete temperature levels.Using these refrigeration levels, heat is removed from the gas at successively lower temperatures. The low level heat removed by the methane cycle is transferred to the ethylene cycle, and the heat removed in the ethylene cycle is transferred to the propane cycle. Final rejection of the heat from the propane system is accomplished with either water or air cooling.

Early facilities used a closed methane refrigeration loop. More modern designs use an open methane loop such as shown in Fig. 16-30 where the methane used for refrigerant is combined with the feed gas and forms part of the LNG product. The efficiency and cost of the process is dependent on the number of refrigeration levels provided in each refrigeration system.

The refrigeration heat exchange units traditionally were based on shell and tube exchangers or aluminum plate fin exchangers. Newer designs incorporate plate fin exchangers in a vessel known as “core-in-kettle” designs. A critical design element in these systems is the temperature approach which can be reached in the heat exchangers.

Mixed Refrigerant Processes

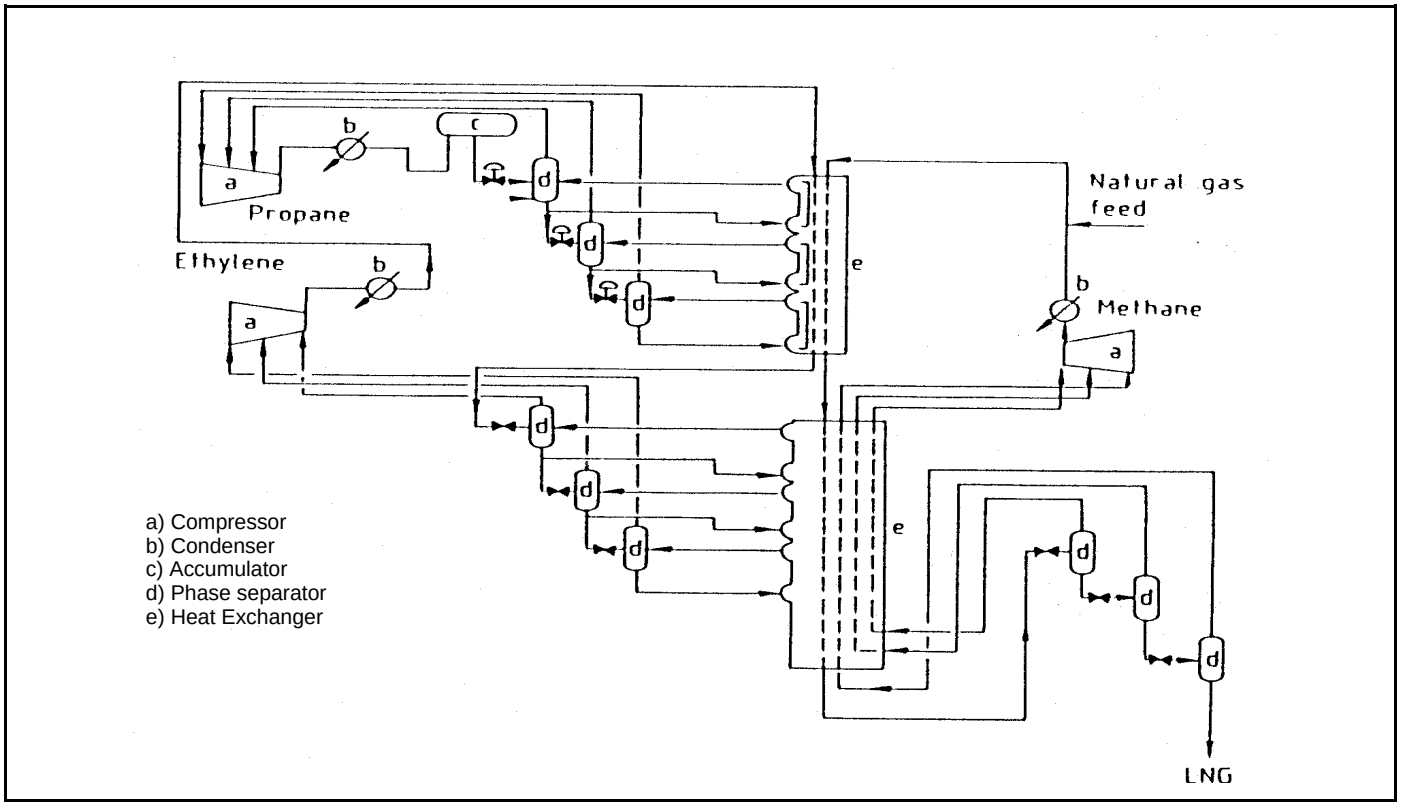
After initial developments of cascade LNG plants, the mixed refrigerant cycle was developed to simplify the refrigeration system. This system uses a single mixed refrigerant composed of nitrogen, methane, ethane, propane, butane and pentane. The refrigerant is designed so that the refrigerant boiling curve nearly matches the cooling curve of the gas being liquefied. The closeness of the match of these two curves is a direct measure of the efficiency of the process.

The process (Fig. 16-31) has two major components: the refrigeration system and the main exchanger cold box. The cold box is a series of aluminum plate fin exchangers which provide very close temperature approaches between the respective process streams. The low pressure refrigerant is compressed and condensed against air or water in a closed system. The refrigerant is not totally condensed before being sent to the cold box. The high pressure vapor and liquid refrigerant streams are combined and condensed in the main exchanger. The condensed stream is flashed across a J-T valve and this low pressure refrigerant provides the refrigeration for both the feed gas and the high pressure refrigerant.

Removal of pentane and heavier hydrocarbons from the feed gas is accomplished by bringing the partially condensed gas out of the cold box and separating the liquid at an intermediate temperature. The liquid removed is then further processed to produce a specification C_5+ product. Light products from this separation are returned to the liquefaction system.

FIG. 16-30

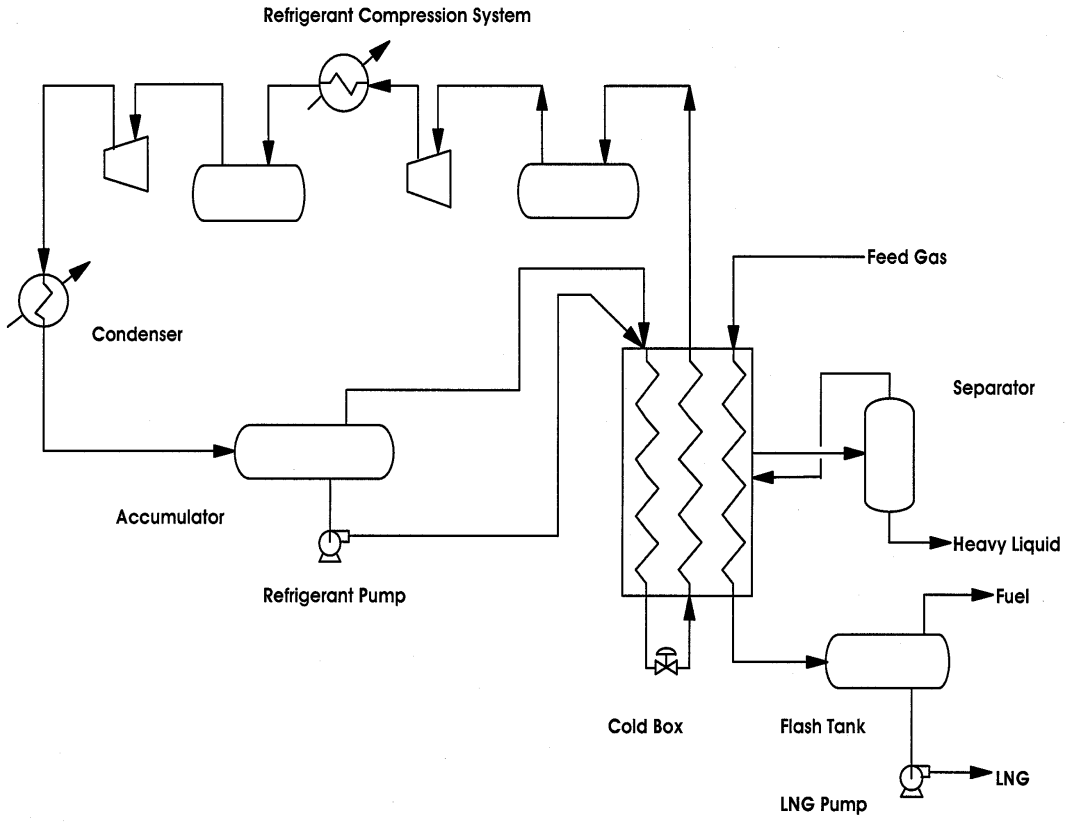
Nine-stage Cascade Liquefaction Process[10]



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FIG. 16-31

Mixed Refrigerant Liquefaction Process[12]



Precooled Mixed Refrigerant Process

The propane precooled mixed refrigerant process (Fig. 16-32) was developed from a combination of the cascade and mixed refrigerant processes. In this process, the initial cooling of the feed gas is accomplished by using a multistage propane refrigeration system.The gas is cooled with this system to around –40°F at which point the gas is processed in a scrub column to remove the heavy hydrocarbons. The gas is then condensed in a two step mixed refrigerant process. The chilling of the gas is accomplished in a single, large, spiral-wound heat exchanger. This exchanger allows extremely close temperature approaches between the refrigerant and the gas to be achieved.

The mixed refrigerant in this process is a lighter mixture composed of nitrogen, methane, ethane and propane with a molecular weight around 25. The mixed refrigerant after recompression is partially cooled with air or water and then further cooled in the propane refrigeration system. The partially condensed refrigerant from the propane chilling is separated and the high pressure vapor and liquid streams sent separately to the main exchanger. The liquid is flashed and provides the initial chilling of the gas. The high pressure vapor is condensed in the main exchanger and provides the low level, final liquefaction of the gas. As in the other processes, the LNG leaves the exchanger subcooled and is flashed for fuel recovery and pumped to storage.

SOLIDS FORMATION

In addition to the obvious need for water removal from the gas stream to protect from blockage in the cryogenic sections of a plant, consideration must be given to the possible formation of other solids or semi-solids in the gas stream. Amines, glycols, and compressor lube oils in the gas stream can form blockages in the system. Generally these contaminants will form a blockage upstream of an expander, in the lower temperature exchange circuit, or on the screen ahead of an expander.

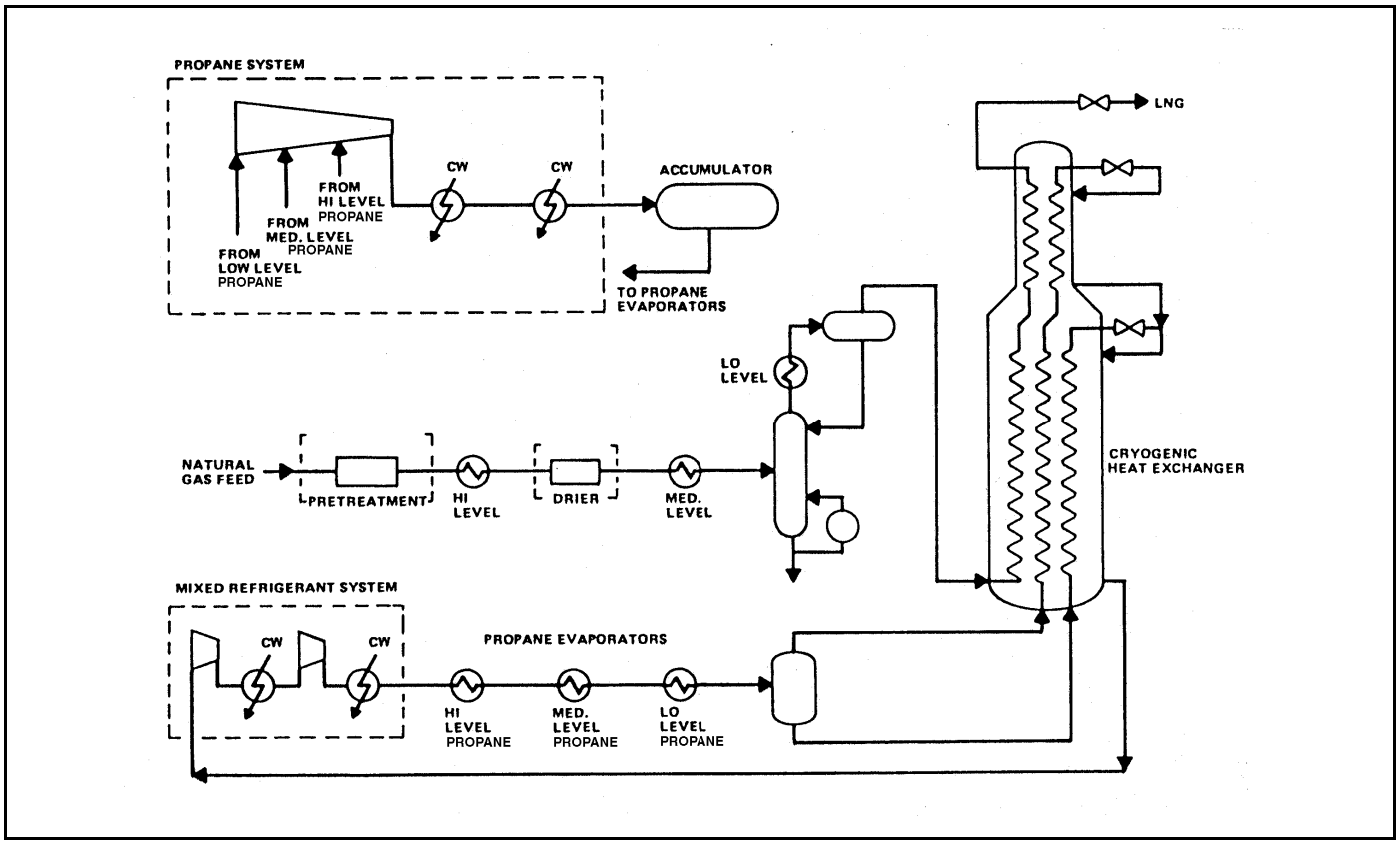
Carbon dioxide can form as a solid in lower temperature systems. Fig. 16-33 will provide a quick estimate for the possibility of formation of solid CO_2. If operating conditions are in the methane liquid region as shown by the insert graph, the dashed solid-liquid phase equilibrium line is used. For other conditions the solid isobars define the approximate CO_2 vapor concentration limits.

For example, consider a pressure of 300 psia. At –170°F, the insert graph (Fig. 16-33) shows the operating conditions to be in the liquid phase region. The dashed solid-liquid phase equilibrium line indicates that 2.1 mol percent CO_2 in the liquid phase would be likely to form solids. However, at the same pressure and –150°F, conditions are in the vapor phase, and 1.28 mole percent CO_2 in the vapor could lead to solids formation. This chart represents an approximation of CO_2 solid formation. Detailed calculations should be carried out if Fig. 16-33 indicates operation in a marginal range.

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FIG. 16-32

Propane Precooled Mixed Refrigerant Process[13]



If the expander liquid is fed to the top tray of a demethanizer, the CO_2 will concentrate in the top equilibrium stages. This means that the most probable condition for solid CO_2 formation may be several trays below the top of the tower rather than at expander outlet conditions. Again, if Fig. 16-33 indicates marginal safety from solids formation, detailed calculations must be carried out.

In addition to CO2 and water which can solidify and cause blockage and damage in cryogenic equipment, hydrocarbons can also solidify at temperatures found in LNG plants. Figure 16-34 shows some freezing point temperatures for pure compounds which can be troublesome in LNG facilities.

Of the compounds listed, all can solidify at LNG temperatures but the solubility of these compounds in LNG are such that only at certain concentrations will there be solid formation. Cyclohexane and benzene are the compounds with the highest freezing points in this list. Cyclohexane is normally not present in significant quantity in produced gas. However, benzene is present in most gases and can be found in level in the 1000 ppm range, well above the solubility at LNG temperatures. Typically benzene and hexane are the compounds which are the most concern due to the combination of concentration in the gas and freezing point.

The solubility of these compounds in LNG streams is composition dependent. Figure 16-35 shows the solubility of benzene in ethane, Figure 16-36 shows the solubility of benzene in ethane. Comparison of these two figures shows that at say –260F, the solubility in methane is about 2 ppm while the solubility in ethane is 75 ppm. Heavier hydrocarbons such as propane and butane have even higher solubility numbers. Thus the composition of the LNG is an important factor in the solid formation concentration of this compound and other components in Figure 16-34. Typically, reduction of the benzene concentration to 10 ppm is sufficient to prevent solid formation. The GPA performed research in this area (See section 1) and has produced a predictive computer program to calculate freezing points for both hydrocarbons and CO2 in LNG streams.

NITROGEN REJECTION

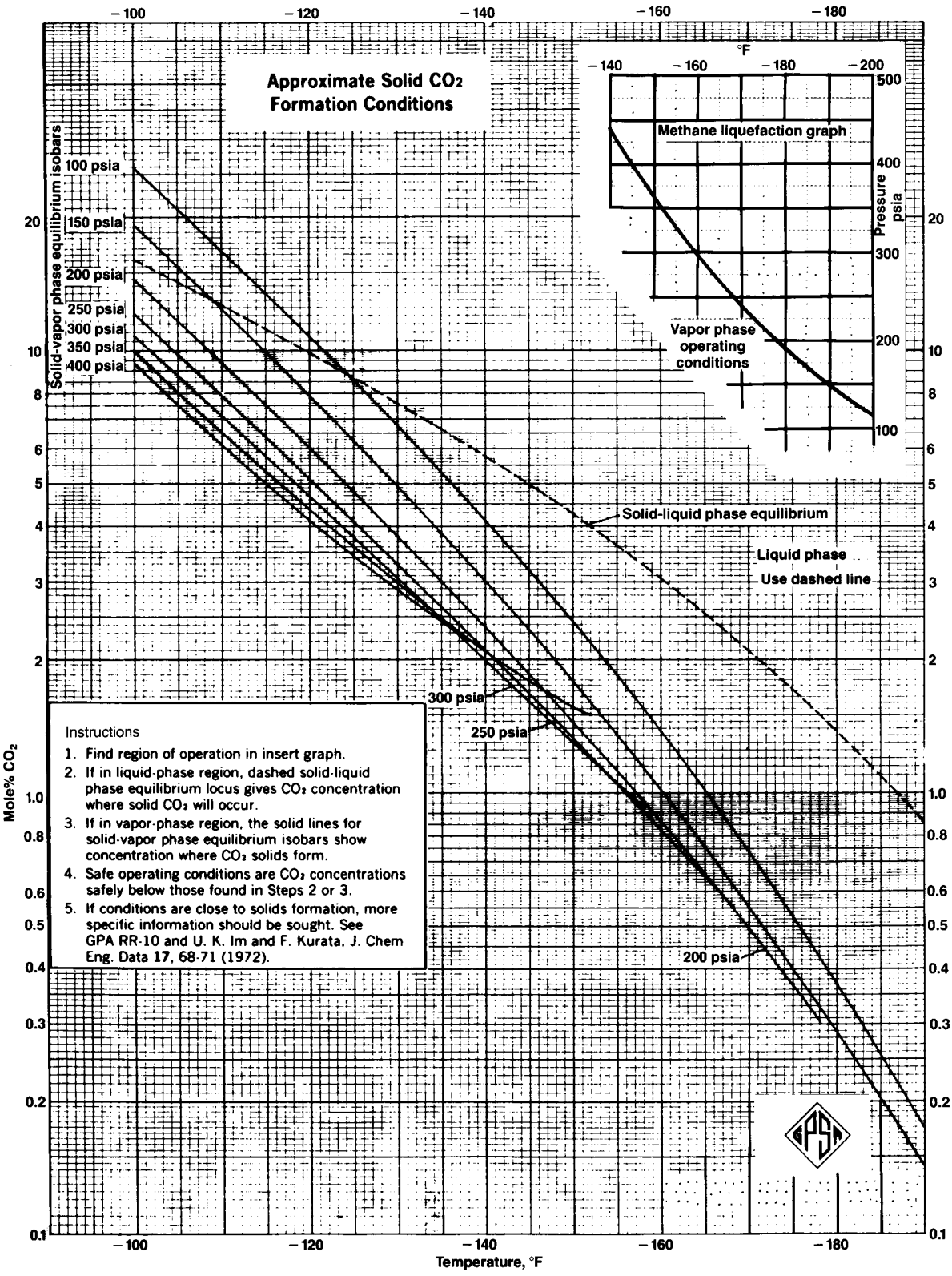
Virtually all natural gas contains some amount of nitrogen which lowers the BTU value of the gas but is no particular problem. However, in some reservoirs gas has been discovered to contain larger amounts of nitrogen than can be tolerated due to contractual considerations on BTU content. In these cases, the operator has three options: 1) blend the gas with richer gas to maintain overall BTU value; 2) accept a reduced price or less secure market; or 3) remove the nitrogen to meet sales specifications. Options 1 and 2 are reasonable approaches to the problem but are very location specific.

When a nitrogen rejection unit (NRU) is selected as a process option for a gas stream, it is often combined with NGL recovery in an integrated plant design. A block flow diagram of a combined NGL/NRU facility is shown in Fig. 16-37. The overall objective of this facility is to produce a nitrogen vent stream, specification sales gas stream, and a specification NGL product. One of the primary contributors to facility cost is the required compression for the inlet gas and the sales gas.

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FIG. 16-33

Approximate Solid CO_2 Formation Conditions



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FIG. 16-34

Problem Compounds in LNG

	Freezing Temp, F
Cyclohexane	43.79
Benzene	41.96
n-Decane	–21.33
n-Nonane	–64.26
n-Octane	–70.17
n-Heptane	–130.99
Toluene	–138.96
n-Hexane	–139.56

Regardless of the technology, recompression of the sales gas is usually required unless the residue gas can be marketed at 300 psig or less. Also, inlet compression is necessary if the gas is available at less than 650 psig.

Cryogenic Technology

Nitrogen rejection is typically carried out using cryogenic distillation technology. Due to the low temperature operation, the gas, after being compressed to required inlet pressure, is fed to a pretreatment unit for CO_2 and water removal. The CO_2 will freeze at –70°F and therefore must be removed to 50-200 ppmv levels. Typically, this removal is accomplished with amine treating which can easily remove CO_2 to acceptable levels. The dehydration step is carried out with molecular sieve dehydration. Another impurity which must be addressed is mercury content of the feed gas. Mercury can attack the aluminum heat exchangers in the low temperature section. Typically removal is accomplished with an adsorbent bed downstream of the dehydration.

The exact design of this nitrogen rejection unit is a strong function of the nitrogen content. For nitrogen contents below 20%, a heat pump cycle such as shown in Fig. 16-38 has been used. The drawback to this process is the heat pump compressor required. A more modern design utilizes a two-column design with a prefractionator. At higher nitrogen contents, a two column system such as in Fig. 16-39 is the choice. This design is quite flexible and can be used at nitrogen contents above 50%. Also, a recycle compressor can be added to handle nitrogen contents below 20%. New proprietary two- and three-column designs have been developed recently which have decreased the cost of NRU distillation cold box designs by about 25%. Variable nitrogen contents require preplanning and careful design to ensure efficient operation over a range of compositions

The NGL recovery may be designed for ethane and heavier recovery or propane and heavier recovery. Since NGL recovery is also a low temperature process, it is easily integrated with the nitrogen rejection into an integrated design. The NGL recovery is a traditional turboexpander setup except that the front-end heat exchange is integrated with the nitrogen and sales gas streams from the NRU section. The incremental cost for NGL recovery may be quite small because many of the required process steps such as dehydration and compression are already present.

The sales gas product from an NRU is produced at low pressure. Recompression to pipeline pressures can represent a large portion of the capital and operating costs. Newer NRU designs have optimized the product pressure by producing two methane streams at different pressures. Approximately two thirds of the sales gas can be produced at 300 psig and the other third at 100 psig. This is in sharp contrast to early designs where all the methane was produced at 100 psig or less. This modification significantly reduces the horsepower requirements.

Recovery Efficiencies

In the separation of nitrogen from natural gas, high purity products are readily achievable. Sales gas purity of 2% nitrogen is common. Higher purities come at a fairly sharp increase in cost. Lesser purities result in some savings but do not usually swing the economics. The hydrocarbon losses in the nitrogen vent stream are typically specified in terms of percent hydrocarbon recovery with 98% hydrocarbon recovery being achievable. Lower recoveries impact the cost of the project, but recoveries below 95% usually result in significant hydrocarbon loss and could be an environmental problem with the nitrogen vent stream. NGL recovery efficiencies associated with an integrated NGL/NRU can be quite high. Ethane recovery of 80 % with virtually complete C_3+ recovery is typical. If ethane recovery is not desired, the process can be designed for high C_3+ recovery and incidental ethane recovery.

New Technology

In addition to improvements in the cryogenic technology, other technologies have been developed for NRUs. The first is the use of a solvent to separate the nitrogen from the hydrocarbon components. This process has the advantage of not requiring CO_2 removal or deep dehydration. The main drawback is that the hydrocarbon components are actually absorbed and regenerated at low pressure. Thus, the recompression costs would be much higher than with the cold box technology. Also, large circulation rates and the corresponding pumping can be required. This technology has not replaced the cryogenic approach but is in the early stages of development.

Another alternative technology utilizes molecular sieves to separate the nitrogen. This technology also tolerates CO_2 and water. Because the molecular sieve bed sizes are proportional to the gas volume being treated, this process has been used for smaller volume applications. The adsorption/desorption cycle is quite similar to molecular sieve dehydration. Such a process could be instrumented quite easily for unattended operation. The major drawback to this process is that the methane product is produced at low pressure requiring more recompression than cold box technology. Also, the waste nitrogen stream may have enough hydrocarbon to preclude venting of the nitrogen. If a fuel requirement is available which would utilize the waste nitrogen stream, hydrocarbon loss could be a minor consideration.

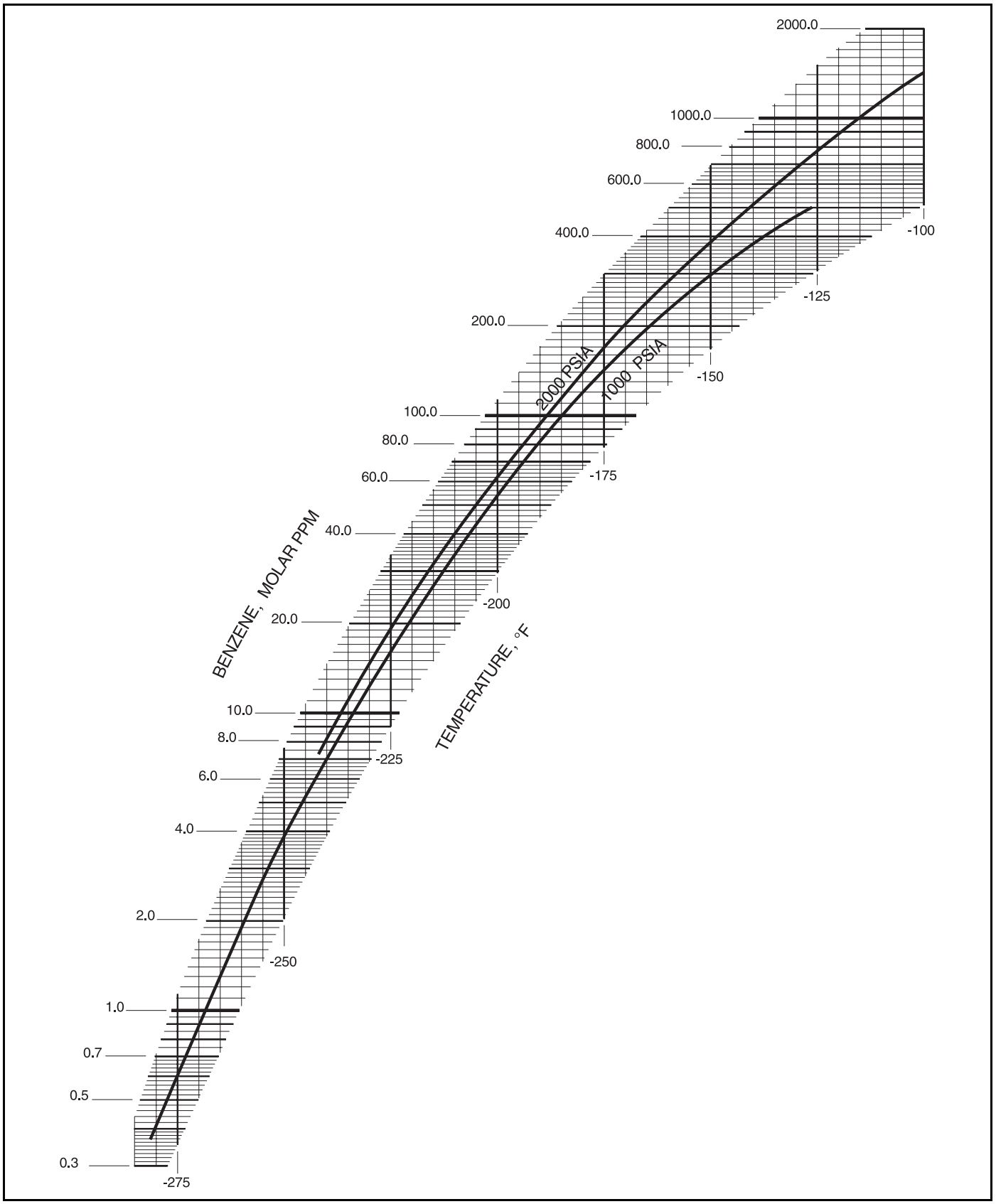
ENHANCED OIL RECOVERY

In order to increase oil production in many reservoirs, the injection of gas for enhanced oil recovery (EOR) has been carried out in numerous projects. The gas injection plan can lead to three different types of processing facilities. First, high methane or high nitrogen gas can be injected for pressure maintenance of the reservoir. In this case the gas is in a separate phase from the oil phase, and any gas produced is simply recycled to the reservoir. Processing of the gas in traditional gas processing facilities is often carried out.

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FIG. 16-35

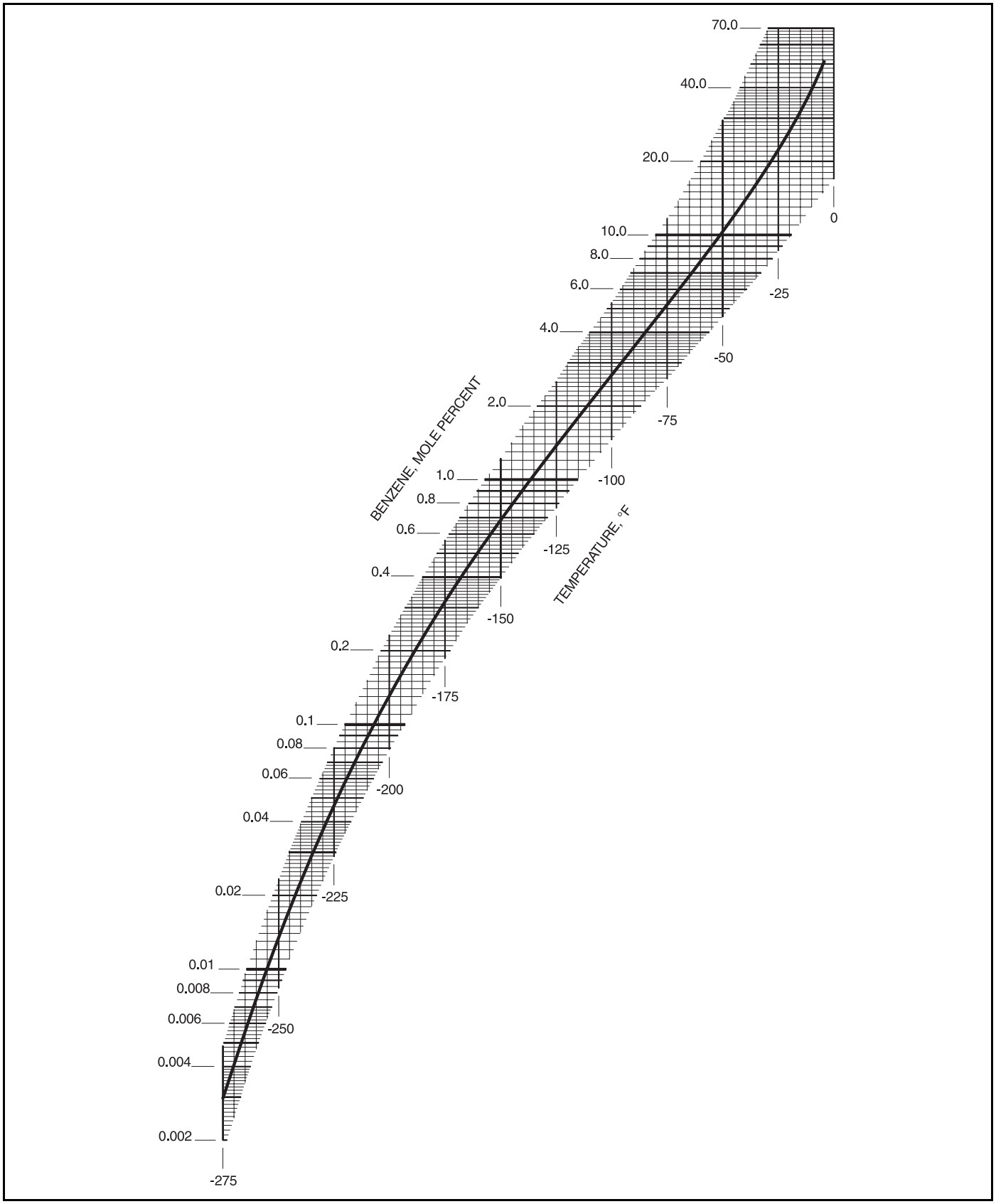
Solubility of Benzene in Methane



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FIG. 16-36

Solubility of Benzene in Ethane



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FIG. 16-37

Nitrogen Rejection Flow Diagram[14]

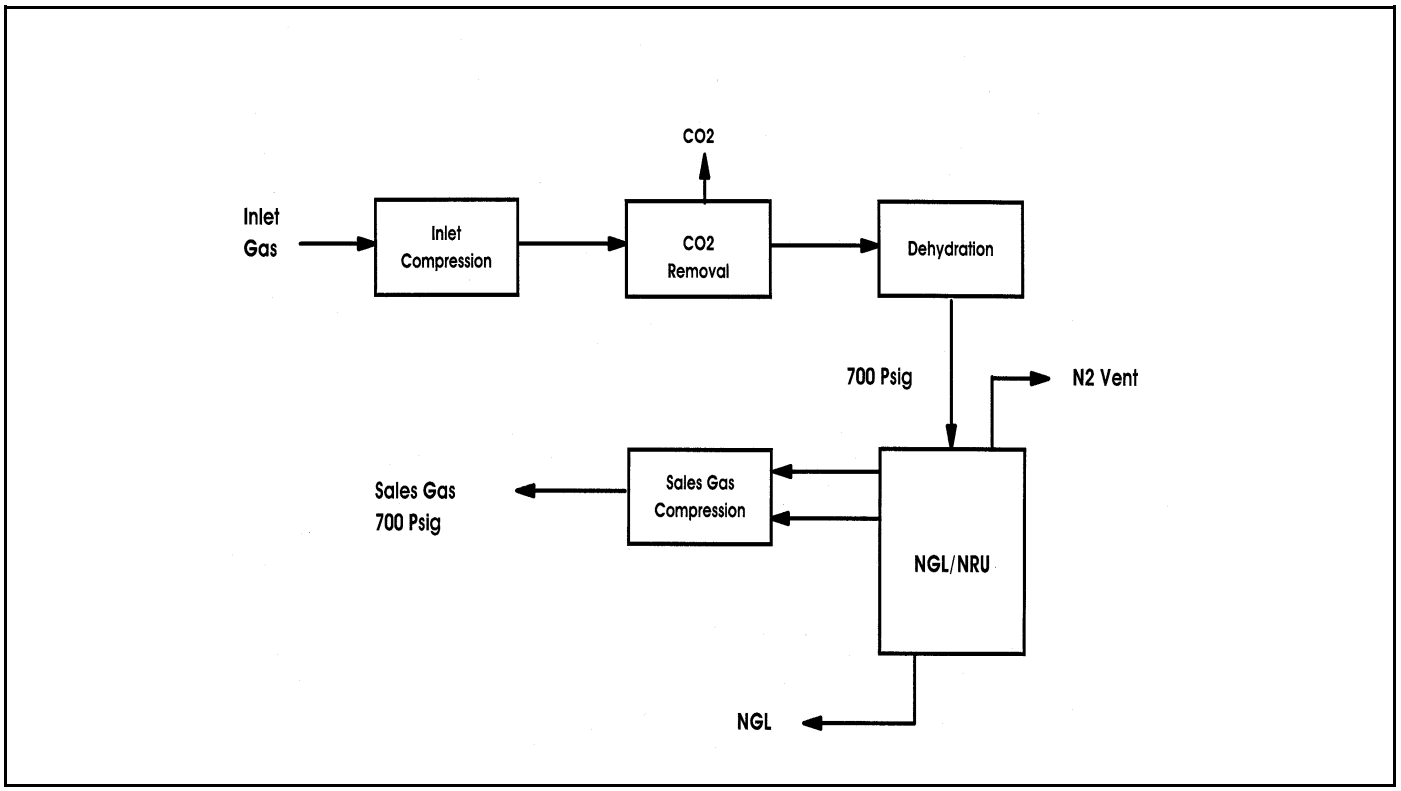


FIG. 16-38

Single-Column NRU[14]

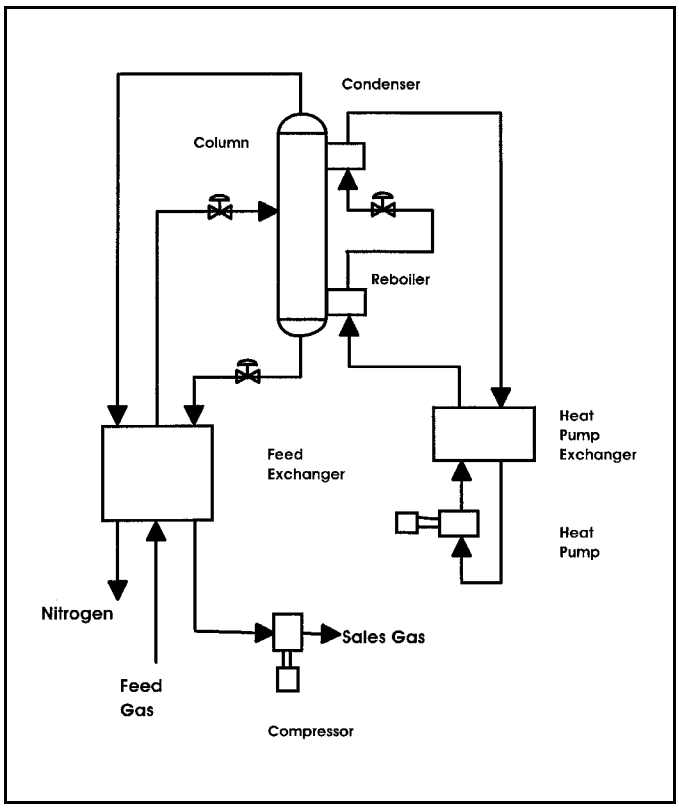
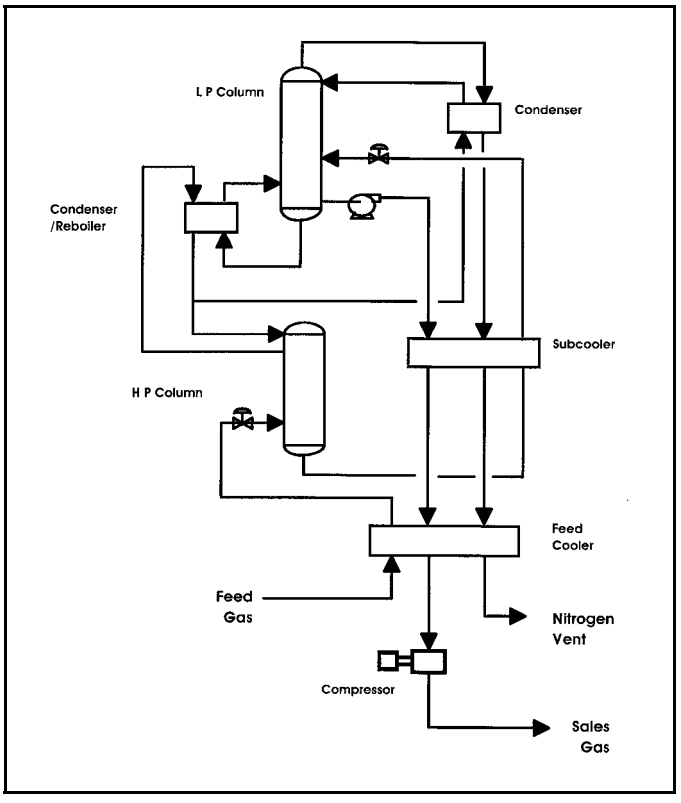


FIG. 16-39

Two-Column NRU[14]



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Second, the gas injected may be nitrogen with little or no hydrocarbons. In this case the injection conditions are chosen such that the nitrogen becomes miscible with the oil phase. As the oil is produced, the nitrogen and associated gas are produced as a mixed gas phase. This produced gas can be reinjected or processed for fuel, sales gas and NGL production. The processes used for this processing are as described in the previous paragraphs. The exact process considerations are somewhat different since the nitrogen is now desired at high pressure for reinjection, but the overall process is as described for naturally occurring high nitrogen gas.

The third type of EOR process involves the injection of CO_2. Large volumes of CO_2 are injected into the reservoir and become miscible with the oil phase. This CO_2 essentially scrubs the oil from the reservoir and can greatly increase oil production. As with the miscible nitrogen injection projects, the CO_2 is produced with the oil and gas and must be handled in the gas processing facilities. The CO_2 that is injected into the reservoir is typically purchased from third party suppliers and is the single greatest operating cost in the EOR project. Therefore, the CO_2 produced with the associated gas is valuable and must be recovered and recycled to the reservoir.

CO_2 Processing for EOR

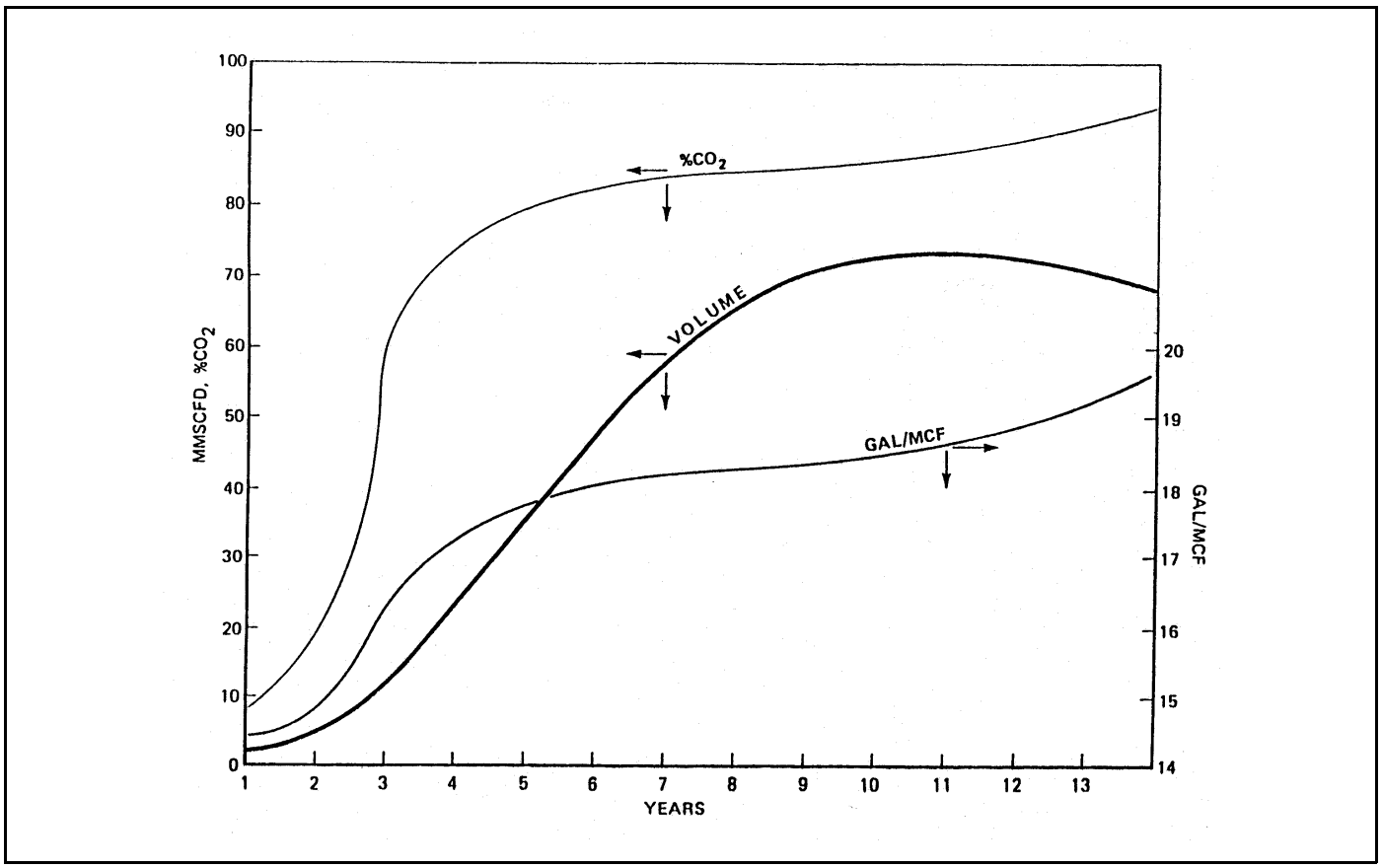
The CO_2 produced in an EOR project can be separated from the hydrocarbon components using solvent or membrane processes as described in Section 21 of this Data Book. However, solvent processes such as amines, potassium carbonate, and physical solvents, as well as membrane systems, were not designed to handle the large volumes of CO_2 which are present in the EOR gas. The capital and operating costs of these systems increase in proportion to the acid gas content. Additionally, the CO_2 is produced at low pressure and typically saturated with water. The EOR project needs high pressure, dry CO_2 for reinjection.

An EOR gas processing plant is designed for three primary separations. First, the methane in the gas is needed for fuel and possibly for gas sale for additional revenue. Second, the produced gas often contains hydrogen sulfide (H_2S) which is removed from the CO_2 stream for safety considerations. Third, EOR gas is typically rich in recoverable NGLs. Fig. 16-40 is an example EOR production profile. This example shows the effect of the EOR operations on the gas to be handled. The CO_2 may start out at a few percent but eventually builds to over 90% as the gas volume increases. The NGL curve in Fig. 16-41 (on a CO_2 free basis) shows that the hydrocarbon portion of the gas gets continually richer. In fact, in most projects, the in-situ oil is actually stripped of the midrange hydrocarbons such that over 10% of the crude production is in the gas phase with the CO_2.

All of the required separations could be performed in a fractionation process which would produce dry CO_2 at elevated pressure as one of the products. Each step of the separation of C_1, CO_2, H_2S, and C_2+ components has technology issues which must be addressed with non-traditional concepts to achieve the necessary separations by fractionation.

FIG. 16-40

Example EOR Production Forecast[15]



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Separation of CO_2 and Methane

The relative volatility of CO_2 and methane at typical operating pressures is quite high, usually about 5 to 1. From this standpoint, distillative separation should be quite easy. However, at processing conditions, the CO_2 will form a solid phase if the distillation is carried out to the point of producing high purity methane. The phase equilibria considerations in this separation are discussed in detail in Section 25 of this Data Book. Fig. 16-41 illustrates the theoretical limits of methane purity which can be obtain in a binary CO_2 /methane system. In practice the purity limits of the methane product are around 10–15% CO_2.

One approach to solving this methane-CO_2 distillation problem is to use an extractive distillation approach developed by Ryan/Holmes. This concept involves adding a heavier hydrocarbon stream to the condenser in a fractionation column. The addition of this stream, which can contain ethane and heavier hydrocarbons, significantly alters the solubility characteristics of the system such that virtually any purity of methane can be produced.

Fig. 16-42 illustrates the effect of adding a third component (in this case n-butane) to a CO_2-methane distillation column producing 2% CO_2 overhead. By adding n-butane, a column operation profile without CO_2 solid formation can be achieved. Adding greater amounts of the additive increases the safety margin away from the CO_2 solid formation region. Other characteristics of this additive addition concept include:

- Raising the operating temperature of the overhead
- Increasing CO_2/methane relative volatility
- Permitting higher pressure operation by raising the mixture critical pressure

In fact, additive flow can be increased to the point that propane refrigeration can be used for the overhead condenser rather than cascade refrigeration.

CO_2-Ethane Separation

The separation of CO_2 and ethane by distillation is limited by the azeotrope formation between these components. An azeotropic composition of approximately 67% CO_2, 33% ethane is formed at virtually any pressure.

Fig. 16-43 shows the CO_2-ethane system at two different pressures. The binary is a minimum boiling azeotrope at both pressures with a composition of about two thirds CO_2 and one third ethane. Thus, any attempt to separate CO_2 and ethane to nearly pure components by distillation cannot be achieved by traditional methods. Extractive distillation is required.

As developed by Ryan and Holmes, the technique involves the addition of a heavier hydrocarbon, usually butane or heavier, to the top section of the distillation column.

The upper dashed line in Fig. 16-43 represents the phase behavior of a multicomponent feed distilled with a butane-plus additive. With this technique, virtually any purity of CO_2 and ethane is thermodynamically possible.

For the CO_2-methane separation, the additive is introduced in the condenser. In the CO_2-ethane separation, the additive is normally introduced several trays below the top of the column. The primary CO_2-ethane distillation is achieved below the additive feed tray. It is in this area that the relative volatility of the CO_2 to ethane is reversed to remain above 1.0 and

FIG. 16-41

Distillation Profile CH_4–CO_2 Binary[17]

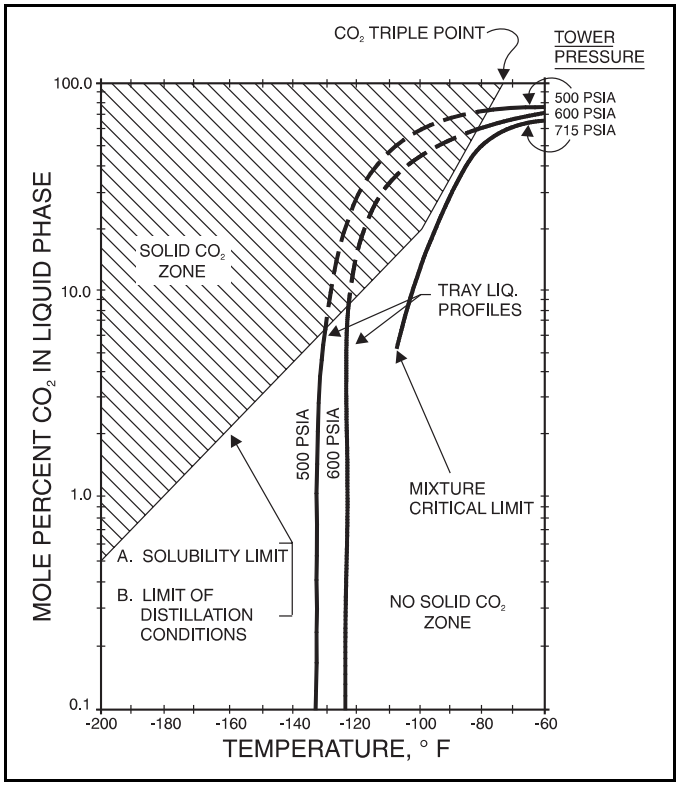
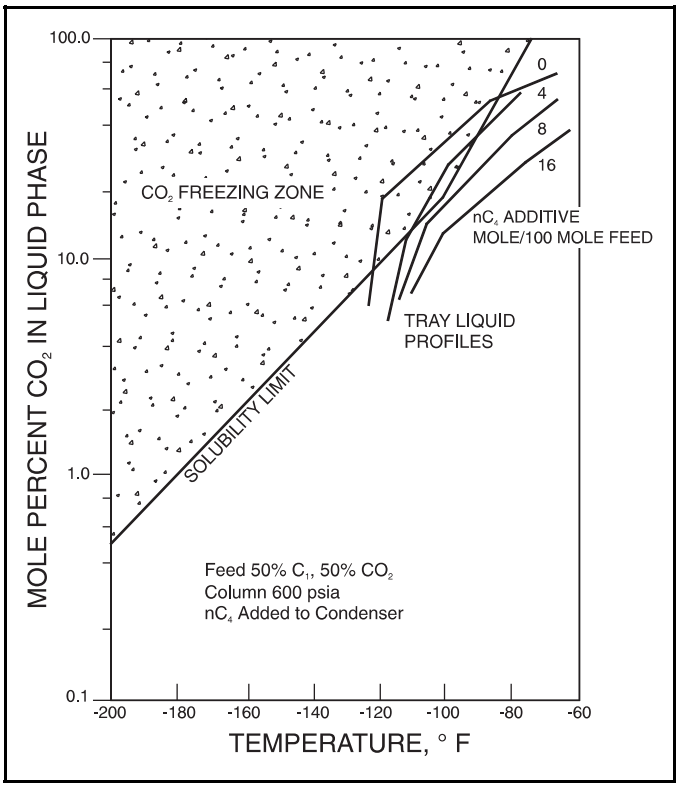


FIG. 16-42

Distillation Profile Binary Feed with nC_4 Additive[16]



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the azeotrope is circumvented. High relative volatilities are obtained at all points on and below the additive feed tray.

In the top portion of the column above the additive feed tray, no resolution of the azeotrope is achieved, as the relative volatility of CO_2 /ethane is less than 1.0. This part of the column serves as a recovery zone for the extractive distillation additive.

Separation of CO_2 and H_2S

The distillative separation of CO_2 and H_2S can be performed with traditional methods. The relative volatility of CO_2 and H_2S is quite small. While an azeotrope between H_2S and CO_2 does not exist, the vapor liquid equilibrium behavior for this binary approaches azeotropic character at high CO_2 concentrations.

In many cases the CO_2 is required to contain less than 100 ppmv H_2S. In order to achieve such purity a very large fractionation tower is required with large energy requirements.

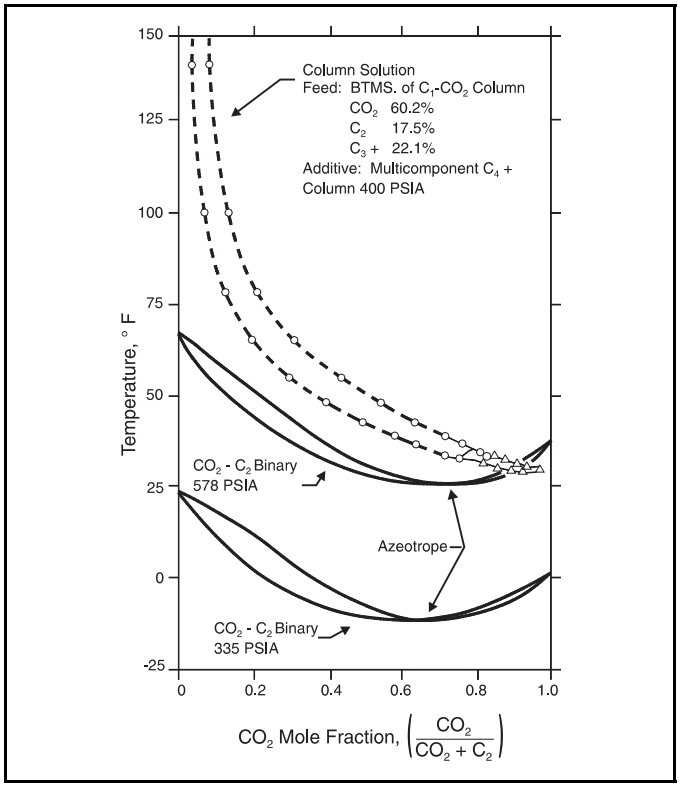
Another aspect to be considered is the CO_2 in the bottom (H_2S concentrated) stream. If fed to a Claus sulfur recovery plant, the CO_2 /H_2S ratio is desired to be less than 2 to 1. Achieving such a low ratio will require high energy input in many cases.

By adding a third component, as in the CO_2-ethane separation system, the relative volatility of CO_2 to H_2S is significantly enhanced. Fig. 16-44 demonstrates the relative volatility enhancement due to addition of n-butane to the CO_2–H_2S binary system.

Thus, if a system containing CO_2, ethane and H_2S is processed in an extractive distillation column, the ethane and H_2S can be separated from the CO_2. The exact specification for purity and recovery will determine the system operating requirements. From a thermodynamic standpoint the CO_2 could be produced overhead with the ethane and the H_2S (and any C_3+ components) produced as a mixed bottom product.

FIG. 16-43

Vapor-Liquid Equilibria CO_2–C_2H_6[16]



Overall Process Configuration

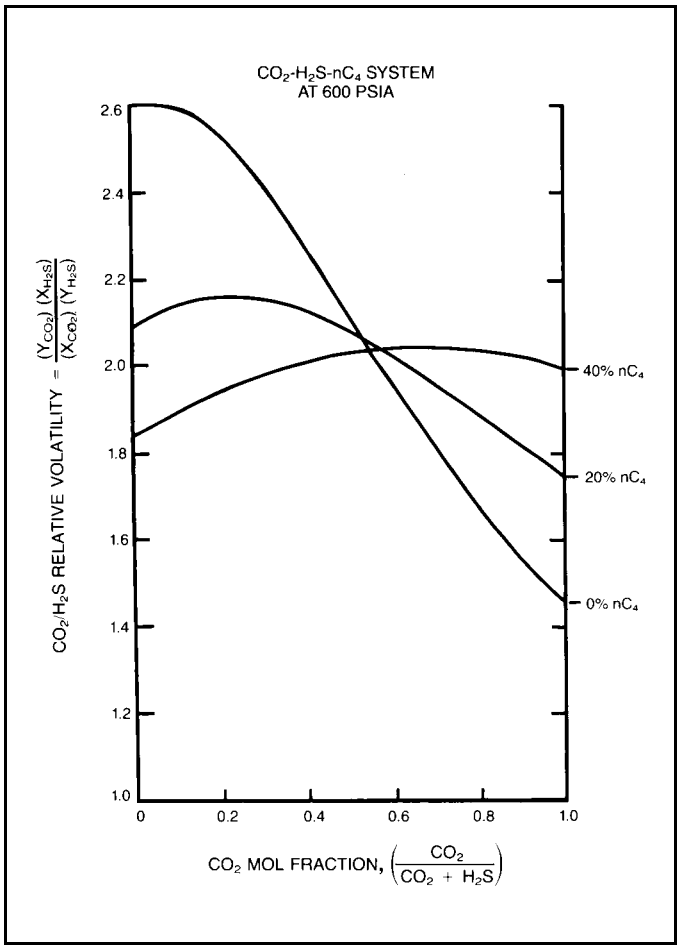
The EOR processing steps can be arranged in a system to achieve all the desired separations. Although the process configuration can take on several variations, the configuration most often used in EOR processing plant is shown in Fig. 16-45.

In this configuration, the first step is the ethane/CO_2 separation in the ethane recovery column. This separation is carried out at pressures in the 350 psig range using refrigeration for reflux in the 0°F range. The CO_2 and lighter components are taken overhead, compressed to around 650 psig and sent to the CO_2 recovery column. This is a bulk removal column which produces CO_2 as a liquid bottom product. This CO_2 can then be pumped to reinjection. The overhead product is essentially a CO_2 /C_1 binary which is limited by CO_2 solid formation considerations. This binary stream is then separated by use of the extractive distillation step to produce a methane stream with low CO_2 content.

The bottoms products from the ethane recovery and demethanizer columns are combined and processed in the additive recovery column. In this column the additive, which is a

FIG. 16-44

CO_2–H_2S–nC_4 System at 600 psia[19]



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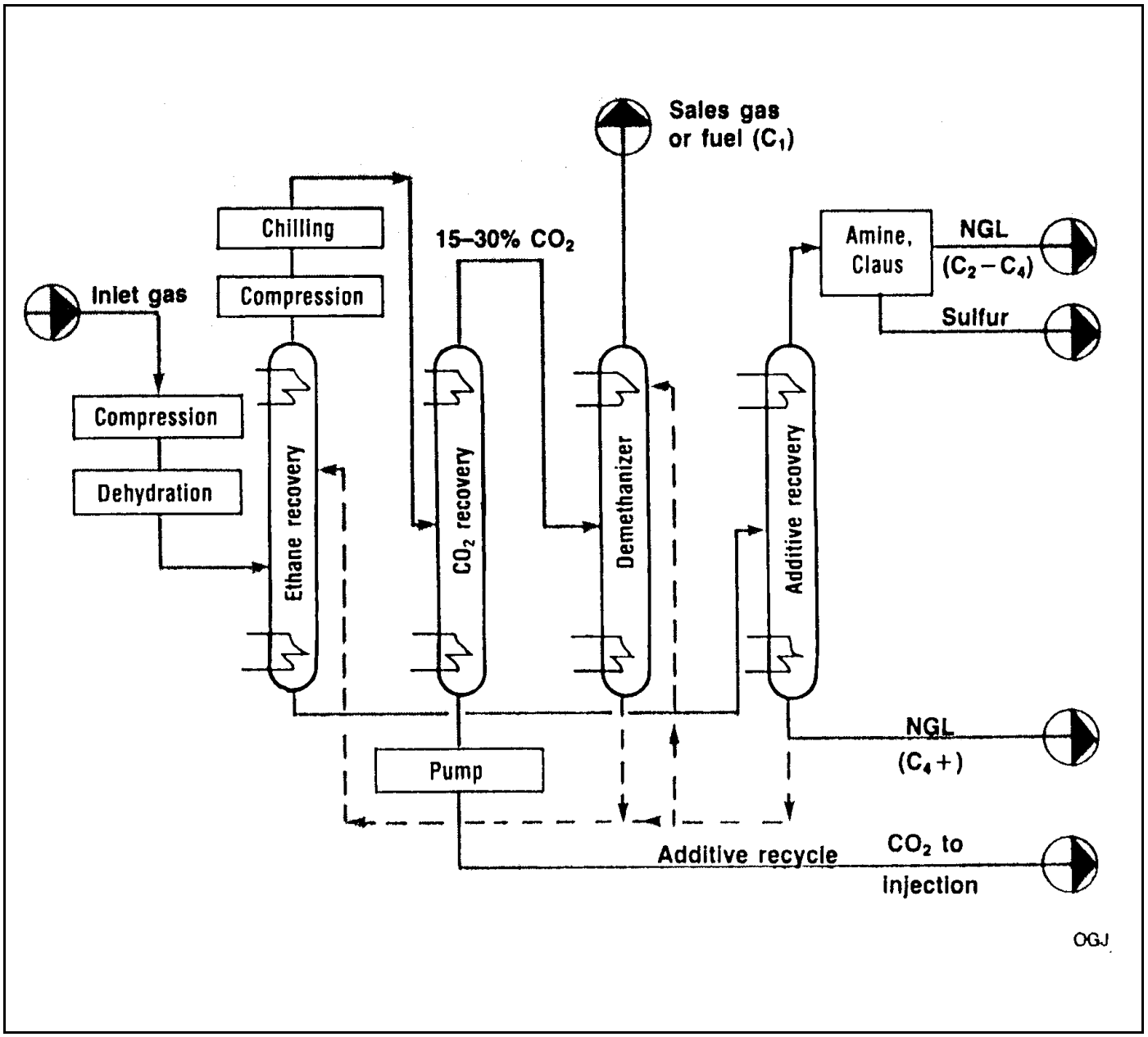
C_4+ stream, is separated from the lighter hydrocarbons for recycle to the distillation columns. A net C_4+ product is also produced. The additive used in the ethane recovery and demethanizer columns is continuously regenerated and reused much the same as lean oil in traditional gas processing applications. The distinct difference in this case is that this C_4+ stream is generated from the feed gas and is used as an extractive distillation agent rather than as an absorption agent.

The light NGL product produced overhead in the additive recovery column also contains any H_2S which was present in the feed gas and some residual CO_2. This product is usually treated in a small amine unit to meet sales specifications. The acid gas may then be sent to a sulfur recovery unit.

This four column EOR processing plant is designed to handle the wide range of feed rates and compositions encountered in EOR projects. In the design effort early, peak and late year cases must be investigated to ensure proper operation over time. This is especially important since the exact timing, flow rate and composition of EOR production are extremely difficult to predict. CO_2 breakthrough to the processing plant can occur rapidly. In some projects the CO_2 volume can triple in less than one year. As the EOR process has matured, other configurations have been developed which mix technologies such as membranes with Ryan/Holmes facilities to optimize the capital and operating costs over the project life.

FIG. 16-45

Four-Column Ryan/Holmes Process[15]



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SECTION 17

Fluid Flow and Piping

Few flow problems can be solved with an acceptable degree of accuracy when using equations designed to fit idealized applications. Flow regimes and associated pressure drops are complex phenomena and require complex equations to predict their relationships. For engineering design purposes, several empirical formulas have been developed to fit particular circumstances in predicting flow capacity and pressure drop.

FIG. 17-1

Nomenclature

- A = pipe cross sectional area, ft^2 ($A = \pi D^2/4$)
- c = sum of allowances for corrosion, erosion, etc., in., Fig. 17-23
- C = design parameter used in Hazen and Williams formula, Eq. 17-33
- C_1 = discharge factor from Fig. 17-8
- C_2 = size factor from Fig. 17-9
- d = internal diameter of pipe, in.
- d_o = outside pipe diameter, in.
- D = internal diameter of pipe, feet
- E = pipeline efficiency factor (fraction)
- E' = longitudinal weld joint factor from ANSI B31.3, Fig. 17-23
- E'' = longitudinal joint factor from ANSI B31.8, Fig. 17-24
- f_f = Fanning friction factor
- f_m = Moody friction factor ($f_m = 4.0\ f_f$)
- f_n = single phase friction factor for Dukler calculation, from Eq 17-44
- f_{tpr} = friction factor ratio for Dukler calculation, Fig. 17-17
- F''' = construction type design factor used in ANSI B31.8, Fig. 17-24
- F_{pv} = volume correction for a non-ideal fluid due to compressibility from Eq 17-13
- $\sqrt{1/f_f}$ = transmission factor
- g = acceleration due to gravity, 32.2 ft/sec^2
- g_c = gravitational constant, 32.2 $(ft \cdot lbm)/(lbf \cdot sec^2)$
- h_L = loss of static pressure head due to fluid flow, feet of fluid
- H = total energy of a fluid at a point above a datum, from Eq 17-1
- H_{Ld} = liquid holdup fraction (Dukler), Fig. 17-18
- H_{Le} = liquid holdup fraction (Eaton), Fig. 17-20
- H_{Lf} = liquid holdup fraction (Flanigan), Fig. 17-19
- I_L = liquid inventory in pipe, ft^3, from Eq 17-57
- L = length of line, feet
- L_m = length of line, miles
- MW = molecular weight
- N_x = Fig. 17-16 horizontal coordinate, ft/sec
- N_y = Fig. 17-16 vertical coordinate, ft/sec
- N_E = abscissa of Eaton correlation, Fig. 17-20
- N_{Lv} = liquid velocity number, from Eq 17-53
- N_{gv} = gas velocity number, from Eq 17-54
- N_d = pipe diameter number, from Eq 17-55
- N_L = liquid viscosity number, from Eq 17-56
- P = pressure, psia
- P_1 = inlet pressure, psia
- P_2 = outlet pressure, psia
- P_{avg} = average pressure, psia, from Eq 17-16
- P_b = base absolute pressure, psia (ANSI 2530 specification: $P_b = 14.73$ psia)
- P_i = internal design pressure, psig
- ΔP_{100} = pressure drop, psi/100 ft equivalent pipe length
- ΔP_e = elevation component of pressure drop, psi
- ΔP_f = frictional component of pressure drop, psi
- ΔP_t = total pressure drop, psi
- q = flow rate, gal./min
- Q = flow rate of gas, cubic feet per day at base conditions
- Q_L = liquid volumetric flow rate at flowing conditions, ft^3/sec
- Q_g = gas volumetric flow rate at flowing conditions, ft^3/sec
- Re = Reynolds number
- Re_y = mixture Reynolds number for Dukler calculation, from Eq 17-45
- S = specific gravity of flowing gas (air = 1.0)
- S' = allowable stress, psi, Fig. 17-23
- S'' = specified minimum yield strength, psi, Fig. 17-24
- t = thickness, in., Figs. 17-23, 17-24
- t_m = minimum required wall thickness, in., Fig. 17-23
- T = absolute temperature of flowing gas, °R
- T'' = temperature derating factor used in ANSI B31.8, Fig. 17-24
- T_{avg} = average temperature, °R, [$T_{avg} = 1/2\ (T_{in} + T_{out})$]
- T_b = base absolute temperature, °R (ANSI 2530 specification: $T_b = 520$°R)
- V = single phase fluid velocity, ft/sec
- V_{sg} = superficial gas velocity, ft/sec, from Eq 17-36
- V_{sL} = superficial liquid velocity, ft/sec, from Eq 17-35
- V_m = mixture velocity, ft/sec, from Eq 17-46

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FIG. 17-1 (Cont'd)
Nomenclature

W = mass flow, lb/hr
X_A = Aziz fluid property correction factor (horizontal axis, Fig. 17-16)
Y_A = Aziz fluid property correction factor (vertical axis, Fig. 17-16)
Y' = coefficient found in Table 304.1.1, ANSI B31.3, Fig. 17-23
Z_{avg} = average compressibility factor
Z_e = pipeline vertical elevation rise, ft
ε = absolute roughness, ft
λ = flowing liquid volume fraction
μ_e = single phase fluid viscosity, $lb_m/(ft \cdot sec)$
μ = single phase fluid viscosity, cp
μ_g = gas viscosity, cp
μ_L = liquid viscosity, cp
μ_n = mixture viscosity for Dukler calculation, cp
ρ = single phase fluid density, lb/ft^3
ρ_{avg} = average density, lb/ft^3 [$\rho_{avg} = 1/2\ (\rho_{in} + \rho_{out})$]
ρ_a = air density at 60°F and 14.7 psia, 0.0764 lb/ft^3
ρ_w = water density at 60°F and 14.7 psia, 62.4 lb/ft^3
ρ_g = gas density, lb/ft^3
ρ_L = liquid density, lb/ft^3
ρ_k = two phase mixture density for Dukler calculation, lb/ft^3
σ = interfacial tension at flowing conditions, dyne/cm
σ_{wa} = interfacial tension of air and water at 60°F and 14.7 psia, 72.4 dyne/cm

Bernoulli's Theorem

The Bernoulli Theorem[1] is a mathematical derivation based on the law of conservation of energy. This theorem states that the total energy of a fluid at any particular point above a datum plane is the sum of the elevation head, the pressure head, and the velocity head. Stated mathematically:

$$H = Z_e + \frac{144\ P}{\rho} + \frac{V^2}{2g} \qquad \textbf{Eq 17-1}$$

If there are no friction losses and no energy is added to or taken from the system, H is constant for any point in the fluid. In reality, whenever fluid is moving there is friction loss (h_L). This loss describes the difference in total energy at two points in the system. Expressing the energy levels at Point 1 versus Point 2 then becomes:

$$Z_{el} + \frac{144\ P_1}{\rho_1} + \frac{V_1^2}{2g} = Z_{e2} + \frac{144\ P_2}{\rho_2} + \frac{V_2^2}{2g} + h_L \qquad \textbf{Eq 17-2}$$

All practical formulas for fluid flow are derived from the above. Modifications to Eq 17-2 have been proposed by many investigators to account for the friction losses.

Fluid Physical Properties

The physical properties of a flowing fluid must be known to predict pressure drop in piping. The two properties entering into the solution of most fluid flow problems are viscosity and density.

Viscosity expresses the readiness with which a fluid flows when it is acted upon by an external force. Two types of viscosity measurements are used, absolute and kinematic. Absolute viscosity is a measure of a fluid's internal resistance to deformation or shear. Kinematic viscosity is the ratio of absolute viscosity to mass density. The absolute viscosity will be used for all calculations in this section.

Viscosity is temperature dependent. The viscosity of most liquids decreases with an increase in temperature, whereas that of gases increases. Pressure has almost no effect on the viscosity of liquids or near perfect gases. On the other hand, the viscosity of saturated or slightly superheated vapors is changed appreciably by pressure changes. The viscosity of steam is readily available, but the viscosity of other vapors may not be known.

Specific volume is the inverse of density. Specific gravity of a liquid is the ratio of the density of the liquid at a specified temperature to the density of water at 60°F. The specific gravity of gas is defined as the ratio of the molecular weight of the gas to the molecular mass of air.

$$S = \frac{MW\,(gas)}{MW\,(air)} \qquad \textbf{Eq 17-3}$$

Flow in Pipes and Reynolds Number

At low velocities, fluid molecules or particles carried by the fluid move in a reasonably straight line. Velocity of the fluid is maximum at the center of the pipe and zero at the pipe wall. This flow pattern is referred to as laminar. If the velocity is increased it will reach a critical point where fluid particles begin to show a random motion transverse to the direction of flow. This is the critical velocity. This random motion is typical of what is referred to as turbulent flow. Above the critical velocity the flow is considered to be completely turbulent even though there is always a boundary layer at the pipe wall where flow is laminar. In the turbulent zone the velocity profile is more nearly straight across the face of the pipe.

Reynolds developed a dimensionless number that may be considered as the ratio of the dynamic forces of mass flow to the shear stress due to viscosity. The Reynolds number is:

$$Re = \frac{DV\rho}{\mu_e} \qquad \textbf{Eq 17-4}$$

If the Reynolds number is less than 2000, flow may be considered laminar. If it is above 4000, the flow is turbulent. In the zone between 2000 and 4000 the flow could be either turbulent or laminar, but cannot be predicted by the Reynolds number.

If a non-circular conduit is encountered, the Reynolds number can be approximated by using an equivalent diameter for D. The equivalent diameter would equal four (4) times the hydraulic radius. The hydraulic radius is defined as:

$$\text{Hydraulic Radius} = \frac{\text{Area of Flowing Fluid}}{\text{Wetted Perimeter}} \qquad \textbf{Eq 17-5}$$

This conversion would not apply to extremely narrow shapes where the width is small relative to the length. In such cases an approximation may be used wherein one-half the width of the passage is equal to the hydraulic radius.

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Pressure Loss Due to Friction

Flow is always accompanied by friction. This friction results in a loss of energy available for work. A general equation for pressure drop due to friction is the Darcy-Weisbach[2] (often referred to as simply the Darcy) equation. This equation can be rationally derived by dimensional analysis, with the exception of the friction factor, fm, which must be determined experimentally. Expressed in feet of fluid this equation is:

$$h_L = \frac{f_m L V^2}{2 g D} \qquad \textbf{Eq 17-6}$$

Converting to pounds per square inch, the equation becomes:

$$\Delta P_f = \frac{\rho f_m L V^2}{(144) D (2g_c)} \qquad \textbf{Eq 17-7}$$

It should be noted that the Moody friction factor3, fm, is used in the equations above. Some equations are shown in terms of the Fanning friction factor, ff, which is one fourth of fm (fm = 4.0 ff). A graph of both Fanning and Moody friction factors as a function of Reynolds number appears in Fig. 17-2.

The Darcy-Weisbach equation is valid for both laminar and turbulent flow of any liquid, and may also be used for gases with certain restrictions. When using this equation, changes in elevation, velocity, or density must be accounted for by applying Bernoulli's theorem. The Darcy-Weisbach equation must be applied to line segments sufficiently short such that fluid density is essentially constant over that segment. The overall pressure drop is the sum of the Δ Pf values calculated for the individual segments. For gas applications the segmental length may be relatively short, as compared to liquid applications, since many gas applications involve compressible gases where gas densities vary with pressure.

Friction Factor and Effect of Pipe Roughness

When the fluid flow is laminar (Re<2000), the friction factor has a direct relationship to the Reynolds number, such that:

$$f_m = 64/Re \quad \text{or} \quad f_f = 16/Re \qquad \textbf{Eq 17-8}$$

Pipe roughness has no effect on the friction factor in laminar flow.

Substitution of the formula for Reynolds number, Eq 17-4, into Eq 17-8, yields the following:

$$f_m = \frac{64 \mu_e}{DV\rho} = \left(\frac{64}{V\rho}\right)\left(\frac{\mu}{1488}\right)\left(\frac{12}{d}\right) \qquad \textbf{Eq 17-9}$$

This expression can then be substituted for the friction factor in Eq 17-7, resulting in the following formula for pressure loss in pounds per square inch:

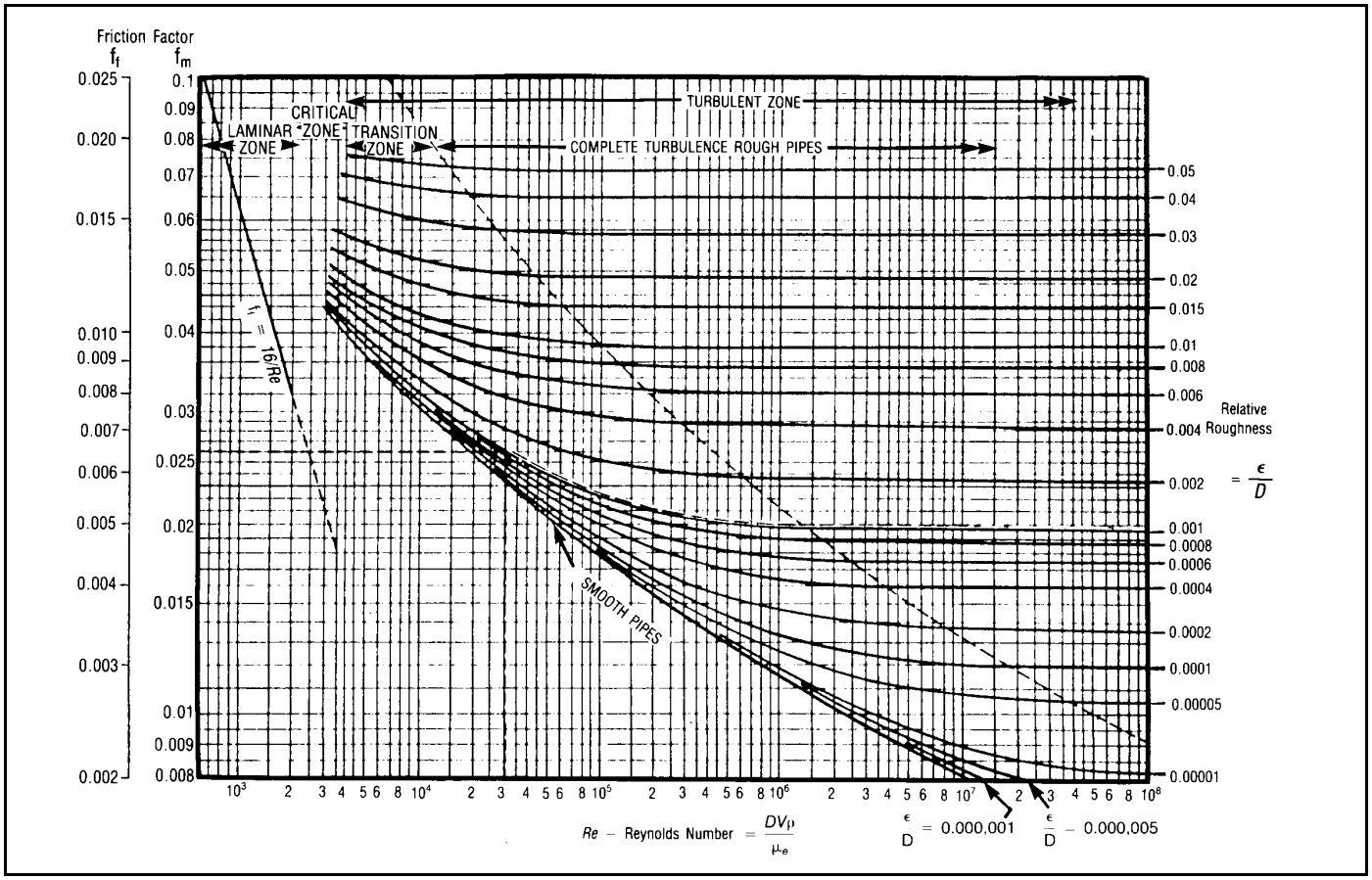
$$\Delta P_f = 0.000668 \frac{\mu LV}{d^2} \qquad \textbf{Eq 17-10}$$

Eq 17-10 is commonly known as Poiseuille's law for laminar flow.

When the flow is turbulent, the friction factor depends on the Reynolds number and the relative roughness of the pipe,

FIG. 17-2

Friction Factors[5]



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ε/D, which is the roughness of the pipe, ε, over the pipe diameter, D. Fig. 17-2 incorporates the relative roughness of the pipe into the determination of the friction factor. Fig. 17-3 indicates relative roughness and friction factors for various piping materials. These figures are based on the iterative solution of the following equation developed by Colebrook.4

$$\frac{1}{\sqrt{f_m}} = -2 \log_{10}\left(\frac{\varepsilon}{3.7\,D} + \frac{2.51}{Re\sqrt{f_m}}\right) \qquad \textbf{Eq 17-11}$$

Various explicit equations have been presented which provide a direct solution for the friction factor. The equation below was proposed by Chen[30] and is accurate and is almost identical to the Colebrook equation over Reynolds Numbers (4000 to $4(10)^8$) and roughness factors (e/D) from 0.05 to $5(10)^{-7}$.

$$A = \log\left[\frac{\left(\frac{\varepsilon}{D}\right)^{1.1098}}{2.8257} + \left(\frac{5.8506}{Re^{0.8981}}\right)\right] \qquad \textbf{Eq 17-11a}$$

$$f_m = \frac{1}{\left(-2 \cdot \log\left(\frac{\frac{\varepsilon}{D}}{3.7065} - \frac{5.0452 \cdot A}{Re}\right)\right)^2} \qquad \textbf{Eq 17-11b}$$

Equivalent Length of Valves and Fittings

The pressure drop effects of valves and fittings can be accounted for by addition of the "equivalent lengths" of the fittings to the actual piping lengths. This augmented pipe length is then used in any of the following pressure drop calculation techniques. A table of equivalent lengths for a number of representative valves and fittings appears in Fig. 17-4.

Compressibility of Gases

For more accurate values of Z, refer to Section 23. For more approximate calculations, the value of the average compressibility factor, Z_{avg}, may be calculated from the following equations:

$$Z_{avg} = \frac{1}{(F_{pv})^2} \qquad \textbf{Eq 17-12}$$

and

$$F_{pv} = \left(1 + \left[\frac{(P_{avg})\,(3.444)\,(10^5)\,(10^{(1.785)(S)})}{T_{avg}^{3.825}}\right]\right)^{0.5} \qquad \textbf{Eq 17-13}$$

Fig. 17-5 contains a plot of the deviation factor, F_{pv}^2.

An estimate for Z_{avg} at pressures below 100 psi is:

$$Z_{avg} = \frac{1}{1 + 0.0002\,P_{avg}} \qquad \textbf{Eq 17-14}$$

SINGLE PHASE FLOW

Transmission Line Gas Flow

Isothermal Flow — The steady-state, isothermal flow behavior of gas in pipelines is defined by a general energy equation of the form:

$$Q = 38.77\left(\frac{T_b}{P_b}\right)E\sqrt{\frac{1}{f_f}}\left[\frac{P_1^2 - P_2^2}{S\,L_m\,T_{avg}\,Z_{avg}}\right]^{0.5} d^{2.5} \qquad \textbf{Eq 17-15}$$

This equation is completely general for steady-state flow, and adequately accounts for variations in compressibility factor, kinetic energy, pressure, and temperature for any typical line section. However, the equation as derived involves an unspecified value of the transmission factor, $\sqrt{1/f_f}$. The correct representation of this friction factor is necessary to the validity of the equation.

The friction factor is fundamentally related to the energy lost due to friction. In the derivation of the general energy equation, all irreversibilities and non-idealities, except for those covered by the real gas law, have been collected into the friction loss term.

Empirical methods historically and currently used to calculate or predict the flow of gas in a pipeline are the result of various correlations of the transmission factor substituted into the general energy equation.

Examination of the relationships presented by various authors shows that their forms differ primarily in the inherent or specified representation of the transmission factor which defines the energy lost in resistance to flow for various pipe sizes, roughnesses, flow conditions, and gases.

To obtain Eq 17-15, which is convenient for general calculations, a number of simplifying assumptions have been made. For other than pipeline sections with a very high pressure gradient, the change in the kinetic energy of the gas is not significant, and is assumed equal to zero. It is also assumed that the gas temperature is constant at an average value for the section considered; the compressibility factor is constant at the value characterized by the average gas temperature and pressure; and in the term giving the effect of elevation change, the pressure is constant at the average value. In the range of conditions to which pipeline flow equations are ordinarily applied, averages are usually sufficiently accurate. Average temperatures are calculated as indicated in Fig. 17-1.

The average pressure in the line can be computed by:

$$P_{avg} = \frac{2}{3}\left(P_1 + P_2 - \frac{P_1 P_2}{P_1 + P_2}\right) \qquad \textbf{Eq 17-16}$$

In the absence of field data indicating otherwise, an efficiency factor, E, of 1.0 is usually assumed.

The AGA Equations — The AGA Equations were developed to approximate partially and fully turbulent flow using two different transmission factors. The fully turbulent flow equation accounts for the relative pipe roughness, ε/D, based on the rough-pipe law.[4] This equation uses the following transmission factor:

$$\sqrt{1/f_f} = 4 \log_{10}\left(\frac{3.7\,D}{\varepsilon}\right) \qquad \textbf{Eq 17-17}$$

When the transmission factor for fully turbulent flow is substituted in the general energy equation (Eq 17-15), the AGA Equation for fully turbulent flow becomes:

$$Q = 38.77\left(\frac{T_b}{P_b}\right)E\left[4 \log_{10}\left(\frac{3.7\,D}{\varepsilon}\right)\right]\left[\frac{P_1^2 - P_2^2}{S\,L_m\,T_{avg}\,Z_{avg}}\right]^{0.5} d^{2.5} \qquad \textbf{Eq 17-18}$$

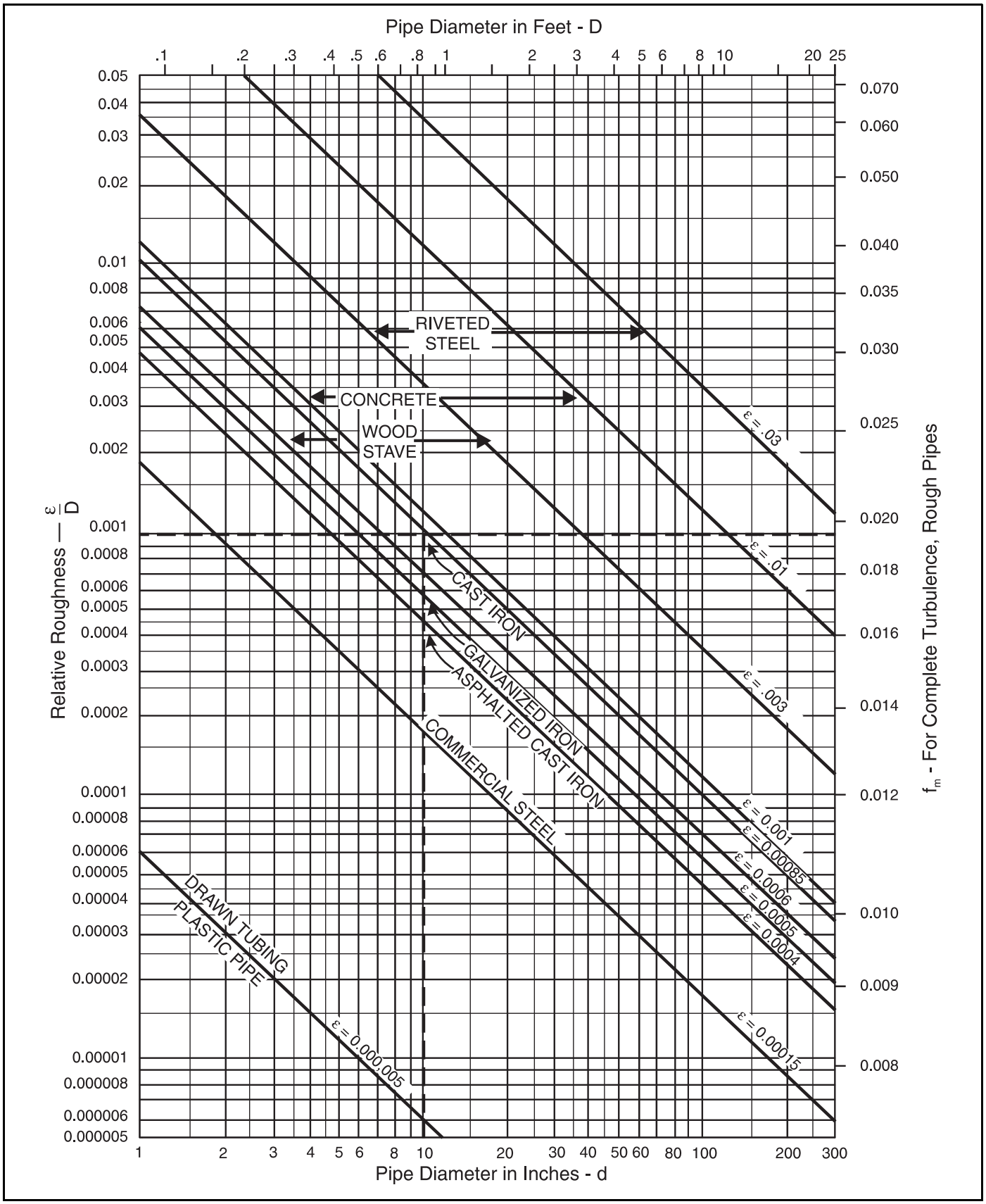
The partially turbulent flow equation is based on the smooth-pipe law[4] and is modified to account for drag-inducing elements. The transmission factor for this equation is:

$$\sqrt{1/f_f} = 4 \log_{10}\frac{R_e}{\sqrt{1/f_f}} - 0.6 \qquad \textbf{Eq 17-19}$$

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FIG. 17-3

Relative Roughness of Pipe Materials and Friction Factors for Complete Turbulence[5]



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FIG. 17-4

Equivalent Length of Valves and Fittings in Feet

Nominal Pipe size in.	Globe valve or ball check valve	Angle valve	Swing check valve	Plug cock	Gate or ball valve	45° ell		Short rad. ell		Long rad. ell		Hard T		Soft T		90° miter bends			Enlargement					Contraction				
																			Sudden			Std. red.		Sudden			Std. red.	
																			Equiv. L in terms of small d									
						Welded	Threaded	Welded	Threaded	Welded	Threaded	Welded	Threaded	Welded	Threaded	2 miter	3 miter	4 miter	d/D = 1/4	d/D = 1/2	d/D = 3/4	d/D = 1/2	d/D = 3/4	d/D = 1/4	d/D = 1/2	d/D = 3/4	d/D = 1/2	d/D = 3/4
1½	55	26	13	7	1	1	2	3	5	2	3	8	9	2	3				5	3	1	4	1	3	2	1	1	–
2	70	33	17	14	2	2	3	4	5	3	4	10	11	3	4				7	4	1	5	1	3	3	1	1	–
2½	80	40	20	11	2	2	–	5	–	3	–	12	–	3	–				8	5	2	6	2	4	3	2	2	–
3	100	50	25	17	2	2		6		4		14		4					10	6	2	8	2	5	4	2	2	–
4	130	65	32	30	3	3		7		5		19		5					12	8	3	10	3	6	5	3	3	–
6	200	100	48	70	4	4		11		8		28		8					18	12	4	14	4	9	7	4	4	1
8	260	125	64	120	6	6		15		9		37		9					25	16	5	19	5	12	9	5	5	2
10	330	160	80	170	7	7		18		12		47		12					31	20	7	24	7	15	12	6	6	2
12	400	190	95	170	9	9		22		14		55		14		28	21	20	37	24	8	28	8	18	14	7	7	2
14	450	210	105	80	10	10		26		16		62		16		32	24	22	42	26	9	–	–	20	16	8	–	–
16	500	240	120	145	11	11		29		18		72		18		38	27	24	47	30	10	–	–	24	18	9	–	–
18	550	280	140	160	12	12		33		20		82		20		42	30	28	53	35	11	–	–	26	20	10	–	–
20	650	300	155	210	14	14		36		23		90		23		46	33	32	60	38	13	–	–	30	23	11	–	–
22	688	335	170	225	15	15		40		25		100		25		52	36	34	65	42	14	–	–	32	25	12	–	–
24	750	370	185	254	16	16		44		27		110		27		56	39	36	70	46	15	–	–	35	27	13	–	–
30	–	–	–	312	21	21		55		40		140		40		70	51	44										
36	–	–	–		25	25		66		47		170		47		84	60	52										
42	–	–	–		30	30		77		55		200		55		98	69	64										
48	–	–	–		35	35		88		65		220		65		112	81	72										
54	–	–	–		40	40		99		70		250		70		126	90	80										
60	–	–	–		45	45		110		80		260		80		190	99	92										

Substituting $\sqrt{1/f_f}$ from Eq 17-19 into Eq 17-15 does not provide an equation which can be solved directly. For partially turbulent flow a frictional drag factor must also be applied to account for the effects of pipe bends and irregularities. These calculations are beyond the scope of this book and the AGA "Steady Flow in Gas Pipelines"[6] should be consulted for a detailed treatment of partially turbulent flow.

The Weymouth Equation — The Weymouth Equation, published in 1912[7], evaluated the coefficient of friction as a function of the diameter.

$$f_f = \frac{0.008}{d^{1/3}} \qquad \textbf{Eq 17-20}$$

$$\sqrt{1/f_f} = 11.18\, d^{1/6} \qquad \textbf{Eq 17-21}$$

When the friction factor, f_f, is substituted in the general energy equation, Weymouth's Equation becomes:

$$Q = (433.5)\left(\frac{T_b}{P_b}\right) E \left[\frac{P_1^2 - P_2^2}{S\, L_m\, T_{avg}\, Z_{avg}}\right]^{0.5} d^{2.667} \qquad \textbf{Eq 17-22}$$

The Weymouth formula for short pipelines and gathering systems agrees more closely with metered rates than those calculated by most other formulae. However, the degree of error increases with pressure. If the Q calculated from the Weymouth formula is multiplied by $\sqrt{1/Z}$, where Z is the compressibility factor of the gas, the corrected Q will closely approximate the metered flow. Fig. 17-5 shows a plot of the deviation factor, $\sqrt{1/Z}$, of a common gas and can be used safely if exact data is not available.

The equation cannot be generally applied to any variety of diameters and roughness, and in the flow region of partially developed turbulence, it is not valid. The Weymouth Equation may be used to approximate fully turbulent flow by applying correction factors determined from the system to which it is to be applied. Graphs showing gas flow calculations based on the Weymouth equation are shown in Fig. 17-6a and 17-6b.

Panhandle A Equation — In the early 1940s Panhandle Eastern Pipe Line Company developed a formula for calculation of gas flow in transmission lines which has become known as the Panhandle A Equation. This equation uses the following expressions of Reynolds number and transmission factor.

$$Re = 1.934\,\frac{Q_s S}{d} \qquad \textbf{Eq 17-23}$$

$$\sqrt{1/f_f} = 7.211\left(\frac{Q_s S}{d}\right)^{0.07305} = 6.872\,(Re)^{0.07305} \qquad \textbf{Eq 17-24}$$

The transmission factor assumes a Reynolds number value from 5 to 11 million based on actual metered experience.

Substituting Eq 17-24 for $\sqrt{1/f_f}$ in the general energy equation (Eq 17-15), the Panhandle A Equation becomes:

$$Q = 435.87\left(\frac{T_b}{P_b}\right)^{1.0788} E \left[\frac{P_1^2 - P_2^2}{S^{0.853}\, L_m\, T_{avg} Z_{avg}}\right]^{0.5392} d^{2.6182}$$

Eq 17-25

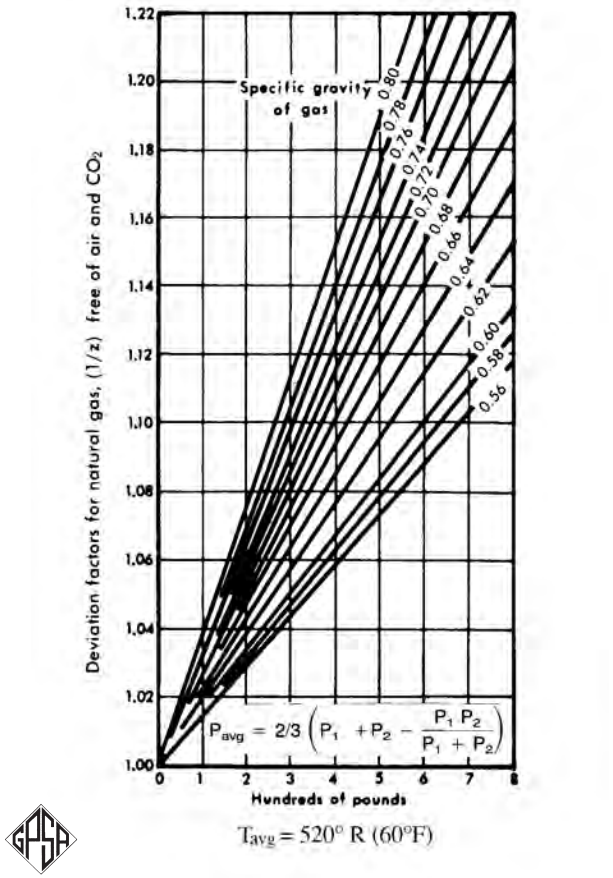
This equation was intended to reflect the flow of gas through smooth pipes. When "adjusted" with an efficiency factor, E, of about 0.90, the equation is a reasonable approximation of the partially turbulent flow equation. The equation becomes less accurate as flow rate increases. Many users of the Panhandle A Equation assume an efficiency factor of 0.92.

Panhandle B Equation — A new or revised Panhandle Equation was published in 1956. This revised equation is known as the Panhandle B Equation and is only slightly

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FIG. 17-5

Deviation Factors[8]



Note: Refer to Section 23 for more accurate compressibility factors.

Reynolds number dependent. Therefore, it more nearly approximates fully turbulent flow behavior. The transmission factor used here is:

$$\sqrt{1/f_f} = 16.70\left(\frac{QS}{d}\right)^{0.01961} = 16.49\,(Re)^{0.01961} \qquad \textbf{Eq 17-26}$$

Substituting Eq 17-23 for $\sqrt{1/f_f}$ in the general energy equation (Eq 17-15), the Panhandle B Equation becomes:

$$Q = 737\left(\frac{T_b}{P_b}\right)^{1.02} E\left[\frac{P_1^2 - P_2^2}{S^{0.961}\,L_m\,T_{avg}Z_{avg}}\right]^{0.51} d^{2.53} \qquad \textbf{Eq 17-27}$$

The equation can be adjusted through the use of an efficiency term that makes it applicable across a relatively limited range of Reynolds numbers. Other than this, however, there are no means for adjustment of the equation to correct it for variations in pipe surface. Adjusted to an average flowing Reynolds number, the equation will predict low flow rates at low Reynolds numbers, and high flow rates at high Reynolds numbers, as compared to a fully turbulent flow equation. Efficiencies based on the Panhandle B equation decrease with increasing flow rate for fully turbulent flow. The efficiency factor, E, used in the Panhandle B equation generally varies between about 0.88 and 0.94.

Conclusions — The successful application of these transmission line flow equations in the past has largely involved compensation for discrepancies through the use of adjustment factors, usually termed "efficiencies." These efficiencies are frequently found in practice by determining the constant required to cause predicted gas equation behavior to agree with flow data. As a result, the values of these factors are specific to particular gas flow equations and field conditions and, under many circumstances, vary with flow rate in a fashion that obscures the real nature of flow behavior in the pipe.

The Reynolds number dependent equations, such as the Panhandle equations, utilize a friction factor expression which yields an approximation to partially turbulent flow behavior in the case of the Panhandle A equation, and an approximation to fully turbulent behavior in the case of the Panhandle B.

These equations suffer from the substitution of a fixed gas viscosity value into the Reynolds number expression, which, in turn, substituted into the flow equation, results in an expression with a preconditioned bias.

Regardless of the merits of various gas flow equations, past practices may dictate the use of a particular equation to maintain continuity of comparative capacities through application of consistent operating policy. A summary of comparisons between transmission factors used in the above gas equations are shown in Fig. 17-7.

Reference should be made to "Steady Flow in Gas Pipelines"[6], published by American Gas Association, for a complete analysis of steady flow in gas pipelines.

Low Pressure Gas Flow

Gas gathering often involves operating pressures below 100 psi. Some systems flow under vacuum conditions. For these low pressure conditions, equations have been developed that give a better fit than the Weymouth or Panhandle equations. Two such formulas are:

The Oliphant Formula[9] for gas flow between vacuum and 100 psi:

$$Q = 42\,(24)\left(d^{2.5} + \frac{d^3}{30}\right)\left(\frac{14.4}{P_b}\right)\left(\frac{T_b}{520}\right)\left[\left(\frac{0.6}{S}\right)\left(\frac{520}{T}\right)\left(\frac{P_1^2 - P_2^2}{L_m}\right)\right]^{1/2} \qquad \textbf{Eq 17-28}$$

The Spitzglass Formula for gas flow below 1 psig at 60°F:

$$Q = (24)\,(3550)\left[\frac{27.69(P_1 - P_{2)}\,d^5}{SL\left(1 + \frac{3.6}{d} + 0.03\,d\right)}\right]^{1/2} \qquad \textbf{Eq 17-29}$$

Plant Piping Gas Flow

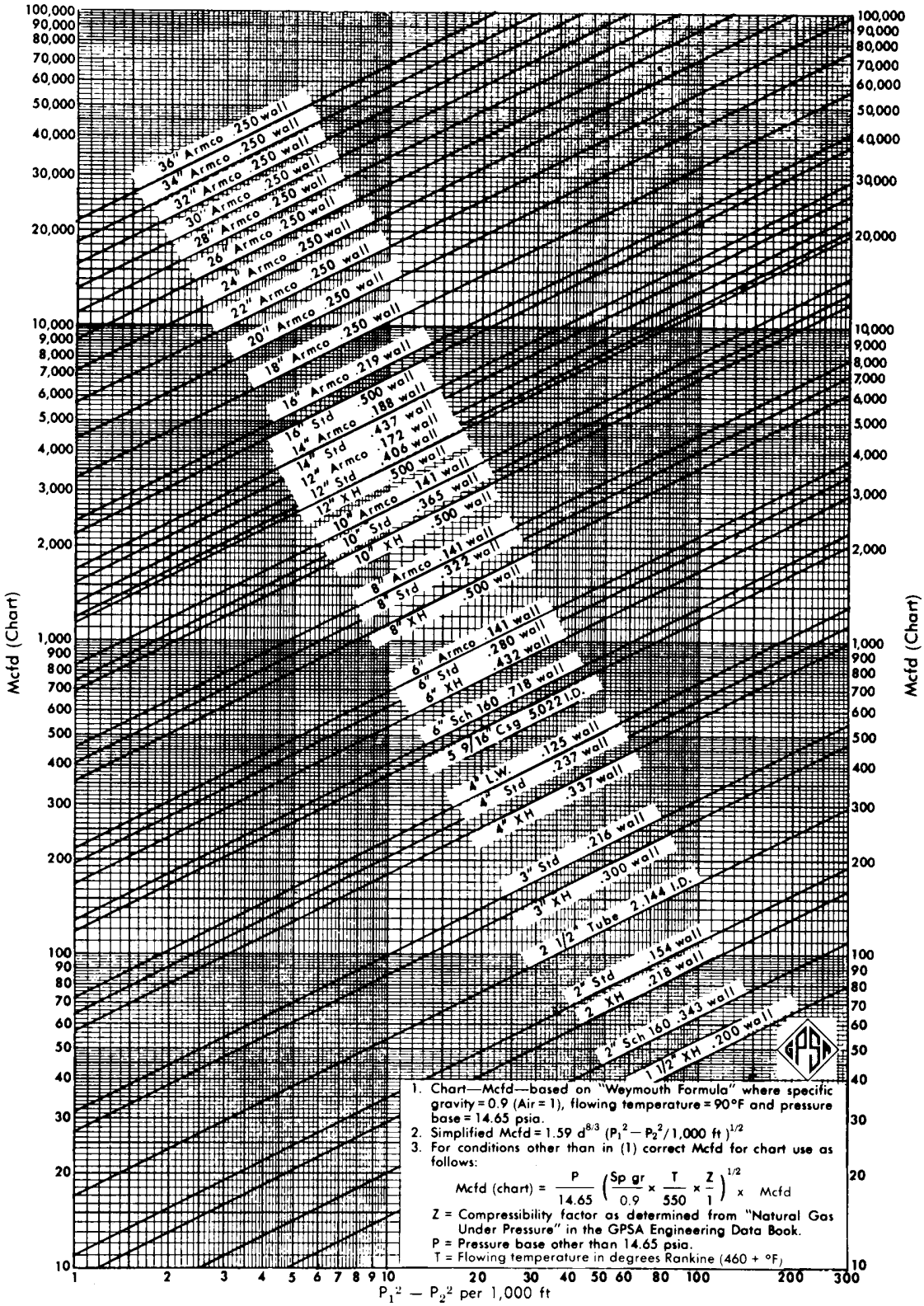
For estimating pressure drop in short runs of gas piping, such as within plant or battery limits, a simplified formula for compressible fluids is accurate for fully turbulent flow, assuming the pressure drop through the line is not a significant fraction of the total pressure (i.e. no more than 10%).

The following method is a simplification of the Darcy formula, which eliminates calculation of f_m, the Moody friction factor. This simplification was checked over a wide range of flows and densities for pressure drops of 0.25 to 1.5 psi/100 ft. Density was varied over a range of 100 to 1; flows varied over a range of 75 to 1. Pressure variation was from atmospheric to 1000 psia. The error from using the simplified approach as compared to the actual friction factor calculated in the Darcy formula was from zero to 5%, with the simplified approach

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FIG. 17-6a

Gas Flow Based On Weymouth Formula



1. Chart—Mcfd—based on "Weymouth Formula" where specific gravity = 0.9 (Air = 1), flowing temperature = 90°F and pressure base = 14.65 psia.
2. Simplified Mcfd = $1.59\ d^{8/3}\ (P_1^2 - P_2^2/1{,}000\ ft)^{1/2}$
3. For conditions other than in (1) correct Mcfd for chart use as follows:

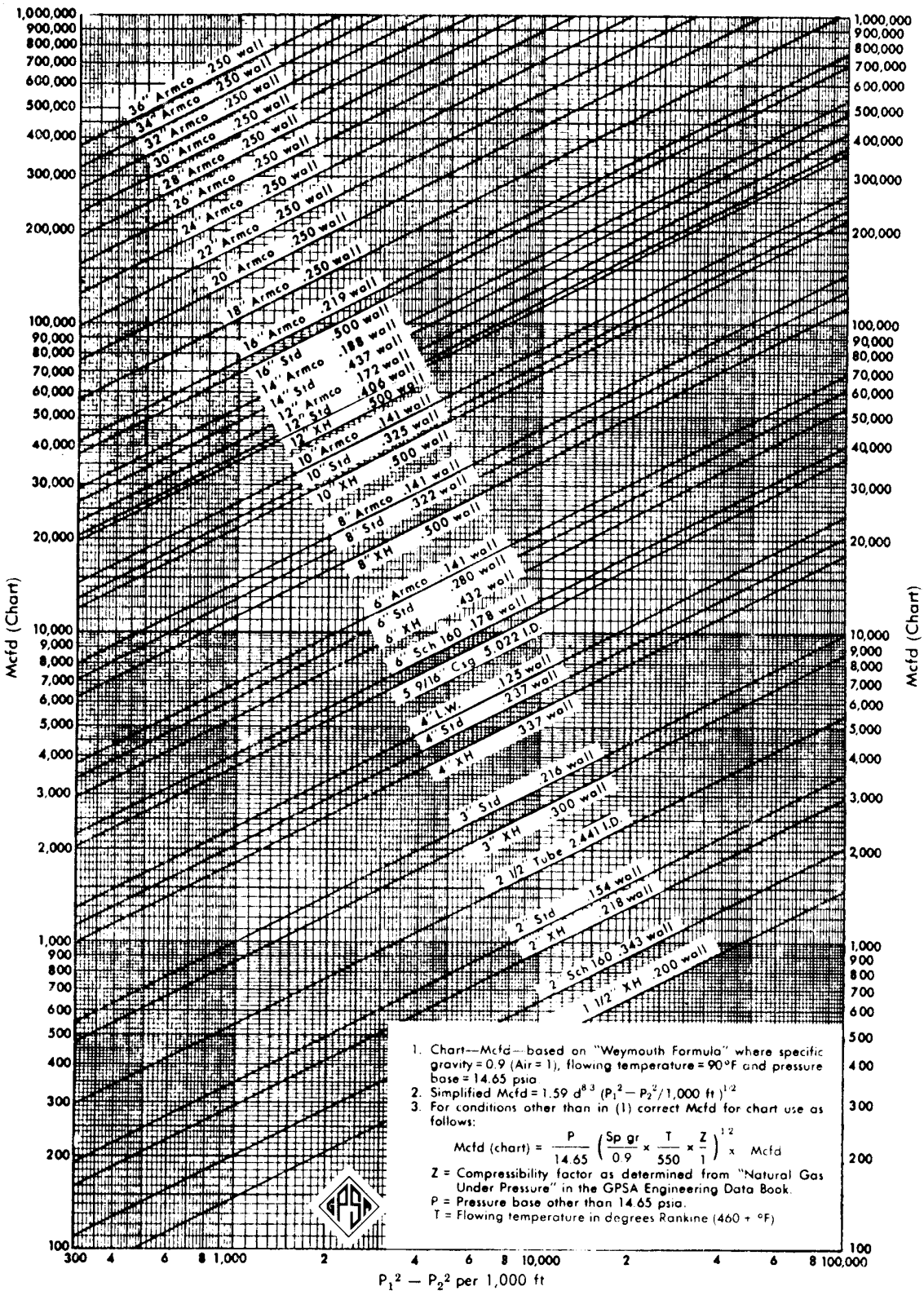
$$\text{Mcfd (chart)} = \frac{P}{14.65}\left(\frac{\text{Sp gr}}{0.9} \times \frac{T}{550} \times \frac{Z}{1}\right)^{1/2} \times \text{Mcfd}$$

Z = Compressibility factor as determined from "Natural Gas Under Pressure" in the GPSA Engineering Data Book.
P = Pressure base other than 14.65 psia.
T = Flowing temperature in degrees Rankine (460 + °F)

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FIG. 17-6b

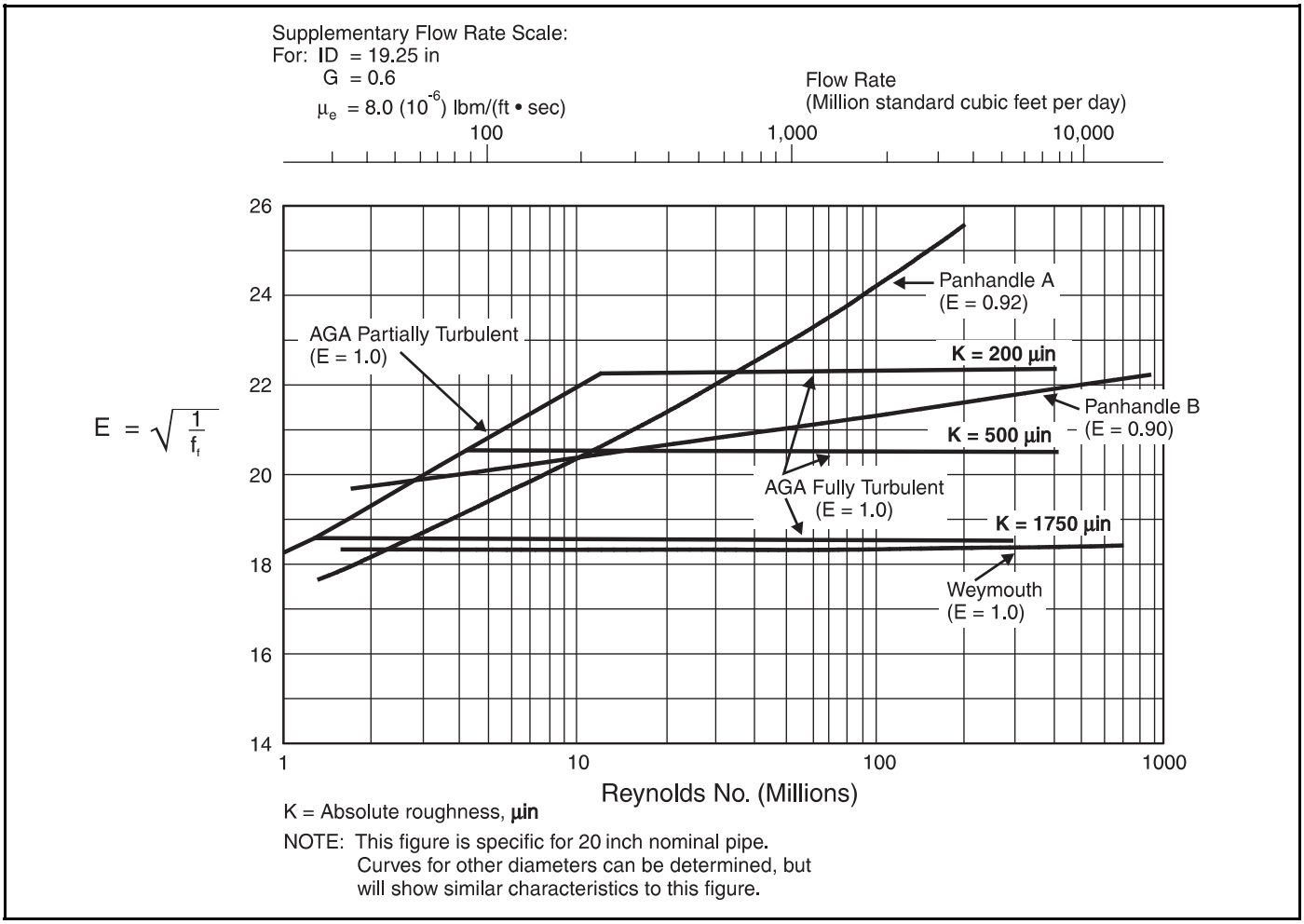
Gas Flow Based On Weymouth Formula



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FIG. 17-7

Comparison of Gas Equation Transmission Factors for Nominal 20 Inch Pipe



giving consistently lower calculated pressure drop for a given flow.

The Darcy formula can be written in the simple form:

$$\Delta P_{100} = \frac{W^2}{\rho}\left(\frac{0.000336\ f_m}{d^5}\right) \qquad \textbf{Eq 17-30}$$

Simplifying, $C_1 = W^2\ (10^{-9})$, and $C_2 = \frac{336{,}000\ f_m}{d^5}$, then

$$\Delta P_{100} = \frac{C_1\ C_2}{\rho} \qquad \textbf{Eq 17-31}$$

$C_1 = \frac{(\Delta P_{100})\ \rho}{C_2}$ = discharge factor from chart, Fig. 17-8

$C_2 = \frac{(\Delta P_{100})\ \rho}{C_1}$ = size factor Fig. 17-9

C_2 incorporates the friction factor, assuming clean steel. Using this simplified approach, new lines can be sized by setting the desired ΔP_{100} and solving for C_2 with a given flow. For a given flow and pipe size, ΔP_{100} can be solved directly.

Example 17-1 — Calculate the pressure drop in a 10-in., Schedule 40 pipe for a flow of 150,000 lb/hr of methane. Temperature is 60°F and pressure is 750 psia. The compressibility factor is 0.905 (from Fig. 23-4).

Solution Steps

$$\rho = \frac{16.042\ (750)}{10.73\ (460 + 60)\ (0.905)} = 2.38\ \text{lb/ft}^3$$

C_1 from Fig. 17-8 is 22.5

C_2 from Fig. 17-9 is 0.0447

$$\Delta P_{100} = \frac{C_1 C_2}{\rho} = \frac{22.5\ (0.0447)}{2.38}$$

= 0.423 psi/100 ft using Eq 17–31

Example 17-2 — Calculate the required line size (of Schedule 40 pipe) to give ΔP_{100} = 1 psi or less when flowing 75,000 lb/hr of methane at 400 psia and 100°F. The compressibility factor is 0.96 (from Fig. 23-6).

Solution Steps

$$\rho = \frac{16.062\ (400)}{10.73\ (460 + 100)\ (0.96)} = 1.11\ \text{lb/ft}^3$$

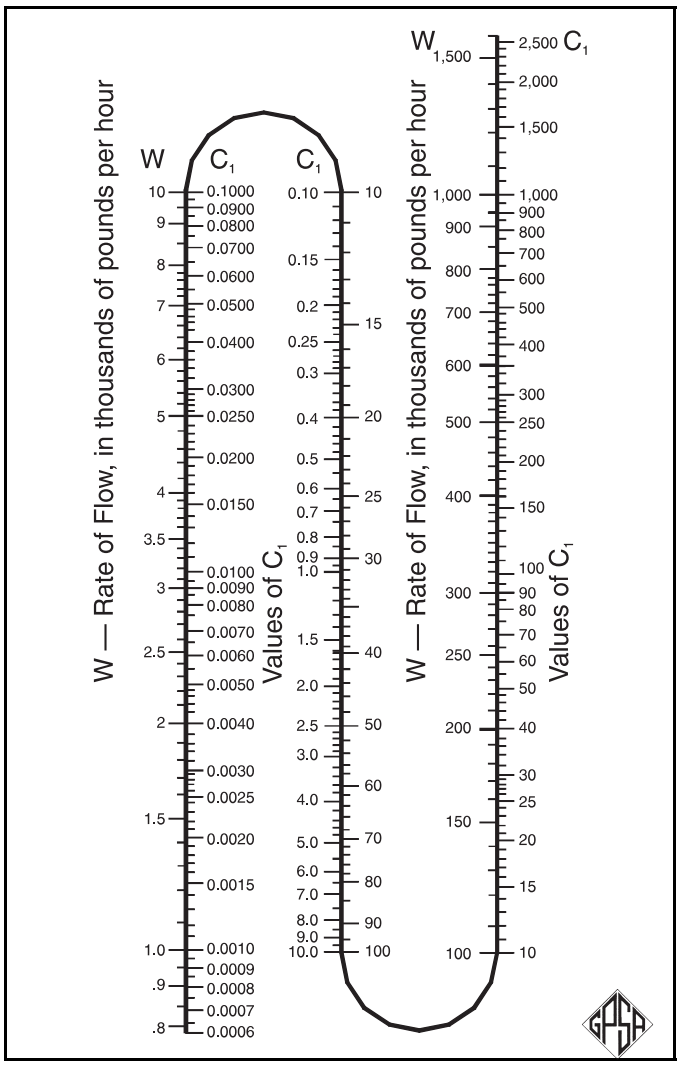
C_1 from Fig. 17-8 is 5.6

$$C_2 = \frac{(\Delta P_{100})\ \rho}{C_1} = \frac{1\ (1.11)}{5.6} = 0.20$$

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FIG. 17-8

Simplified Flow Formula for Compressible Fluids[5]
Values of C_1



From Fig. 17-9 the smallest size of Schedule 40 pipe with C_2 less than 0.20 is 8-in. pipe. For 8 in. Sch 40 pipe, C_2 is 0.146. The actual pressure drop can then be calculated as:

$$\Delta P_{100} = \frac{5.6\ (0.146)}{1.11} = 0.74 \text{ psi/100 ft}$$

using Eq 17-31 for the above flow conditions.

Liquid Flow

For the calculation of pressure drop in liquid lines, the Darcy-Weisbach method, Eq 17-6, can be used. The calculation is simplified for liquid flows since the density can reasonably be assumed to be a constant. As a result, the Darcy-Weisbach calculation can be applied to a long run of pipe, rather than segmentally as dictated by the variable density in gas flow. In addition, several graphical aids are available for pressure drop calculation. Elevation pressure drops must be calculated separately using Eq 17-32. These elevation pressure gains or losses are added algebraically to the frictional pressure drops.

$$\Delta P_e = (0.00694)\ \rho_L\ Z_e \qquad \textbf{Eq 17-32}$$

Water — A graph showing pressure drop for water per 100 feet as a function of flow rate in gallons per minute and pipe size is shown in Fig. 17-10. These data are based on the Hazen and Williams empirical formula[10] using a "C" constant of 100 which is commonly used for design purposes in welded and seamless steel pipe.

Hazen and Williams formula for flow of water:

$$q = 0.442\ d^{2.63}\ C \left(\frac{P_1 - P_2}{L}\right)^{0.54} \qquad \textbf{Eq 17-33}$$

Where:

C = 140 for new steel pipe

C = 130 for new cast iron pipe

C = 100 is often used for design purposes to account for pipe fouling, etc.

Hydrocarbon — A graph showing pressure drop for hydrocarbons per 100 feet as a function of flow rate in gallons per minute and pipe size is shown in Fig. 17-11. This graph assumes a specific gravity of 1.0 (water). To correct for different liquid densities, the value read from Fig. 17-11 must be multiplied by the actual specific gravity to obtain the correct pressure loss.

Steam Flow

Fig. 17-12 contains a graphical representation of Fritzsche's formula[11] for calculating pressure drop in steam lines. Fritzsche's formula and instructions for the chart usage are given in Fig. 17-12.

The Babcock formula[5] for steam flow is:

$$\Delta P_f = 3.63\ (10^{-8}) \left(\frac{d + 3.6}{d^6}\right) \frac{W^2\ L}{\rho} \qquad \textbf{Eq 17-34}$$

Fire Stream Flow

Fig. 17-13 is a table permitting rapid computation of the behavior of various sized fire nozzles. The table also includes the estimated pressure drop in 100 feet of 2½ inch diameter fire hose.

TWO PHASE FLOW

Two-phase flow presents several design and operational difficulties not present in single phase liquid or vapor flow. Frictional pressure drops are much harder to calculate. For cross-country pipelines, a terrain profile is needed to calculate elevation pressure drops. Commercial software is available to simulate these complex two-phase flow situations.

At the downstream end of a pipeline, it is frequently necessary to separate the liquid and vapor phases in a separator. The presence of liquid slugs complicates this process, and a slug catcher may be required.

Flow Regime Determination

Several empirical flow regime maps have been presented that determine vapor-liquid flow patterns as a function of fluid properties and flow rates. Diagrams of these flow patterns are shown in Fig. 17-14. One map commonly used was developed by Gregory, Aziz, and Mandhane[12] for horizontal flow. This map appears as Fig. 17-15. The coordinates of the map are:

V_{sL} = superficial liquid velocity

$$= Q_L/A \qquad \textbf{Eq 17-35}$$

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FIG. 17-9

Simplified Flow Formula for Compressible Fluids[5]

Values of C_2

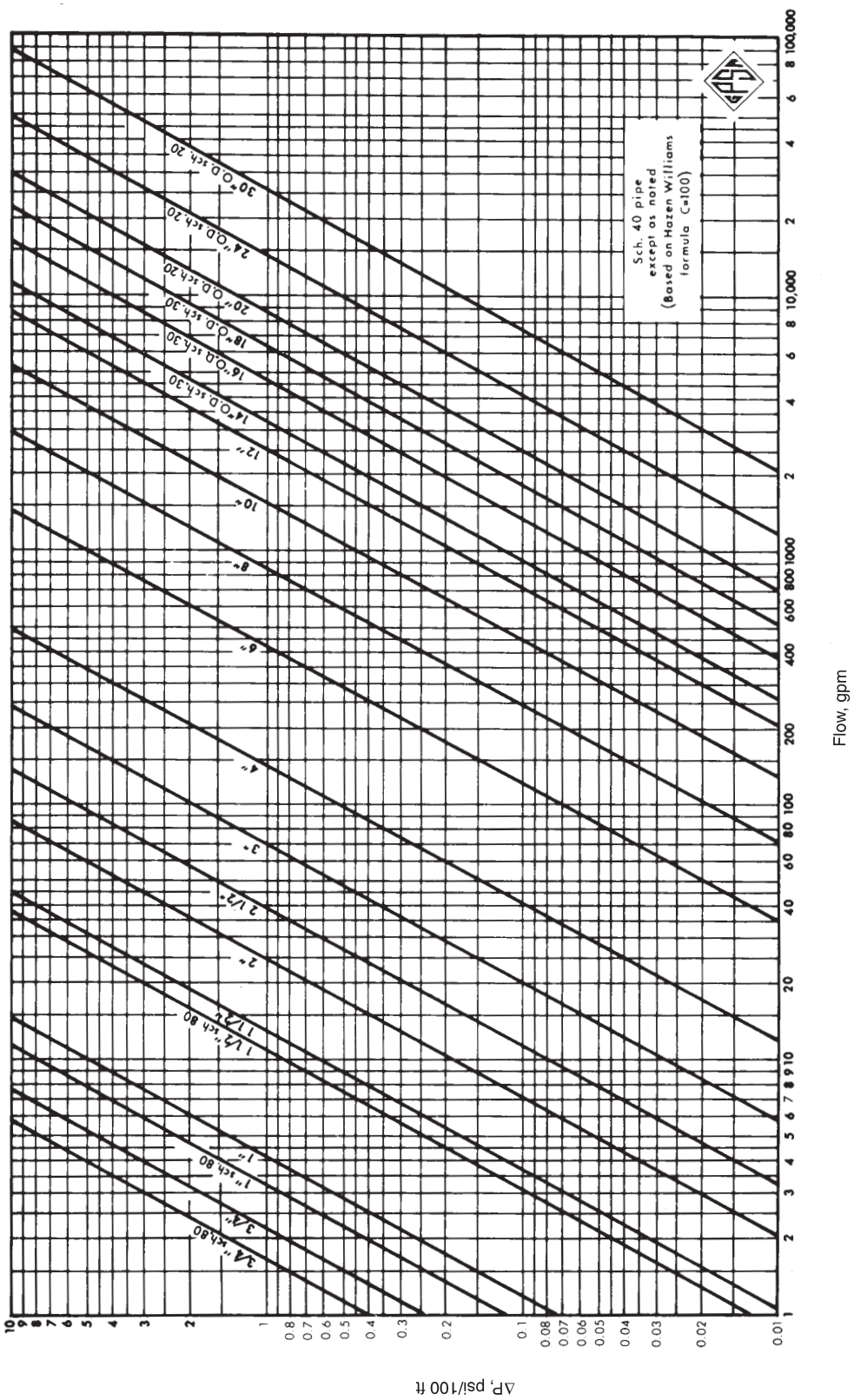
Nominal pipe size in.	Schedule number	Value of C_2
1/8	40 s	7 920 000.
	80 x	26 200 000.
1/4	40 s	1 590 000.
	80 x	4 290 000.
3/8	40 s	319 000.
	80 x	718 000.
1/2	40 s	93 500.
	80 x	186 100.
	160	430 000.
	... xx	11 180 000.
3/4	40 s	21 200.
	80 x	36 900.
	160	100 100.
	... xx	627 000.
1	40 s	5 950.
	80 x	9 640.
	160	22 500.
	... xx	114 100.
1 1/4	40 s	1 408.
	80 x	2 110.
	160	3 490
	... xx	13 640.
1 1/2	40 s	627.
	80 x	904.
	160	1 656.
	... xx	4 630.
2	40 s	169.
	80 x	236.
	160	488.
	... xx	899.
2 1/2	40 s	66.7
	80 x	91.8
	160	146.3
	... xx	380.0
3	40 s	21.4
	80 x	28.7
	160	48.3
	... xx	96.6
3 1/2	40 s	10.0
	80 x	13.2
4	40 s	5.17
	80 x	6.75
	120	8.94
	160	11.80
	... xx	18.59
5	40 s	1.59
	80 x	2.04
	120	2.69
	160	3.59
	... xx	4.93
6	40 s	0.610
	80 x	0.798
	120	1.015
	160	1.376
	... xx	1.861
8	20	0.133
	30	0.135
	40 s	0.146
	60	0.163
	80 x	0.185
	100	0.211
	120	0.252
	140	0.289
	... xx	0.317
	160	0.333
10	20	0.039 7
	30	0.042 1
	40 s	0.044 7
	60 x	0.051 4
	80	0.056 9
	100	0.066 1
	120	0.075 3
	140	0.090 5
	160	0.105 2
12	20	0.015 7
	30	0.016 8
	... s	0.017 5
	40	0.018 0
	... x	0.019 5
	60	0.020 6
	80	0.023 1
	100	0.026 7
	120	0.031 0
	140	0.035 0
	160	0.042 3
14	10	0.009 49
	20	0.009 96
	30 s	0.010 46
	40	0.010 99
	... x	0.011 55
	60	0.012 44
	80	0.014 16
	100	0.016 57
	120	0.018 98
	140	0.021 8
	160	0.025 2
16	10	0.004 63
	20	0.004 83
	30 s	0.005 04
	40 x	0.005 49
	60	0.006 12
	80	0.007 00
	100	0.008 04
	120	0.009 26
	140	0.010 99
	160	0.012 44
18	10	0.002 47
	20	0.002 56
	... s	0.002 66
	30	0.002 76
	... x	0.002 87
	40	0.002 98
	60	0.003 35
	80	0.003 76
	100	0.004 35
	120	0.005 04
	140	0.005 73
	160	0.006 69
20	10	0.001 41
	20 s	0.001 50
	30 x	0.001 61
	40	0.001 69
	60	0.001 91
	80	0.002 17
	100	0.002 51
	120	0.002 87
	140	0.003 35
	160	0.003 85
24	10	0.000 534
	20 s	0.000 565
	... x	0.000 597
	30	0.000 614
	40	0.000 651
	60	0.000 741
	80	0.000 835
	100	0.000 972
	120	0.001 119
	140	0.001 274
	160	0.001 478
30	10	0.0001681
	... s	0.0001719
	20 xs	0.0001797
	30	0.0001879
36	10	0.0000642
	... s	0.0000654
	20 xs	0.0000678
	30	0.0000704
	40	0.0000731

Note: The letters s, x, and xx in the columns of Schedule Numbers indicate Standard, Extra Strong, and Double Extra Strong pipe respectively.

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FIG. 17-10

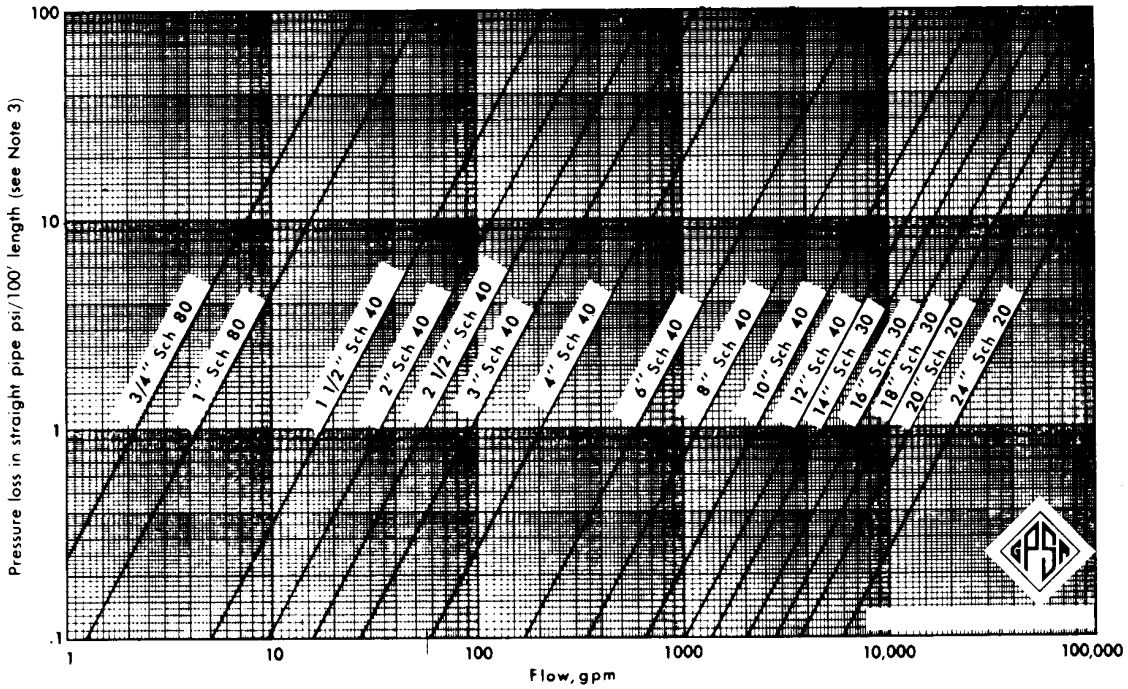
Pressure Drop for Flowing Water



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FIG. 17-11

Pressure Drop for Hydrocarbon Liquids in Smooth Pipe



Notes:

1. Curves calculated using the Fanning equation:

$$\Delta P_{100} = \frac{5.35\, f_f\, q^2\, \rho_L}{d^5\, \rho_w}$$

2. For this chart $\epsilon = 0.00015$ ft

3. This chart assumes specific gravity = 1.0. For other values multiply pressure loss from chart by actual specific gravity (ρ_L/ρ_w).

4. For viscous fluids, use this chart only if the flow is fully turbulent (see Fig. 17-2). For viscous fluids in the partially turbulent range, use Fig. 17-2 to obtain f_m and use Eq. 17-7 to calculate ΔP_f.

V_{sg} = superficial gas velocity

$$= Q_g/A \qquad \textbf{Eq 17-36}$$

Mandhane proposed a fluid property correction to the superficial velocities, but concluded that the fluid property effects are insignificant compared to the errors in the empirical map. The map reports the flow regimes: stratified, wavy, annular mist, bubble, slug, and dispersed. Care should be taken in the interpretation of these flow maps as the regime boundaries are strongly affected by pipe inclination. In particular, horizontal flow regime maps must not be used for vertical flow, and vertical flow regime maps must not be used for horizontal flow. The Mandhane map given in Fig. 17-15 was developed for horizontal lines flowing air and water at near atmospheric pressure. Inclinations in the range of 0.1-1.0 degrees can cause substantial regime boundary movement. In addition, flow regime boundary adjustment has been observed due to fluid pressure, pipe diameter, and surface tension.[13,22] The gas density increase caused by high pressure acts to move the slug-mist boundary to lower superficial gas velocities, while increased pipe diameter acts to increase the stratified wavy flow regime at the expense of the slug flow regime. In addition, foamy fluids having a high surface tension have been observed to flow in the dispersed flow regime even though Mandhane would have predicted superficial liquid velocities too low to cause dispersed flow. A flow regime map generated by Taitel and Dukler[13] contains explicit inclination effects and should be used for inclined pipes. This latter method also contains explicit pipe diameter effects but lacks any way of accounting for surface tension.

For vertical flow, the stratified flow regime cannot exist as there is no preferred direction for the liquid to settle. An empirical flow regime map developed by Aziz[14] for vertical upward flow is shown in Fig. 17-16. The coordinates for this flow map are the same as for the Mandhane map in Fig. 17-15 except that fluid property corrections are used. The coordinates used in the Aziz vertical map are:

$$N_x = V_{sg}\, X_A \qquad \textbf{Eq 17-37}$$

$$N_y = V_{sL}\, Y_A \qquad \textbf{Eq 17-38}$$

$$X_A = \left(\frac{\rho_g}{\rho_a}\right)^{0.333} Y_A \qquad \textbf{Eq 17-39}$$

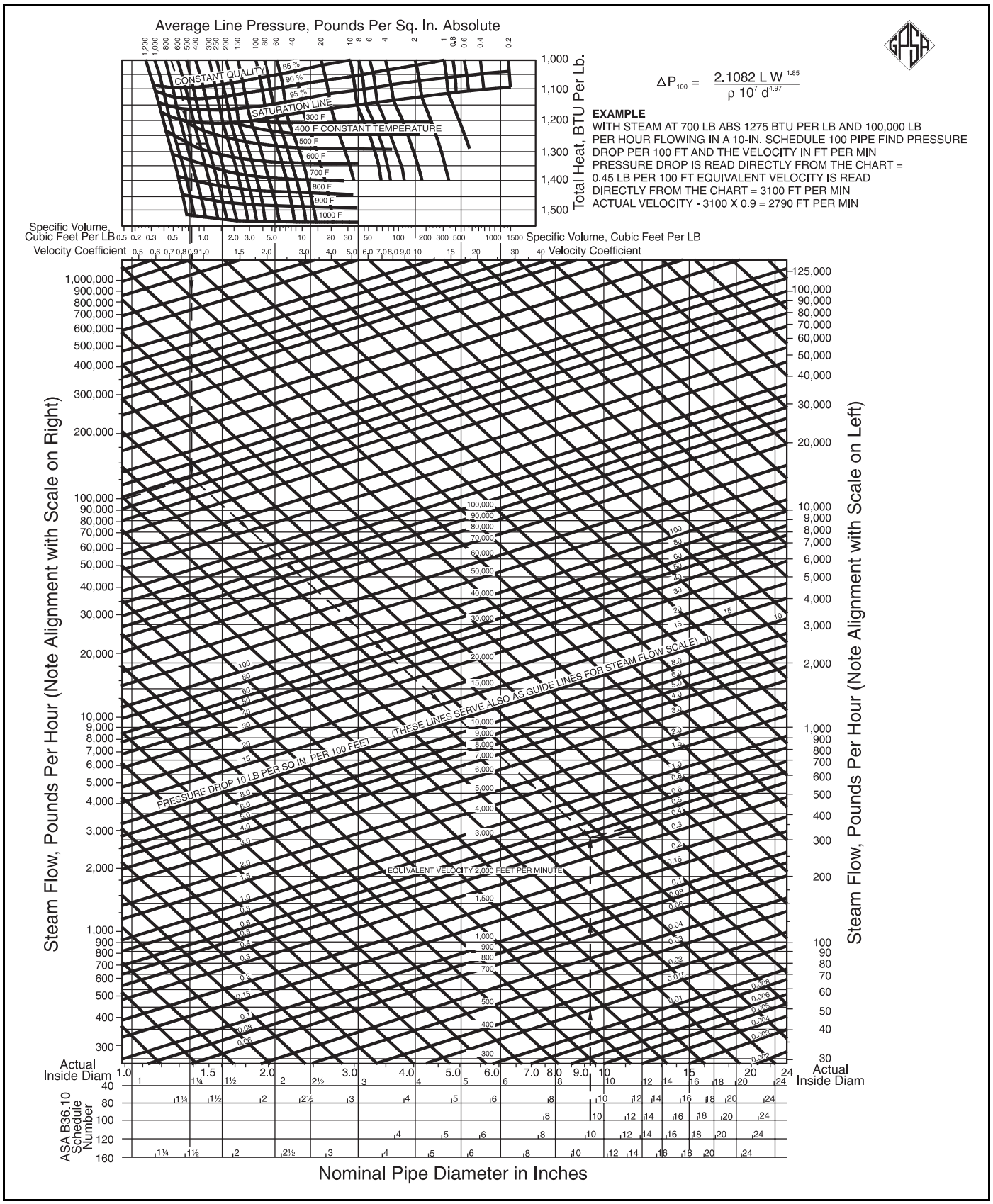
$$Y_A = \left(\frac{\rho_L \sigma_{wa}}{\rho_w \sigma}\right)^{0.25} \qquad \textbf{Eq 17-40}$$

For pipe inclinations greater than 10-20 degrees, flow regime patterns resemble those of vertical flow more than those

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FIG. 17-12

Pressure Drop in Steam Pipes by Fritzsche's Formula[11]



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FIG. 17-13

Table of Effective Fire Streams

Smooth nozzles, size	¾"						⅞"						1"					
Pressure at hydrants, psi.	32	43	54	65	75	85	34	46	57	69	80	91	37	50	62	75	87	100
Pressure at nozzle, psi	30	40	50	60	70	80	30	40	50	60	70	80	30	40	50	60	70	80
Pres. lost in 100 ft. 2½ in. hose psi	2	3	4	5	5	6	4	6	7	9	10	11	7	10	12	15	17	20
Vertical height, ft.	48	60	67	72	76	79	49	62	71	77	81	85	51	64	73	79	85	89
Horizontal distance, ft	37	44	50	54	58	60	42	49	55	61	66	70	47	55	61	67	72	76
Gal discharge/ min.	90	104	116	127	137	147	123	142	159	174	188	201	161	186	208	228	246	263
Smooth nozzles, size	**1⅛"**						**1¼"**						**1⅜"**					
Pressure at hydrants, psi	42	56	70	84	98	112	49	65	81	97	113	129	58	77	95	116	135	154
Pressure at nozzle, psi	30	40	50	60	70	80	30	40	50	60	70	80	30	40	50	60	70	80
Pres. lost in 100 ft 2½ in hose psi	12	16	20	24	28	30	19	25	31	37	43	49	28	37	36	56	65	74
Vertical height, ft	52	65	75	83	88	92	53	67	77	85	91	95	55	69	79	87	92	97
Horizontal distance, ft	50	59	66	72	77	81	54	63	70	76	81	85	56	66	73	79	84	88
Gal discharge/min	206	238	266	291	314	336	256	296	331	363	392	419	315	363	406	445	480	514

Using 100 ft of 2½ in. ordinary best quality rubber lined hose between nozzle and hydrant or pump.

The vertical and horizontal distance in above table are "effective" streams. The "effective stream" is one that has not broken up into a spray and which will project three fourths of the water through a circle 10 in. in diameter, at the distance indicated.

The bulk of the stream and extreme drops will carry a greater distance, but the stream is spread out too much to penetrate a hot fire and reach the burning materials before evaporation. The vertical height "h" in feet, which the bulk of the stream will carry, may be computed by formula $h = 0.91 \frac{V^2}{2g}$

The gallons/minute discharge in the above table check approximately with the formula: $V = C\sqrt{2gH} = \frac{0.321 \times gpm}{A}$

then $gpm = \frac{V A}{0.321}$ V = Velocity in feet per second g = Acceleration due to gravity, = 32.16 ft/sec^2

A = Area of nozzle, in square inches C = Coefficient for smooth nozzles = 0.98 H = Head in feet = pressure x 2.31

Reference: Fire Protection Handbook, 14th Edition, 1976, National Fire Protection Association

FIG. 17-14

Two Phase Flow Regimes

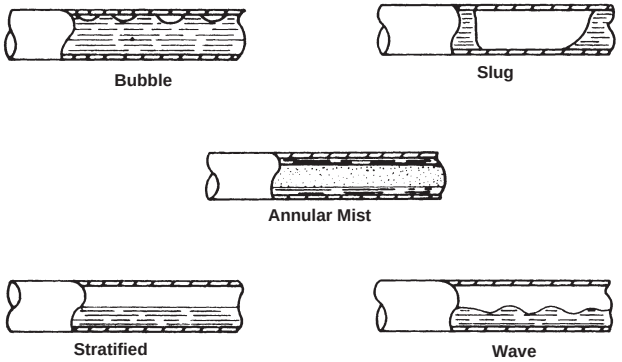
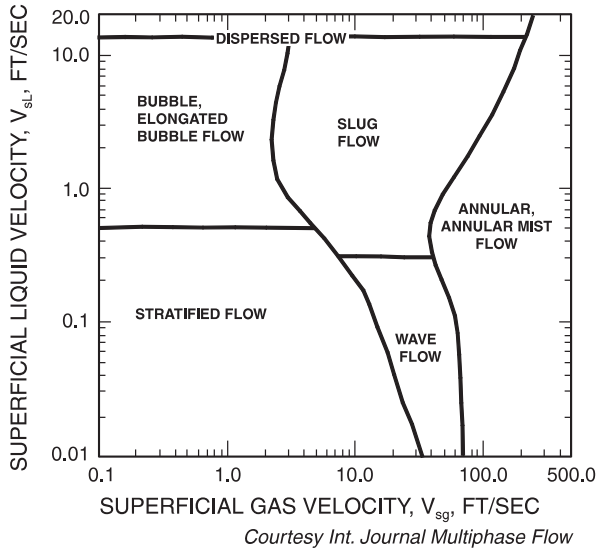


FIG. 17-15

Mandhane et al. Horizontal Flow Regime Map[12]

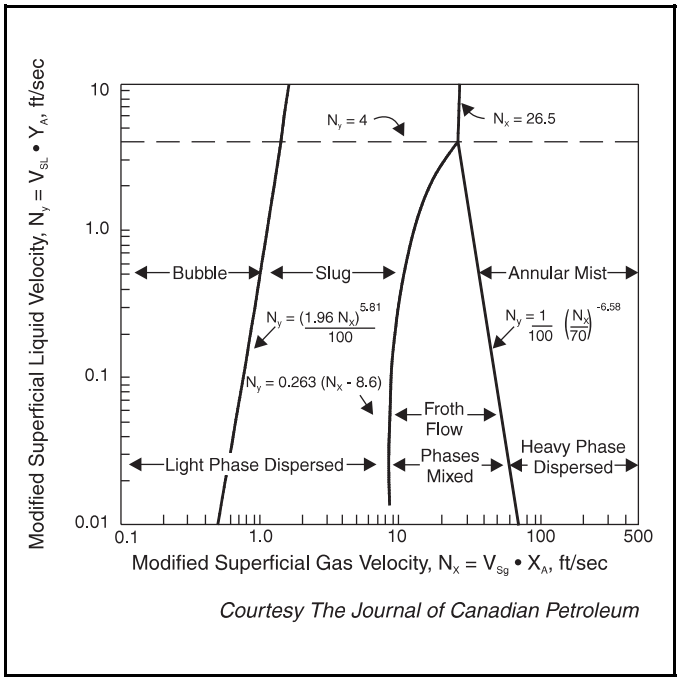


Courtesy Int. Journal Multiphase Flow

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FIG. 17-16

Aziz et al. Vertical Up-Flow Regime Map[14]



Courtesy The Journal of Canadian Petroleum

of horizontal flow, and the Aziz vertical map should be used. For vertical downward flow, the flow patterns can be more complicated. A generally accepted vertical down-flow map is not available.

Although the designer frequently does not have the choice, avoidance of the slug flow regime in horizontal flow and the slug and froth flow regimes in vertical flow is desirable. Slug flow introduces a flow rate and pressure intermittency that may be troublesome to process control. In some cases, slug flow may be avoided by the choice of smaller pipe sizes. Of course, frictional pressure drop may be increased by use of this smaller pipe. In vertical upflow, oversizing the pipe may result in a bubble flow regime, and a large liquid inventory. This liquid inventory may cause excessive hydrostatic presure drops.

Example 17-3 — A vapor-liquid mixture is flowing vertically upward in a pipe having an inside diameter of 8.0 inches. The fluid is a hydrocarbon liquid-hydrocarbon vapor mixture. The liquid density is 52 lb/ft^3 and the vapor density is 2.0 lb/ft^3. The interfacial surface tension is 20 dynes/cm. The liquid volumetric flow rate is 0.17 ft^3/sec and the vapor flow rate is 0.5 ft^3/sec measured at acutal conditions. What flow regime is to be expected?

Solution Steps

$$Y_A = \left[\frac{(52.0)\ (72.4)}{(62.4\ (20)}\right]^{0.25} = 1.32 \qquad \text{using Eq 17-40}$$

$$X_A = \left[\frac{(2.0)}{0.0764}\right]^{0.333} (1.32) = 3.91 \qquad \text{using Eq 17-39}$$

$$V_{sg} = \frac{0.5}{(\pi/4)\ (8/12)^2} = 1.43 \text{ ft/sec} \qquad \text{using Eq 17-36}$$

$$V_{sL} = \frac{0.17}{(\pi/4)\ (8/12)^2} = 0.49 \text{ ft/sec} \qquad \text{using Eq 17-35}$$

$$N_x = (1.43)\ (3.91) = 5.60 \text{ ft/sec} \qquad \text{using Eq 17-37}$$

$$N_y = (0.49)\ (1.32) = 0.64 \text{ ft/sec} \qquad \text{using Eq 17-38}$$

Fig. 17-16 shows that this flow is in the slug flow regime.

Pressure Drop Calculation

Calculation of pressure drop in two-phase flow lends itself better to computer calculation than to hand calculation. Several two-phase pressure drop correlations are available for both horizontal and vertical flows.[15,16,17] Due to the complexity of two-phase flow, uncertainties associated with pressure drop calculations are much greater than uncertainties in single-phase pressure drop calculations. As a result, errors in calculated two-phase pressure drops in the order of plus or minus twenty percent may normally be anticipated, especially in circumstances where fluid velocities are unusually high or low, where terrain is rugged, or where fluid properties are inadequately known. In addition, different two-phase flow correlations may give significantly different pressure drops. In order to evaluate these differences, several correlations should be used. A method suggested by the American Gas Association[18] can serve as a basis for hand calculation generated by Dukler[19] and an elevation pressure drop correlation by Flanigan.[20]

Frictional Component[18] — Using the Dukler frictional pressure drop calculation method, the frictional pressure drop is given by the equation:

$$\Delta P_f = \frac{f_n\ f_{tpr}\ \rho_k\ V_m^2\ L_m}{(0.14623)d} \qquad \textbf{Eq 17-41}$$

where

$$\rho_k = \frac{\rho_L\ \lambda^2}{H_{Ld}} + \frac{\rho_g\ (1-\lambda)^2}{(1-H_{Ld})} \qquad \textbf{Eq 17-42}$$

and

$$\lambda = \frac{Q_L}{Q_L + Q_g} \qquad \textbf{Eq 17-43}$$

The single phase friction factor, f_n, can be obtained from the correlation:[19]

$$f_n = 0.0056 + 0.5\ (Re_y)^{-0.32} \qquad \textbf{Eq 17-44}$$

The mixture Reynolds number, Re_y, is calculated according to the equation:

$$Re_y = \frac{(124.0)\ \rho_k\ V_m\ d}{\mu_n} \qquad \textbf{Eq 17-45}$$

Calculation of this Reynolds number requires determination of mixture velocity, V_m, and mixture viscosity, μ_n. These quantities can be determined according to:

$$V_m = V_{sL} + V_{sg} \qquad \textbf{Eq 17-46}$$

$$\mu_n = \mu_L\ \lambda + \mu_g\ (1-\lambda) \qquad \textbf{Eq 17-47}$$

The two-phase friction factor ratio, f_{tpr}, representing a two-phase frictional "efficiency" can be determined by reference to Fig. 17-17 or by the equation:

$$f_{tpr} = 1 + \left[\frac{y}{1.281 - 0.478y + 0.444y^2 - 0.094y^3 + 0.00843y^4}\right] \qquad \textbf{Eq 17-48}$$

where $y = -\ln(\lambda)$.

The remaining quantity to be calculated in the Dukler scheme is an estimate of the liquid holdup, H_{Ld}. This holdup can be estimated using Fig. 17-18. This figure gives liquid holdup as a function of λ and Re_y. Since Re_y is itself a function of

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liquid holdup, the calculation is, in general, iterative. For most calculations, however, the Re_y line can be used for a first estimate.

Elevation Component — The elevation component of pressure drop can be found using the Flanigan method. In this method, the elevation component is calculated using the equation:

$$\Delta P_e = \frac{\rho_L H_{Lf}}{144} \Sigma Z_e \qquad \textbf{Eq 17-49}$$

where H_{Lf} is determined from Fig. 17-19 or calculated according to the formula:

$$H_{Lf} = \frac{1}{1 + 0.3264 (V_{sg})^{1.006}} \qquad \textbf{Eq 17-50}$$

The term Z_e is the vertical elevation rise of a hill. The rises are summed. No elevation drops are considered. This is tantamount to ignoring any possible hydrostatic pressure recoveries in downhill sections of pipeline and may lead to a considerable error in the pressure drop analysis.

Once the frictional component or pressure drop is found using the Dukler method, and the elevation component is found using the Flanigan method, the overall two-phase pressure drop is found by summing the friction and elevation components.

$$\Delta P_t = \Delta P_e + \Delta P_f \qquad \textbf{Eq 17-51}$$

Since fluid properties and liquid holdups can change rapidly in a two-phase line, accuracy is improved if this AGA calculation procedure is performed segmentally. The need for segmental calculations is one of the reasons why two-phase calculations are best suited for computer calculation.

Liquid Holdup — The liquid holdup correlation given in Fig. 17-18 is intended only for use in the Dukler friction pressure drop calculation. A correlation by Eaton et al.[21] is better suited for liquid holdup determination in liquid inventory calculations.

The Eaton[21] holdup correlation is shown in Fig. 17-20. In this figure, the holdup fraction, H_{Le}, is plotted directly as a function of the dimensionless group, N_E. This dimensionless group is of the form:

$$N_e = \frac{1.84 (N_{Lv})^{0.575} \left(\frac{P_{avg}}{P_b}\right)^{0.05} (N_L)^{0.1}}{N_{gv} (N_d)^{0.0277}} \qquad \textbf{Eq 17-52}$$

where

$$N_{Lv} = 1.938 V_{sL} \left(\frac{\rho_L}{\sigma}\right)^{0.25} \qquad \textbf{Eq 17-53}$$

$$N_{gv} = 1.938 V_{sg} \left(\frac{\rho_L}{\sigma}\right)^{0.25} \qquad \textbf{Eq 17-54}$$

$$N_d = 10.073\, d \left(\frac{\rho_L}{\sigma}\right)^{0.50} \qquad \textbf{Eq 17-55}$$

$$N_L = 0.15726\, \mu_L \left(\frac{1}{\rho_L \sigma^3}\right)^{0.25} \qquad \textbf{Eq 17-56}$$

The Eaton correlation has been found reasonably accurate by several investigators, particularly for low holdup flows.

The liquid holdup fraction, H_{Le}, is the fraction of the flow area of the pipe occupied by liquid. To calculate the liquid inventory in the pipe, I_L, the pipe internal volume is multiplied by this holdup fraction.

$$I_L = (28.80) H_{Le} d^2 L_m \qquad \textbf{Eq 17-57}$$

Since holdup fractions may change along the length of the pipe, a segmental calculation is more accurate.

Example 17-4 — A pipeline segment with a 6-inch inside diameter, 0.75 miles long, transports a mixture of gas and oil. The pipeline has a gradual upward slope and rises 100 feet over the 0.75 mile length. The inlet pressure of the pipeline is 400 psia, liquid viscosity is 20 cp, the vapor viscosity is 0.015 cp, and the interfacial surface tension is 15 dynes/cm. The liquid flow rate is 10 ft^3/min and the vapor flow rate is 250 actual ft^3/min. The density of the liquid phase is 55 lb/ft^3, and the density of the gas phase is 1.3 lb/ft^3 at operating conditions. What is the pressure at the downstream end of the line segment, and what is the liquid inventory of the line?

Solution Steps

Calculate the flowing liquid volume fraction using Eq 17-43.

$$\lambda = \frac{10}{250 + 10} = 0.038$$

Calculate the mixture viscosity, μ_n using Eq 17-47.

$$\mu_n = (20)(0.038) + (0.015)(1.0 - 0.038) = 0.774 \text{ cp}$$

For a first guess, assume $H_{Ld} = \lambda$ and estimate ρ_k using Eq 17-42.

$$\rho_k = \frac{(55)(0.038)^2}{0.038} + \frac{(1.3)(1.0 - 0.038)^2}{(1.0 - 0.038)} = 3.341 \text{ lb/ft}^3$$

Calculate the superficial velocities and the mixture velocity.

$$V_{sL} = \frac{10.0}{(\pi/4)(6/12)^2 (60)} = 0.849 \text{ ft/sec using Eq 17-35}$$

$$V_{sg} = \frac{250}{(\pi/4)(6/12)^2 (60)} = 21.22 \text{ ft/sec using Eq 17-36}$$

$$V_m = 0.849 + 21.22 = 22.07 \text{ ft/sec using Eq 17-46}$$

Calculate an estimate of the mixture Reynolds number, Re_y, using Eq 17-45

$$Re_y = \frac{(124.0)(3.341)(22.07)(6.0)}{(0.774)} = 70{,}878$$

From Fig. 17-18, determine a better estimate for the holdup fraction H_{Ld} using $\lambda = 0.038$, $Re_y = 70{,}878$

$$H_{Ld} = 0.12$$

Using this improved H_{Ld}, recalculate ρ_k using Eq 17-42

$$\rho_k = \frac{(55)(0.038)^2}{(0.12)} + \frac{(1.3)(1.0 - 0.038)^2}{1.0 - 0.12} = 2.029 \text{ lb/ft}^3$$

Using this improved ρ_k recalculate Re_y using Eq 17-45

$$Re_y = \frac{(124.0)(2.029)(22.07)(6.0)}{(0.774)} = 43{,}044$$

From Fig. 17-18 with $\lambda = 0.038$ and $Re_y = 43{,}044$, $H_{Ld} = 0.16$. Another iteration using $H_{Ld} = 0.16$ indicates $Re_y = 40{,}923$ and $H_{Ld} = 0.16$.

Calculate the single phase friction factor with $Re_y = 40{,}923$, using Eq 17-44

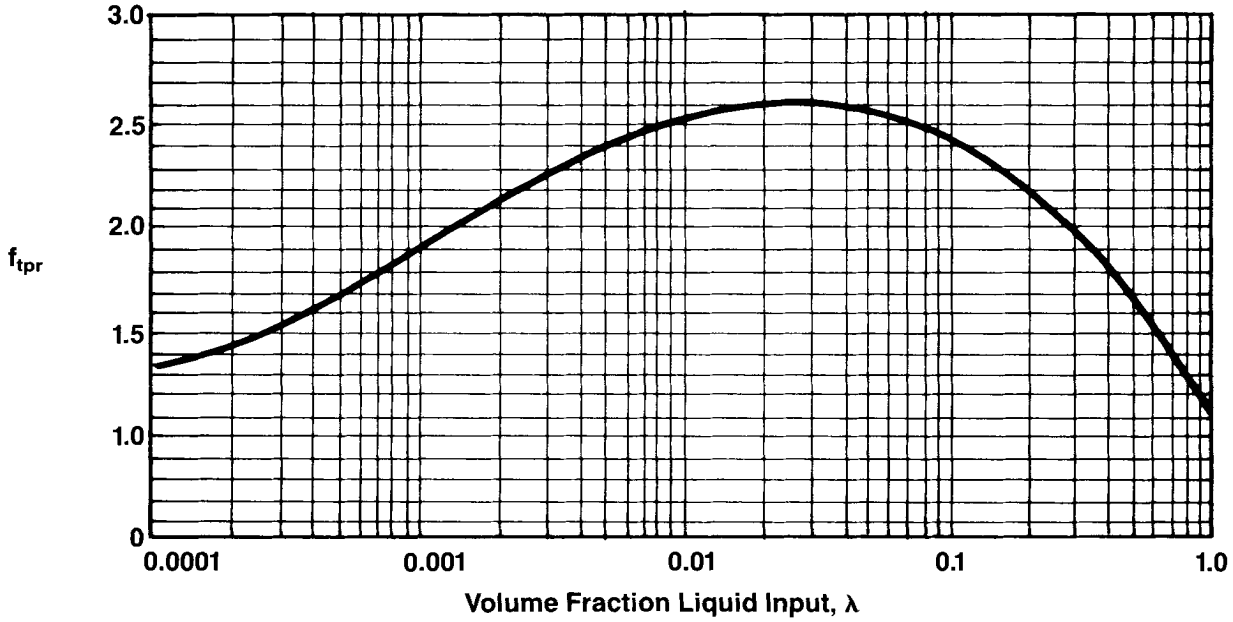
$$f_n = 0.0056 + 0.5 (40{,}923)^{-0.32} = 0.0223$$

Determine the two-phase friction factor, f_{tpr}, from Fig. 17-17 using $\lambda = 0.038$

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FIG. 17-17

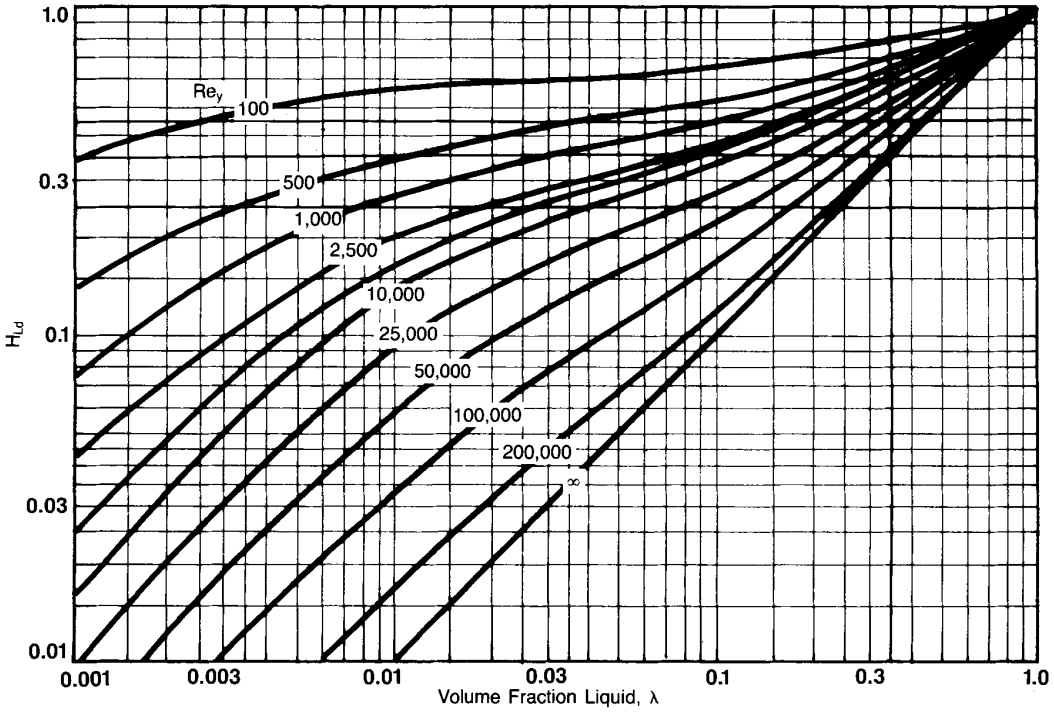
Two-Phase Friction Factor Ratio[19]



Courtesy AIChE Journal

FIG. 17-18

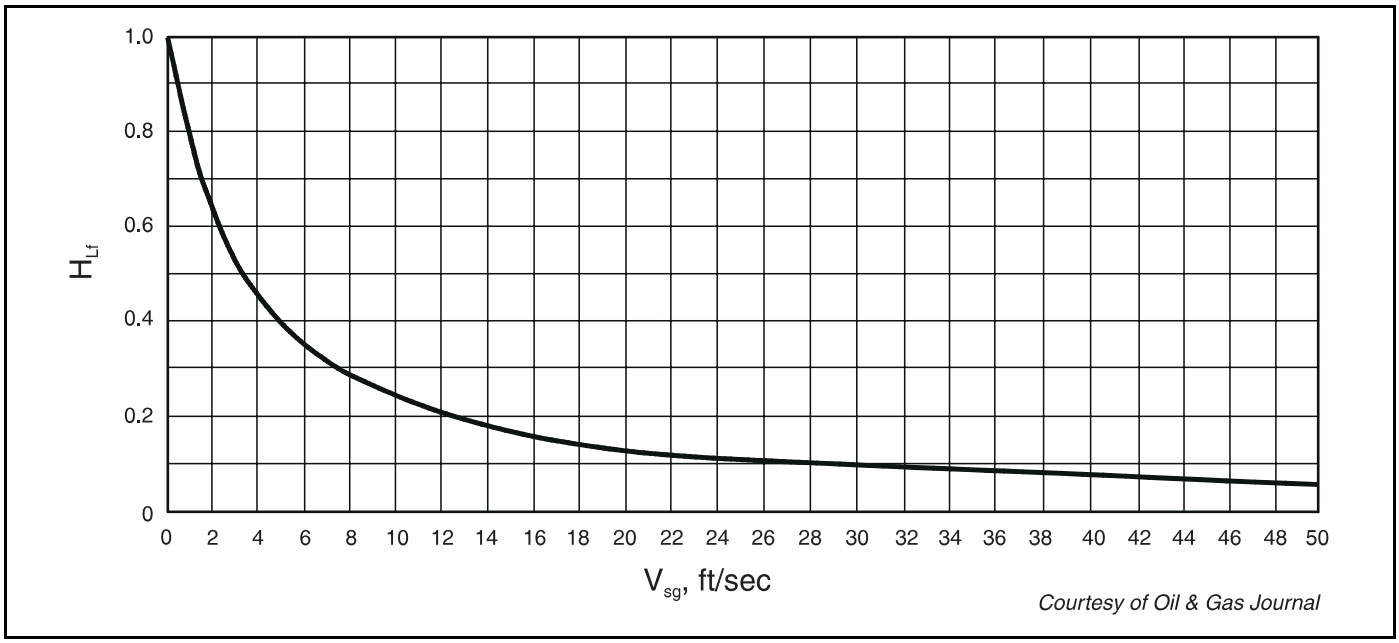
Liquid Holdup Correlation[19]



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FIG. 17-19

Flanigan Liquid Holdup Correlation[20]



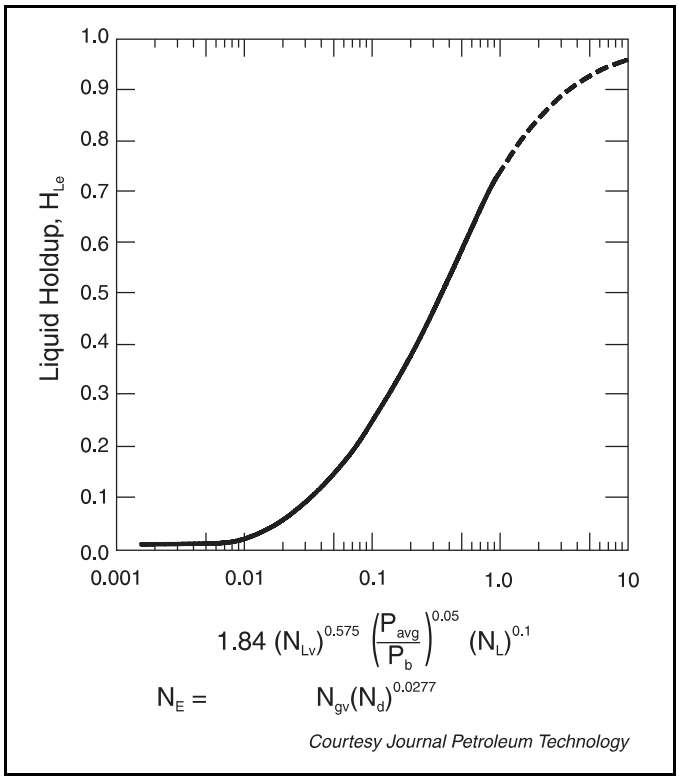
$f_{tpr} = 2.59$

Now for $\lambda = 0.038$, $H_{Ld} = 0.16$ then $\rho_k = 1.929$ using Eq 17-42.

Calculate the frictional component of pressure drop ΔP_f using Eq 17-41

FIG. 17-20

Eaton Liquid Holdup Correlation[21]



$$\Delta P_f = \frac{(0.0223)\,(2.59)\,(1.929)\,(22.07)^2\,(0.75)}{(0.14623)\,(6.0)} = 46.39 \text{ psi}$$

Find H_{Lf} from Fig. 17-19 using $V_{sg} = 21.22$ ft/sec

$H_{Lf} = 0.13$

Determine the elevation component of pressure drop, ΔP_e, using Eq 17-49

$$\Delta P_e = \frac{(55)\,(0.13)\,(100)}{(144)} = 4.97 \text{ psi}$$

Find the total pressure drop, ΔP_t, using Eq 17-51

$\Delta P_t = 46.39 + 4.97 = 51.36$ psi

Find the segment discharge pressure

$P_2 = 400 - 51.36 = 348.64$ psia

The pipeline segment has a discharge pressure of 348.64 psia.

To calculate the liquid inventory, the liquid holdup fraction from Eaton's correlation must be found. First determine the nondimensional parameters:

$N_{Lv} = (1.938)\,(0.849)\,(55/15)^{0.25} = 2.277$ using Eq 17-53

$N_{gv} = (1.938)\,(21.22)\,(55/15)^{0.25} = 56.91$ using Eq 17-54

$N_d = (10.073)\,(6.0)\,(55/15)^{0.5} = 115.73$ using Eq 17-55

$$N_L = (0.15726)\,(20.0)\left[\frac{1}{(55)\,(15)^3}\right]^{0.25} = 0.152$$

using Eq 17-56

Determine Eaton's nondimensional abscissa, N_E, using Eq 17-52

$$N_E = \frac{(1.84)\,(2.277)^{0.575}\,(400/14.73)^{0.05}\,(0.152)^{0.1}}{(56.91)\,(115.73)^{0.0277}} = 0.0444$$

From Fig. 17-20, read the holdup fraction, H_{Le}

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FIG. 17-21

Multiple Pipe Slug Catcher

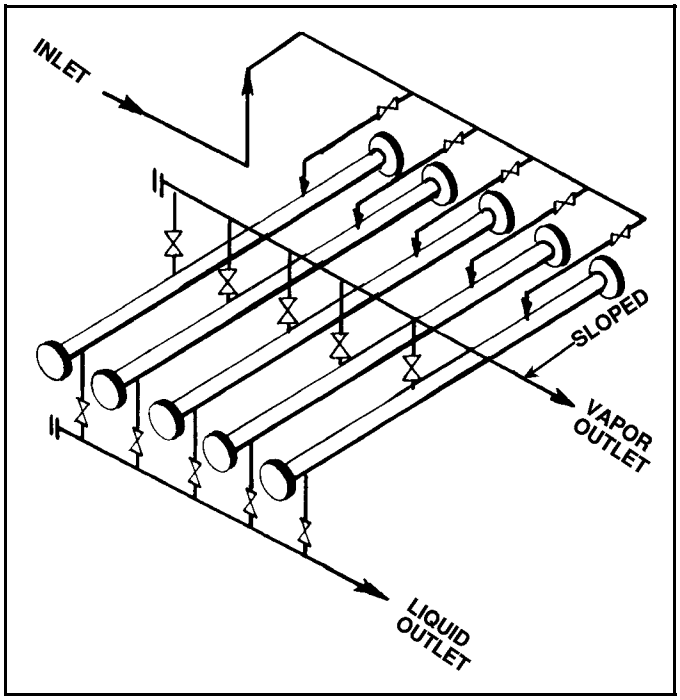
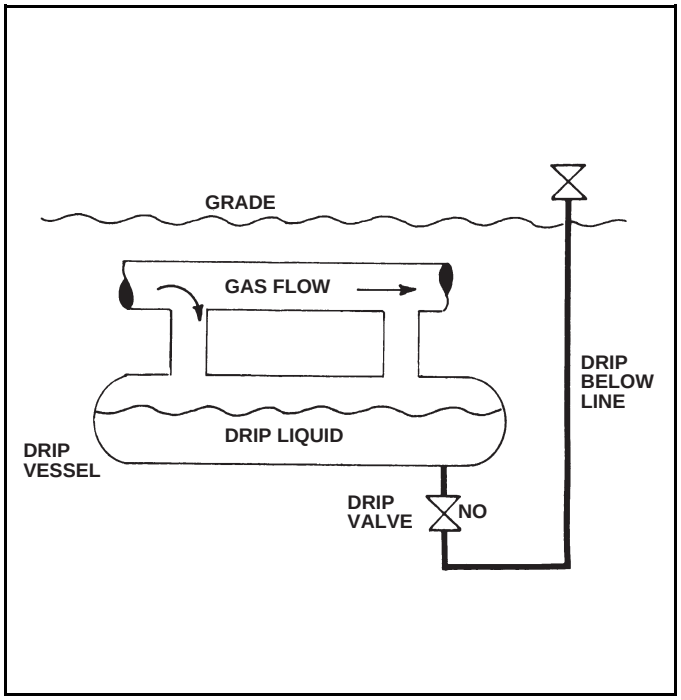


FIG. 17-22

Example Line Drip



$H_{Le} = 0.14$

Note that this estimate is close to the H_{Lf} predicted in Fig. 17-19 for elevation pressure drop determination. It also coincides closely with the value of 0.16 from Fig. 17-18.

Calculate the pipeline segment liquid inventory from Eq 17- 57

$$I_L = (28.80)\,(0.14)\,(6.0)^2\,(0.75) = 108.86 \text{ ft}^3$$

The pipeline segment contains 108.86 cubic feet of liquid at any instant.

Liquid Slugging

Purpose of Separators — The slug flow regime is frequently encountered for pipe sizes and flow rates used in process and transmission piping. Liquid slugging introduces an additional design and operational difficulty as liquid and vapor must generally be separated at the downstream end of the two-phase flow line. The downstream separator serves both as a liquid-vapor disengaging device and as a surge vessel to absorb the fluctuating liquid flow rates caused by slugging. In order to size the separator or slug catcher, the length of the incoming slugs must be determined. Slug length calculation methods are not well developed, and there is large uncertainty in slug length determination.

Mechanisms of Slug Generation — Liquid slug lengths are difficult to determine in part because there are at least four identifiable mechanisms for liquid slug generation. Slugs can form as the result of wave formation at the liquid-gas interface in a stratified flow. When the liquid waves grow large enough to bridge the entire pipe diameter, the stratified flow pattern breaks down and a slug flow is formed.

Slugs can also form due to terrain effects. Liquid collects at a sag in the pipeline and blocks the gas flow. The pressure in this blocked gas rises until it blows the accumulated liquid in the sag out as a slug. Changes in pipeline inlet flow rate can also cause slugs. When the inlet flow rate increases, the liquid inventory in the pipeline decreases, and the excess liquid forms a slug or series of slugs. Finally, pigging can cause very large liquid slugs as the entire liquid inventory of the line is swept ahead of the pig. Of the four mechanisms described, wave growth normally produces the shortest slugs, followed in length by terrain generated slugs. Methods for calculating wave induced slugs were described by Greskovich and Shrier[22], and by Brill et al.[23] A preliminary scheme for calculating terrain generated slugs was reported by Schmidt.[24] Analytical methods for determining inlet flow rate generated slugs were given by Cunliffe,[25] and a method of analyzing pigging dynamics was given by McDonald and Baker.[26]

Slug Catchers — Slug catchers are devices at the downstream end or other intermediate points of a pipeline to absorb the fluctuating liquid inlet flow rates through liquid level fluctuation. Slug catchers may be either a vessel or constructed of pipe. All size specifications discussed in Section 7 to provide residence time for vapor-liquid disengagement also apply to vessels used as slug catchers. In addition, sufficient volume must be provided for liquid level fluctuation. Particularly for high pressure service, vessel separators may require very thick walls.

In order to avoid thick wall vessels, slug catchers are frequently made of pipe. Lengths of line pipe tens or hundreds of feet long are used as long, slender horizontal separators. The pipe is generally inclined from one to ten degrees and banks of these slightly inclined pipes are frequently manifolded together. Pipe type slug catchers are frequently less expensive than vessel type slug catchers of the same capacity due to thinner wall requirements of smaller diameter pipe. The manifold nature of multiple pipe slug catchers also makes possible the later addition of additional capacity by laying more parallel pipes. A schematic of a multiple pipe (harp) slug catcher appears in Fig. 17-21. Different pipe inclinations and different manifolding arrangements are favored by different designers.

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An example of a line drip catcher is shown in Fig. 17-22. A drip vessel is connected to the incoming pipeline and often laid beneath it. A flow line from the drip vessel is used to blow the liquids out to a storage or surge vessel as they accumulate.

Pigging — Pipelines are pigged for several reasons. If water is present in the line, it must be removed periodically in order to minimize corrosion. This water accumulates in sags in the pipeline, and these low spots are particularly susceptible to corrosion. Pipelines are also pigged to improve pressure drop-flow rate performance. Water or hydrocarbon liquids that settle in sags in the pipeline constitute partial blockages that increase pressure drop. Pigging can remove these liquids and improve pipeline efficiency. Pigging can also be used as a means of limiting the required slug catcher size. By pigging at frequent intervals, liquid inventory buildup in a pipeline can be reduced, and the maximum slug size can be limited. The required downstream slug catcher size must take into account pigging frequency.

Operational hazards are associated with pigging. The very large slugs swept ahead of the pig may overwhelm inadequately sized downstream facilities. Pigs may also occasionally be destroyed in the pipeline and the resulting debris may damage downstream fittings or equipment. Even worse, the pig may become stuck in the line and require an expensive shutdown for location and removal.

FIG. 17-23

Working Pressures Refinery Piping

To determine allowable internal working pressure for straight sections of pipe in accordance with ANSI B31.3, "Code for Pressure Piping, Petroleum Refinery Piping", use the following:

$$t_m = t + c$$

$$t = \frac{P_i d_o}{2(S'E' + P_i Y')} \quad \text{or} \quad P_i = \frac{2\,tS'E'}{d_o - 2\,tY'}$$

For $t > \frac{d_o}{6}$ or $\frac{P_i}{S'\,E'} > 0.385$ calculation of pressure design thickness requires special consideration.

where:

t_m = minimum required thickness, satisfying requirements for pressure, and mechanical, corrosion, and erosion allowances, inches. Selected thickness shall be no less than t_m plus the manufacturer's negative tolerance. The typical negative tolerance is 12.5%.

t = pressure design thickness, in.

c = the sum of the mechanical allowances (thread depth and groove depth), corrosion, and erosion allowances, in.

P_i = internal design pressure, psig.

d_o = outside diameter of pipe, in.

S' = allowable stresses, psi.

E' = longitudinal weld joint factor:
Seamless = 1.000, ERW = 0.85

Y' = coefficient having values for ferritic steels as follows: 0.4 up to and including 900°F
0.5 for 950°F
0.7 for 1,000°F and above

PIPE AND FLANGE DATA

The Petroleum Refinery Piping Code (ANSI B31.3) is used to determine the allowable pressure limits for piping inside refineries and other processing facilities. Refer to Fig. 17-23 for the calculation method.

FIG. 17-24

Working Pressures Transmission Lines

To determine allowable internal working pressures for piping outside of refineries and other processing facilities in accordance with ANSI B31.8-1999, "Code of Pressure Piping, Gas Transmission and Distribution Piping," use the following:

$$P_i = \frac{2\,S''\,t}{d_o}(F'')(E'')(T'')$$

Where

P_i = Design pressure, psig

S'' = Specified minimum yield strength, psi

d_o = Nominal outside diameter, in.

t = Nominal wall thickness, in.

F'' = Construction type design factor, Table 841.114A and Par. 840.2 (see note)

Location	Class	F″
1	Div 1	.80
	Div 2	.72
2		.60
3		.50
4		.40

Complete details are covered in Par. 841.

E'' = Longitudinal joint factor, Table 841.115A
Normally a factor of 1.0 is used for seamless and welded pipe except for the following:

Fusion Welded A 134 and A 139	0.80
Spiral Welded A 211	0.80
Furnace Butt Welded ASTM-A53, API-5L	0.60

T'' = Temperature derating factor, Table 841.116A

Temp, °F	Factor T″
250 or less	1.000
300	0.967
350	0.933
400	0.900
450	0.867

For intermediate temperatures, interpolate for derating factor.

Note: Factor reflecting location of line, proximity to roads, public or private land, etc.

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FIG. 17-25

Representative Allowable Stresses in Tension for Materials
(Developed from ASME B31.3, 2002, Tables A-1, A-1B)

Material	Specification	Grade	Class	Factor (E)	Tensile Strength min. psi	Yield Strength min. psi	(6) Min. Temp.	BASIC ALLOWABLE STRESSES IN TENSION, psi (1) Metal Temperature, °F (7) Min. Temp. to 100	200	300	400	500	600	650	700	750	800	850	900	950	1000	1050	1100
CARBON STEEL																							
Seamless Pipe																							
	ASTM A53	A	Type S		48000	30000	–20	16000	16000	16000	16000	16000	14800	14500	14400	10700	9300	7900	6500	4500	2500	1600	1000
	ASTM A53	B	Type S		60000	35000	–20	20000	20000	20000	20000	18900	17300	17000	16500	13000	10800	8700	6500	4500	2500	1600	1000
	ASTM A106	A			48000	30000	–20	16000	16000	16000	16000	16000	14800	14500	14400	10700	9300	7900	6500	4500	2500	1600	1000
	ASTM A106	B			60000	35000	–20	20000	20000	20000	20000	18900	17300	17000	16500	13000	10800	8700	6500	4500	2500	1600	1000
	ASTM A106	C			70000	40000	–20	23300	23300	23300	22900	21600	19700	19400	19200	14800	12000						
	ASTM A120						–20	12000	11400														
	ASTM A333	1			55000	30000	–50	18300	18300	17700	17200	16200	14800	14500	14400	12000	10200	8300	6500	4500	2500	1600	1000
	ASTM A334	1			55000	30000	–50	18300	18300	17700	17200	16200	14800	14500	14400	12000	10200	8300	6500	4500	2500	1600	1000
	ASTM A333	6			60000	35000	–50	20000	20000	20000	20000	18900	17300	17000	16500	13000	10800	8700	6500	4500	2500	1600	1000
	ASTM A334	6			60000	35000	–50	20000	20000	20000	20000	18900	17300	17000	16500	13000	10800	8700	6500	4500	2500	1600	1000
	API 5L	A			48000	30000	–20	16000	16000	16000	16000	16000	14800	14500	14400	10700	9300	7900	6500	4500	2500	1600	1000
	API 5L	B			60000	35000	–20	20000	20000	20000	20000	18900	17300	17000	16500	13000	10800	8700	6500	4500	2500	1600	1000
	API 5LX	X42			60000	42000	–20	20000	20000	20000	20000												
	API 5LX	X46			63000	46000	–20	21000	21000	21000	21000												
	API 5LX	X52			66000	52000	–20	22000	22000	22000	22000												
	API 5LX	X52			72000	52000	–20	24000	24000	24000	24000												
Electric Resistance Welded Pipe																							
	ASTM A53	A	Type E	0.85	48000	30000	–20	13800	13800	13600	13600	13600	12600	12300	12250	9100	7900	6700	5500	3800	2150	1350	850
	ASTM A53	B	Type E	0.85	60000	35000	–20	17000	17000	17000	17000	16100	14700	14500	14000	11000	9200	7350	5500	3800	2150	1350	850
	ASTM A120			0.85			–20	10200	9600														
LOW AND INTERMEDIATE ALLOY STEEL & STAINLESS STEEL (4.40) - Seamless Pipe																							
3 1/2 Ni	ASTM A333	3			65000	35000	–150	21700	19600	19600	18700	17800	16800	16300	15500	13900	11400	9000	6500	4500	2500	1600	1000
3 1/2 Ni	ASTM A334	3			65000	35000	–150	21700	19600	19600	18700	17800	16800	16300	15500	13900	11400	9000	6500	4500	2500	1600	1000
Ni-Cr-Cu-Al	ASTM A333	4			60000	35000	–150	20000	19100	18200	17300	16400	16500	15000									
2 1/4 Ni	ASTM A333	7			65000	35000	–100	21700	19600	19600	18700	17600	16800	16300	15500	13900	11400	9000	6500	4500	2500	1600	1000
2 1/4 Ni	ASTM A334	7			65000	35000	–100	21700	19600	19600	18700	17600	16800	16300	15500	13900	11400	9000	6500	4500	2500	1600	1000
9 Ni	ASTM A333	8			100000	75000	–320	31700	31700														
9 Ni	ASTM A334	8			100000	75000	–320	31700	31700														
18Cr-8Ni Pipe	ASTM A376	TP304			75000	30000	–425	20000	*20000*	*20000*	18700	17500	16400	16200	16000	15600	15200	14900	14600	14400	*13800*	*12200*	9700
18Cr-8Ni Pipe	ASTM A376	TP304H			75000	30000	–325	20000	*20000*	*20000*	18700	17500	16400	16200	16000	15600	15200	14900	14600	14400	*13800*	12200	9700

Note: ASME 31.3 Appendix A includes notes which may additionally limit allowable stress values or application of the above materials due to temperature limitations, wall thickness, heat treating, material composition, etc. Refer to ASME 31.3 Appendix A notes for these limitations or special requirements applicable to particular materials.

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FIG. 17-26

Design Properties and Allowable Working Pressures for Piping ASTM A106, grade B seamless pipe—Petroleum Refinery Piping Code for Pressure Piping ANSI B31.3-2002—Corrosion allowance = 0.05 inch

Nom pipe size in.	Sch. No.	Weight of pipe lb./ft.	O.D. in.	Wall thk. in.	I D (d) in.	Flow area sq ft	Allowable working pressures for temperatures (in °F) not to exceed.						
							–20 to 100	200	300	400	500	600	700
1/2	S40	.851	.840	.109	.622	.00211	2258	2258	2258	2258	2134	1953	1863
3/4	S40	1.131	1.050	.113	.824	.00371	1933	1933	1933	1933	1827	1672	1595
	X80	1.474		.154	.742	.00300	3451	3451	3451	3451	3261	2985	2847
1	S40	1.679	1.315	.133	1.049	.00600	2103	2103	2103	2103	1988	1819	1735
	X80	2.172		.179	.957	.00499	3468	3468	3468	3468	3277	3000	2861
	160	2.844		.250	.815	.00362	5720	5720	5720	5720	5405	4948	4719
	XX	3.659		.358	.599	.00196	9534	9534	9534	9534	9010	8247	7866
1-1/2	S40	2.718	1.900	.145	1.610	.01414	1672	1672	1672	1672	1580	1446	1379
	X80	3.632		.200	1.500	.01225	2777	2777	2777	2777	2625	2402	2291
	160	4.866		.281	1.338	.00976	4494	4494	4494	4494	4247	3887	3707
	XX	6.409		.400	1.100	.00660	7228	7228	7228	7228	6831	6253	5963
2	S40	3.653	2.375	.154	2.067	.02330	1469	1469	1469	1469	1388	1270	1212
	X80	5.022		.218	1.939	.02050	2488	2488	2488	2488	2351	2152	2053
	160	7.445		.343	1.687	.01556	4600	4600	4600	4600	4347	3979	3795
	XX	9.030		.436	1.503	.01232	6284	6284	6284	6284	5939	5436	5185
3	S40	7.58	3.500	.216	3.068	.05130	1640	1640	1640	1640	1550	1419	1353
	X80	10.25		.300	2.900	.04587	2552	2552	2552	2552	2412	2207	2105
	160	14.33		.438	2.624	.03755	4122	4122	4122	4122	3895	3566	3401
	XX	18.58		.600	2.300	.02885	6089	6089	6089	6089	5754	5267	5024
4	S40	10.79	4.500	.237	4.026	.08840	1439	1439	1439	1439	1360	1244	1187
	X80	14.99		.337	3.826	.07986	2275	2275	2275	2275	2150	1968	1877
	160	22.51		.531	3.438	.06447	3978	3978	3978	3978	3760	3441	3282
	XX	27.54		.674	3.152	.05419	5307	5307	5307	5307	5015	4590	4378
6	S40	18.98	6.625	.280	6.065	.2006	1205	1205	1205	1205	1139	1042	994
	X80	28.58		.432	5.761	.1810	2062	2062	2062	2062	1948	1783	1701
	160	45.30		.718	5.187	.1469	3753	3753	3753	3753	3546	3246	3097
	XX	53.17		.864	4.897	.1308	4659	4659	4659	4659	4403	4030	3844
8	S40	28.56	8.625	.322	7.981	.3474	1098	1098	1098	1098	1037	950	906
	X80	43.4		.500	7.625	.3171	1864	1864	1864	1864	1761	1612	1537
	XX	72.4		.875	6.875	.2578	3554	3554	3554	3554	3359	3074	2932
	160	74.7		.906	6.813	.2532	3699	3699	3699	3699	3496	3200	3052
10	S40	40.5	10.750	.365	10.020	.5475	1022	1022	1022	1022	966	884	843
	X60	54.7		.500	9.750	.5185	1484	1484	1484	1484	1403	1284	1224
	160	115.7		1.125	8.500	.3941	3736	3736	3736	3736	3531	3232	3082
12	S	49.6	12.750	.375	12.000	.7854	888	888	888	888	839	768	732
	X	65.4		.500	11.750	.7528	1245	1245	1245	1245	1177	1077	1027
	160	160.3		1.312	10.126	.5592	3699	3699	3699	3699	3496	3200	3052
14	10	36.7	14.000	.250	13.500	.9940	486	486	486	486	460	421	401
	S30	54.6		.375	13.250	.9575	807	807	807	807	763	698	666
	X	72.1		.500	13.000	.9211	1132	1132	1132	1132	1069	979	934
16	10	42.1	16.000	.250	15.500	1.310	425	425	425	425	402	368	351
	S30	62.6		.375	15.250	1.268	705	705	705	705	666	609	581
	S40	82.8		.500	15.000	1.227	987	987	987	987	933	854	815
18	10	47.4	18.000	.250	17.500	1.670	377	377	377	377	357	326	311
	S	70.6		.375	17.250	1.622	625	625	625	625	591	541	516
	X	93.5		.500	17.000	1.575	876	876	876	876	828	757	722
20	10	52.7	20.000	.250	19.500	2.074	339	339	339	339	321	293	280
	S20	78.6		.375	19.250	2.021	562	562	562	562	531	486	464
	X30	104.1		.500	19.000	1.969	787	787	787	787	743	680	649
24	10	63.4	24.000	.250	23.500	3.012	282	282	282	282	267	244	233
	S20	94.6		.375	23.250	2.948	468	467	467	467	442	404	386
	X	125.5		.500	23.000	2.883	660	654	654	654	618	565	539

Note: The above allowable working pressures are calculated from Fig. 17-23 using a reduction in t_m to 87.5% of the wall thickness shown above to recognize mill wall tolerance of 12.5%.

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FIG. 17-27

Gas Transmission and Distribution Piping
Code for Pressure Piping ANSI B31.8-1999
Carbon Steel and High Yield Strength Pipe
(Values apply to A106, API 5L and API 5LX pipe having the same specified minimum yield strength as shown**)**

Nom Pipe Size	O.D.	Wall Thk.	Allowable Working Pressures up to 250°F, in psig																			
			Construction Type Design Factors																			
			Type A, F = 0.72*					Type B, F = 0.60					Type C, F = 0.50					Type D, F = 0.40				
			GR.B					GR.B					GR.B					GR.B				
			35,000	42,000	46,000	52,000	60,000	35,000	42,000	46,000	52,000	60,000	35,000	42,000	46,000	52,000	60,000	35,000	42,000	46,000	52,000	60,000
2	(STD)	.154	3268					2723					2270					1816				
	2.375	.218	4626					3855					3213					2570				
3	3.500 (STD)	.125	1800					1500					1250					1000				
		.156	2246					1872					1560					1248				
		.188	2707					2256					1880					1504				
		.216	3110					2592					2160					1728				
		.250	3600					3000					2500					2000				
		.281	4046					3372					2810					2248				
		.300	4320					3600					3000					2400				
4	4.500 (STD)	.125	1400	1680	1840			1167	1400	1533			973	1167	1278			778	933	1022		
		.156	1747	2097	2296			1456	1747	1913			1214	1456	1595			971	1165	1276		
		.188	2105	2526	2767			1754	2105	2306			1462	1755	1922			1170	1404	1537		
		.219	2453	2943	3223			2044	2453	2686			1704	2044	2239			1363	1635	1791		
		.237	2654	3185	3488			2212	2654	2907			1844	2212	2423			1475	1770	1938		
		.250	2800	3360	3680			2333	2800	3067			1945	2333	2556			1556	1869	2044		
		.281	3147	3776	4136			2623	3147	3447			2186	2622	2873			1748	2098	2298		
		.312	3494	4193	4593			2912	3494	3827			2427	2912	3190			1941	2330	2552		
		.337	3774	4530	4961			3145	3775	4134			2621	3146	3445			2097	2516	2756		
6	6.625 (STD)	.156	1187	1424	1560	1763		989	1187	1300	1469		824	989	1083	1224		659	791	866	980	
		.188	1429	1716	1880	2124		1192	1430	1567	1770		993	1192	1306	1475		794	954	1044	1180	
		.219	1666	2000	2190	2475		1388	1666	1825	2063		1157	1389	1521	1719		926	1111	1216	1375	
		.250	1902	2282	2500	2826		1585	1902	2083	2355		1321	1585	1736	1963		1057	1268	1389	1570	
		.280	2130	2556	2799	3164		1775	2130	2333	2637		1479	1775	1944	2198		1183	1420	1555	1758	
		.312	2373	2848	3120	3527		1978	2374	2600	2933		1649	1978	2167	2449		1319	1582	1733	1959	
		.375	2853	3424	3750	4237		2377	2853	3125	3531		1981	2378	2604	2943		1585	1902	2083	2354	
		.432	3287	3943	4319	4883		2739	3286	3599	4069		2283	2738	3000	3391		1826	2191	2400	2713	
8	8.625 (STD)	.156	912	1094	1198	1354		760	912	998	1128		633	760	832	940		506	608	666	752	
		.188	1098	1318	1444	1632		915	1098	1203	1360		763	915	1003	1133		610	732	802	907	
		.203	1186	1424	1559	1762		989	1186	1299	1469		824	989	1083	1224		659	791	866	979	
		.219	1280	1535	1681	1901		1067	1280	1401	1584		889	1067	1168	1320		711	853	934	1056	
		.250	1461	1753	1920	2170		1217	1461	1600	1809		1014	1217	1333	1507		812	974	1067	1206	
		.277	1618	1942	2128	2405		1349	1618	1773	2004		1124	1349	1478	1670		899	1079	1182	1336	
		.312	1823	2189	2396	2709		1520	1823	1997	2258		1266	1520	1664	1881		1013	1216	1331	1505	
		.322	1882	2258	2473	2796		1568	1882	2061	2329		1307	1568	1717	1941		1045	1254	1374	1553	
		.344	2011	2412	2642	2988		1676	2011	2202	2490		1396	1676	1835	2075		1117	1340	1468	1660	
		.375	2191	2628	2880	3256		1826	2191	2399	2713		1521	1826	1999	2261		1217	1460	1599	1808	
		.438	2560	3071	3364	3803		2133	2560	2804	3170		1778	2133	2336	2641		1422	1706	1869	2113	
		.500	2922	3506	3840	4341		2435	2922	3200	3617		2029	2435	2667	3014		1623	1948	2133	2412	
10	10.750 (STD)	.188	881	1058	1158	1310		733	881	965	1091		612	735	804	909		490	588	644	728	
		.203	959	1143	1251	1415		794	952	1043	1179		661	794	869	983		529	635	695	786	
		.219	1026	1231	1348	1525		855	1026	1124	1271		713	855	936	1059		570	684	749	847	
		.250	1172	1407	1540	1741		977	1172	1284	1451		814	977	1070	1209		651	781	856	967	
		.279	1309	1570	1719	1944		1091	1309	1433	1620		909	1091	1194	1350		727	872	955	1080	
		.307	1440	1728	1892	2138		1200	1440	1577	1782		1000	1200	1314	1486		800	960	1051	1189	
		.344	1613	1935	2120	2396		1344	1613	1767	1997		1120	1344	1473	1664		896	1075	1178	1331	
		.365	1711	2054	2249	2542		1426	1711	1874	2119		1188	1426	1562	1766		951	1141	1249	1412	
		.438	2054	2464	2700	3051		1712	2054	2250	2543		1426	1712	1875	2119		1141	1369	1500	1695	
		.500	2344	2813	3081	3483		1953	2344	2567	2902		1628	1953	2140	2419		1302	1563	1712	1935	
12	12.750 (STD)	.188	743	892	977	1104		619	743	814	920		516	619	678	767		413	495	543	613	
		.203	803	963	1055	1193		669	803	879	995		558	669	733	829		446	535	586	663	
		.219	866	1039	1138	1287		722	866	948	1073		601	722	790	894		481	577	632	715	
		.250	988	1186	1299	1468		824	988	1082	1224		686	824	902	1020		549	659	722	816	
		.281	1111	1332	1460	1651		926	1111	1217	1376		771	926	1014	1146		617	740	811	917	
		.312	1233	1480	1620	1832		1028	1233	1350	1527		856	1028	1125	1273		685	822	900	1018	
		.330	1305	1566	1715	1939		1088	1305	1430	1616		906	1088	1191	1346		725	870	953	1077	
		.344	1359	1631	1786	2020		1133	1359	1488	1683		944	1133	1240	1403		755	906	992	1122	
		.375	1482	1779	1948	2202		1235	1482	1624	1835		1029	1235	1353	1529		824	988	1082	1224	
		.406	1606	1926	2110	2385		1338	1606	1758	1988		1115	1338	1465	1656		892	1070	1172	1325	
		.438	1732	2077	2275	2572		1443	1732	1896	2144		1203	1443	1580	1786		962	1154	1264	1429	
		.500	1976	2372	2598	2936		1647	1976	2165	2447		1373	1647	1804	2039		1098	1318	1443	1631	

* Type A construction also applicable to "Liquid Petroleum Transportation Piping Code," ANSI B31.4-2002

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FIG. 17-27 (Cont'd.)

Gas Transmission and Distribution Piping

Nom Pipe Size	O.D.	Wall Thk.	Allowable Working Pressures up to 250°F, in psig																			
			Construction Type Design Factors																			
			Type A, F = 0.72*					Type B, F = 0.60					Type C, F = 0.50					Type D, F = 0.40				
			GR.B					GR.B					GR.B					GR.B				
			35,000	42,000	46,000	52,000	60,000	35,000	42,000	46,000	52,000	60,000	35,000	42,000	46,000	52,000	60,000	35,000	42,000	46,000	52,000	60,000
16	16.000 (STD)	.219	689	828	905	1024	1183	575	689	755	854	986	479	575	629	711	822	383	460	503	569	657
		.250	786	945	1035	1170	1350	656	788	863	975	1125	547	656	719	813	938	438	525	575	650	750
		.281	886	1063	1164	1316	1518	738	886	970	1097	1265	615	738	809	914	1054	492	591	647	731	843
		.312	982	1179	1291	1460	1685	818	982	1076	1217	1404	682	819	896	1014	1170	546	655	717	811	936
		.344	1084	1300	1424	1609	1858	903	1084	1187	1341	1548	753	903	989	1118	1290	602	722	791	894	1032
		.375	1181	1418	1553	1755	2025	984	1181	1294	1463	1688	820	984	1078	1219	1407	656	788	863	975	1125
		.438	1379	1655	1813	2049	2365	1149	1379	1511	1707	1971	958	1149	1259	1423	1643	766	919	1007	1138	1314
		.500	1575	1890	2070	2340	2700	1313	1575	1725	1950	2250	1094	1313	1438	1625	1875	875	1050	1150	1300	1500
		.625	1969	2363	2588	2925	3375	1641	1969	2157	2438	2812	1368	1641	1796	2031	2344	1094	1313	1438	1625	1875
20	(STD) 20.000	.250	630	756	828	936	1080	525	630	690	780	900	438	525	575	650	750	350	420	460	520	600
		.281	709	851	931	1053	1214	591	709	776	878	1012	492	591	647	731	843	394	473	518	585	674
		.312	786	943	1033	1168	1348	656	786	861	973	1123	547	656	719	813	936	438	525	575	650	749
		.344	867	1040	1139	1289	1486	723	868	950	1074	1238	603	723	791	895	1032	482	578	633	716	826
		.375	945	1134	1242	1404	1620	788	945	1035	1170	1350	656	788	863	975	1125	525	630	690	780	900
		.406	1023	1228	1345	1520	1754	853	1023	1121	1267	1462	710	853	934	1056	1218	568	682	747	844	974
		.438	1103	1324	1450	1639	1892	919	1103	1208	1366	1577	766	919	1007	1138	1314	613	735	805	910	1051
		.500	1260	1512	1656	1872	2160	1050	1260	1380	1560	1800	875	1050	1150	1300	1500	700	840	920	1040	1200
		.625	1575	1890	2070	2340	2700	1313	1575	1725	1950	2250	1094	1313	1438	1625	1875	875	1050	1150	1300	1500
		.750	1890	2268	2484	2808	3240	1575	1890	2070	2340	2700	1313	1575	1725	1950	2250	1050	1260	1380	1560	1800
24	(STD) 24.000	.281	590	709	776	877	1012	492	591	647	731	843	410	492	539	609	703	328	394	431	487	562
		.312	655	786	861	973	1123	547	656	719	812	936	456	547	599	677	780	365	438	479	542	624
		.344	722	866	949	1073	1238	602	722	791	894	1032	502	602	659	745	860	401	481	527	596	688
		.375	788	945	1035	1170	1350	656	788	862	975	1125	547	656	719	813	938	438	525	575	650	750
		.406	853	1024	1121	1267	1462	711	853	935	1056	1218	592	711	779	880	1015	474	569	623	704	812
		.438	919	1103	1208	1366	1577	766	919	1006	1138	1314	638	766	839	948	1095	510	613	671	758	876
		.500	1050	1260	1380	1560	1800	875	1050	1150	1300	1500	729	875	958	1083	1250	583	700	767	867	1000
		.625	1312	1575	1725	1950	2250	1094	1313	1437	1625	1875	911	1094	1198	1354	1563	729	875	958	1083	1250
		.750	1575	1890	2070	2340	2700	1313	1575	1725	1950	2250	1094	1313	1438	1625	1875	875	1050	1150	1300	1500
26	26.000 (STD)	.281	545	654	717	810	934	454	545	597	675	778	379	454	498	563	649	303	363	398	450	519
		.312	604	727	796	900	1037	503	604	663	750	864	421	505	553	625	720	337	404	442	500	576
		.344	667	800	876	990	1143	556	666	730	825	953	463	555	606	688	794	370	444	487	550	635
		.375	726	872	955	1080	1246	606	727	796	900	1039	505	606	663	750	866	404	485	531	600	692
		.406	787	945	1035	1170	1349	656	787	863	975	1124	547	656	719	813	937	437	525	575	650	750
		.438	848	1018	1115	1260	1456	707	848	929	1050	1213	589	707	774	875	1011	471	565	619	700	809
		.500	969	1163	1274	1440	1662	808	969	1062	1200	1385	673	808	885	1000	1154	538	646	708	800	923
		.625	1211	1454	1592	1800	2077	1010	1212	1327	1500	1731	841	1010	1106	1250	1442	673	808	885	1000	1154
		.750	1454	1745	1911	2160	2492	1212	1454	1592	1800	2077	1010	1212	1327	1500	1731	808	969	1062	1200	1385
30	(STD) 30.000	.312	525	630	690	780	899	438	525	575	650	749	365	438	479	542	624	292	350	383	433	499
		.344	578	693	759	858	991	482	577	632	715	826	401	481	527	596	688	321	385	422	477	550
		.375	630	756	828	936	1080	525	630	690	780	900	437	525	575	650	750	350	420	460	520	600
		.406	682	819	897	1014	1169	568	682	747	845	974	474	569	623	704	812	379	455	498	563	650
		.438	735	882	966	1092	1261	612	735	805	910	1051	510	612	671	758	876	408	490	537	607	701
		.500	840	1008	1104	1248	1440	700	840	920	1040	1200	583	700	767	867	1000	467	560	613	693	800
		.625	1050	1260	1380	1560	1800	875	1050	1150	1300	1500	729	875	958	1083	1250	583	700	767	867	1000
		.750	1260	1512	1656	1872	2160	1050	1260	1380	1560	1800	875	1050	1150	1300	1500	700	840	920	1040	1200

* Type A construction also applicable to "Liquid Petroleum Transportation Piping Code," ANSI B31.4-2002

Notes: 1. All dimensions are in inches
2. See Fig 17-24

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FIG. 17-28

Pressure-Temperature Ratings for Pipe Flanges and Flanged Fittings from ANSI B16.5-1996

CLASS	150	300	400	600	900	1500	2500
Material Group 1.1			**(Carbon Steel)**			**A105 (1), A216–WCB (1), A515–70 (1) A516–70 (1) (2) A350–LF2 (1), A537–C1.1 (3)**	
°F	Pressures are in pounds per square inch, gauge (psig)						
–20 to 100	285	740	990	1480	2220	3705	6170
200	260	675	900	1350	2025	3375	5625
300	230	655	875	1315	1970	3280	5470
400	200	635	845	1270	1900	3170	5280
500	170	600	800	1200	1795	2995	4990
600	140	550	730	1095	1640	2735	4560
650	125	535	715	1075	1610	2685	4475
700	110	535	710	1065	1600	2665	4440
750	95	505	670	1010	1510	2520	4200
800	80	410	550	825	1235	2060	3430
850	65	270	355	535	805	1340	2230
900	50	170	230	345	515	860	1430
950	35	105	140	205	310	515	860
1000	20	50	70	105	155	260	430
Material Group 2.1			**(Type 304)**			**A182–F304 (5), A182–F304H A240–304 (5), A351–CF8 (5) A351–CF3 (4)**	
–20 to 100	275	720	960	1440	2160	3600	6000
200	230	600	800	1200	1800	3000	5000
300	205	540	720	1080	1620	2700	4500
400	190	495	660	995	1490	2485	4140
500	170	465	620	930	1395	2330	3880
600	140	435	580	875	1310	2185	3640
650	125	430	575	860	1290	2150	3580
700	110	425	565	850	1275	2125	3540
750	95	415	555	830	1245	2075	3460
800	80	405	540	805	1210	2015	3360
850	65	395	530	790	1190	1980	3300
900	50	390	520	780	1165	1945	3240
950	35	380	510	765	1145	1910	3180
1000	20	320	430	640	965	1605	2675
1050		310	410	615	925	1545	2570
1100		255	345	515	770	1285	2145
1150		200	265	400	595	995	1655
1200		155	205	310	465	770	1285
1250		115	150	225	340	565	945
1300		85	115	170	255	430	715
1350		60	80	125	185	310	515
1400		50	65	90	145	240	400
1450		35	45	70	105	170	285
1500		25	35	55	80	135	230

Notes:
(1) Upon prolonged exposure to temperatures above about 800°F (425°C), the carbide phase of carbon steel may be converted to graphite: permissible but not recommended for prolonged use above 800°F
(2) Not to be used over 850°F
(3) Not to be used over 700°F
(4) Not to be used over 800°F
(5) At temperatures over 1000°F (540°C), use only when the carbon content is 0.04 percent or higher
(6) For temperatures above 1000°F (540°C), use only if the material is heat treated by heating it to a temperature of at least 1900°F (1040°C) and quenching in water or rapidly cooling by other means

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The table of allowable stresses, Fig. 17-25, is extracted from ANSI B31.3. The designer is strongly urged to consult the latest ANSI B31.3 publication for full description of the code. A tabular compilation of maximum allowable working pressures calculated according to ANSI B31.3 appears in Fig. 17-26.

For piping outside of refineries and other processing facilities, a separate code applies for determining allowable pressure limits, ANSI B31.8. Refer to Fig. 17-24 for the calculation method.

The designer is encouraged to refer to the latest ANSI B31.8 standard for comprehensive code description. A tabular compilation of maximum allowable working pressures computed according to ANSI B31.8 appears in Fig. 17-27.

Fig. 17-28 provides pressure ratings for steel flanges and flanged fittings.

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SECTION 18

Utilities

Well designed and functioning utilities are essential to reliable operation of gas processing plants. The extent of the utilities required for gas processing plants varies widely with the type of facility and process units involved in the project. Also, in many situations some of the utilities are provided by third parties or shared with other facilities.

Utility systems are covered broadly in this Section. Many of the equipment components and systems in utility systems are covered in other Sections of the Data Book. The following utility systems will be covered in this Section:

- Steam Systems
- Heat Medium Systems
- Instrument Air Systems
- Nitrogen Systems
- Fuel Systems
- Flare/Relief Systems
- Water Treating Systems
- Electrical Systems

In addition, general information on plant spacing and maintenance procedures is included in this Section.

FIG. 18-1

Nomenclature

A = ampere
AC = alternating current
BD = blowdown, gpm
DC = direct current
E = voltage, volts
eff = efficiency, percent
F = filtering rate, gpm
hp = horsepower
I = current, amperes
kV = kilovolt
kW = kilowatt
kVA = kilovolt-ampere
KVAr = reactive kilovolt-amperes, kilovar
N.C. = normally closed
N.O. = normally open
ppmw = part per million by weight
pAlk = $\log\left(\frac{1}{\text{ppmw of M alkalinity}}\right)$ (see Fig. 18-22)
pCa = $\log\left(\frac{1}{\text{ppmw of Ca}}\right)$ (see Fig. 18-22)
pH_S = calculated pH at saturation with calcium carbonate (see Fig. 18-22)
PF = power factor, decimal
R = resistance, ohms
SS_F = final suspended solids content, ppmw
SS_I = initial suspended solids content, ppmw
V = electromotive force, volts
W = watt
~ = frequency, Hertz
φ = symbol for phase, usually preceded by a number

Alkalinity: The acid neutralizing capacity of a water. It is usually expressed as "M" alkalinity (the methyl orange endpoint at a pH ≅ 4.3) and "P" alkalinity (the phenolphthalein endpoint at a pH ≅ 8.3).

Several ions contribute to alkalinity, but it is generally due to bicarbonate (HCO_3^{-1}), carbonate (CO_3^{-2}), and hydroxyl (OH^{-1}) ions.

Alkalinity and pH relationships: The alkalinity of naturally occurring waters is usually due to calcium and magnesium bicarbonate and occasionally to some sodium bicarbonate. Carbonate or hydroxide alkalinity is rarely encountered in raw waters.

"M" alkalinity = all bicarbonate + all carbonate + all hydroxide
"P" alkalinity = 1/2 carbonate + all hydroxide
If 2P < M, hydroxide = 0
If 2P = M, bicarbonate and hydroxide = 0
If 2P > M, bicarbonate = 0
If P = 0, all alkalinity is bicarbonate
If P = M, all alkalinity is hydroxyl
M-2P = bicarbonate alkalinity
2P-M = hydroxide alkalinity

Ampacity: The continuous current-carrying capacity of electric conductors expressed in amperes under specific operating temperatures.

Biochemical Oxygen Demand (BOD): A measure of the oxygen consumed in the oxidation of organic and oxidizable inorganic materials in wastewater (expressed in ppm).

Blowdown: The removal of a portion of the water in a boiler or cooling water system to reduce concentrations of dissolved and/or suspended solids.

Bonding: The permanent joining of metallic parts to form an electrically conductive path which will assure electrical continuity and the capacity to conduct safely any current likely to be imposed.

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FIG. 18-1 (Cont'd)

Nomenclature

Branch Circuit: The circiut conductors between the final overcurrent device protecting the circuit and the outlet(s).

Bus: A conductor, or group of conductors, that serve as a common connection for two or more circuits.

Cathodic Protection: A means of reducing or preventing corrosion of a metal by making it the cathode in a conducting medium by means of an impressed or galvanic direct electric current.

Caustic Embrittlement: A peculiar type of boiler corrosion characterized by cracking of the metal along the grain boundaries which may occur when highly stressed metal is exposed to concentrated boiler water. It is usually associated with high concentrations of sodium hydroxide.

Circuit Breaker: A device designed to open and close a circuit by nonautomatic means and to open the circuit automatically on a predetermined overcurrent without injury to itself when properly applied within its rating. The automatic opening means can be integral, direct acting with the circuit breaker, or remote from the circuit breaker.

Adjustable: A qualifying term indicating that the circuit breaker can be set to trip at various values of current and/or time within a predetermined range.

Instantaneous Trip: A qualifying term indicating that no delay is purposely introduced in the tripping action of the circuit breaker.

Inverse Time: A qualifying term indicating there is purposely introduced a delay in the tripping action of the circuit breaker, which delay decreases as the magnitude of the current increases.

Nonadjustable: A qualifying term indicating that the circuit breaker does not have any adjustment to alter the value of current at which it will trip or the time required for its operation.

Setting: (of Circuit Breaker) The value of current and/or time at which an adjustable circuit breaker is set to trip.

Conductivity: The ability of water to conduct an electrical current. As such, it is the opposite of resistivity and is related to the concentration of dissolved (ionizable) solids in the water. The measure of conductivity is conductance (the reciprocal of resistance) whose units are normally microhms equal to 1,000,000/ohms. The relationship between conductance and dissolved solids concentration will vary depending on the compounds present in the water as shown in Fig. 18-8. Temperature is also a factor and most conductivity meters provide for temperature compensation.

Conductor: A wire or combination of wires not insulated from one another, suitable for carrying a single electric current.

Continuous Load: A load where the maximum current is expected to continue for three hours or more.

Controller: A device or group of devices that serves to govern, in some predetermined manner, the electric power delivered to the apparatus to which it is connected.

Demand Factor: The ratio of the maximum demand of a system, or part of a system, to the total connected load of a system or the part of the system under consideration.

Duty:

Continuous Duty: Operation at a substantially constant load for an indefinitely long time.

Intermittent Duty: Operation for alternate intervals of (1) load and no load; or (2) load and rest; or (3) load, no load, and rest.

Non-plugging, Non-jogging Duty: The rate of operation shall not exceed five openings or closings per minute and shall be not more than 10 in a 10-minute period.

Periodic Duty: Intermittent operation in which the load conditions are regularly recurrent.

Plug-Stop, Plus-Reverse, and Jogging Duty: Require repeated interruption of stalled motor current or repeated closing of high transient currents encountered in rapid motor reversal.

Short-Time Duty: Operation at a substantially constant load for a short and definitely specified time.

Varying Duty: Operation at loads, and for intervals of time, both of which may be subject to wide variation.

Enclosure: The case or housing of apparatus, or the fence or walls surrounding an installation to prevent personnel from accidentally contacting energized parts, or to protect the equipment from physical damage. See text section "NEMA Enclosures."

Explosion-proof Apparatus: Apparatus enclosed in a case that is capable of withstanding an explosion of a specified gas or vapor which may occur within it and of preventing the ignition of a specified gas or vapor surrounding the enclosure by sparks, flashes, or explosion of the gas or vapor within, and which operates at such an external temperature that a surrounding flammable atmosphere will not be ignited thereby.

Feeder: All circuit conductors between the service equipment, or the generator switchboard of an isolated plant, and the final branch-circuit overcurrent device.

Fitting: An accessory such as a locknut, bushing, or other part of a wiring system that is intended primarily to perform a mechanical rather than an electrical function.

Flammable and Combustible Liquids: A flammable liquid is one that has a closed cup flash point below 100°F (38°C) and a vapor pressure not exceeding 40 psia (276 kPa) at 100°F (38°C). Combustible liquids have a closed cup flash point at or above 100°F (38°C).

Ground: A conducting connection, whether intentional or accidental, between an electrical circuit or equipment and the earth, or to some conducting body that serves in place of the earth.

Ground-Fault Circuit Interrupter: A device intended for the protection of personnel that functions to de-energize a circuit or portion thereof within an established period of time when a current to ground exceeds some predetermined value that is less than that required to operate the overcurrent protective device of the supply circuit.

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FIG. 18-1 (Cont'd.)

Nomenclature

Ground Water: Water from wells and springs is classified as ground water. Ground waters are usually relatively free of suspended solids. The composition of a ground water usually remains fairly constant with time.

Hertz: The unit of frequency, one cycle per second.

Hardness: A property of water which is usually caused by the presence of calcium and magnesium ions. Hardness causes excessive soap consumption domestically and is the source of most scale formation in boiler and cooling water systems. Waters with up to 50 ppmw hardness (as $CaCO_3$) are considered soft; waters with more than 200 ppmw hardness (as $CaCO_3$) are considered hard. Carbonate hardness is usually due to calcium and magnesium bicarbonate; noncarbonate hardness is due to calcium and magnesium salts of sulfate, chloride, and nitrate.

Impedance: The equivalence of resistance in an alternating current circuit, consisting of the sum of orthogonal components of resistance and reactants, measured in ohms.

InSight From (Within Sight From, Within Sight): Where the NEC specifies that one equipment shall be "in sight from," "within sight from," or "within sight," etc., of another equipment, one of the equipments specified shall be visible and not more than 50 feet (15.24 m) distant from the other.

Interrupting Rating: The highest current at rated voltage that an overcurrent protective device is intended to interrupt under specified test conditions. Equipment intended to break current at other than fault levels may have its interrupting rating implied in other ratings, such as horsepower or locked rotor current.

Intrinsically Safe: Equipment and wiring that are incapable of releasing sufficient electrical energy under normal or abnormal conditions to cause ignition of a specific hazardous atmospheric mixture in its most easily ignited concentration.

Ions, Anions, Cations: Electrically charged atoms or groups of atoms. In electrolysis, the negatively charged ions (anions, containing an excess of electrons denoted by minus signs such as Cl^{-1}, SO_4^{-2}) move toward the anode while the positively charged ions (cations, deficient in electrons denoted by plus signs such as Na^{+1}, Ca^{+2}) move toward the cathode.

Langelier Scaling Index (LSI), Ryznar Scaling Index (RSI): Empirical indices often used to predict the tendency of cooling water to form scale (Fig. 18-22).

$$LSI = pH - pH_S$$

$$RSI = 2pH_S - pH$$

pH = a measurement of the acidity or alkalinity of a system. The reference temperature for pH is 25°C (77°F) and the pH scale runs from 0 (highly acidic) to 14 (highly basic) with pH = 7.0 being neutral.

Motor-Circuit Switch: A switch, rated in horsepower, capable of interrupting the maximum operating overload current of a motor of the same horsepower rating as the switch at the rated voltage.

Motor Control Center: Motor Control Centers consist of a mechanical grouping of combination motor control, feeders, or other units arranged in a convenient assembly. They may or may not include interwiring or interlocking between units or to remotely mounted devices.

Outlet: A point of the wiring system at which current is taken to supply utilization equipment.

Overcurrent: Any current in excess of the rated current of equipment or the ampacity of a conductor. It may result from overload (see definition), starting, short circuit, or ground fault. A current in excess of rating may be accommodated by certain equpment and conductors for a given set of conditions. Hence, the rules for overcurrent protection are specific for particular situations.

Overload: Operation of equipment in excess of normal, full-load rating, or of a conductor in excess of rated ampacity which, when it persists for a sufficient length of time, would cause damage or dangerous overheating. A fault, wuch as a short circuit or ground fault, is not an overload. (See "Overcurrent").

Panelboard: A single panel or group of panel units designed for assembly in the form of a single panel; including buses, automatic overcurrent devices, and with or without switches for the control of light, heat, or power circuits; designed to be placed in a cabinet or cutout box placed in or against a wall or partition and accessible only from the front. (See "Switchboard").

Power Factor: Ratio of total watts to the total root-mean-square volt-amperes.

Raceway: An enclosed channel designed expressly for holding wires, cables, or busbars, with additional functions as permitted in the NEC. Raceways may be of metal or insulating material, and the term includes rigid metal conduit, rigid nonmetallic conduit, intermediate metal conduit, liquid-tight flexible metal conduit, electrical metallic tubing, underfloor raceways, cellular concrete floor raceways, cellular metal floor raceways, surface raceways, wireways, and busways.

Receptacle: A receptacle is a contact device installed at the outlet for the connection of a single attachment plug. A single receptacle is a single device on the same yoke. A multiple receptacle is a single contact device containing two or more receptacles.

Remote-Control Circuit: Any electric circuit that controls any other circuit through a relay or an equivalent device.

Service Drop: The overhead service conductors from the last pole or other aerial support to and including the splices, if any, connecting to the service-entrance conductors at the building or other structure.

Service Equipment: The necessary equipment, usually consisting of a circuit breaker or switch and fuses, and their accessories, located near the point of entrance of supply conductors to a building or other structure, or an otherwise defined area, and intended to constitute the main control and means of cutoff of the supply.

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FIG. 18-1 (Cont'd.)

Nomenclature

Short Circuit: A connection of comparatively low resistance accidentally or intentionally made between points on a circuit between which the resistance is normally much greater.

Solids (suspended, dissolved, total): Suspended solids are those which can be removed by filtration. Dissolved solids are in true solution, while total solids are the sum of the suspended and dissolved solids. Usually expressed in ppmw or mg/liter.

Surface Water: Water from lakes and streams is considered to be surface water. The composition of surface waters tends to vary widely with time.

Synchronism: The state where connected alternating-current systems, machines, or a combination operating at the same frequency and where the phase-angle displacements between voltages in them are constant, or vary about a steady and stable average value.

Synchronous Speed: Speed of rotation of the magnetic flux, produced by or linking the primary winding.

Switchboard: A large single panel, frame, or assembly of panels on which are mounted, on the face or back or both, switches, overcurrent and other protective devices, buses, and usually instruments. Switchboards are generally accessible from the rear as well as from the front and are not intended to be installed in cabinets. (See "Panelboard").

Switchgear: A form of switchboard in which all the equipment required to control an individual circuit, including bus, circuit breaker, disconnecting devices, current and potential transformers, controls, instruments, and relays, is assembled in one metal cubicle and the circuit breaker is provided with means for ready removal from the cubicle. Circuit breakers can be of the oil or air type, although the trend is strongly to the use of air circuit breakers.

Thermal Cutout: An overcurrent protective device that contains a heater element in addition to and affecting a renewable fusible member which opens the circuit. It is not designed to interrupt short-circuit currents.

Thermal Protector: (As applied to motors) A protective device for assembly as an integral part of a motor or motor-compressor and which, when properly applied, protects the motor against dangerous overheating due to overload and failure to start.

Voltage (of a Circuit): The greatest root-mean-square (effective) difference of potential between any two conductors of the current concerned. Some systems, such as 3-phase 4-wire, single-phase 3-wire, and 3-wire direct-current may have various circuits of various voltages.

Voltage, Norminal: A nominal value, assigned to a circuit or system for the purpose of conveniently designating its voltage class (as 120/240, 480Y/277,600, etc.). The actual voltage at which a circuit operates can vary from the nominal within a range that permits satisfactory operation of equipment.

Voltage to Ground: For grounded circuits, the voltage between the given conductor and that point or conductor of the circuit that is grounded; for ungrounded circuits, the greatest voltage between the given conductor and any other conductor of the circuit.

Useful Conversion and Equivalence Factors

	Parts per Million (ppmw)	Grains per Gallon	Grams per Liter	Milligrams per Liter	Wt%
1 part per million by weight	1.0	0.0584	0.001	1.0	0.0001
1 grain per gallon	17.1	1.000	0.017	17.1	0.0017
1 gram per liter	1000	58.4	1.0	1000	0.1
1 milligram per liter	1.0	0.058	0.001	1.0	0.0001
1 percent (wt)	10000	584	10.0	10000	1.0

1 cu ft water @ 60°F = 62.37 lbs = 7.481 gal.
1 gal. = 231 cu in. = 0.1337 cu ft

1 lb water = 27.741 cu in. @ 60°F
1 lb water = 0.1201 gal. @ 60°F

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STEAM SYSTEMS

Steam generation can be accomplished with stand alone boilers or by utilizing gas turbine exhaust waste heat recovery. The steam requirements may be low pressure process steam such as is needed for amine unit reboilers or fractionator reboilers. These systems are easily developed with standard equipment.

More complex systems are used which generate high pressure steam for driving steam turbines as well as providing process steam needs. Fig. 18-2 shows an example integrated steam system. Information on steam turbine drivers can be found in Section 15 of this Data Book.

Information to enable calculations on steam systems can be found in the steam tables in Section 24.

Steam systems are also integrated into sulfur recovery units to handle the waste heat generated by the sulfur unit and aid in controlling the overall system. Examples of how steam generation is integrated into sulfur recovery units can be found in Section 22.

Proper water treating for steam system makeup is critical to the successful operation of a steam system. Information on water treating can be found in the Water Treating subsection of this Section. Also, information on handling boiler blowdown can also be found in this Section.

HEAT MEDIUM SYSTEMS

Heat medium systems, like steam systems are used to provide process heat needs in varoius units of gas processing plants. Heat medium systems have become popular in lieu of steam systems due to the elimination of makeup water treatment and handling of waste water. This may be important for environmental reasons as well as in areas where water makeup supply is problematic.

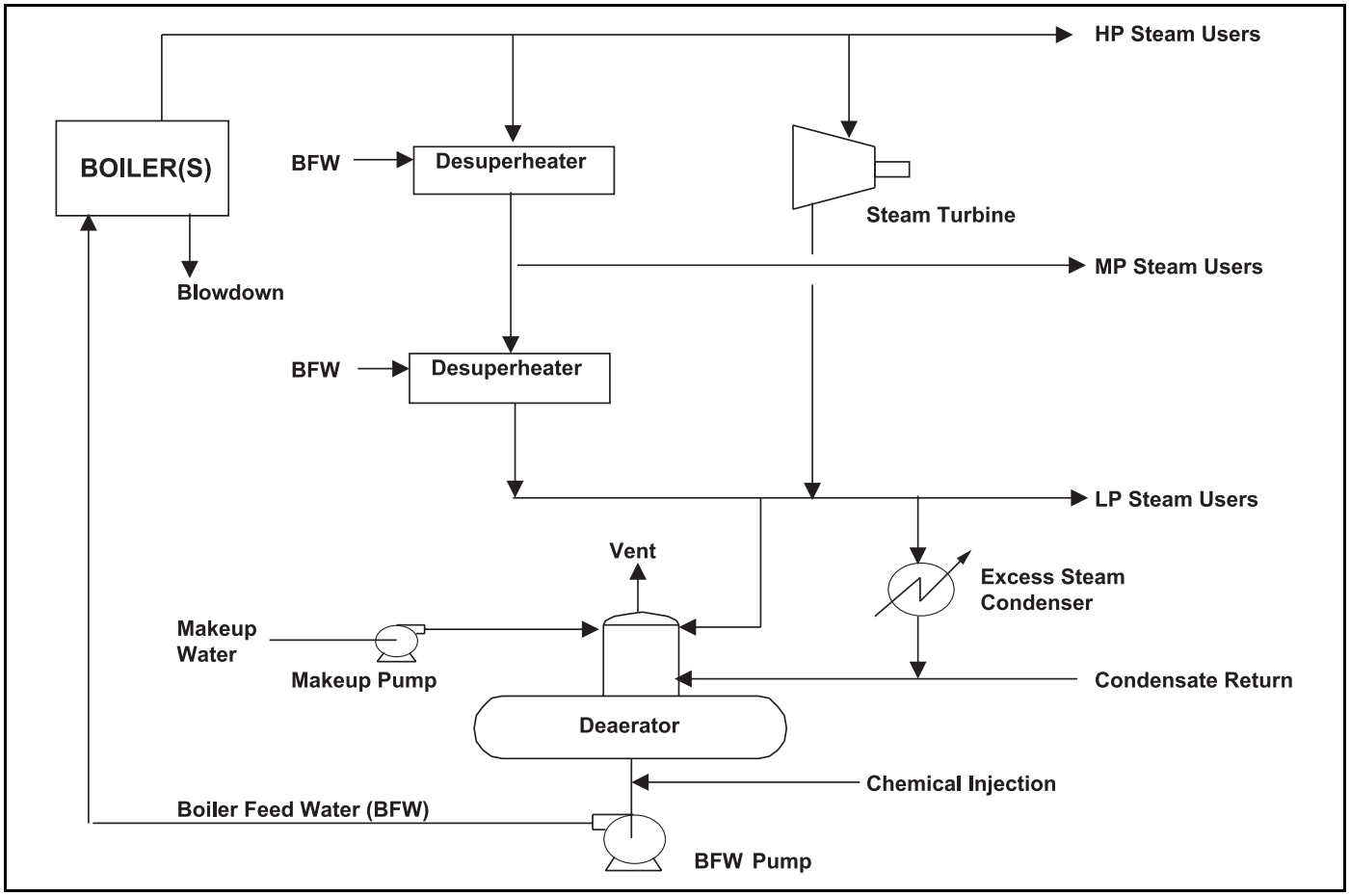
There are a number of heat transfer fluids which are used in the industry. Generally, the heat transfer fluids used in gas processing facilities are liquid phase. Fig. 18-3 provides data on some commercially available fluids.

Section 8 of this Data Book contains information on Fired Heaters and a discussion of heat medium systems.

One important design issue with the use of heat transfer fluids is in amine reboilers. Care must be taken to limit the film temperature in the reboiler to avoid amine degradation. A temperature approach of 75°F maximum is recommended.

FIG. 18-2

Example Integrated Steam System



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FIG. 18-3

Properties of Heat Transfer Fluids

Supplier	Trade Name	Product	Composition	Temperature Range (F)	Flash Point (F)	Fire Point (F)	Vapor Pressure Autoignition	
							Temp. (F)	At (temp) psia
DOW CHEMICAL	Dowtherm	A	Diphenyll oxide and biphenyl	60-750	236		1139	152 @ 750
		G	Di-, tri-aryl ethers	20-680	266		1083	49.1 @ 680
		J	Alkylated aromatic	-100 to 600	136		788	175 @ 600
		HT	Partially hydrogenated terphenyl	25-650	342		662	14.2 @ 650
		Q	Diphenylethane and alkylated aromatics	-30 to 625	249		773	48.1 @ 625
		RP	Diaryl Alkyl	30 to 660	381		725	13.6 @ 660
		MX	Alkylated aromatics	-10 to 625	329		788	15.1 @ 625
		T	C14 to C30 Alkyl Benzene Derivatives	14 to 550	370		707	2.6 @ 550
		SR-I	Inhibited ethylene glycol	-34 to 250	N/A	N/A	N/A	
		4000	Inhibited ethylene glycol	-34 to 350	N/A	N/A	N/A	
	Syltherm	800	Polydimethyl siloxane	-40 to 750	320		725	197 @ 750
		XLT	Polycimethyl siloxane	-150 to 500	116		662	75.5 @ 500
		HF	Polydimethyl siloxane	-100 to 500	145		671	39.8 @ 500
	Dowfrost		Inhibited propylene glycol	-28 to 250	N/A	N/A	N/A	
		HD	Inhibited propylene glycol	-28 to 350	N/A	N/A	N/A	
	Dowcal	10	Inhibited ethylene glycol	-34 to 350	N/A	N/A	N/A	
		20	Inhibited propylene glycol	-28 to 325				
		N	Inhibited propylene glycol	-18 to 250				
SASOL	Marlotherm	X	Diethyl benzene	-94 to 572	133		770	158 @ 572
		LH	Benzyl toluene	32-680	266		842	70@ 680
		SH	Dibenzyl toluene	158-662	392		842	12.5 @ 680
		N	Alkyl benzene	140-572	356		626	3.4 @ 572
		FP						
SOLUTIA	Therminol	LT	Alkyl substituted aromatic	-100 to 358	134	150	805	228 @ 600
		D-12	Synthetic hydrocarbon mixture	-120 to 500	138	160	531	57.4 @ 500
		FS	Inhibited propylene glycol in H20	-50 to 250	N/A	N/A	N/A	104 @ 200
		XP	White mineral oil	0-600	360	385	615	6.1 @ 600
		55	Synthetic hydrocarbon mixture	15-500	380	420	690	7 @ 600
		59	Alkyl substituted aromatic	-50 to 600	295	310	760	23.6 @ 600
		66	Modified terphenyl	30-650	375	420	750	11 @ 650
		VP-1	Diphenyl oxide and biphenyl	54-750	255	260	1150	156 @ 750
		VP-3	Phenylcyclohexane and bicyclohexyl	36 to 625	219	235	663	99.4 @ 625
PARA-THERM		HE	Paraffinic hydrocarbon	150-600	440	500	700	0.87 @ 600
		NF	Hydrotreated hydrocarbon	120-600	345	385	690	4.7 @ 600
		MR	Paraffinic hydrocarbon	30 to 550	300	325	621	3.2 @ 550
		OR	Hydrotreated hydrocarbon	175 to 550	350	395	630	0.95 @ 500
RADCO	Xceltherm	MKI	Diphenyl oxide and biphenyl	60 to 750	255	265	1150	435 @ 750
		XT	Alkyl aromatic	-70 to 650	275	283	803	61 @ 650
		500	Polyalphaolefin	-80 to 500	325	350	625	5.2 @ 500
		550	Mineral oil	-9 to 550	350	380	640	1.5 @ 550
		600	White oil	-4 to 600	380	420	680	3.6 @ 600
		HT	Alkyl aromatic	-35 to 660	417	425	842	5.9 @ 660
		LV1	Diphenylethan and	45 to 700	251	263	1120	419 @ 700
		LV2	Dipheyl	32 to 675	255	267	1120	416 @ 650
		LV3	Oxide (All LV's)	-35 to 650	266	278	1120	436 @ 650
		445FP	Parafinnic blend	5 to 550	445	480	715	1.5 @ 550

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INSTRUMENT AIR

Instrument air systems are critical to the proper operation of gas processing facilities since all the instruments and controls depend on dry, pressurized instrument air for operation. A typical instrument air system is shown in Fig. 18-4. Most systems are designed with 100% (or more) backup in the air compressor systems. Systems are generally designed to provide 100 psig air pressure for users. While most instrumentation components do not require this high pressure, often large valves with rapid closure requirements need this pressure to operate properly.

Drying of the instrument air is critical to prevent fouling and possible freezing in the air system and instruments. A –40°F dew point specification is common but specifications vary according to the climatic conditions of the site. Drying is usually accomplished with activated alumina or molecular sieve fixed bed driers similar to natural gas dehydrators (see Section 20). Heated regeneration similar to that shown in Section 20 is often used. The second type of regeneration is the "heatless" regeneration. In this system the beds are regenerated by depressuring the bed and using some of the dry air to drive off the water. The "wet" air is vented. Instrument air is also sometimes dried by using refrigeration to chill the air and condense out the water. The air is then reheated to ambient user conditions.

A number of different style compressors are used for instrument air systems. Since the air is needed at 100 psig, the compression ratio is over 7.5. If reciprocating compressors are used, multiple stages are necessary. Screw compressors (both oil flooded and oil free) are the most widely used style of compressors in this service (See Section 13).

In large gas processing facilities, multiple instrument air receivers may be used at multiple locations in the plant. In this way sufficient air volume can be provided near to large users of air without pulling down the system pressure.

NITROGEN SYSTEMS

Most gas processing facilities benefit from having an onsite source of nitrogen for purging seals in rotating equipment, purging air from equipment and components and for other uses such as blanketing. Fig. 18-5 lists flammability characteristics of common gases and liquids and the threshold levels of oxygen above which explosion could occur.

Consideration of this data is necessary when considering the use, sizing and purity of the nitrogen being generated.

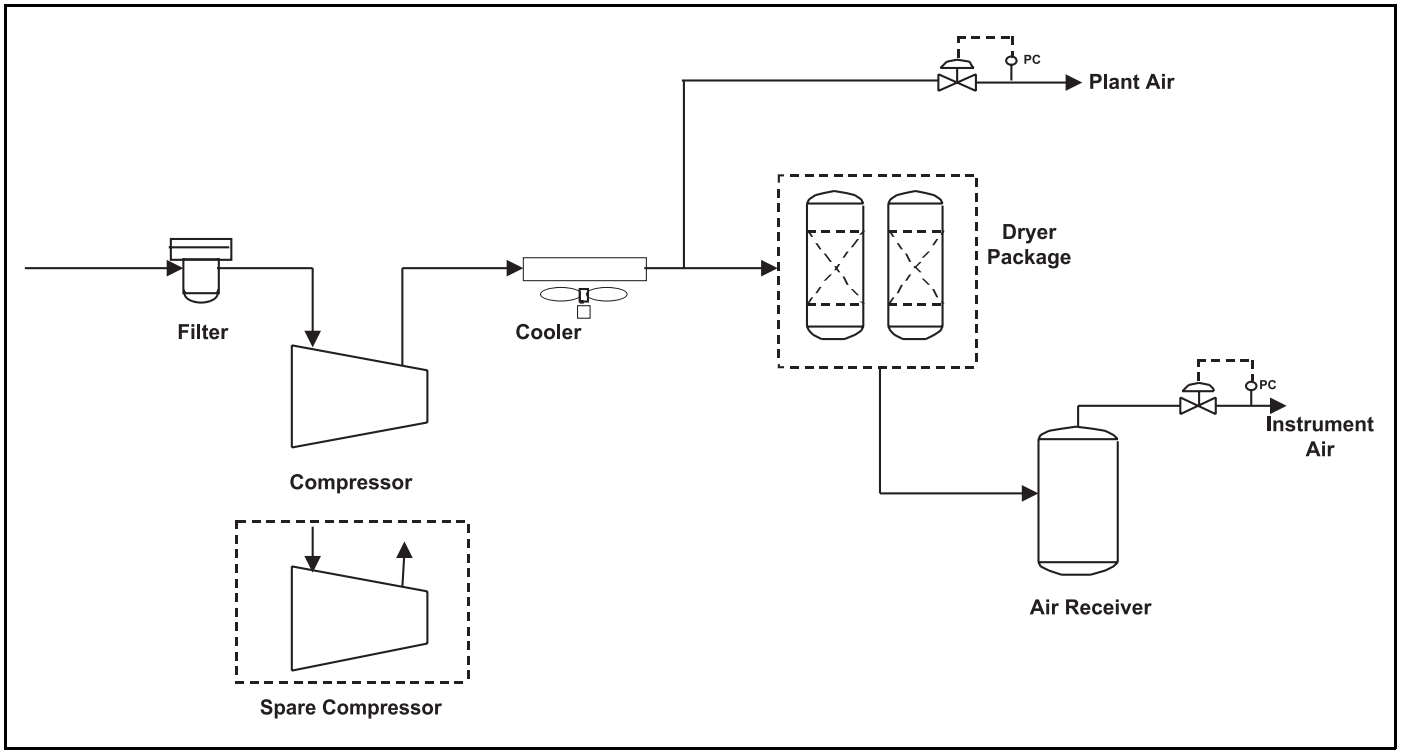
For facilities near industrial areas, it is often economical to have a nitrogen tank and vaporizer on site which is refilled by a third party nitrogen supplier. The nitrogen is then resupplied as needed.

In remote facilities or in facilities which require larger volumes (such as LNG facilities), onsite generation is often necessary. Nitrogen can be generated from a number of different processes such as pressure swing adsorption (PSA), membranes separation, or cryogenic separation.

Selection of the process is dependent on the purity of nitrogen required, the expected usage rate, and the variability of the nitrogen needs. PSA and membrane units can produce nitrogen from 95% to 99.9% purity in standard unit sizes up to about 100,000 scfh. Water dewpoints of –70 to –90°F are achievable. Nitrogen produced cryogenically usually has a residual oxygen content of less than 20 ppm (99.998% purity).

FIG. 18-4

Example Instrument Air System



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FIG. 18-5

Flammability Characteristics of Gases and Liquids

Product	Boiling Point Temperature °F (1)	Flashpoint °F (2)	Autoignition Temperature °F (3)	Flammability Limit in Air Vol. % (4)		Maximum Oxygen Content Vol. % (5)
				Lean (LEL)	Rich (UEL)	
Acetylene	-119	–	571	1.5	100	–
Ammonia	-28	–	1,204	15.5	27	15
Benzene	176	12	1,044	1.2 (at 212-F)	8	11.20
1,3-Butadiene	24	–	804	2	12.5	10.40
Butane	31	–	761	1.5	9	12.10
1-Butene	21	–	723	1.60	10	11.40
2-butene	34	–	615	1.6	10	11.70
Carbon disulfide	115	-22	212	1.30	44	5.40
Carbon monoxide	-313	–	1,128	12.50	74	5.60
Cyclopropone	-27.4	–	928	2.40	10.40	11.70
2, 2-Dimethylbutane	121	-54	797	1.20	7	12.10
Ethane	-127	–	959	2.9	13	11
Ethanol	173	-55	793	3.3	19	10.60
Ethylene	-155	–	842	2.7	36	10
Gasoline	–	-49	996	1.40	7	–
Gasoline (octane 60)	–	-45	536	1.40	7.60	11.60
Gasoline (octane 92)	–	–	734	1.50	7.60	11.60
Gasoline (octane 100)	–	-36	853	1.40	7.40	11.60
Heptane	209	25	433	1	7	11.60
Hexane	156.20	7	453	1.1	7.7	11.90
Hydrogen	-423	–	1,085	4	74.2	5
Isobutane	11	–	864	1.80	8.5	12
Isopropanol	179.60	70	860	2	12	12
Methane	-259	–	999	5	15	12.10
Methanol	148	52	867	5.5	44	9.70
Methyl butene	87.4	<20	–	–	–	11.40
N-butanol	244.40	95	649	1.40	11.20	11.30
Pentane	97	<-40	588	1.4	8.3	12.10
Propane	-44	–	871	2	9.5	11.40
Propylene	-54.4	–	770	2	11.7	11.50
Toluene	231	39.20	996	1.2	7.1	9.10
Xylene	282	85	867	1	7	8

1. Boiling point temperature at standard atmospheric pressure
2. Flashpoint is the minimum temperature at which vapors of a combustible liquid will be ignited by a flame in certain experimental conditions
3. Autoignition temperature is the minimum temperature at which a product will spontaneously oxidize in air
4. Flammability limit is the volume percentage of combustible gas in air such that below the lean limit (LEL) or above the rich limit (UEL), the mixture is considered nonflammable
5. Maximum oxygen content is the oxygen percentage in a combustible gas mixture below which the mixture is non-flammable

Water content is essentially zero as the nitrogen has been processed at around –300°F. The cryogenic process also has the ability to produce liquid and vapor. Many units in remote locations produce vapor for daily use and some liquid which can be stored as a backup supply. An example cryogenic nitrogen production system is shown in Fig. 18-6.

FUEL SYSTEMS

Fuel systems in gas processing facilities are necessary to provide the proper fuel for a variety of users in the plant. Low pressure users are items such as boilers, fired heaters and reciprocating engines. Higher pressure users are gas turbines. All fuel systems need to be kept free of solid contaminants which can plug instrumentation and fuel nozzles. In addition, fuel streams need to be maintained above the hydrocarbon dewpoint to prevent any liquid slugs in the fuel users.

Gas turbines require more rigorous fuel specifications than do lower pressure systems. Fig. 18-7 shows an example fuel gas specification for a commercial gas turbine. Specifications for a particular turbine can be obtained from the manufacturer.

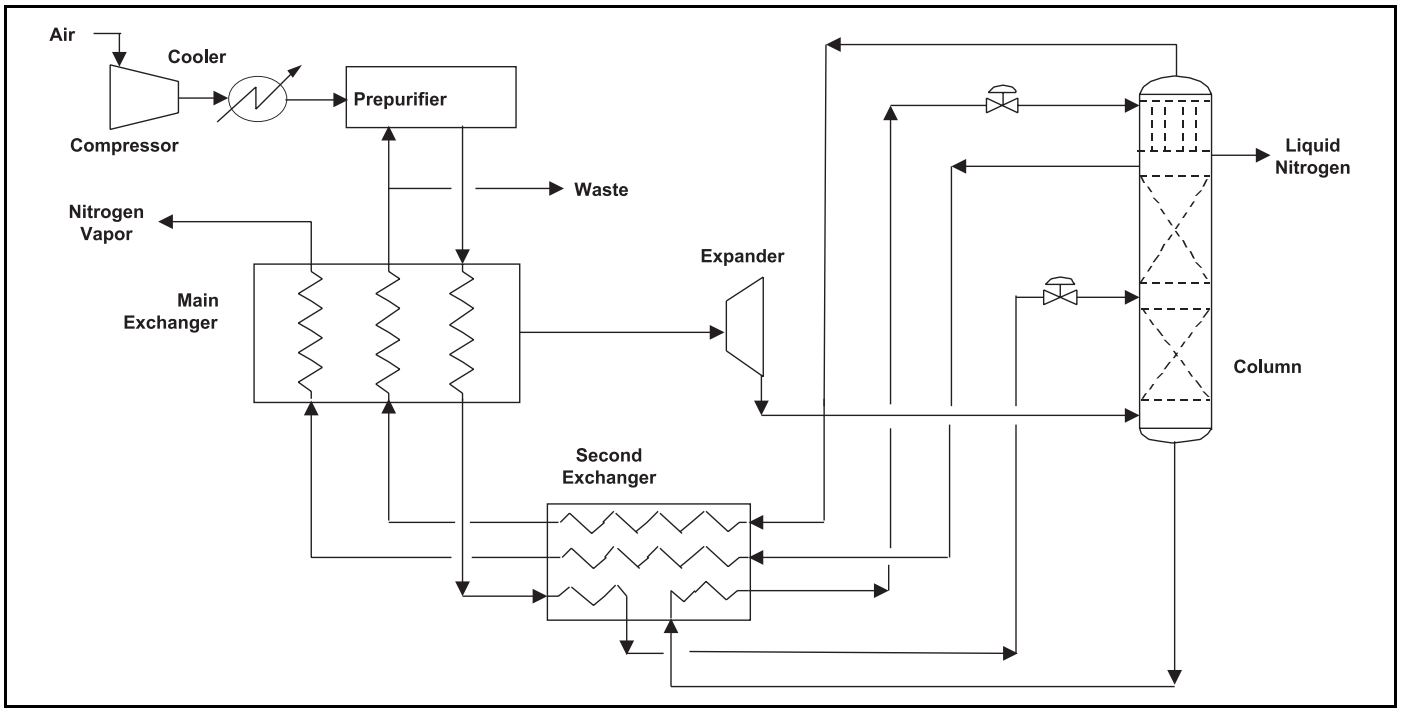
(1) The turbines can be designed to handle higher or lower values of LHV but are designed for a particular range by the vendor.

(2) Feed gas pressure is entirely dependent on the type of turbine used. Most smaller turbines and industrial turbines require 300 to 400 psia. Large aeroderivative tur-

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FIG. 18-6

Example Air Separation Plant



bines can require fuel in the 600 psia range. Fuel systems are usually designed to provide fuel at 100 psi greater than the compressor exit pressure of the turbine.

(3) Virtually all turbine manufacturers require 30-50ºF of superheat in the fuel stream.

The superheating of the gas can be accomplished in several ways. One way is simply to heat the feed stream directly. If the fuel is compressed before entering the fuel header, the temperature of the gas from the discharge cooler can be controlled to ensure proper superheat.

If the fuel is supplied from a higher pressure system by pressure let down, the stream often needs some processing to prevent condensation. This can be provided by chilling the stream, scrubbing and then reheating. Fuel gas conditioning systems based on Low Temperature Separation schemes are commercially available to accomplish this fuel conditioning.

FLARE/RELIEF SYSTEMS

Flare systems are needed in most gas processing facilities to safely dispose of waste gas streams and often are used to collect and dispose of discharges from safety relief systems. Design of these systems is covered in depth in API RP 520 and API RP 521 and in this Data Book in Section 5.

FIG. 18-7

Example Turbine Fuel Gas Specifications

	Maximum	Minimum
Lower Heating Value, Btu/SCF (1)	1200	900
Fuel Pressure, psia (2)	375	275
Supply Temperature, (3)	200ºF	41ºF or 36ºF above hydrocarbon dewpoint whichever is greater
Liquid Hydrocarbons/Dust, ppmw	20	
Liquid Droplet Size, microns	5	
Dust Particle Size, microns	10	
Water	No Free Water	
Sodium Content, ppmw	1	

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WATER TREATING

Water treating requirements for gas processing plants depend upon (1) the quality of the source or makeup water, (2) the manner in which the water is used, (3) environmental regulations, and (4) site climatic conditions governing wastewater disposal. These factors should be considered in selecting the overall plant process and utility systems. Many gas processing plants, especially smaller plants, are designed "water free", utilizing air for all cooling services, a heating medium for process heat requirements, and electric motor drivers. Such plants have essentially no makeup water requirements and wastewater treatment requirements are minimized.

Source Waters

Source or makeup water is normally either ground water or surface water, neither of which is ever chemically pure. Ground waters contain dissolved inorganic impurities which came from the rock and sand strata through which the water passed. Surface waters often contain silt particles in suspension (suspended solids) and dissolved organic matter in addition to dissolved inorganic impurities (dissolved solids). Fig. 18-8 lists some of the common properties or characteristics and the normal constituents of water, together with corresponding associated operating difficulties and potential methods of water treatment.

Water Analysis

Water analyses are conventionally expressed, for both cations and anions, in parts per million by weight (ppmw) except for hardness and alkalinity which are usually expressed in ppmw of calcium carbonate ($CaCO_3$). These ppmw values can be converted to a common basis (such as milli-equivalents/liter) by dividing by the equivalent weight of the ion and multiplying by the specific gravity of the water solution. This permits the summation of oppositely-charged ions such that total cations will then equal total anions. Cation and anion concentrations in milli-equivalents/liter can be converted to ppmw $CaCO_3$ by multiplying by the equivalent weight of $CaCO_3$ (100.08/2 = 50.04) and dividing by the specific gravity of the water solution.

Example 18-1 — Water analysis calculation

Water Analysis Ion	ppmw	MW	Equivalent Weight
Calcium (Ca^{+2})	100.1	40.08	$\frac{40.08}{2} = 20.04$
Magnesium (Mg^{+2})	20.4	24.32	$\frac{24.32}{2} = 12.16$
Sodium (Na^{+1})	12.0	23.00	$\frac{23.0}{1} = 23.0$
Bicarbonate ($HCO3^{-1}$)	366.0	61.02	$\frac{61.02}{1} = 61.02$
Sulfate (SO_4^{-2})	48.1	96.06	$\frac{96.06}{2} = 48.03$
Chloride (Cl^{-1})	7.1	35.46	$\frac{35.46}{1} = 35.46$

	Cations	
Ion	Milli-equivalents/ liter (Sp Gr = 1.0)	ppmw $CaCO_3$
Ca^{+2}	100.1/20.04 = 5.00	(5.0) (50.04) = 250
Mg^{+2}	20.4/12.16 = 1.68	(1.68) (50.04) = 84
Na^{+1}	12.0/23 = 0.52	(0.52) (50.04) = 26
$HCO3^{-1}$	—	—
SO_4^{-2}	—	—
Cl^{-1}	—	—
Totals	7.20	360

	Anions	
Ion	Milli-equivalents / liter (Sp Gr = 1.0)	ppmw $CaCO_3$
Ca^{+2}	—	—
Mg^{+2}	—	—
Na^{+1}	—	—
$HCO3^{-1}$	366/61.02 = 6.00	(6) (50.04) = 300
SO_4^{-2}	48.1/48.03 = 1.00	(1.0) (50.04) = 50
Cl^{-1}	7.1/35.46 = 0.20	(0.20) (50.04) = 10
Totals	7.20	360

Total hardness is the sum of calcium and magnesium and is therefore equal to 334 ppmw as $CaCO_3$ (250 + 84). Correspondingly, alkalinity is the sum of CO_3^{-2}, HCO_3^{-1}, and OH^{-1} ions and is equal to 300 ppmw as $CaCO_3$.

Boiler Water Systems

Water treatment is employed to prevent or minimize:

- Scaling of boiler heat transfer surfaces by salts of hardness ions, by silica and/or by metallic oxides.
- Boiler corrosion by oxygen, water or acids, and of the steam/condensate system by oxygen or carbon dioxide.
- Carryover from the boiler because of foaming.
- Caustic embrittlement.

Boiler Water Chemistry

There are four types of impurities of concern in water to be used for the generation of steam:

- Scale-forming solids which are usually the salts of calcium and magnesium along with boiler corrosion products. Silica, manganese, and iron can also form scale.
- The much more soluble sodium salts (see Fig. 18-9) which do not normally form scale, but can concentrate under scale deposits to enhance corrosion or in the boiler water to increase carryover due to boiler water foaming.
- Dissolved gases, such as oxygen and carbon dioxide, which can cause corrosion.
- Silica, which can volatilize with the steam in sufficient concentrations to deposit in steam turbines.

Boiler Blowdown

Blowdown is employed to maintain boiler water dissolved solids at an appropriate level of concentration. At equilibrium, the quantities of dissolved solids removed by blowdown exactly equals those introduced with the feedwater plus any in-

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FIG. 18-8

Water Impurities and Characteristic Treatment

Constituent	Chemical Formula	Difficulties Caused	Means of Treatment
Turbidity	None, usually expressed in Jackson Turbidity Units	Imparts unsightly appearance to water; deposits in water lines, process equipment, boilers, etc.; interferes with most process uses.	Coagulation, settling, and filtration
Color	None	Decaying organic material and metallic ions causing color may cause foaming in boilers; hinders precipitation methods such as iron removal, hot phosphate softening; can stain product in process use	Coagulation, filtration, chlorination, adsorption by activated carbon.
Hardness	Calcium, magnesium, barium, and strontium salts expressed as $CaCO_3$	Chief source of scale in heat exchange equipment, boilers, pipe lines, etc.; forms curds with soap; interferes with dyeing, etc.	Softening, distillation, internal boiler water treatment, surface active agents, reverse osmosis, electrodialysis
Alkalinity	Bicarbonate (HCO_3^{-1}), carbonate (CO_3^{-2}), and hydroxyl (OH^{-1}), expressed as $CaCO_3$	Foaming and carryover of solids with steam; embrittlement of boiler steel; bicarbonate and carbonate produce CO_2 in steam, a source of corrosion	Lime and lime-soda softening, acid treatment, hydrogen zeolite softening, demineralization, dealkalization by anion exchange, distillation, degasifying
Free Mineral Acid	H_2SO_4, HCl, etc. expressed as $CaCO_3$, titrated to methyl orange end-point.	Corrosion	Neutralization with alkalies
Carbon Dioxide	CO_2	Corrosion in water lines and particularly steam and condensate lines	Aeration, deaeration, neutralization with alkalies, filming and neutralizing amines
pH	Hydrogen Ion concentration defined as $pH = \log \frac{1}{(H^{+1})}$	pH varies according to acidic or alkaline solids in water; most natural waters have a pH of 6.0-8.0	pH can be increased by alkalies and decreased by acids
Sulfate	$(SO_4)^{-2}$	Adds to solids content of water, but, in itself, is not usually significant; combines with calcium to form calcium sulfate scale	Demineralization, distillation, reverse osmosis, electrodialysis
Chloride	Cl^{-1}	Adds to solids content and increases corrosive character of water	Demineralization, distillation, reverse osmosis, electrodialysis
Nitrate	$(NO_3)^{-1}$	Adds to solid content, but is not usually significant industrially; useful for control of boiler metal embrittlement	Demineralization, distillation, reverse osmosis, electrodialysis
Fluoride	F^{-1}	Not usually significant industrially	Adsorption with magnesium hydroxide, calcium phosphate, or bone black; alum coagulation; reverse osmosis; electrodialysis
Silica	SiO_2	Scale in boilers and cooling water systems; insoluble turbine blade deposits due to silica vaporization	Hot process removal with magnesium salts; adsorption by highly basic anion exchange resins, in conjunction with demineralization; distillation
Iron	Fe^{+2} (ferrous) Fe^{+3} (ferric)	Discolors water on precipitation; source of deposits in water lines, boilers, etc.; interferes with dyeing, tanning, paper mfr., etc.	Aeration, coagulation, and filtration, lime softening, cation exchange, contact filtration, surface active agents for iron retention
Manganese	Mn^{+2}	same as iron	same as iron
Oil	Expressed as oil or chloroform extractable matter, ppmw	Scale, sludge and foaming in boilers; impedes heat exchange; undesirable in most processes	Baffle separators, strainers, coagulation and filtration, diatomaceous earth filtration
Oxygen	O_2	Corrosion of water lines, heat exchange equipment, boilers, return lines, etc.	Deaeration, sodium sulfite, corrosion inhibitors, hydrazine or suitable substitutes
Hydrogen Sulfide	H_2S	Cause of "rotten egg" odor; corrosion	Aeration, chlorination, highly basic anion exchange
Ammonia	NH_3	Corrosion of copper and zinc alloys by formation of complex soluble ion	Cation exchange with hydrogen zeolite, chlorination, deaeration, mixed-bed demineralization
Conductivity	Expressed as microhms, specific conductance	Conductivity is the result of ionizable solids in solution; high conductivity can increase the corrosive characteristics of a water	Any process which decreases dissolved solids content will decrease conductivity; examples are demineralization, lime softening
Dissolved Solids	None	"Dissolved solids" is measure of total amount of dissolved matter, determined by evaporation; high concentrations of dissolved solids are objectionable because of process interference and as a cause of foaming in boilers	Various softening process, such as lime softening and cation exchange by hydrogen zeolite, will reduce dissolved solids; demineralization; distillation; reverse osmosis; electrodialysis
Suspended Solids	None	"Suspended solids" is the measure of undissolved matter, determined gravimetrically; suspended solids plug lines, cause deposits in heat exchange equipment, boilers, etc.	Subsidence, filtration, usually preceded by coagulation and setting
Total Solids	None	"Total solids" is the sum of dissolved and suspended solids, determined gravimetrically	See "Dissolved Solids" and "Suspended Solids"

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jected chemicals, Fig. 18-10. The concentration of feedwater solids and the acceptable level of boiler water solids concentration determine the blowdown rate.

ABMA and ASME Standards

The American Boiler Manufacturers' Association (ABMA) and the American Society of Mechanical Engineers (ASME) have developed suggested limits for boiler water composition which depend upon the type of boiler and the boiler operating pressure. These control limits for boiler water solids are based upon one or more of the following factors:

- Sludge and Total Suspended Solids — These result from the precipitation in the boiler of feedwater hardness constituents due to heat and to interaction of treatment chemicals, and from corrosion products in the feedwater. They can contribute to boiler tube deposits and enhance foaming characteristics, leading to increased carryover.
- Total Dissolved Solids — These consist of all salts naturally present in the feedwater, of soluble silica, and of any chemical treatment added. Dissolved solids do not normally contribute to scale formation but excessively high concentrations can cause foaming and carryover or can enhance "under deposit" boiler tube corrosion.
- Silica — This may be the blowdown controlling factor in softened waters containing high silica. High boiler water silica content can result in silica vaporization with the steam, and under certain circumstances, siliceous scale. This is illustrated by Fig. 18-11 and by Example 18-2. Silica content of the boiler water is not as critical for steam systems without steam turbines.
- Iron — Occasionally in high pressure boilers where the iron content is high in relation to total solids, blowdown may be based upon controlling iron concentrations. High concentrations of suspended iron in boiler water can produce serious boiler deposit problems and are often indications of potentially serious corrosion in the steam/steam condensate systems.

Example 18-2 — A 400 psig boiler operating with 500 ppmw SiO_2 in the water within the boiler could generate steam containing 0.07 ppmw of SiO_2 (Fig. 18-11). When this steam is expanded through a turbine to 100 psig, the solubility of SiO_2 decreases to about 0.01 ppmw. The silica coming out of solution (0.07 – 0.01 = 0.06 ppmw) could coat turbine blades and eventually result in extensive turbine maintenance. This problem could be avoided as shown in Fig. 18-11 if the silica content of the water in the boiler were kept below 100 ppmw.

While there are other considerations (such as corrosive or deposit forming tendencies) in establishing limits for boiler water composition, the ABMA recommendations (Fig. 18-12) clearly indicate that boiler feedwater purity becomes more important as operating pressures increase. The ASME publishes the "Consensus on Operating Practices for the Control of Feed Water and Boiler Water Chemistry in Modern Industrial Boilers."[8] This contains a series of tables for various boiler types.

Boiler Water Treatment–General

Boiler system water treatment is classified as either external or internal. The most common chemical reactions in both external and internal water treatment are shown in Fig. 18-13.

External treatment is the reduction or removal of impurities from water outside the boiler; it includes solids removal, precipitation softening, ion exchange processes (softening, demin-

FIG. 18-9

Solubility of Some Common Compounds in Water (in ppmw as $CaCO_3$)

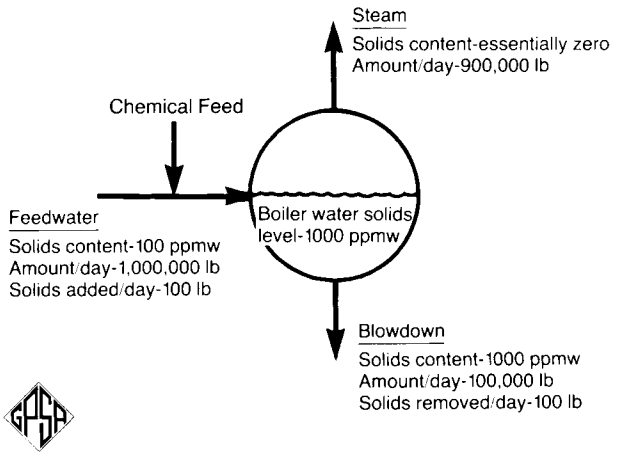
	32°F	212°F
Calcium		
Bicarbonate	1,620	Decomposes
Carbonate	15	13
Sulfate	1,290	1,250
Magnesium		
Bicarbonate	37,100	Decomposes
Carbonate	101	75
Sulfate	170,000	356,000
Sodium		
Bicarbonate	38,700	Decomposes
Carbonate	61,400	290,000
Chloride	225,000	243,000
Hydroxide	370,000	970,000
Sulfate	33,600	210,000

General Rules

1. Hardness salts tend to: decrease in solubility as temperature rises; decrease in solubility as alkalinity increases; increase in solubility as carbon dioxide increases.
2. Sodium salts tend to increase in solubility as temperature rises.
3. Silica (SiO_2) solubility increases with increased alkalinity.
4. Iron and manganese solubilities decrease with increased alkalinity.

FIG. 18-10

Example Showing How Boiler Water Solids are Controlled by Blowdown



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eralization, dealkalization), evaporation, reverse osmosis, electrodialysis, and deaeration.

Internal treatment is the conditioning of impurities within the boiler. This involves adding chemicals to scavenge oxygen, control scale, condition sludge, control pH and foaming, and mitigate corrosion.

Boiler Water Treatment–External

Solids Removal Methods — include settling, clarification, and filtration. Selection of the appropriate suspended solids removal system depends upon the nature and concentration of suspended solids and the degree of solids removal required.

A substantial degree of suspended solids removal is frequently achieved through settling of untreated water under relatively quiescent conditions. This is termed settling; it removes only relatively coarse solids.

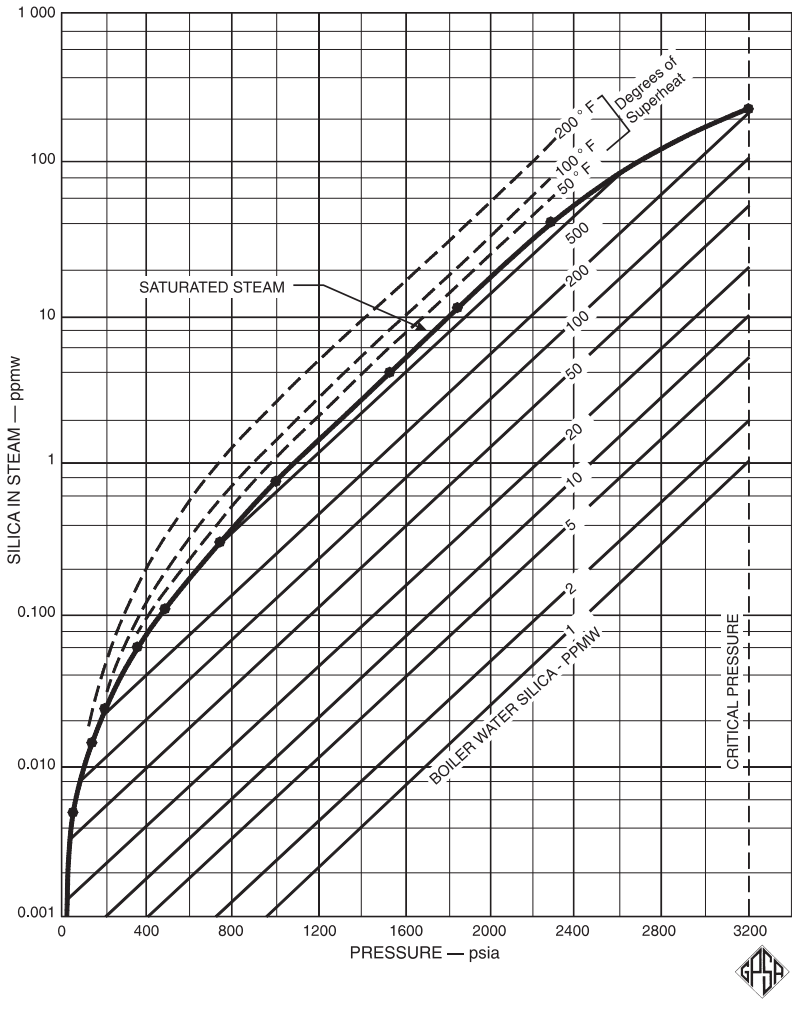
Clarification involves treating the water with various chemicals including alum, iron salts, or polymeric materials to agglomerate smaller particles, then settling to achieve a significantly higher degree of solids removal. Reactor-clarifiers of various designs are available to facilitate the clarification process. Settling is sometimes necessary prior to clarification to prevent overload of the clarifier; this also provides some surge volume of water upstream of the clarifier, facilitating process control.

Filtration of water through a bed of sand, anthracite, or some similar medium can be used as a stand-alone process or for additional suspended solids removal after subsidence or clarification. Both gravity and pressure filters are available. Filters are cleaned of suspended solids by backwashing.

Precipitation Softening — usually involves the addition of lime or a combination of lime and soda ash to remove various constituents from water by precipitation; this is followed by clarification and usually filtration. Concentrations of calcium, magnesium, alkalinity, and silica can be reduced. When only lime is used, a reduction in total dissolved solids can also be obtained. The precipitation products of either lime or lime-soda ash softening are primarily calcium carbonate and magnesium hydroxide. The softening process is carried out at either ambient (cold process) or elevated (hot process) temperature. Because of the inverse temperature solubilities

FIG. 18-11

Relationships Between Boiler Pressure, Boiler Water Silica Content, and Silica Solubility in Steam[4]



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FIG. 18-12

Recommended Boiler Water Limits and Estimates of Carryover Limits That Can Be Achieved

Drum Pressure psig	Maximum Boiler Water Solids, ppmw	Maximum Total Alkalinity as $CaCO_3$, ppmw	Maximum Suspended Solids, ppmw	Steam TDS Corresponding to Maximum Boiler Water TDS	Maximum Fractional Carryover, FCO (Note 2)
0 – 300	3500	Note 1	15	1.0	0.0003
301 – 450	3000	"	10	1.0	0.0003
451 – 600	2500	"	8	1.0	0.0004
601 – 750	1000	"	3	0.5	0.0005
751 – 900	750	"	2	0.5	0.0006
901 – 1000	625	"	1	0.5	0.0007
1001 – 1800	100	*	1	0.1*	0.001
1801 – 2350	50	*	1	0.1*	0.002
2351 – 2600	25	*	1	0.05*	0.002
2601 – 2900	15	*	1	0.05*	0.003

*Not Applicable

Note 1 – 20% of Actual Boiler Water Solids. For TDS ≤ 100 ppmw, the total alkalinity is dictated by the boiler water treatment.

Note 2 – Does not include vaporous silica caryover

TDS = Total Dissolved Solids

FCO = Fractional Carryover

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of calcium carbonate and magnesium hydroxide, hot process softening is more effective. However, the hot process is not always used because of other factors such as consideration of additional downstream treatment needs, ultimate use of the softened water, and overall equipment and operating costs.

Ion Exchange Processes — include softening, demineralization, and dealkalization. The reactions involved in these ion exchange processes are illustrated in Fig. 18-14.

In softening, calcium and magnesium ions (hardness ions) are exchanged for the more soluble sodium ions.

In demineralization, cations are exchanged for hydrogen ions (H^{+1}) and anions are exchanged for hydroxyl ions (OH^{-1}); the result is relatively pure water ($H^{+1} + OH^{-1} = H_2O$).

In dealkalization, the ions contributing to alkalinity (carbonate, bicarbonate, and hydroxyl ions) are exchanged for chloride ions.

A typical ion-exchange bed is shown in Fig. 18-15. Ion exchange units are usually installed with two parallel beds to permit continuous service during regeneration. During normal operation, water enters the top of the vessel through a distributor pipe and as it flows through the bed of ion exchange material, undesirable ions in the water are exchanged for more acceptable ions. The treated water is drawn off by collector piping at the bottom. Following exhaustion of the ion exchange material, the unwanted ions are removed from the bed by regenerating with a solution containing the more acceptable ions.

Regeneration of the exchange material normally involves three separate steps: backwashing, introducing the regenerant chemicals, and rinsing.

Backwashing involves introducing water upflow through the bed at a controlled rate to remove accumulated suspended matter and bed fines and to classify the bed to ensure evenly-distributed flow. This is usually done immediately before the regenerant chemical solution is introduced. Regenerant chemicals are usually introduced at the top of the bed and removed through the bottom outlet.

Rinsing is usually a two-step process. A slow rinse (low flow rate) displaces the bulk of the excess regenerant chemical and unwanted ions from the bed. This is followed by a fast rinse (high flow rate) which continues until the effluent water is of satisfactory quality.

Operating costs for ion exchange units are determined by the amounts of regenerant chemicals and rinse water, bed replacement expense, and spent regenerant disposal requirements, all of which are roughly proportional to the amount of dissolved solids removed from the water. Generally, ion exchange units are most suitable for waters of 1,500 ppmw or less dissolved solids or where essentially complete removal of an undesirable ion (or ions) is required.

Evaporation — involves vaporizing the water to separate it from the dissolved solids. Vapor compression and multistage flash evaporators have largely replaced the traditional submerged-tube evaporators because of better energy efficiency and the capability, with appropriate water treatment, of operating free of scale for relatively longer periods. Vapor compression and flash evaporators can produce water of high purity from brackish and sea waters.

Operating costs are related principally to the cost of heat, and, to a lesser extent, the cost of utilities (cooling water, elec-

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FIG. 18-13

Chemical Reactions in Treatment of Boiler Water

$CaSO_4$	+	Na_2CO_3	=	**$CaCO_3$**	+	Na_2SO_4
$CaCl_2$	+	Na_2CO_3	=	**$CaCO_3$**	+	$2NaCl$
$Ca(NO_3)_2$	+	Na_2CO_3	=	**$CaCO_3$**	+	$2NaNO_3$
$MgSO_4$	+	Na_2CO_3	=	**$MgCO_3$**	+	$2Na_2SO_4$
$MgCl_2$	+	Na_2CO_3	=	**$MgCO_3$**	+	$2NaCl$
H_2SO_4	+	Na_2CO_3	=	H_2CO_3	+	Na_2SO_4
$Na_2CO_3+H_2O$	+	Boiler heat	=	$2NaOH$	+	$CO_2 + H_2O$
$Ca(HCO_3)_2$	+	Boiler heat	=	**$CaCO_3$**	+	$CO_2 + H_2O$
$Mg(HCO_3)_2$	+	Boiler heat	=	**$MgCO_3$**	+	$CO_2 + H_2O$
$MgSO_4$	+	$2NaOH$	=	**$Mg(OH)_2$**	+	Na_2SO_4
$MgCl_2$	+	$2NaOH$	=	**$Mg(OH)_2$**	+	$2NaCl$
H_2SO_4	+	$2NaOH$	=	Na_2SO_4	+	$2H_2O$
H_2CO_3	+	$2NaOH$	=	**Na_2CO_3**	+	$2H_2O$
$Ca(HCO_3)_2$	+	$2NaOH$	=	**$CaCO_3$**	+	$Na_2CO_3 + 2H_2O$
$Mg(HCO_3)_2$	+	$4NaOH$	=	**$Mg(OH)_2$**	+	$2Na_2CO_3 + 2H_2O$
$3CaSO_4$	+	$2Na_3PO_4$	=	**$Ca_3(PO_4)_2$**	+	$3Na_2SO_4$
$3MgSO_4$	+	$2Na_3PO_4$	=	**$Mg_3(PO_4)_2$**	+	$3Na_2SO_4$
$3MgCl_2$	+	$2Na_3PO_4$	=	**$Mg_3(PO_4)_2$**	+	$6NaCl$
$CaSO_4$	+	Na_2SiO_3	=	**$CaSiO_3$**	+	Na_2SO_4
$MgSO_4$	+	Na_2SiO_3	=	**$MgSiO_3$**	+	Na_2SO_4
$MgCl_2$	+	Na_2SiO_3	=	**$MgSiO_3$**	+	$2NaCl$
H_2CO_3	+	$Ca(OH)_2$	=	**$CaCO_3$**	+	$2H_2O$
$Ca(HCO_3)_2$	+	$Ca(OH)_2$	=	**$2CaCO_3$**	+	$2H_2O$
$Mg(HCO_3)_2$	+	$2Ca(OH)_2$	=	**$Mg(OH)_2$**	+	**$2CaCO_3$** $+ 2H_2O$
$CaSO_4$	+	$Ba(OH)_2$	=	**$BaSO_4$**	+	$Ca(OH)_2$
$MgSO_4$	+	$Ba(OH)_2$	=	**$Mg(OH)_2$**	+	**$BaSO_4$**
H_2CO_3	+	$Ba(OH)_2$	=	**$BaCO_3$**	+	$2H_2O$
$CaSO_4$	+	$BaCO_3$	=	**$BaSO_4$**	+	**$CaCO_3$**
$MgSO_4$	+	$BaCO_3$	=	**$BaSO_4$**	+	**$MgCO_3$**
$MgSO_4$	+	$2NaCl$	=	$MgCl_2$	+	Na_2SO_4
$MgCl_2$	+	$2H_2O$	=	$Mg(OH)_2$	+	$2HCl$
$FeCl_2$	+	$2H_2O$	=	$Fe(OH)_2$	+	$2HCl$
$FeSO_4$	+	$2H_2O$	=	$Fe(OH)_2$	+	H_2SO_4
$CaSO_4$	+	Na_2Z	=	CaZ*	+	Na_2SO_4
$MgSO_4$	+	Na_2Z	=	MgZ*	+	Na_2SO_4
$CaCl_2$	+	Na_2Z	=	CaZ*	+	$2NaCl$
$MgCl_2$	+	Na_2Z	=	MgZ*	+	$2NaCl$
$Ca(HCO_3)_2$	+	Na_2Z	=	CaZ*	+	$2NaHCO_3$
$Mg(HCO_3)_2$	+	Na_2Z	=	MgZ*	+	$2NaHCO_3$

*Upon regeneration with a strong salt (NaCl) brine, the zeolite is converted back to Na_2Z. The calcium and magnesium chlorides formed during the "exchange" regeneration (CaZ or MgZ + 2NaCl = Na_2Z + $CaCl_2$ or $MgCl_2$) are disposed of as waste.

The formulas in **heavy type** indicate precipitates, or sludges.

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FIG. 18-14

Types of Ion-Exchange Processes

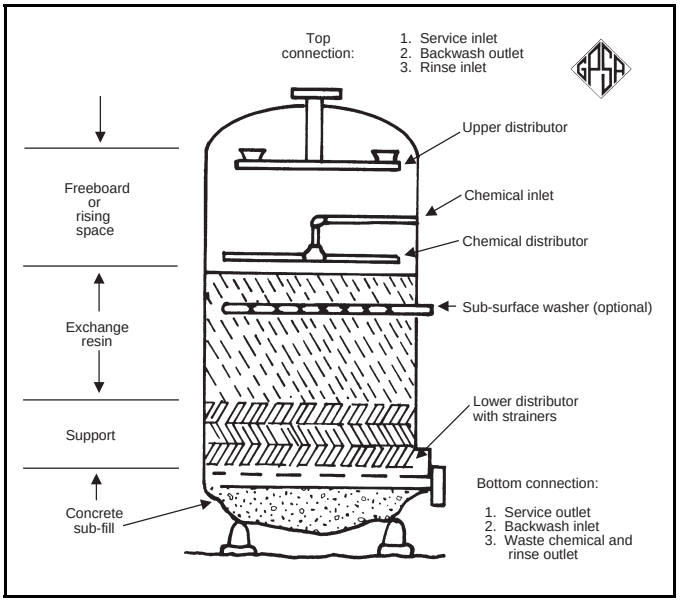
(A)	$Ca(HCO_3)_2$	→	Cation Na^{+1} Exchanger	→	$NaHCO_3$
	$CaSO_4$	→		→	Na_2SO_4
(B)	$Ca(HCO_3)_2$	→	Cation H^{+1} Exchanger	→	H_2CO_3
	$CaSO_4$	→		→	H_2SO_4
(C)	Na_2SO_4	→	Anion Cl^{-1} Exchanger	→	NaCl
	$NaHCO_3$	→		→	NaCl
(D)	H_2CO_3	→	Anion OH^{-1} Exchanger	→	H_2O
	H_2SO_4	→		→	H_2O

Conventional Softening — Process (A)

Dealkalization by Split Stream Softening — Blending Effluents from (A) and (B)

FIG. 18-15

Typical Ion-Exchange Bed



tricity, etc.) and water treating chemicals. Heat (energy) costs are relatively independent of the feed water composition.

Reverse Osmosis — involves separating water from dissolved solids by forcing the water to pass through a semi-permeable membrane which retains most of the dissolved solids. As illustrated in Fig. 18-16, this is accomplished by providing sufficient pressure on the system feedwater to overcome the normal osmotic pressure and produce a reasonable flow rate through the membrane.

A typical brackish water with a dissolved solids content of 1500 ppmw will have an osmotic pressure of about 15 psi; seawater with a dissolved solids content of about 35000 ppmw has an osmotic pressure of about 350 psi. The applied pressure for brackish water purification is typically in the range of 400-600 psig and for seawater purification, in the range of 800-1000 psig. Recovery of product (desalted) water with reverse osmosis units ranges from 50 to 90% of the feedwater depending upon the feedwater composition, the product water quality requirement, and the number of stages utilized.

Operating costs consist mainly of pumping costs (the pressure drop across the membrane may be from 250 psi to 1000 psi, depending upon dissolved solids content and membrane selection) and membrane cleaning and replacement costs. For water containing from about 250 to 1500 ppmw dissolved solids, an economic comparison of ion exchange and reverse osmosis is frequently necessary to select the more cost effective process. Reverse osmosis has been successfully employed for desalination of seawater. In many cases, the reverse osmosis product water must be treated by one of the ion exchange processes if high quality boiler feedwater is required.

A pretreatment system is needed to avoid fouling or excessive degradation of the membrane. Typically, pretreatment will include filtration to remove suspended particles and addition of chemicals to prevent scaling and biological growth. Because the optimum operating temperature for reverse osmosis systems is about 75-80°F, it is frequently desirable to heat the feedwater. This represents an additional operating cost; however, because reverse osmosis is a continuous process which does not require regenerant chemicals, the cost of disposing of the waste water from the reverse osmosis system may be less than that of waste water from an ion exchange unit.

Electrodialysis — involves separating water from dissolved solids by passing the dissolved solids (ions) through a semi-permeable membrane which is relatively impervious to water. This is accomplished by means of a direct current electrical field which transports the ions through the membranes. Fig. 18-17 shows a basic electrodialysis system with alternating cation-selective and anion-selective membranes.

Recovery of product (deionized) water with electrodialysis units ranges from 50 to 90% of the feedwater depending upon the number of stages and degree of recirculation utilized. Operating costs consist mainly of power costs (typically 6-10 kwh/1000 gallons of product water) and membrane cleaning and replacement costs. Based upon combined capital and operating costs, the electrodialysis process is most economical when used to desalt brackish water (1000 to 5000 ppmw dissolved solids) to a product water concentration of about 500 ppmw dissolved solids.

A pretreatment system is usually needed to prevent fouling or degradation of the membranes. Electrodialysis units can operate over a pH of 1 to 13 and at temperatures up to about 110°F.

Deaeration (Degasifying) — Although other gases (e.g. H_2S, ammonia, methane) can be present in source or makeup water, the dissolved gases of primary concern in boiler feedwater and steam condensate are oxygen and carbon dioxide. Both are highly corrosive and should be removed to the greatest extent possible because the presence of these gases can result in significant damage to piping and equipment and the resulting corrosion products can foul boiler heat transfer surfaces. If a steam condensate treater (polisher) is utilized, high concentrations of corrosion products increase its load and oxygen can attack the ion exchange resin of the treater, espe-

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cially at higher temperatures. Dissolved oxygen can also cause pitting-type corrosion in the boiler itself.

Dissolved gases can be substantially removed from water physically by stripping with, for example, air (to remove H_2S) or methane (to remove oxygen) or by applying a vacuum (Fig. 18-18). Boiler feedwater degasifiers (deaerating heaters and deaerators) utilize low pressure steam for stripping and, depending upon the design of the unit, will reduce dissolved oxygen concentrations to, respectively, about 0.03 cc/liter (4.04 ppmw) and about 0.005 cc/liter (0.007 ppmw) or less. Deaerators operating at pressures of 2 to 5 psig will usually also remove free carbon dioxide completely but not bicarbonate and carbonate ions which can decompose and release CO_2 at boiler temperatures.

Deaerators are of two basic types – the tray type and the spray type. In the tray type (Fig. 18-19), the water is distributed over trays and steam is injected to strip the dissolved gases from the water as it cascades down from tray to tray. The spray type (Fig. 18-20) uses spray nozzles to "atomize" the water into droplets. While deaerators can reduce oxygen to very low concentration levels, chemical treatment may still be needed to remove the last traces.

Boiler Water Treatment – Internal

Internal treatment complements external treatment by taking care of any residual impurities entering the boiler with the feedwater. Internal treatment alone can sometimes be used, especially for low pressure boilers and when the makeup water is low in dissolved solids. Chemical dosages for internal water treatment are based on the amounts and types of impurities in the feedwater and are generally fed at rates slightly in excess of stoichiometric requirements to provide a residual in the boiler water. The boiler water is then tested for this residual chemical which serves as the basis for control of treating chemical feed rate and ensures that sufficient chemical is available in the event of unexpected increases in feedwater impurities concentrations.

Oxygen Scavenging — Some oxygen remains in the boiler feedwater after deaeration and this residual oxygen must be removed to control boiler system corrosion. Chemical oxygen scavengers such as sodium sulfite and hydrazine are commonly used. These chemicals remove the oxygen by the following reactions:

$$2\ Na_2SO_3 + O_2 \rightarrow 2\ Na_2SO_4 \qquad \textbf{Eq 18-1}$$

$$N_2H_4 + O_2 \rightarrow 2\ H_2O + N_2 \qquad \textbf{Eq 18-2}$$

Oxygen scavengers are usually introduced into the boiler system immediately downstream of deaeration, frequently into the deaerator storage tank, in order to minimize corrosion of as much of the system as possible.

Sodium sulfite reacts rapidly with oxygen at temperatures as low as 212°F, is easy to handle, and involves simple control tests. The use of sodium sulfite is usually limited to lower pres-

FIG. 18-16

Principle of Reverse Osmosis Used to Obtain Purified Water from a Salt Solution[2]

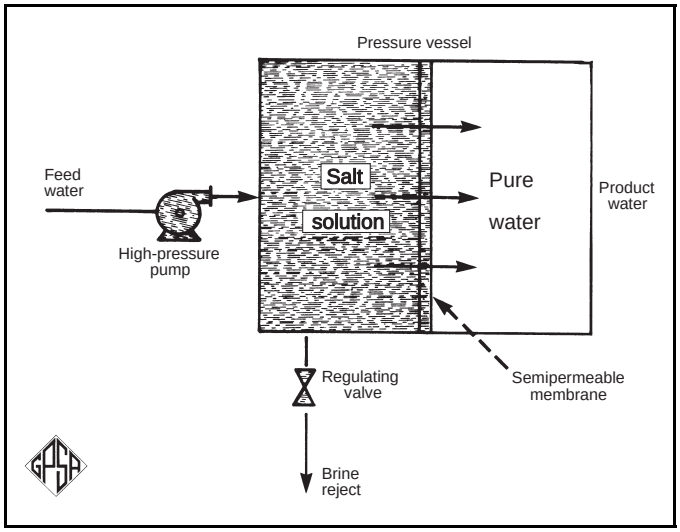


FIG. 18-17

Electrodialysis Process Desalts Water Via Membranes of Alternating Ion Selectivity[2]

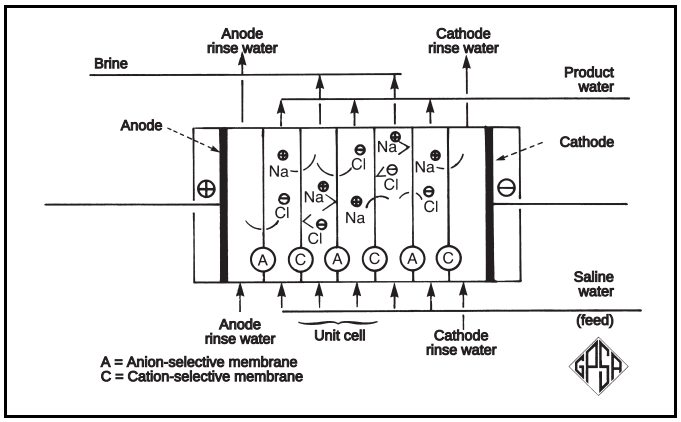
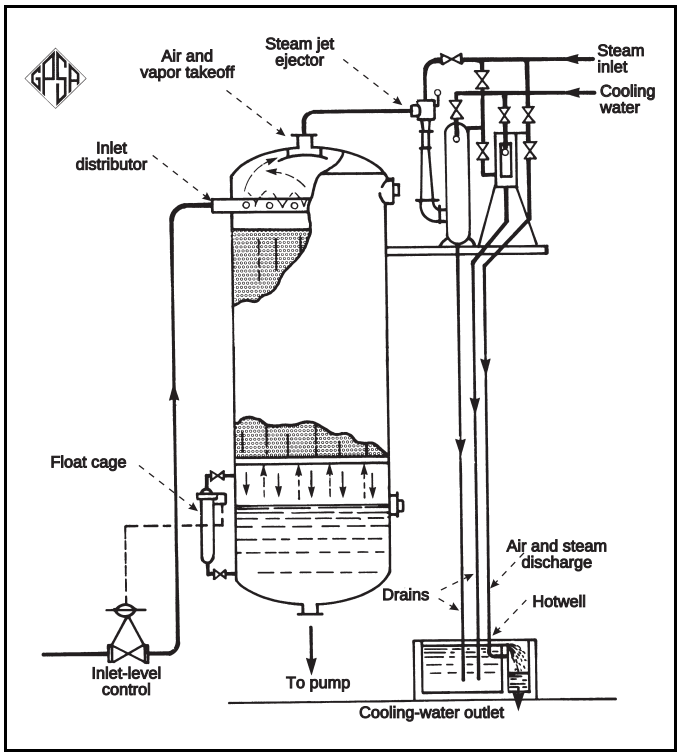


FIG. 18-18

Vacuum Deaerator[5]



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FIG. 18-19

Tray/Spray Deaerator[5]

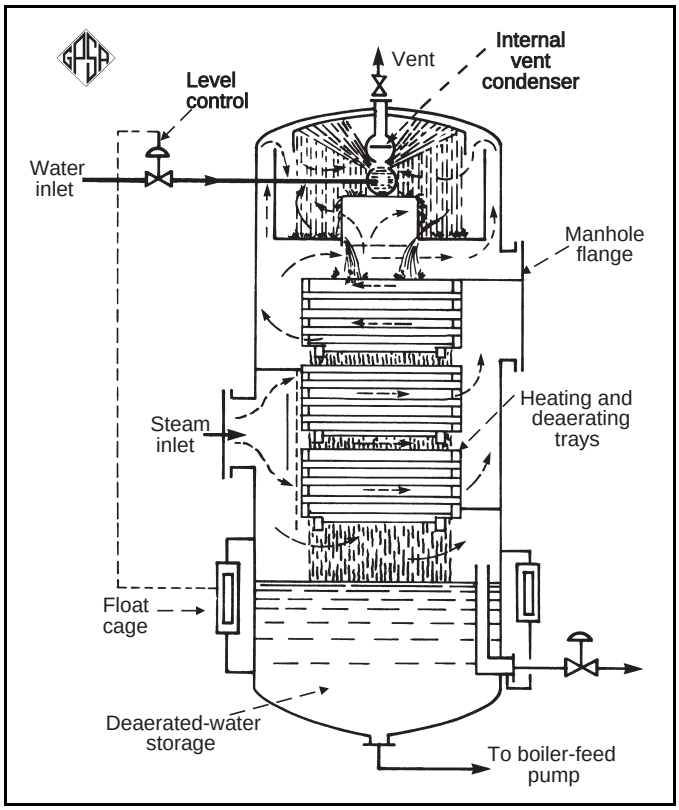
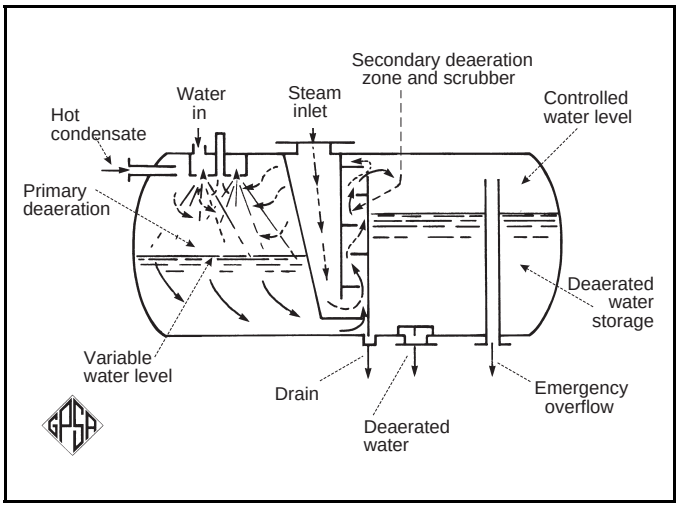


FIG. 18-20

Spray-Type Deaerator[5]



sure boilers because at higher boiler pressures, it can decompose and form potentially corrosive sulfur compounds such as sulfur dioxide (SO_2) and hydrogen sulfide (H_2S). In addition, the use of sodium sulfite will result in an increase in boiler water solids unless blowdown is increased. Because the oxygen-sulfite reaction (Eq 18-1) is inhibited by some boiler waters, catalyzed sodium sulfite containing materials which speed the reaction to completion is frequently used instead of the uncatalyzed material.

Catalyzed hydrazine will react with oxygen at an acceptable rate at low water temperatures. The use of hydrazine and catalyzed hydrazine is economically attractive principally in high pressure boiler systems where extremely low boiler water solids content is essential. Hydrazine reacts too slowly with oxygen at low temperatures to provide effective scavenging, is toxic, and requires special handling precautions and equipment. Control testing for hydrazine residuals is difficult and it decomposes in the boiler to form ammonia which can cause excessive corrosion of copper and copper alloys.

Scale Control — Scale formation involves the deposition of insoluble salts on heat transfer surfaces. The most common method of controlling scale is to precipitate potential scale-forming ions as non-adhering solids, or sludges, or as loosely-adhering scales. Calcium ions are preferably precipitated as calcium hydroxyapatite [$3Ca_3(PO_4)_2 \cdot Ca(OH)_2$]; magnesium is preferably precipitated as serpentine [$2MgSiO_3 \cdot Mg(OH)_2 \cdot H_2O$]. These sludges are more flocculent or fluid when precipitated at a pH above about 9.5. Caustic soda, soda ash, or a blend of phosphates can be fed to provide this alkalinity if there is inadequate natural alkalinity in the feedwater. Proper control of phosphate and silicate residuals avoids the formation of magnesium phosphate (a sticky precipitate) and calcium silicate (normally a dense, hard scale).

In higher pressure boilers and some lower pressure boilers with high purity feedwater, coordinated phosphate-pH control is practiced. This control method provides both the phosphate residual and the pH desired in the boiler by feeding a combination of disodium and trisodium phosphates. Its purpose is to avoid the presence of free hydroxide, thus eliminating the potential for caustic attack of boiler surfaces.

Chelating agents provide an alternative approach to scale control that may be attractive for some low pressure boiler systems. These chemicals form soluble complexes with ions such as calcium and magnesium. Some chelating agents will also solubilize iron and copper ions. Chelating agents should be supplemented with an antifoam agent and an oxygen scavenger. The boiler feedwater must be low in hardness (1-2 ppmw or less) for chelating agents to demonstrate an economic advantage over the precipitation scale control methods. Chelating agents have not been successfully utilized in high pressure boilers.

Sludge Conditioning — Various organic materials are often used to condition the boiler precipitates or sludges to make them fluid or free-flowing for easier removal by blowdown. These are usually derivatives of tannin or lignin, synthetic materials, or, in some cases, derivatives of seaweed. Starch is sometimes used in high silica waters. Sludge conditioners are frequently combined with phosphates and chelating agents. Antifoam materials, for smoother boiler operation, are sometimes also incorporated in these formulations.

Foam Control — Foaming can cause entrainment of boiler water with the steam although this carryover may also be the result of poor boiler design, ineffective steam-separating equipment, or high water levels. Foaming can be caused by high levels of dissolved solids, suspended solids, alkalinity, or by the introduction of foaming-promoting materials into the boiler, for example, by the use of oil-contaminated steam condensate. Although effective antifoam agents are available to suppress foam formation, it is usually more economical to reduce or eliminate the problem by adjusting boiler water treatment (external and/or internal), increasing boiler blowdown,

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eliminating foam-promoting contaminants from recycled steam condensate, etc.

Corrosion Mitigation — Corrosion in boiler and steam/steam condensate systems is usually due to the effect of either low pH or the presence of oxygen.

Low pH (below neutral pH = 7) is usually caused by dissolved carbon dioxide and the resulting corrosion is normally of a general nature over the entire metal surface. This acidic corrosion can be mitigated by raising the pH. Soda ash (Na_2CO_3) and caustic soda are often used for this purpose in boiler feedwater systems. In boilers, the proper water treatment for sludge and scale control will normally result in a satisfactorily high pH of 10-11.

Pretreatment of the boiler feedwater to reduce carbonate alkalinity will result in an equivalent reduction in the potential carbon dioxide content of the steam and the carbonic acid content of the steam condensate. Filming amines, which form a thin protective layer on metal surfaces, and neutralizing amines, which react with carbon dioxide and raise the pH of the steam condensate to a sufficiently high level (8.5 to 9.5), are frequently used to mitigate corrosion in steam condensate systems.

Filming amines, which tend to decompose at higher temperatures, are often fed to the steam headers at a rate sufficient to form and maintain the desired corrosion-resistant film. Filming amines will also protect the steam condensate system from corrosion due to oxygen. Neutralizing amines, which are quite stable, are usually added to the boiler feedwater at a rate proportional to the carbon dioxide content of the steam. Neutralizing amines can be used in high temperature, high pressure steam systems, but these amines will not protect against oxygen attack and are usually not economical in steam systems containing high concentrations of carbon dioxide. Ammonia is sometimes substituted for neutralizing amines; however, it should not be used in systems containing copper or most copper alloys.

Oxygen may be present in the makeup water or may result from air leaks into the steam/steam condensate systems; the resulting corrosion is generally in the form of pitting. Oxygen-related corrosion can be mitigated by deaeration of boiler feedwater, the use of chemical oxygen scavengers, and the addition to the steam/steam condensate systems of a filming amine.

Caustic Embrittlement — Caustic embrittlement is intercrystalline cracking of boiler steel which may occur in the presence of all of the following factors:

- The metal must be subjected to a high level of stress.
- There must be some mechanism (a crevice, seam, leak, etc.) permitting concentration of the boiler water on the stressed metal.
- The concentrated boiler water must possess embrittling characteristics and chemically attack the boiler metal. Of these three factors, the embrittling characteristics of the boiler water generally can best be shown to be present or absent in a boiler. An Embrittlement Detector developed by the U.S. Bureau of Mines can be used to determine this water characteristic. As an alternative, since there are no simple chemical tests to measure embrittlement and there is always the possibility of embrittlement occurring, a chemical embrittlement inhibitor, generally sodium nitrate, is often added to the boiler. A definite ratio of sodium nitrate to caustic alkalinity in the boiler water is required for inhibition according to the formula,

$$\frac{NaNO_3}{NaOH}\ \text{Ratio} = \frac{(\text{Nitrate as } NO_3, \text{ ppmw})\ (2.14)}{\left(\begin{matrix}\text{M alkalinity as}\\ CaCO_3, \text{ ppmw}\end{matrix}\right) - \left(\begin{matrix}\text{Phosphate as}\\ PO_4, \text{ ppmw}\end{matrix}\right)}$$

Eq 18-3

This ratio depends upon the operating pressure of the boiler as recommended by the U.S. Bureau of Mines in Fig. 18-21.

FIG. 18-21

Recommended $NaNO_3$/NaOH Ratio for Boilers

Boiler Operating Pressure	$NaNO_3$/NaOH Ratio
Up to 250 psi	0.20
250-400 psi	0.25
400-700 psi	0.40

OPEN COOLING WATER SYSTEMS

In an open recirculating cooling water system, warm water from the coolers, condensers, etc., is routed to a cooling tower where cooling of the water is effected primarily by evaporation of a portion of the circulating water. This concentrates the dissolved solids in the water; the level of concentration of dissolved solids is controlled by blowdown of some of the circulating water. At equilibrium, the rate of dissolved-solids loss with blowdown and windage or drift (droplets of water leaving the tower or pond) equals that gained with the water added as makeup to replace water lost by evaporation, drift, and blowdown. Water treatment is employed to prevent or minimize:

- scaling or heat exchanger surfaces by salts of hardness ions, silica, or silicates
- corrosion of the system by oxygen or low pH
- attack of cooling tower wood by algae, bacteria, or fungi, and
- fouling of heat exchanger surfaces by suspended solids and marine organisms

See Section 11 for additional information about cooling towers, including heat and material balance calculations.

Scale Control

Scale is an adherent deposit laid down during operation, causing impaired heat transfer and restricting flow in the cooling water system. The scale-forming tendency of a water increases with increasing cycles of concentration of dissolved solids in a recirculating system. Calcium carbonate, the principal scale found in cooling water systems, forms when calcium and alkalinity levels become too high. Because it has an inverse temperature solubility, calcium carbonate tends to deposit on warmer heat transfer surfaces.

Several scaling indices have been developed and are often used as guides to predict the tendency of cooling water to form scale. These include the Langelier Saturation Index (LSI) and

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the Ryznar Stability Index (RSI). The main objective in using the Langelier or the Ryznar index is to adjust the cooling water to a non-scaling, non-corrosive condition. A positive LSI indicates a tendency to deposit calcium carbonate scale; a negative LSI indicates an unsaturated condition with respect to calcium carbonate and a tendency to dissolve any existing calcium carbonate and to be corrosive. Similarly, a RSI less than 6.0 indicates a tendency to deposit calcium carbonate; a RSI greater than 6.0 indicates a tendency to dissolve existing calcium carbonate deposits and to be corrosive. Fig. 18-22 can be used to calculate pH_S, the pH at which the water is in equilibrium with calcium carbonate, and Fig. 18-23 is a comparison of scaling tendency as characterized by the two indices.

A common water treatment strategy is to adjust the cooling water to a slightly scaling condition (assumed therefore to be a non-corrosive condition) and to use a scale inhibitor. However, it should be emphasized that the LSI and RSI are only measures of the tendency to deposit or dissolve calcium carbonate scale and that the two indices often give inconsistent indications.

Two different approaches to scale control are often followed. The alkalinity can be maintained at a level at which calcium carbonate clearly will not form, or a scale inhibitor can be used.

Low alkalinities may be maintained in some cases by limiting the cycles of concentration; however, this increases blowdown requirements, increasing water consumption and wastewater production. In most cases, sulfuric acid is used to reduce alkalinity by converting bicarbonate and carbonate alkalinity to carbon dioxide and water. Unfortunately, this in-

FIG. 18-22

Nomograph for Determination of Ryznar and Langelier Scaling Indexes[7]

Example:

Given the following data, find the values of both the Langelier and the Ryznar Indexes:

pH = 6.9

Temp. = 68°F (20°C)

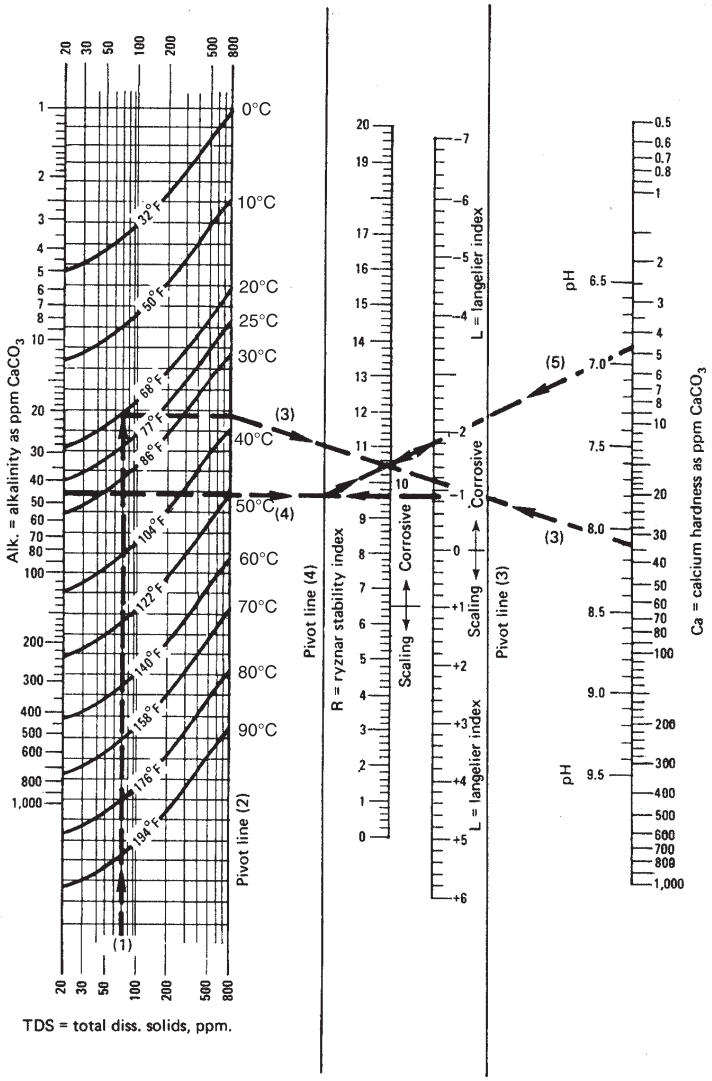
TDS = 72 ppm

Calcium hardness as $CaCO_3$ = 47 ppm

Methyl orange alkalinity as $CaCO_3$ = 47 ppm

Solution:

1. Reading at the bottom of the left-hand side, find TDS = 72 and note the intersection of this reading with the curved 70°F line.
2. Carry this intersection horizontally to pivot line 2.
3. Connect that point with Ca hardness = 34 on the right-hand scale.
4. Note the intersection on pivot line 3.
5. Connect that point with alkalinity = 47 on the left-hand scale.
6. Note the intersection on pivot line 4. Connect this intersection to pH = 6.9.
7. The Langelier Index = –1.8 and the Ryzner Index = 10.5. This water would be said to be very corrosive.



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FIG. 18-23

Scaling Tendency of Water According to Langelier's and Ryznar's Indices[3]

LSI	RSI	Condition
3.0	3.0	Extremely severe
2.0	4.0	Very severe
1.0	5.0	Severe
0.5	5.5	Moderate
0.2	5.8	Slight
0.0	6.0	Stable water*
–0.2	6.5	No scaling, very slight tendency to dissolve scale
–0.5	7.0	No scaling, slight tendency to dissolve scale
–1.0	8.0	No scaling, moderate tendency to dissolve scale
–2.0	9.0	No scaling, strong tendency to dissolve scale
–3.0	10.0	No scaling, very strong tendency to dissolve scale
* No scaling, no tendency to dissolve scale		

creases the sulfate content of the water and, consequently, the potential for calcium sulfate scale formation. Although calcium sulfate also has an inverse temperature solubility, it is considerably more soluble than calcium carbonate, so the tendency toward scale formation is reduced. Generally, calcium sulfate will not be a problem if the calcium concentration in the circulating water is maintained below about 900 ppmw (as calcium carbonate). Calcium and alkalinity levels can also be reduced by softening the makeup water or a sidestream from the circulating water system (see "Boiler Water Treatment-External" under "Boiler Water Systems") or by using a makeup water with low dissolved solids such as the "fast rinse" water from a demineralizer.

Addition of acid to the cooling water system should preferably be controlled automatically. The acid might be fed in proportion to makeup water flow and trimmed by a circulating water pH signal. Acid should be introduced into the tower basin remote from the circulating pumps at a location where intimate mixing can occur.

Among the materials in common use to inhibit calcium carbonate scale formation are inorganic polyphosphates and various organic materials, including phosphonates, phosphate esters, and polyacrylates. Inorganic polyphosphates and phosphate esters tend to hydrolyze to form orthophosphate. Calcium phosphate deposits can form if the orthophosphate level becomes too high. Many scale inhibitors tend to control calcium sulfate scale formation as well as calcium carbonate.

Silica levels are usually maintained below about 150 ppmw to avoid formation of siliceous scales within the system. Where the silica level of the makeup water is inordinately high, it can be reduced by precipitation softening. Alternatively, precipitation softening of a sidestream from the circulating water system can be used to remove silica.

Corrosion Control

Factors contributing to the corrosiveness of cooling water are: dissolved oxygen concentration, pH, calcium and alkalinity concentrations, dissolved solids concentration, water temperature, and circulating-system metallurgy. Successful application of inhibitors requires a detailed understanding of the various corrosion processes that are possible in a given system. Typical inhibitors are polyphosphates, chromates and dichromates, silicates, nitrates, ferrocyanides, and molybdates. Inhibitors specific to control of copper and copper alloy corrosion are sometimes used, particularly when the circulating water pH tends to be low.

Polyphosphates were used at one time as corrosion inhibitors in concentrations of 10 to 15 ppmw. Polyphosphates are seldom used now, however, because they revert to orthophosphate which can result in an undesirable calcium phosphate scale.

Chromates alone are effective inhibitors at concentrations of 100 to 300 ppmw; however, such high concentrations are seldom used because of environmental restrictions on chromate discharges and the high chemical makeup cost. Lower chromate concentrations are likely to promote pitting; however, satisfactory corrosion inhibition can be obtained at these lower chromate levels by adding zinc salts. Addition of phosphates as well as zinc salts further improves corrosion inhibition with chromates, but this inhibition system requires a close control of pH.

Proprietary formulations are available that provide satisfactory corrosion protection under broad operating conditions and at reasonable costs. Most of these formulations are blends of chromate, zinc salts, phosphates, and organic compounds. Increased restrictions on chromate discharges with blowdown streams have stimulated research on non-chromate inhibitors. Chromate can be removed from the cooling tower blowdown by precipitation and filtering or by ion exchange.

Biological Fouling

A cooling tower is an ideal environment for the development and growth of microorganisms. Algae can develop in the tower where sunlight is present while slime can develop in almost any part of the system. These deposits can cause local corrosion as well as plugging and reduction of heat transfer.

Growth of the microorganisms can be controlled by using chlorine, chlorinated phenols, organometallic salts, quaternary ammonium compounds, and various other biocides. Chlorination is probably the most widely used control method. A chlorine residual of 0.3 to 1.0 ppmw is usually effective. The most appropriate treatment is best determined experimentally. Proprietary compounds of several biocides have frequently been found to be more effective than any single material. These compounds are sometimes used alternately with chlorine.

Chlorination programs may be either continuous or intermittent. A generally successful program has been to chlorinate daily until a 1 ppmw free chlorine residual has been maintained for one hour. Chlorine can cause deterioration of cooling tower wood, so prolonged exposure to concentrations over 1 ppmw should be avoided. Limitations on chlorine concentrations in effluent waters have necessitated closer control of chlorine dosage. Several techniques have been employed to reduce chlorine residuals in cooling tower blowdown. The chlorine can be removed by reaction with reducing agents such as sulfur dioxide or sodium bisulfite, or blowdown can be discon-

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tinued until the chlorine residual of the circulating water has fallen to an acceptable level. In the latter technique, it is usually necessary to blowdown at a somewhat higher rate prior to the initiation of chlorination to ensure that cycles of concentration do not exceed control levels when blowdown is shut off.

Solids Removal

Continuous filtration of a portion of the total circulating water has been used in cooling systems for controlling the quantity of suspended solids. Antifouling agents can reduce or eliminate the need for mechanical filtration. Both chemical antifoulants and mechanical side-stream filters are sometimes used to combat very difficult suspended-solids problems.

When sand or mixed media filters are used, they can be sized using the following equation:

$$F = \left[\left(\frac{SS_I}{SS_F}\right) - 1\right] BD \qquad \textbf{Eq 18-4}$$

To provide 80% removal of suspended solids, a side-stream filter is often sized at four times the normal blowdown rate.

A disadvantage of side-stream filtration is the requirement of a significant quantity of water for backwashing. If this water is withdrawn immediately from the system at the required backwash rate, upsets in system concentrations can occur. A better approach is to withdraw the backwash water continuously from the circulating system and store this water until needed for backwashing. Backwash water must be discarded and cannot be permitted to reenter the cooling system.

ONCE-THROUGH COOLING WATER SYSTEMS

In a once-through system, no evaporation takes place. Since there is no increase in concentration of dissolved solids but only an increase in the water temperature, required water treatment is usually significantly reduced. The water is often obtained from a river, lake, or bayou, and aside from rough screening to protect circulating water pumps, removal of suspended solids is rarely practiced. Water treatment is sometimes employed to prevent or minimize scaling and corrosion, but more frequently, its purpose is to mitigate fouling from suspended solids and marine organisms. Discharge water temperature must be compatible with state and federal regulations. Permits for once-through systems, except for coastal (seawater) applications, can be difficult to obtain.

Various antifouling materials including polyacrylates, natural organic materials, and other organic polymers are used to control deposition of solids. The Langelier Saturation Index will provide some indication as to whether the water will tend to be scale-forming, corrosive, or neither. Calcium carbonate, the most common scale in once-through systems, is usually inhibited by applying one or a combination of several deposit-control materials such as polyphosphates, phosphonates, and polyacrylates. Shock treatment with chlorine may also be used to control biological fouling. As with recirculating water systems, chlorine residuals in once-through cooling water system discharges must comply with environmental regulations.

Corrosion of piping and exchangers in a once-through cooling water system can be a serious problem. Because it is usually impractical to use corrosion inhibitors, the problem is usually handled by using fiberglass reinforced plastic, cement-lined, plastic-lined, or other corrosion-resistant pipe and corrosion-resistant condenser and cooler tubing materials, such as 90/10 Cupro-Nickel and titanium.

CLOSED COOLING WATER SYSTEMS

The small amount of makeup water required for closed cooling water systems significantly reduces water-caused problems. Steam condensate or demineralized water is usually used in these systems so scaling is not a problem. High concentrations of corrosion inhibitor can be economically used. Antifreeze may be added for cold weather operation.

OTHER WATER SYSTEMS

Water treatment for potable (drinking) water systems must meet state and federal drinking water standards. Water treatment is not normally provided for systems such as fire water, utility water, etc., although the water in these systems must be reasonably free of suspended solids and relatively noncorrosive.

WASTEWATER TREATMENT AND DISPOSAL

Wastewater treatment and disposal methods must normally meet environmental regulations. These regulations usually consider technology limitations, volume of discharge and concentration of pollutants, method of disposal, nature of the receiving stream, etc. Some wastewater streams either with or without treatment may be recycled for use in systems requiring water of lesser quality. Final treatment usually requires removal of oil and suspended solids, reduction of biochemical and chemical oxygen demand (BOD and COD), and removal of toxic contaminants.

Surface disposal of plant wastewater (except for once-through cooling water system effluent which can generally be discharged directly if chlorine residuals are acceptable) using properly-lined evaporation ponds is sometimes allowed and can be used where evaporation rates are favorable. Underground disposal of wastewaters is permitted in some instances. In such cases, a thorough geological investigation is often required to ensure against contamination of protected aquifers. Removal of suspended solids and additional treatment to ensure compatibility among the various wastewater sources and the receiving aquifer must frequently be implemented in order to eliminate plugging of the underground reservoir. Treatment of wastewater prior to disposal to surface streams is almost always required. Reuse or recycle of wastewater streams within the plant can be considered and is often required by regulatory agencies. This often reduces overall plant wastewater treatment requirements significantly.

Boiler blowdown streams are alkaline (pH ~ 10), low in volume, and generally high in total dissolved solids content (although blowdown from high pressure boilers is normally low in dissolved solids). After cooling, this wastewater is normally compatible with other wastewater streams but may require neutralization prior to discharging. Because it is usually oil free, boiler blowdown may bypass any conventional oil-water separation step. High pressure boiler blowdown can be reused as cooling tower makeup or cooled, deionized, and reused as boiler makeup.

Cooling tower blowdown is often the major source of plant wastewater. Discharge limitations may apply to concentrations of total dissolved solids, specific ions such as sulfate, suspended solids, corrosion inhibitors such as hexavalent chromium or phosphates, biological control agents including

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chlorine, and various miscellaneous chemicals. The quantity of cooling tower blowdown may frequently be reduced, thereby reducing treatment requirements, by observing higher circulating water control limits, using more effective scale inhibitors, or treating cooling tower makeup water or a sidestream from the system. If the dissolved solids level exceeds established discharge limits, it is usually necessary to blow down at a higher rate in order to lower the concentration, although in some situations pretreatment of the makeup water will effect the necessary reduction. Another alternative would be to concentrate the blowdown by mechanical evaporation to facilitate disposal. High sulfate concentrations may result from using sulfuric acid for neutralization of alkalinity. Where sulfate concentrations are specifically limited, use of another acid, such as hydrochloric, precipitation softening of makeup water, or use of a scale inhibitor to allow operation at higher alkalinity levels are possible approaches to resolving this problem. Suspended solids can, of course, be reduced by filtration. Sidestream filtration, which would also improve cooling system operation might be utilized. A non-chromate corrosion inhibitor can be substituted for a chromate-based material, or the hexavalent chromium can be removed by chemical reduction, precipitation, clarification, and filtration or by ion exchange. Phosphate compounds can be handled by chemical or biological methods. If high intermittent concentrations of biological control agents are unavoidable, diversion of the blowdown to a holding pond for blending with better quality blowdown may be necessary.

Process water is usually contaminated with hydrocarbons and may be sour (contain dissolved hydrogen sulfide). Normally all wastewater contaminated with heavy hydrocarbons is handled with an API separator or corrugated plate interceptor (Fig. 18-24) where the oil is skimmed from the water. Wastewater contaminated with light hydrocarbons is often handled with a flash tank where the hydrocarbon vapors are sent to flare. Sour water is normally handled with a sour water stripper where the hydrogen sulfide is vented to incinerator or flare or sent to a sulfur recovery unit. Stripped sour water may be reusable as cooling tower or boiler makeup. Additional treatment may be needed before reuse is possible. In some cases, conventional treatment techniques are not adequate for process wastewater treatment. Such supplementary techniques as air flotation, biological treatment, activated carbon adsorption, ion exchange, ultraviolet irradiation, ozonation, chlorination, hydrogen peroxide oxidation, and precipitation and clarification may be necessary. Fig. 18-25 is an example of a complete wastewater treating system.

Produced water is normally contaminated with hydrocarbons, may be sour, and may range from very low to extremely high total dissolved solids. Treatment can be similar to that of process water. Produced water is often reusable in reservoir formation flooding operations.

Ion exchange process waste streams can have high concentrations of sodium chloride, acid or base, and are high in total dissolved solids. Adjustment of pH may be necessary before discharge with the other plant wastewater streams. In some cases, concentration by evaporation is needed to facilitate disposal. Reverse osmosis wastes are generally not as high in total dissolved solids and can frequently be reused as cooling tower makeup. Wastewater disposal requirements can often be significantly reduced by selecting the proper makeup water treatment system.

Chemical cleaning wastewaters can be acidic or alkaline, and contain high concentrations of dissolved metals. Adjustment of the pH, chemical precipitation of the metals, and removal of the precipitates by clarification and filtration is often necessary.

Plant runoff waters may have to be retained for flow equalization and oil and suspended solids removal prior to discharge. Adjustment of pH may also be necessary. If contaminated from process leaks, treatment similar to that described above for process water may be required, depending upon the degree and type of contamination. Removal of heavy metals, such as dissolved iron, is sometimes required. This is often accomplished by raising the pH to precipitate the metals as oxides or hydroxides, and then clarifying and filtering. Other approaches may be needed, depending upon the type of contamination and required degree of removal.

Plant sewage is generally treated by extended aeration, a modification of the activated sludge process. Package treatment plants are available for this purpose.

FIG. 18-24

Corrugated Plate Interceptor (CPI) Oil Separator[1]

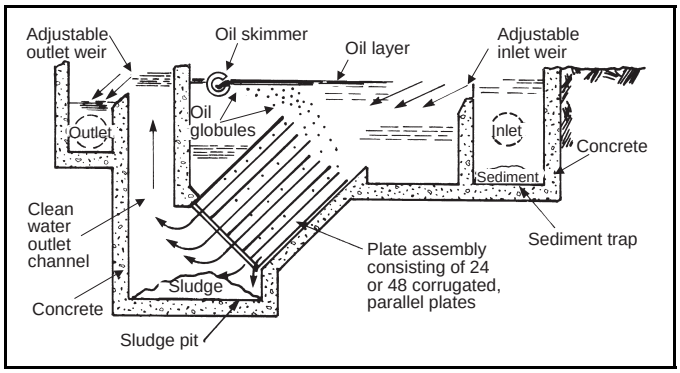
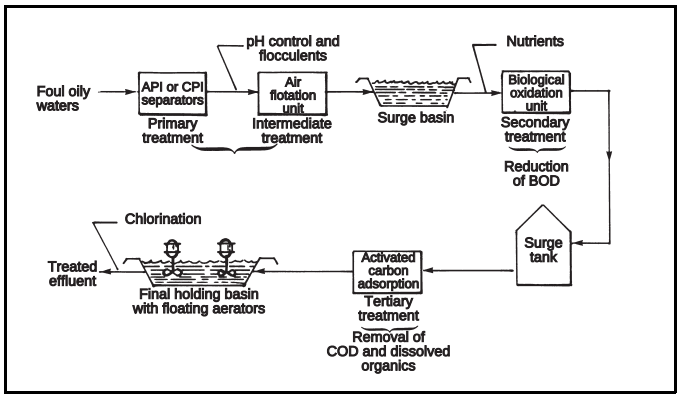


FIG. 18-25

Complete System for Treating Plant Wastewater[1]



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ELECTRICAL SYSTEMS

Electric-power applications in a modern gas processing plant are many, including: power distribution, illumination, space heating, heat tracing of water and product lines, communication, automation, signal transmission for process control, data logging, cathodic protection, grounding, and others.

The National Electrical Code (NEC), which is revised every three years, serves as the minimum acceptable standard.

Fig. 18-26 provides formulas for calculation and conversion of various electrical terms used throughout this section. Fig. 18-27 covers symbols used in electrical one-line diagrams. One-line diagrams are utilized extensively in electrical design to show the connection and relationship of electrical system components. Figure 18-28 shows an example one-line for a simple power system.

Power Supply System

It is important to identify the utilization voltage of each piece of equipment in order to properly design the electrical system. Once this has been accomplished, local loads may be grouped to be served from motor control centers and/or switchgear, which in turn may be served from other switchgear and ultimately served from transformers. These transformers are used to reduce the incoming service voltage. A typical system might take 69 kV or 138 kV power at a substation and reduce the voltage to 13.8 kV for distribution to local substations which in turn reduce the voltage to 480 volts, 3 phase for the utilization equipment. See Fig. 18-28. Consultation with the local electric utility is recommended to determine what supply voltages are available.

The capacity of the supply system may not need to be as great as the sum of nameplate ratings of each connected load. This is due to the fact that all the equipment may not be operating at the same time or, if operating, may not all be taking full-load current from the system at the same time.

In gas plants where the usage of each motor is generally known, making a load list is the best way to determine the system requirements in terms of the operating load. The load list should list the hp rating of each motor as well as its operating hp (brake hp), and whether the motor will run continuously, intermittently, or is a standby for other motors. The brake hp can either be obtained from the equipment designers, or calculated by the formulas given in other sections of this data book.

When the above list is completed, the kW of each motor should be calculated by the hp to kW formula given in Fig. 18-26 of this section, using the brake horsepower. In the absence of specific user guidelines these kW's may be added up using the following:

Motors

- Largest Motor (1.25) (kW)
- All Continuous Motors (1.00) (kW)
- All intermittent (to be determined by evaluating each use and plant requirements) (0.20) (kW)
- Standby motors which *cannot* run when another is running can be ignored.

Other Loads

- All flood lighting load (1.00) (kW)
- Building lighting loads (consult the National Electrical Code, Article 220, for loads of various building occupancies). (2 watts/sq ft of floor space)
- Larger of air conditioning or electrical heating (1.00) (kW)
- Heat Tracing (1.00) (kW)
- Miscellaneous Loads — Computers, laboratories, office machinery, etc. (1.00) (Actual)

This total load is the *minimum* value to use in sizing the supply capacity. This does not leave any spare capacity for future additions. Other things should also be considered. If one motor is large in relationship to the total load, or if two or more motors must be started at the same time, it will generally be necessary to increase the supply capacity to provide the starting current which is approximately 5.5 times normal running current.

Whether purchasing or generating power, the starting loads need to be considered in addition to the above calculations. If the motors will be started one at a time, the locked rotor current listed on the nameplate of the largest motor should be used in the above calculations instead of the kW • 1.25. If two or more motors need to be started at the same time, their combined locked rotor current needs to be used if it is larger than the locked rotor current of the largest motor.

Transformer Connections

Various connections of single-phase transformers commonly used in plant substations have their limitations, benefits, and advantages. Fig. 18-29 shows the most commonly used schematic diagrams of single-phase transformer connections.

Open Delta — The units will transform 86.6% of their rating, that is, two 100 kVA units connected open delta will each transform 86.6 kVA for a total of 173.2 kVA. The line currents must equal the winding currents; therefore, the transformer bank rating is reduced by the ratio of normal transformer current to normal line current (1/1.73), or 57.7%. The individual transformation in terms of kVA is (57.7%) (3/2) = 86.6%, since 3-phase voltage is delivered with only two units.

With the open delta connection, it is not necessary for the transformers to have the same impedance.

The voltage regulation of an open delta bank is poor and different for each phase resulting in unbalanced voltage conditions that may be detrimental to 3-phase induction motor operations.

Closed Delta — When three transformers are operated in a closed delta bank, care should be taken to make certain the impedances of the three units are practically the same. Transformers having more than 10% difference in impedance rating should not be operated together in a closed delta bank unless a reactor is used to increase the impedance of the unit having the lower impedance rating to a value equal to the other units.

If the voltage ratio of all three of the transformers is not the same, there will be a circulating current inside the delta. The current will be limited by the impedance of the three transformers considered as a series circuit.

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FIG. 18-26

Electrical Formulas

Desired Data	Alternating Current		Direct Current
	Single Phase	Three Phase	
kilowatts	$\frac{V \cdot I \cdot PF}{1{,}000}$	$\frac{1.73 \cdot V \cdot I \cdot PF}{1{,}000}$	$\frac{V \cdot I}{1{,}000}$
kVA	$\frac{V \cdot A}{1{,}000}$	$\frac{1.73 \cdot V \cdot I}{1{,}000}$	
Reactive kVa	$\frac{V \cdot I \sqrt{1 - PF^2}}{1{,}000}$	$\frac{1.73 \cdot V \cdot I \sqrt{1 - PF^2}}{1{,}000}$	
Horsepower (Output)	$\frac{V \cdot I \cdot eff \cdot PF}{(746)(100)}$	$\frac{1.73 \cdot V \cdot I \cdot eff \cdot PF}{(746)(100)}$	$\frac{V \cdot I \cdot eff}{(746)(100)}$
Amperes (When horsepower is known)	$\frac{hp(746)(100)}{V \cdot eff \cdot PF}$	$\frac{hp(746)(100)}{1.73 \cdot V \cdot eff \cdot PF}$	$\frac{hp(746)(100)}{V \cdot eff}$
Amperes (When kilowatts are known)	$\frac{kW \cdot 1{,}000}{V \cdot PF}$	$\frac{kW \cdot 1{,}000}{1.73 \cdot V \cdot PF}$	$\frac{kW \cdot 1{,}000}{V}$
Amperes (When kVA is known)	$\frac{kVA \cdot 1{,}000}{V}$	$\frac{kVA \cdot 1{,}000}{1.73 \cdot V}$	

$PF = \frac{kW}{kVA} = \frac{kW \cdot 1{,}000}{1.73 \cdot V \cdot I}$ (for 3–phase)

PF = Power factor

eff = efficiency

Motor kilowatts $= \frac{hp\ (0.746)\ (100)}{eff}$

Motor kVA $= \frac{hp\ (0.746)(100)}{eff \cdot PF} = \frac{kW}{PF}$

Motor full–load torque $= \frac{5{,}250 \cdot \text{Full– load hp}}{\text{Speed in rpm}}$

Synchronous speed in rpm $= \frac{120 \cdot \text{frequency}}{\text{Number of poles}}$

It is good practice, before applying voltage to three transformers in closed delta, to insert a fuse wire between the leads coming from the high voltage bushings of two transformers closing the delta bank. The fuse wire should be of sufficient size to carry the exciting current of the transformers. This fuse wire offers a very simple means of making certain the transformers have the proper polarity.

Wye Delta — Transformers are connected for delta-delta to wye-delta to take advantage of 1.732 times the delta transmission voltage. It is not necessary that the impedance of the three transformers be the same.

If single-phased on the primary, fully-loaded motors connected on the secondary will draw 200% current in one phase and 100% in the other two phases. This requires overload elements in each phase for full protection.

Delta-Wye Grounded — With a delta-wye grounded connection, a combination of single and three-phase loads may be connected. This is the most common connection used to obtain a grounded secondary system. A grounded system is readily relayed for phase-to-ground faults, and the problem of high transients due to arcing grounds is minimized.

It is not necessary that the impedances of each unit in the bank be the same. A combination of single and 3-phase loads may be connected without causing any circulating currents. Three overload elements are required to protect a fully loaded motor for a single phase on the primary system.

Transformer Locations

Indoors

Transformers rated over 35,000 volts shall be installed in a vault. A transformer vault is a room with concrete walls, roof, and floor to meet a minimum fire resistance of three hours. It shall comply with NEC Sections 450-41 through 450-48.

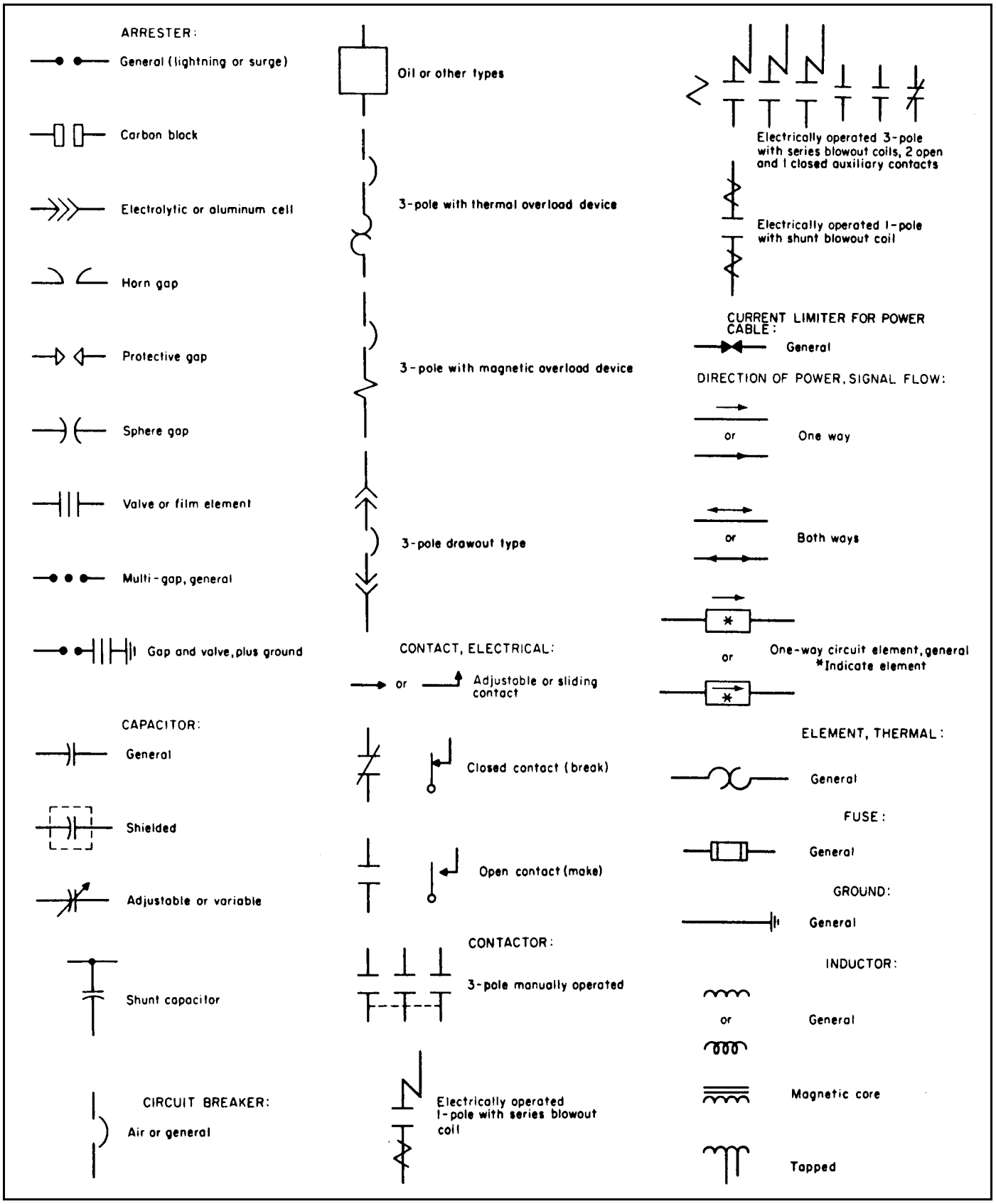
Dry Type Transformers — Transformers installed indoors and rated 112½ kVA or less shall have a separation of at least 12 inches (305 mm) from combustible material unless separated therefrom by a fire-resistant, heat-insulating barrier, unless its rating is not over 600 volts and it is completely enclosed except for ventilating openings.

Transformers of more than 112½ kVA rating shall be installed in a transformer room of fire-resistant construction, unless the transformer has an 80°C rise or higher insulation and has proper fire barrier or distance separation to combustible material.

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FIG. 18-27

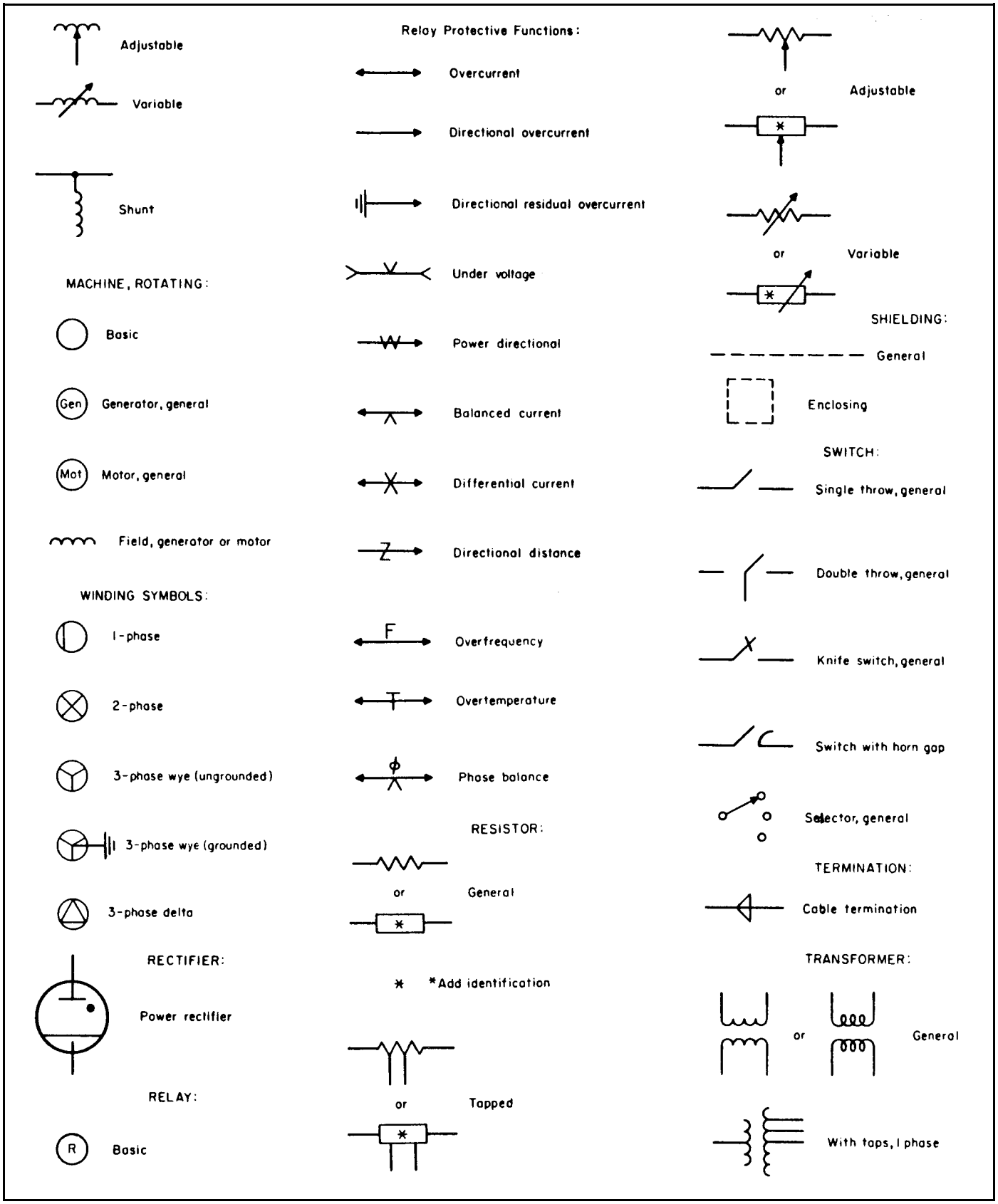
Graphical Symbols for One-Line Electrical Diagrams



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FIG. 18-27 (Cont'd)

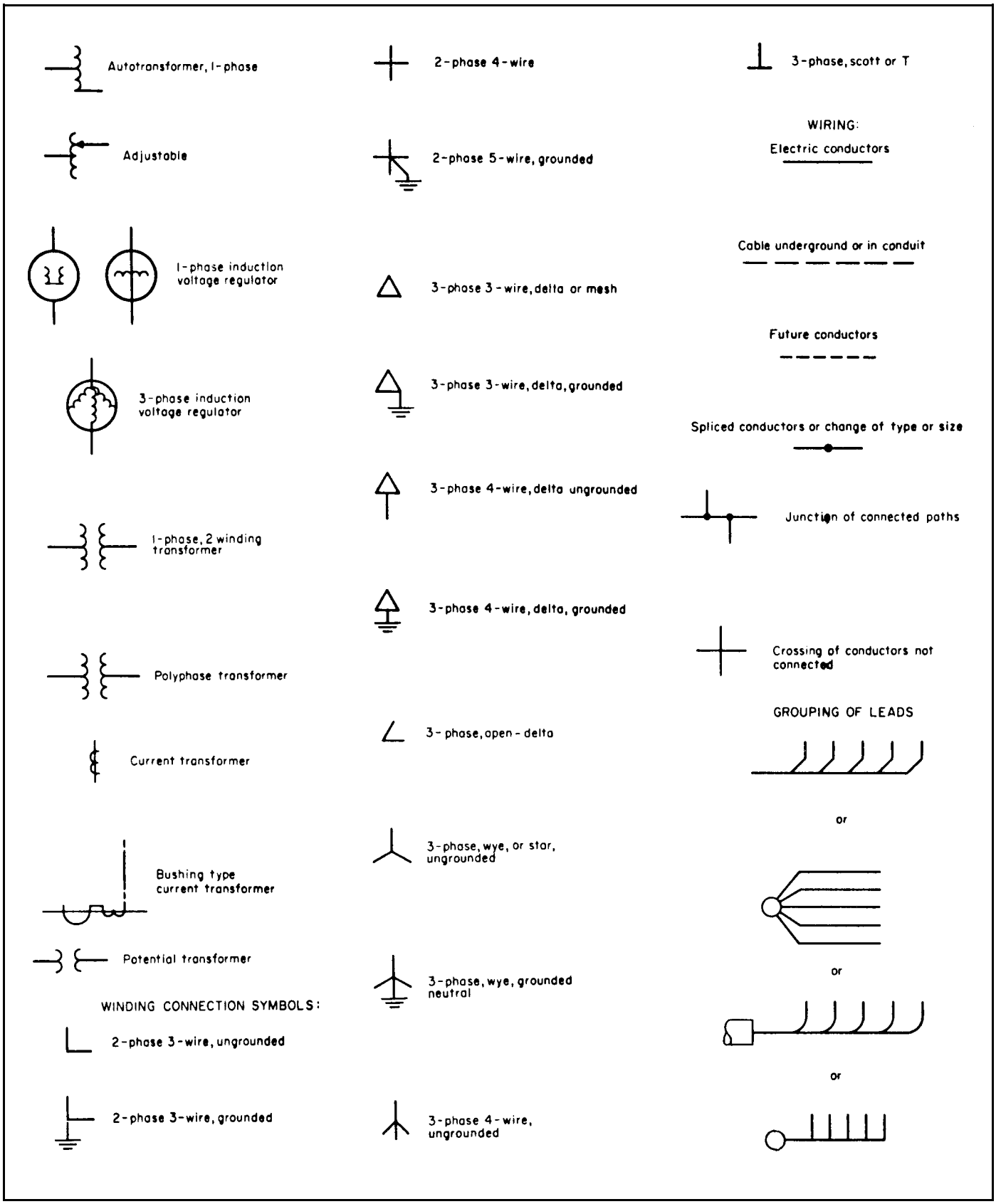
Graphical Symbols for One-Line Electrical Diagrams



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FIG. 18-27 (Cont'd)

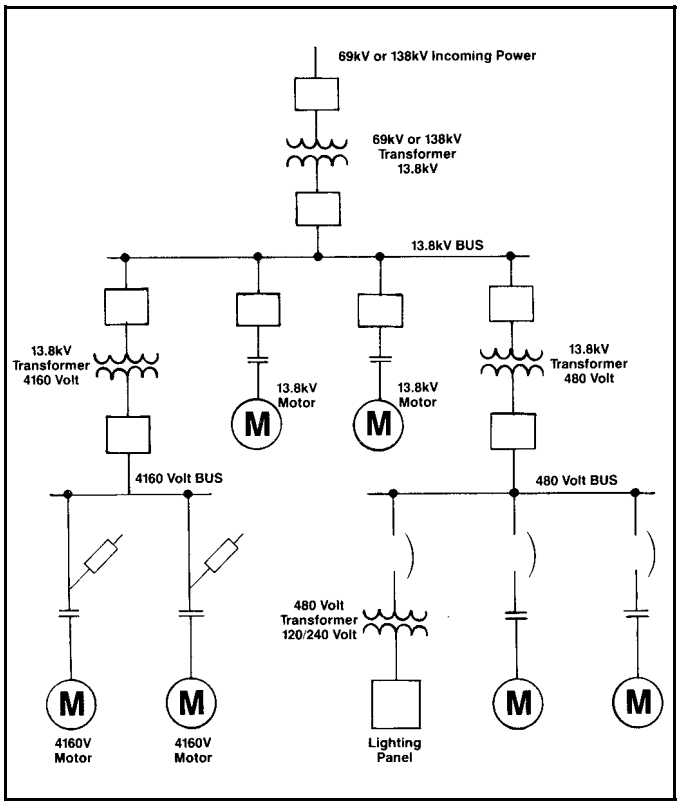
Graphical Symbols for One-Line Electrical Diagrams



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FIG. 18-28

Example Electrical Power System One-Line Diagram



High Fire Point Liquid-Insulated Transformers — Transformers insulated with listed less-flammable liquids shall be permitted to be installed without a vault in noncombustible occupancy areas of noncombustible buildings, provided there is a liquid confinement area and the minimum clearances required by the heat release rates of the listed liquid are maintained.

Such indoor transformer installations not meeting the clearance requirements of the liquid listing, or installed in combustible buildings or combustible occupancy areas, shall be provided with an automatic fire extinguishing system or shall be installed in a vault.

For purposes of this section, a less-flammable liquid is one with a fire point not less than 300°C. Fire point is defined by ASTM D92-72.

Nonflammable Fluid-Insulated Transformers — Transformers insulated with a dielectric fluid identified as nonflammable shall be permitted to be installed indoors or outdoors.

For the purpose of this section, a nonflammable dielectric fluid is one which does not have a flash point or fire point, and is not flammable in air.

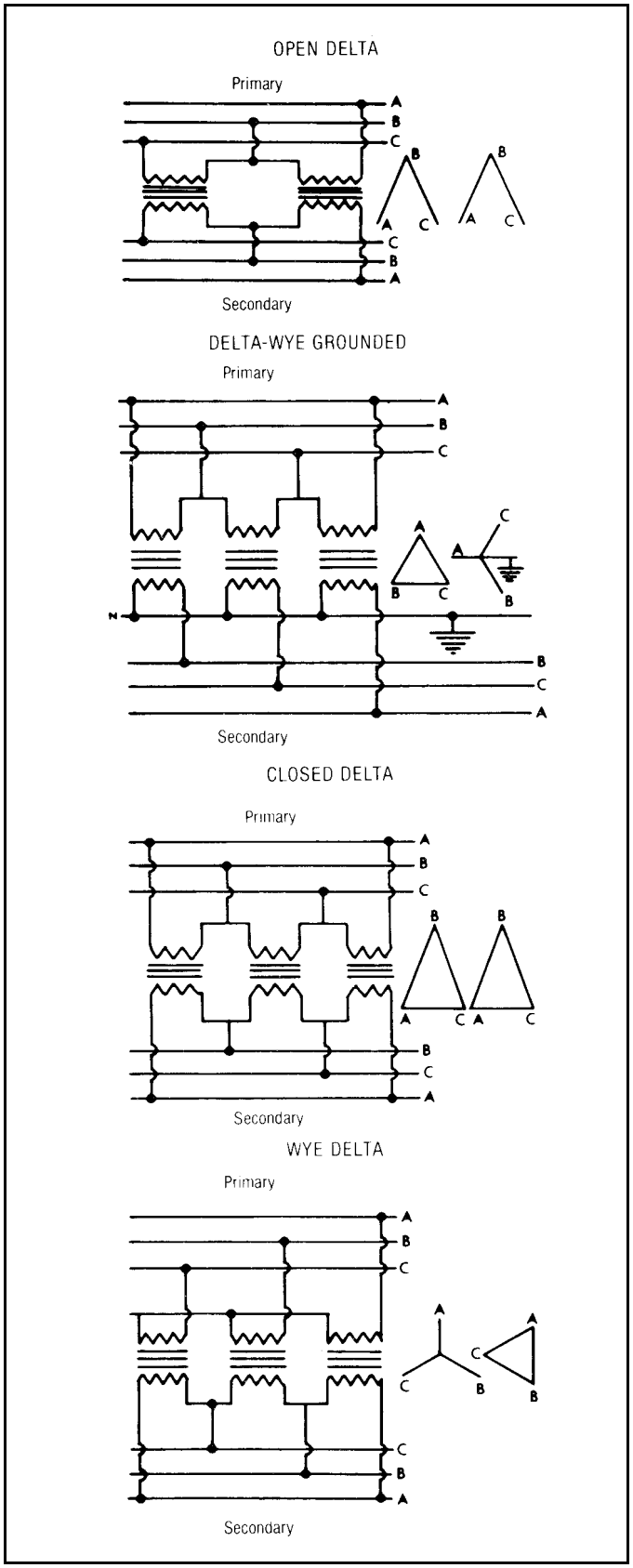
Oil-Insulated Transformers — Oil-insulated transformers installed indoors shall be installed in a vault.

Exceptions:

- Where the nominal voltage does not exceed 600, a vault shall not be required if suitable arrangements are made to prevent a transformer oil fire from igniting other ma-

FIG. 18-29

Transformer Connection Schematics



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terials, and the total capacity in one location does not exceed 10 kVA in a section of the building classified as combustible, or 75 kVA where the surrounding structure is classified as fire-resistant construction.

- Transformers shall be permitted to be installed in a detached building if neither the building nor its contents presents a fire hazard to any other building or property, and if the building is used only in supplying electric service and the interior is accessible only to qualified persons.

Outdoors

Dry-type Transformers — Dry-type transformers installed outdoors shall have a weatherproof enclosure.

Transformers exceeding 112½ kVA shall not be located within 12 in. (305 mm) of combustible materials of buildings.

Oil-Insulated Transformers — Combustible material, combustible buildings, and parts of buildings, fire escapes, and door and window openings shall be safeguarded from fires originating in oil-insulated transformers installed on roofs, attached to, or adjacent to a building or combustible material.

Space separations, fire-resistant barriers, automatic water spray systems, and enclosures that confine the oil or a ruptured transformer tank are recognized safeguards. One or more of these safeguards shall be applied according to the degree of hazard involved in cases where the transformer installation presents a fire hazard. Transformers installed on poles or structures or underground shall conform to the National Electrical Safety Code (ANSI C2-1984).

MOTOR CONTROLS

Protective Devices

Motor Protection — The basic type of motor, its size, and service to which it is applied, will have a large influence on the system of protection used. The hazards for which protection is applied to induction motors are:

- Short circuits in the motor windings or branch circuits.
- Overloads or locked rotor.
- Reduction or loss of supply voltage.
- Phase unbalance.
- Phase reversal.
- Line surge.

Actually, several of these hazards will result in an overload condition. Locked rotor is a severe overload condition. Reduced voltage may result in an overload. Also, unbalanced phase voltage or single-phasing results in overload. The overload protection employed, therefore, will also give some degree of protection from these hazards, depending on the motor and transformation connections.

Therefore, overload and short circuit protection is all that is provided for a large percentage of induction motors.

Several types of overload protective devices (Fig. 18-30), are used: the replica type, such as thermal bi-metallic relays, is the most commonly used to protect small and medium sized motors. For induction motors, rated up to 30 hp, there is no particular problem of matching the thermal relay characteristics with the motor capability.

Above 30 hp, more care should be exercised in selecting overload relays to be sure that adequate protection is provided. The rotor circuit, rather than the stator winding of large motors, particularly high speed motors, may be the limiting part.

Short Circuit Protection — The branch circuit overcurrent protection device is used for the purpose of protecting against short circuits and grounds that produce short-circuit currents. It is not necessarily sized to provide running overcurrent protection for the branch circuit, as this function is provided by the motor-running overcurrent device.

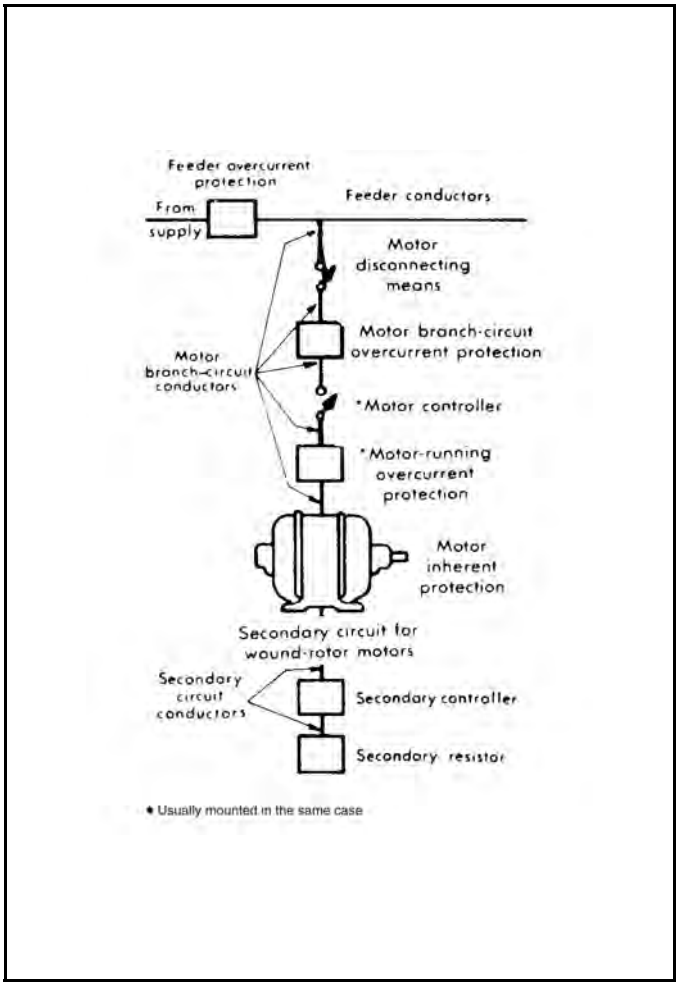
When using inherent type of protectors which operate on the basis of temperature, particular attention should be given to selecting the rating of the branch circuit overcurrent protection device to obtain running protection.

Available short-circuit protection for faults in any branch circuit can readily be calculated. If the available fault current should exceed the interrupting capacity of the motor branch circuit overcurrent protective device normally used, there are several solutions:

- Use the scheme of cascading the motor branch circuit-protecting device with the feeder circuit overcurrent-protecting device. (Use with caution.)
- Install current-limiting fuses in the feeder serving the motor branch circuit. (Use with caution.)

FIG. 18-30

Motor Feeder and Branch Circuits (Based on 1984 NEC Diagram 430-1)



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- Install current-limiting reactors in the feeder circuit.
- Use higher-than-normal interrupting-capacity-motor branch circuit breakers.
- Install current-limiting fuses in combination with molded case breakers.
- Reduce the size of transformer serving the motor bus or use a high-impedance transformer.

Controllers

Ratings — As shown in Fig. 18-31, NEMA has established horsepower ratings for manual and magnetic controllers in low voltage (600 volts and below) sizes. High voltage sizes to 5000 volts are also established, but are not shown here. These ratings change for duties other than continuous duty, such as: jogging, plug stopping, control of constant-horsepower multiple-speed motors, part winding, and reduced-voltage starting.

Starting Methods — When voltage is applied to a squirrel cage motor, it may be compared to energizing a transformer with the secondary short circuited. As the motor comes up to speed, the rotor back emf causes a reduction in line currents and a corresponding rise in motor terminal voltage. The motor torque available is proportional to the square of the terminal voltage; hence, terminal voltage, load torque, and total angular momentum must be considered when determining the starting method to be used and whether a motor will start.

When the motor is small in comparison to the system, across-the-line starting may be used. Where voltage sensitive loads are present in the system or when a motor exceeds 15 to 25% of the system capacity, reduced voltage starting is likely to be required.

Reduced voltage starting isolates the high starting requirements of a motor from the system and reduces these requirements by lowering the motor terminal voltage. Since the motor torque drops off as the square of the voltage, starting and acceleration problems may develop. A detailed analysis of motor starting is recommended for all large reciprocating compressors and large pumps and compressors that are to be started while fully loaded.

Electrical Control Devices

There are two basic motor control schemes for controlling process equipment as shown in Fig. 18-32. They are two-wire control and three-wire control. The two-wire control device could be a hand switch, thermostat, float switch, limit switch, or other maintained contact device. When the contacts of the control device close, they complete the coil circuit of the starter, causing it to pick up and connect the motor to the line. When the control device opens, the starter is de-energized, stopping the motor.

Two-wire control provides low voltage release, but no low voltage protection. Depending upon the nature of the control device, the starter will function automatically in response to the direction of the control device without the attention of an operator. After a power dip or power outage, restoration of power will cause process equipment to restart if the control device is closed at that time. Consequently, the demand on the supply and distribution system may be excessive.

A three-wire control circuit uses momentary contact start-stop buttons and a holding circuit interlock, wired in parallel with the start button, to maintain the circuit.

Pressing the N.O. start button completes the circuit to the coil. The power circuit contacts close, completing the circuit to the motor and the holding circuit contacts (mechanically linked with the power contacts) also close. Once the starter has picked-up, the contacts provide an alternate current path around the reopened start contacts.

Pressing the N.C. stop button will open the circuit to the coil, causing the starter to drop-out. An overload condition which causes the overload contact to open, a power failure, or a drop in voltage to less than seal-in value would also de-energize the starter. When the starter drops out, the interlock contact re-opens, and both current paths to the coil, through the start button and the interlock, are now open.

FIG. 18-31

Ratings for Single-Speed Full-Voltage Magnetic Controllers for Nonplugging and Nonjogging Duty (Based on NEMA ICS 2-321B, May 1974)
Horsepower Ratings

Size of Controller	Continuous Current Rating,* Amperes	Three-Phase Horsepower † at				Single-Phase Horsepower at 60 Hertz	
		60 Hertz		50 Hertz	60 Hertz		
		200 Volts	230 Volts	380 Volts	460 or 575 Volts	115 Volts	230 Volts
00	9	1½	1½	1½	2	⅓	1
0	18	3	3	5	5	1	2
1	27	7½	7½	10	10	2	3
1P	36	–	–	–	–	3	5
2	45	10	15	25	25	3	7½
3	90	25	30	50	50	–	–
4	135	40	50	75	100	–	–
5	270	75	100	150	200	–	–
6	540	150	200	300	400	–	–
7	810	–	300	–	600	–	–
8	1215	–	450	–	900	–	–
9	2250	–	800	–	1600	–	–

kW= 0.746 x hp *See ICS 2-321 A.20 † Based on locked rotor current ratings given in Table ICS 2-327B-1

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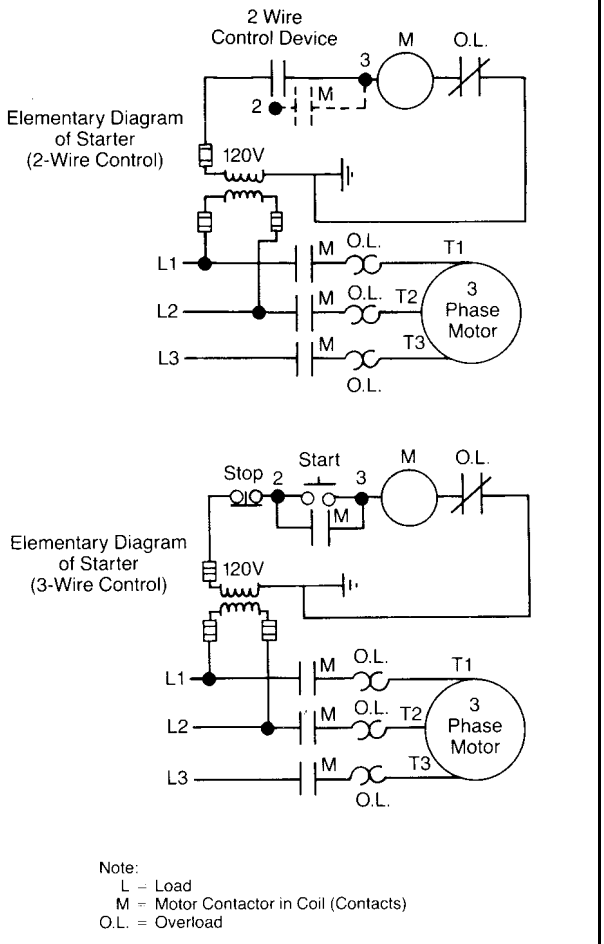
To guard against nuisance shutdowns, a time-delay undervoltage device (TDUV) can be added in addition to the mechanical interlock around the N.O. momentary start push button. This will restart the process equipment within a three to four second time interval to avoid shutdown on a power dip, but it will need to be restarted after a power failure.

A maintained contact control device is one which when operated will cause a set of contacts to open (or close) and stay open (or closed) until a deliberate reverse operation occurs. A conventional thermostat is a typical maintained contact device. Maintained contact control devices are used with 2-wire control systems.

A standard push button is a typical momentary contact control device. Pushing the button will cause N.O. contacts to close and N.C. contacts to open. When the button is released, the contacts revert to their original state. Momentary contact devices are used with 3-wire control or jogging service.

FIG. 18-32

Typical 2 and 3 Wire Control Wiring Diagrams



Note:
L = Load
M = Motor Contactor in Coil (Contacts)
O.L. = Overload

Power Factor Correction

Capacitors can be installed to reduce the cost of reactive power, to release system capacity, to relieve overload, and to improve voltage. The effects of adding capacitors are: reduction of the lagging component of current, increased power factor at the source, decreased kVA demand, reduction in the I^2R losses, and a consequent reduction of the purchased power costs.

When capacitors are applied for overall plant power factor correction and primarily for their effect on power costs, they are usually located near the service entrance. If there is a large variation in power factor due to varying loads, a series of capacitor banks may be installed to turn on and off automatically as required by means of power factor relays.

Group correction, with capacitors installed at each load center, is usually the most practical method. This takes advantage of the load diversity factor and provides the most effective correction for a given amount of kVA. It serves to reduce feeder losses and to improve voltage regulation.

Individual correction can be applied to motors with the capacitors located at the motor terminals and switched on and off with the motor. Caution must be exercised, however, in the application of individual capacitors, especially on motors driving high inertia loads which may cause a motor to run a relatively long time after power is cut off. The capacitor is an excitation source to the motor and could cause a dangerously high induced voltage immediately after shutdown. The danger would be if the line switch were reclosed at the time when the induced voltage would be out of phase with the line voltage.

If the plant in question has its own generating equipment and the power factor of the load is less than 0.8 lagging, it may be advisable to correct to approximately 0.9 to prevent excessive voltage drops on feeders, excessive I^2R losses, and reduction in generator capacity.

It is impractical to make any general recommendations on power factor correction when there are large variations in load conditions because severe overvoltages can result with an excess of capacitors on a lightly loaded bus. Therefore, it is suggested that if there is a low power factor problem, a study of the plant system be made with consideration given to the many intangible advantages and variables. A good knowledge of the basics of power factor will facilitate such a study.

LIGHTING

Lighting Sources

Various types of light sources are available, depending on the quantity and quality of the light desired. The most commonly used sources are fluorescent (usually limited to interior spaces), mercury vapor, metal halide, and high pressure sodium. Of all the currently used sources, high pressure sodium is the most efficient in terms of lumens (source intensity) per watt.

For determining lighting levels, see the Illuminating Engineering Society of American Handbook; see also Fig.18-33.

ELECTRICAL HEAT TRACING

The most common type of electrical heat trace materials is the resistance type heat cable. The resistive material in the heat cable is generally nichrome wire. The nichrome wire

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FIG. 18-33

Suggested Lighting Levels (Based on API RP 540 1974)

Location	In-Service Footcandle Level
Walkways, stairways	3
Operating platforms	3
Toilets and washrooms	10
Warehouse	5-30
Compressor building	20-25
Maintenance area	15-50
Boiler house	20
Control room	
General	30
Console desk	30
Panel	30
Back of panel	10
Switch Room	30
Laboratories and office, general	30-50
Business machine operation	50
Outdoor areas	
General	1
Cooling towers, tanks, etc.	3
Switchyards	2

comes into contact with the bus wires (one hot and one neutral) at predetermined intervals along the length of cable. The nichrome wire creates heat (I^2R) as current passes through it. A temperature switch is used to turn the heat trace on and off as the temperature drops close to the solidification point of the substance to be kept from freezing.

Another type of heat trace cable is the current limiting type cable. Similar to the resistive cable, the current limiting cable uses a resistive material to generate its heat, but with a special property or alloy in the material such that the current is limited in proportion to the change in temperature. As temperature increases, the resistance of the heat element increases. Since

$$I = \frac{V}{R}$$

as R increases, I decreases. If temperature decreases, so does R which leads to an increase in I.

A third type of electric heat trace is the skin effect type used for heating long lengths of pipe. Lengths of 10 miles or more can be heated uniformly, at a continuous rate and from one power source, using the skin effect method. This type of heat trace is associated with pipelines and is not generally used in a plant environment.

STAND-BY POWER

The use of back-up or stand-by power systems in gas processing plants is needed in the event there is a power dip or a complete failure in the primary AC power source.

There are two types of back-up systems in general use, the Uninterruptible Power Supply (UPS) system and the standby generator system. The UPS system generally consists of a rectifier/battery charger, battery, DC to AC inverter, and transfer or bypass switch. The output of the inverter supplies regulated, transient-free (uninterrupted) power to critical loads such as plant control systems (Section 4). The amount of battery back-up or time back-up is user specified. The battery bank could be sized to carry the load through a power dip, through a shutdown sequence, or until an alternate power supply system (such as an engine driven generator) is brought on line. Where it is crucial for a plant or parts of a plant to continue operating, a standby generator system is used to drive heavier loads such as motors and lighting systems. These standby generators can take from seconds to minutes to be brought on line.

PROGRAMMABLE CONTROLLERS

A Programmable Logic Controller (PLC) is a solid-state device designed to perform logic decision making for industrial control applications. The PLC can be used as a direct replacement for relays or solid-state electronics in an industrial environment. See Section 4 for detailed discussion.

GROUNDING

Equipment Grounding

Equipment grounding is one of the most important factors in safety to personnel in industrial plants. It covers the connecting to ground of non-current-carrying metal parts such as motor-control centers, motor frames, switchgear, metal raceways, building steel, etc.

Equipment grounding is installed to limit potential between non-current-carrying parts and between these parts and earth, to a safe value under normal and abnormal operating conditions.

To ensure this condition, all parts of structure and apparatus are metallically connected to the plant grounding system, thus placing all at the same potential, as well as to place personnel at the same potential, at all times.

System Grounding

A system ground is the grounding of one of the current carrying leads to earth. There are many variations of ground systems from solid grounding to impedance grounding.

A study should be made before selecting a particular system giving consideration to voltage level, service continuity, etc. Equipment grounding is separate from system grounding. Both are required to provide adequate protection.

Grounding Principles

A study of grounding indicates that it requires more than just good ground rods to ensure low-resistance ground. The conductance of soils, especially subsoils, is an important factor in ground resistance, and this conductance can vary through a rather wide range.

The various factors which affect the conductance of soil or the resistance of a ground are the chemical ingredients, the amount of moisture in the soil, and type of soil. Resistance values may range from 2 ohms to as much as 3,000 ohms. A desirable value should be less than 25 ohms.

Earth temperature also has an effect on resistivity. As the water in the soil freezes and the temperature drops, the resistivity rises, and the resistance of the ground connection is increased.

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Ground Resistivity Test

Ground-resistance measurements are usually made with self-contained direct reading instruments. These meters require two auxiliary grounds when making the measurements.

CATHODIC PROTECTION

Cathodic protection is a means of reducing or preventing destructive corrosion which results from galvanic or electrochemical attack. The most familiar galvanic or electro-chemical corrosion occurs when two dissimilar metals are in contact in the presence of an electrolyte. This forms a galvanic couple which is short-circuited on itself through the electrolyte. The metal of higher potential becomes the anode which goes into solution in the electrolyte, and therefore corrodes. The electrolyte needs to be only rainwater with impurities dissolved from the air, the ground, or the surface of the metal itself.

The principal method of minimizing corrosion is to isolate the metal from its environment by means of an envelope of more corrosion-resistant material: paint, organic coatings, or electro-deposits. If electro-deposits of metals are used, and if the deposited metal is less noble than the base is, zinc on steel for example, the zinc protects the steel galvanically, by so-called sacrificial action. It becomes the anode and the steel becomes the cathode of the galvanic cell, and the steel does not corrode until all the zinc in its immediate neighborhood is consumed.

Underground pipes and cables are corroded by electrolytic action from unidirectional electric currents in the ground. These currents may result from galvanic couples in the ground or many other causes. One way to reduce these currents from electrical equipment is by reducing the electric resistance of the metal and thus increasing the resistance of the ground circuit. The method of widest use is by the application of an external source of DC voltage. In doing this, the underground metal to be protected becomes lower in potential than the surrounding soil, and thus becomes a cathode instead of an anode. Usually if the pipe or other metallic structure is 0.25 to 0.30 V negative to the soil or liquid surrounding the pipe, corrosion is prevented.

This voltage is obtained by using small generators, batteries, or rectifiers. The negative lead is connected to the metal structure to be protected; and the positive lead, to a ground some distance away. Another means is to sink magnesium or zinc rods in to the ground and externally connect them to the pipe. They protect the pipe in a sacrificial manner, since they become an anode to the pipe. Due to varying conditions, such as size of pipe, type and condition of protective coatings, and resistance and chemical conditions of the soil, it is not possible to calculate the number of units that will be required. It has been found that one unit may protect anywhere from one-fourth mile of bare pipe to as much as 20 miles of well coated line. One method to determine the number required is to install temporary units at various intervals along the pipeline until the proper voltage level is achieved between the pipe and ground.

BUILDING AND AREA CLASSIFICATION

For methods of determining classification of building and areas in hydrocarbon plants, refer to the latest edition of API-RP-500 for the proper application of electrical equipment and material and the latest edition of NEC Section 500.

Types of Hazardous Classified Locations

Class I — Locations in which flammable gases or vapors are or may be present in air in quantities sufficient to produce an explosion or ignition.

Class II — Locations in which combustible dusts may be present.

Class III — Locations in which combustible fibers or flyings may be present.

Hazardous Gases

Hazardous locations are divided into these groups, based on atmospheric contaminant:

Group A — Atmospheres that may contain acetylene.

Group B — Atmospheres that may contain hydrogen, such as manufactured gases with more than 30 vol % hydrogen.

Group C — Atmospheres that may contain ethyl ether vapors, ethylene, cyclopropane, carbon monoxide, hydrogen sulfide, and others.

Group D — Atmospheres that may contain vapors of hydrocarbons and natural gas, alcohols, ketones, solvents, ethers, esters, and others.

Group E — Atmospheres that may contain dust of aluminum, magnesium, or similar metals and alloys.

Group F — Atmospheres that may contain carbon black, coal, or coke dust.

Group G — Atmospheres that may contain flour, starch, or grain dusts.

Hazardous Divisions

Hazardous location Classes and Groups are subdivided into Divisions 1 or 2, based on the probability of an ignitable mixture being present in the atmosphere.

Class I, Division 1 areas are locations in which one of these conditions exists:

- Ignitable concentrations of flammable gases or vapors exist under normal operating conditions.
- Ignitable concentrations of such gases or vapors may exist frequently because of repair or maintenance operations or because of leakage.
- Breakdown or faulty operation of equipment or processes might release ignitable concentrations of flammable gases or vapors and at the same time cause simultaneous failure of the electrical equipment.

All electrical equipment, fittings, and wiring materials in a Class I, Division 1 area shall be explosion-proof and suitable for the atmospheric group designation. Seal fittings are installed in conduit and cable systems to prevent the passage of gases, vapors, or flames from one portion of the electrical installation to another through the conduit. Such communication through Type MI cable is inherently prevented by construction of the cable.

Class I, Division 2 areas are locations in which one of these conditions exists:

- Flammable liquids or flammable gases are handled, processed, or used, but in which the liquids, vapors, or gases will normally be confined within closed containers

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or closed systems from which they can escape only in case of accidental rupture or breakdown of such containers or systems, or in case of abnormal operation of equipment.

- Ignitable concentrations of gases or vapors are normally prevented by positive mechanical ventilation and which might become hazardous through failure or abnormal operation of the ventilating equipment.
- The area is adjacent to a Class I, Division 1 location, and to which ignitable concentrations of gases or vapors might occasionally be communicated unless such communication is prevented by adequate positive pressure ventilation from a source of clear air, and effective safeguards are provided against ventilation failure.

All electrical equipment, fittings, and junction boxes in a Class I, Division 2 area need not always be explosion-proof. All arcing devices, however, shall be hermetically sealed or shall be installed in explosion-proof enclosures suitable for the atmospheric group designation. Lighting fixtures may be of the enclosed and gasketed type if the lamp temperature of the fixture being considered does not exceed 80% of the ignition temperature of the gas or vapor likely to be present in the atmosphere. Otherwise the fixtures must be explosion-proof. See the National Electrical Code, Section 501 for more explicit information regarding wiring rules in Class I, Division 2 locations.

Purging/Pressurization

Through the exercise of ingenuity in the layout of electrical installations for hazardous (classified) locations, it is frequently possible to locate much of the equipment in less hazardous or in nonhazardous locations and thus to reduce the amount of special equipment required. In some cases, hazards may be reduced or hazardous (classified) locations limited or eliminated by a purging/pressurization system.

For hazardous locations, sealed cast enclosures or sheet metal enclosures with pressurization may be used. As a typical example, if an installation had many electronic instruments that could be enclosed in a single sheet metal enclosure, the installation would lend itself to the purging/pressurization system. However, if the instruments, due to their nature, had to be installed in separate enclosures, then the cast, hazardous location housing would almost invariably prove more economical. Pressurized enclosures require:

- A source of clean air or inert gas.
- A compressor to maintain the required pressure on the system.
- Pressure control valves, to prevent the power from being applied before the enclosures have been purged, and to de-energize the system should pressure fall below a safe value.

In addition, door-interlock switches are required to prevent access to the equipment while the circuits are energized. It can readily be seen that all of these accessories can add up to a considerable expenditure.

For further information, see Purged and Pressurized Enclosures for Electrical Equipment in Hazardous Location, ANSI/NFPA 496-1982.

Intrinsically Safe Design

Equipment and associated wiring approved as intrinsically safe shall be permitted in any hazardous (classified) location for which it is approved, and the provisions of NEC Articles 500 through 517 shall not be considered applicable to such installation.

Abnormal conditions shall include accidental damage to any field-installed wiring, failure of electrical components, application of overvoltage, adjustment and maintenance operations, and other similar conditions.

The use of intrinsically safe equipment is primarily limited to process control instrumentation, since these electrical systems lend themselves to the low energy requirements.

For further information, see Intrinsically Safe Apparatus and Associated Apparatus for Use in Class I, II, and III, Division I Hazardous Locations, NFPA 493-1978 (ANSI) and Installation of Intrinsically Safe Instrument Systems in Class I Hazardous Locations (ANSI/ISA RP 12.6-1976).

Need for Classification

The need for classification is indicated by an affirmative answer to one of these questions:

- Is the presence of flammable liquids or vapors having flash points less than 70°F likely?
- Are any flammable liquids or vapors having flash points under 200°F likely to be handled, processed, or stored at temperatures above their flash points?
- For a more detailed explanation see the API RP-500A.

NEMA ENCLOSURES

Type 1 – General Purpose

A general-purpose enclosure is intended primarily to prevent accidental contact with the enclosed apparatus. It is suitable for general-purpose applications indoors where it is not exposed to unusual service conditions.

A Type 1 enclosure serves as a protection against dust and light indirect splashing, but is not dust tight.

Type 2 – Drip Proof – Indoors

A driptight enclosure is intended to prevent accidental contact with the enclosed apparatus and, in addition, is so constructed as to exclude falling moisture or dirt, but is not dust tight.

Type 2 enclosure is suitable for application where condensation may be severe, such as is encountered in cooling rooms and laundries.

Type 3 – Dust Tight, Rain Tight, and Sleet (Ice) Resistant – Outdoor

A weather-resistant enclosure is intended to provide suitable protection against specified weather hazards. It is suitable for use outdoors.

A Type 3 enclosure is suitable for application outdoors, if ice is not a serious problem.

Type 3R – Rain Proof, Sleet (Ice) Resistant – Outdoor

An outdoor enclosure designed to protect against rain. It is not dust tight, snow, or sleet (ice) proof.

Type 3S – Dust Tight, Rain Tight, and Sleet (Ice) Proof – Outdoor

An outdoor enclosure designed to protect against dust and water and to operate covered with ice or sleet.

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Type 4 – Water Tight and Dust Tight

An enclosure so designed that there will be no leakage of water into the enclosure under a specified hose test.

A Type 4 enclosure is suitable for application outdoors on ship docks, and in dairies, breweries, etc.

Type 4X – Water Tight, Dust Tight, and Corrosion Resistant

A Type 4 enclosure that is also corrosion resistant.

Type 6 – Submersible

Type 6 enclosures are intended for indoor or outdoor use primarily to provide a degree of protection against the entry of water during occasional temporary submersion at a limited depth. They are not intended to provide protection against conditions such as internal condensation, internal icing, or corrosive environments.

A Type 6 enclosure is suitable for application where the equipment may be subject to submersion, as in quarries, mines, and manholes. The design of the enclosure will depend upon the specified conditions of pressure and time. It is also dust tight and sleet (ice) resistant.

Type 7 (A, B, C, or D) Hazardous Locations – Class I Air Break

These enclosures are designed to meet the applicable requirements of the National Electrical Code for Class I hazardous locations which may be in effect. In this type of equipment, the circuit interruption occurs in air.

Specifically note that Type 7 (explosion-proof) enclosures and their associated conduit systems are neither gas nor liquid tight. Consequently, corrosive gases such as hydrogen sulfide and water from rain or internal condensation can accumulate within the enclosure. Premature failure of electrical devices and interconnections often results when preventative measures such as drains, air purges, and dual rated enclosures are not used to remove or exclude these corrosive elements.

Type 8 (A, B, C, or D) Hazardous Locations – Class I Oil Immersed

These enclosures are designed to meet the application requirements of the National Electrical Code for Class I hazardous locations which may be in effect from time to time. The apparatus is immersed in oil.

Type 9 (E, F, or G) Hazardous Locations – Class II

These enclosures are designed to meet the application requirements of the National Electrical Code for Class II hazardous locations which may be in effect.

The letter or letters following the type number indicates the particular group or groups of hazardous locations (as defined in the National Electrical Code) for which the enclosure is designed. The designation is incomplete without a suffix letter or letters.

Type 10 – Bureau of Mines – Explosion Proof

A Type 10 enclosure is designed to meet the explosion proof requirements of the U.S. Bureau of Mines which may be in effect. It is suitable for use in gassy coal mines.

Type 11 – Acid and Fume Resistant – Oil Immersed

A Type 11 enclosure is suitable for application indoors where the equipment may be subject to corrosive acid or fumes, as in chemical plants, plating rooms, sewage plants, etc. The apparatus is immersed in oil.

Type 12 – Industrial Use

A Type 12 enclosure is designed for use in those industries where it is desired to exclude such materials as dust, lint fibers and flyings, oil seepage, or coolant seepage.

Type 13 – Oil Tight and Dust Tight – Indoor

An indoor enclosure for pilot devices such as limit switches, selector switches, foot switches, push buttons, and pilot lights for protection against lint, dust seepage, external condensation, and spraying of water, oil, or coolant.

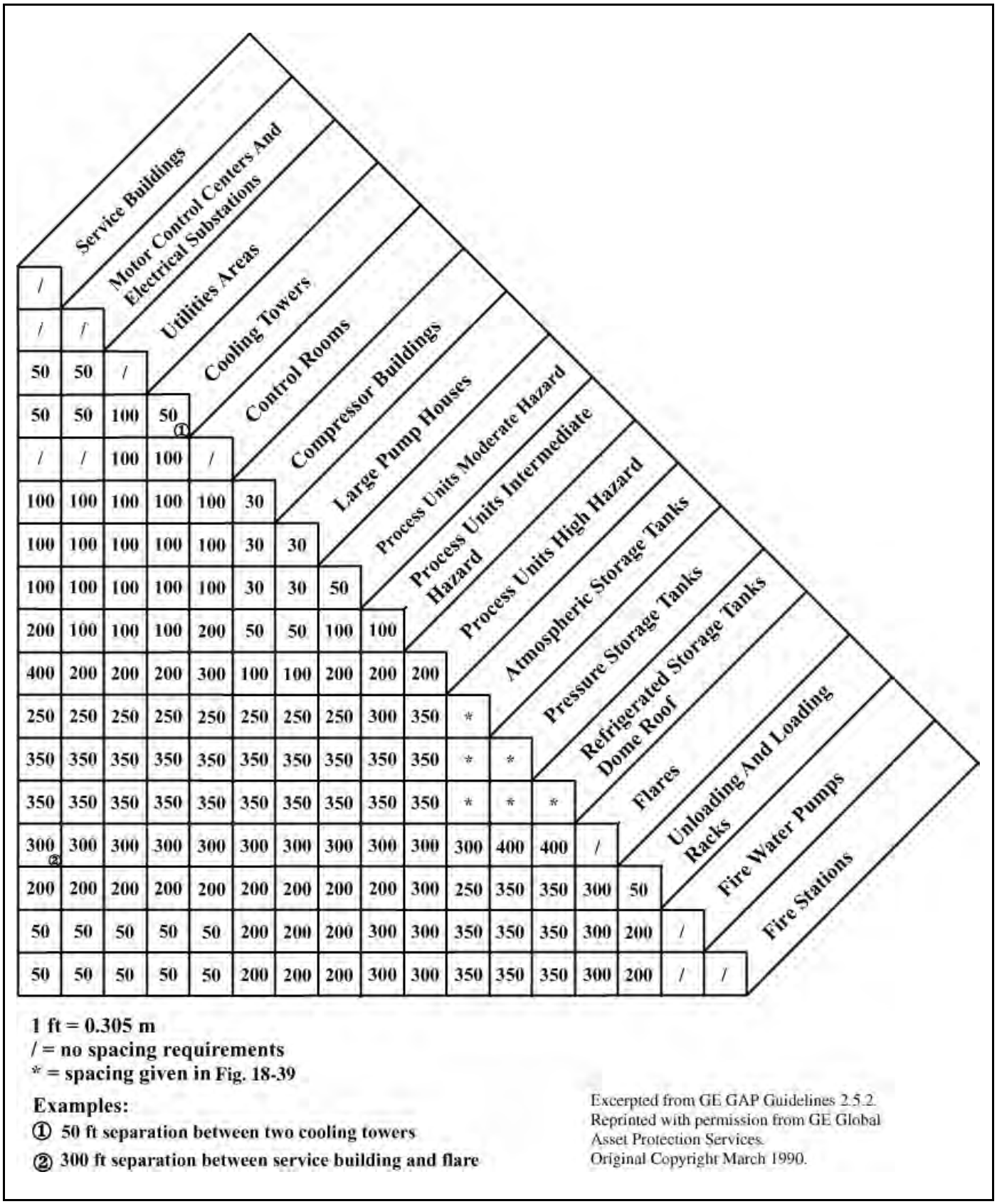
PLANT SPACING GUIDELINES

Plant layout applies to the spacing of both process units and process equipment within a facility. Industrial Risk Insurers published guidelines for plant layout and spacing which are used extensively in the Gas Processing Industry. These tables shown in Fig. 18-34 through 18-36 can be used as a guideline for plant and equipment spacing. The ultimate decision on a layout should be a combination of industry experience and risk assessment.

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FIG. 18-34

Interunit Spacing Guidelines



1 ft = 0.305 m
/ = no spacing requirements
*** = spacing given in Fig. 18-39**

Examples:

① 50 ft separation between two cooling towers

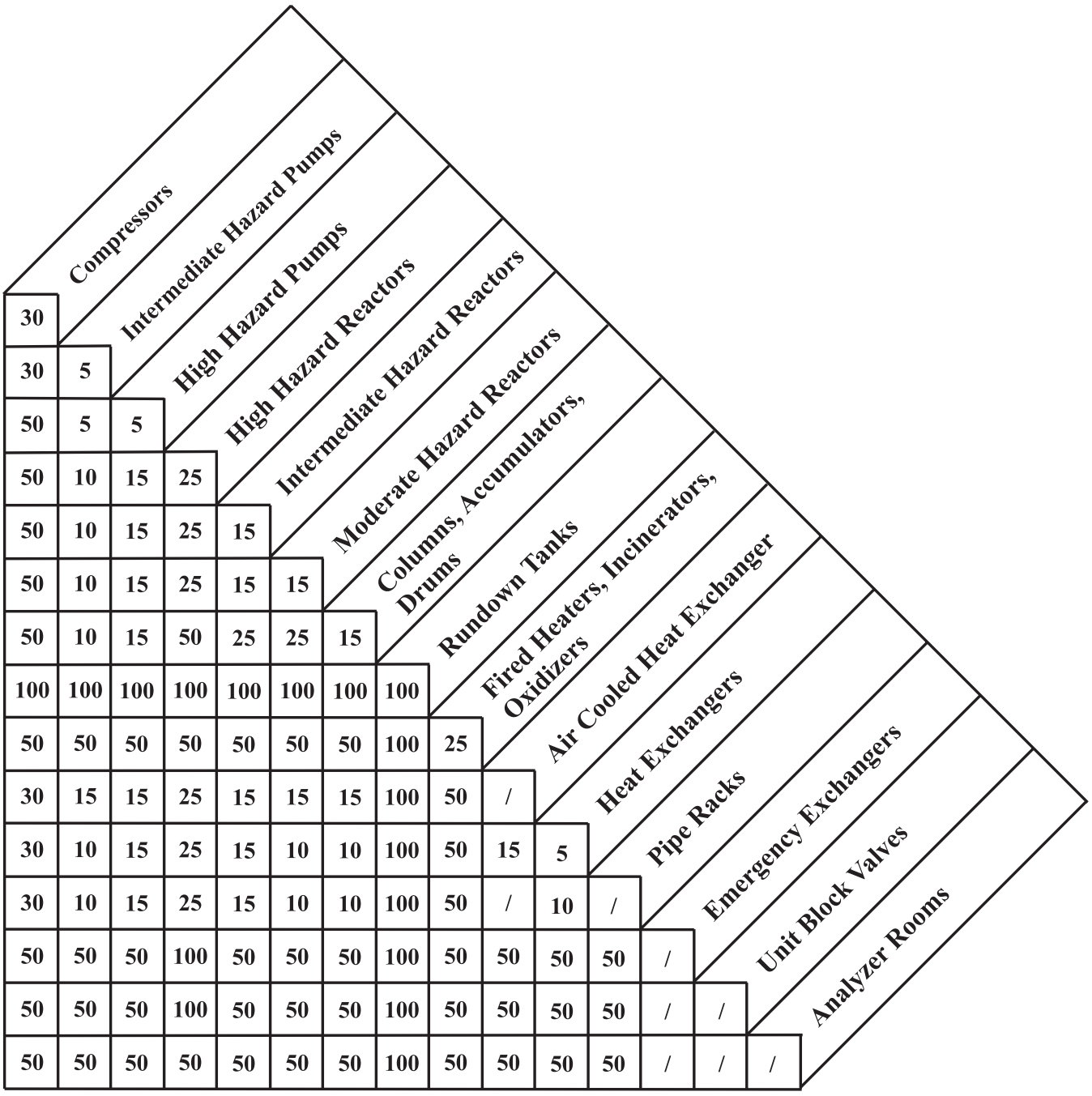
② 300 ft separation between service building and flare

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FIG. 18-35

Intra-Unit Spacing Guidelines



	Compressors	Intermediate Hazard Pumps	High Hazard Pumps	High Hazard Reactors	Intermediate Hazard Reactors	Moderate Hazard Reactors	Columns, Accumulators, Drums	Rundown Tanks	Fired Heaters, Incinerators, Oxidizers	Air Cooled Heat Exchanger	Heat Exchangers	Pipe Racks	Emergency Exchangers	Unit Block Valves	Analyzer Rooms
Compressors	30														
Intermediate Hazard Pumps	30	5													
High Hazard Pumps	50	5	5												
High Hazard Reactors	50	10	15	25											
Intermediate Hazard Reactors	50	10	15	25	15										
Moderate Hazard Reactors	50	10	15	25	15	15									
Columns, Accumulators, Drums	50	10	15	50	25	25	15								
Rundown Tanks	100	100	100	100	100	100	100	100							
Fired Heaters, Incinerators, Oxidizers	50	50	50	50	50	50	50	100	25						
Air Cooled Heat Exchanger	30	15	15	25	15	15	15	100	50	/					
Heat Exchangers	30	10	15	25	15	10	10	100	50	15	5				
Pipe Racks	30	10	15	25	15	10	10	100	50	/	10	/			
Emergency Exchangers	50	50	50	100	50	50	50	100	50	50	50	50	/		
Unit Block Valves	50	50	50	100	50	50	50	100	50	50	50	50	/	/	
Analyzer Rooms	50	50	50	50	50	50	50	100	50	50	50	50	/	/	/

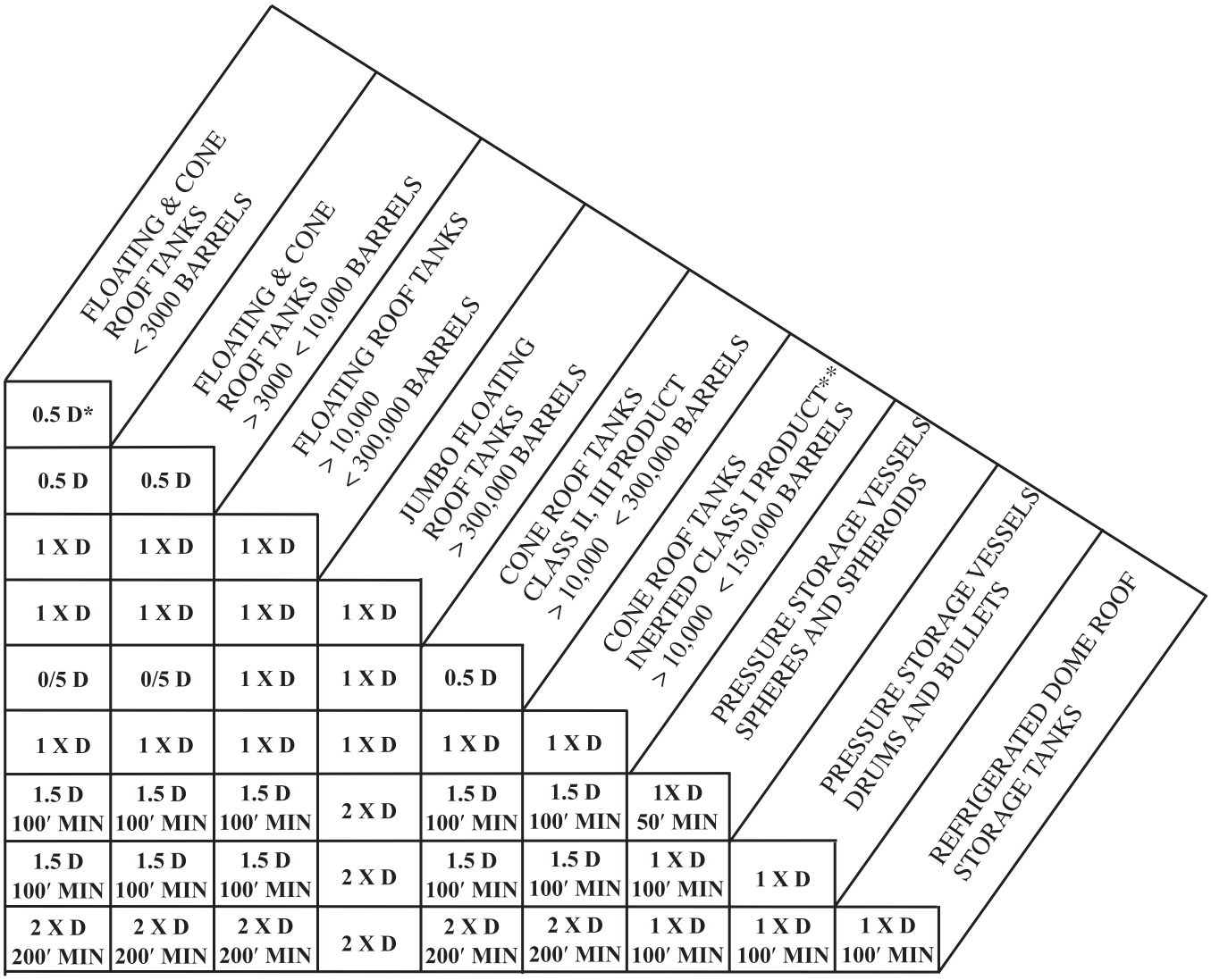
1 ft = 0.305 m
/ = no spacing requirements

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FIG. 18-36

Storage Tank Spacing Guidelines



D = Largest Tank Diameter
1 barrel = 42 Gallons = 159 l
***C = (*F• 32) x 0.555**
1 ft = 0.305 m

*** For Class II, III products, 5 ft spacing is acceptable.**
**** Or Class II or III operating at temperatures > 200° F.**

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MAINTENANCE GUIDELINES

Proper maintenance is an important activity for safe, reliable and profitable operation of gas processing facilities. GPA has developed a separate publication addressing Maintenance Practices (ref 18.201). The intent of the above referenced publication is "... to provide a basic understanding of maintenance management practices and information on some of the tools available to assist in improving safety, environmental, and overall asset performance." Definitions in maintenance management are given in Fig. 18-37, Nomenclature.

Introduction

There is terminology and several concepts that are routinely used in maintenance practices. Some of these are explained below.

Overall Unit Efficiency (OEE):

A comprehensive indicator of a plant's or equipment item's condition that takes into account operating time, performance and quality.

OEE = Absolute Availability
× (Actual Production Rate/Design Production Rate)
× (On Spec Production/Actual Production)
× 100 **Eq 18-5**

Utilization:

Percentage of equipment operating hours (runtime) during a given calendar period. Utilization can be expressed mathematically as:

$$\text{Utilization (\%)} = \frac{\text{THIP} - (\text{SM} + \text{UM} + \text{ND})}{\text{THIP}} \times 100 \quad \textbf{Eq 18-6}$$

Availability:

Availability is the probability that an equipment item will be available to produce production when it is needed. The method by which Availability is calculated varies based on what it is being used for. The following are the most common calculations for Availability:

Absolute Availability — Percentage of hours during which the equipment is available for operation during a given calendar period. Absolute Availability can be expressed mathematically as:

$$\text{Absolute Availability (\%)} = \frac{\text{THIP} - (\text{SM} + \text{UM})}{\text{THIP}} \times 100 \quad \textbf{Eq 18-7}$$

Operating Availability — This definition is the same as that of Absolute Availability except that maintenance performed during no demand (ND) downtime is not included in the scheduled maintenance (SM) or unscheduled maintenance (UM) downtime charged to the equipment. Operating Availability can be expressed mathematically as:

$$\text{Operating Availability (\%)} = \frac{\text{THIP} - (\text{SM}^1 + \text{UM}^1)}{\text{THIP}} \times 100 \quad \textbf{Eq 18-8}$$

Process Availability — Percentage of hours during which the equipment is available for operation when such operation is required by the process where the equipment is installed. Process Availability can be expressed mathematically as:

$$\text{Process Availability (\%)} = \frac{\text{PHIP} - (\text{SM} + \text{UM})}{\text{PHIP}} \times 100 \quad \textbf{Eq 18-9}$$

FIG. 18-37

Nomenclature

— **ND** —	Hours during which equipment operation is not required due to either no demand or to other process downtime not chargeable to the equipment under analysis.
— **PHIP** —	Total hours in period under analysis during which equipment is required to operate in process service. As compared to THIP, PHIP can be defined mathematically as **THIP-ND**.
— **SM** —	Hours during which equipment is unavailable for operation due to performance of scheduled maintenance.
— **SM^1** —	Hours during which equipment is required for operation but unavailable due to performance of scheduled maintenance. As compared to **SM**, this term excludes any scheduled maintenance hours performed during no demand **(ND)** downtime.
— **THIP** —	Total calendar hours in period under analysis (e.g., 8760 hours per calendar year)
— **UM** —	Hours during which equipment is unavailable for operation due to performance of unscheduled maintenance.
— **UM^1** —	Hours during which equipment is required for operation but unavailable due to performance of unscheduled maintenance. As compared to **UM**, this term excludes any unscheduled maintenance hours performed during no demand **(ND)** downtime.
— **PM** —	Preventive Maintenance
— **PdM** —	Predictive Maintenance

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To illustrate the variance in measured "availability," consider the following situation:

THIP = 8760 hours (one calendar year)
PHIP = 7000 hours (79.91% demand for equipment operation during calendar year)
SM = 50 hours
SM[1] = 10 hours
UM = 30 hours
UM[1] = 20 hours
ND = 1760 hours

Measured "availability" for this piece of equipment would be:

Absolute Availability = 99.09%

Operating Availability = 99.66%

Process Availability = 99.57%

Reliability:

The probability that equipment item will perform its intended function without failure for a specific time period. The method by which Reliability is calculated varies based on what it is being used for. The following are the most common calculations for Reliability:

Absolute Reliability — Percentage of hours during which the equipment is not down for unscheduled maintenance during a given calendar period. Absolute Reliability can be expressed mathematically as:

$$\text{Absolute Reliability (\%)} = \frac{\text{THIP} - \text{UM}}{\text{THIP}} \times 100 \qquad \textbf{Eq 18-10}$$

Operating Reliability — This definition is the same as that of Absolute Reliability except that unscheduled maintenance performed during no demand (ND) downtime is not included in the unscheduled maintenance (UM) downtime charged to the equipment. Operating Reliability can be expressed mathematically as:

$$\text{Operating Reliability (\%)} = \frac{\text{THIP} - \text{UM}^1}{\text{THIP}} \times 100 \qquad \textbf{Eq 18-11}$$

Process Reliability — Percentage of hours during which the equipment is not down for unscheduled maintenance when operation is required by the process where the equipment is installed. Process Reliability can be expressed mathematically as:

$$\text{Process Reliability (\%)} = \frac{\text{PHIP} - \text{UM}}{\text{PHIP}} \times 100 \qquad \textbf{Eq 18-12}$$

Using the same assumptions as the measured "availability" example, the measured "reliability" for this piece of equipment would be as follows:

Absolute Reliability = 99.66%

Operating Reliability = 99.77%

Process Reliability = 99.71%

Equipment Life Cycle:

The time period starting when an equipment item is put into service until it is permanently taken out of productive service. For an example the life cycle of an engine can be several decades even though it might go through several Maintenance Life Cycles during this time period.

Maintenance Life Cycle:

The time period between the highest maintenance level regimen required in the equipment's maintenance program. This may be expressed as the time between zero hour reconditioning, major overhauls, or similar terminology. At the completion of a maintenance life cycle, the maintenance program "clock" is reset to zero, and (with the possible exception of some life-limited components) the equipment's maintenance regimen can restart as if the equipment were new.

Planned Maintenance:

Maintenance, which has been scheduled, some predetermined time period prior to the maintenance work being performed. The predetermined time period is set by each facility to meet its business requirements. As a rule this time period ranges between seven and thirty-one days.

Preventive Maintenance:

Maintenance which is planned and performed on a scheduled basis. Most preventative maintenance is done strictly on a calendar basis however it can be scheduled based on meter reading such as equipment run hours.

Optimization of Preventative Maintenance requires the performance of the minimum amount of maintenance at the longest maintenance interval possible while still keeping an equipment item within required operating parameters.

Condition Based Maintenance:

Maintenance based on point-in-time measurement of key equipment operating parameters. Examples might include: (1) changing a fuel gas injection valve on an engine based on leakage detected by an engine-compressor analyzer, or (2) inspecting bearings based on a high bearing wear metal report from lubricating oil analysis.

Predictive Maintenance:

A maintenance technology predominantly based on analysis of historical equipment operation and maintenance experience with extrapolated forecasting from which future maintenance requirements can be determined. Predictive Maintenance normally incorporates both planned and condition based maintenance technologies and tools as a source of data to determine when maintenance is required. A Planned Maintenance example would be the change out of a component during a planned inspection based on the determination of the component's statistical life expectancy or mean time between failure in a Predictive Maintenance analysis.

Proactive Maintenance:

A maintenance strategy, which strives to eliminate all failures before they happen by applying the findings and recommendations of root cause failure analysis to all operating equipment and in the design and procurement of new equipment. Maintainability and life cycle costs are key decision factors the procurement of new equipment.

Zero Hour:

Restoration of equipment item to its design specifications.

CMMS:

Computerized maintenance management system.

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Master Equipment List (MEL):

A comprehensive list of all equipment items in a facility. As a minimum a MEL must contain the name of the equipment item, where it is located, a unique identifier, either numeric or alpha numeric, and what type of equipment it is. A MEL can contain more information such as specific details about the equipment item, its criticality rating, whether it is spared, etc.

Key Performance Indicator (KPI):

A performance measure that is utilized to benchmark the effectiveness of various systems and functions within an organization.

Criticality:

A ranking based on an equipment item's inherent reliability, impact of its failure on the system and the consequence of its failure with respect to safety, the environment, production and repair costs.

Criticality can be determined through sophisticated modeling techniques or simple "What-If" type methodology. The level of sophistication used is generally determined by a facility's profitability and/or perceived risks to employees or the public.

Maintenance Drivers

In order to remain competitive, it is important to know where and why money is spent, particularly when it comes to maintenance and reliability. Market conditions change often requiring a shift in business strategies. The Maintenance, Operations and Engineering organizations that support an asset have to be able to change and adapt to these ever-changing business conditions. In order to understand where and how to make these changes, these organizations must first understand what is required out of the facility in terms of availability, and ultimately deliverability to meet market or contractual requirements.

"Availability is concerned with all levels of performance with respect to sustained deliverability rather than just visible uptime and downtime. It is also concerned with the design, management and support resources and work processes behind specified achievable performance." **(I)** A plant is a collection of systems that interact with each other to perform the function of producing a product. Each individual piece of equipment has its own inherent reliability and when taken in context with its maintainability, produces an availability. These systems taken as a whole will then result in an overall availability for the plant.

The Maintenance Drivers are the reasons why maintenance should be carried out. Maintenance Drivers should be documented in the following three (3) major categories (you may elect to group these differently, but it should be done for each facility).

Safety and Environmental

Maintenance carried out in support of Health, Safety and Environmental concerns with a goal of no accidents, no harm to people and no damage to the environment.

Safety — protection of your employees and the general public from any danger created from failure to maintain equipment.

Health — protection of the long-term health of your employees and the general public from any concern resulting from failure to maintain equipment.

Environmental — protection of the environment that could result from failure to maintain equipment.

Mechanical Integrity — as required by OSHA regulations, the integrity of vessels and equipment must be maintained.

Regulatory Requirements — rules and regulations like OSHA and others require certain maintenance procedures and actions to be taken. These may be the maintenance drivers at times.

Production

Maintenance which supports the achievement of the business plan production targets.

Planning/Predictability — maintenance that is done in concert with the business plan or timed to coincide with other maintenance. Many times this type of maintenance is done in conjunction with turnarounds or partial shutdown within a large facility.

Optimization of Investment — maintenance that is done to allow optimization whether for production increases, increase through puts or just being able to fully utilize a facility.

Protection of Investment/assets — maintenance that is done as part of an overall plan to protect the entire facility.

Resource Utilization planning — maintenance that ties closely to planning but is done at prescribed times to allow for ultimate utilization of your assets.

Optimized Life Cycle — maintenance done to prolong (optimize) your ability to utilize that equipment.

Achievement of long-term or short-term goals — maintenance that is done or delayed to meet either long term or short term goals such as expenses to fall within certain quarters or business cycles.

Commercial

Maintenance carried out to prevent or limit equipment failure especially where to cost of repair or replacement is high.

Cost of lost production — maintenance that is done to prevent or avert lost opportunity to make production.

Repair Costs — maintenance that is done to prevent the extremely high cost of repair or replacement.

Contractual — maintenance that is done to comply with contractual requirements especially when a downstream customer is dependent on the supply you provide.

Customer Satisfaction — maintenance that is done to provide satisfaction to a customer or in conjunction with a customer.

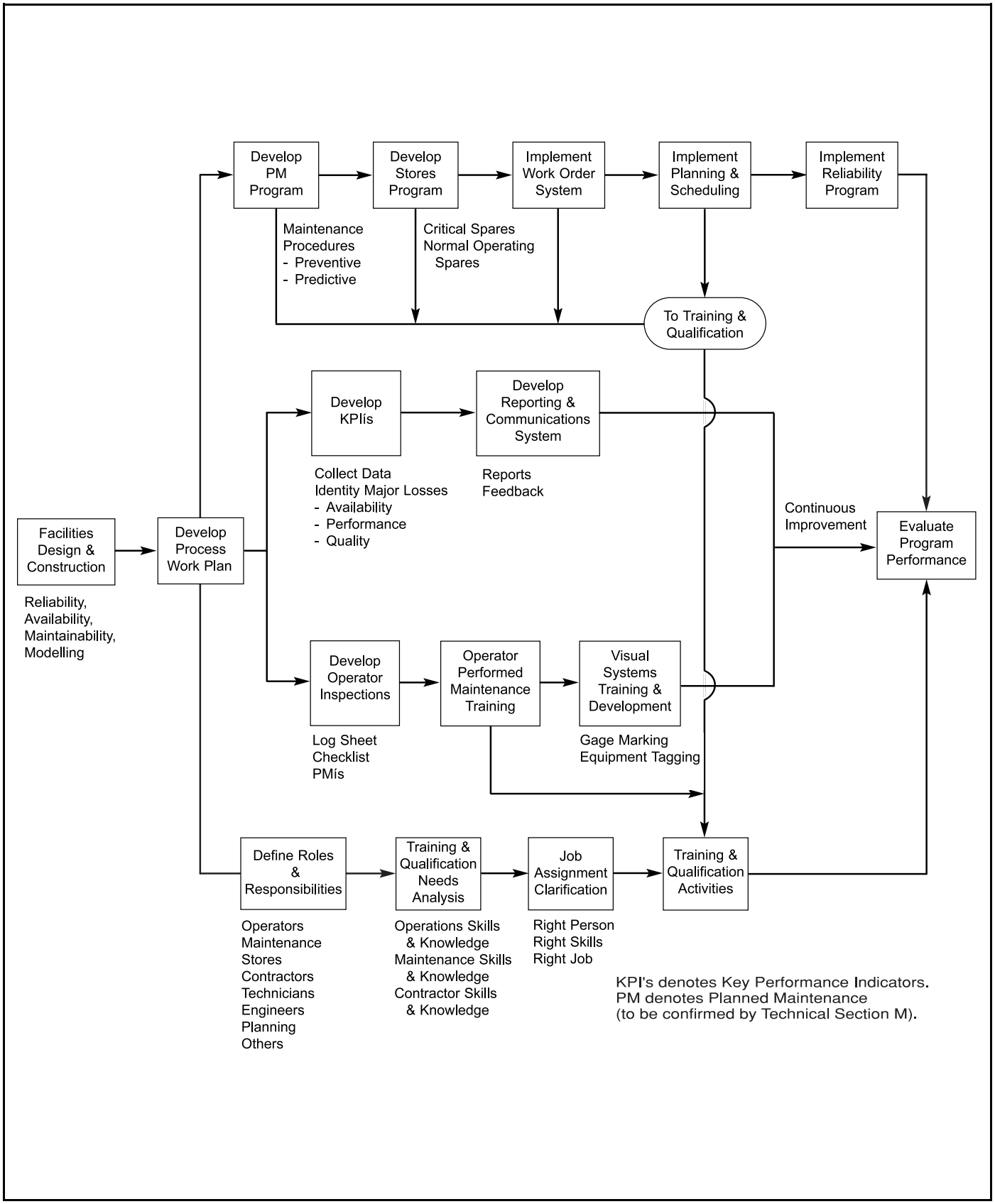
MAINTENANCE PROGRAM DEVELOPMENT

This is an important part of developing maintenance strategies. Figure 18-38 shows steps in developing a maintenance program. This figure shows the maintenance planning beginning during the initial facilities design and construction. The planning culminates in an on-going cycle of evaluation and continuous improvement.

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FIG. 18-38

Maintenance Program Development



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RELIABILITY, AVAILABILITY AND MAINTAINABILITY

Reliability, Availability and Maintainability (RAM) are evaluated during the design stage. The inputs for a RAM study are illustrated in Figure 18-39. One result of a RAM study in an Equipment Criticality Listing. This listing ranks equipment systems according to their impact on production losses. Criticality affects the sparing philosophy.

PLANNED MAINTENANCE VALIDATION

Figure 18-40 addresses some important maintenance management activities. This figure can be used in establishing the level of maintenance required. It can help strike a balance between insufficient maintenance (higher levels of unscheduled shutdowns and lost production) and excessive maintenance (unnecessary maintenance expense)

SUMMARY

The full GPA Maintenance Practices document contains the following sections:

Introduction

Definitions

Maintenance Drivers

Developing Maintenance

Strategies

Maintenance Tools and Applications

Selection of Computerized Maintenance Management System

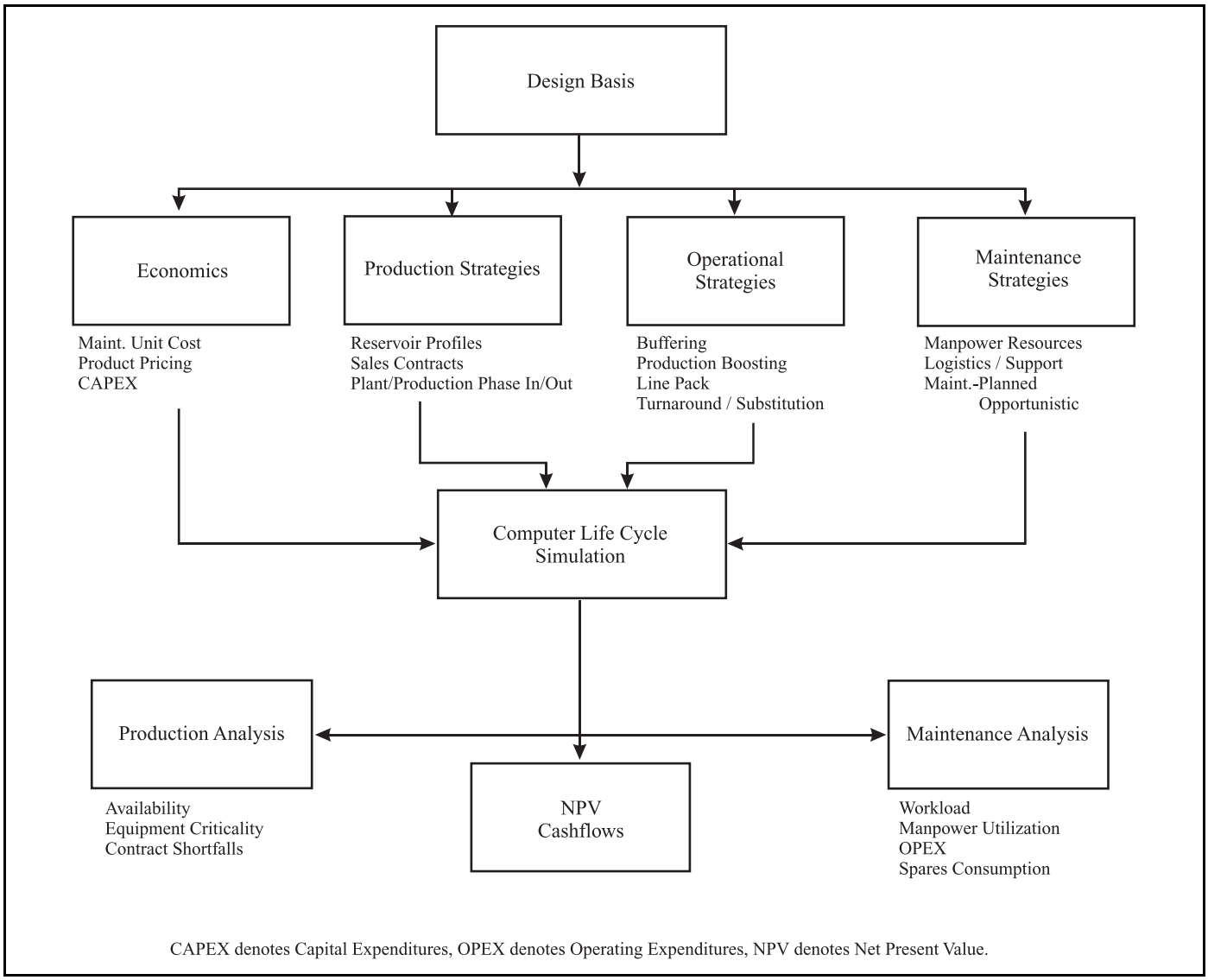
Maintenance Procedure Development

Planning and Scheduling

Continuous Improvement

FIG. 18-39

Reliability, Availability and Maintainability

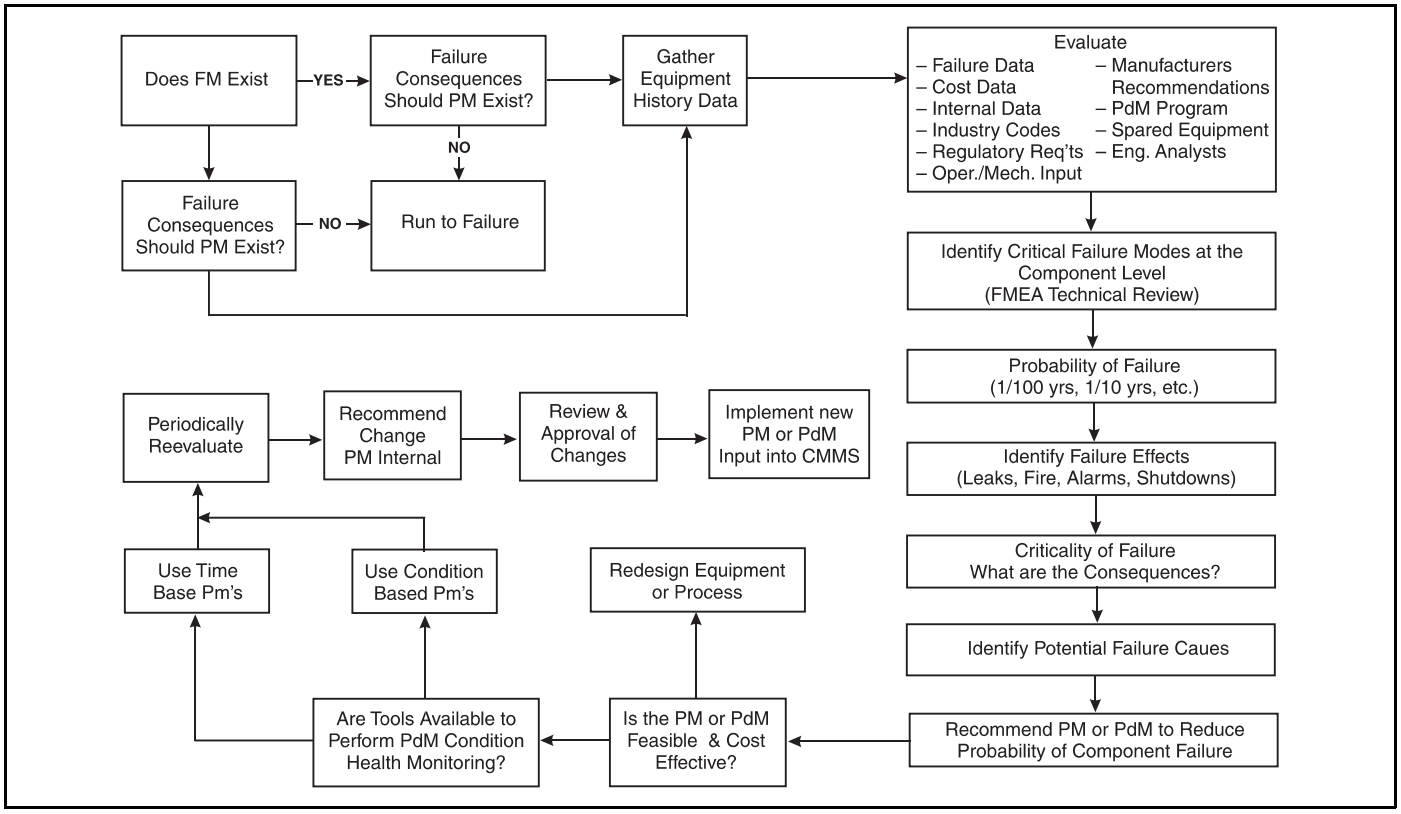


CAPEX denotes Capital Expenditures, OPEX denotes Operating Expenditures, NPV denotes Net Present Value.

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FIG. 18-40

PM Validation Process



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10. Christensen, D. R. and Conn, B. R, "Waste-Water Treating is Successful", Oil & Gas J., pp. 199-204 (September 20, 1976).

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    Recommended Practices:
    a. API RP-500A–Recommended Practice for Classification of Locations for Electrical Installations in Petroleum Refineries.
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SECTION 19

Fractionation and Absorption

Fractionation

Fractionation is a unit operation utilized to separate mixtures into individual products. Fractionation involves separating components by relative volatility (α). The difficulty of a separation is directly related to the relative volatility of the components and the required purity of the product streams.

FIG. 19-1

Nomenclature

a'_t	=	tube flow area, ft^2
a_t	=	total tube flow area, ft^2
A	=	absorption factor used in Eq 19-28
A_c	=	cross sectional area, ft^2
A_t	=	heat transfer surface, ft^2
AAM	=	tray active area, ft^2
ADM	=	tray downcomer area, ft^2
ATM	=	tower cross sectional area, ft^2
b	=	exponent in Eq 19-5 and 19-6
B	=	bottoms product rate, moles/unit time
C	=	coefficient in Eq 19-11, ft/hr
CAF	=	vapor capacity factor, corrected, ft/sec
CAF_o	=	vapor capacity factor, uncorrected, ft/sec
CFS	=	vapor loading, ft^3/sec
D′	=	diameter, ft
D	=	distillate (overhead) product rate, moles/unit time
D_T	=	tower diameter, ft
E_a	=	absorption efficiency, Eq 19-30
E_s	=	stripping efficiency, Eq 19-32
f	=	friction factor (Moody friction factor/144), ft^2/in^2
F	=	feed rate, moles/unit time
F_p	=	packing factor
FF	=	flooding factor used in Eq 19-17
FPL	=	flow path length, ft
g_c	=	conversion factor, 32.174 $(ft \cdot lb_m)/(lb_f \cdot sec^2)$
G_t	=	mass velocity, $lb/(hr \cdot ft^2)$
G_p	=	tower vapor loading, $lb/(ft^2 \cdot sec)$
GPM	=	tower liquid loading, gal./min
H	=	enthalpy, Btu/lb
HETP	=	height of packing equivalent to a theoretical plate
HTU	=	height of a transfer unit
K	=	equilibrium K-value, y/x
L_o	=	liquid reflux rate, moles/unit time
L_p	=	liquid loading, $lb/(ft^2 \cdot sec)$
L	=	liquid rate, moles/unit time
L_t	=	tube length, ft
L_{m+1}	=	rich oil entering the stripper, moles/unit time
m	=	number of stripping stages
M	=	mass flow rate, lb/hr
n	=	number of absorber stages
N_m	=	minimum number of theoretical stages
NP	=	number of passes in a tray
N_t	=	number of tubes
ΔP	=	pressure drop, psi
q	=	moles of saturated liquid in the feed per mole of feed
Q	=	heat transfer duty, Btu/hr
Q_c	=	condenser duty, Btu/hr
R	=	reflux ratio, moles of reflux divided by moles of net overhead product
Re	=	Reynolds number, dimensionless
s	=	specific gravity
S	=	number of stages
S_T	=	stripping factor used in Eq 19-31
S_F	=	separation factor defined by Eq 19-1
TS	=	tray spacing, inches
U_D	=	overall heat transfer coefficient, $Btu/(hr \cdot ft^2 \cdot °F)$
v	=	specific volume, ft^3/lb
v_{max}	=	maximum velocity, ft/hr
v_i	=	specific volume of the inlet, ft^3/lb
v_o	=	specific volume of the outlet, ft^3/lb
V	=	vapor rate, moles/unit time
V_1	=	vapor rate leaving top tray, moles/unit time
V_{max}	=	volumetric vapor flow rate, ft^3/hr
VD^*_{dsg}	=	downcomer velocity (uncorrected), gpm/ft^2
VD_{dsg}	=	downcomer velocity (corrected), gpm/ft^2
V_{load}	=	vapor loading defined by Eq 19-13, ft^3/sec
V_o	=	stripping medium rate, moles/unit time
w	=	weight flow, lb/hr
x	=	liquid mole fraction
X	=	liquid rate, moles/unit time
X_{m+1}	=	moles of a component in the rich oil entering a stripper per mole of rich oil entering the stripper
x_1	=	moles of a component in the lean oil per mole of rich oil
X_o	=	moles of a component in the liquid in equilibrium with the stripping medium per mole of entering rich oil
y	=	vapor mole fraction
Y_i	=	moles of any component in the lean gas leaving the absorber per mole of rich gas

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FIG. 19-1 (Cont'd)

Y_{n+1} = moles of any component in the entering rich gas per mole of rich gas
Y_o = moles of any component in the gas in equilibrium with the entering lean oil, per mole of rich gas
Z = static head, ft

Greek

α = relative volatility
β_{ij} = volatility factor defined in Eq 19-5
θ = correlating parameter in Eq 19-7, 19-8
σ = surface tension, dyne/cm
ρ = density, lb/ft^3
ε = efficiency
μ = viscosity, cp

Subscripts

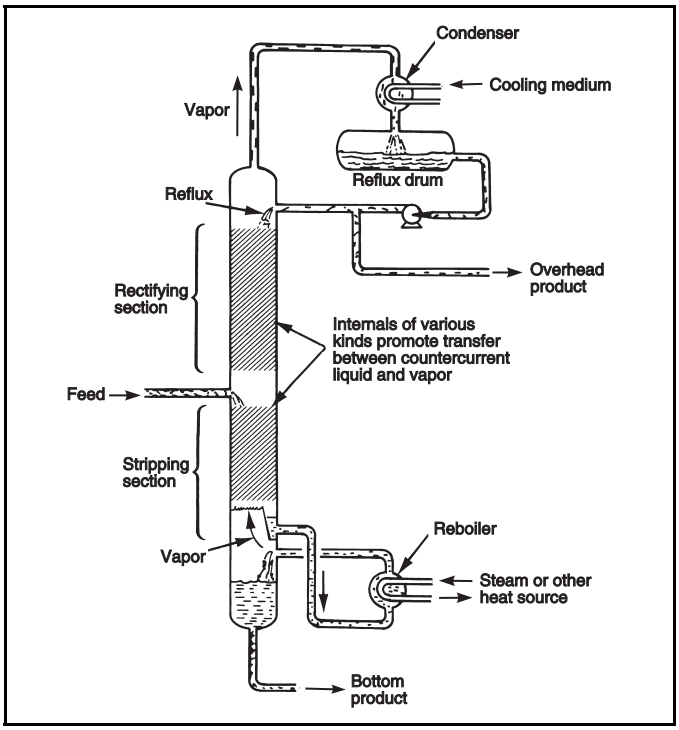
avg = average value
B = bottoms
BP = bubble point feed stream
bottom = bottom of the column
calc = calculated value
corr = corrected value
D = distillate (overhead)
F = feed
G = gas
HK = heavy key
i = any component
L = liquid
LK = light key
m = minimum
n = tray number
top = top of the column

Virtually all gas processing plants producing natural gas liquids require at least one fractionator to produce a liquid product which will meet sales specifications. The schematic of an example fractionator in Fig. 19-2 shows the various components of the system. Heat is introduced to the reboiler to produce stripping vapors. The vapor rises through the column contacting the descending liquid. The vapor leaving the top of the column enters the condenser where heat is removed by some type of cooling medium. Liquid is returned to the column as reflux to limit the loss of heavy components overhead.

Internals such as trays or packing promote the contact between the liquid and vapor streams in the column. Intimate contact of the vapor and liquid phases is required for efficient separation. Vapor entering a separation stage will be cooled which results in some condensation of heavier components. The liquid phase will be heated which results in some vaporization of the lighter components. Thus, the heavier components are concentrated in the liquid phase and eventually become the bottom product. The vapor phase is continually enriched in the light components which will make up the overhead product.

FIG. 19-2

Fractionation Schematic Diagram



The vapor leaving the top of the column may be totally or partially condensed. In a total condenser, all vapor entering the condenser is condensed to liquid and the reflux returned to the column has the same composition as the distillate or overhead product. In a partial condenser, only a portion of the vapor entering the condenser is condensed to liquid. In most partial condensers only sufficient liquid will be condensed to serve as reflux for the tower. In some cases, however, more liquid will be condensed than is required for reflux and there will actually be two overhead products, one a liquid having the same composition as the reflux and the other a vapor product which is in equilibrium with the liquid reflux.

Equilibrium Stage Concept

All calculations are performed using theoretical (equilibrium) stages. A fractionation column may be considered as a series of equilibrium flashes with two feeds and two product streams (Fig. 19-3). The vapor enters the flash from the stage below at a higher temperature and the liquid stream enters from the stage above at a lower temperature. Heat and mass transfer occur in this stage such that the exiting streams are a bubble point liquid and dew point vapor at the same temperature and pressure. The compositions of these phases are related by the equilibrium relationship of $y_i = K_i x_i$ (See Section 25). This relationship, along with heat and material balance considerations, is the basis for all fractionator design.

Types of Fractionators

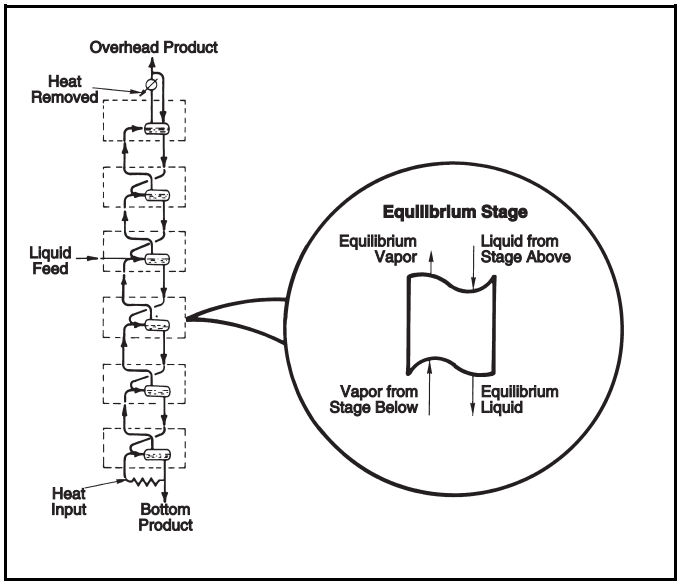
The number and type of fractionators required depend on the number of products to be made and the feed composition. Typical NGL products from a fractionation process include:

- Demethanized Product (C_2+)
- Deethanized Product (C_3+)
- Ethane/Propane mixtures (EP)
- Commercial Propane
- Propane/Butane mixture (LPG)
- Butane(s)

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FIG. 19-3

Basic Fractionation Model



- Butane/Gasoline mixtures
- Natural Gasoline
- Mixtures with a vapor pressure specification

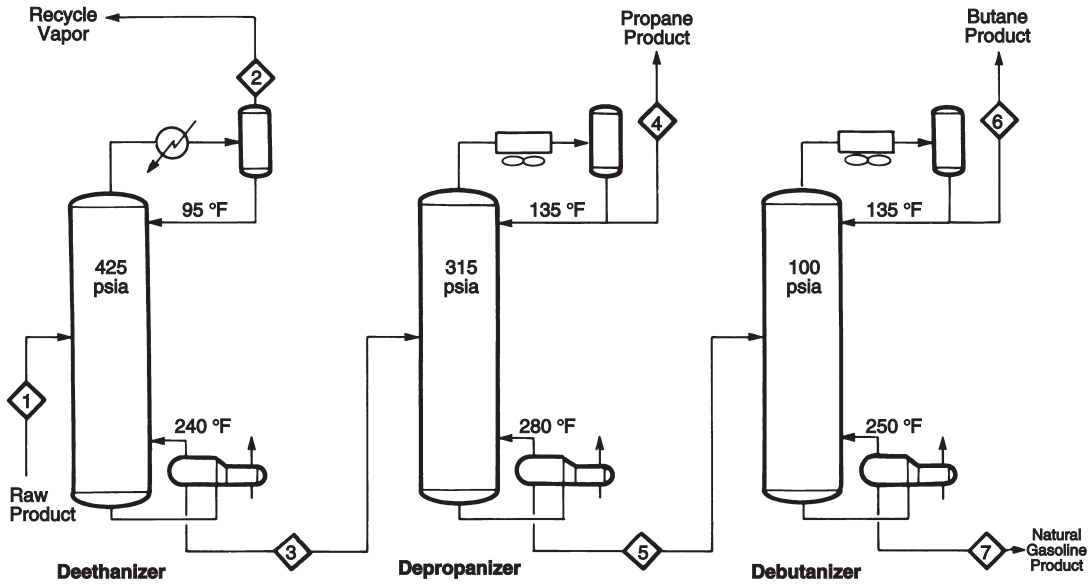
See Section 1 for definitions and Section 2 for product specifications.

An example fractionation train used to produce three products is illustrated in Fig. 19-4. The feed stream contains too much ethane to be included in the products; thus, the first column is a deethanizer. The overhead stream is recycled to the upstream processing plant or sent to a fuel system. The bottom product from this column could be marketed as a deethanized product. The second column, a depropanizer, produces a specification propane product overhead. The bottom product, a butane-gasoline mixture, is often sold to a pipeline without further processing. The third column, a debutanizer, separates the butane and gasoline products. This separation is controlled to limit the vapor pressure of the gasoline. The overhead butane product can be sold as a mixture or an additional column can be used to separate the iso-butane and normal-butane.

Another class of fractionators uses no external reflux condenser to produce liquid for contact with the fractionator vapor. One such tower is a demethanizer as is found in cryogenic

FIG. 19-4

Fractionation Train



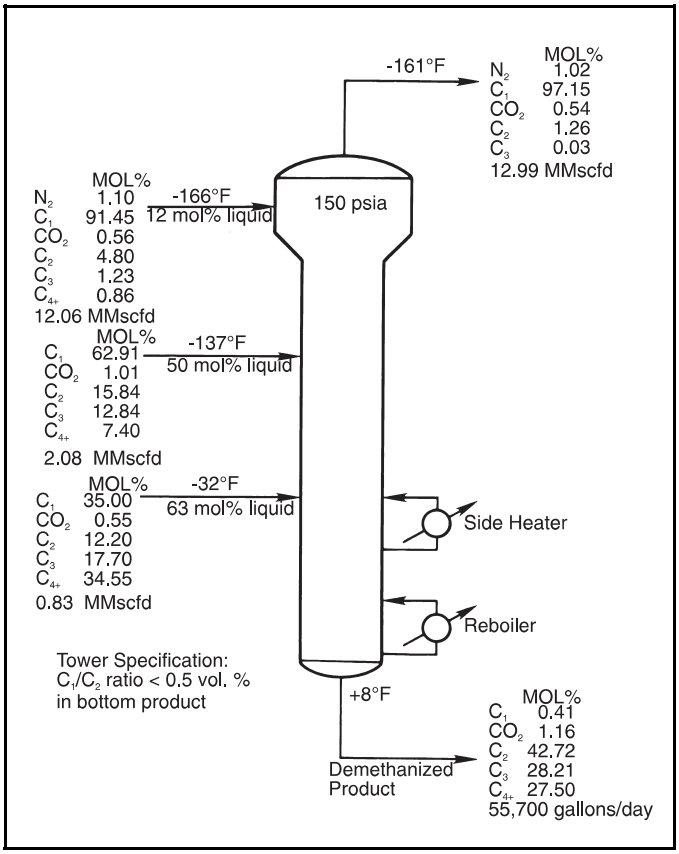
	Moles/hr						
	◇1	◇2	◇3	◇4	◇5	◇6	◇7
C_1	1.5	1.5					
C_2	24.6	22.2	2.4	2.4			
C_3	170.3	7.5	162.8	161.9	0.9	0.9	
iC_4	31.0		31.0	0.9	30.1	30.1	
nC_4	76.7		76.7		76.7	72.1	4.6
C_{5+}	76.5		76.5		76.5	0.9	75.6
Total	380.6	31.2	349.4	165.2	184.2	104.0	80.2
gal./day				41,340		31,160	29,290

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plants (Fig. 19-5). The top feed being 12 mol % liquid at low temperature provides the reflux. This liquid along with the other feeds provides the liquid loading for this tower. The reboiler is the control point for the bottom product purity. The overhead composition is a function of the upstream process units.

FIG. 19-5

Demethanizer Example



Applications also exist for a fractionator with a top liquid feed. These are commonly used for crude stabilizers or deethanizers. As with the demethanizer, this column produces a specification bottom product and an overhead stream whose composition is determined by upstream process units. This is an economical approach to producing a single product but is limited in separation efficiency. Better recovery or sharper separation can be achieved by adding a reflux condenser and rectifying section.

Product Specifications

A material balance around the column is the first step in fractionation calculations. In order to perform this balance, assumption of the product stream compositions must be made. There are three ways of specifying a desired product from a fractionator:

- A percentage recovery of a component in the overhead or bottom stream.
- A composition of one component in either product.
- A specific physical property, such as vapor pressure, for either product.

The recovery and composition specifications can be used directly in the material balance. However, property specifications are used indirectly. For instance if vapor pressure is a desired specification of a product, a material balance is performed with an assumed component split. The calculated vapor pressure of the resulting stream is then compared with the desired value and the material balance redone until reasonable agreement is reached.

In a multicomponent mixture, there are typically two components which are the "keys" to the separation. The light key component is defined as the lightest component in the bottom product in a significant amount. The heavy key component is the heaviest component in the overhead product in a significant amount. Normally, these two components are adjacent to each other in the volatility listing of the components. For hand calculations, it is normally assumed for material balance purposes that all components lighter than the light key are produced overhead and all components heavier than the heavy key are produced with the bottom product. By definition, the key components will be distributed between the product streams.

Example 19-1 — For the given feed stream, estimate the product stream compositions for 98% propane recovered in the overhead product with a maximum iso-butane content of the overhead stream of 1%.

Feed:		
	C_2	2.4
	C_3	162.8
	iC_4	31.0
	nC_4	76.7
	C_5	76.5
		349.4 moles

Solution Steps

For Propane (light key):

Moles in overhead = (0.98) 162.8 = 159.5

Moles in bottoms = 162.8 – 159.5 = 3.3

For Ethane:

Moles in overhead = 2.4 (100% to overhead)

Since the isobutane (the heavy key) is 1% of the overhead stream, the sum of propane and ethane must be 99% (all n-C_4 and C_5+ are in the bottoms). Thus:

$$\text{Total Overhead Moles} = \frac{159.5 + 2.4}{0.99} = \frac{161.9}{0.99} = 163.5$$

Moles of iC_4 = 163.5 – 161.9 = 1.6

The overall balance is:

Comp.	Feed	Overhead		Bottoms	
	Moles	Moles	Mole %	Moles	Mole %
C_2	2.4	2.4	1.5	—	
C_3	162.8	159.5	97.5	3.3	1.8
iC_4	31.0	1.6	1.0	29.4	15.8
nC_4	76.7	—	—	76.7	41.2
C_5	76.5	—	—	76.5	41.2
Total	349.4	163.5	100.0	185.9	100.0

In actual operation, the lighter than light key components and heavier than heavy key components will not be perfectly separated. For estimation purposes and hand calculations, perfect non-key separation is a useful simplifying assumption.

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Key Parameters

Two important considerations which affect the size and cost of a fractionation column are degree of separation and component volatility.

The degree of separation or product purity has a direct impact on the size of the column and the required utilities. Higher purity will require more trays, more reflux, larger diameter, and/or a reduced product quantity. One quantitative measure of the difficulty of a separation is the separation factor, S_F, defined as:

$$S_F = \left(\frac{X_D}{X_B}\right)_{LK}\left(\frac{X_B}{X_D}\right)_{HK} \qquad \textbf{Eq 19-1}$$

Note that Eq 19-1 defines the specification for the tower design.

Typically, for most fractionation problems this factor ranges from around 500 to 2000. However, for sharp separations, it can be in the 10,000 range. The number of trays will be roughly proportional to the log of the separation factor for a given system.

The volatility of the components is usually expressed as relative volatility, α. This quantity is computed as the ratio of the equilibrium K-values of two components at a given temperature and pressure. For fractionation calculations the α of the key components is important. Therefore:

$$\alpha = K_{LK}/K_{HK} \qquad \textbf{Eq 19-2}$$

This is a measure of the ease of separation. The larger α is, the easier is the separation.

DESIGN CONSIDERATIONS

Operating Pressure

Before any design calculations can be made on a fractionation problem, a tower operating pressure must be determined. One of the primary considerations for operating pressure is the cooling medium available for the reflux condenser. The overhead product will be at bubble point conditions for a liquid product or at dew point conditions for a vapor product. The bubble point (or dew point) pressure is fixed by a desired component separation and the temperature of the cooling medium.

The cooling media typically used are air, water, and refrigerant. Air cooling is normally the least expensive cooling method. Practical exchanger design limits the process to a 20°F approach to the ambient summer temperature. This translates to a process temperature of 115 to 125°F in most locations. With cooling water, process temperatures of 95 to 105°F are possible. Below about 95°F, mechanical refrigeration must be used to achieve the desired condensing temperature. This is the most expensive cooling method from both a capital and operating cost standpoint. Generally, it is desirable to operate at as low a pressure as possible to maximize the relative volatility between the key components of the separation. However, if reducing the pressure requires a change to a more expensive cooling method, this is usually not a desirable choice.

In some cases, the overhead from the column must be compressed to sales or another process unit. In this case a higher operating pressure may be desired to reduce compression horsepower.

Other items must be considered which will limit pressure selection. If an operating pressure is too high, the critical temperature of the bottom product may be exceeded and the desired separation cannot be achieved. Additionally, the pressure cannot exceed the critical pressure of the desired overhead product.

The selection of a partial or total condenser is fixed by the disposition of the overhead product. A total condenser is used for a liquid product and a partial condenser for a vapor product. However, a liquid product can be produced as a vapor and subsequently cooled and/or compressed to produce a liquid product. There may be cases where this downstream liquefaction is economically attractive. In most cases, the fractionation system for a partial condenser will be cheaper and will have to be balanced against the cost of additional downstream equipment. Before a reliable economic comparison can be made, the column design must be made for each type condenser for a number of reflux ratios and operating pressures.

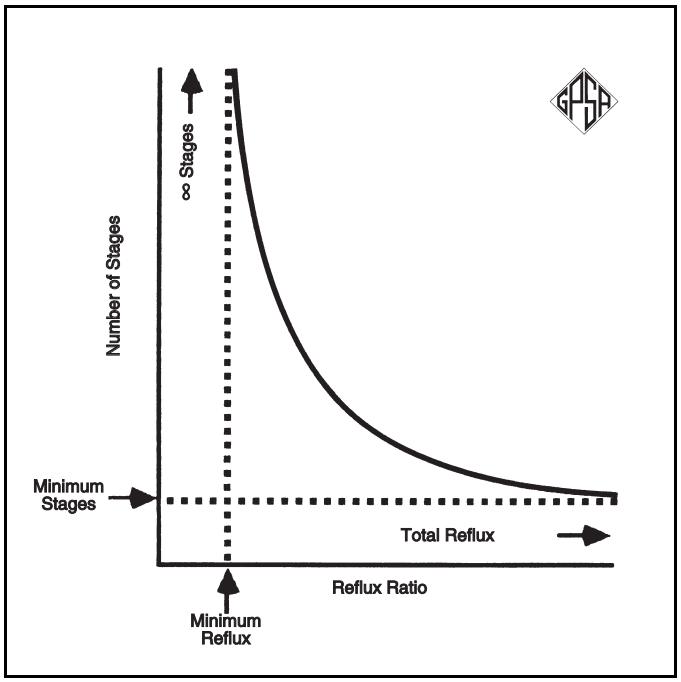
Reflux Ratio and Number of Stages

The design of a fractionation column is a capital cost versus energy cost trade-off problem. The primary parameters are the number of stages and the reflux ratio. Reflux ratio may be defined in several ways. For most calculations, reflux ratio is defined as the ratio of the molar rate of reflux liquid divided by the molar rate of net overhead product. The reboiler duty is a direct function of the reflux ratio as the fractionating column must maintain an overall heat and material balance for a given separation.

A fractionation column can only produce a desired separation between the limits of minimum reflux and minimum stages. Fig. 19-6 illustrates the relationship between reflux ratio and number of stages for a given separation. At minimum reflux an infinite number of stages is required. At total reflux a minimum number of stages is required. Neither of these situations represents actual operation but are the extreme limits

FIG. 19-6

Relationship Between Reflux Ratio and Number of Stages



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of possible design configurations. Methods have been developed to calculate both these cases in a rigorous manner.[1, 2] However, these methods require a computer solution of tray-by-tray calculations. In order to begin a detailed design, estimates of minimum reflux ratio and minimum trays should be generated from simple methods using a binary key component analysis.

Minimum Stages

The minimum stages can be calculated for most multicomponent systems by the Fenske equation.[3]

$$S_m = \frac{\log S_F}{\log (\alpha_{avg})} \qquad \textbf{Eq 19-3}$$

S_m in this equation includes a partial reboiler and a partial condenser if these items are used.

The α_{avg} is the column average relative volatility of the key components in the separation. Various averaging techniques have been proposed such as square root averaging of the α at the top and bottom of the column. The most common approach is to use an arithmetic average:

$$\alpha_{avg} = \frac{\alpha_{top} + \alpha_{bottom}}{2} \qquad \textbf{Eq 19-4}$$

If volatility varies widely, the approach of Winn[4] is suggested, in which a modified volatility is used:

$$\beta_{ij} = K_{LK} / K_{HK}^{b} \qquad \textbf{Eq 19-5}$$

where the exponent b is obtained from K-value plots over the range of interest.

The minimum stage calculation is:

$$S_m = \frac{\log \left[\left(\frac{X_D}{X_B} \right)_{LK} \left(\frac{X_B}{X_D} \right)^{b}_{HK} \left(\frac{B}{D} \right)^{1-b} \right]}{\log \beta_{ij}} \qquad \textbf{Eq 19-6}$$

Note that S_m includes the partial condenser and partial reboiler if they exist.

Minimum Reflux Ratio

The Underwood method[5] is the most widely used of the methods for calculating minimum reflux ratio. Underwood assumed constant relative volatility and constant molal overflow in the development of this method. The first step is to evaluate θ by trial and error:

$$1 - q = \sum_{i=1}^{n} \frac{X_{Fi}}{(\alpha_i - \theta)/\alpha_i} \qquad \textbf{Eq 19-7}$$

Once θ is determined, the minimum reflux ratio is:

$$(L_o/D)_m + 1 = R_m + 1 = \sum_{i=1}^{n} \frac{X_{Di}}{(\alpha_i - \theta)/\alpha_i} \qquad \textbf{Eq 19-8}$$

Number of Stages

The number of theoretical stages required for a given separation at a reflux ratio between minimum and total reflux can be determined from empirical relationships. Erbar and Maddox[6] made an extensive investigation of tray-by-tray fractionator calculations and developed the correlation in Fig. 19-7. This correlation relates the ratio of minimum stages to theoretical stages to the minimum reflux ratio, R_m, and the operating reflux ratio, R (where $R = L_o/D$).

Fig. 19-7 can be used to determine an operating reflux for a given number of stages by entering the figure at the value of S_m/S, moving up to the line representing the value of $R_m/(R_m + 1)$ and reading a value of $R/(R + 1)$. The optimum operating reflux ratio has been found to be near the minimum reflux ratio. Values of 1.2 to 1.3 times the minimum are common.[7] Thus for a given R, a value of S can be determined from Fig. 19-7.

This correlation is generated on the basis of bubble point feed. If the feed is between the bubble point and dew point then the operating reflux should be corrected. Erbar and Maddox[6] proposed the following relationship to adjust the vapor rate from the top tray for non-bubble point feed:

$$V_{corr} = V_{calc} + \frac{\left(1 - \frac{D}{F}\right)[F(H_{VF} - H_{BP})]}{\left(\frac{Q_C}{L_o}\right)_{calc}} \qquad \textbf{Eq 19-9}$$

The reflux rate can then be adjusted by material balance since:

$$L_o = V_1 - D \qquad \textbf{Eq 19-10}$$

Computation Method

In order to determine the design parameters for a fractionation problem, the following method is recommended:

1. Establish feed composition, flow rate, temperature, and pressure.
2. Make product splits for the column and establish condenser temperature and column pressure. From column pressure, calculate the reboiler temperature.
3. Calculate minimum number of theoretical stages from the Fenske equation (Eq 19-3).
4. Calculate minimum reflux rate from the Underwood equations (Eq 19-7 and 19-8).
5. Obtain theoretical stages/operating reflux relation from Fig. 19-7.
6. Adjust actual reflux for feed vaporization if necessary (Eq 19-9, 19-10).

Example 19-2 — For the given feed stream, 291,000 gal./day (bubble point feed).

Desire: 98% C_3 in the overhead (relative to the feed)
1% iC_4 in the overhead

Air cooling (120°F Condensing Temperature)

Feed Composition	Mol %	Moles/hr
C_2	2.07	21.5
C_3	48.67	505.6
iC_4	10.11	105.0
nC_4	24.08	250.1
iC_5	5.41	56.2
nC_5	4.81	50.0
C_6	4.85	50.4
	100.00	1038.8

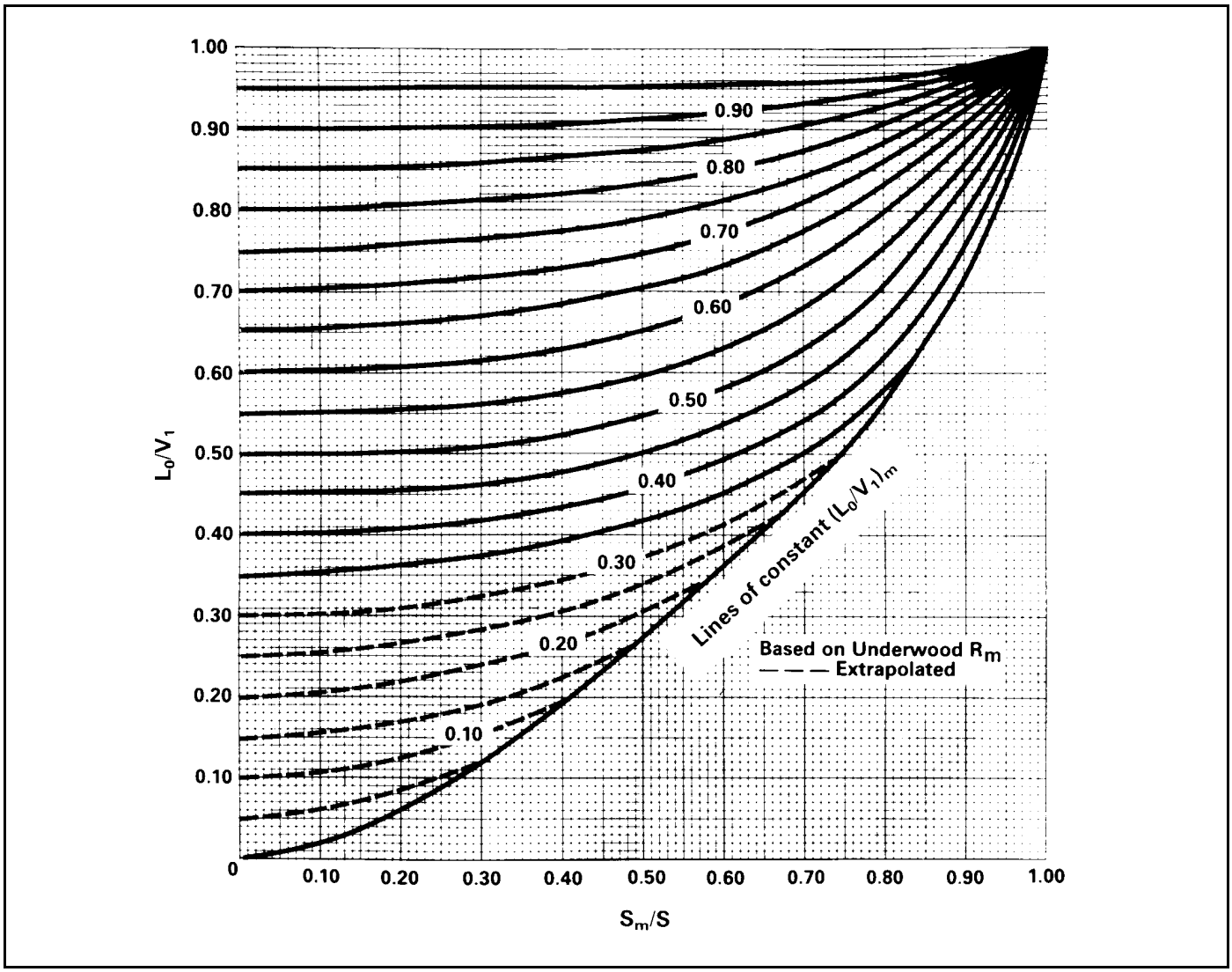
Find the:

- Minimum trays required
- Minimum reflux ratio

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FIG. 19-7

Erbar-Maddox Correlation of Stages vs Reflux[6]



- Actual trays at 1.3 times the minimum reflux ratio

Solution Steps

Estimate Product Splits from Material Balance:

	Overhead		Bottoms	
	Moles	Mol %	Moles	Mol %
C_2	21.5	4.1	—	—
C_3	495.4	94.9	10.2	2.0
iC_4	5.2	1.0	99.8	19.3
nC_4	—	—	250.1	48.4
iC_5	—	—	56.2	10.9
nC_5	—	—	50.0	9.7
C_6	—	—	50.4	9.7
Totals	522.1	100	516.7	100

Get tower pressure at 120°F (bubble point calculation). Using K-values from Section 25:

	K	α	
C_2	2.80		
C_3	0.93	2.067	
iC_4	0.45		bubble point pressure = 280 psia

Estimate the bottom temperature using K-values at 280 psia (bubble point calculation) assuming negligible pressure drop:

	K	α	
C_3	2.30	1.643	
iC_4	1.40		bubble point temperature = 250°F
nC_4	1.15		
iC_5	0.68		
nC_5	0.62		
C_6	0.15		

α_{avg} = 1.855

Determine the minimum number of trays (Eq 19-3):

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$$S_F = \left(\frac{94.9}{2.0}\right)\left(\frac{19.3}{1.0}\right) = 915.8$$

$$S_m = \frac{\log (915.8)}{\log (1.855)} = 11 \text{ trays}$$

Correct for change in relative volatility by using Eq 19-6:

$$K_{LK} = 0.93 = \beta_{ij} (0.45)^b \text{ (condenser)}$$

$$K_{LK} = 2.30 = \beta_{ij} (1.4)^b \text{ (reboiler)}$$

dividing gives $2.473 = (3.111)^b$

$$b = 0.798; \beta_{ij} = 1.759$$

$$S_m = \frac{\log\left[\left(\frac{495.4}{10.2}\right)\left(\frac{99.8}{5.2}\right)^{0.798}\left(\frac{516.7}{522.1}\right)^{1-0.798}\right]}{\log (1.759)}$$

$$S_m = \frac{\log (512.1)}{\log (1.759)} = 11.05$$

Thus correcting for changing α did not affect the minimum tray calculation in this example.

Find the minimum reflux, R_m (Eq 19-7, 8):

	x_F	α_{avg} relative to C_6+	$\alpha x_F/(a-\theta)$ $\theta = 16$	$\theta = 15$	$\theta = 15.8$
C_2	0.0207	68.33	0.0270	0.0265	0.0269
C_3	0.4867	26.67	1.2165	1.1123	1.1941
iC_4	0.1011	13.83	-0.6443	-1.1951	-0.7098
nC_4	0.2408	11.00	-0.4506	-0.6622	-0.5518
iC_5	0.0541	5.83	-0.0310	-0.0344	-0.0316
nC_5	0.0481	5.00	-0.0219	-0.0241	-0.0223
C_6	0.0485	1.00	-0.0032	-0.0035	-0.0033
Total			0.0925	-0.7805	-0.0978

$$\theta = 15.9$$

$$R_m + 1 = \frac{68.33\ (0.041)}{68.33 - 15.9} + \frac{26.67\ (0.949)}{26.67 - 15.9} + \frac{13.83\ (0.01)}{13.83 - 15.9}$$

$$R_m + 1 = 2.336$$

$$R_m = 1.336$$

Theoretical trays at $R = (1.3)\, R_m = 1.737$

$$L_o/V_1 = \frac{R}{R+1} = \frac{1.737}{(1.737 + 1.0)} = 0.635$$

$$(L_o/V_1)_m = \frac{R_m}{R_m + 1} = \frac{1.336}{(1.336 + 1.0)} = 0.572$$

$S_m/S = 0.54$ (Fig. 19-7)

$S = 20.46$ trays (use 21 trays)

TRAYED COLUMNS

Internals

Various types of trays are used in fractionation columns. Fig. 19-8 presents an isometric sketch of the top two trays in a fractionation column with bubble caps. The bubble caps, along with the weirs and downcomers, maintain a liquid level on the trays. The liquid flows across the tray, into the downcomer, and across the next tray in the opposite direction. The vapor flows up through the caps and through the slots mixing with the liquid.

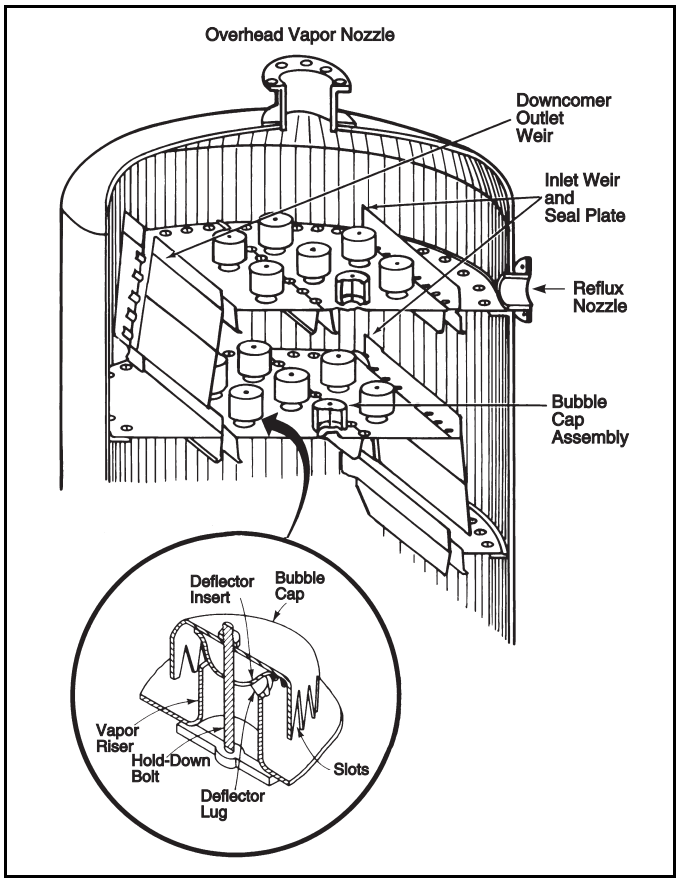
Fig. 19-9 shows the vapor flow through bubble cap trays, sieve trays, and valve trays. Due to the riser in the bubble cap, it is the only tray which can be designed to prevent liquid from "weeping" through the vapor passage. Sieve or valve trays control weeping by vapor velocity. The bubble cap tray has the highest turndown ratio, with designs of 8:1 to 10:1 ratio being common. Bubble cap trays are almost always used in glycol dehydration columns.

Valve and sieve trays are popular due to the lower cost and increased capacity over bubble cap trays for a given tower diameter. Fig. 19-10 shows two valve designs. The upper drawing shows a floating valve free to open and close with varying vapor flow rates. The lower drawing shows a "caged" valve which prevents valve loss due to erosion of the tray. Various other designs are common such as using multiple disks and rectangular valves. Valves of assorted weights have also been used to increase flexibility.

The sieve or perforated tray is the simplest construction of the three general types and thus is the least expensive option. The sieve tray is simply a plate with holes for vapor passage. Although the sieve tray generally has higher capacity, its main disadvantage is that sieve trays will be susceptible to "weep-

FIG. 19-8

Top Two Trays of a Bubble-cap Column[28]



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FIG. 19-9

Flow Through Vapor Passages[28]

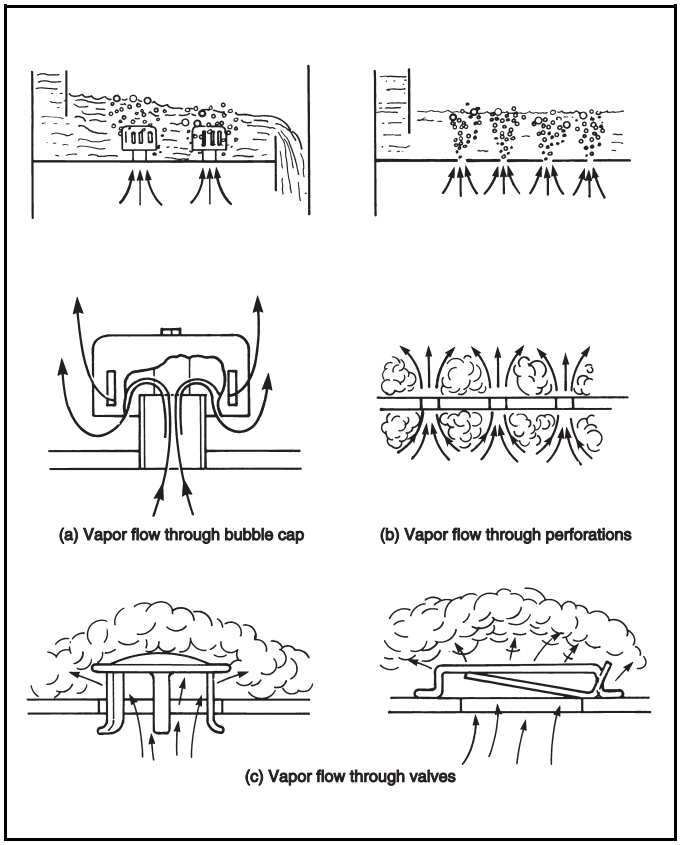
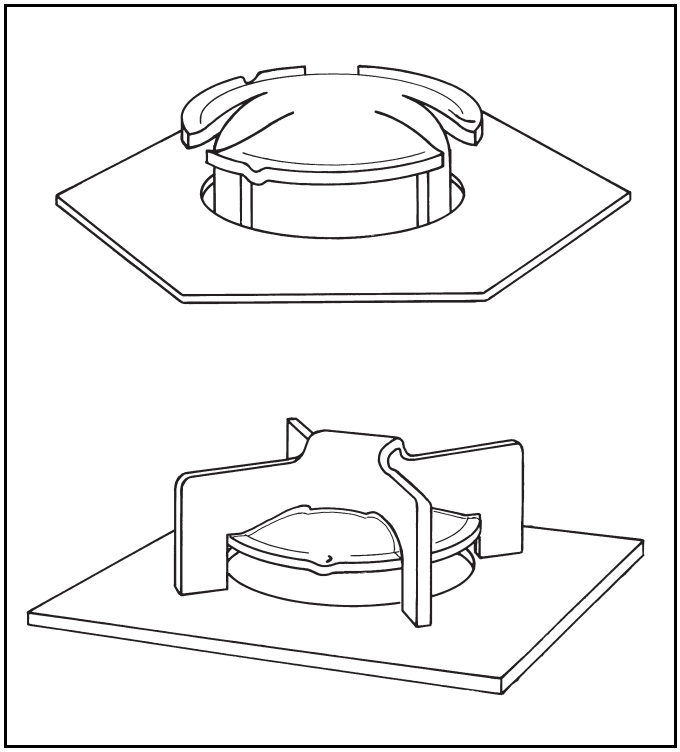


FIG. 19-10

Valve Types[28]



ing" or "dumping" of the liquid through the holes at low vapor rates and its turndown capacity is limited.

Trayed columns generally provide satisfactory operation over a wide range of vapor and liquid loadings. Fig. 19-11 shows operating characteristics for a representative system. The vapor and liquid rates can vary independently over a broad range and the column will operate satisfactorily. At low vapor rates unsatisfactory tray dynamics may be characterized by vapor pulsation, dumping of liquid, or uneven distribution. At high vapor rates, the tower will eventually flood as liquid is backed-up in the downcomers. At low liquid rates, poor vapor-liquid contact can result. High liquid rates can cause flooding and dumping as the liquid capacity of the downcomers is exceeded.

In order to handle higher liquid rates, more downcomer area is required. This is often achieved by using multiple pass trays. Multipass trays increase liquid handling capacity for a given diameter due to reductions in the flow path length and weir crest. Fig. 19-12 shows various configurations beyond a one pass tray where the liquid phase is split into two to four flow paths to increase liquid handling capacity.

Sizing

"C" Factor Method — Many design methods for sizing trayed fractionators have been used. Generally these methods are oriented toward liquid entrainment limitations or correlations for flooding limits. A simple method called the Souders and Brown equation[8] involves using a Stokes' Law type formula:

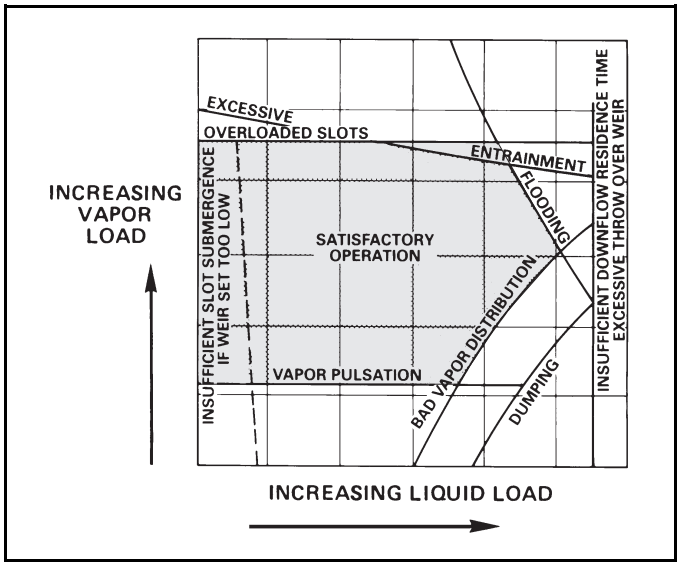
$$v_{max} = C\sqrt{\frac{\rho_L - \rho_v}{\rho_v}} \qquad \textbf{Eq 19-11}$$

Note that ρ_L and ρ_v are at flowing temperature and pressure.

The value of C can be found from Fig. 19-13 based on tray spacing and liquid surface tension. The column diameter is:

FIG. 19-11

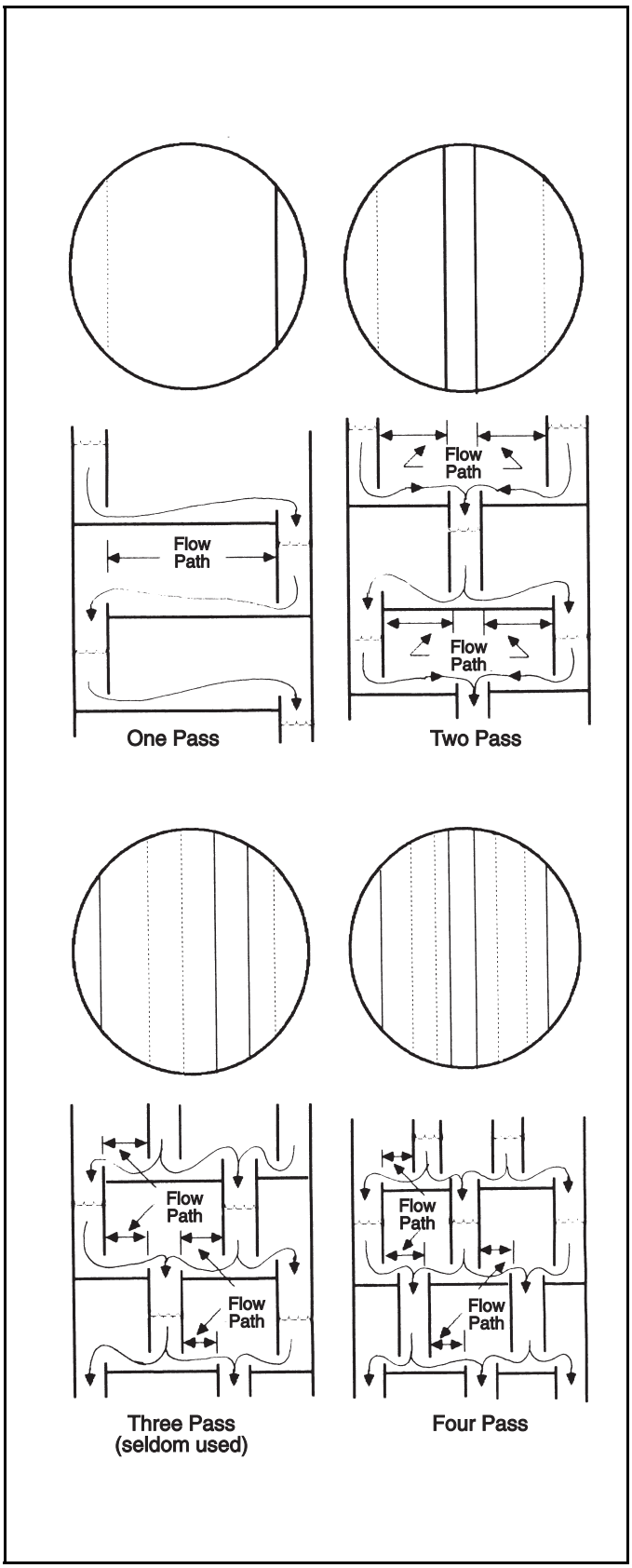
Limits of Satisfactory Tray Operation for a Specific Set of Tray Fluid Properties[8]



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FIG. 19-12

Alternative Liquid Flow Paths



$$D_T = \sqrt{\frac{V_{max}}{v_{max}\,(0.7854)}} \qquad \textbf{Eq 19-12}$$

This method was originally developed for bubble cap trays and gives a conservative diameter, especially for other types of trays.

Nomograph Method — Manufacturers of valve trays have developed design methods for their trays. Design procedures are made available[9, 10, 11] for preliminary studies. One such procedure starts with the nomograph in Fig. 19-14.[10] This is a simple relationship of liquid rate (GPM) and a quantity V_{load} defined as:

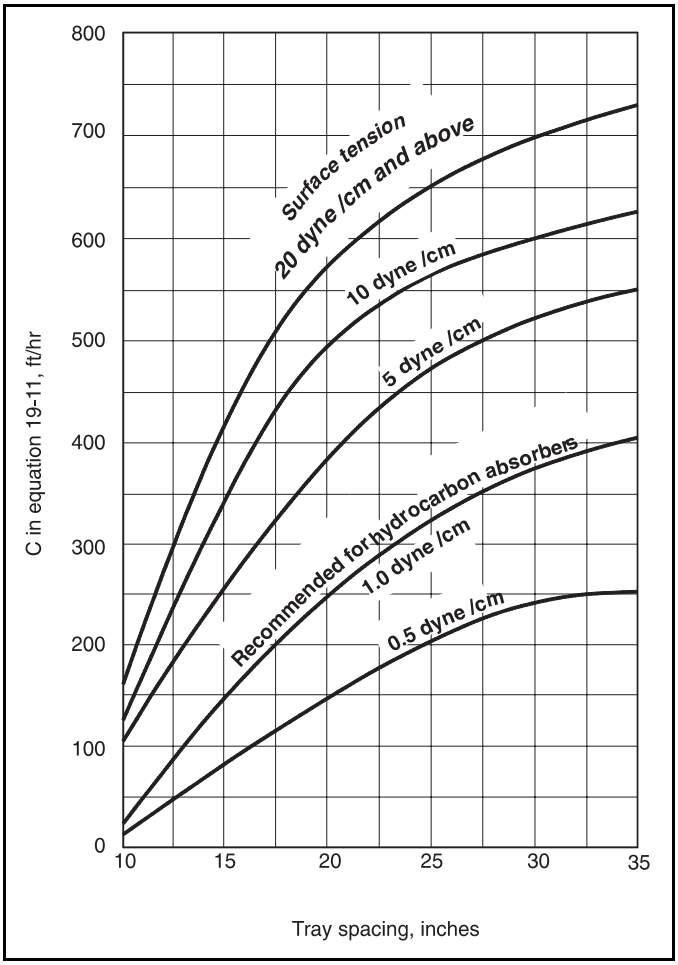
$$V_{load} = CFS\sqrt{\frac{\rho_v}{(\rho_L - \rho_v)}} \qquad \textbf{Eq 19-13}$$

Detailed Method — Fig. 19-14 is an approximation only and does not take into account foaming which is a major consideration in many systems. In order to compensate for foaming, a System Factor is used to adjust the vapor and liquid capacities (Fig. 19-15).

The downcomer velocity VD^*_{dsg} is found from Fig. 19-16. VD^*_{dsg} is corrected by the System Factor:

FIG. 19-13

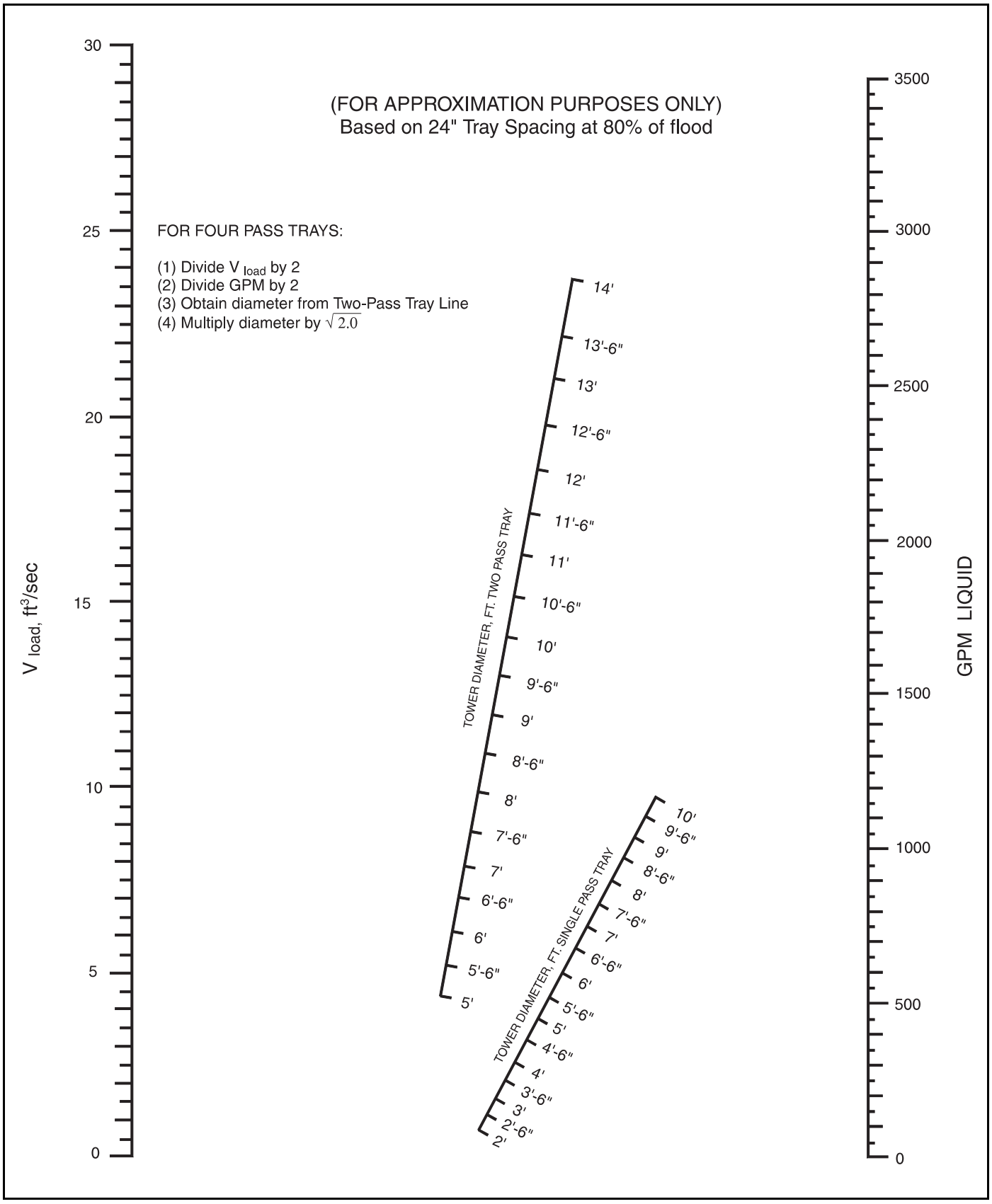
Souders-Brown Correlation for Approximate Tower Sizing[8]



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FIG. 19-14

Valve Tray Diameter[10]



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FIG. 19-15

System Factors[9]

Systems with foaming tendencies are taken into account by using a factor to derate the capacity of a given tray design. A list of the more common foaming systems and their recommended factor is below.

System	Factor
Absorbers (over 0°F)	0.85
Absorbers (below 0°F)	0.80
Amine Contactor	0.80
Vacuum Towers	0.85
Amine Stills (Amine Regenerator)	0.85
H_2S Stripper	0.85
Furfural Fractionator	0.85
Top Section of Absorbing Type Demethanizer/ Deethanizer	0.85
Glycol Contactors	0.50
Glycol Stills	0.65
CO_2 Absorber	0.80
CO_2 Regenerator	0.85
Caustic Wash	0.65
Caustic Regenerator, Foul Water, Sour Water Stripper	0.60
Alcohol Synthesis Absorber	0.35
Hot Carbonate Contactor	0.85
Hot Carbonate Regenerator	0.90
Oil Reclaimer	0.70

The capacity of a given tray design used in *high pressure fractionation service* with a vapor density of 1.8 lb per cu ft and higher should be derated by a system factor calculated by the following formula:

$$\text{System factor} = \frac{1.21}{(\rho_V)^{0.32}}$$

$$VD_{dsg} = VD^{*}_{dsg}\ (\text{System Factor}) \qquad \textbf{Eq 19-14}$$

The other factor required for this design method is the vapor capacity factor CAF.

$$CAF = CAF_o\ (\text{System Factor}) \qquad \textbf{Eq 19-15}$$

CAF_o is read from Fig. 19-17. In order to compute the column cross sectional area, three quantities are needed.

The flow path length, FPL:

$$FPL = 9\ D_T/NP \qquad \textbf{Eq 19-16}$$

D_T and NP are found from Fig. 19-14.

The active area, AAM:

$$AAM = \frac{V_{load} + [(GPM(FPL/13000)]}{CAF \cdot FF} \qquad \textbf{Eq 19-17}$$

FF, the flooding factor commonly used is 0.82 for most systems.

The downcomer area, ADM:

$$ADM = GPM/(VD_{dsg} \cdot FF) \qquad \textbf{Eq 19-18}$$

If ADM is less than 11% of AAM, use 11% of AAM or double ADM, whichever is smaller.

The tower cross sectional area is then:

$$ATM = AAM + 2\ (ADM) \qquad \textbf{Eq 19-19}$$

or

$$ATM = \frac{V_{load}}{0.78 \cdot CAF \cdot FF} \qquad \textbf{Eq 19-20}$$

The larger of these two values is used. Then:

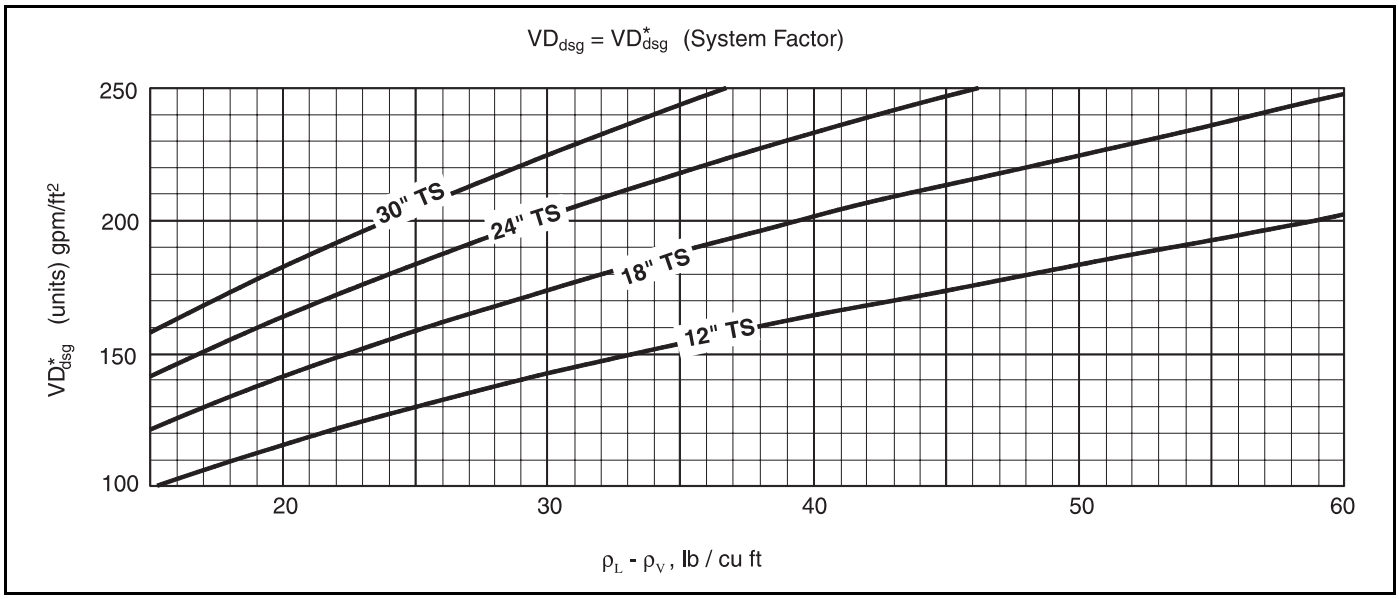
$$D_T = \sqrt{ATM / 0.7854} \qquad \textbf{Eq 19-21}$$

Example 19-3 — Determine the diameter of a depropanizer with the following data:

vapor rate: 70418 ft^3/hr

FIG. 19-16

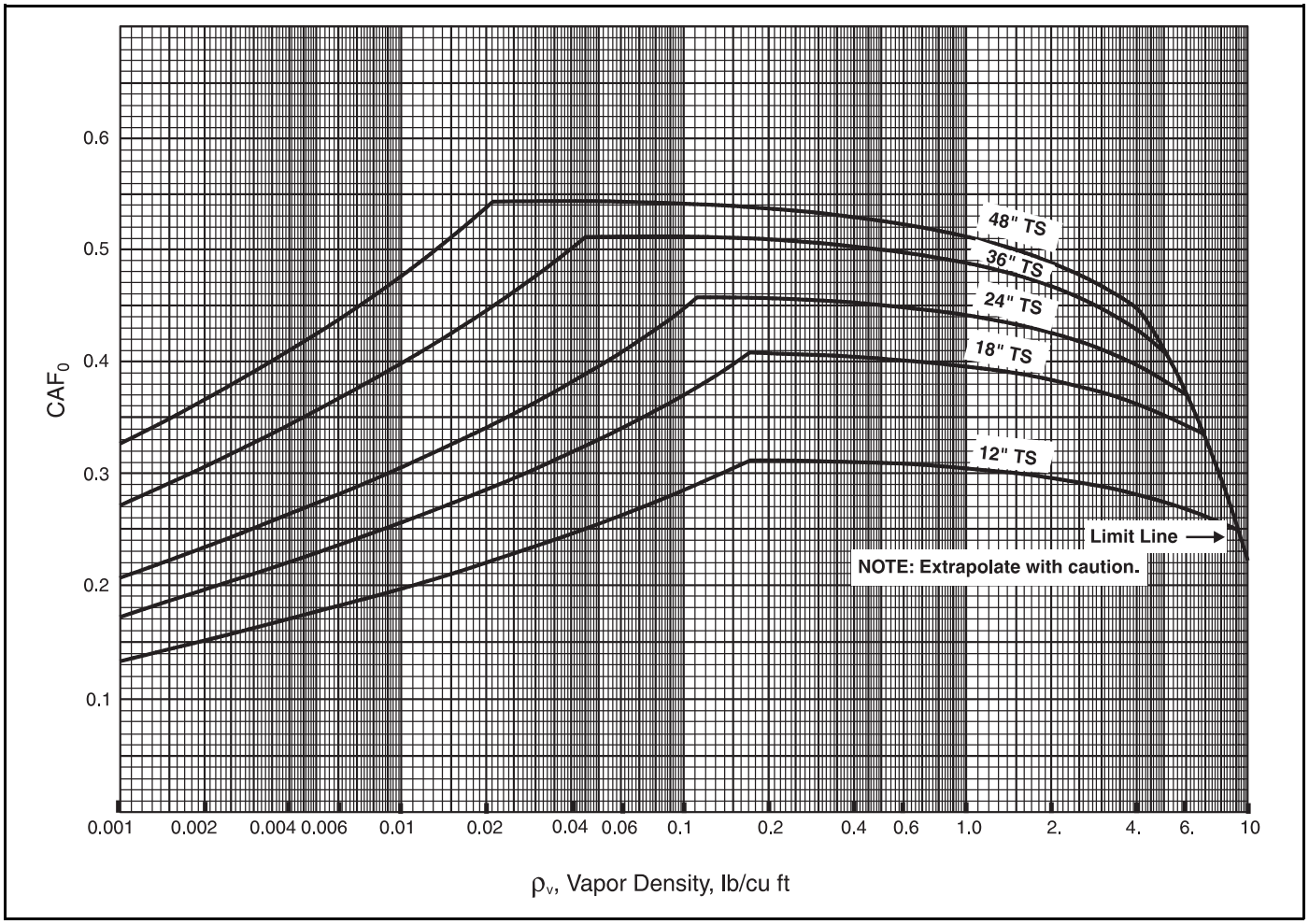
Downcomer Design Velocity[10]



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FIG. 19-17

Approximate Flood Capacity of Valve Trays[10]



vapor density: 3.0 lb/ft^3
liquid rate: 1190 gpm
liquid density: 28.8 lb/ft^3
liquid surface tension: 3.3 dyne/cm
tray spacing: 24"

"C" Factor Method

From Fig. 19-13: C ≅ 430

$$v_{max} = 430\sqrt{\frac{28.8-3.0}{3.0}} = 1261 \text{ ft/hr} \quad \text{from Eq 19-11}$$

$$D_T = \sqrt{\frac{70418}{1261\,(0.7854)}} = 8.4 \text{ ft} \quad \text{from Eq 19-12}$$

Nomograph (Fig. 19-14)

$$V_{load} = \frac{70418}{3600}\sqrt{\frac{3}{28.8-3}} = 6.67 \text{ ft}^3/\text{sec} \quad \text{from Eq 19-13}$$

then from Fig. 19-14 @ GPM = 1190

D_T ≅ 9′6″ for a 1 pass tray
7′6″ for a 2 pass tray

Detailed Method

VD^*_{dsg} = 186 gpm/ft^2 at $\rho_L - \rho_v$ = 25.8

$$\text{System Factor} = \frac{1.21}{(3)^{0.32}} = 0.85 \text{ (Fig. 19-15)}$$

VD_{dsg} = 186 (0.85)
= 158.1 gpm/ft^2

From Fig. 19-17:

CAF_o = 0.412 ft/sec

CAF = (0.412) (0.85) = 0.350 ft/sec

$$FPL = \frac{9(7.5)}{2} = 33.75 \text{ ft} \quad \text{from Eq 19-16}$$

$$AAM = \frac{6.67 + [1190\ (33.75/13000)]}{(0.350)\ (0.82)}$$

= 34.00 ft^2 from Eq 19-17

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$$ADM = \frac{1190}{(158.1)\,(0.82)} = 9.18\ ft^2 \qquad \text{from Eq 19-18}$$

$$ATM = 34.00 + 2(9.18) = 52.36\ ft^2 \qquad \text{from Eq 19-19}$$

$$ATM = \frac{6.67}{(0.78)\,(0.350)\,(0.82)} = 29.8\ ft^2 \qquad \text{from Eq 19-20}$$

$$D_T = \sqrt{\frac{52.36}{0.7854}} = 8.16\ ft \qquad \text{from Eq 19-21}$$

A comparison of the methods (rounded to the nearest 6")

C Factor	102"
Nomograph	90" (114" for single pass)
Detailed Method*	96"

*At at tray spacing different than 24" or for a different flooding factor, the diameter could change considerably.

Tray Efficiency

All column design work is performed using theoretical trays. An actual tray will not achieve equilibrium due to limitations of vapor-liquid contact time. In an actual column, more trays are required to obtain the desired separation. This determination is usually accomplished by the use of an overall tray efficiency defined as:

$$\varepsilon = \frac{\text{theoretical trays}}{\text{actual trays}} \qquad \textbf{Eq 19-22}$$

The determination of tray efficiencies from theoretical parameters is the topic of numerous technical articles.[12, 13, 14] A detailed discussion of this subject is beyond the scope of this book.

O'Connell[15] correlated the tray efficiencies of fractionators and absorbers. For fractionators, this correlation considered thirty-eight systems of which 27 are hydrocarbon fractionators. The correlation, shown in Fig. 19-18, relates overall tray efficiency to relative volatility computed at average column conditions and the feed viscosity at average column conditions.

Example 19-4 — Evaluate the tray efficiency for the system in Example 19-2.

Average column temperature = 185°F

Feed viscosity @ 185°F = 0.076 cp

Average α = 1.854

Solution Steps

$(\alpha)(\mu) = 0.141$

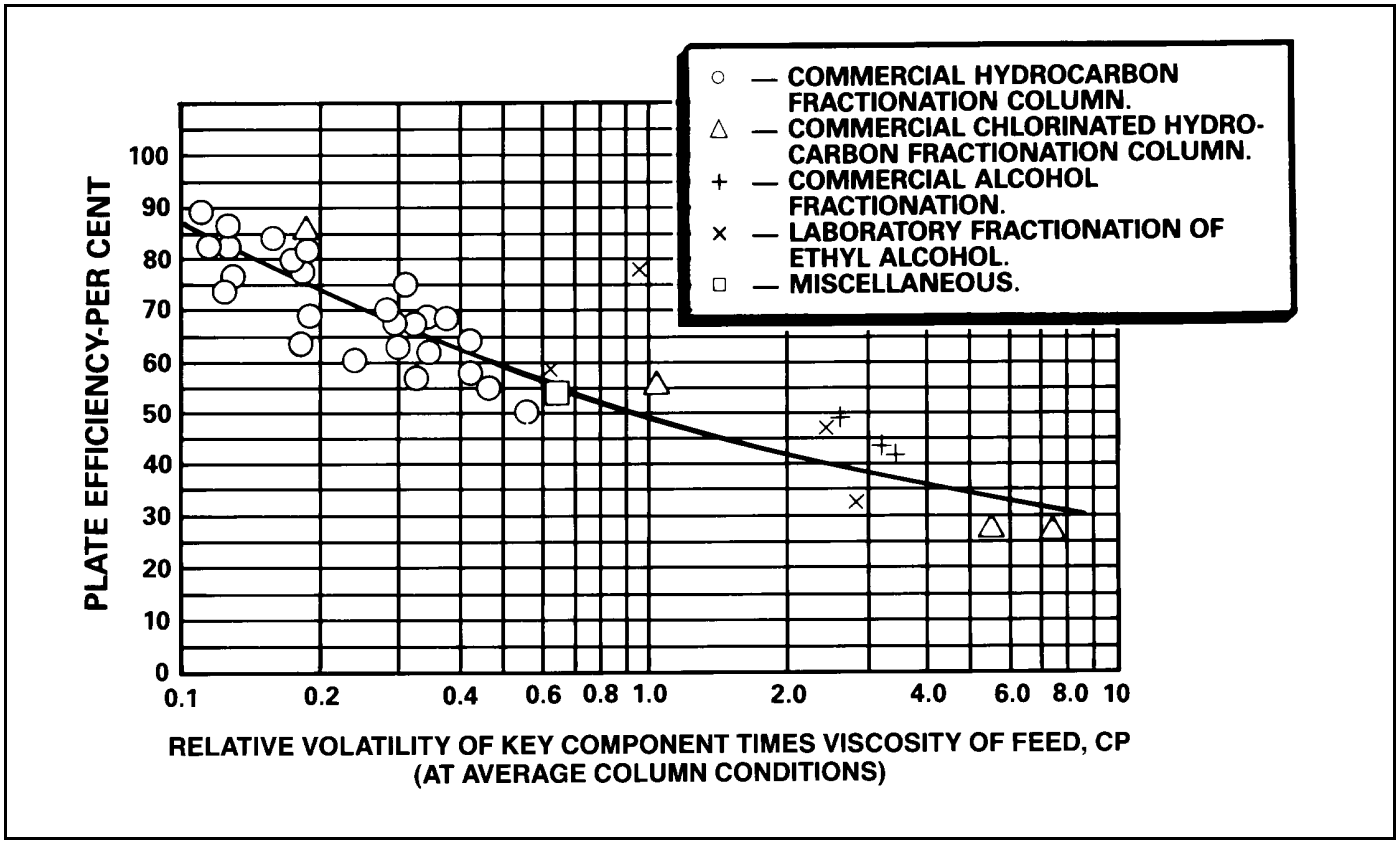
From Fig. 19-18, $\varepsilon \cong 80\%$

The system in Example 19-2 required 21 theoretical stages including the reboiler. The total actual trays is:

$$\frac{21-1}{0.80} \cong 25 \text{ trays}$$

FIG. 19-18

Effect of Relative Volatility and Viscosity on Plate Efficiency of Fractionating Columns



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FIG. 19-19

Typical Fractionator Parameters

	Operating Pressure, psig	Number of Actual Trays	Reflux[1] Ratio	Reflux[2] Ratio	Tray Efficiency, %
Demethanizer	200 - 400	18-26	Top Feed	Top Feed	45 - 60
Deethanizer	375 - 450	25-35	0.9 - 2.0	0.6 - 1.0	60 - 75
Depropanizer	240 - 270	30-40	1.8 - 3.5	0.9 - 1.1	80 - 90
Debutanizer	70 - 90	25-35	1.2 - 1.5	0.8 - 0.9	85 - 95
Butane Splitter	80 - 100	60-80	6.0 -14.0	3.0 - 3.5	90 - 100
Rich Oil Fractionator (Still)	130 - 160	20-30	1.75 - 2.0	0.35 - 0.40	Top 67 Bottom 50
Rich Oil Deethanizer	200 - 250	40	–	–	Top 25-40 Bottom 40-60
Condensate Stabilizer	100 - 400	16-24	Top Feed	Top Feed	50-75

[1]Reflux ratio relative to overhead product, mol/mol

[2]Reflux ratio relative to feed, gal./gal.

Typically an extra tray is added to the tray count for each feed tray and each side exchanger. Using this criteria, this column should have 26 trays.

Typical operating pressures, tray counts, reflux ratio, and tray efficiencies for various gas processing systems are shown in Fig. 19-19. These are *not* design values; rather guidelines for typical values in previous applications. The actual selection depends on many factors such as feed composition, energy cost, and capital cost.

HIGH CAPACITY TRAYS

The 90s saw the proliferation of High Capacity Trays by distillation equipment vendors and users. These trays employ unconventional downcomer and deck configurations to effect vapor and/or liquid handling capability increases, when used to revamp distillation columns. High Capacity Trays have been particularly effective in demethanizers, deethanizers, depropanizers and butane columns.

One such High Capacity Tray, the NYE TRAY®, is shown in Fig. 19-20. This tray increases vapor capacity by raising the receiving pan and increasing the area available for vapor flow. This, and similar trays, employ a crossflow arrangement with liquid traveling horizontally across the decks and vapor bubbling up through the liquid, creating a froth where the mass transfer occurs. Examples of other High Capacity crossflow trays include the following:

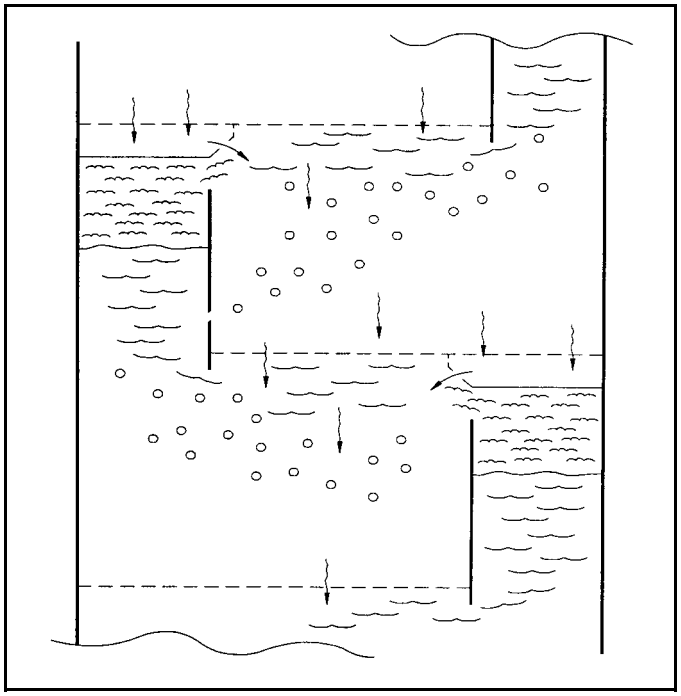
MAC-FRAC®	(Koch-Glitsch)
Bi-FRAC™	(Koch-Glitsch)
SUPERFRAC®	(Koch-Glitsch)
Pro-Value	(St. Gobain)
Triton	(St. Gobain)
MVG	(Sulzer ChemTech)

Another style of High Capacity Trays employs a configuration sometimes called "counterflow," where the liquid spends only a short time on the tray decks and where the predominant liquid direction is vertical (downward) rather than horizontal. Examples of counterflow trays include the following:

MD™	(UOP)
ECMD™	(UOP)
VGMD™	(UOP and Sulzer ChemTech)
Hi-Fi	(Shell Global Solutions)
Vortex Downcomer	(Sulzer ChemTech)

FIG. 19-20

NYE TRAY Schematic



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Efficiencies of these counterflow trays are often lower than those of crossflow trays due to the reduced contact time between the phases. Capacities can be quite high, and tray spacings quite small, due to the very long outlet weir that these trays are capable of providing.

Still another tray configuration, called "cocurrent flow," is expected to gain greater acceptance in the future. With cocurrent flow, the vapor and liquid phases are allowed to flow together, unidirectionally, for awhile inside contacting elements. Examples of such trays are ULTRA-FRAC® (Koch-Glitsch) and ConSep (Shell Global Solutions). Some such trays are only capable of functioning at low liquid rates such as those that are encountered in glycol dehydration columns. Little information is publicly available regarding the efficiency of cocurrent flow trays. Sizing for these, and in fact most High Capacity Trays, is regarded as proprietary by their vendors.

PACKED COLUMNS

Traditionally the majority of fractionation columns in gas processing plants were equipped with trays. However, an option to trayed columns is to use packing. With packed columns, contact between the vapor and liquid phases is achieved throughout the column rather than at specific levels.

There are generally three types of packed columns:

- Random packing wherein discrete pieces of packing are dumped in a random manner into a column shell. These packings are of a variety of designs. Each design has particular surface area, pressure drop and efficiency characteristics. Examples of various packing types are shown in Fig. 19-21. Random packing have gone through various development phases from the first generation packings which were two basic shapes, the Rashig Ring and the Berl Saddle. Second generation packings include the Pall Ring and the Inatalox Saddle which are still used extensively today. Third generation packings come in a multitude of geometries most of which evolved from the Pall Ring and The Intalox Saddle. (Fig. 19-22 and 19-23).
- Structured packing where a specific geometric configuration is achieved. These types of packing can either be the knitted-type mesh packing or sectionalized beds made of corrugated sheets (Fig. 19-24). There are a number of commercially available packings which differ in the angle of the crimps, the surface grooves and the use of perforations.
- Grids which are systematically arranged packing which use an open lattice structure. These types of packings have found application in vacuum operation and low pressure drop applications. Little use of these types of packings are seen in high pressure services.

Structured packing have found application in low liquid loading applications which are below 20 gpm/ft^2. Structured

FIG. 19-21

Various Types of Packing[28]

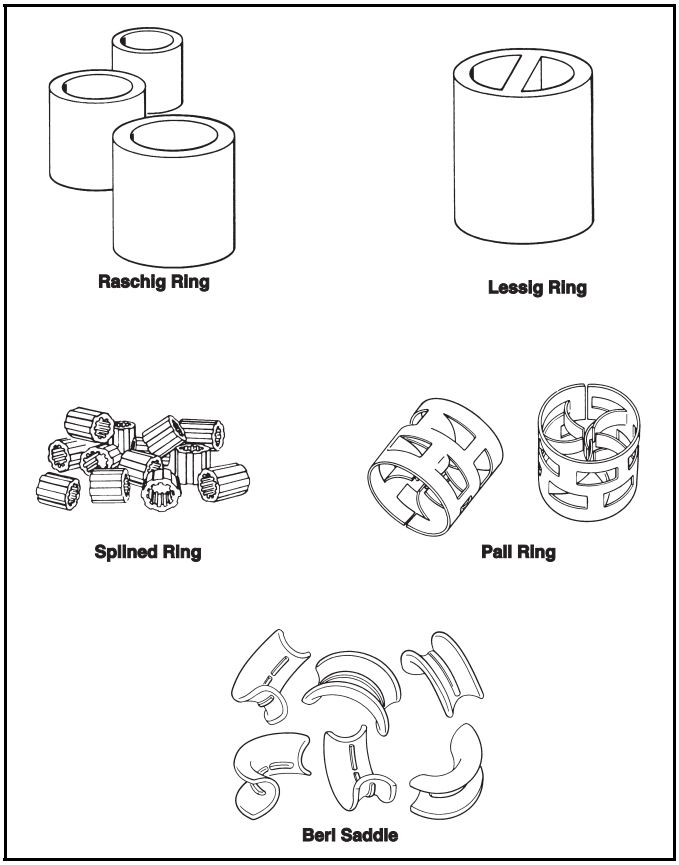


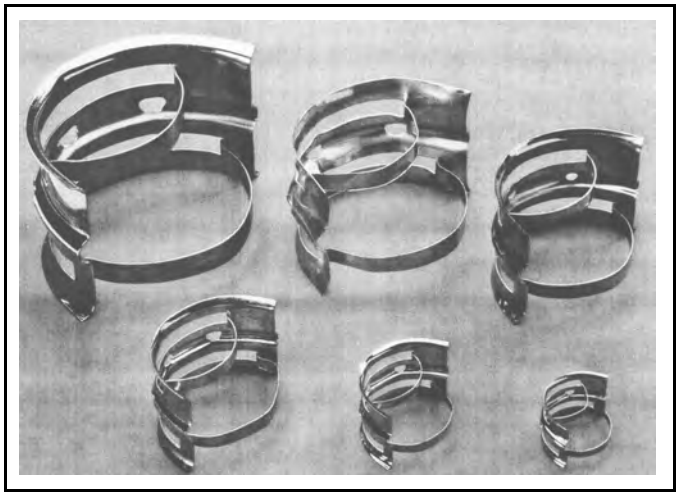
FIG. 19-22

Flexipak®, Cascade Mini Rings® and Fleximax® packings



FIG. 19-23

Nutter Ring™ Metal Packings



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packing has performed very well in extremely low liquid loading applications such as glycol dehydration (See Section 20). The high surface tension in glycol dehydrators also helps the structured packing to perform well. Above 20 gpm/ft^2, random packings are more advantageous. Structured packings have been tried in fractionators with little success. Numerous case of structured packing failures have been experienced in high pressure and/or high-liquid rate services. Structured packings generally have lower pressure drop per theoretical stage then random packings. This can be important in low pressure applications but not for high pressure NGL fractionators.

Column Sizing

The Eckert generalized pressure drop correlation (GPDC)[16] is often used for sizing randomly packed columns. The chart in Fig. 19-26, which is a modified correlation, can be used to predict pressure drop for a given loading and column diameter. Alternatively, for a given pressure drop the diameter can be determined.

Most packed columns are designed for pressure drop of between 0.20 and 0.60 inches of water per foot of packed depth with 1.0 inches of water being the maximum.

The packing factors for various packings are shown in Fig. 19-25. Broadly speaking, packings smaller than 1 inch size are intended for towers one foot or smaller in diameter, packings 1 inch or 1½ inch in size for towers over one foot to three feet in diameters, and 2 or 3 inch packings are used for towers three or more feet in diameter. This results from tradeoffs of capacity and efficiency. The designer should select the proper size of packing, and therefore the proper packing factor for calculations.

The packing factors in Fig. 19-25 are average values which are sufficient for preliminary sizing but specific packing vendors should be contacted for design applications.

The GPDC has limitations in describing the performance of packings. Efforts to improve the correlation for specific packing geometries have led to the development and publication of charts for each packing which strive to correlate packing performance information with the same abscissa and ordinate as the GPDC chart. Kister[31] published a series of 96 charts for a wide variety of packings.

Example 19-5 — Determine the packed column diameter for example 19-3 using 2" plastic Pall rings.

Given: $\mu = 0.076$ cp

$\Delta P = 0.5$ in. water/ft of packing

Solution Steps

$$M_L = \frac{(1190)(60)(28.8)}{(7.48)} = 274{,}909 \text{ lb/hr}$$

$$M_G = (70418)(3) = 211{,}254 \text{ lb/hr}$$

$$\frac{L_p}{G_p}\sqrt{\frac{\rho_v}{\rho_L}} = \frac{M_L}{M_G}\sqrt{\frac{\rho_v}{\rho_L}} = \frac{274{,}909}{211{,}254}\sqrt{\frac{3}{28.8}} = 0.42$$

From Fig. 19-26 at $\Delta P = 0.5$ in. water/ft of packing:

$$\frac{G_p^2 \mu_L^{0.1} F_p (\rho_w / \rho_L)^{0.1}}{32.17 \rho_v (\rho_L - \rho_v)} = 0.024$$

From Fig. 19-25 $F_p = 26$, then:

$$G_p^2 = \frac{(0.024)(32.17)(28.8 - 3.0)(3.0)}{(0.076)^{0.1}(26)(62.4/28.8)^{0.1}} = 2.753$$

$$G_p = 1.659 \text{ lb/(ft}^2 \bullet \text{sec)}$$

$$A_c = \frac{211254}{(1.659)(3600)} = 35.37 \text{ ft}^2$$

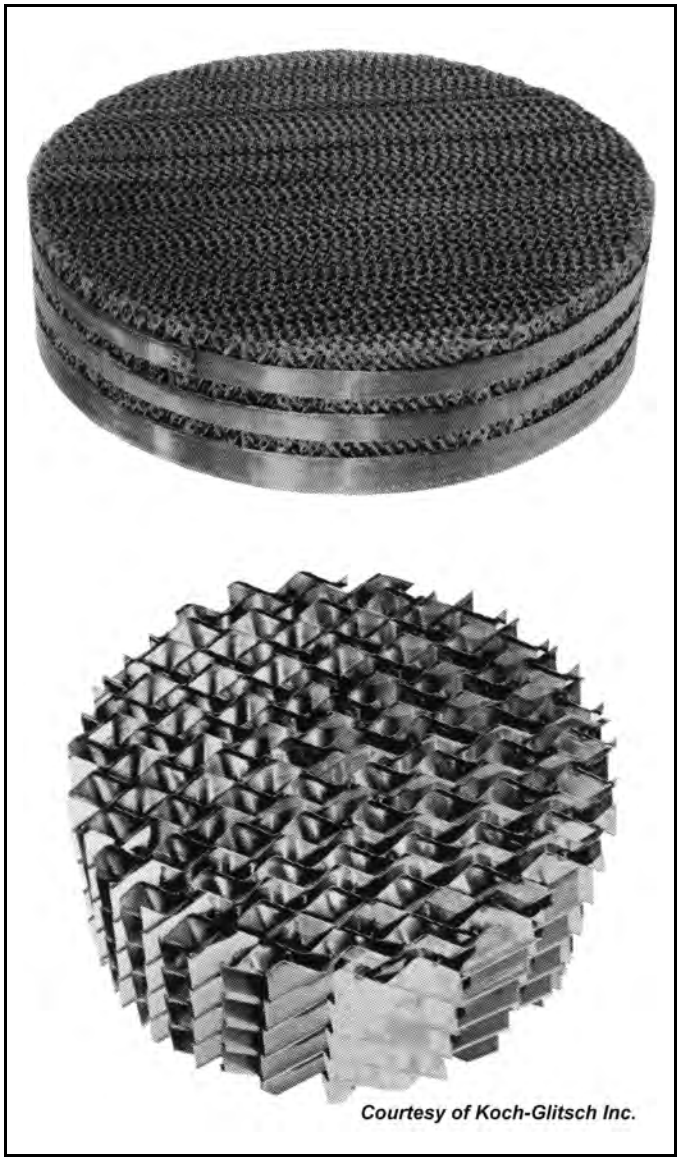
$$D_T = 6.71 \text{ ft (use a 7 ft column)}$$

Packing Height

In order to determine the height of a packed column bed, the height of a theoretical plate, HETP, is required. HETP times the number of theoretical stages gives the height of the packing. Generally HETPs range from 12 to 36 in. but can be as high as 60 in. Packed columns have found wide usage in cryogenic plant demethanizers. Typical HETP's for demethanizers are 36 inches for the upper section and 30 inches for the lower section.

FIG. 19-24

Structured Packing



Courtesy of Koch-Glitsch Inc.

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The prediction of the HETP from theory or empirical relations is a complex subject.[17] Recent research by Fractionation Research Inc. has underscored the sensitivity of HETP with a number of variables. HETP is a function of flow rates and properties of the system as well as the specific geometric and mechanical factors. In order to determine packing requirements, a packing manufacturer should be consulted.

Fig. 19-27 provides some example HETPs for hydrocarbon systems in the gas processing industry.[18]

HETP's are also a function of the packing size. In general, the smaller packings have lower HETP values. Fig. 19-28 shows an example trend of packing HETP's for one type of packing.

Packed Column Internals

A critical consideration in packed columns is the control of the vapor and liquid phases. Fig. 19-29 shows a cross section of a packed tower with various internals. Each section of packing is supported by a support plate or grid whose function is to carry the weight of the bed with minimum pressure drop. Hold-down grids are used at the top to prevent lifting of the bed by the vapor phase.

Liquid distribution is a critical consideration in packed columns. Poor liquid distribution causes dramatic loss of efficiency. Various designs have been used to distribute liquid feeds and to collect and redistribute the liquid at various points in the tower. Generally the liquid should be redistributed every 20 ft of packing height or every 10 column diameters, whichever is smaller.

Dumped Packing Versus Trays

Packed columns have been used extensively in the chemical industry for many years. Packings are selected instead of trays for several reasons:

- Pressure drop—Packed towers usually yield a lower pressure drop per theoretical stage. This can be important for low pressure operations. At the elevated pressures encountered in natural gas processing, column pressure drop is usually not a major issue.
- High liquid loading—for high liquid-to-vapor ratio systems, a packed column will have more capacity for a given diameter. Some fractionation applications are characterized by low liquid/vapor ratios and packing has less of an advantage for these designs.
- Corrosion—for corrosive systems, packing can be fabricated from ceramics or plastics. Trays may have to be fabricated from expensive alloy materials.

Packed columns also have several disadvantages which must be taken into account in a fractionation design:

- Turndown—Packed columns usually have limited turndown capabilities. Whereas trays can be operated as low as 10-15% of full load, packings are limited to about a 50% turndown. This can be important in situations where gas production is phased in and throughput rates build up over time.
- Liquid distribution—In trayed columns, the liquid phase is forced to flow across a tray surface. With gas bubbling through the liquid, contact is assured. In packed towers, the liquid and vapor are free to seek their own flow paths, and channeling can occur. It is critical that the liquid phase be properly distributed at the top of the column

FIG. 19-25

Packing factors (F_p) (Dumped Packing)

Packing Type	Material	Nominal Packing Size (Inches)										
		1/4	3/8	1/2	5/8	3/4	1	1.25	1.50	2	3	3.5
IMTP®	Metal				51		40		24	18	12	
Hy-Pak™	Metal						45		29	26		16
Super Intalox Saddles®	Ceramic						60			30		
Super Intalox Saddles®	Plastic						40			28		18
Pall Rings	Plastic				75		55		40	26		17
Pall rings	Metal				70		56		40	27		18
Intalox Saddles®	Ceramic	725	330	200		145	92		52	40	22	
Raschig Rings	Ceramic	1600	1000	580	380	255	155	125	95	65	37	
Raschig Rings	1/32" Metal	700	390	300	170	155	115					
Raschig Rings	1/16" Metal			410	300	220	144	110	93	62	32	
Berl Saddles	Ceramic	900		240		170	110		65	45		
Flexiring	Metal						49			23		16
Fleximax	Metal						35		26	17	11	
Cascade Mini Rings	Metal						39	36	33	26	18	
Cascade Mini Rings	Plastic						44		33	20	17	

NOTE: Values in this table are average values for the packing factor (F_p). F_p is actually a function of loading. Specific correlations for each packing from the vendors should be used for design purposes.

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FIG. 19-26

Packed Column Pressure Drop Correlation

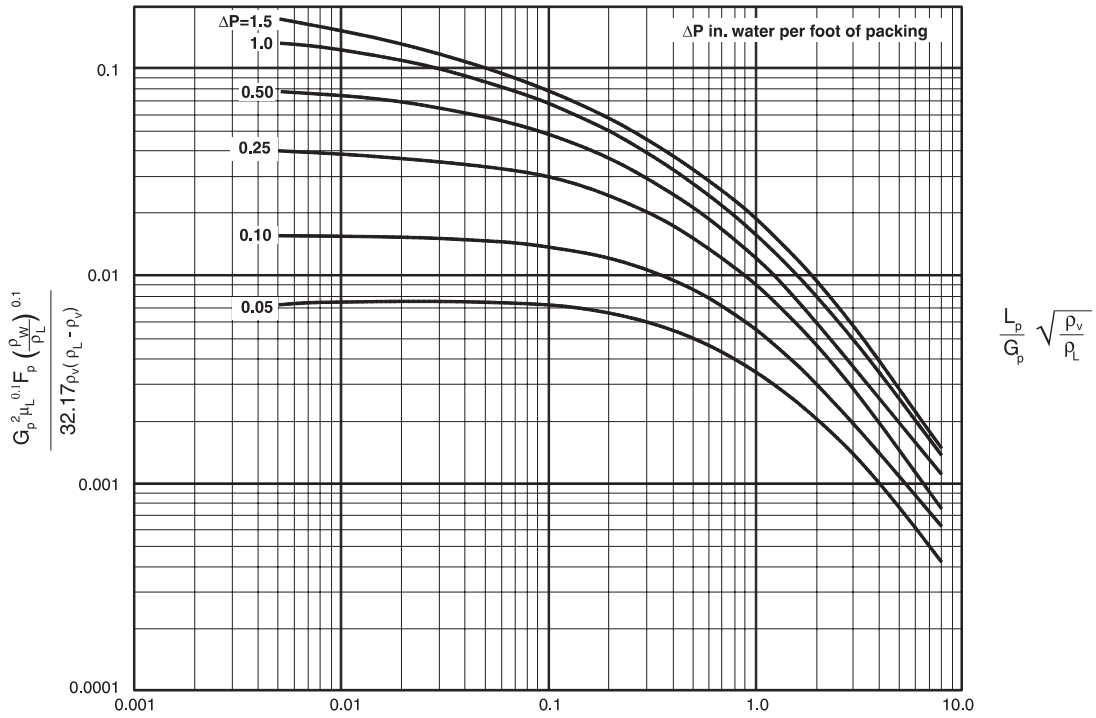


FIG. 19-27

Typical Packing Depths[18]

System	L/G, lb/(hr-sq ft)	Diam. in.	Packing		Bed depth, ft	HETP, ft	HTU, ft	System press., psia	ΔP, in H_2O/ ft pkg	% Overhead
			Type	Size, in.						
Absorber	8300/ 11000	36	Pall rings	2	23.0	2.8	–	865	0.55	–
L.O.-Top fractionator	3600/ 4700	36	Pall rings	2	17.0	2.5	–	157	0.12	–
L.O.-Bottom fractionator	10600/ 5600	48	Pall rings	2	17.0	2.8	–	157	0.30	–
Deethanizer top	11000/ 4600	18	Pall rings	1½	20.0	2.9	–	300	0.20	–
Deethanizer bottom	19000/ 4500	30.0	Pall rings	2	18.0	3.3	–	300	0.30	–
Depropanizer top	5700/ 4200	23.4	Pall rings	1½	16.0	3.2	–	270	0.30	–
Depropanizer bottom	5700/ 4200	23.4	Pall rings	1½	24.0	2.4	–	270	0.30	–
Debutanizer top	1900/ 3100	19.5	Pall rings	1½	12.0	2.4	–	90	0.12	–
Debutanizer bottom	1900/ 3100	19.5	Pall rings	1½	18.0	2.0	–	90	0.12	–
Pentane-iso-pentane	2100/ 1900	18.0	Pall rings	1	9.0/7.6	1.5	–	Atmos.	0.40	–
Light and heavy naphtha	660/ 1250	15.0	Pall rings	1	10.0	2.00	2.05	100 mm. Hg	1.10	95.0
	320/ 600	15	Pall rings	1	10.0	3.25	2.50	100 mm. Hg	0.20	95.0
	620/ 1450	15	Pall rings	1	10.0	1.45	1.25	100 mm. Hg	1.75	97.5
	260/ 650	15	Pall rings	1	10.0	1.45	1.30	100 mm. Hg	0.20	97.5
	370/ 850	15	Intalox	1	10.0	2.30	1.90	100 mm. Hg	0.80	93.0
	210/ 500	15	Intalox	1	10.0	2.70	2.10	100 mm. Hg	0.22	99.0
	340/ 800	15	Raschig rings	1	10.0	1.95	1.40	100 mm. Hg	1.11	91.6
	210/ 500	15	Raschig rings	1	10.0	2.70	1.97	100 mm. Hg	0.40	96.5
Iso-octane Toluene	1970/ 2300	15	Pall rings	1	10.0	1.34	1.35	Atmos.	0.70	82.0
	950/ 2100	15	Pall rings	1	10.0	1.90	2.17	Atmos.	0.10	76.0
	2100/ 2660	15	Pall rings	1	10.0	0.80	1.02	Atmos.	1.70	84.0
	960/ 1200	15	Pall rings	1	10.0	1.53	1.42	Atmos.	0.15	74.0
	1110/ 1300	15	Pall rings	1	10.0	1.34	1.29	100 mm. Hg	1.08	92.5
	510/ 600	15	Pall rings	1	10.0	1.88	1.81	100 mm. Hg	0.20	87.0
	1020/ 1300	15	Pall rings	1	10.0	1.67	1.60	100 mm. Hg	1.14	92.0
	470/ 600	15	Pall rings	1	10.0	2.07	2.00	100 mm. Hg	0.20	89.0

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and be redistributed at 20 foot intervals or every 10 column diameters, whichever is smaller.

- Plugging—Packed towers will be more susceptible to plugging from dirt and other foreign materials.
- Packing Height—The HETP for a packed column is an uncertain matter. Often they must be determined by testing or field applications. HETP's can vary from a few inches to several feet.
- Inspection—It is difficult to inspect internals without removing all the contents of a column.

MECHANICAL CONSIDERATIONS

Once the diameter and height of a fractionator have been determined, consideration must be given to the column internals and heat exchanger arrangements. There are many options in each of these areas and a sound design must consider many details to ensure proper operation. For additional information on heat exchangers see Section 9.

Reboiler Arrangements[19]

There are several reboiler configurations which have been used in fractionation service.[20] The most common types are:

- Forced circulation
- Once-through natural circulation
- Vertical thermosyphon
- Horizontal thermosyphon
- Flooded bundle (kettle type)

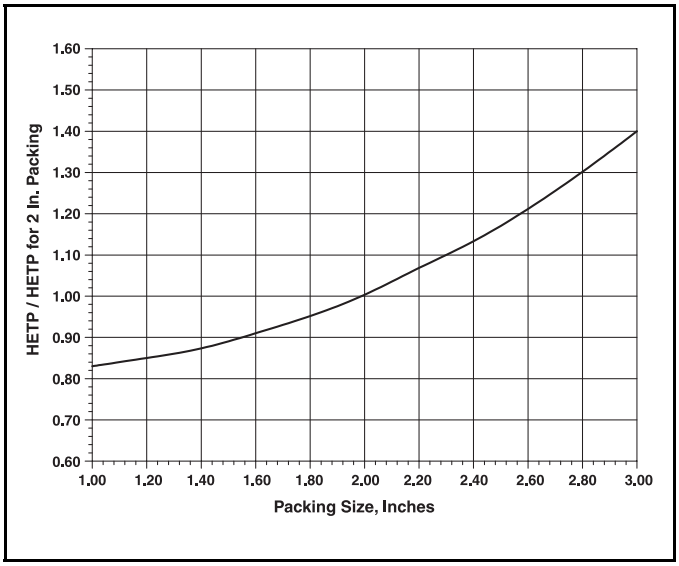
These types of reboilers are shown in Fig. 19-30 through Fig. 19-35. Modifications of these types are also used; for example, forced circulation reboilers are not necessarily in vertical orientation. Also, internal "stab-in" type reboilers have been used but are not common.

Each type of reboiler has its special advantages and disadvantages. Selection criteria of a reboiler configuration should include:

- Heat transfer surface required
- Space and piping requirements

FIG. 19-28

Example Effect of Packing Size on HETP

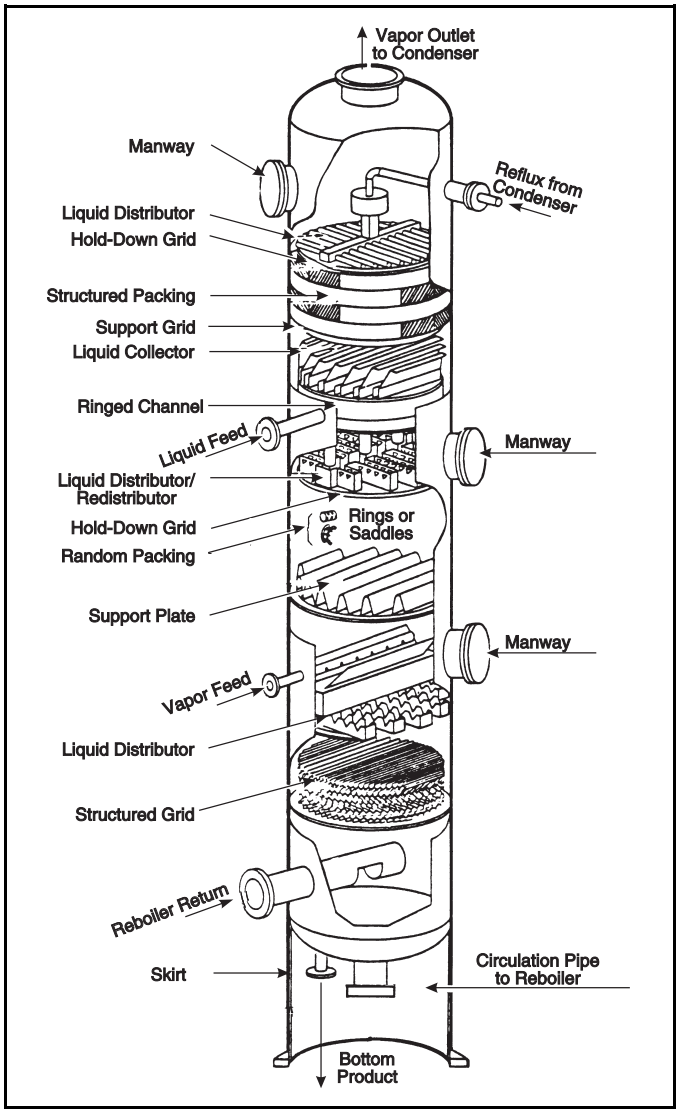


- Ease of maintenance
- Fouling tendency
- Operating stability
- Operating cost
- Column and skirt elevation requirements

Forced Circulation — A typical arrangement for forced circulation reboilers is shown in Fig. 19-30. This type is also called a pumped-through reboiler. All the liquid from the bottom tray is carried by a downcomer to below the liquid level in the bottom of the column. The liquid can be circulated through the reboiler as many times as is economically feasible to control the percent vaporization. The bottom product is drawn off the line to the reboiler. This type arrangement is usually used in installations where piping pressure drop is so high that natural circulation is not practical. Remotely located reboilers or installations where the reboiler heat is provided by several sources may require forced circulation. The main advantages of forced circulation are the abilities to closely control circulation rate and to handle viscous or solid containing

FIG. 19-29

Example Packed Column Internals[29]



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fluids. The continuous operating cost of the pump makes natural circulation designs more desirable.

Natural Circulation — By far the greater number of reboiler installations employ natural circulation. This can be achieved in either of two ways as shown on Fig. 19-31a and b. In Fig. 19-31a all the liquid on the bottom tray is circulated directly to the reboiler, where it is partially vaporized. The unvaporized portion, on being disengaged under the bottom tray, is withdrawn as bottom product. In Fig. 19-31b the liquid passes through the downcomer below the liquid level of the column as in forced circulation. The bottom liquid is free to recirculate through the reboiler as many times as the hydrostatic pressure difference between Z_1 and Z_3 will permit. Because there is no opportunity for recirculation in the arrangement in Fig. 19-31a, it is called a once-through reboiler arrangement. Fig. 19-31b is referred to as a recirculating reboiler.

Vertical Thermosyphon — The vertical thermosyphon reboiler shown in Fig. 19-32 is usually a one tube pass-one shell pass exchanger with the channel end up. The upper tube sheet is placed close to the liquid level in the bottom of the fractionation column. This type exchanger is capable of high heat transfer rates (minimum area) and requires simple piping. It is not easily fouled and has generally good controllability. Because of the vertical orientation, additional column skirt is required and maintenance can be awkward.

Recirculation Ratios — The recirculation ratio is determined from the difference between hydrostatic head in the column corresponding to the tube length of the reboiler and the weight of the vapor-liquid mixture.

Recirculation ratios of 4:1 or greater are usually employed. Referring to the vertical thermosyphon in Fig. 19-32, there are five principal resistances:

- Frictional pressure drop through the inlet piping
- Frictional pressure drop through the reboiler
- Expansion or acceleration loss due to vaporization in the reboiler
- Static pressure of a column of mixed liquid and vapor (Z_3) in the reboiler
- Frictional pressure drop through the outlet piping

Detailed calculation of the hydraulics of this system is complex due to the two-phase flow involved.[20] The simplified method presented by Kern[19] can be used to estimate this system:

Expansion Loss Due to Vaporization — This is taken as two velocity heads based on the mean of the inlet and outlet densities.

$$\Delta P_1 = \frac{G^2}{144\, g_c\, \rho_{avg}} \qquad \textbf{Eq 19-23}$$

Particularly where the recirculation ratio and the operating pressure are great, the difference in the densities between the inlet and outlet is not very large and the expansion loss is negligible.

Weight of a Column of Mixed Liquid and Vapor— This is difficult to evaluate if precision is required, since the expansion of the vapor is a function of the recirculation ratio, average specific volume of the vapor, coefficient of expansion of the liquid, etc. For nearly all practical cases it may be assumed that the variation of the density is linear between the inlet and the outlet. If v is the specific volume at any height, h, in the vertical tube whose total length is L_t and whose inlet and outlet specific volumes are v_i and v_o:

$$v = v_i + \frac{(v_o - v_i)h}{L_t} \qquad \textbf{Eq 19-24}$$

If the weight of the column of mixture is m, the change in weight with height is dm, and if a is the cross-section flow area,

$$dm = \frac{a}{v}\, dh \qquad \textbf{Eq 19-25}$$

If the static pressure of the column of liquid and vapor is designated by $Z_3\rho_{avg}$ and the cross-section area, a, is unity, then:

$$Z_3\rho_{avg} = \int^{L_t} \frac{dx}{v} = \int \frac{dx}{v_i + (v_o - v_i)\, x/L_t} \qquad \textbf{Eq 19-26}$$

Integrating and dividing by 144 to obtain the static head per square inch:

$$\frac{Z_3\, \rho_{avg}}{144} = \frac{2.3\, L_t}{144\, (v_o - v_i)} \log \frac{v_o}{v_i} \qquad \textbf{Eq 19-27}$$

Rational solutions for the recirculation ratio can be established by taking all the heads in the circuit into account as functions of the mass velocity, G, and upon solution for G, the recirculation rate can be obtained directly. Because the gravity of the reboiler outlet mixture also varies with the recirculation ratio, the expression becomes complex and it is simpler to solve

FIG. 19-30

Forced-Circulation Reboiler Arrangement

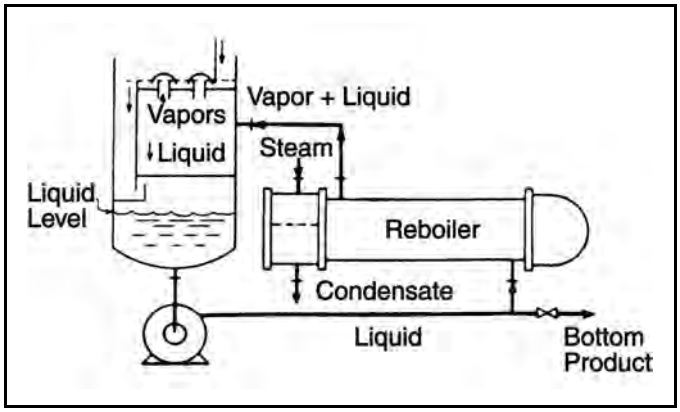
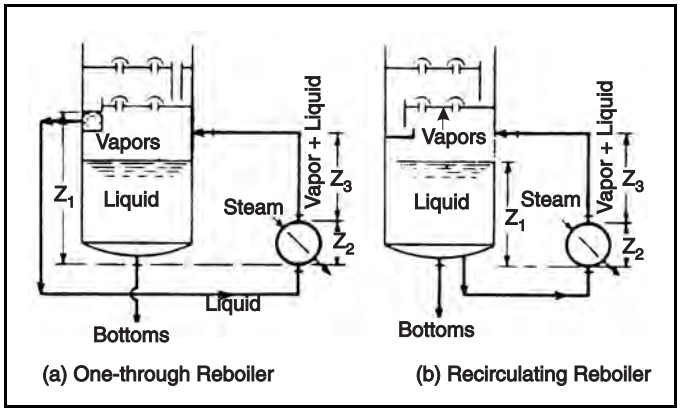


FIG. 19-31

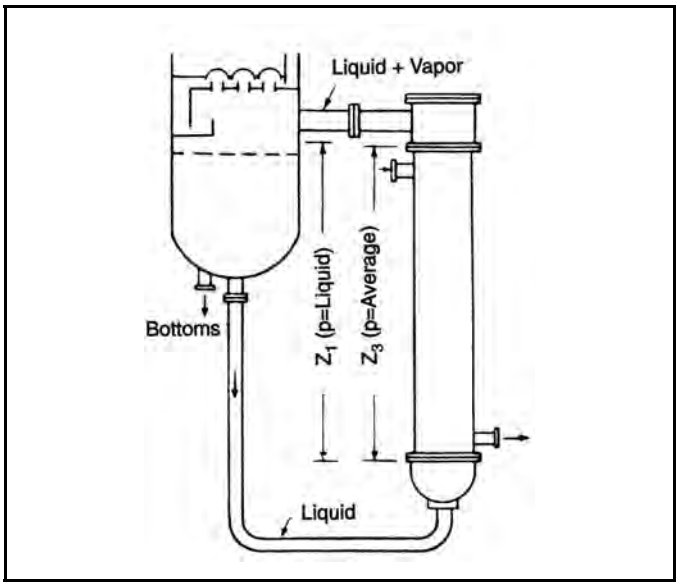
Natural-Circulation Reboiler Arrangements



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FIG. 19-32

Vertical Thermosyphon Reboiler Connected to Tower



by trial and error. If the height of an existing reboiler is given, the recirculation ratio can be computed. If the recirculation ratio is given, the required head, $Z_1\rho_L$, may be computed.

Example 19-6 — A vertical thermosyphon reboiler is to provide 40,800 lb/hr of vapor which is almost pure butane. The column operates at a pressure of 275 psig corresponding to a nearly isothermal boiling point of 228°F. Heat will be supplied by saturated steam at 125 psig. A recirculation ratio of 4:1 or greater should be employed. What is the optimum exchanger to fulfill this requirement? (Assume negligible inlet and outlet piping pressure drops.)

Given:

Tube Data:

3/4 in., 16 BWG, 1-in. triangular pitch
I.D. = 0.62 in.
Surface Area = 0.1963 ft^2/ft
Internal Tube Area = .302 $in.^2$
Vapor Density = 2.27 lb/ft^3
Liquid Viscosity = 0.1 cp
Liquid Specific Gravity = 0.43

Solution Steps

Heat balance:

Enthalpy of liquid at 228°F and 290 psia = 241 Btu/lb
Enthalpy of vapor at 228°F and 290 psia = 338 Btu/lb
Q = 40,800 (338 – 241) = 3,960,000 Btu/hr
Steam, 3,960,000/868 = 4570 lb/hr
Isothermal boiling, ΔT = LMTD = 353° – 228° = 125°F

Trial 1:

When establishing reboiler surface the first trial should always be taken for the maximum allowable flux (12,000 Btu/ft^2):

$$A_t = \frac{Q}{Q/A_t} = \frac{3{,}960{,}000}{12{,}000} = 330 \text{ ft}^2$$

Assume 16′0″ long tubes to reduce the shell diameter and provide the cheapest reboiler. However, the long tubes will also require the greatest elevation of the column.

$$\text{Number of tubes} = \frac{330}{(16)\,(0.1963)} = 105$$

Static pressure of reboiler leg (Eq 19-27):

Vapor density,

$$\rho_v = \frac{58}{(359)\,(688/492)\,(14.7/290)} = 2.28 \text{ lb/ft}^3$$

$$v_v = \frac{1}{2.28} = 0.44 \text{ ft}^3/\text{lb}$$

$$v_L = v_i = \frac{1}{(62.4)\,(0.43)} = 0.0373 \text{ ft}^3/\text{lb}$$

Weight flow of recirculated liquid = (4) 40,800
= 163,200 lb/hr

Total volume out of reboiler:

Liquid	(163,200)	0.0373	= 6,100 ft^3
Vapor	(40,800)	0.44	= 17,950 ft^3
Total			24,050 ft^3

$$v_o = \frac{24{,}050}{(163{,}200 + 40{,}800)} = 0.1179 \text{ ft}^3/\text{lb}$$

Static pressure of leg, (Eq 19-27)

$$\frac{Z_3\,\rho_{avg}}{144} = \frac{(2.3)\,16}{144\,(0.1179 - 0.0373)} \log \frac{0.1179}{0.0373}$$

$$= 1.59 \text{ psi}$$

Frictional resistance:

Flow area:

$$a_t = N_t \frac{a'_t}{144} = (105)\frac{0.302}{144} = 0.220 \text{ ft}^2$$

$$G_t = \frac{w}{a_t} = \frac{163{,}200 + 40{,}800}{0.220} = 927{,}273 \text{ lb/(hr} \cdot \text{ft}^2)$$

At 228°F, $\mu = (0.10)\,2.42 = 0.242$ lb/(ft • hr)

$$D' = \frac{0.62}{12} = 0.0517 \text{ ft}$$

$$Re = \frac{D'\,G_t}{\mu} = \frac{(0.0517)\,927{,}273}{0.242} = 198{,}100$$

$f = 0.000127 \text{ ft}^2/\text{in.}^2$

$$s_{avg} = \frac{[0.43 + (1/0.1179)\,/\,62.4]}{2} = 0.283$$

$$\Delta P_t = \frac{f\,G_t^2\,L}{(5.22)\,(10^{10})\,D s_{avg}}$$

$$= \frac{(0.000127)\,(927{,}273)^2\,(16)}{(5.22)\,(10^{10})\,(0.0517)\,(0.283)} = 2.29 \text{ psi}$$

Total resistance = 1.59 + 2.29 = 3.88 psi

Driving force, $\frac{Z_1\,\rho_L}{144} = (16)\,(0.43)\,(62.4/144) = 2.99$ psi

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The resistances are greater than the hydrostatic head can provide; hence the recirculation ratio will be less than 4:1. Of the resistances, the frictional pressure drop may be reduced by the square of the mass velocity if the tubes are made shorter. The other alternative is to raise the liquid level in the column above the upper tube sheet.

Trial 2:

Assume 12′0″ tubes and 4:1 recirculation ratio:

$$\text{Number of tubes} \cong 330 \text{ ft}^2 = \frac{330}{(12)\,(0.1963)} = 140$$

$v_i = 0.0373$ as before

$v_o = 0.1179$

Static pressure,

$$\frac{Z_3\,\rho_{avg}}{144} = \frac{(2.3)\,12}{144\,(0.1179 - 0.0373)} \log \frac{0.1179}{0.0373} = 1.19 \text{ psi}$$

Frictional resistance:

$$a_t = (140)\,\frac{0.302}{144} = 0.294 \text{ ft}^2$$

$$G_t = \frac{204{,}000}{0.317} = 694{,}000 \text{ lb/(hr} \cdot \text{ft}^2)$$

$$\text{Re} = \frac{(0.0517)\,694{,}000}{0.242} = 148{,}000$$

$f = 0.000135 \text{ ft}^2/\text{in.}^2$

$$\Delta P_t = \frac{(0.000135)\,(694{,}000^2)\,(12)}{(5.22)\,(10^{10})\,(0.0517)\,(0.285)} = 1.01 \text{ psi}$$

Total resistance = 1.19 + 1.01 = 2.20 psi

$$\text{Driving force,} \quad \frac{Z_1\,\rho_L}{144} = (12)\,(0.43)\,\frac{62.4}{144} = 2.24 \text{ psi}$$

Since the driving force is slightly greater than the resistances, a recirculation ratio better than 4:1 is assured.

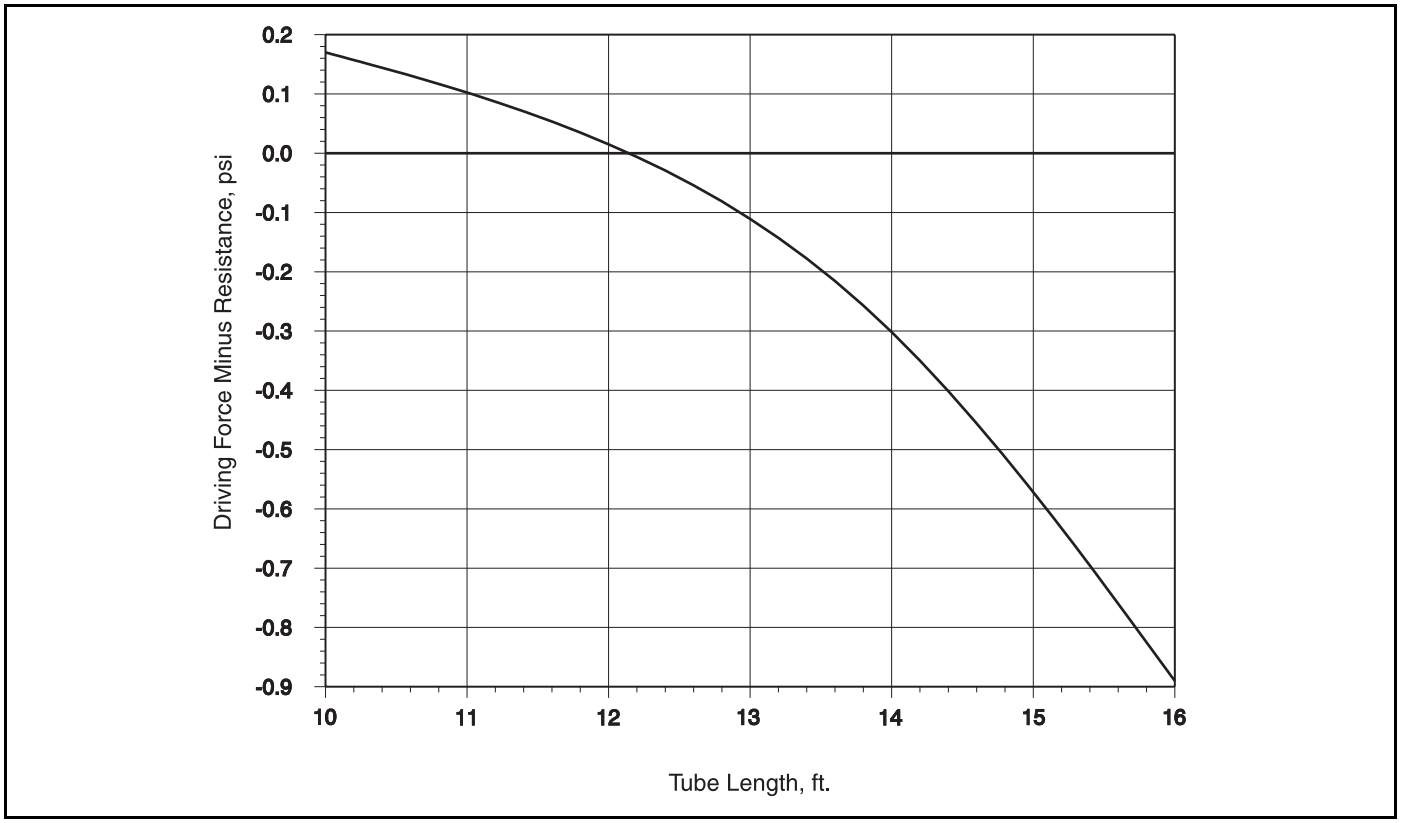
If the solution is not reached, a plot of ΔP (driving force – resistance), can be developed to determine the maximum length to achieve a pressure balance where the driving force exceeds the resistance. Fig. 19-33 shows a plot for this example at various lengths.

Horizontal Thermosyphon—The horizontal thermosyphon (Fig. 19-34) is similar in nature to the vertical thermosyphon reboiler. However, less skirt height is required to provide circulation head. It consists of centrally located inlet and outlet nozzles, a vertical support plate between the nozzles, and a horizontal longitudinal baffle. The liquid enters the bottom, flowing in two directions around the longitudinal baffle and back together at the outlet. Vapor disengagement takes place in the column. The horizontal thermosyphon can be natural or forced circulation.

Kettle Reboilers—Kettle reboilers are quite different in their configuration than other types (Fig. 19-35). Liquid from the bottom tray is gravity fed to the reboiler from a draw-off on the bottom of the column. A weir maintains the liquid level

Fig. 19-33

Thermosyphon Reboiler Driving Force Curve



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FIG. 19-34

Horizontal Thermosyphon Reboiler

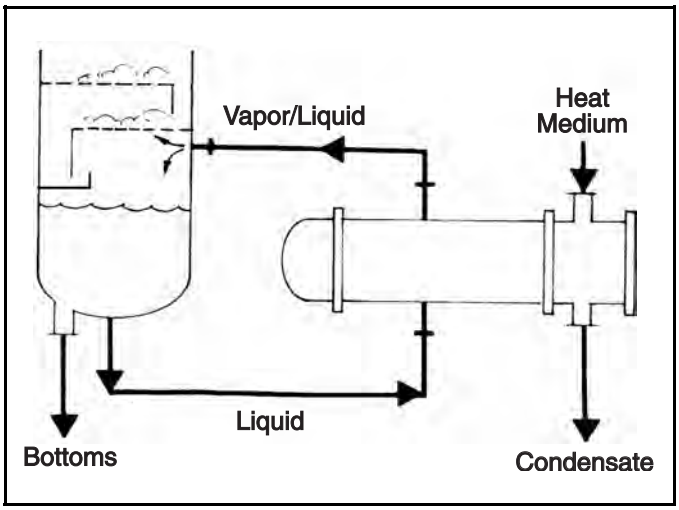


FIG. 19-35

Kettle Reboiler Arrangement

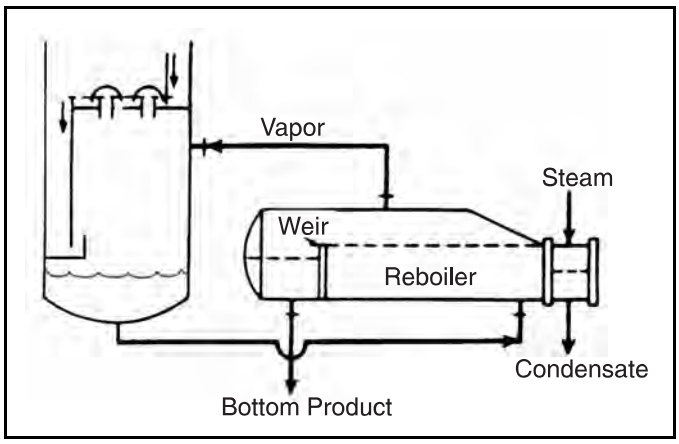
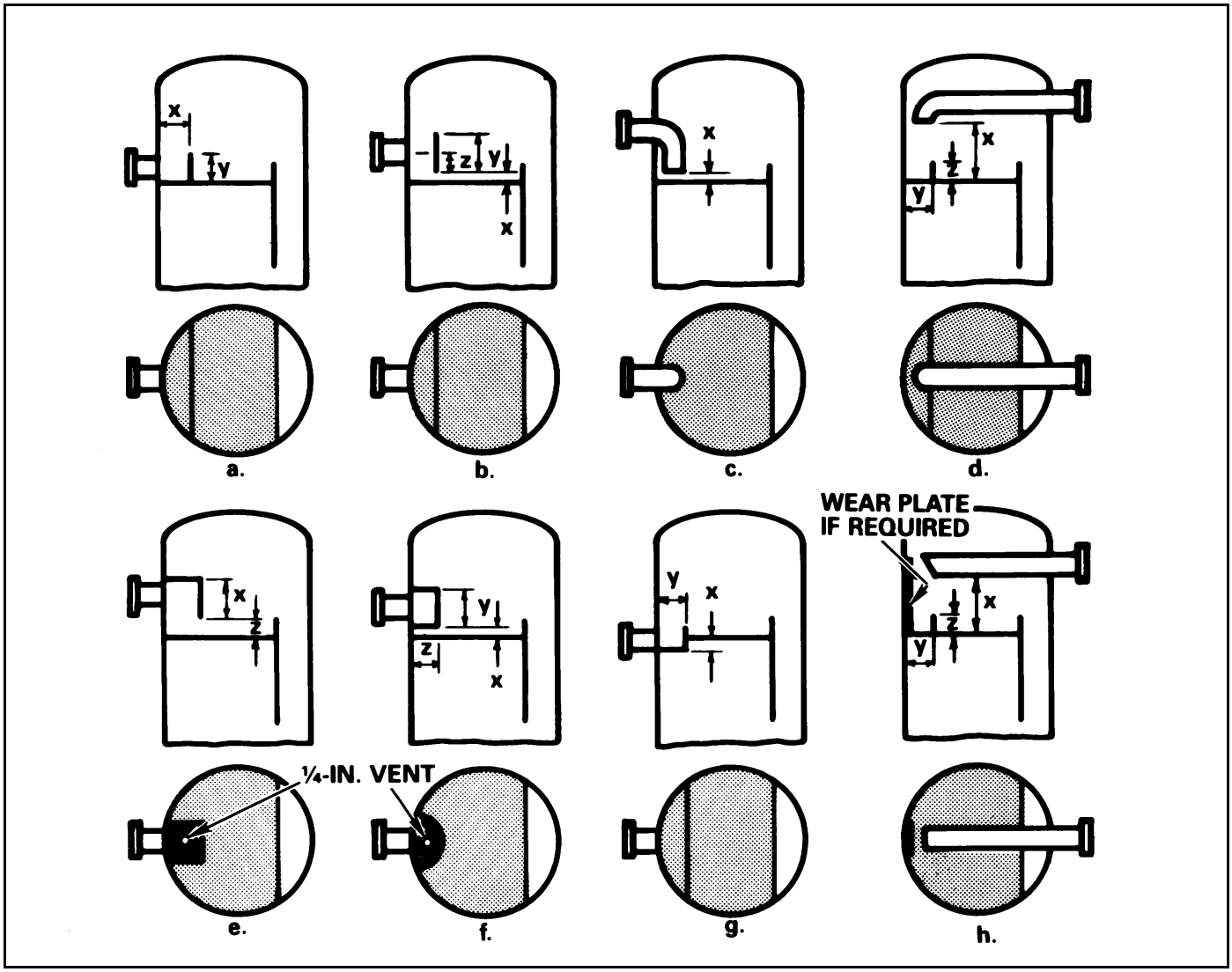


FIG. 19-36

Example Top Feed Nozzles[21]



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FIG. 19-37

Design Parameters for Top Feed Nozzles[21]

Dimensions for top feed/reflux inlet arrangements								
	See Fig. 19-36							
	a	**b**	**c**	**d**	**e**	**f**	**g**	**h**
Maximum nozzle dia., in.	6	–	–	6	–	–	6	–
Note	3	3	–	–	1	1	–	2
Pure-liquid feed								
Dimension x, in.	W_d	h_{cl}	$d_n/2$	>12	$2d_n$	$d_n/2$	4	>12
Dimension y, in.	4 to 6	$2d_n$	–	W_d	$2d_n$	$2d_n$	W_d	W_d
Dimension z, in.	–	d_n	–	4 to 6	d_n	$1.5d_n$	–	4 to 6
Vapor/liquid feed	NS		NS			NS	NS	
Dimension x, in.		$2d_n$		>12	$2d_n$			>12
Dimension y, in.		$2d_n$		W_d	$2d_n$			W_d
Dimension z, in.		d_n		4 to 6	$2d_n$			4 to 6

d_n = Inlet pipe dia., in.
h_{cl} = Clearance under downcomer, in.
W_d = Downcomer width, in.
NS = Not suitable

Note 1: Drill a ¼-in. vent hole on top.

Note 2: Wear plate may be required.

Note 3: Ensure nozzle enters behind the baffle. If it does not, hydraulic jump could be a problem.

Internal inlet pipes should be removable for maintenance.

in the reboiler such that the tube bundle is always submerged. Vapor disengaging space is provided in the exchanger. The vapor is piped back to the column to provide stripping vapor for the bottom tray. Bottom product is drawn from the reboiler.

Kettle reboilers are attractive due to the ease of control. No two-phase flow or circulation rate considerations are required. The kettle is also equivalent to a theoretical tray. Due to the vapor disengagement requirement, kettles are constructed with an expanded shell. The additional cost of this shell is offset to some extent by a reduced tower skirt requirement.

Column Internals

The most common causes of startup and operating problems are the column internals. These items are usually small details that are often overlooked and later become operating difficulties. Correct location and orientation of inlet and outlet nozzles and other internal considerations must be addressed to eliminate problems. Kister[21] presented a series of articles which discussed these areas in detail.

Top Feed Nozzles — Fig. 19-36 illustrates various arrangements used for top-tray feed and reflux nozzles. Fig. 19-37 lists factors and restrictions in each design. For cost reasons, arrangements of Fig. 19-36a, b, c, e, and f are preferred. However, for a two-phase stream only b, d, e, and h are suitable. Most installations use arrangement a or c for all-liquid feed while b and e are popular for a two-phase feed.

Tray sections and baffles that are contacted by an entering feed should be strengthened. Feed nozzles and internal liquid distributors should be anchored to the tower shell. Feed lines containing two phase flow should be designed to minimize slugging which causes column instability and possible tray damage. For liquid feeds, the nozzle velocity should not exceed 3 ft/sec.

Intermediate Feed Nozzles — Fig. 19-38 shows various methods for introducing intermediate column feeds. Fig.19-39 summarizes the application area for each design. Fig. 19-38a is only suitable for subcooled liquids. Vapor containing or hot feeds would cause flashing in the downcomer and loss of capacity. Fig. 19-38b is only suitable for low-velocity liquid feeds and is seldom recommended. Fig. 19-38c and d show a similar nozzle location with a baffle to direct the feed stream. These are both designed for two-phase streams with d being the preferred arrangement. Fig. 19-38c can be used for virtually any feed except for high velocity feeds where a baffle plate is added as in Fig. 19-38f.

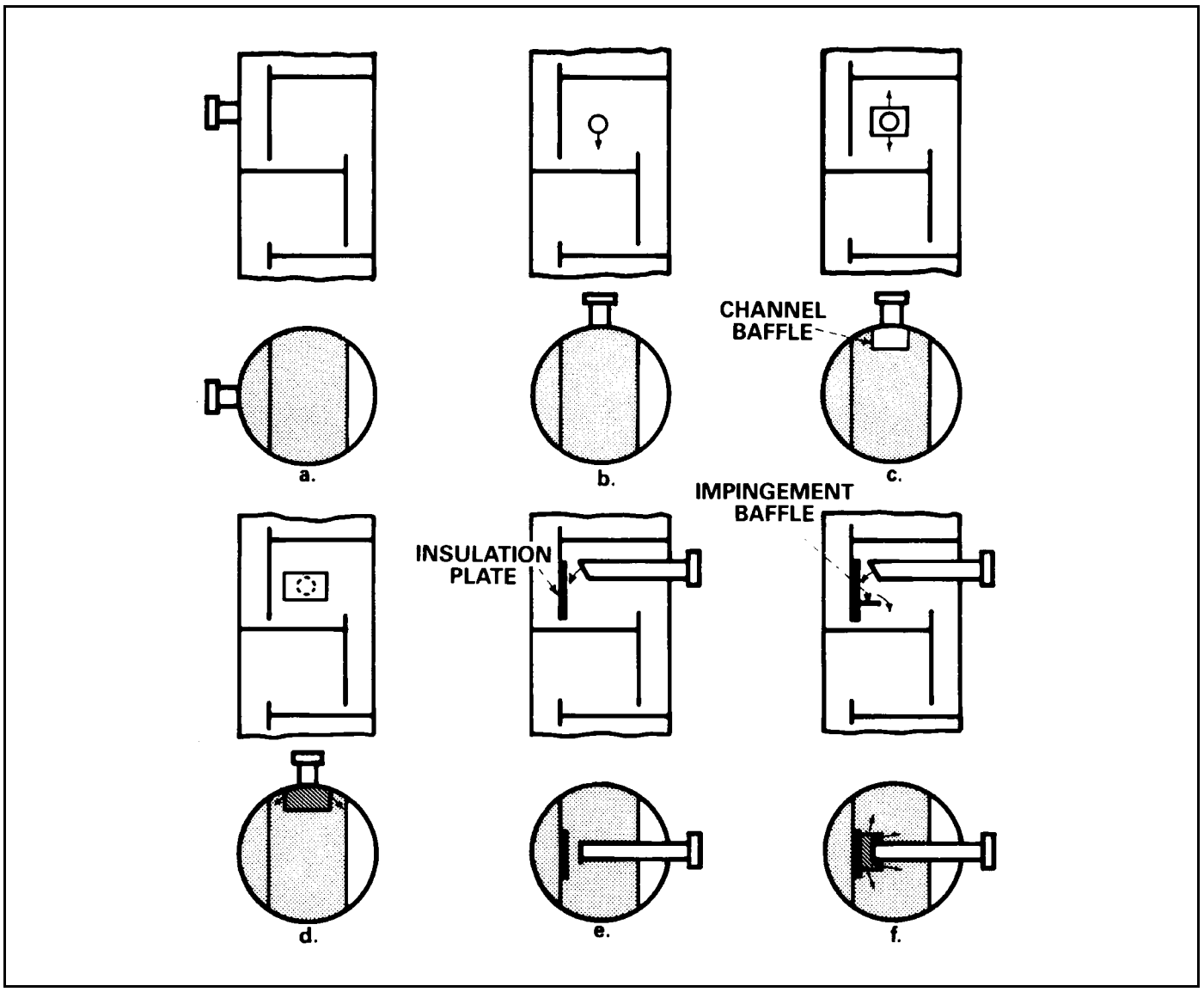
Bottom Vapor Inlet[22] — The optimum vapor inlet below the bottom tray is shown at location A in Fig. 19-40. The vapor is introduced parallel to the bottom downcomer at a recommended spacing of 24 in. below the bottom tray. A vapor inlet nozzle, causing impingement of the vapor stream against the downcomer and/or liquid overflow as shown by location B, should be provided with vapor inlet baffle or piping. The vapor velocity can be controlled by the hood outlet area. For multipass trays, it is very important to feed each compartment equally and allow for vapor equalization between sections.

Liquid Outlet — Sufficient residence time must be provided in the liquid draw-off sump. Fig. 19-41 presents recommended residence times for various situations. These guidelines are intended to provide sufficient times for vapor disengagement, to smooth out column upsets, and to give operating personnel time to correct operating problems. For

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FIG. 19-38

Example Intermediate Feed Nozzle Arrangements[21]



large residence time requirements, an external vessel should be considered in lieu of a large sump volume.

Bottom Sump Arrangements — A common design practice is to divide the bottoms sump into a reboiler-feed compartment and bottoms-drawoff compartment by installing a preferential baffle. Typical arrangements are shown in Fig. 19-42. The baffle has the advantage of providing an additional theoretical tray, supplying a constant head to the reboiler, and increasing the bottoms-outlet sump residence time. The installation of such a baffle is recommended when thermosyphon reboilers are used.

Each sump must have its own drainage facilities. This can frequently be achieved by drilling a hole through the baffle, or by using an external dump line at a low point to interconnect the liquid outlet lines from each compartment.

Either one of the arrangements shown in Fig. 19-42a or b is satisfactory. The arrangement of Fig. 19-42b has slightly better mass-transfer characteristics; however, it is somewhat more complicated than that of Fig. 19-42a. A baffle similar to that on the left-hand side of Fig. 19-42b can also be incorporated in arrangements such as shown in Fig. 19-42c and d.

The arrangement of Fig. 19-42d is preferable to that of Fig. 19-42c for two-pass trays. The latter forces the vapor to flow through a curtain of liquid while ascending to the first tray, which may cause entrainment or premature flooding.

Draw-off Arrangements—Total draw-off is normally accomplished with a chimney tray or draw pan as indicated in Fig. 19-43. The chimney tray has an advantage over the draw pan because it catches tray weepage during startup and at low vapor rates. Chimneys are normally sized for approximately 15% of tower area. The chimneys should be located or hooded to prevent liquid flow downward through the chimney. Elevating the draw nozzles flush with the draw tray in many cases eliminates the need for weep holes. A spill-over baffle can be provided for the draw pan to maintain tower circulation for

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FIG. 19-39

Intermediate Feed Nozzle Applications[21]

	See Fig. 19-38					
	a	b	c	d	e	f
Cold-liquid feed	Yes	Yes	Yes	Yes	Yes	Yes
Vapor/liquid feed	No	No	Yes	Yes	Yes	Yes
Vapor feed	No	No	Yes	Yes	Yes	Yes
Hot feed	No	Yes	Yes	Yes	Yes*	Yes*
High-velocity feed	No	No	No	Yes	No	Yes
High-pressure application	No	Yes	Yes	Yes	Yes	Yes
Downcomer capacity critical	No	Yes	Yes	Yes	Yes	Yes
*Assuming insulation plate is provided.						

cases where a draw-off may not be required during operation. A vortex breaker is suggested for outlet nozzles.

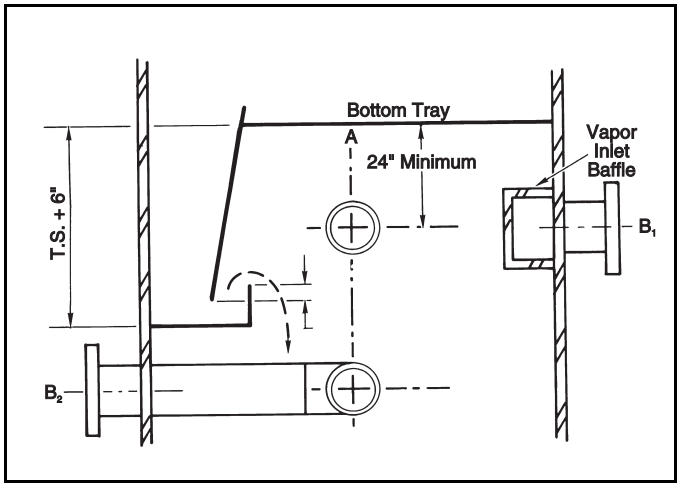
If the liquid on the chimney tray seals the downcomer from the tray above, particular care must be taken with the design of this downcomer. The liquid in the downcomer is aerated, while most of the liquid on the tray is degasified. The degasified liquid on the tray produces a greater hydrostatic head than the column of aerated liquid in the downcomer. This effect is aggravated if two phases are separated. If these effects are not allowed for, and sufficient height is not provided, downcomer backup may exceed the spacing between the liquid level and the tray above, and lead to premature flooding.

Fig. 19-44 shows two types of partial draw-off arrangements. When a chimney tray is used, a partition (sometimes insulated by application of two plates) can be provided to allow a draw-off and return on the same tray. Elevating the partition will determine total separation or recycling. The return nozzle should be located above the liquid level if vapor content is expected.

Partial draw from a recessed pan is frequently used. The draw pan saves shell length at the sacrifice of surge capacity. It is advisable to provide a positive downcomer seal.

FIG. 19-40

Bottom Vapor Inlet[22]



Water draw-off has been successfully accomplished by using the design shown in Fig. 19-45. The perforated plate normally contains 25% of the pan area as hole area. Water draw pans are usually sloped for multipass trays in large towers. A weld-in pan with a flush fitting draw nozzle is recommended.

Mechanical Design

Special care should be given to designing the trussing structure at heavily loaded areas, such as draw pan and draw trays where additional liquid levels are anticipated.

Where total draw-off arrangements are required, it is generally recommended that seal welding should be applied in lieu of gasketing, as gasketing may not maintain its sealing effectiveness at operating conditions. For large towers and higher temperatures, expansion joints should be provided. Good inspection can, in many cases, detect errors which could lead to column operation problems. It is, therefore, important

FIG. 19-41

Residence Time for Liquid in the Sump[21]

Operating condition	Minimum residence time, min
Liquid is withdrawn by level control and feeds another column directly by pressure.	2
Liquid is withdrawn by level control and pumped away. Spare pump starts manually.	3
Liquid is withdrawn by level control and pumped away. Spare pump starts automatically.	1
Liquid is withdrawn by level control and feeds a unit that is some distance away or that has its instruments on a different control board.	5-7
Liquid is withdrawn by flow control.	3-5
Liquid flows through a thermosyphon reboiler without a level controller, to maintain a level in the sump.	1

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FIG. 19-42

Example Baffle Arrangements for Bottom Sumps for Recirculating Reboilers[21]

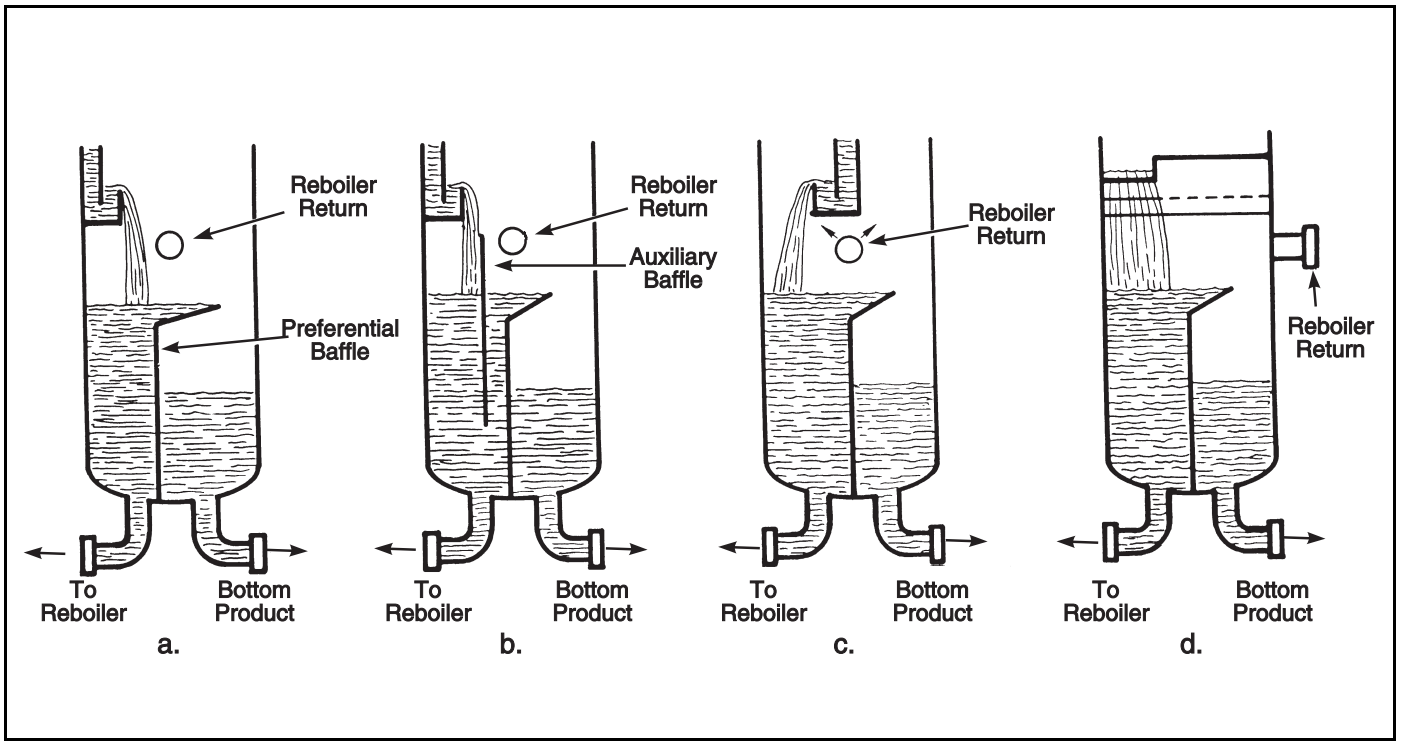
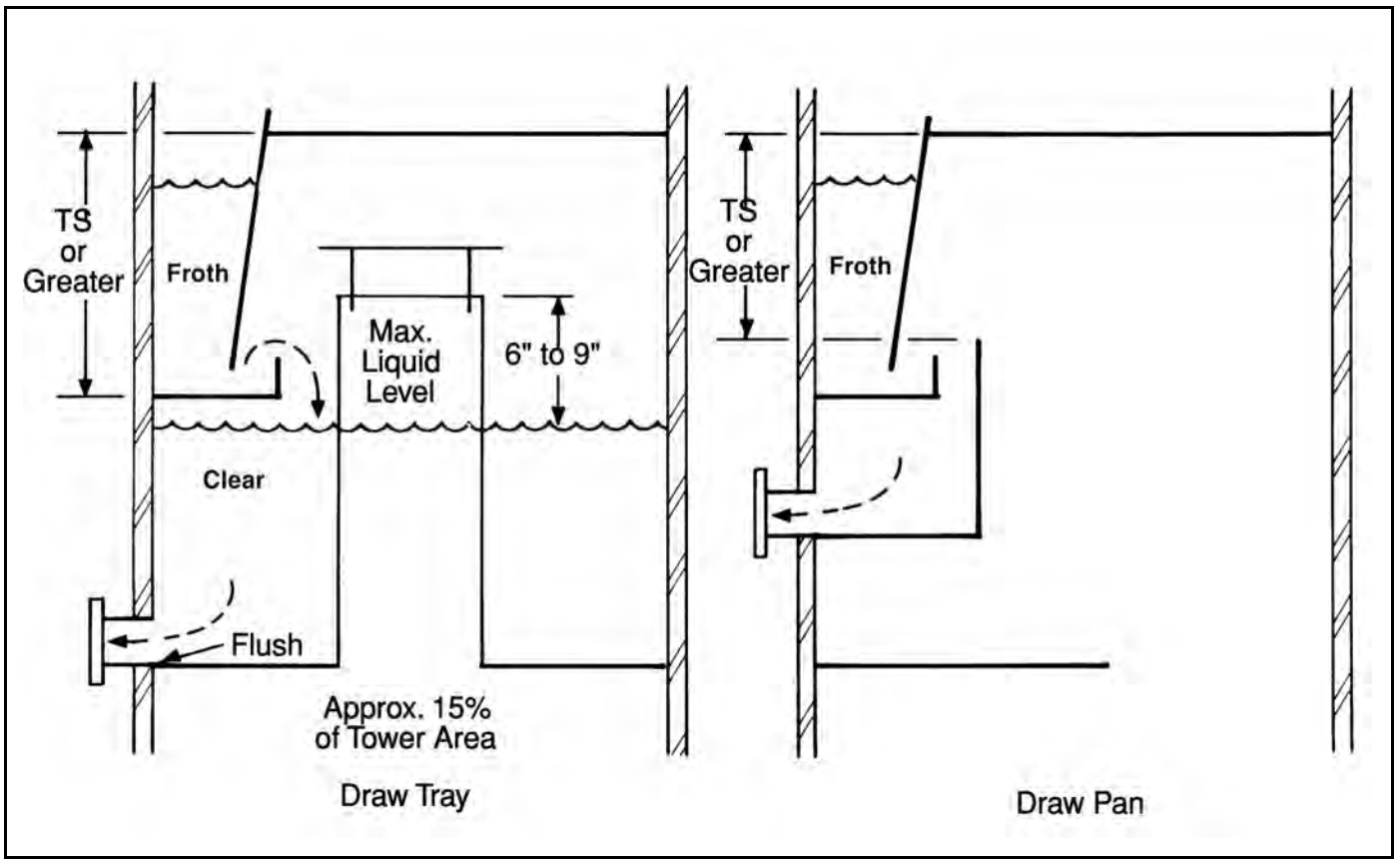


FIG. 19-43

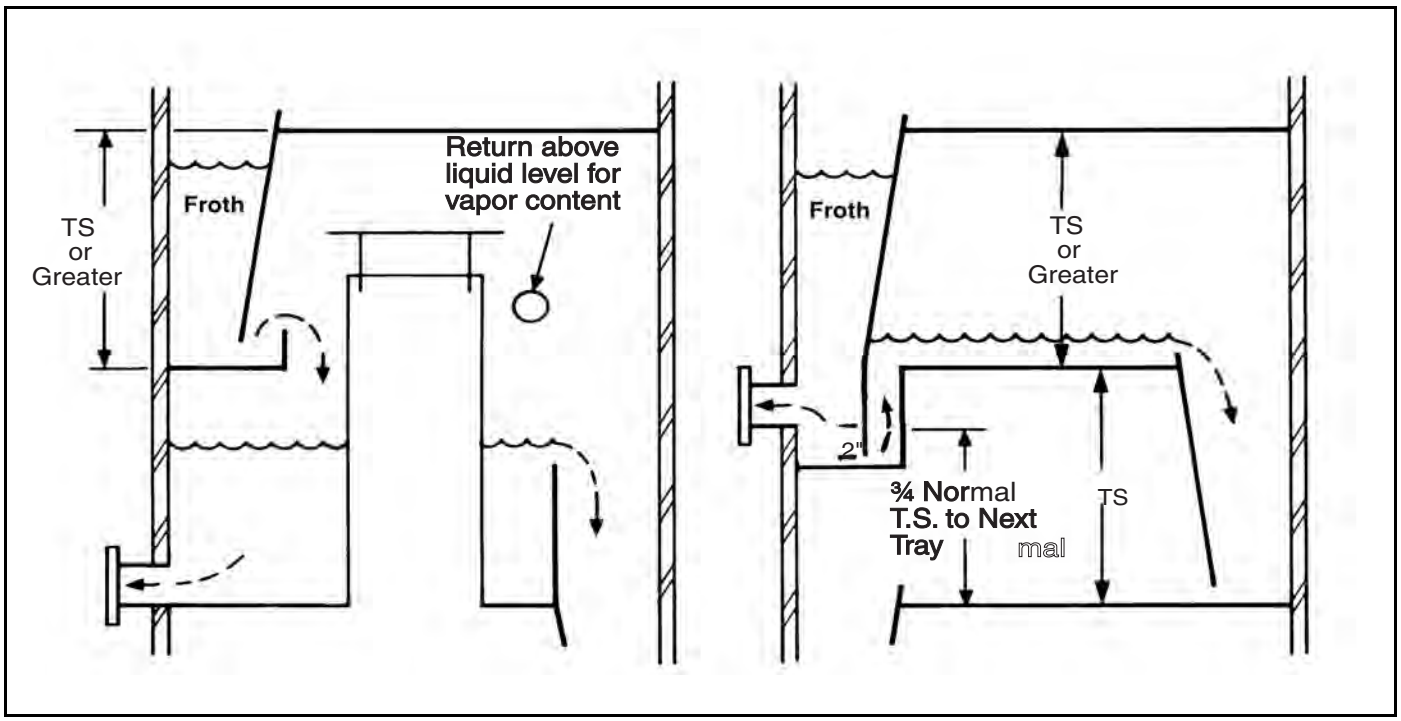
Example Total Draw-off[22]



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FIG. 19-44

Example Partial Draw-off[22]



that an inspector be well informed on internal design fundamentals including feed and draw-off arrangements. The following recommended inspection check list can be an invaluable tool for discovering errors and providing a record for future reference:

- Weir levelness
- Tray levelness
- Is hardware properly installed?
- Have correct materials been used (general spot check)?
- Are downcomers properly sealed to prevent vapor from escaping into downcomer area?
- Are nozzles oriented properly with respect to feed and draw-off requirements?
- All special internal designs as well as feed and draw nozzles should be checked for restrictions
- Are trays clean and clear of obstruction from foreign material?
- Are all internal parts secured?

FIG. 19-45

Example Water Draw-off[22]

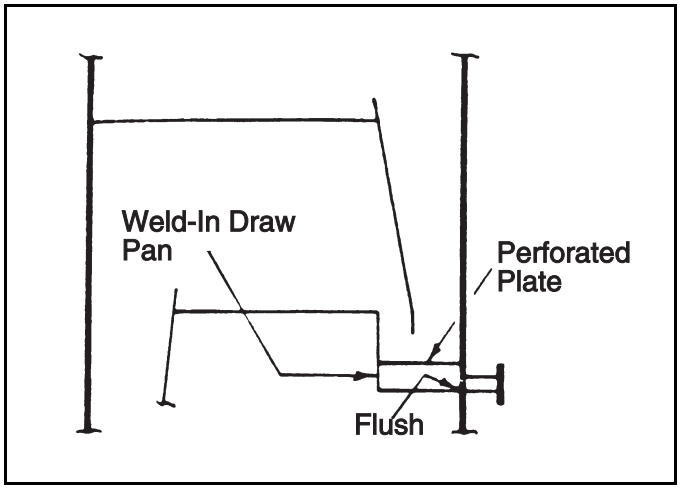
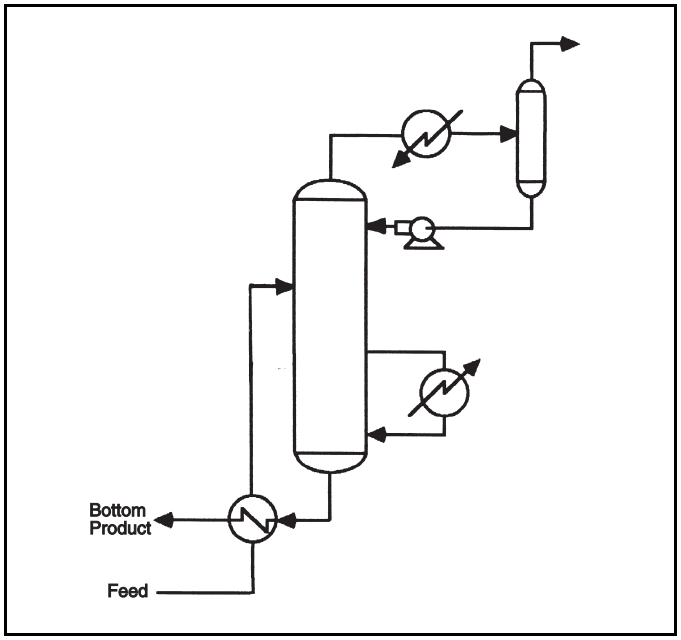


FIG. 19-46

Example Feed/Product Exchanger



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ENERGY EFFICIENT DESIGN CONSIDERATIONS

Fractionators require energy input in the form of heat to the reboiler. Regardless of the exact arrangement, fuel is often required and represents a major operating cost. Minimization of fuel usage is a common design goal.

To provide reflux for the fractionator, a utility is required to remove the heat to an appropriate heat sink. For columns utilizing air or water cooling, all the utilities use a common temperature heat sink. However, for columns using refrigeration, the temperature level is very important. A lower temperature refrigeration level increases both the capital and operating cost of a unit. If the condenser duty can be applied to a higher temperature system, considerable savings can be realized.

Feed/Product Exchangers

One of the simplest ways to reduce the reboiler fuel requirement is to preheat a liquid feed stream. This can be accomplished with a feed/product exchanger as shown in Fig. 19-46.

In general this heat input will decrease the reboiler duty. However, since the feed is now partially vaporized, the overhead condenser duty will tend to increase (see Eq 19-9). This increased condenser duty must be offset by reboiler duty. The net reboiler savings will be close to, but not equal to, the heat input to the feed. The net effect will depend on many system parameters; but feed/product exchange is generally an attractive heat conservation application.

Side Heaters

Side heaters (Fig. 19-47) can be used to add heat to a tower several trays up from the reboiler. Because of the temperature gradient in the column, this heat is applied at a much lower temperature than the reboiler. The heat source for this side heater can be any stream which requires cooling and is at a high enough temperature level to be useful. Often, the bottom product is used to side-heat the column. In cryogenic plants, the feed gas often supplies the reboil heat.

One penalty for side heating is the additional column height required for the liquid draw-off tray and vapor disengagement of the two-phase return stream. Typically, this will add about 6-8 feet to the column height.

For small amounts of side heat up to 25% of the reboiler duty, the side heater has little effect on the column design and condenser duty. As this heat is increased, the condenser duty will rise, requiring more total heat and/or more trays. In general, a good rule of thumb is to limit the side heat duty to no more than 50% of the total heat requirement.

One other possible benefit of side heating is that tower loading below the side heat tray is reduced. In many towers the bottom trays have the greatest loading. Judicious application of side heating can "smooth" the column vapor and liquid profiles in the lower section, reducing the required diameter.

Side Coolers/Condensers

Side coolers can be used to extract heat from a tower at an intermediate point above the feed tray. Due to the tower gradient this heat removal can be accomplished with a higher temperature cooling medium. This can be particularly attractive if the condenser uses refrigeration.

For large quantities of heat removal a side condenser can be effective. However, this is a bit more complicated than a single phase cooler. A side condenser requires a vapor draw-off and provision for a two phase return and separation section.

One place where side coolers are used is in absorber applications. The cooler draw-off is located in the middle part of the absorber to remove the heat of absorption from the liquid phase. This helps limit the temperature rise throughout the tower thus increasing absorption recovery.

Heat Pumping

One technique for energy conservation in fractionation systems is the use of a heat pump. Heat pumping usually employs an external working fluid as shown in Fig. 19-48. Compression is used to raise the temperature of the working fluid above that required for the reboiler. The fluid leaving the reboiler is then flashed and used to condense the reflux. The net result is that the heat absorbed in the condenser is used to reboil the column. The main operating cost then becomes the compressor rather than the normal heating and cooling utilities.

An alternative to the basic heat pump is to use the column overhead as the working fluid. This alternative, vapor compression, eliminates the overhead condenser (Fig. 19-49).

It is often difficult to find a working fluid to reboil and condense in a single fractionator. However, often plants have several fractionators with condensers and reboilers at a variety of temperatures. It may be possible to link a condenser and reboiler from separate columns to utilize a heat pump configuration.

Absorption

Absorption is one of the oldest unit operations used in the gas processing industry. Rich gas enters the bottom of the absorber and flows upward contacting the countercurrent lean oil stream. The lean oil preferentially absorbs the heavier components from the gas and is then termed "rich oil". The rich oil is sent to a stripper (or still) where the absorbed components are removed by heating and/or stripping with steam. The lean oil is recycled to the absorber to complete the process loop.

For a given gas, the fraction of each component in the gas that is absorbed by the oil is a function of the equilibrium phase relationship of the components and lean oil, the relative flow rates, and the contact stages. The phase relation is a function of pressure, temperature, and the composition of the lean oil. Nomenclature for an absorber is shown in Fig. 19-50.

As components are absorbed, the temperature of the gas and oil phases will increase due to heat of absorption. The heat released is proportional to the amount of gas absorbed. In many cases, side coolers are used on the absorber to limit the temperature rise and aid in absorption.

Lean oil will have a molecular weight in the 100 to 200 range. For ambient temperature absorbers, a heavy lean oil of 180 to 200 molecular weight will normally be used. For refrigerated absorbers, a lighter lean oil of 120 to 140 molecular weight is used. A lower molecular weight lean oil will contain more moles per gallon resulting in a lower circulation rate. However, lower molecular weight lean oil will have higher vaporization losses.

The stripping column is operated at low pressure and high temperatures. In older plants, "live" steam is injected into the bottom of the column to strip the NGL components. The steam lowers the partial pressure of the light hydrocarbons which is equivalent to lowering the effective operating pressure.

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Refrigerated lean oil plants normally use direct fired heaters to vaporize a portion of the rich oil in the stripper (still) to provide the necessary stripping vapor.

ABSORBER CALCULATIONS

Absorber and stripper calculations, like fractionation column calculations, can be accomplished with tray-by-tray computer models. However, hand calculations can be performed to estimate the absorption of components in a lean oil absorber. The stripping operation is essentially the reverse of absorption and can be handled in a similar fashion.

Many attempts have been made to define an "average" absorption factor method to short-cut the time consuming rigorous calculation procedures. The sole restriction of such a method is how well the average factor, as it is defined, will represent the absorption that actually occurs. One of the simplest definitions of an average absorption factor was by Kremser and Brown.[23, 24] They defined it as:

$$A = L_o/(K_{avg}V_{n+1}) \qquad \textbf{Eq 19-28}$$

or $$L_o = A\,(K_{avg})\,(V_{n+1}) \qquad \textbf{Eq 19-29}$$

Using an average absorption factor, the extraction of any component from a rich gas can be described by:

$$\frac{Y_{n+1} - Y_1}{Y_{n+1} - Y_o} = \frac{A^{n+1} - A}{A^{n+1} - 1} = E_a \qquad \textbf{Eq 19-30}$$

Fig. 19-48 provides a graphical solution of Eq 19-30.

FIG. 19-47

Example Side Heater

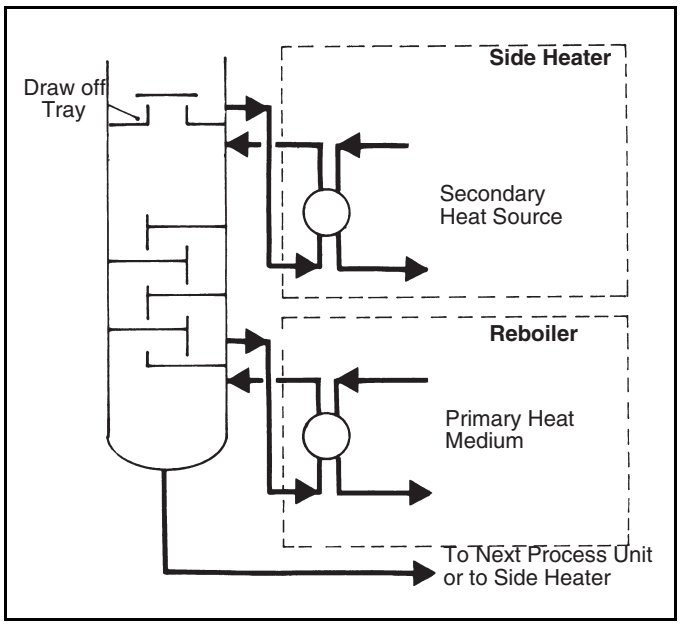


FIG. 19-48

Heat Pumping

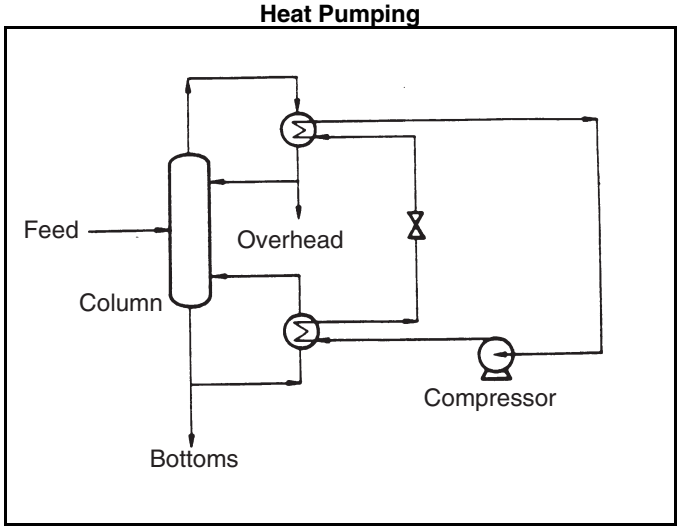


FIG. 19-49

Vapor Recompression

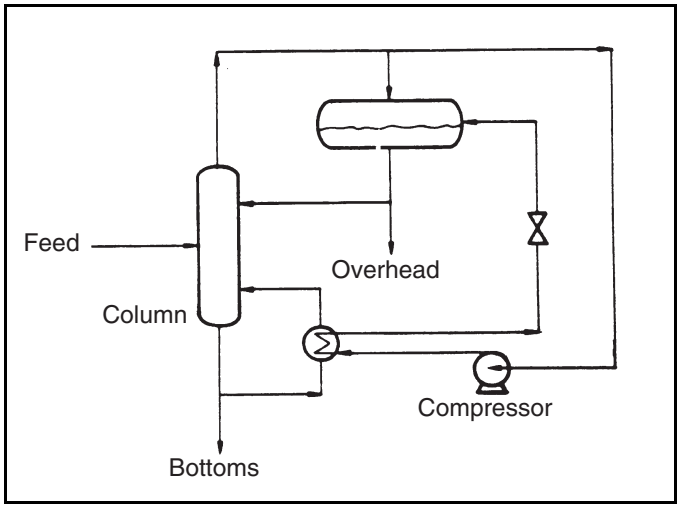
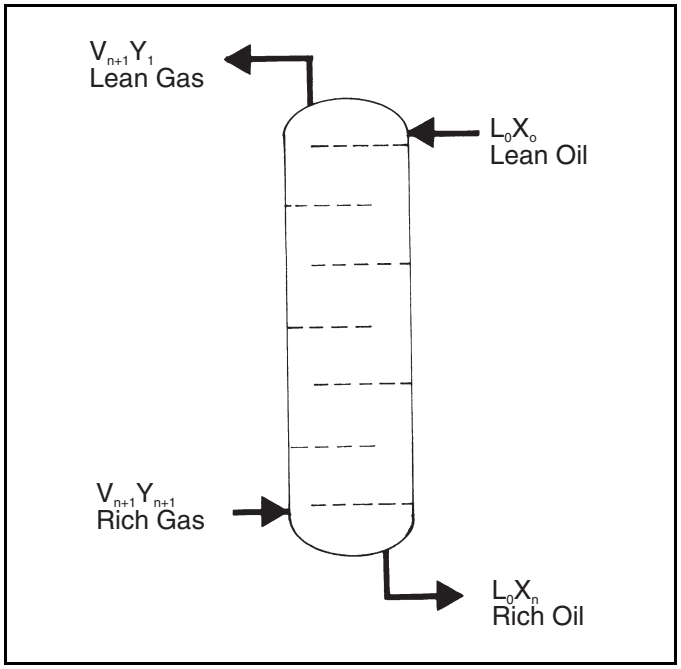


FIG. 19-50

Absorption Nomenclature



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Example 19-7 — Oil absorption is to be used to recover 75 percent of the propane from 100 moles of the rich gas stream shown below. The absorber is to have six theoretical plates. What oil circulation rate is to be used if the average temperature and pressure of the absorber are 104°F and 1,000 psig? The entering lean oil is assumed to be completely stripped or denuded of rich gas components. What will be the composition of the residue gas leaving the absorber?

Solution Steps

Using the equilibrium ratio charts (Section 25), obtain the K-value for each component at 104°F and 1,000 psig.

From Fig. 19-51 at $E_a = 0.75$, $A = 0.80$

Using Eq 19-29:

$$L_o = (0.8)(0.37)(100) = 29.6 \text{ moles/hr}$$

(based on 100 moles of gas)

Using Eq 19-28, the oil rate calculated and the component K-values determine the absorption factor "A" for the remaining components.

For example, for methane:

$$A = \frac{29.6}{3.25\,(100)} = 0.091$$

Using the absorption-factor values read values of E_a for each component (Fig. 19-51).

Solve Eq. 19-30 for each component to determine the moles of components in the residue gas, Y_1.

For example, for methane:

$$\frac{Y_{n+1} - Y_2}{Y_{n+1} - Y_o} = \frac{90.6 - Y_1}{90.6 - 0} = 0.091$$

$$Y_1 = 82.36$$

Note: For this example, $Y_o = 0$ since entering lean oil is assumed completely stripped of rich gas components. This assumption will not be true for all cases.

Calculate the moles of each component in the rich oil. For example, for methane:

$$I = Y_{n+1} - Y_1 + Y_o = 90.6 - 82.36 + 0 = 8.24$$

Comp	Mol %	K	A	E_a	Y_1	I
C_1	90.6	3.25	0.091	0.091	82.36	8.24
C_2	4.3	0.9	0.329	0.329	2.89	1.41
C_3	3.2	0.37	0.80	0.75	0.80	2.40
iC_4	0.5	0.21	1.41	0.96	0.02	0.48
nC_4	1.0	0.17	1.74	0.985	0.015	0.985
C_6	0.4	0.035	8.46	1.0	0.0	0.40
Total	100.0				86.085	13.915

The use of an average absorption factor, as defined in Eq 19-28, ignores the change in gas volume from inlet to outlet. Also, the assumptions of average temperature and K-values can cause significant errors in the preceding calculation method.

Fig. 19-51 can also be used to determine the trays required for a given lean oil rate or to calculate recoveries with a given oil rate and tray count. Fig. 19-51 shows that oil rate declines with increasing number of trays and that beyond about eight theoretical trays little increase in efficiency is achieved.

Since higher oil rates require more energy for heating, cooling, and pumping, the optimum design is usually one that uses the minimum possible oil rate with a reasonable size absorber.

The lowest molecular weight lean oil should be used. This will be fixed by oil vapor pressure and absorber operating temperature. Most problems in absorber operation center around oil quality and rates. Proper stripping of the oil is necessary to minimize lean oil losses to the gas and to maximize absorption capacity.

STRIPPER CALCULATIONS

In a calculation sense, a stripper is simply an upside-down absorber. For hand calculations, a stripping factor is defined as

$$S_T = \frac{KV}{L} \qquad \textbf{Eq 19-31}$$

then:

$$\frac{X_{m+1} - X_1}{X_{m+1} - Y_o} = \frac{S_T^{m+1} - S_T}{S_T^{m+1} - 1} = E_s \qquad \textbf{Eq 19-32}$$

Fig. 19-51 can be used to perform stripper calculations in a similar manner to absorber calculations.

SOUR WATER STRIPPERS

Sour water is a term used for water containing dissolved hydrogen sulfide. Facilities for processing sour gas may have several sources of sour water. These include water from inlet separators, water from compressor discharge scrubbers, quench water from certain Claus unit tail-gas cleanup processes, and water from the regeneration of solid bed product treaters or dehydrators. In some plants it is possible to dispose of this water by using it for makeup to the gas treating solution. However, most sour gas plants have an excess of water and the hydrogen sulfide must be removed to a level of 1 to 2 ppmw before disposing of the water. Sour water strippers are used for this purpose.

Sour water strippers commonly have 10 to 15 trays or 20 to 30 feet of packing. The feed enters at the top and heat is supplied either by a reboiler or by steam injection directly below the bottom tray. Typical operating conditions are:

Pressure, psig	10 - 15
Feed Temperature, °F	200 - 230
Bottom Temperature, °F	240 - 250
Reboil Heat, Btu/gal.	1000 - 2000
Residual H_2S, ppmw	0.5 - 2.0

Overhead vapors from sour water strippers contain hydrogen sulfide, steam, trace amounts of hydrocarbons and, in some plants, carbon dioxide. These vapors are usually sent to the regenerator (still) condenser in plants using aqueous treating solutions. Alternatively, the vapors may be sent directly to the sulfur recovery unit, or incinerated if emission standards are not exceeded.

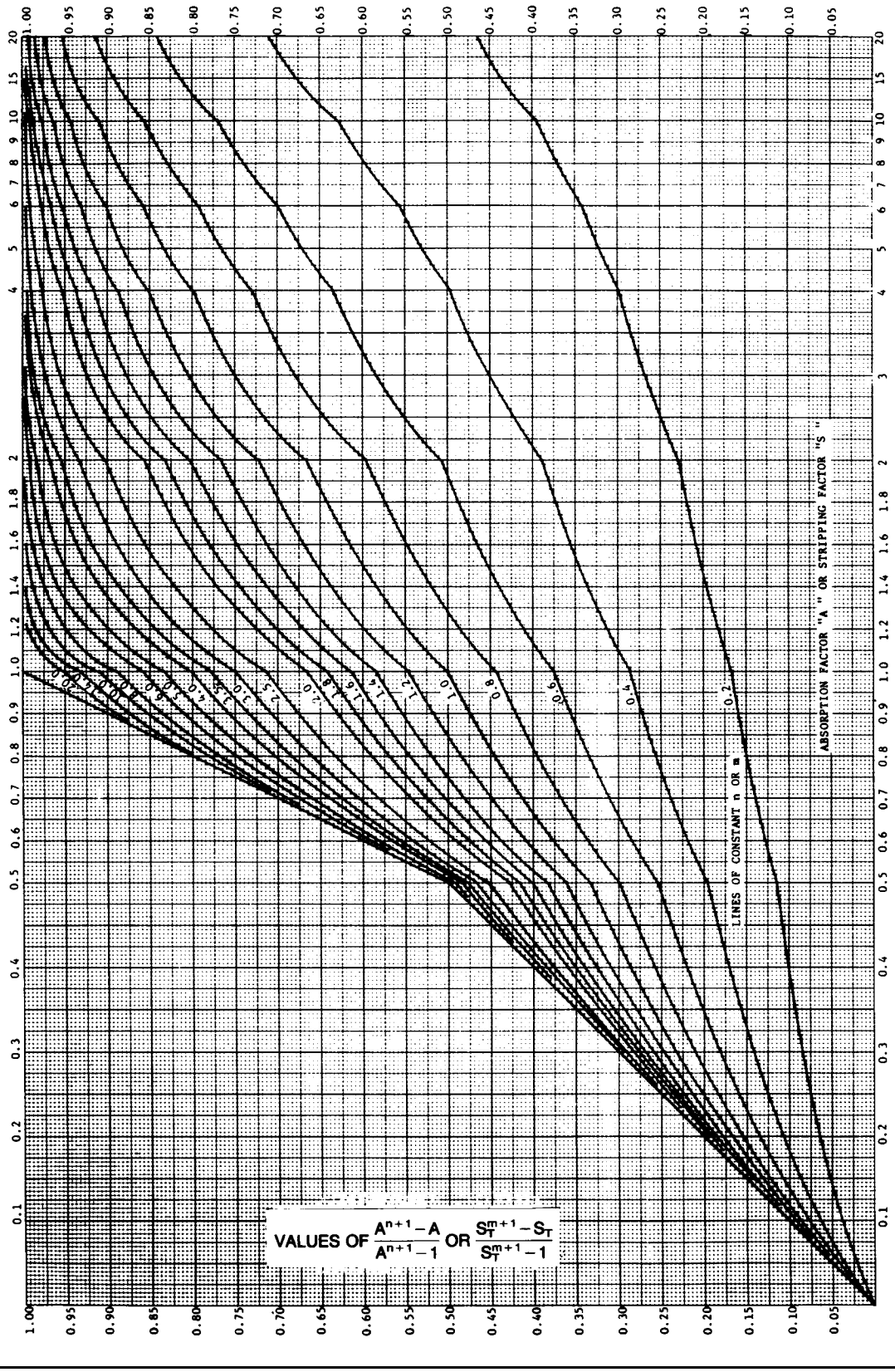
Foaming occurs in sour water strippers and the tower diameter should be based on operation at 50 to 70 percent of the flooding loads for a non-foaming system.[25]

The required number of theoretical trays and stripping vapor quantity can be calculated as shown in the following example. However, the results of such calculations must be used only as a guide to the relative effects of changing vapor rates

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FIG. 19-51

Absorption and Stripping Factor Correlation



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and trays. This is because tray efficiencies or packing HETPs are not known accurately and the effects of other components in the sour water change the apparent solubility of hydrogen sulfide. Ammonia, which is common in refinery sour waters, can increase the hydrogen sulfide solubility by a factor of 10 or more. A more detailed design procedure is then required for refining sour water strippers than that given in the following example.[26]

Example 19-8 — Sour water containing 2500 ppmw of hydrogen sulfide is to be stripped to 1.5 ppmw. Enough indirect reboiler heat is provided to allow 0.75 pounds of steam to leave the top tray for each gallon of feed. The feed rate is 10 gpm and the tower top is to operate at 21.0 psia. Determine the number of theoretical trays required.

Set desired overall material balance:

Feed = 10 gpm (8.33 lb/gal) (60 min/hr) = 5000 lb/hr

Overhead steam = 10 (60) 0.75 = 450 lb/hr

	Feed lb/hr	Bottoms lb/hr	Overhead lb/hr
H_2S	12.50	0.007	12.493
Water	4987.50	4537.500	450.000
	5000.00	4537.507	462.493

Required fraction of H_2S to be stripped:

12.493/12.50 = 0.99944

Estimate top temperature:

Fraction water vapor in overhead

450/462.493 = 0.973

Partial pressure water in overhead

0.973 (21) = 20.4 psia

Temperature (from steam table, Fig. 24-37) at 20.4 psia = 229°F

Estimate the K-value for H_2S at top conditions:

K = Henry's Constant/Total pressure

Henry's Constant for H_2S at 229°F = 2.05 (10^4) psia (Fig. 19-52)

K = 2.05 (10^4)/21.0 = 976.2

V = mols vapor leaving top tray

$$= \frac{12.493}{34} + \frac{450}{18} = 25.37$$

L = mols liquid to top tray

$$= \frac{12.5}{34} + \frac{4987.5}{18} = 277.5$$

Use Eq 19-31 to calculate fraction H_2S stripped:

$$S_T = \frac{(976)\,(25.37)}{277.5} = 89.2$$

$$E_s = \frac{S_T^{(m+1)} - S_T}{S_T^{(m+1)} - 1}$$

Assume various values for "m" and calculate "E_s":

Results are:

m	E_s
1	0.98891
2	0.99988
3	0.99999

Two theoretical trays would be required for the stated conditions. Since tray efficiencies or packing HETPs are not predictable, 10 actual trays or 20 feet of packing would be used.

The relative effect of various operating pressures and reboiler heat rates can be estimated by the above method.

FIG. 19-52

Henry's Constants for H_2S in Water

Temp, °F	H (H_2S), psia
100	1.10 (10^4)
200	1.82 (10^4)
300	2.6 (10^4)

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SECTION 20

Dehydration

Natural gas and associated condensate are often produced from the reservoir saturated (in equilibrium) with water. In addition, the gas and condensate often contain CO_2 and H_2S which might require removal. This is frequently accomplished with aqueous solutions such as amines, potassium carbonate, etc. which saturate the gas or condensate with water. Liquid hydrocarbons may also contain water downstream of product treaters or upon removal from underground storage.

Dehydration is the process used to remove water from natural gas and natural gas liquids (NGLs), and is required to:

- prevent formation of hydrates and condensation of free water in processing and transportation facilities,
- meet a water content specification, and
- prevent corrosion

FIG. 20-1

Nomenclature

A	=	area, ft^2
B	=	constant in Equation 20-11
C	=	constant in Equation 20-11
C_p	=	heat capacity, Btu/(lb • °F)
C_g	=	gravity correction factor for water content
C_s	=	salinity correction factor for water content
C_{ss}	=	saturation correction factor for sieve
C_T	=	temperature correction factor
D	=	diameter, ft
d	=	depression of the water dewpoint or the gas hydrate freezing point, °F
EOS	=	Equation of State
F_s	=	sizing parameter for packed towers, $\sqrt{\text{lb} / (\text{ft} \bullet \text{sec})}$
G	=	mass velocity, lb /(ft^2 • hr)
H	=	enthalpy, BTU/lb
ΔH	=	latent heat of vaporization, Btu/lb
K_{vs}	=	vapor/solid equilibrium K-value
L	=	length of packed bed, ft
L_g	=	glycol flow rate, U.S. gal./hr
L_{MTZ}	=	length of packed bed mass transfer zone, ft
L_s	=	length of packed bed saturation zone, ft
$\dot{m}$	=	mass flow rate, lb/hr
MTZ	=	mass transfer zone
MW	=	molecular weight
MW_I	=	molecular weight of inhibitor0
N	=	number of theoretical stages
P	=	pressure, psia
ΔP	=	pressure drop, psi
q	=	actual gas flow rate, ft^3/min
Q	=	heat duty, Btu/hr
Q_c	=	reflux condensing heat duty, Btu/gal.
Q_{hl}	=	regeneration heat loss duty, Btu
Q_r	=	total regeneration heat duty, Btu/gal.
Q_s	=	sensible heat, Btu/gal.
Q_{si}	=	duty required to heat mole sieve to regeneration temperature, Btu
Q_{st}	=	duty required to heat vessel and piping to regeneration temperature, Btu
Q_{tr}	=	total regeneration heat duty, Btu
Q_v	=	vaporization of water heat duty, Btu/gal.
Q_w	=	desorption of water heat duty, Btu
S_s	=	amount molecular sieve req'd in saturation zone, lb
t	=	thickness of the vessel wall, in.
T	=	temperature, °F
T_{rg}	=	regeneration temperature, °F
v	=	vapor velocity, ft/sec
V	=	superficial vapor velocity, ft/min
$\dot{w}$	=	water rate, lb/hr
W	=	water content of gas, lb/MMscf
W_{bbl}	=	water content of gas, bbl/MMSCF
W_r	=	water removed per cycle, lb
x	=	mole fraction in the liquid phase
X	=	mass fraction in the liquid phase
y	=	mole fraction in the gas phase
z	=	compressibility factor
γ	=	specific gravity
μ	=	viscosity, cp
ρ	=	density, lb/ft^3

Subscripts

i	=	inlet
o	=	outlet
l	=	liquid
v	=	vapor
t	=	total
CO_2	=	carbon dioxide
H_2S	=	hydrogen sulfide
HC	=	hydrocarbon
s	=	solid phase
L	=	lean inhibitor
R	=	rich inhibitor
I	=	inhibitor
H_2O	=	water
H	=	hydrate
rg	=	regeneration
f	=	feed
p	=	permeate

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Techniques for dehydrating natural gas, associated gas condensate and NGLs include:

- Absorption using liquid desiccants,
- Adsorption using solid desiccants,
- Dehydration with $CaCl_2$,
- Dehydration by refrigeration,
- Dehydration by membrane permeation,
- Dehydration by gas stripping, and
- Dehydration by distillation

WATER CONTENT OF GASES AND LIQUIDS

Water Solubility in Liquid Hydrocarbons

Fig. 20-2 shows the solubilities of water in sweet liquid hydrocarbons. It is based on experimental data developed in GPA RR 169.[49] In sour hydrocarbon liquids, water solubility can be substantially higher.

GPA RR-62[1] provides water solubility data for selected hydrocarbons in both sweet and sour systems. Equations-of-State (EOS) may be used to estimate water solubilities in hydrocarbon systems. GPA RR-42[2] provides a comparison of experimental versus calculated values using a modified Soave-Redlich-Kwong (SRK) EOS. Results from EOS methods should be used with caution and verified with experimental data when possible.

Fig. 20-3 gives hydrocarbon solubilities in water, which in general are considerably less than water in hydrocarbons. This figure is based on experimental data developed in GPA RR 169.[49] Some experimental data is available in GPA RR-62. Yaws, *et. al.*[3] provide a general correlation which may be used to estimate the solubility of over 200 hydrocarbons in water.

Water Content of Natural Gases

The saturated water content of a gas depends on pressure, temperature, and composition. The effect of composition increases with pressure and is particularly important if the gas contains CO_2 and/or H_2S. For lean, sweet natural gases containing over 70% methane and small amounts of heavy hydrocarbons, generalized pressure-temperature correlations are suitable for many applications. Fig. 20-4[4] is an example of one such correlation which has been widely used for many years in the design of "sweet" natural gas dehydrators. It was first published in 1958 and was based on experimental data available at that time. The gas gravity correlation should never be used to account for the presence of H_2S and CO_2 and may not always be adequate for certain hydrocarbon effects, especially for the prediction of water content at pressures above 1500 psia. The hydrate formation line is approximate and should not be used to predict hydrate formation conditions.

Fig. 20-5 extends Fig. 20-4 from 300 to 400°F. This is based on data in the high-temperature region published by Olds et. al.[50]

The following examples are provided to illustrate the use of Figs. 20-4 and 20-5:

Example 20-1 — Determine the saturated water content for a sweet lean hydrocarbon gas at 150°F and 1,000 psia.

From Fig. 20-4 or Fig. 20-5

$$W = 220 \text{ lb/MMscf}$$

For a 26 molecular weight gas,

$$C_g = 0.98 \quad \text{(Fig. 20-4)}$$

$$W = (0.98)(220) = 216 \text{ lb/MMscf}$$

For a gas in equilibrium with a 3% brine,

$$C_s = 0.93 \quad \text{(Fig. 20-4)}$$

$$W = (0.93)(220) = 205 \text{ lb/MMscf}$$

Water Content of High CO_2/H_2S Gases

Both H_2S and CO_2 contain more water at saturation than methane or sweet natural gas mixtures. The relative amounts vary considerably with temperature and pressure. Fig. 20-6[7] and 20-7[6] display saturated water content of pure CO_2 and H_2S, respectively, at various temperatures and pressures. Fig. 20-8 shows the saturated water contents of pure CH_4, CO_2 and selected mixtures vs. pressure at 100°F. Fig. 20-9[5] exhibits the saturated water content of pure CH_4, CO_2 and a 95% CO_2 – 5% CH_4 mixture vs. pressure at 100°F. Several significant observations can be made from these figures and other available data.

1. Saturated water content of pure CO_2 and H_2S can be significantly higher than that of sweet natural gas, particularly at pressures above about 700 psia at ambient temperatures.
2. Corrections for H_2S and CO_2 should be applied when the gas mixture contains more than 5% H_2S and/or CO_2 at pressures above 700 psia. These corrections become increasingly significant at higher concentrations and higher pressures.
3. The addition of small amounts of CH_4 or N_2 to CO_2 or H_2S can dramatically reduce the saturated water content compared to the pure acid gas.

Acid gas water content is a very complex subject. The data and methods presented here should not be used for final design. Fig. 20-6, 20-7, 20-8 and 20-9 are all based on experimental data. A cursory study of these figures reveals the complexities involved. An accurate determination of water content requires a careful study of the existing literature and available experimental data. In most cases additional experimental data is the best way to verify predicted values. Even the most sophisticated EOS techniques may give results of questionable reliability.

Below 40% acid gas components, one method of estimating the water content uses Eq 20-1 and Fig. 20-4, 20-10, and 20-11.[8]

$$W = y_{HC} W_{HC} + y_{CO_2} W_{CO_2} + y_{H_2S} W_{H_2S} \qquad \textbf{Eq 20-1}$$

Note that Fig. 20-10 and 20-11 provide values for what is termed the "effective" water content of CO_2 and H_2S in natural gas mixtures for use only in Eq 20-1. These are not pure CO_2 and H_2S water contents.

Another method for estimation of the saturated water content of acid gas mixtures up to 10,000 psia uses Fig. 20-12, 20-13, and 20-14.[9] With gases containing CO_2, the CO_2 must be converted to an "equivalent" H_2S concentration. For purposes of this method, it is assumed the CO_2 will contribute 75% as much water to the gas mixture, on a molar basis, as H_2S.

Water contents for pressures in between the values in the figures (for example at pressure P_{bbl} between pressures P_{bbl1} and P_{bbl2}) can be determined by plotting on log-log paper or by logarithmic interpolation using the following equation:

$$\log (W_{bbl}) = \log (W_{bbl1}) + (\log(W_{bbl2}/W_{bbl1})) \cdot (\log (P_{bbl}/P_{bbl1})) / (\log(P_{bbl2}/P_{bbl1}) \qquad \textbf{Eq 20-2}$$

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A third method is Fig. 20-15.[51] The CO_2 is converted to equivalent H_2S as for the second method, but the factor is 70% instead of 75%.

Example 20-2 — Determine the saturated water content of an 80% C_1, 20% CO_2 mixture at 160 °F and 2000 psia. The experimentally determined water content was 172 lb/MMscf.

Method One

W_{HC} = 167 lb/MMscf (Fig. 20-4)

W_{CO_2} = 240 lb/MMscf (Fig. 20-11)

W = (0.80)(167) + (0.20)(240)

= 182 lb/MMscf

Method Two

First the composition must be converted for use with Fig. 20-12.

y_{H_2S} (pseudo) = (0.75)(y_{CO_2}) = (0.75)(0.20) = 0.15

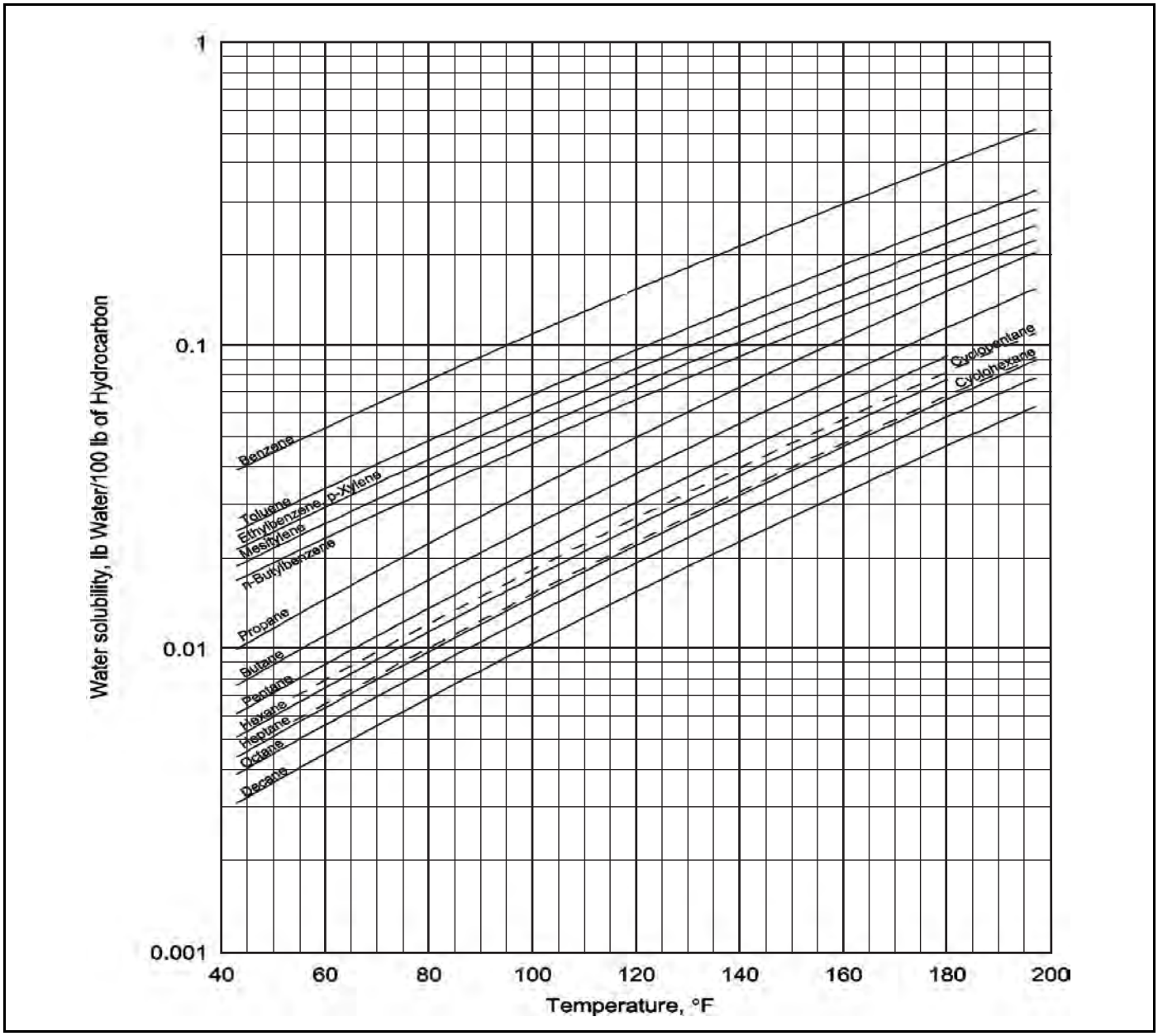
W = 0.49 bbl/MMscf (Fig. 20-12)

Density of water = 350 lb/bbl

= (0.49)(350) = 172 lb/MMscf

FIG. 20-2

Solubility of Water in Liquid Hydrocarbons



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Method Three

First the composition must be converted for use with Fig. 20-15.

y_{H_2S} (pseudo) = 0.70 (y_{CO_2}) = 0.70(0.20) = 0.14

Enter the left side of Fig. 20-15 at 160°F and move to the % H_2S Equivalent line (14%). Proceed vertically upward to the Pressure, psia line (2000 psia), and move horizontally to the left to Water Content Ratio scale (ratio of 1.16).

W = (1.16)(167) = 194 lb/MMscf

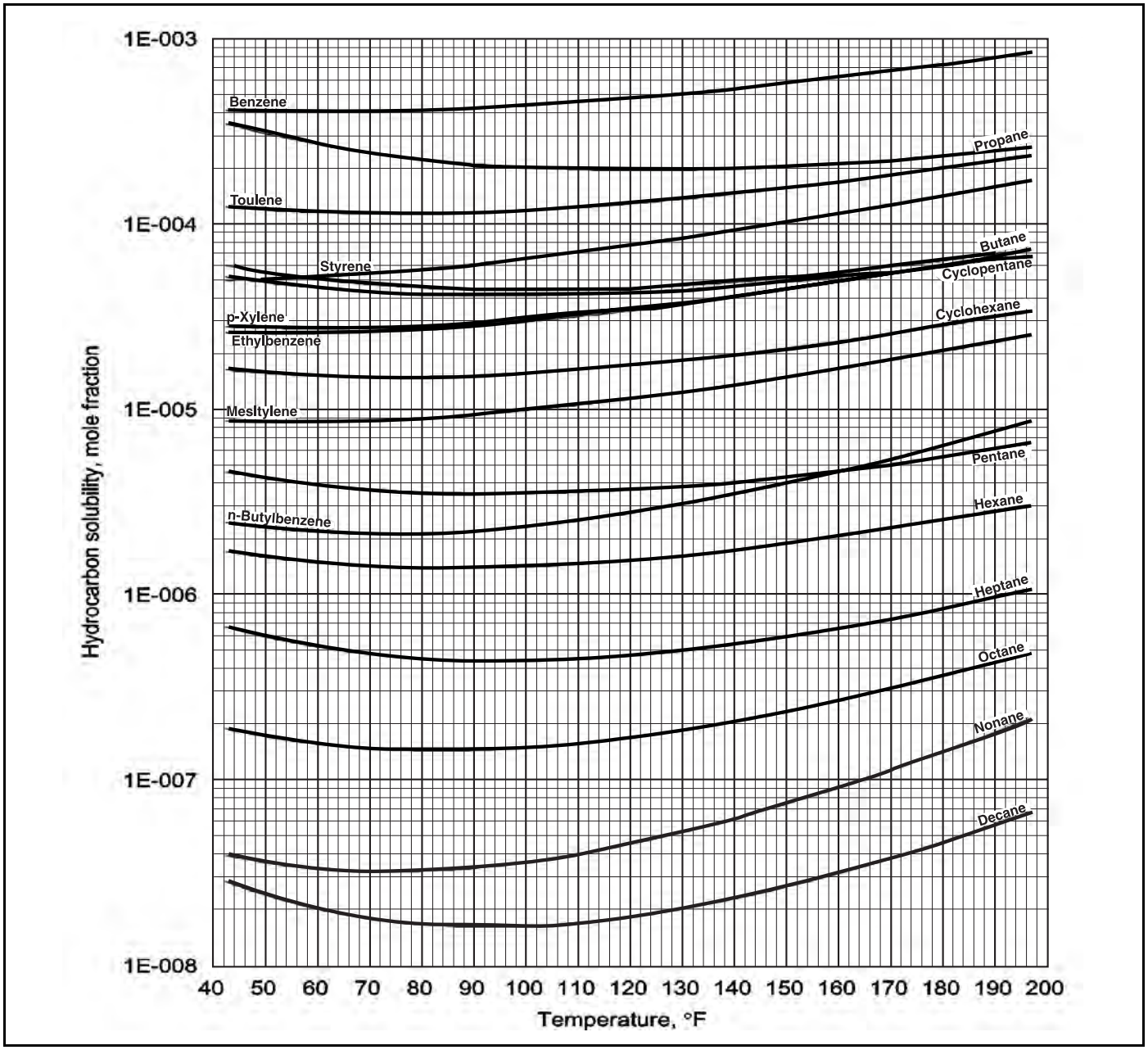
Fig. 20-16 compares the three methods presented for saturated water content determination of high CO_2/H_2S gas mixtures with some of the available experimental data. The last four data points shown in Fig. 20-16 indicate the dangers involved with extrapolation to higher CO_2 or H_2S contents. In one case, the estimated water content agrees within 11% of the experimental value. In another case, the experimental value is over 6 times the estimated water content.

Water Content in the Hydrate Region

Fig. 20-4 is based on the assumption that the condensed water phase is a liquid. However, at temperatures below the hydrate temperature of the gas, the "condensed" phase will be a solid

FIG. 20-3

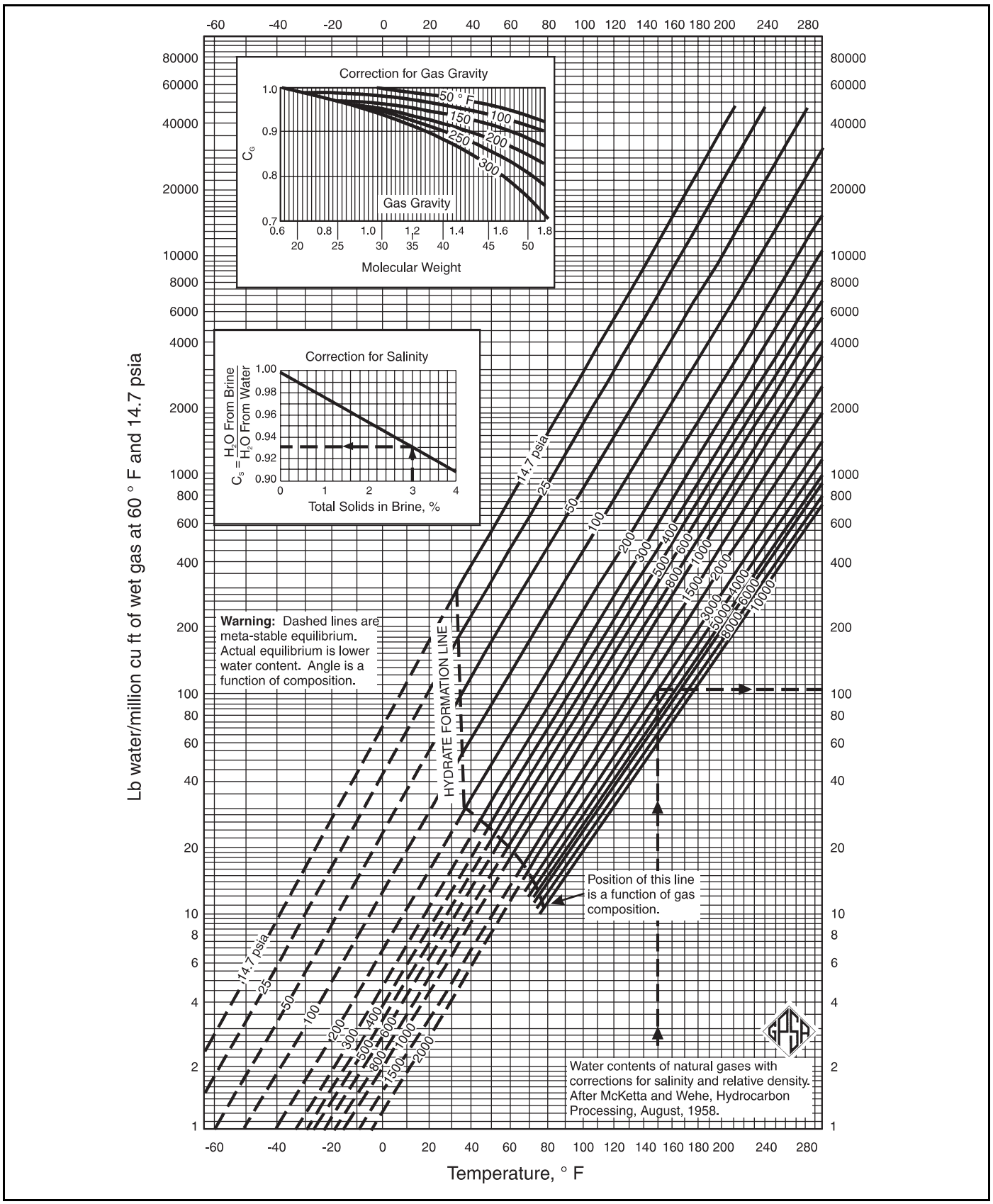
Solubility of Hydrocarbons in Water



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FIG. 20-4

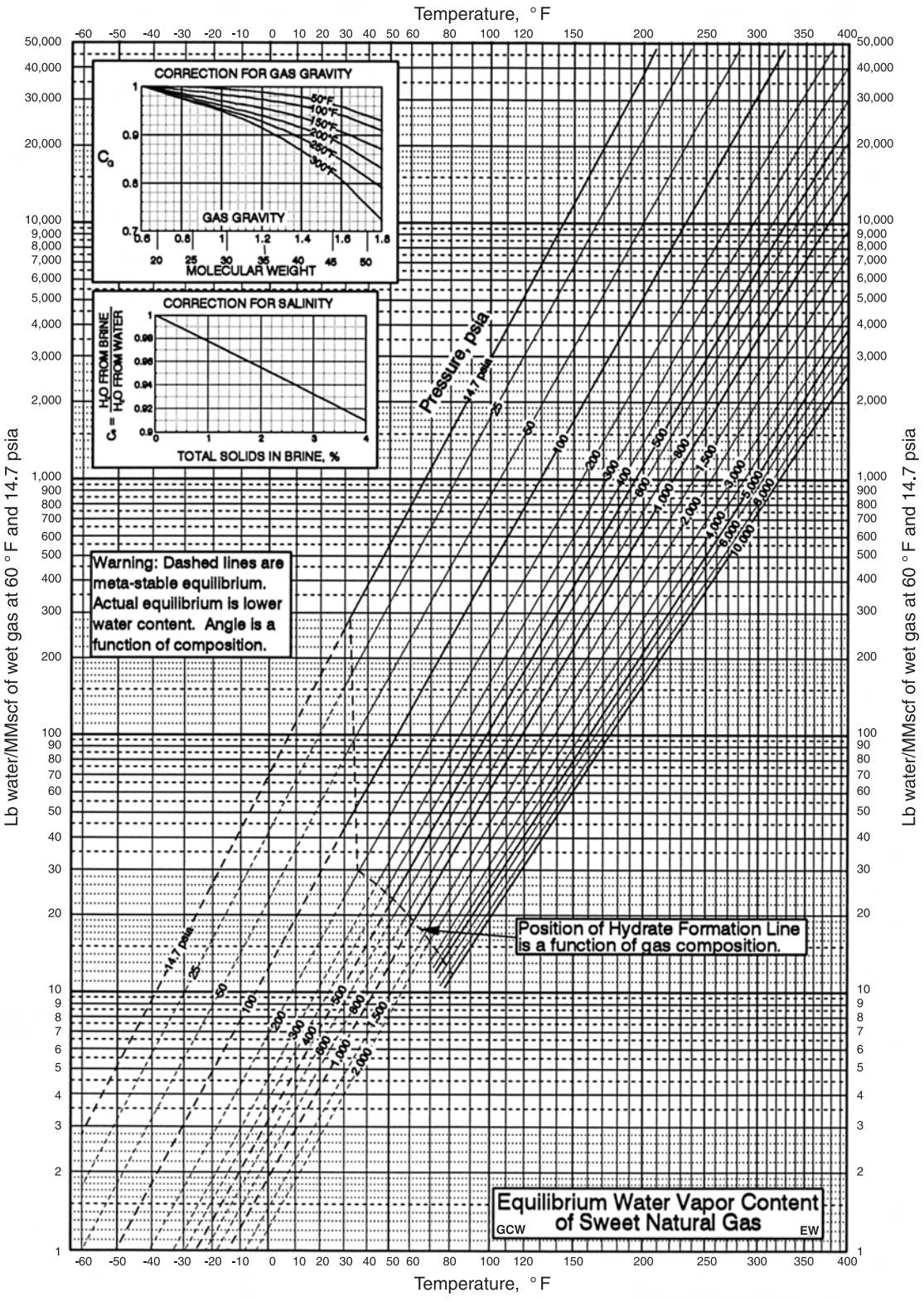
Water Content of Hydrocarbon Gas



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FIG. 20-5

Water Content of Hydrocarbon Gas



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FIG. 20-6

Water Content of CO_2

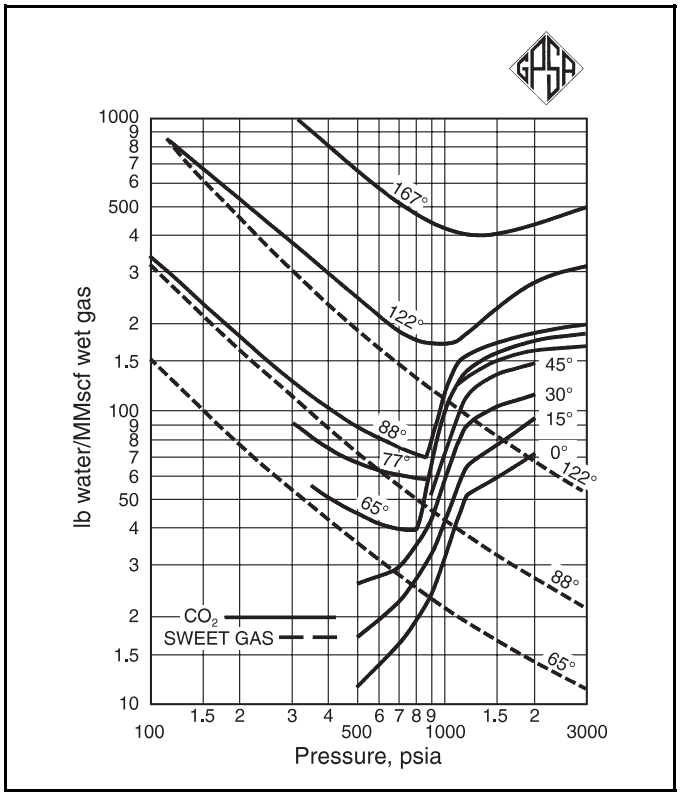


FIG. 20-8

Experimental Values for Water Content of Acid Gases

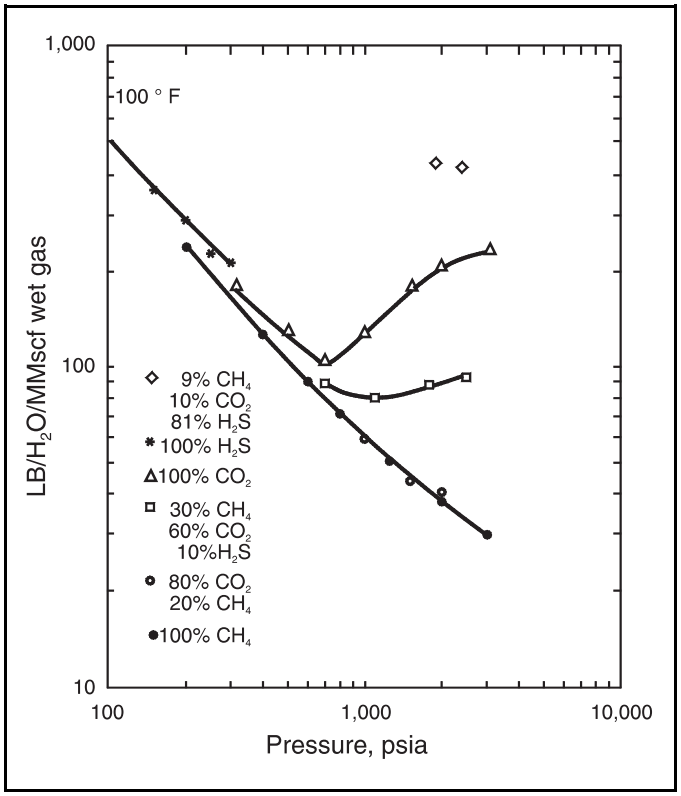


FIG. 20-7

Water Content of Hydrogen Sulfide

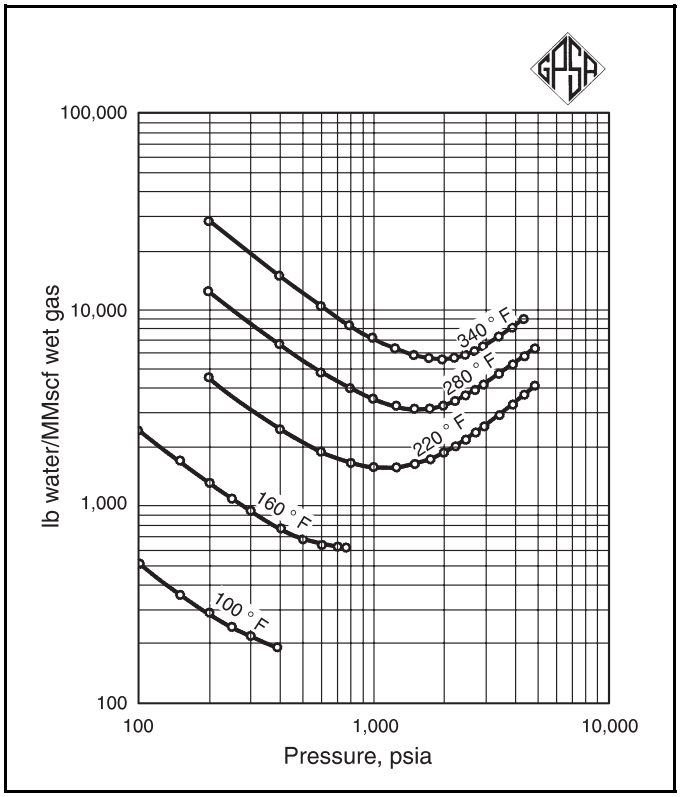
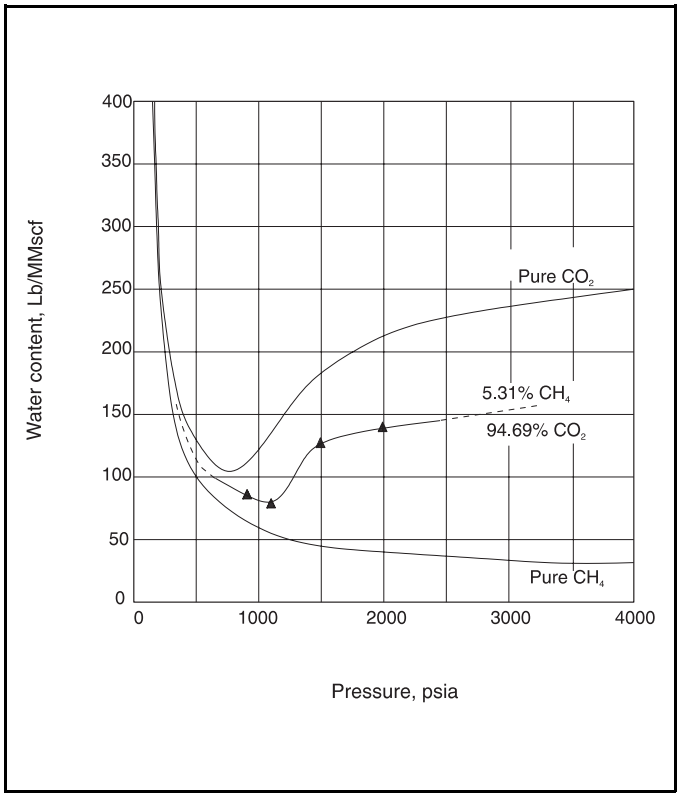


FIG. 20-9

Saturated Water Content of CO_2 - Rich Mixtures at 100°F



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FIG. 20-10

Effective Water Content of H_2S in Natural Gas Mixtures vs. Temperature at Various Pressures

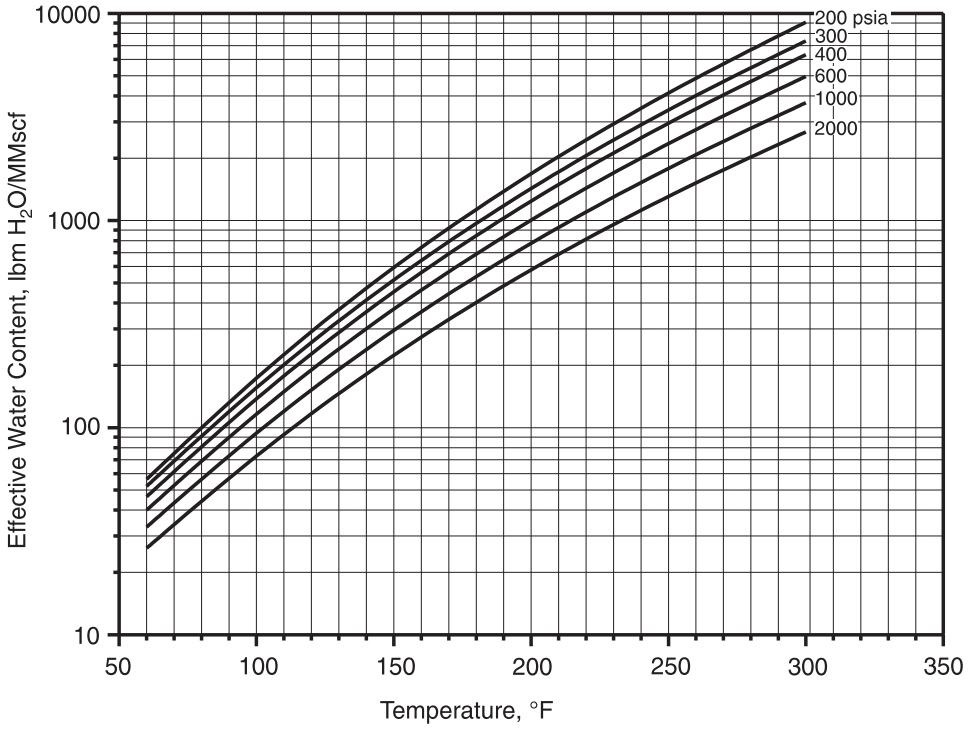
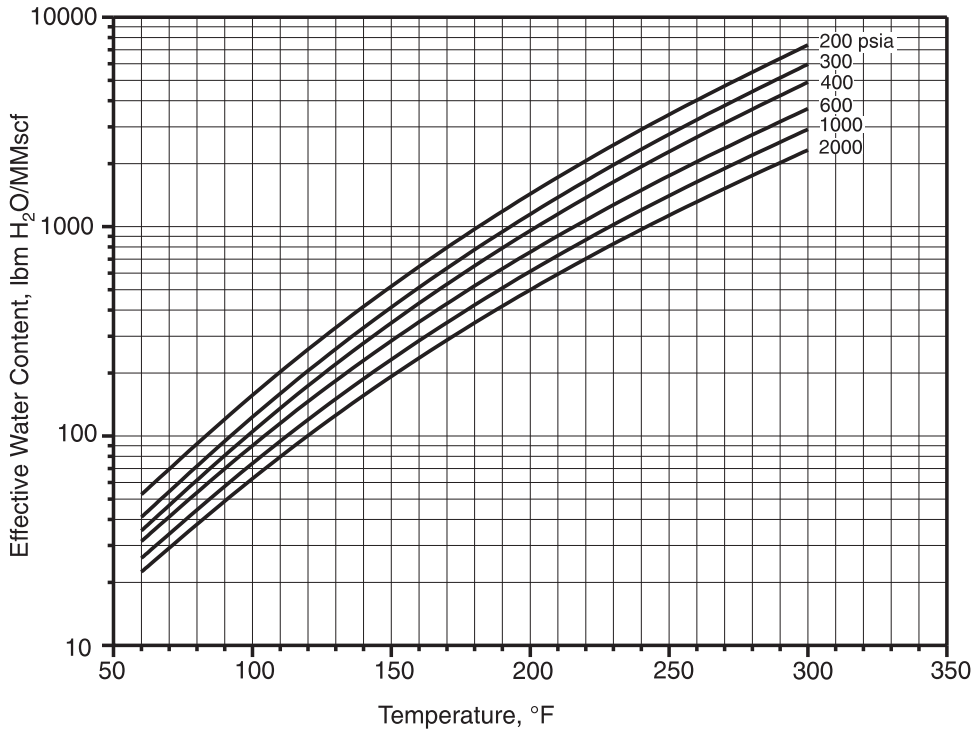


FIG. 20-11

Effective Water Content of CO_2 in Natural Gas Mixtures vs. Temperature at Various Pressures



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FIG. 20-12

Calculated Water Content of Acid Gas Mixtures to 2000 psia

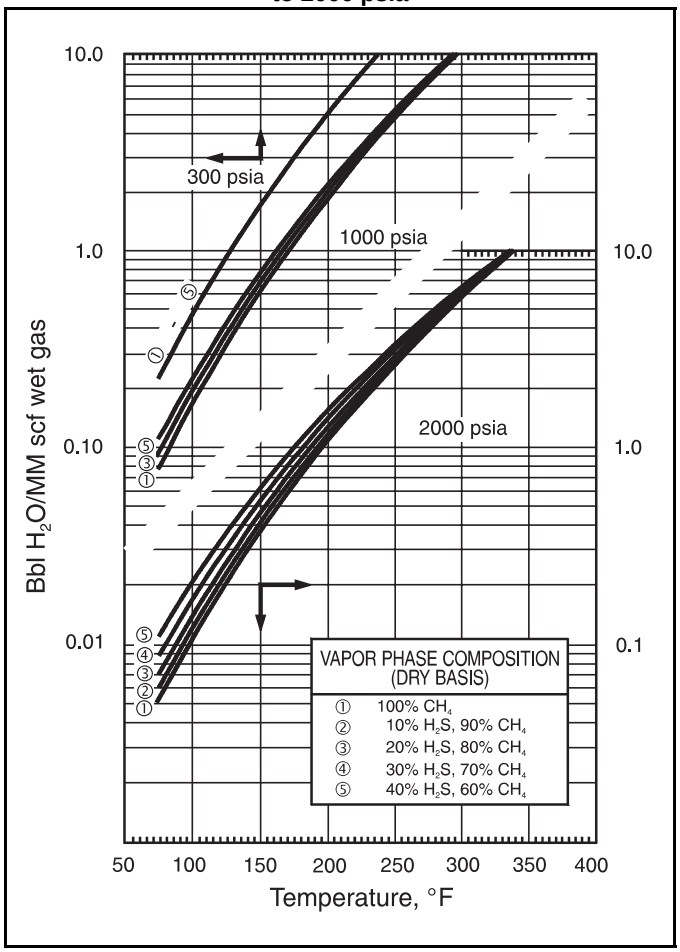
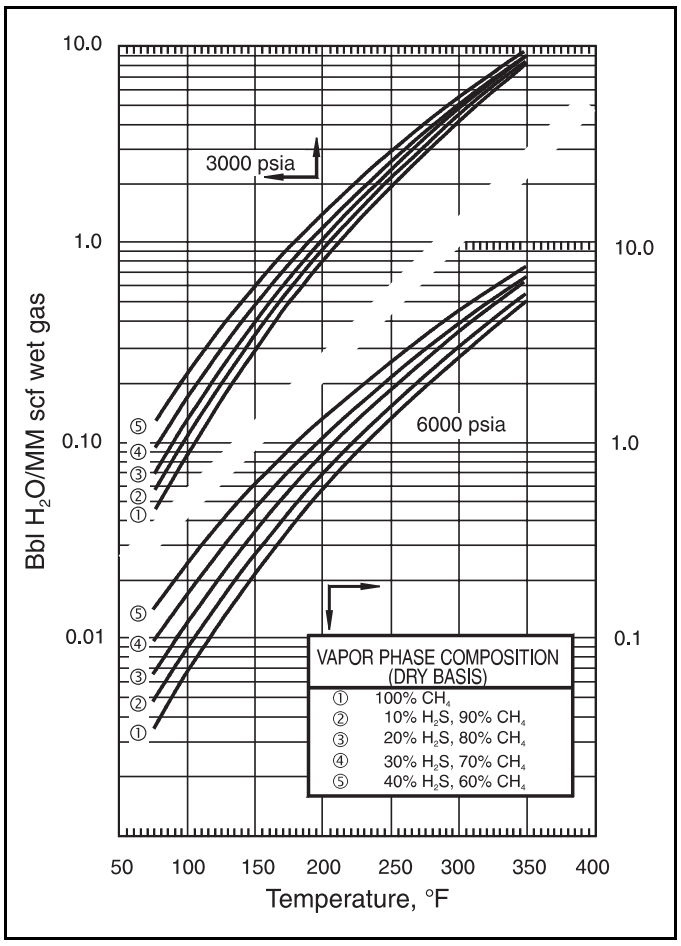


FIG. 20-13

Calculated Water Content of Acid Gas Mixtures to 6000 psia



(hydrate). The water content of a gas in equilibrium with a hydrate will be lower than equilibrium with a metastable liquid. This is acknowledged in the "Warning" in Fig. 20-4.

Hydrate formation is a time dependent process. The rate at which hydrate crystals form depends upon several factors including gas composition, presence of crystal nucleation sites in the liquid phase, degree of agitation, etc. During this transient "hydrate formation period" the liquid water present is termed "metastable liquid". Metastable water is liquid water which, at equilibrium, will exist as a hydrate.

GPA RR-45[11], 50[10] and 80[12] present experimental data showing equilibrium water contents of gases above hydrates. Data from RR-50 is presented in Fig. 20-17. For comparative purposes, the metastable water content of a sweet gas from Fig. 20-4 is also shown. Water content of gases in the hydrate region is a strong function of composition. Fig. 20-17 should not be extrapolated to other compositions.

When designing dehydration systems (particularly TEG systems) to meet extremely low water dewpoint specifications, it is necessary to determine the water content of the gas in equilibrium with a hydrate using a correlation like that presented in Fig. 20-17. If a metastable correlation is used, one will overestimate the saturated water content of the gas at the dewpoint specification. This, in turn, may result in a dehydration design which is unable to meet the required water removal. Where experimental data is unavailable, utilization of a sound thermodynamic-based correlation can provide an estimate of water content in equilibrium with hydrates.

Water Content Measurement

Specifications for water content measurement are given in GPA Publication 2140. These include the Valve Freeze Method, the Bureau of Mines Dew Point Tester, and the Cobalt Bromide Method. Cobalt bromide color change occurs at about 25-30 ppmw.

There are several commercial instruments available for monitoring water content based on other principles. Measuring water contents of less than 20 ppmw or making dewpoint determinations at less than –40°F can be very difficult.

HYDRATES IN NATURAL GAS SYSTEMS

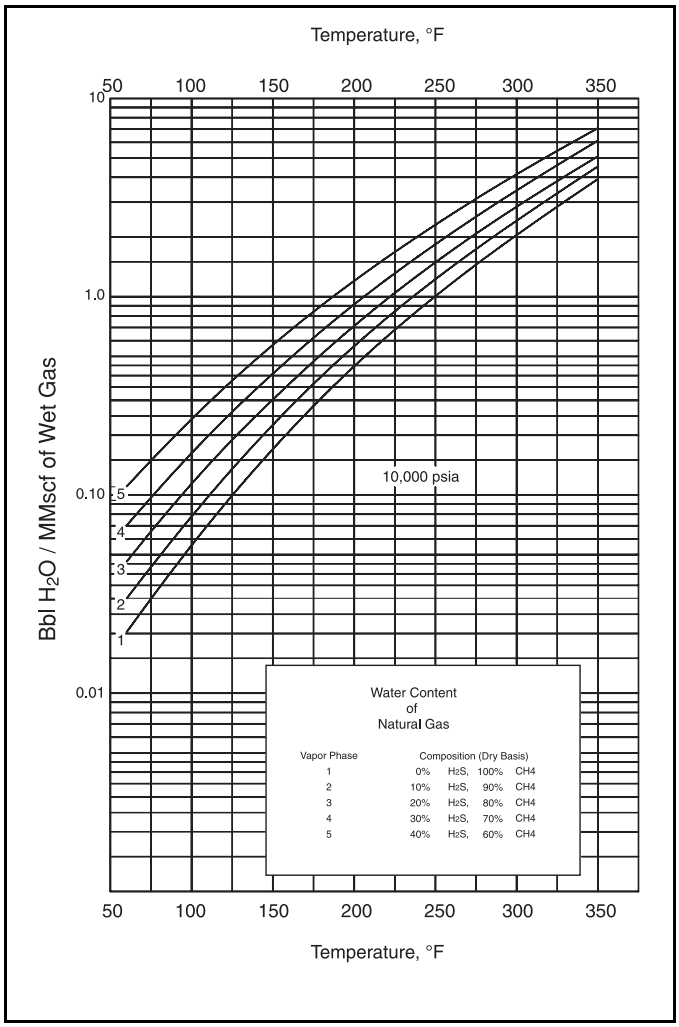
A hydrate is a physical combination of water and other small molecules to produce a solid which has an "ice-like" appearance but possesses a different structure than ice. Their formation in gas and/or NGL systems can plug pipelines, equipment, and instruments, restricting or interrupting flow.

There are three recognized crystalline structures for such hydrates. In both, water molecules build the lattice and hydrocarbons, nitrogen, CO_2 and H_2S occupy the cavities. Smaller molecules (CH_4, C_2H_6, CO_2, H_2S) stabilize a body-centered cu-

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FIG. 20-14

Calculated Water Content of Acid Gas Mixtures to 10,000 psia



bic called Structure I. Larger molecules (C_3H_8, i-C_4H_{10}, n-C_4H_{10}) form a diamond-lattice called Structure II.

Normal paraffin molecules larger than n-C_4H_{10} do not form Structure I and II hydrates as they are too large to stabilize the lattice. However, some isoparaffins and cycloalkanes larger than pentane are known to form Structure H hydrates.[13]

Gas composition determines structure type. Mixed gases will typically form Structure II. Limiting hydrate numbers (ratio of water molecules to molecules of included gaseous component) are calculated using the size of the gas molecules and the size of the cavities in H_2O lattice.

From a practical viewpoint, the structure type does not affect the appearance, properties, or problems caused by the hydrate. It does, however, have a significant effect on the pressure and temperature at which hydrates form. Structure II hydrates are more stable than Structure I. This is why gases containing C_3H_8 and i-C_4H_{10} will form hydrates at higher temperatures than similar gas mixtures which do not contain these components. The effect of C_3H_8 and i-C_4H_{10} on hydrate formation conditions can be seen in Fig. 20-19. At 1000 psia, a 0.6 sp. gr. gas (composition is shown in Fig. 20-22) has a hydrate formation temperature which is 12-13°F higher than pure methane.

The presence of H_2S in natural gas mixtures results in a substantially warmer hydrate formation temperature at a given pressure. CO_2, in general, has a much smaller impact and often reduces the hydrate formation temperature at fixed pressure for a hydrocarbon gas mixture.

The conditions which affect hydrate formation are:

Primary Considerations

- Gas or liquid must be at or below its water dew point or saturation condition (NOTE: liquid water does not have to be present for hydrates to form)
- Temperature
- Pressure
- Composition

Secondary Considerations

- Mixing
- Kinetics
- Physical site for crystal formation and agglomeration such as a pipe elbow, orifice, thermowell, or line scale
- Salinity

In general, hydrate formation will occur as pressure increases and/or temperature decreases to the formation condition.

Prediction of Sweet Natural Gas Hydrate Conditions

Fig. 20-18, based on experimental data, presents the hydrate pressure-temperature equilibrium curves for pure methane, ethane, propane, and for a nominal 70% ethane 30% propane mix.

Fig. 20-19 through 20-21, based on gas gravity, may be used for first approximations of hydrate formation conditions and for estimating permissible expansion of sweet natural gases without the formation of hydrates.

The conditions at which hydrates can form are strongly affected by gas composition. Compositions used for the construction of Fig. 20-19 through Fig. 20-21 are given in Fig. 20-22. The gases are saturated with water.

Example 20-3 — Find the pressure at which hydrate forms for a gas with the following composition. T = 50°F.

Component	Mole Fraction	Mole Wt	lb per lb-mol of Mixture
C_1	0.784	16.043	12.58
C_2	0.060	30.070	1.80
C_3	0.036	44.097	1.59
iC_4	0.005	58.124	0.29
nC_4	0.019	58.124	1.10
N_2	0.094	28.013	2.63
CO_2	0.002	44.010	0.09
Total	1.000		20.08

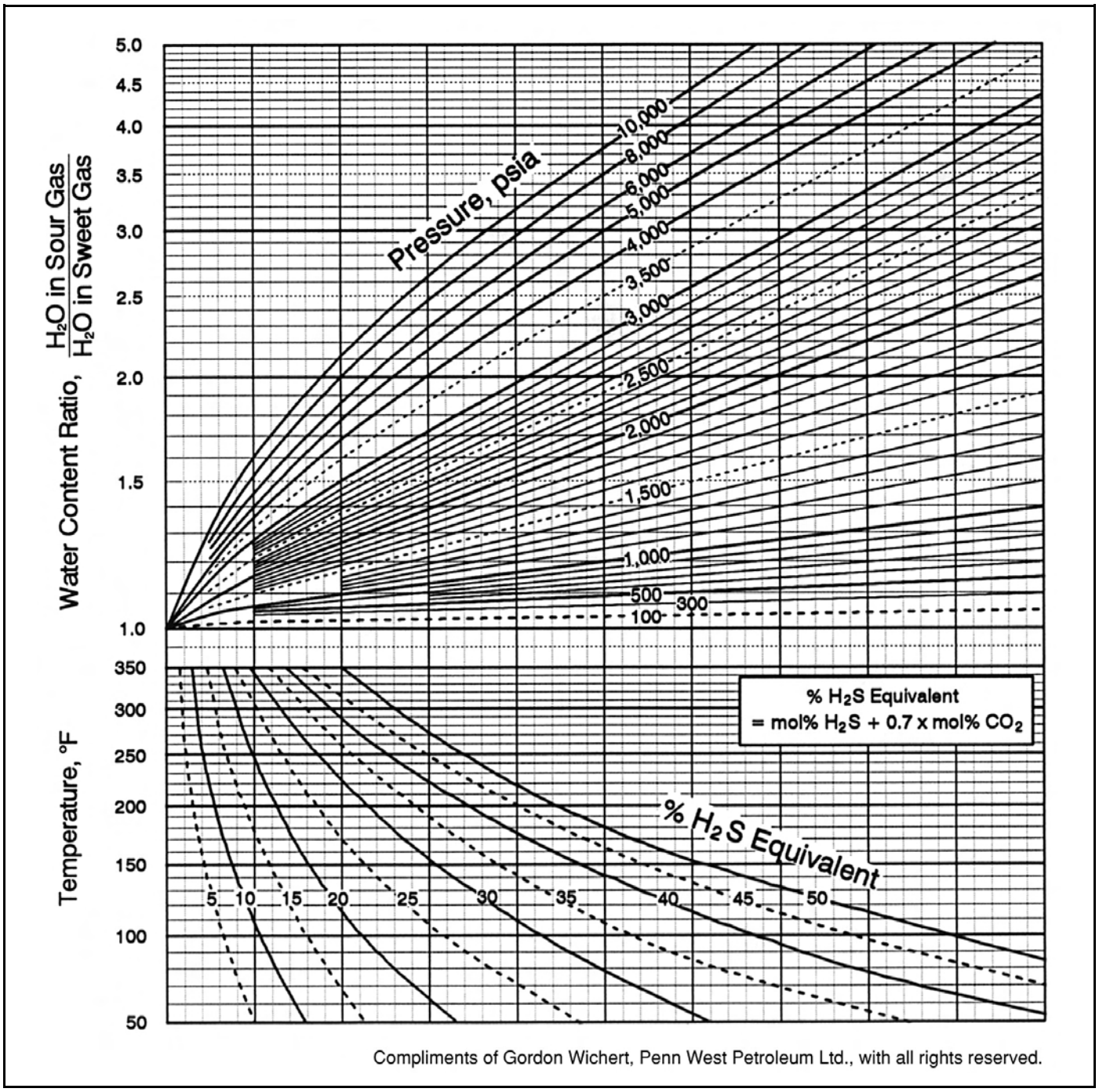
Mole wt. of gas mixture = 20.08

$$\gamma = \frac{MW_{gas}}{MW_{air}} = \frac{20.08}{28.964} = 0.693$$

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FIG. 20-15

Calculated Water Content of Acid Gas Mixtures



From Fig. 20-19 at 50°F

P = 320 psia for 0.7 gravity gas

Example 20-4 — The gas in Example 20-3 is to be expanded from 1,500 psia to 500 psia. What is the minimum initial temperature that will permit the expansion without hydrate formation?

The 1,500 psia initial pressure line and the 500 psia final pressure line intersect just above the 110°F curve on Fig. 20-21. Approximately 112°F is the minimum initial temperature.

Example 20-5 — How far may a 0.6 gravity gas at 2,000 psia and 100°F be expanded without hydrate formation?

On Fig. 20-20 find the intersection of 2,000 initial pressure line with the 100°F initial temperature curve. Read on the x-axis the permissible final pressure of 1100 psia.

Example 20-6 — How far may a 0.6 gravity gas at 2,000 psia and 140°F be expanded without hydrate formation?

On Fig. 20-20, the 140°F initial temperature curve does not intersect the 2,000 psia initial pressure line. Therefore, the gas may

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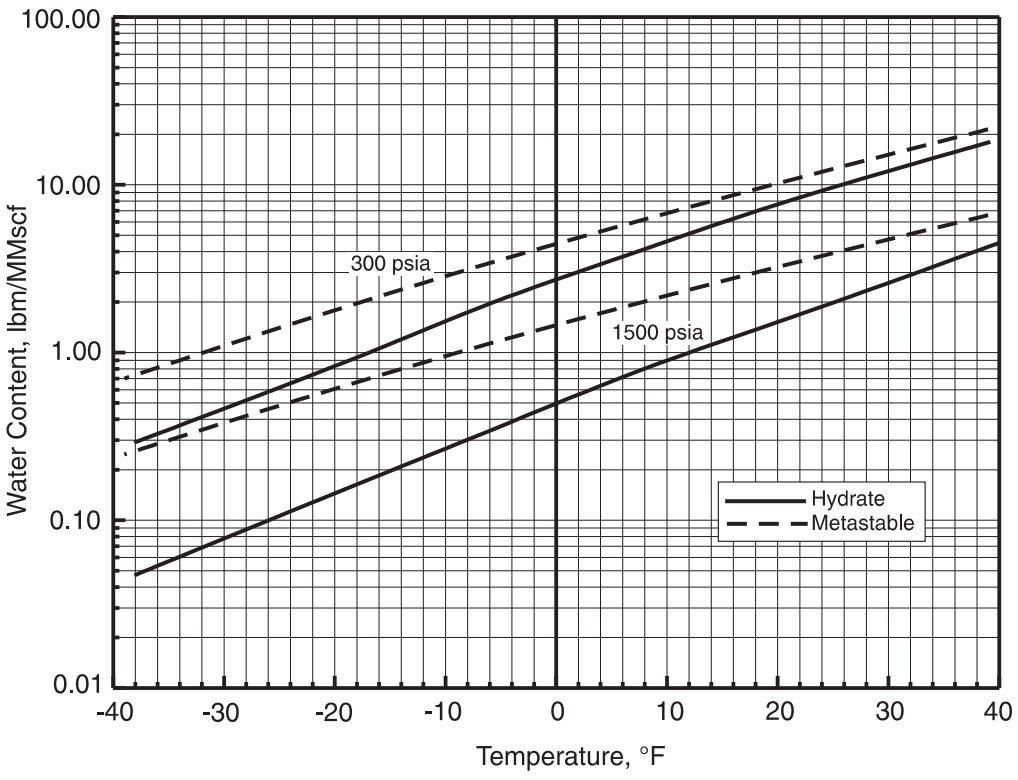
FIG. 20-16

Comparison of Experimental vs. Calculated Water Contents for Acid Gases

Mixture	T, °F	P, psia	Water Content lb/MMscf			
			Experimental	Eq 20-1	Fig. 20-12 & 20-13	Fig. 20-15
11% CO_2/89% C_1	100	2000	40.6	42	39.2	43
11% CO_2/89% C_1	160	1000	286	277	287	285
20% CO_2/80% C_1	100	2000	40.6	43	44.1	46
20% CO_2/80% C_1	160	1000	282	278	287	290
20% CO_2/80% C_1	160	2000	172	182	172	194
8% H_2S/92% C_1	130	1500	111	105	112	106
27.5% H_2S/72.5% C_1	160	1367	247	258	273	260
17% H_2S/83% C_1	160	1000	292	278	290	293
$C_1/CO_2/H_2S$ 30%/60%/10%	100	1100	81	72	NA	86
$C_1/CO_2/H_2S$ 9%/10%/81%	100	1900	442	72	NA	NA
5.31% C_1/94.69% CO_2	77	1500	109.2	38	NA	NA
5.31% C_1/94.69% CO_2	122	2000	164.6	105	NA	NA

FIG. 20-17

Water Content of 5.31% C_3/94.69% C_1 Gas in Equilibrium with Hydrate



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be expanded to atmospheric pressure without hydrate formation.

Conditions predicted by Fig. 20-19 through 20-21 may be significantly in error for compositions other than those used to derive the charts. For more accurate determination of hydrate formation conditions, the following procedures should be followed. In addition, Fig. 20-20 and 20-21 do not account for liquid water and liquid hydrocarbons present or formed during the expansion. These can have a significant effect on the outlet temperature from the pressure reduction device.

Hydrate Prediction Based on Composition for Sweet Gases

Several correlations have proven useful for predicting hydrate formation of sweet gases and gases containing minimal amounts of CO_2 and/or H_2S. The most reliable ones require a gas analysis. The Katz method[14,15] utilizes vapor solid equilibrium constants defined by the Eq 20-3.

$$K_{vs} = \frac{y}{x_s} \qquad \textbf{Eq 20-3}$$

WARNING: Not good for pure components – only mixtures.

The applicable K-value correlations for the hydrate forming molecules (methane, ethane, propane, isobutane[16], normal butane[17], carbon dioxide, and hydrogen sulfide) are shown in Fig. 20-23 to 20-29. Normal butane cannot form a hydrate by itself but can contribute to hydrate formation in a mixture.

For calculation purposes, all molecules too large to form hydrates have a K-value of infinity. These include all normal paraffin hydrocarbon molecules larger than normal butane. Nitrogen is assumed to be a non-hydrate former and is also assigned a K-value of infinity.

The K_{vs} values are used in a "dewpoint" equation to determine the hydrate temperature or pressure. The calculation is iterative and convergence is achieved when the following objective function (Eq 20-4) is satisfied.

$$\sum_{i=1}^{i=n} (y_i / K_{vs}) = 1.0 \qquad \textbf{Eq 20-4}$$

Prudence should be exercised when some higher molecular weight isoparaffins and certain cycloalkanes are present as they can form Structure H hydrates.

Example 20-7 — Calculate the pressure for hydrate formation at 50°F for a gas with the following composition.

Component	Mole Fraction in Gas	at 300 psi		at 400 psi	
		K_{vs}	y/K_{vs}	K_{vs}	y/K_{vs}
Methane	0.784	2.04	0.384	1.75	0.448
Ethane	0.060	0.79	0.076	0.50	0.120
Propane	0.036	0.113	0.319	0.072	0.500
Isobutane	0.005	0.046	0.109	0.027	0.185
n-Butane	0.019	0.21	0.090	0.21	0.090
Nitrogen	0.094	*	0.000	*	0.000
Carbon dioxide	0.002	3.0	0.001	1.9	0.001
Total	1.000		0.979		1.344

* Infinity — Interpolating linearly, $\Sigma y/K_{vs} = 1.0$ at 305 psia

FIG. 20-18

Conditions for Hydrate Formation for Light Gases

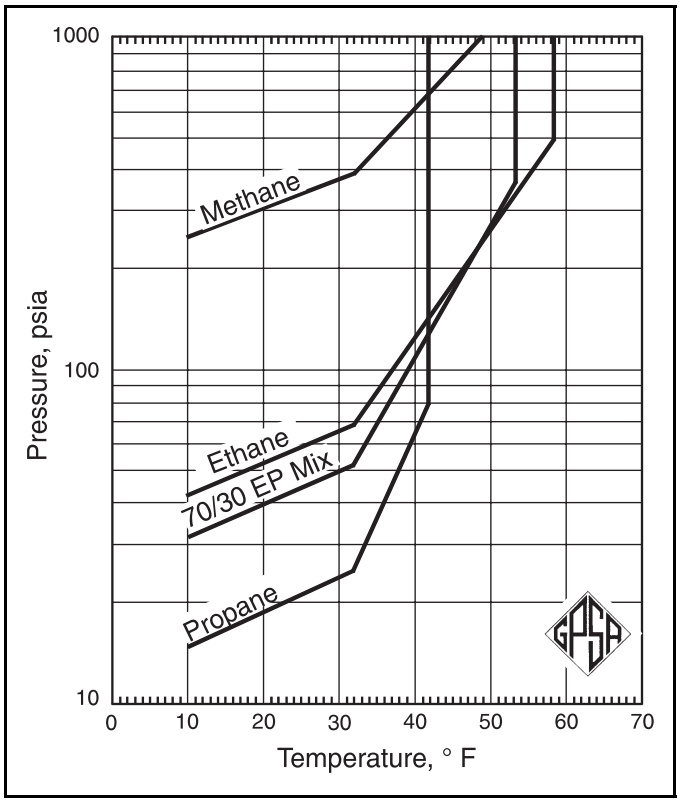
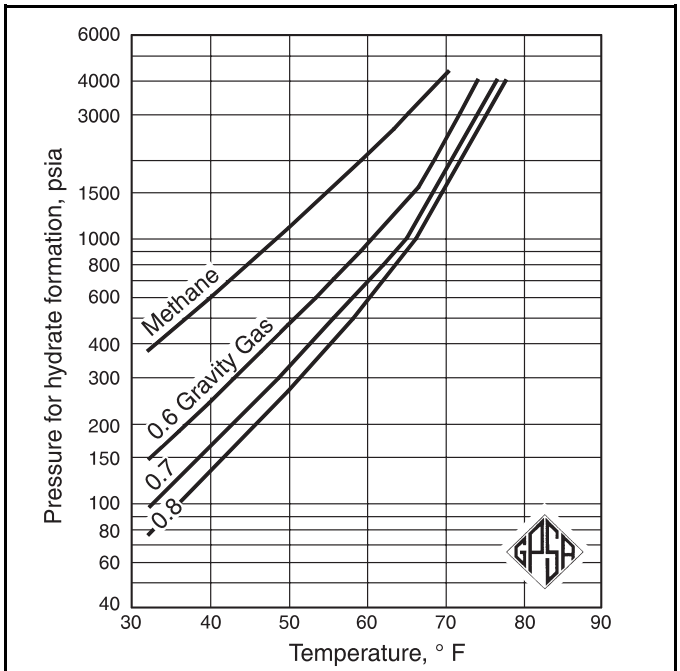


FIG. 20-19

Pressure-Temperature Curves for Predicting Hydrate Formation



CAUTION: Figures 20-19 through 20-21 should only be used for first approximations of hydrate formation conditions. For more accurate determination of hydrate conditions make calculations with K_{v-s}.

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The experimentally observed hydrate-formation pressure at 50°F was 325 psia.

Example 20-8 — The gas with the composition below is at 3500 psia and 150°F. What will be the hydrate conditions when this gas is expanded?

Component	Mole Fraction
C_1	0.9267
C_2	0.0529
C_3	0.0138
iC_4	0.0018
nC_4	0.0034
nC_5	0.0014
Total	1.0000

Solution Steps:

1. Make several adiabatic flash calculations at different pressures and plot on a pressure versus temperature graph. (See Fig. 20-30)

Initial Pressure, psia	Initial Temperature, °F	Final Pressure, psia	Final Temperature, °F
3500	150	300	38
3500	150	400	45
3500	150	500	52
3500	150	600	58
3500	150	700	64

2. Assume some temperature and predict the hydrate formation pressure for this gas using the solid-vapor K-data. Plot the results on Fig. 20-30. Sample calculations for 200 and 300 psia are provided below. This calculation has been repeated for 400, 500, 800 and 1000 psia to develop Fig. 20-30.

T = 40°F	y	200 psia		300 psia	
		K_{vs}	y/K_{vs}	K_{vs}	y/K_{vs}
C_1	0.9267	2.25	0.4119	1.75	0.5295
C_2	0.0529	0.50	0.1058	0.205	0.2580
C_3	0.0138	0.055	0.2509	0.030	0.4600
iC_4	0.0018	0.0225	0.0800	0.0105	0.1714
nC_4	0.0034				
C_5	0.0014				
Total	1.0000		0.8486		1.4189

$\Sigma y/K_{vs}$ = 1.0 @ 227 psia

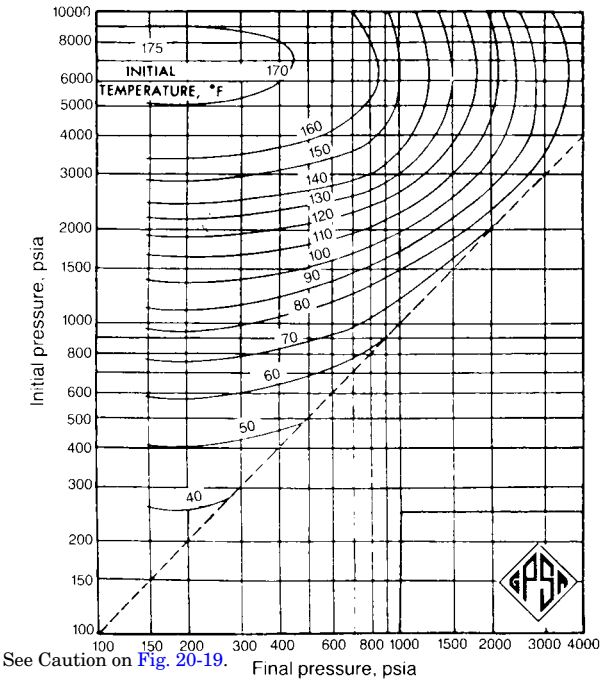
3. The intersection of the lines in Fig. 20-30 will be the point at which hydrates start to form. In this example, the result is 500 psia and 52°F.

Note: Fig. 20-20 would predict permissable expansion only to a pressure around 700 psia.

The Katz correlation is not recommended above 1000-1500 psia, depending on composition. Prediction of hydrate formation conditions at higher pressures requires the use of other methods. Sloan, et.al.[18] present an alternate set of K_{vs} values which, in general, are valid to 4000 psia. McLeod & Campbell[19] present experimental hydrate data for natural gas mixtures

FIG. 20-20

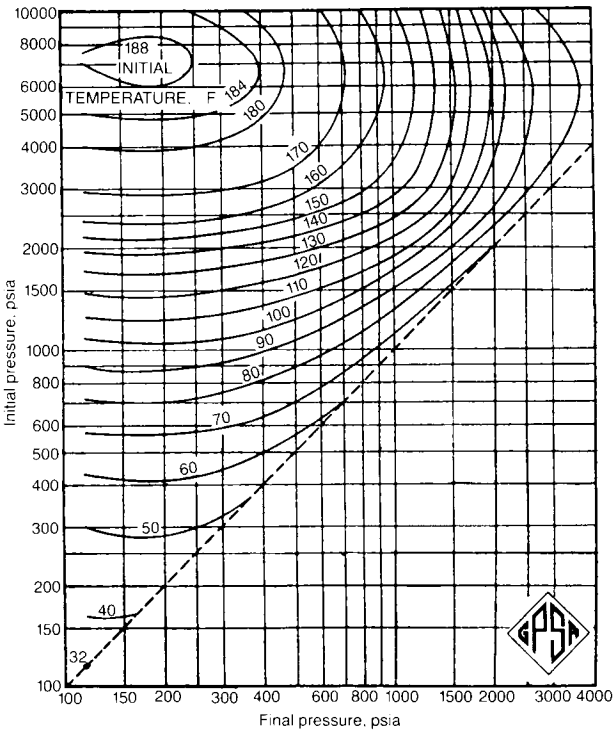
Permissible Expansion of a 0.6-Gravity Natural Gas Without Hydrate Formation



See Caution on Fig. 20-19.

FIG. 20-21

Permissible Expansion of a 0.7-Gravity Natural Gas Without Hydrate Formation



See Caution on Fig. 20-19.

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up to 10,000 psia as well as a correlation for estimating high pressure hydrate formation conditions. Blanc & Tournier-Lasserve[20] provide experimental hydrate data to 14,500 psia and compare prediction correlations with experimental data.

Hydrate Predictions for High CO_2/H_2S Content Gases

The Katz method of predicting hydrate formation temperature gives reasonable results for sweet paraffin hydrocarbon gases. The Katz method should not be used for gases containing significant quantities of CO_2 and/or H_2S despite the fact that K_{vs} values are available for these components. Hydrate formation conditions for high CO_2/H_2S gases can vary significantly from those composed only of hydrocarbons. The addition of H_2S to a sweet natural gas mixture will generally increase the hydrate formation temperature at a fixed pressure.[21]

A method by Baille & Wichert for predicting the temperature of high H_2S content gases is shown in Fig. 20-31[22]. This is based on the principle of adjusting the propane hydrate conditions to account for the presence of H_2S as illustrated in the following example.

FIG. 20-22

Gas Compositions Used for Fig. 20-19 through 20-21

	Mole Fraction		
C_1	0.9267	0.8605	0.7350
C_2	0.0529	0.0606	0.1340
C_3	0.0138	0.0339	0.0690
iC_4	0.0018	0.0084	0.0080
nC_4	0.0034	0.0136	0.0240
nC_5	0.0014	0.0230	0.0300
Sp. Gr.	0.603	0.692	0.796

Example 20-9 — Estimate the hydrate formation temperature at 610 psia of a gas with the following analysis using Fig. 20-31.

Component	mol %
N_2	0.30
CO_2	6.66
H_2S	4.18
C_1	84.27
C_2	3.15
C_3	0.67
iC_4	0.20
nC_4	0.19
C_{5+}	0.40
MW = 19.75	γ = 0.682

Solution Steps:

1. Enter left side of Fig. 20-31 at 600 psia and proceed to the H_2S concentration line (4.18 mol%)
2. Proceed down vertically to the specific gravity of the gas (γ = 0.682)
3. Follow the diagonal guide line to the temperature at the bottom of the graph (T = 63.5°F).
4. Apply the C_3 correction using the insert at the upper left. Enter the left hand side at the H_2S concentration and proceed to the C_3 concentration line (0.67%). Proceed down vertically to the system pressure and read the correction on the left hand scale (–2.7°F)

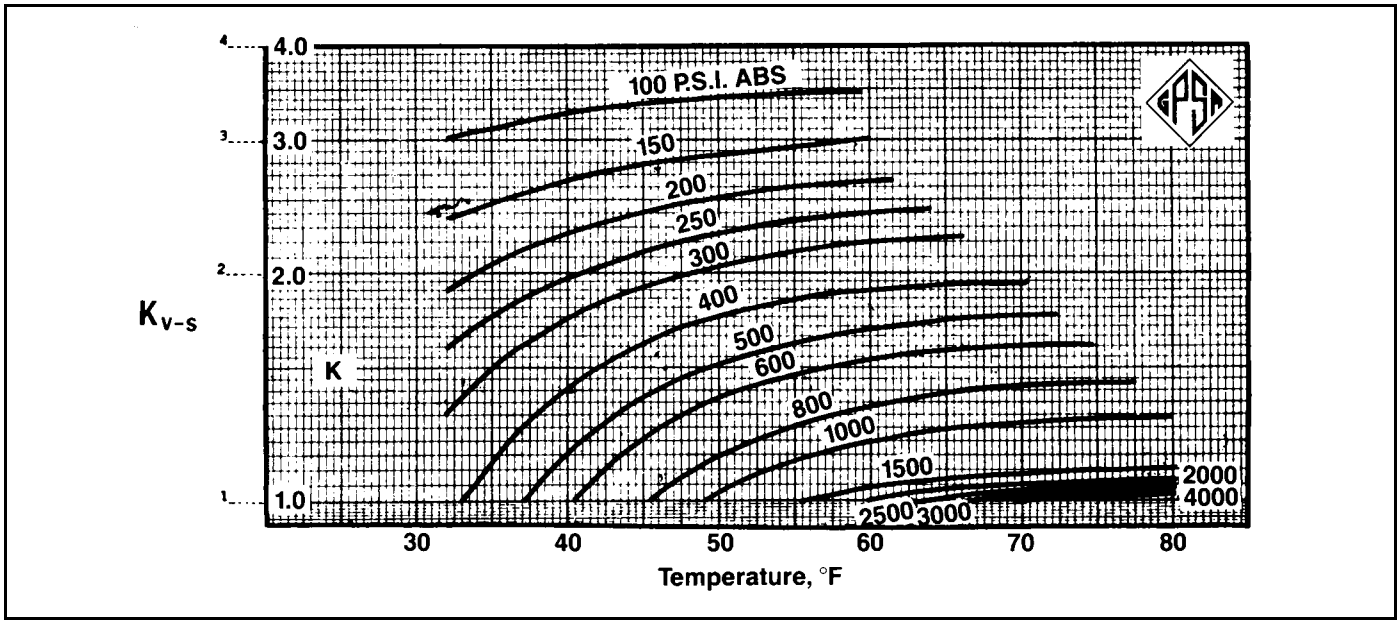
Note: The C_3 temperature correction is negative when on the left hand side of the graph and positive on the right hand side.

$T_H = 63.5 - 2.7 = 60.8°F$

Fig. 20-31 was developed based on calculated hydrate conditions using the Peng-Robinson EOS. It has proven quite accurate when compared to the limited amount of experimental

FIG. 20-23

Vapor-Solid Equilibrium Constants for Methane



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data available. It should only be extrapolated beyond the experimental data base with caution.

Fig. 20-32[23] presents experimental hydrate formation data for three mixtures of methane, propane and hydrogen sulfide. Results of selected hydrate prediction methods are also shown.

The addition of CO_2 to pure methane will slightly increase the hydrate temperature at a fixed pressure.[24] However, the addition of CO_2 to a "typical" sweet natural gas mixture will often lower the hydrate formation temperature at a fixed pressure. Fig. 20-33 is provided to portray these compositional effects. The hydrate curves for four gas compositions are shown. These were generated using a commercial hydrate program employing the Peng-Robinson EOS. The four gas compositions are:

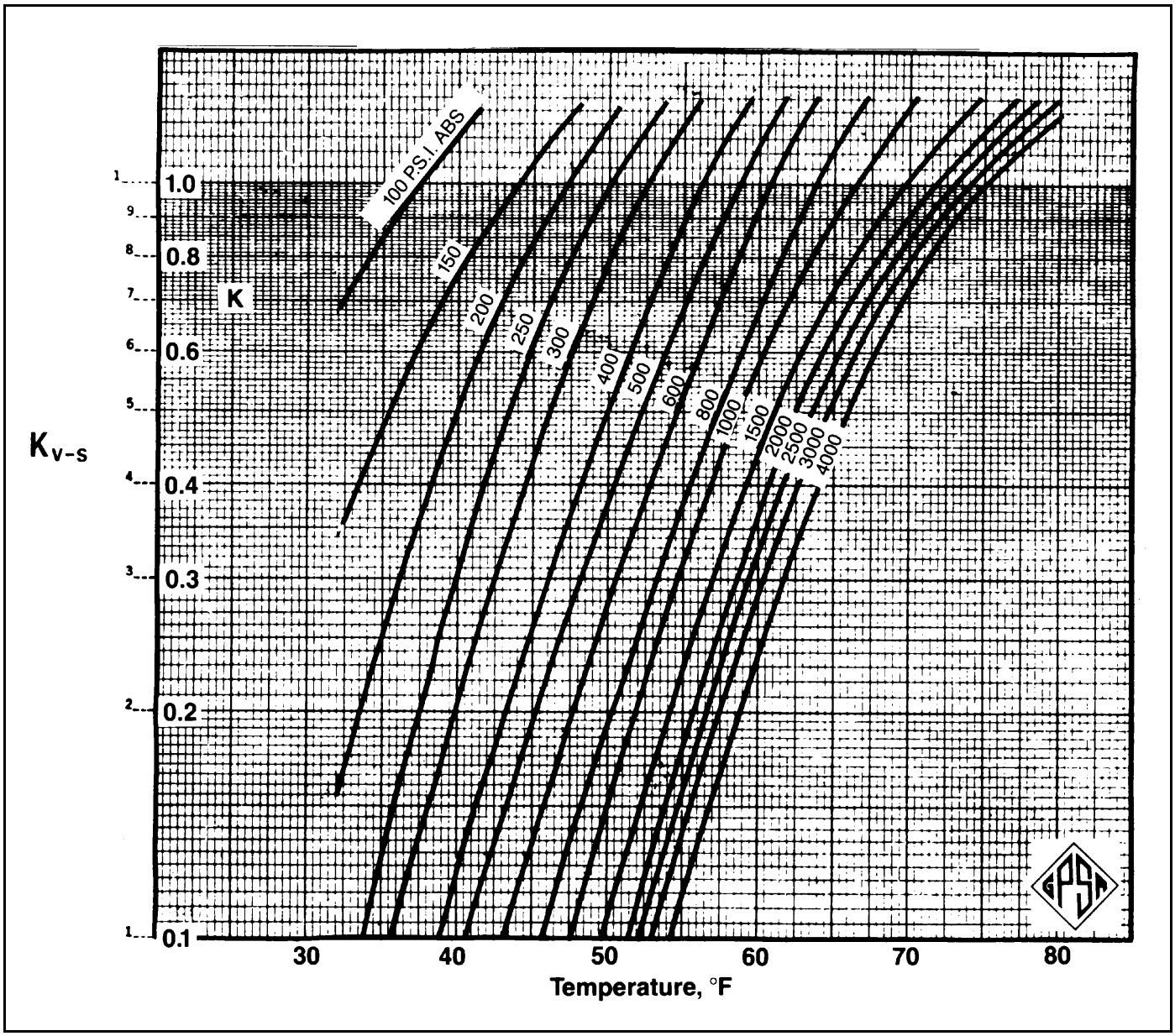
Sweet Gas (0.6 sp. gr. gas from Fig. 20-22)
Sweet Gas containing 10% CO_2
Sour Gas containing 10% H_2S
Sour Gas containing 10% CO_2 and 10% H_2S

Note that H_2S significantly increases the hydrate temperature of a sweet natural gas. In this example, at 1000 psia, the addition of H_2S (10 mol%) to a sweet gas mixture increases the hydrate temperature by 15°F. On the other hand, CO_2 has a minor effect on the hydrate formation temperature and slightly decreases the hydrate temperature for both the "sweet" and "sour" gases in this case.

EOS-based computer programs are probably the most consistent method of predicting hydrate formation temperatures today. Accuracy when compared to experimental data is usually ± 2°F. This is generally adequate for design.

FIG. 20-24

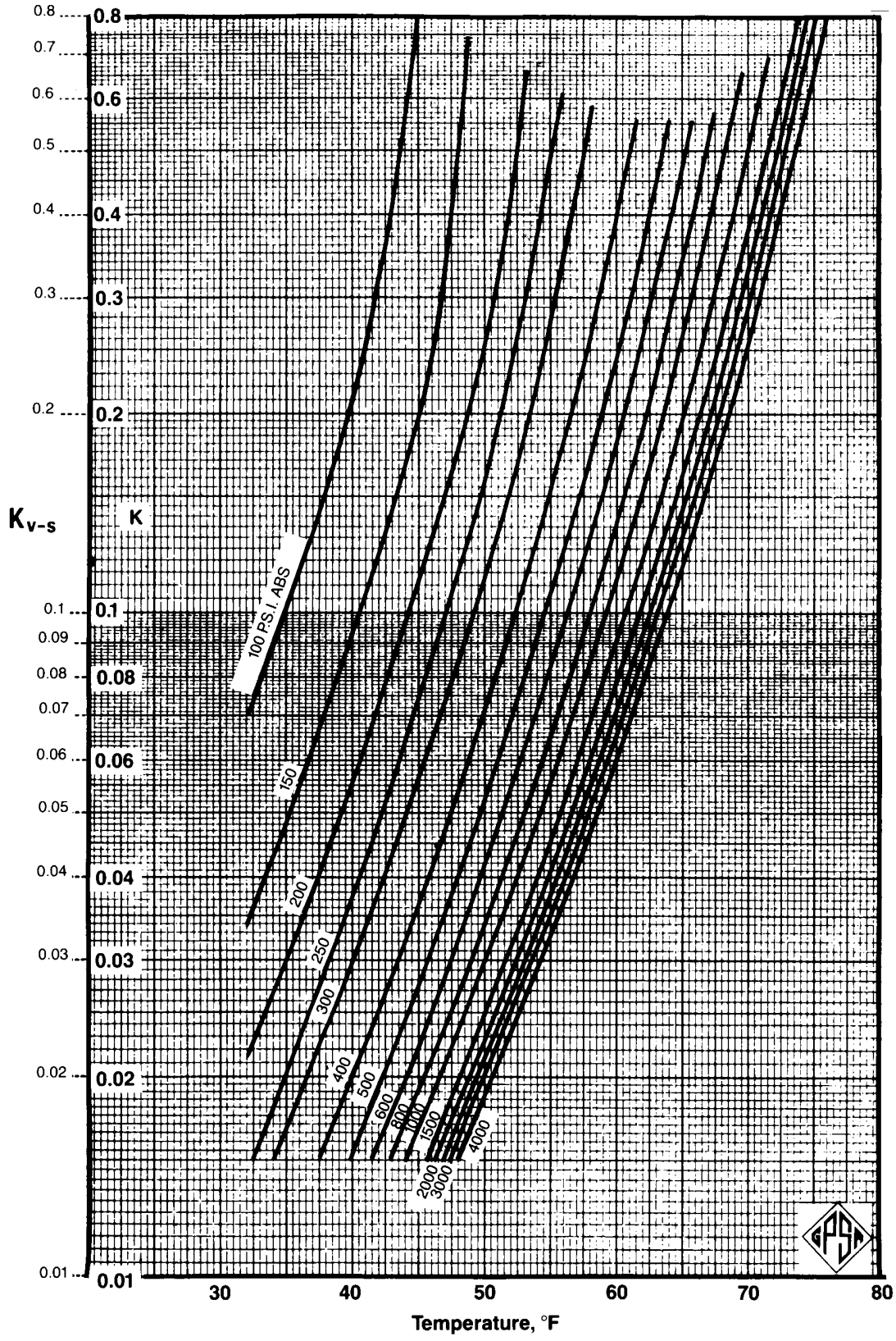
Vapor-Solid Equilibrium Constants for Ethane



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FIG. 20-25

Vapor-Solid Equilibrium Constants for Propane



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FIG. 20-26

Vapor-Solid Equilibrium Constants for Iso-Butane

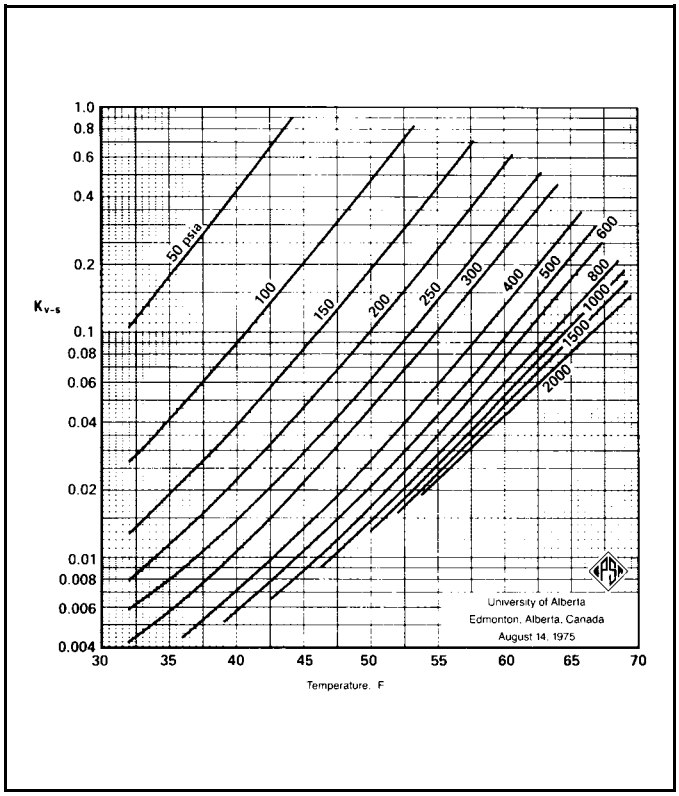


FIG. 20-27

Vapor-Solid Equilibrium Constants for N-Butane

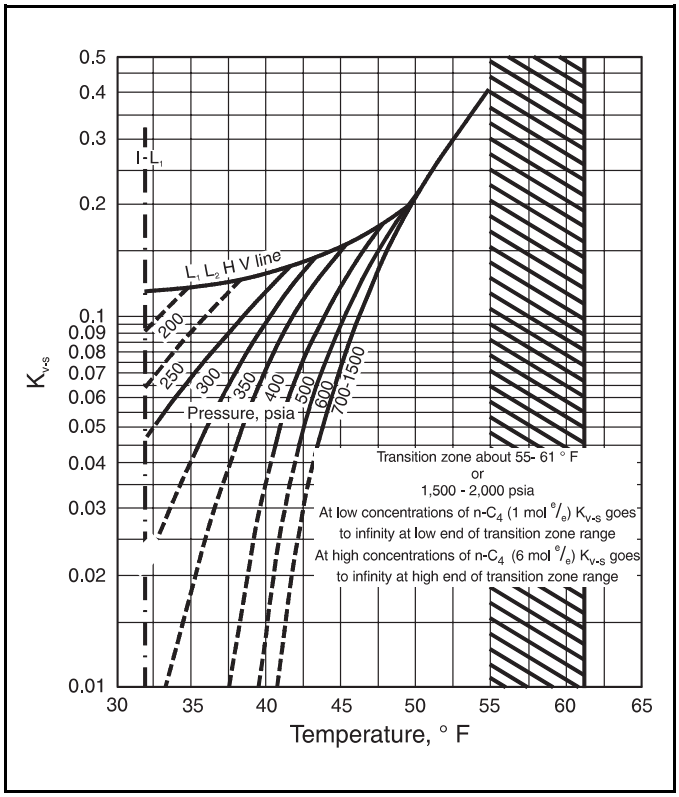


FIG. 20-28

Vapor-Solid Equilibrium Constants for Carbon Dioxide

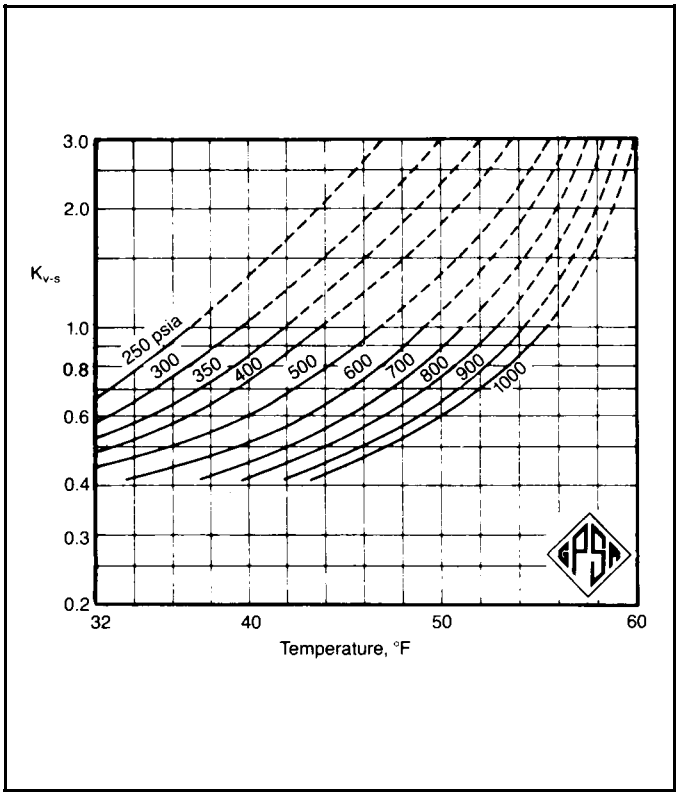
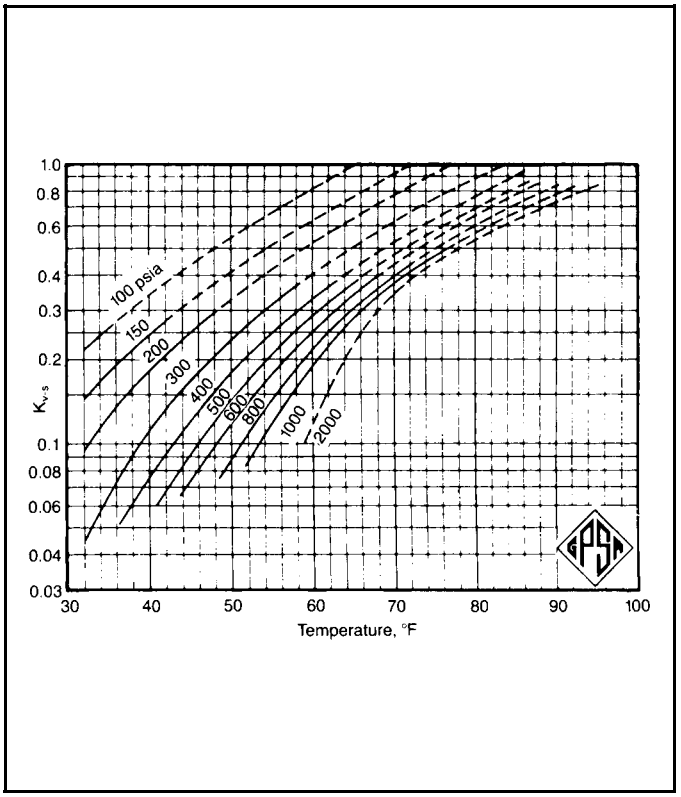


FIG. 20-29

Vapor-Solid Equilibrium Constants for Hydrogen Sulfide



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Hydrate Inhibition

The formation of hydrates can be prevented by dehydrating the gas or liquid to eliminate the formation of a condensed water (liquid or solid) phase. In some cases, however, dehydration may not be practical or economically feasible. In these cases, chemical inhibition can be an effective method of preventing hydrate formation. Chemical inhibition utilizes injection of thermodynamic inhibitors or low dosage hydrate inhibitors (LDHIs). Thermodynamic inhibitors are the traditional inhibitors (i.e., one of the glycols or methanol), which lower the temperature of hydrate formation. LDHIs are either kinetic hydrate inhibitors (KHIs) or antiagglomerants (AAs). They do not lower the temperature of hydrate formation, but do diminish its effect. KHIs lower the rate of hydrate formation, which inhibits its development for a defined duration. AAs allow the formation of hydrate crystals but restrict them to sub-millimeter size.

Thermodynamic Inhibitors — Inhibition utilizes injection of one of the glycols or methanol into a process stream where it can combine with the condensed aqueous phase to lower the hydrate formation temperature at a given pressure. Both glycol and methanol can be recovered with the aqueous phase, regenerated and reinjected. For continuous injection in services down to –40°F, one of the glycols usually offers an economic advantage versus methanol recovered by distillation. At cryogenic conditions (below –40°F) methanol usually is preferred because glycol's viscosity makes effective separation difficult.

Ethylene glycol (EG), diethylene glycol (DEG), and triethylene glycol (TEG) glycols have been used for hydrate inhibition. The most popular has been ethylene glycol because of its lower cost, lower viscosity, and lower solubility in liquid hydrocarbons.

Physical properties of methanol and methanol-water mixtures are given in Fig. 20-34 through Fig. 20-37. Physical properties of the most common glycols and glycol-water mixtures are given in Fig. 20-38 through Fig. 20-49. Tabular information for the pure glycols and methanol is provided in Fig. 20-56.

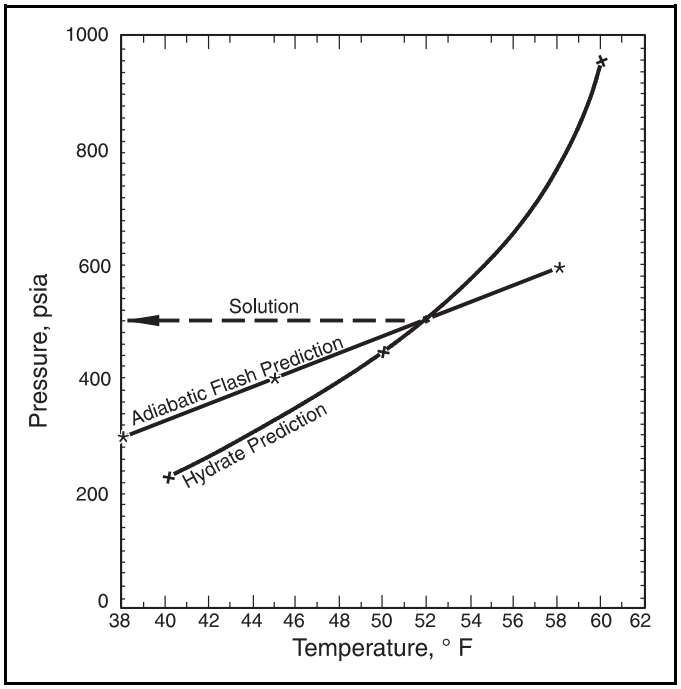
To be effective, the inhibitor must be present at the very point where the wet gas is cooled to its hydrate temperature. For example, in refrigeration plants glycol inhibitors are typically sprayed on the tube-sheet faces of the gas exchangers so that it can flow with the gas through the tubes. As water condenses, the inhibitor is present to mix with the water and prevent hydrates. Injection must be in a manner to allow good distribution to every tube or plate pass in chillers and heat exchangers operating below the gas hydrate temperature.

The viscosities of ethylene glycol and its aqueous solutions increase significantly as temperature decreases, and this must be allowed for in the rating of refrigeration-plant exchangers and chillers.

The inhibitor and condensed water mixture is separated from the gas stream along with a separate liquid hydrocarbon stream. At this point, the water dewpoint of the gas stream is essentially equal to the separation temperature. Glycol-water solutions and liquid hydrocarbons can emulsify when agitated or when expanded from a high pressure to a lower pressure, e.g., JT expansion valve. Careful separator design will allow nearly complete recovery of the diluted glycol for regeneration and reinjection. Fig. 20-57 shows a flow diagram for a typical EG injection system in a refrigeration plant.

FIG. 20-30

Solution Sketch for Example 20-8



The regenerator in a glycol injection system should be operated to produce a regenerated glycol solution that will have a freezing point below the minimum temperature encountered in the system. This is typically 75-80 wt%. Fig. 20-58 shows the freezing point of various concentrations of glycol water solutions.

The minimum inhibitor concentration in the free water phase may be approximated by Hammerschmidt's equation.[25]

$$d = \frac{K_H X_I}{MW_I (1 - X_I)} \qquad \textbf{Eq 20-5}$$

$$X_I = \frac{dMW_I}{K_H + dMW_I} \qquad \textbf{Eq 20-6}$$

Where K_H (glycols) = 2335 to 4000 and
K_H (methanol) = 2335

The K_H range of 2335 to 4000 for glycols reflects the uncertainty in the value of this parameter. At equilibrium, such as for a laboratory test, 2335 is applicable as illustrated on Fig. 20-60. In some field operations, however, hydrate formation has been prevented with glycol concentrations corresponding with K_H values as high as 4000. This is because hydrate suppression with glycols depends on the system's physical and flow characteristics (i.e., the system dynamics, configuration, location and method of glycol injection, amount of free water, etc.) as well as the properties of the gas and the glycol. Therefore, in the absence of reliable field-test data, a system should be designed for a K_H of 2335. Once the system is operating, the glycol concentration can be reduced to tolerable levels.

Eq 20-5 and Eq 20-6 should not be used beyond 20-25 wt% for methanol and 60-70 wt% for the glycols. For methanol concentrations up to about 50%, the Nielsen-Bucklin equation[26] provides better accuracy:

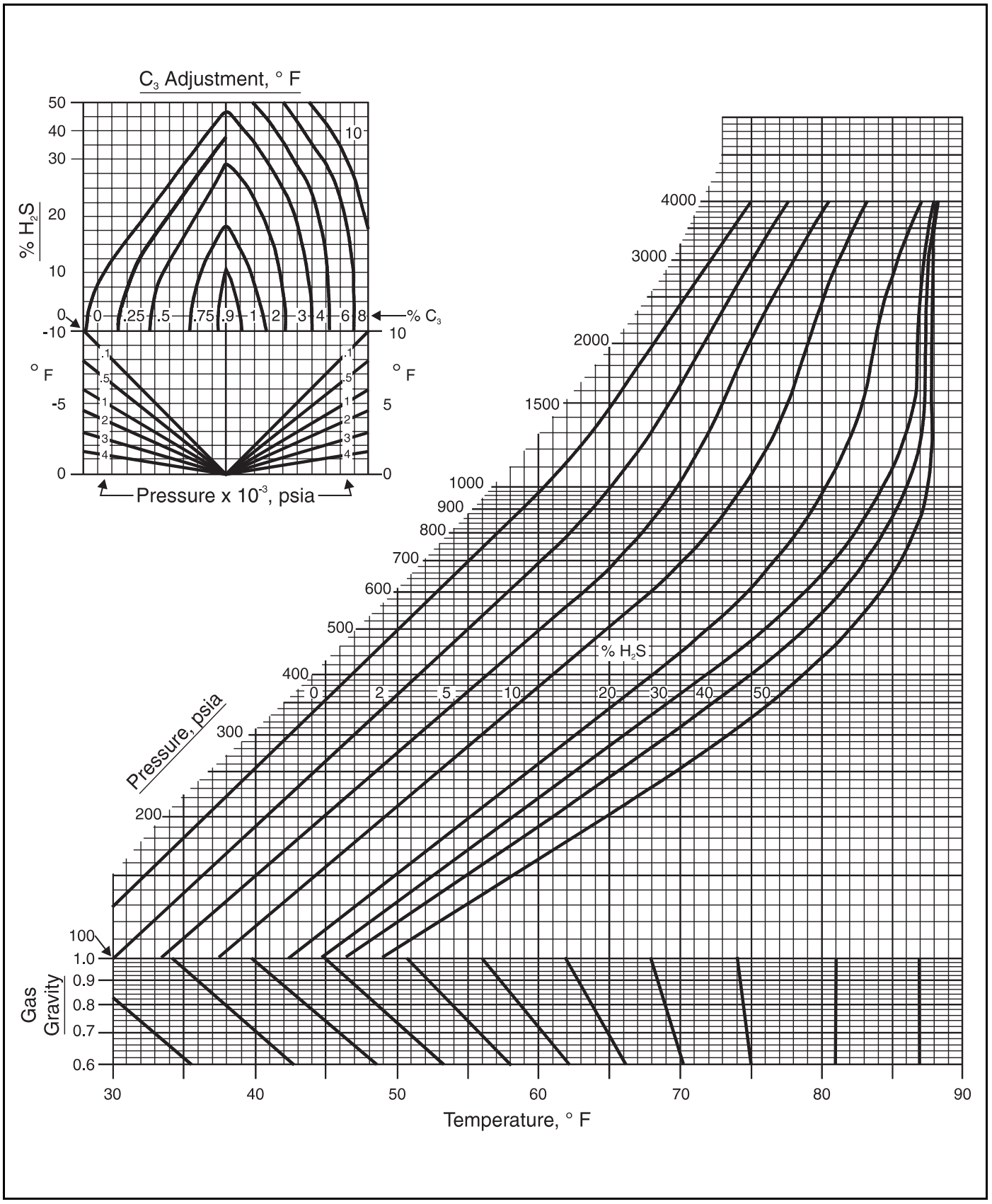
$$d = -129.6 \ln(x_{H_2O}) \qquad \textbf{Eq 20-7}$$

Note that "x_{H_2O}" in Eq 20-7 is a mole fraction, not a mass fraction. Expressing mole fraction in terms of mass fraction, dew-

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FIG. 20-31

Hydrate Chart for Gases Containing H_2S



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point depression is plotted against the weight percent methanol in Fig. 20-59.

Maddox *et al.*[27] presents a method of estimating the required inhibitor concentration for both methanol and EG. The method is iterative but converges easily after a few iterations.

Figs. 20-60 thru 20-64 provide a comparison of various inhibitor correlations with experimental data.[28,29,30] Experimental data at very high inhibitor concentrations is limited.

Once the required inhibitor concentration has been calculated, the mass of inhibitor required in the water phase may be calculated from Eq 20-8

$$m_I = \frac{X_R \cdot m_{H_2O}}{X_L - X_R} \qquad \textbf{Eq 20-8}$$

The amount of inhibitor to be injected not only must be sufficient to prevent freezing of the inhibitor water phase, but also must be sufficient to provide for the equilibrium vapor phase content of the inhibitor and the solubility of the inhibitor in any liquid hydrocarbon. The vapor pressure of methanol is high enough that significant quantities will vaporize. Methanol vaporization losses may be estimated from Fig. 20-65.[31] Fig. 20-65 is extrapolated above 700 psia. Recent studies indicate Fig. 20-65 may underestimate vapor phase methanol losses at higher pressures. Glycol vaporization losses are generally very small and are typically ignored in calculations.

Inhibitor losses to the hydrocarbon liquid phase are more difficult to predict. Solubility is a strong function of both the water phase and hydrocarbon phase compositions. Fig. 20-66 presents experimental data[32,33,34] showing solubility of methanol in a paraffinic hydrocarbon liquid as a function of temperature and methanol concentration. Methanol solubility in naphthenic hydrocarbons is slightly less than paraffinic, but solubility in aromatic hydrocarbons may be four to six times higher than in parafins.

Solubility of EG in the liquid hydrocarbon phase is extremely small.[29] A solubility of 0.3 lb per 1000 gal. (U.S.) of NGL is often used for design purposes. However, entrainment and other physical losses may result in total losses significantly higher than this.

Example 20-10—100 MMscf/d of natural gas leaves an offshore platform at 100°F and 1200 psia. The gas comes onshore at 40°F and 900 psia. The hydrate temperature of the gas is 65°F. Associated condensate production is 10 Bbl/MMscf. The condensate has an API gravity of 50 and a MW of 140. Calculate the amount of methanol and 80 wt% EG inhibitor required to prevent hydrate formation in the pipeline.

Solution Steps:

Methanol

1. Calculate the amount of water condensed per day

   from Fig. 20-4, $W_{in} = 53.0$ lb / MMscf

   $W_{out} = 9.5$ lb / MMscf

   $\Delta W = 43.5$ lb / MMscf

   Water condensed = (100)(53 – 9.5) = 4350 lb/day

2. Calculate required methanol inhibitor concentration from Eq 20-5 and 20-7 (with Fig. 20-59).

   d = 25°F MW = 32

   Solving for X_I,

   $X_I = 0.255$, Eq 20-5

   $X_I = 0.275$, Eq. 20-7 (use this value in subsequent calculations)

3. Calculate mass rate of inhibitor in water phase from Eq. 20-8 (assume 100% methanol is injected)

   $$m_I = \frac{X_R \cdot m_{H_2O}}{X_L - X_R} = \frac{(0.275)\,(4350)}{(1 - 0.275)} = 1650 \text{ lb/day}$$

4. Estimate vaporization losses from Fig. 20-65.

   @ 40°F and 900 psia, losses = $1.05 \frac{\text{lb/MMscf}}{\text{wt\% MeOH}}$

   daily losses = (1.05)(100)(27.5) = 2890 lb/day

5. Estimate losses to hydrocarbon liquid phase from Fig. 20-66.

   @ 40°F and 27.5 wt% MeOH, $x_{MeOH} \approx 0.2$ mol%

   lb • mols of condensate per day–

   $$\left(\frac{100 \text{ MMscf}}{\text{day}}\right)\left(\frac{10 \text{ bbl}}{\text{MMscf}}\right)\left(\frac{(350)(0.78) \text{ lb}}{\text{bbl}}\right)\left(\frac{1 \text{ lb} \cdot \text{mol}}{140 \text{ lb}}\right)$$

   = 1950 lb–mols/day

   lb • mols methanol = (1950)(0.002)

   = 3.9 lb • mols/day

   lb methanol = (3.9)(32) = 125 lb/day

   Total methanol injection rate = 1650 + 2890 + 125

   = 4665 lb/day

Methanol left in the gas phase can be recovered by condensation with the remaining water in downstream chilling processes. Likewise, the methanol in the condensate phase can be recovered by water by downstream water washing.

80 wt% EG

1. Calculate required inhibitor concentration from Eq 20-6.

   d = 25°F MW = 62 $K_H = 2335$

   Solving for X_I, $X_I = 0.40$

2. Calculate mass rate of inhibitor in water phase from Eq. 20-8.

   $$\dot{m}_I = \frac{(0.40)(4350)}{(0.8 - 0.40)} = 4350 \text{ lb / day}$$

Vaporization and liquid hydrocarbon losses are negligible.

Inhibitor losses represent a significant operating cost and can cause problems in downstream process units. Efficient inhibitor separation should be provided.

Low Dosage Hydrate Inhibitors (LDHIs) — LDHIs can provide significant benefits compared to thermodynamic inhibitors including:

- Significantly lower inhibitor concentrations and therefore dosage rates. Concentrations rante from 0.1 to 1.0 weight percent polymer in the free water phase, whereas alcohols can be as high as 50%
- Lower inhibitor loss caused by evaporation, particularly compared to methanol
- Reduced capital expenses through decreased chemial storage and injection rate requirements; and no need for regeneration because the chemicals are not currently recovered. These are especially appropriate for offshore where weight and space are critical to costs
- Reduced operating expenses in many cases through decreased chemical consumption and delivery frequency
- Increased production rates, where inhibitor injection capacity or flowline capacity is limited

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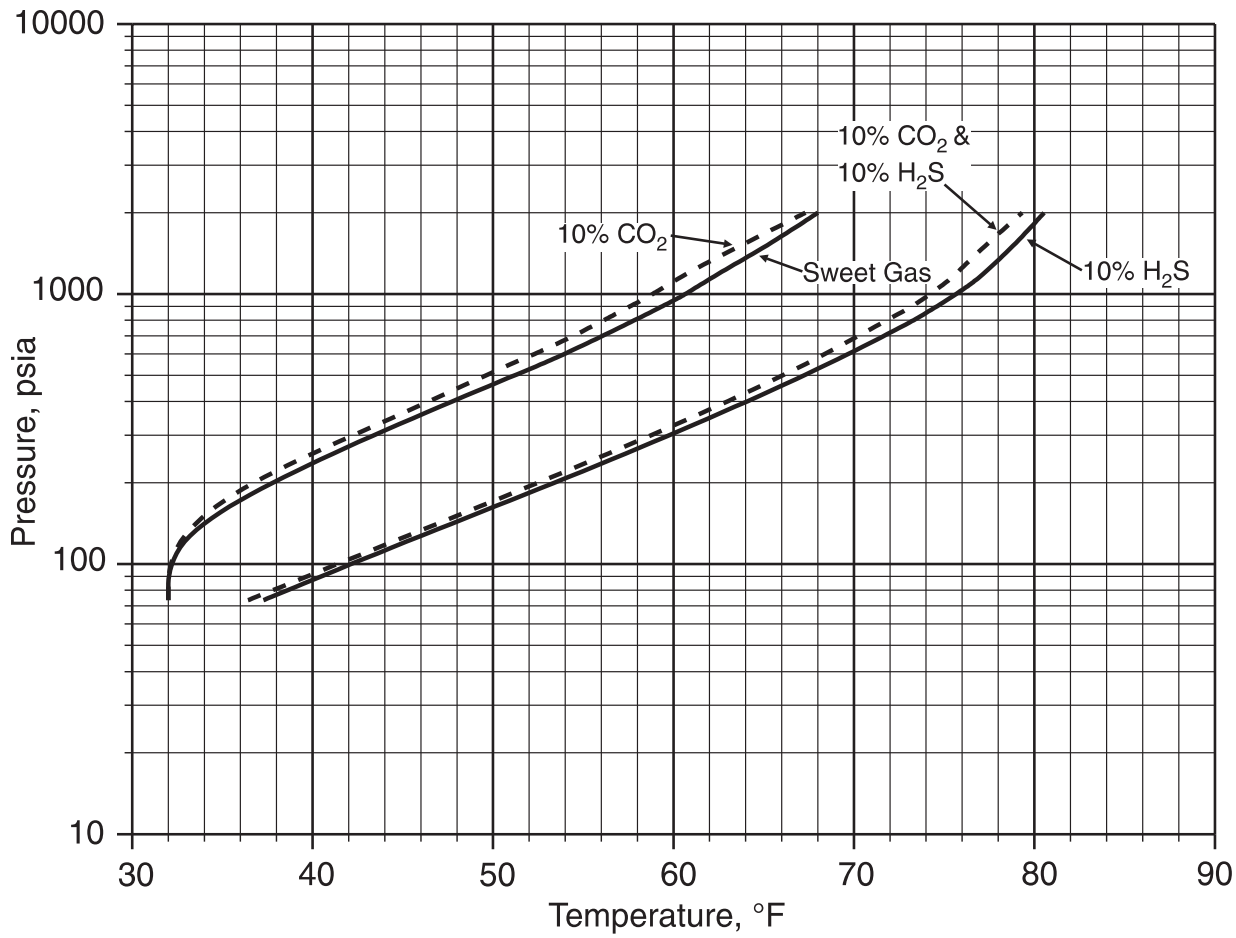
FIG. 20-32

Experimental vs. Predicted Hydrate Conditions for Gases Containing C_1, C_3, and H_2S

Composition, mol %				Experimental Data[18]		Predicted Temperature,°F		
C_1	C_3	H_2S	γ	Temperature, °F	Pressure, psia	Fig. 20-19	Eq 20-4	Fig. 20-31
88.654	7.172	4.174	0.649	40.3	102.4	NA	36.6	41.8
88.654	7.172	4.174	0.649	51.8	205.8	41	47.2	52.3
88.654	7.172	4.174	0.649	57.6	293.5	45	52.2	57.3
88.654	7.172	4.174	0.649	64.4	488.3	53	58.9	65.2
81.009	7.016	11.975	0.696	50.7	118.5	34	41.2	51.4
81.009	7.016	11.975	0.696	67.1	408	53	58.9	70.7
60.888	7.402	31.71	0.823	55.6	99.5	37	44.7	55.8
60.888	7.402	31.71	0.823	66.4	209.5	47	59.6	68.5
60.888	7.402	31.71	0.823	75.7	371	55	67.5	76.6
60.888	7.402	31.71	0.823	82.0	620	62	75.3	83.6

FIG. 20-33

Hydrate Formation Conditions for Sweet Gas Showing Effects of CO_2 and H_2S



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FIG. 20-34

Density of Aqueous Methanol Solutions at Various Temperatures

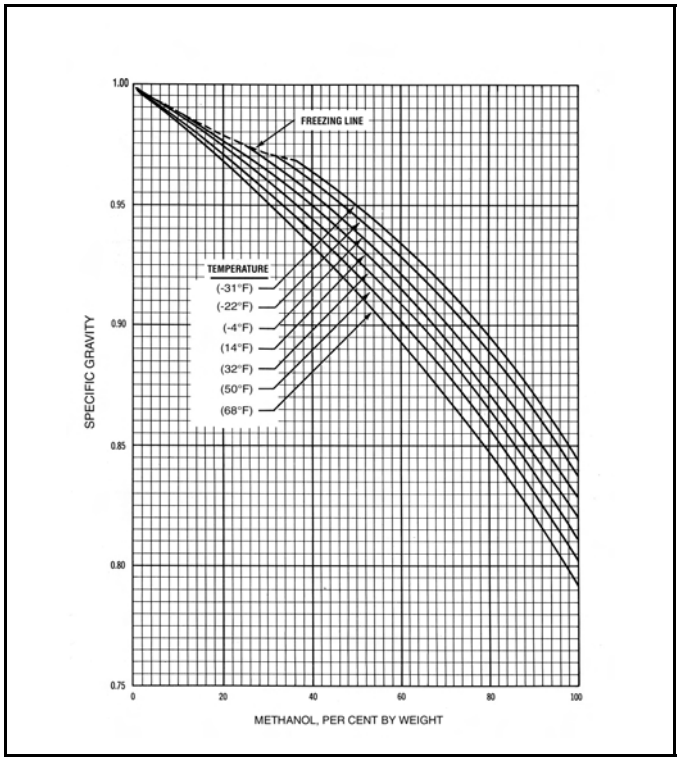


FIG. 20-35

Vapor Pressure of Aqueous Methanol Solutions at Various Temperatures

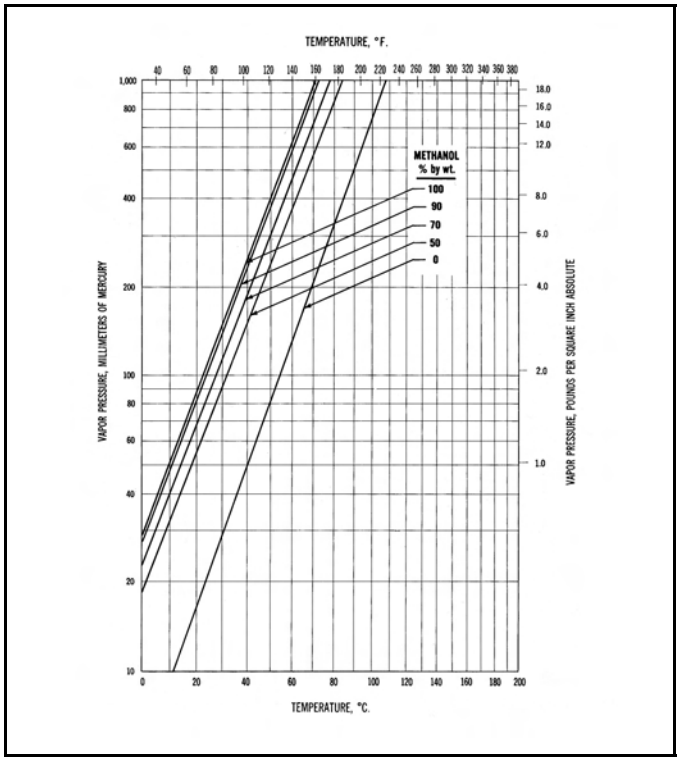


FIG. 20-36

Heat of Vaporization of Methanol Versus Temperature

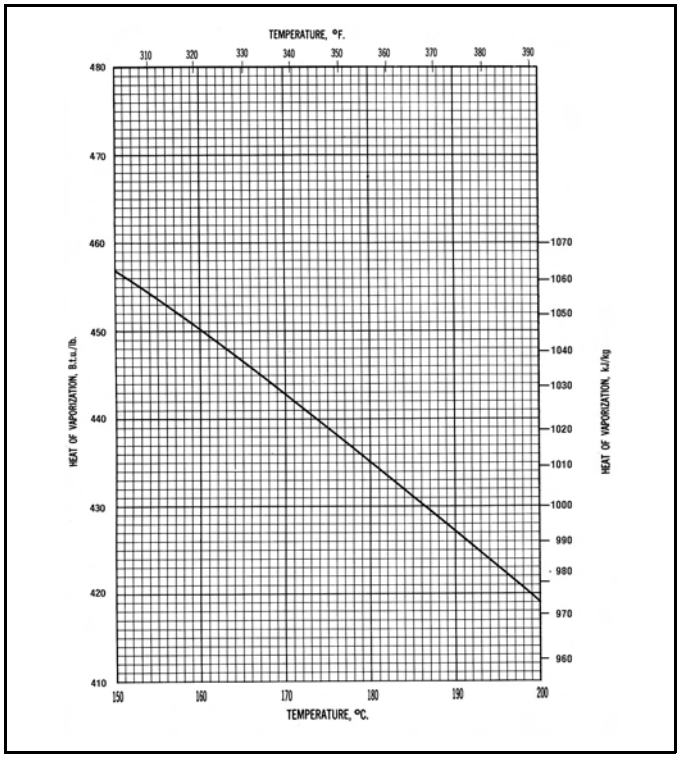
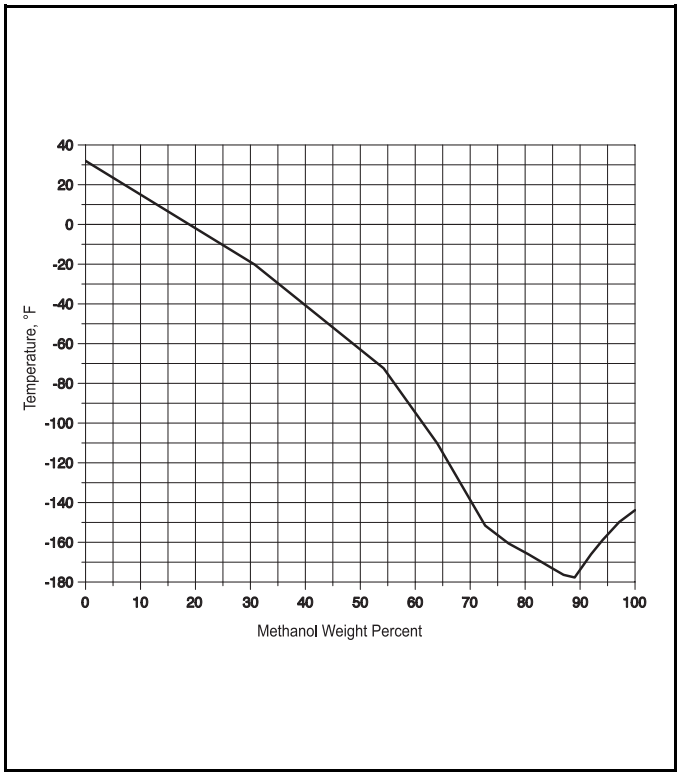


FIG. 20-37

Freezing Points of Aqueous Methanol Solutions



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FIG. 20-38

Densities of Aqueous Ethylene Glycol Solutions

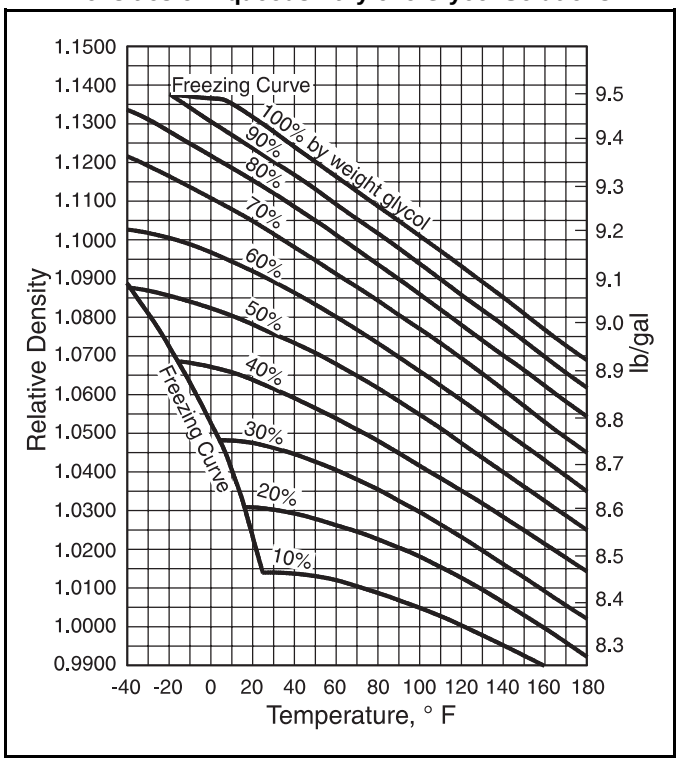


FIG. 20-39

Densities of Aqueous Diethylene Glycol Solutions

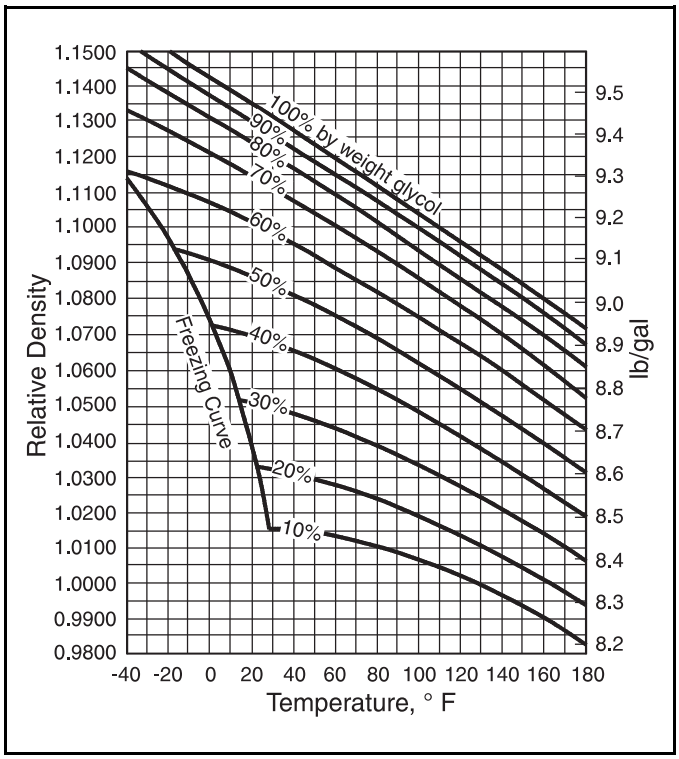


FIG. 20-40

Densities of Aqueous Triethylene Glycol Solutions

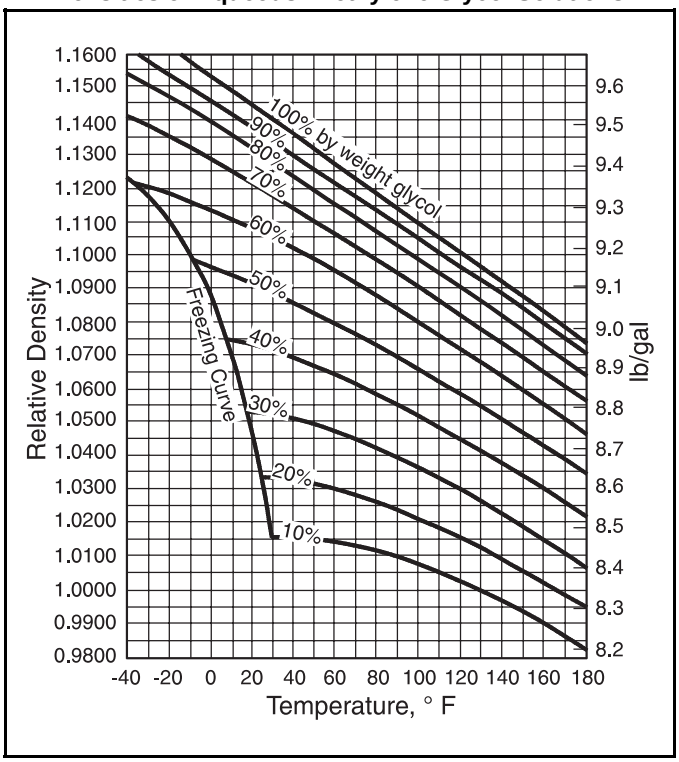
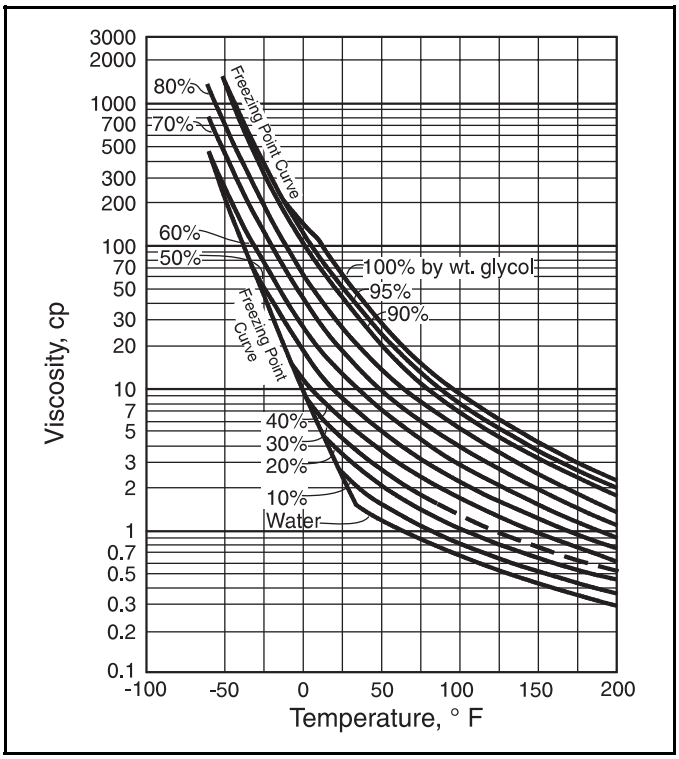


FIG. 20-41

Viscosities of Aqueous Ethylene Glycol Solutions



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FIG. 20-42

Viscosities of Aqueous Diethylene Glycol Solutions

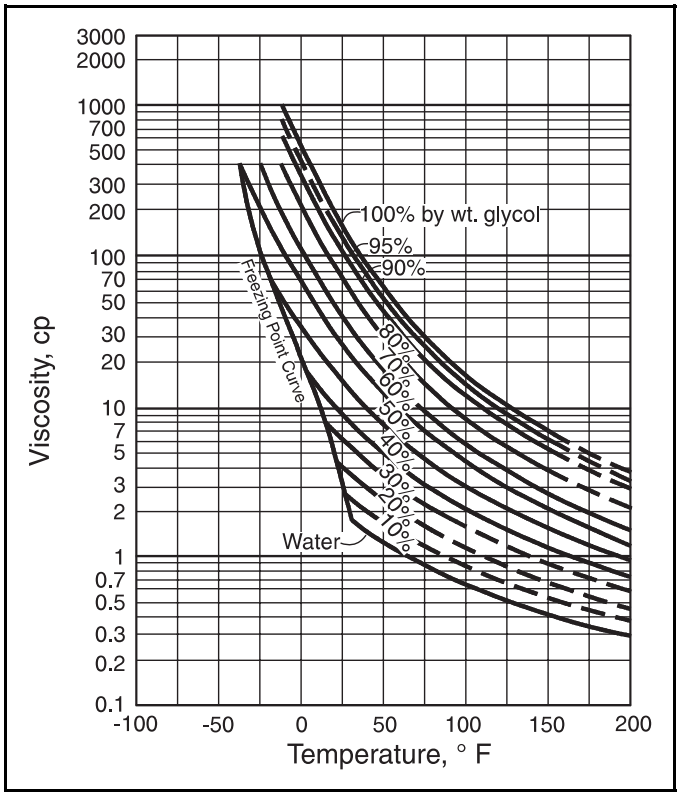


FIG. 20-43

Viscosities of Aqueous Triethylene Glycol Solutions

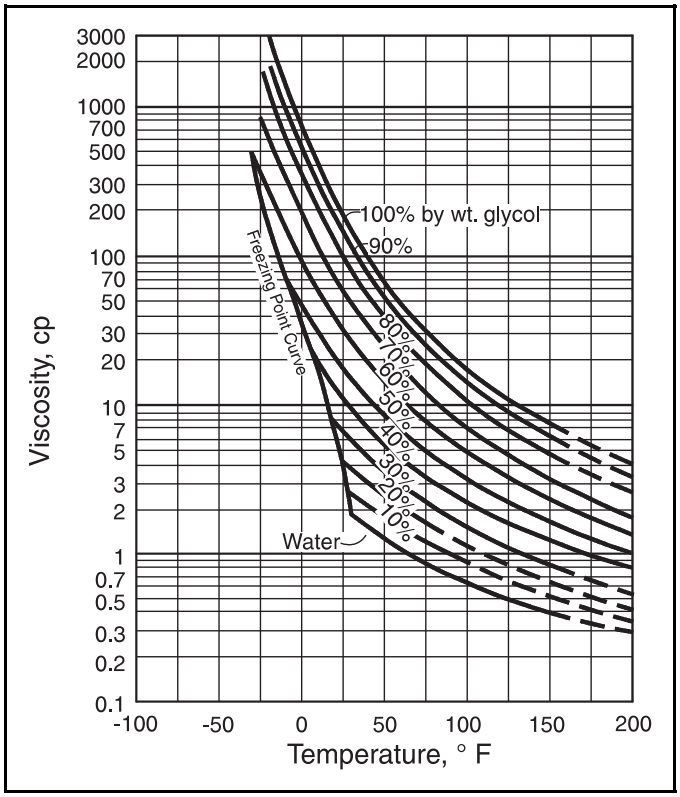


FIG. 20-44

Heat Capacities of Aqueous Ethylene Glycol Solutions

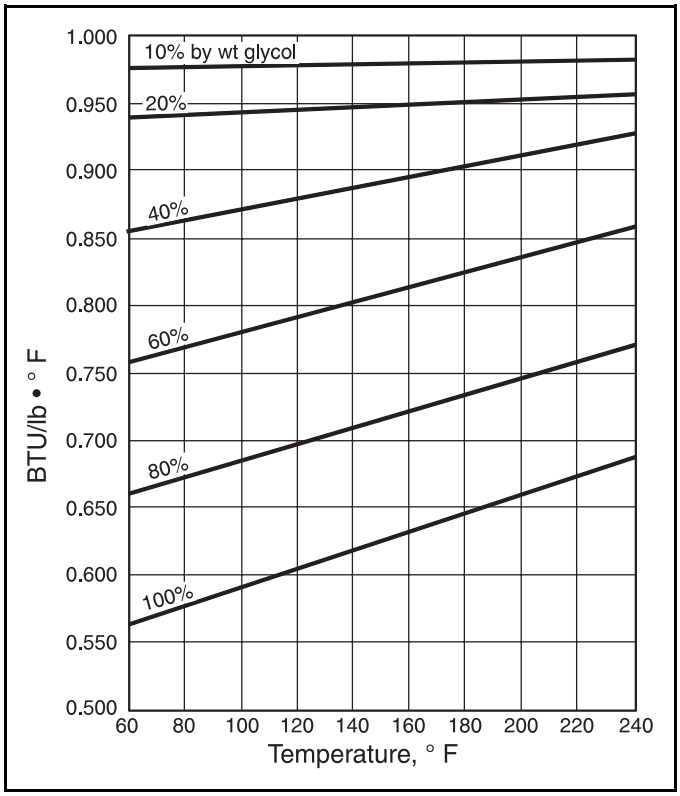
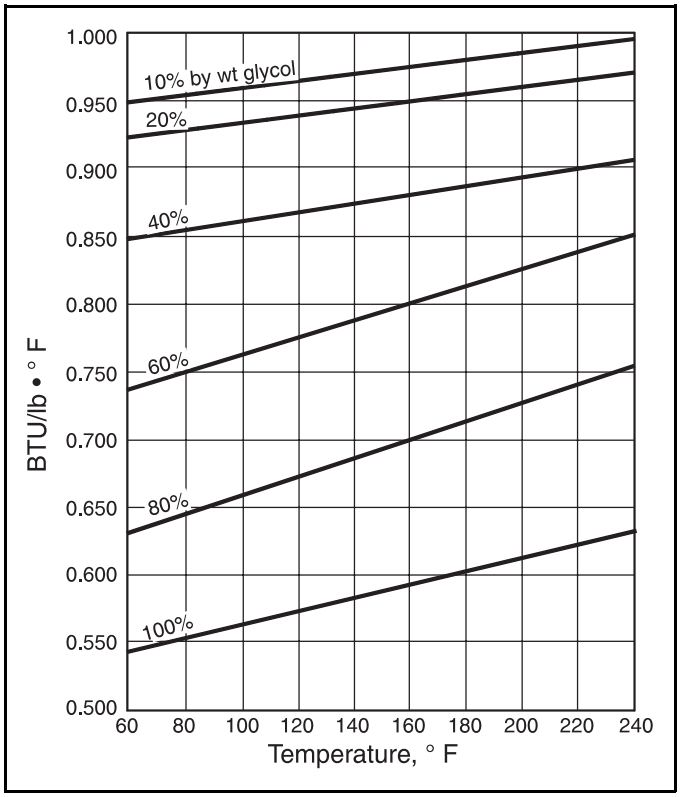


FIG. 20-45

Heat Capacities of Aqueous Diethylene Glycol Solutions



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FIG. 20-46

Heat Capacities of Aqueous Triethylene Glycol Solutions

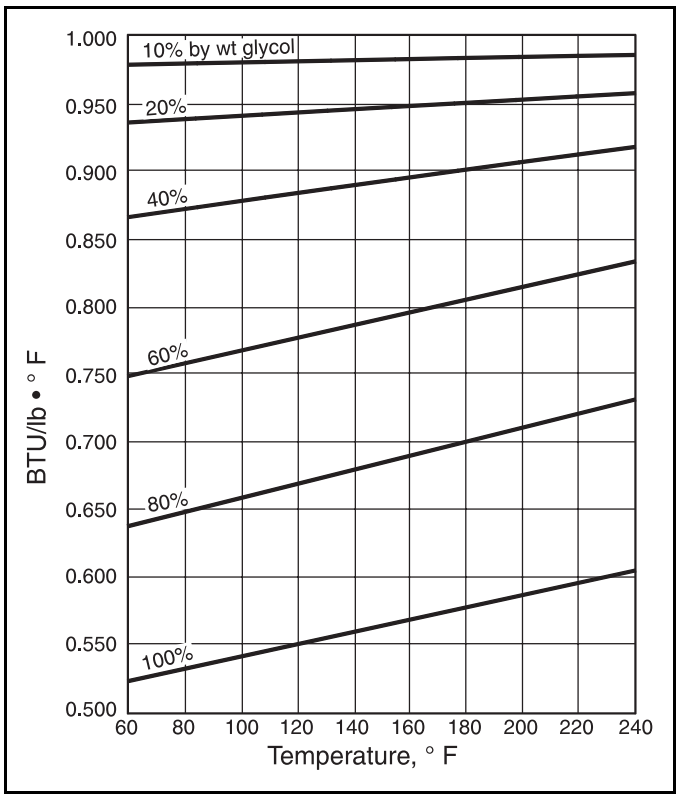


FIG. 20-47

Thermal Conductivity of Ethylene Glycol–Water Mixtures

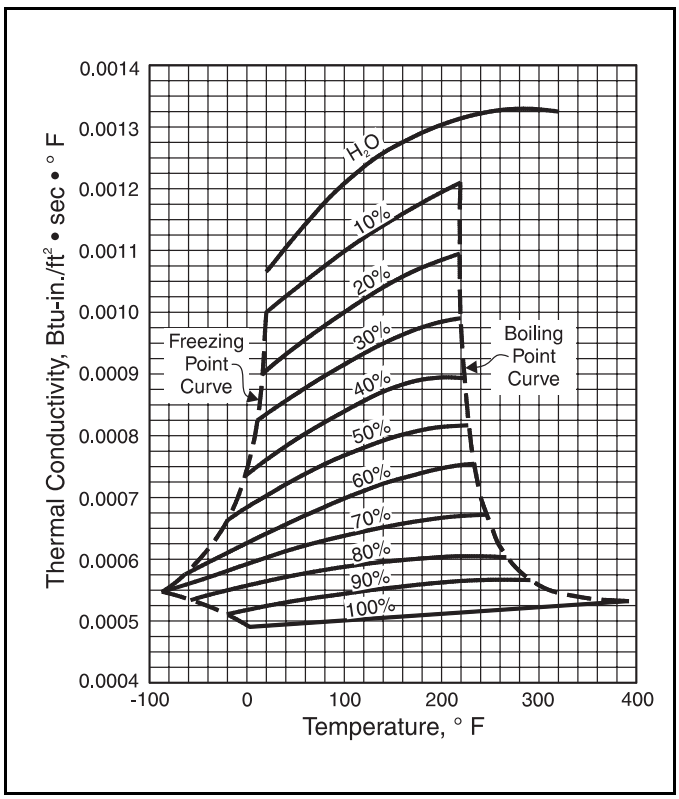


FIG. 20-48

Thermal Conductivity of Diethylene Glycol–Water Mixtures

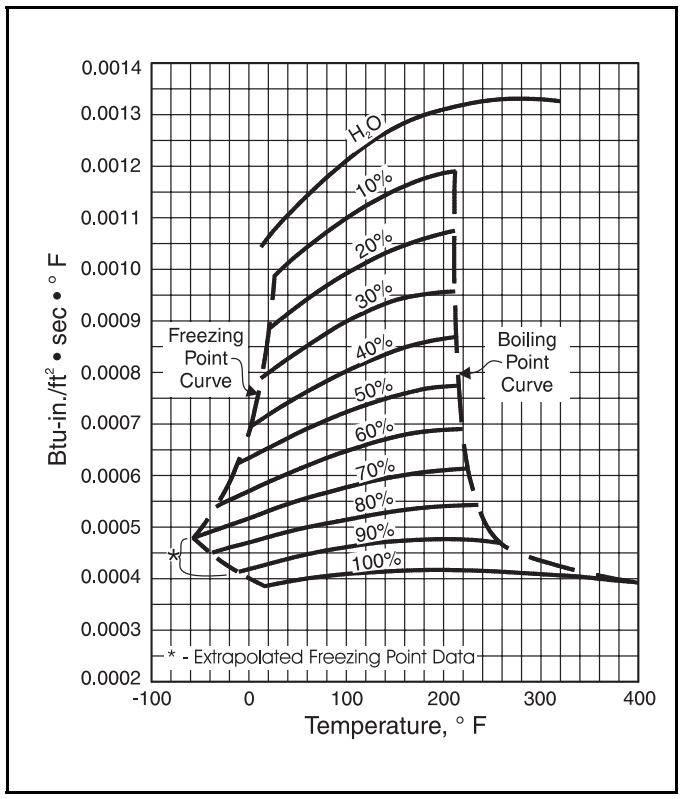
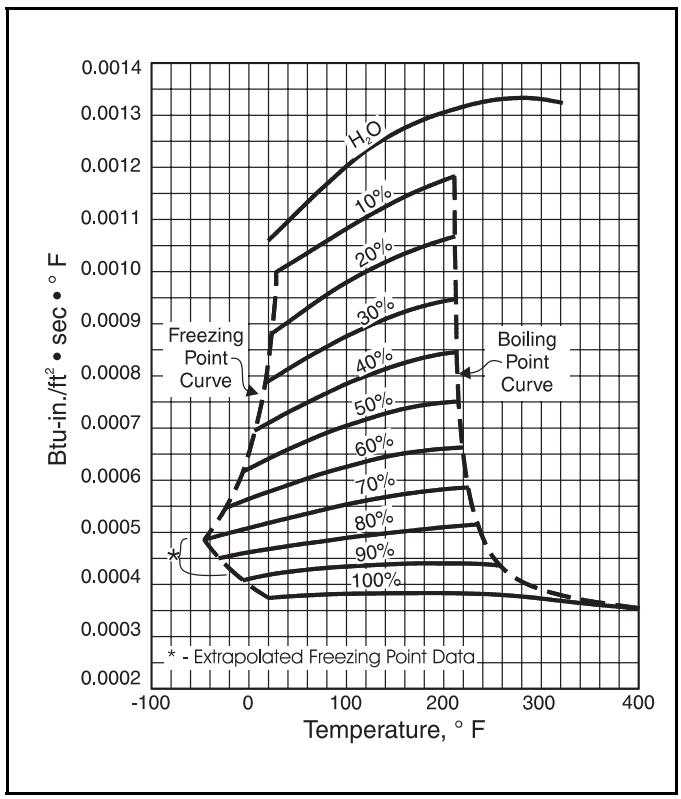


FIG. 20-49

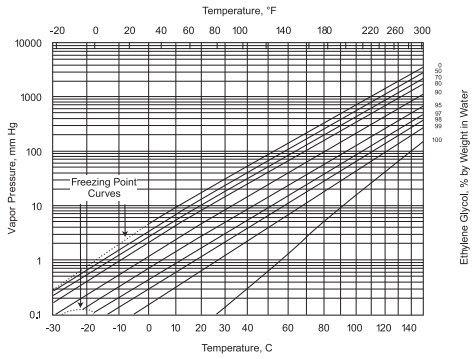
Thermal Conductivity of Triethylene Glycol–Water Mixtures



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FIG. 20-50

Vapor Pressures of Ethylene Glycol at Various Temperatures



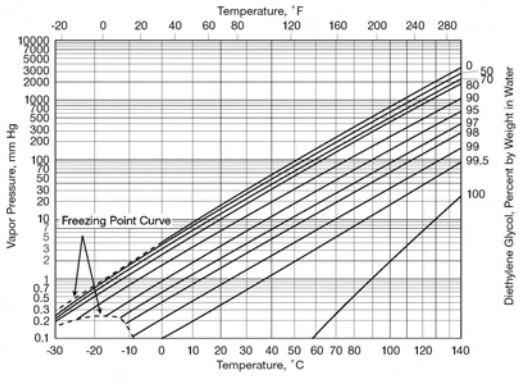
Ethylene Glycol Antoine Constants for Calculating Vapor Pressure
3-Constant Equation
$Log_{10}(P) = A - B/(T + C)$
P = mmHg, T = °C

EG, Wt%	A	B	C
0	7.966820	1668.210	228.000
50	7.901886	1691.452	229.778
70	7.833380	1712.369	231.166
80	7.775839	1736.188	232.689
90	7.685032	1792.464	235.836
95	7.856193	2019.846	251.898
97	8.123192	2273.083	267.910
98	8.384100	2493.364	279.584
99	9.189807	3103.597	309.713
100	8.212109	2161.907	208.429

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FIG. 20-51

Vapor Pressures of Aqueous Diethylene Glycol Solutions at Various Temperatures



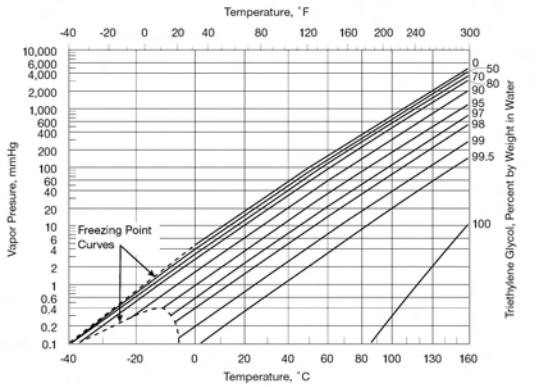
Diethylene Glycol Antoine Constants for Calculating Vapor Pressure
3-Constant Antoine Equation
$Log_{10}(P) = A - B/(T + C)$
P = mm Hg, T = °C

DiEG, Wt%	A	B	C
0	7.959199	1663.545	227.575
50	7.849221	1646.755	226.918
70	7.720100	1632.771	226.643
80	7.605747	1630.455	227.213
90	7.411919	1649.970	229.847
95	7.246397	1699.218	233.944
97	7.254579	1813.670	243.670
98	7.299095	1951.128	254.593
99	7.626717	2329.389	281.281
99.5	8.405776	3045.472	325.327
100	7.700795	2019.255	173.622

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FIG. 20-52

Vapor Pressures of Aqueous Triethylene Glycol Solutions at Various Temperatures



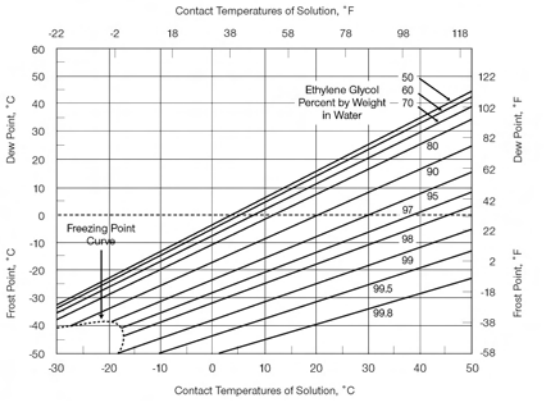
Triethylene Glycol Antoine Constants for Calculating Vapor Pressure
3-Constant Antoine Equation
$Log_{10}(P) = A - B/(T + C)$
P = mm Hg, T = °C

TriEG, Wt%	A	B	C
0	7.959199	1663.545	227.575
50	7.922294	1671.501	228.031
70	7.878546	1681.363	228.237
80	7.837076	1697.006	228.769
90	7.726126	1728.047	229.823
95	7.620215	1806.257	236.227
97	7.495349	1841.522	238.048
98	7.404435	1881.474	240.666
99	7.211145	1926.114	242.799
99.5	7.042989	1970.802	242.865
100	7.472115	2022.898	152.573

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FIG. 20-53

Dew Points of Aqueous Ethylene Glycol Solutions at Various Contact Temperatures



Dew or Frost Point = A + BT
T = Temperature, °C

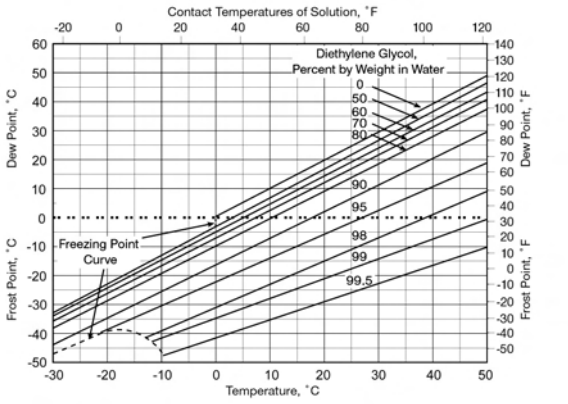
EG, Wt%	A	B
50.0	-3.532	0.96530
60.0	-5.043	0.95130
70.0	-7.231	0.93130
80.0	-10.663	0.90020
90.0	-17.081	0.84200
95.0	-23.575	0.77810
97.0	-28.124	0.72850
98.0	-31.807	0.69790
99.0	-37.996	0.65700
99.5	-43.626	0.61100
99.8	-50.671	0.55450

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FIG. 20-54

Dew Points of Aqueous Diethylene Glycol Solutions at Various Contact Temperatures



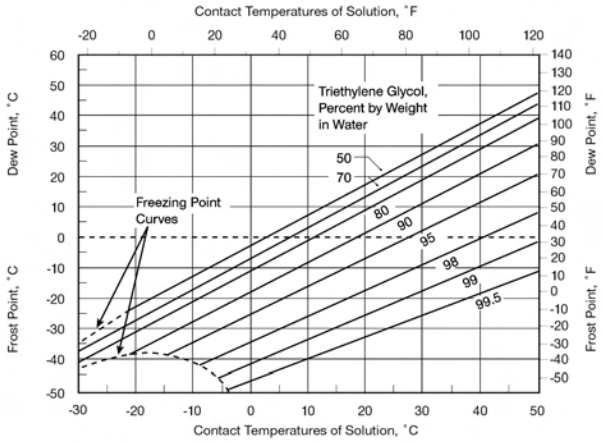
Dew or Frost Point = A + BT
T = Temperature, °C

DEG, Wt%	A	B
0	0.0000	0.99202
50	-3.1257	1.00710
60	-5.0603	0.97853
70	-7.1426	0.96426
80	-10.127	0.95719
90	-16.857	0.93572
95	-22.731	0.82862
98	-31.334	0.80003
99	-35.064	0.69450
99.5	-41.845	0.62866

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FIG. 20-55

Dew Points of Aqueous Triethylene Glycol Solutions at Various Contact Temperatures



Dew or Frost Point = A + BT
T = Temperature, °C

TriEG, Wt%	A	B
50	-3.0308	1.01050
70	-7.0009	1.01610
80	-10.745	1.01160
90	-17.923	0.98187
95	-25.252	0.93019
98	-34.675	0.85598
99	-41.419	0.80150
99.5	-47.195	0.73263

Courtesy of The Dow Chemical Company. All rights reserved.

- Lower toxicity

Kinetic Hydrate Inhibitors — KHIs were designed to inhibit hydrate formation in flowlines, pipelines, and downhole equipment operating within hydrate-forming conditions such as subsea and cold-weather environments. Their unique chemical structure significantly reduces the rate of nucleation and hydrate growth during conditions thermodynamically favorable for hydrate formation, without altering the thermodynamic hydrate formation conditions (i.e., temperature and pressure). This mechanism differs from methanol or glycol, which depress the thermodynamic hydrate formation temperature so that a flowline operates outside hydrate-forming conditions.

KHIs Compared to Methanol or Glycols— KHIs inhibit hydrate formation at a concentration range of 0.1–1.0 weight percent polymer in the free water phase. At the maximum recommended dosage, the current inhibition capabilities are 28°F of subcooling in a gas system and 20°F in an oil system with efforts continuing to expand the region of effectiveness. For relative comparison, methanol or glycol typically may be required at concentrations ranging 20 to 50 weight percent respectively in the water phase.

KHI Screening Considerations — Although KHIs are applicable under most producing conditions, certain conditions must be considered when evaluating a potential application, which include water salinity, freezing conditions, hold time (i.e., period of effectiveness), water saturation, and high-temperature processes.

- At water salinity levels greater than approximately 17% NaCL, the polymer may come out of solution, thereby reducing KHI effectiveness.
- A solution of KHI in water does not provide protection from freezing or icing conditions, neither in the line being treated nor in the KHI storage tank. If ambient temperatures are expected to fall below freezing, the KHI storage volume must be freeze-protected through the use of insulation on the container and piping or addition of antifreeze (typically ethylene glycol) to the KHI solution.
- A solution of KHI cannot be used for melting ice or hydrate plugs. It is recommended to have other strategies, such as a small quantity of ethylene glycol or methanol for remediation purposes in the event of a blockage.
- The KHI delivery system must be capable of providing sufficient dosage to achieve a hold time greater than the water residence time in the piping. Factors to consider include:
  - — The design basis duration of hydrate forming conditions for an unplanned shut-in.
  - — The potential for water to pool in low sections of piping (e.g., turn-down hydraulics, flowline profile, pigging frequency, flowline interconnects that are not used continuously) and dead legs.
  - — The seasonal duration of the cold point temperature below hydrate temperature, if applicable.
- If the gas is undersaturated with respect to water, the water in the KHI solution will evaporate and leave a high viscosity fluid. This can be addressed by using a more

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FIG. 20-56

Physical Properties of Selected Glycols and Methanol

	Ethylene Glycol	Diethylene Glycol	Triethylene Glycol	Tetraethylene Glycol	Methanol
Formula	$C_2H_6O_2$	$C_4H_{10}O_3$	$C_6H_{14}O_4$	$C_6H_{18}O_5$	CH_3OH
Molecular Weight	62.1	106.1	150.2	194.2	32.04
Boiling Point* at 760 mm Hg, °F	387.1	472.6	545.9	597.2	148.1
Boiling Point* at 760 mm Hg, °C	197.3	244.8	285.5	314	64.5
Vapor Pressure at 77°F (25°C) mm Hg	0.12	<0.01	<0.01	<0.01	120
Density (g/cc) at 77°F (25°C)	1.110	1.113	1.119	1.120	0.790
(g/cc) at 140°F (60°C)	1.085	1.088	1.092	1.092	
Pounds Per Gallon at 77°F (25°C)	9.26	9.29	9.34	9.34	6.59
Freezing Point, °F	8	17	19	22	–144.0
Pour Point, °F	—	–65	–73	–42	
Viscosity in centipoise at 77°F (25°C)	16.5	28.2	37.3	44.6	0.52
at 140°F (60°C)	4.68	6.99	8.77	10.2	
Surface Tension at 77°F (25°C), dynes/cm	47	44	45	45	22.5
Refractive Index at 77°F (25°C)	1.430	1.446	1.454	1.457	0.328
Specific Heat at 77 °F (25°C) Btu/(lb•°F)	0.58	0.55	0.53	0.52	0.60
Flash Point, °F (PMCC)	240	255	350	400	53.6
Fire Point, °F (C.O.C.)	245	290	330	375	

* Glycols decompose at temperatures below their atmospheric boiling point. Approximate decomposition temperatures are:

Ethylene Glycol 329°F Triethylene Glycol 404°F

dilute KHI solution, or by changing the KHI carrier fluid to ethylene glycol.

- The KHI and water from the KHI solution will form separate phases if the inhibited fluid is above the lower critical solution temperature (LCST) of the KHI solution.
- The KHI polymer suffers degradation effects at temperatures above 480°F.

Antiagglomerant Inhibitors — Antiagglomerants were developed out of the necessity to extend the range of subcooling for LDHIs beyond that of KHIs, and AAs can achieve subcooling of greater than 40°F. Unlike KHIs, which delay the formation of hydrates, AAs allow their formation at normal rates, but as small nonagglomerating hydrate crystals that are dispersed into an oil or condensate preventing the formation and accumulation of large hydrate crystals. Thus, AAs are suitable only in the presence of liquid hydrocarbon. The mechanism of dispersion is emulsification with the AAs acting as emulsification agents.

AAs Compared to Methanol or Glycols — The comparisons of AAs are similar for KHIs except AAs achieve greater subcooling.

AA Screening Considerations — Although AAs are applicable under most producing conditions, certain conditions must be considered when evaluating a potential application. These conditions include water salinity, emulsification and de-mulsification (i.e., separation), pipeline hydraulics, water cuts, material compatibility, water treating, and downstream impacts.

- Some AAs have a maximum salinity criterion that is normally not exceeded with produced water.
- Since AAs are based on dispersing (i.d., emulsifying) polar hydrate crystals in a nonpolar oil or condensate phase (i.e., continuous phase), they may sometimes require a de-emulsifier for oil and water separation. Further, the addition of a heater upstream or heat coil inside a separator may be required to melt the hydrate crystals.
- Since AAs form crystals that are then dispersed in the liquid hydrocarbon phase, careful consideration of the potential impact on viscosity should be considered including steady state flow, shut-in flow and restart conditions.
- An additional consideration for AAs is that the water cuts (i.e., percent water in the liquids) should be less than 50%. Higher water cuts can invert the emulsion (i.e., change the continuous liquid phase from liquid hydrocarbon to water) and make the AA ineffective.
- AAs can impact the performance of some metallurgy and elastomers, so impacts on existing hardware should be reviewed.

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- AAs typically partition (i.e., disperse) to the liquid hydrocarbon phase, but low residuals can remain in the produced water, which can impact toxicity test results.
- Residual AA concentration in the hydrocarbon liquid phase could possibly impact downstream processes and should be considered in the context of overall contribution to a total feed-stream.

GAS DEHYDRATION

Glycol Dehydration Systems

In those situations where inhibition is not feasible or practical, dehydration must be used. Both liquid and solid desiccants may be used, but economics frequently favor liquid desiccant dehydration when it will meet the required dehydration specification.

Liquid desiccant dehydration equipment is simple to operate and maintain. It can easily be automated for unattended operation; for example, glycol dehydration at a remote production well. Liquid desiccants can be used for sour gases, but additional precautions in the design are needed due to the solubility of the acid gases in the desiccant solution. At very high acid gas content and relatively higher pressures the glycols can also be "soluble" in the gas.

Glycols are typically used for applications where dew point depressions of the order of 60° to 120°F are required. Diethylene glycol (DEG), triethylene glycol (TEG), and tetraethylene glycol (TREG) are used as liquid desiccants, but TEG is the most common for natural gas dehydration.

Good practice dictates installing an inlet gas scrubber, even if the dehydrator is near a production separator. The inlet gas scrubber will prevent accidental dumping of large quantities of water (fresh or salty), hydrocarbons, treating chemicals or corrosion inhibitors into the glycol contactor. Even small quantities of these materials can result in excessive glycol losses due to foaming, reduced efficiency, and increased maintenance. Integral separators at the bottom of the contactor are common.

Following the process flow in Fig. 20-67, the regenerated glycol is pumped to the top tray of the contactor (absorber). The glycol absorbs water as it flows down through the contactor countercurrent to the gas flow. Water-rich glycol is removed from the bottom of the contactor, passes through the reflux condenser coil, flashes off most of the soluble gas in the flash tank, and flows through the rich-lean heat exchanger to the regenerator. In the regenerator, absorbed water is distilled from the glycol at near atmospheric pressure by application of heat. The regenerated lean glycol exits the surge drum, is partly cooled in the lean-rich exchanger and is pumped through the glycol cooler before being recirculated to the contactor.

Evaluation of a TEG system involves first establishing the minimum TEG concentration required to meet the outlet gas water dewpoint specification. Fig. 20-68 shows the water dewpoint of a natural gas stream in equilibrium with a TEG solution at various temperatures and TEG concentrations. Fig. 20-68 can be used to estimate the required TEG concentration for a particular application or the theoretical dewpoint depression for a given TEG concentration and contactor temperature. Actual outlet dewpoints depend on the TEG circulation rate and number of equilibrium stages, but typical approaches to equilibrium are 10-20°F. Equilibrium dewpoints are relatively

FIG. 20-57

Typical Glycol Injection System

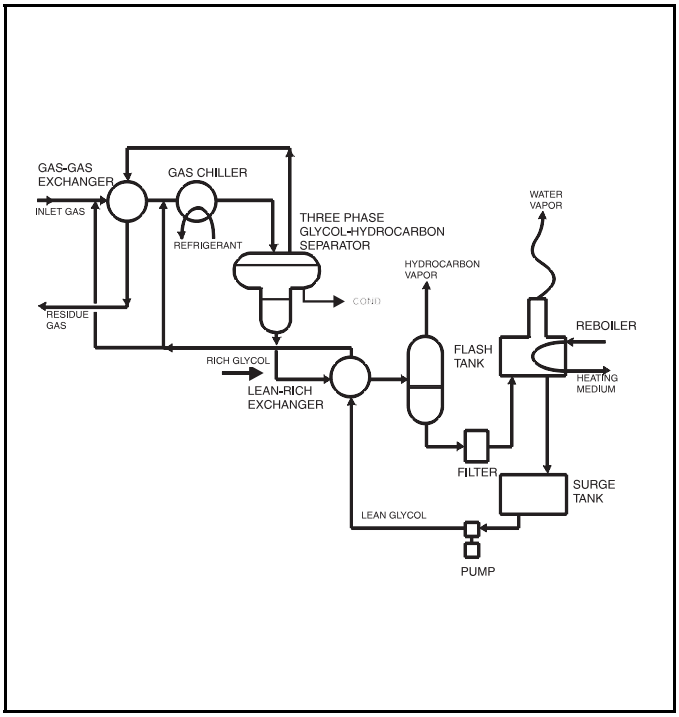
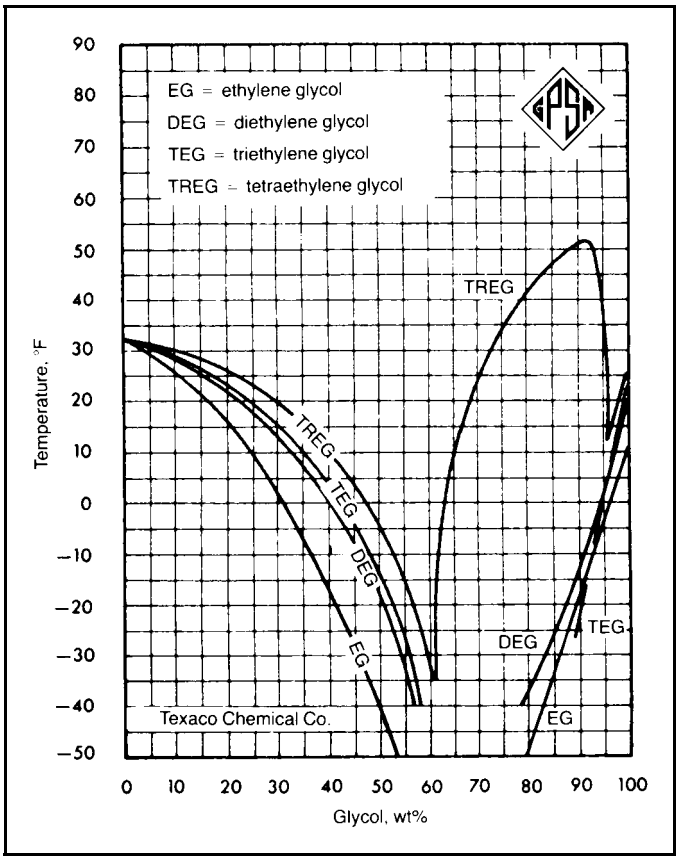


FIG. 20-58

Freezing Points of Aqueous Glycol Solutions



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insensitive to pressure and Fig. 20-68 may be used up to 1500 psia with little error.

Fig. 20-68 combines the results published by Parrish, et al.[35] covering TEG purity up to 99.99 weight percent and those reported by Bucklin and Won in 1987[52] covering TEG purity up to 99.999 weight percent. Several equilibrium correlations[36,37,38,39,40,52] have been presented since 1950. Previous editions of the GPSA data book presented an equilibrium correlation based on the work of Worley[38]. In general, the correlations of Worley,[38] Rosman[39] and Parrish[35] agree reasonably well and are adequate for most TEG system designs. All are limited by the ability to measure accurately the equilibrium concentration of water in the vapor phase above TEG solutions. The Parrish et al. and Won correlation has been included in this edition because equilibrium water concentrations in the vapor phase were determined at infinite dilution (essentially 100% TEG). The other correlations use extrapolations of data at lower concentrations to estimate equilibrium in the infinite dilution region.

Please note that the equilibrium water dewpoints on the ordinate of Fig. 20-68 are based on the assumption the condensed water phase is a metastable liquid. At low dewpoints the true condensed phase will be a hydrate. The equilibrium dewpoint temperature above a hydrate is higher than that above a metastable liquid. Therefore, Fig. 20-68 predicts dewpoints which are colder than those which can actually be achieved. The difference is a function of temperature, pressure and gas composition but can be as much as 15-20°F (see Fig. 20-17). When dehydrating to very low dewpoints, such as those required upstream of a refrigeration process, the TEG concentration must be sufficient to dry the gas to the hydrate dewpoint.

Once the lean TEG concentration has been established, the TEG circulation rate and number of trays (height of packing) must be determined. Most economical designs employ circulation rates of about 2-5 gal. TEG/lb H_2O absorbed. The relationship between circulation rate and number of equilibrium stages employs the absorption calculation techniques set out in Chapter 19. This has been done for TEG systems with the results presented in Figs. 20-69 through 20-74.

The graphs in these figures apply only if the feed gas is water saturated. They are based on feed-gas and therefore contactor temperatures of 80°F, but are essentially independent of temperature. Although the K values in the absorption factors (i.e., L/VK) do increase with temperature, the required TEG rates also increase, and this tends to compensate for the increasing K values and keep the absorption factors fairly constant.

Conversion from equilibrium stages to actual trays can be made assuming an overall tray efficiency of 25-30%. For random and structured packing, Height of Packing Equivalent to a Theoretical Plate (HETP) varies with TEG circulation rate, gas rate, gas density, and packing characteristics but a value of about 60 inches is usually adequate for planning purposes. When the gas density exceeds about 6 lb/ft^3 (generally at very high pressures), the above conversions may not provide sufficient packing height and number of trays. Also when the contactor temperature is less than about 60°F, the increased viscosity of the TEG can reduce mass transfer efficiency, and temperatures in this range should be avoided.

Typical tray spacing in TEG contactors is 24 inches. Therefore, the total height of the contactor column will be based on the number of trays or packing required plus an additional 6-10 ft to allow space for vapor disengagement above the top tray, inlet gas distribution below the bottom tray, and rich glycol surge volume at the bottom of the column. Bubble cap trays have historically been used in glycol contactors due to the low liquid rates versus gas flow, but structured packing is widely used. Generally, structured packing allows a significantly smaller contactor diameter and a slightly smaller contactor height. In 1991, ARCO published a report on its testing and application of structured packing to TEG dehydration.[53]

Contactor diameter is set by the gas velocity. Sizing is identical to that outlined for separators in Section 7. Recommended values for K-factors and C-factors are shown in Fig. 20-75.

Structured packing vendors frequently quote an F_s value for sizing glycol contactors, where F_s is defined in Eq 20-9.

$$F_s = v\sqrt{\rho_v} \qquad \textbf{Eq 20-9}$$

Values of F_s = 2.5 to 3.0 will generally provide a good estimate of contactor diameter for structured packing.

FIG. 20-59

Hydrate Temperature Depression vs. Methanol Concentration

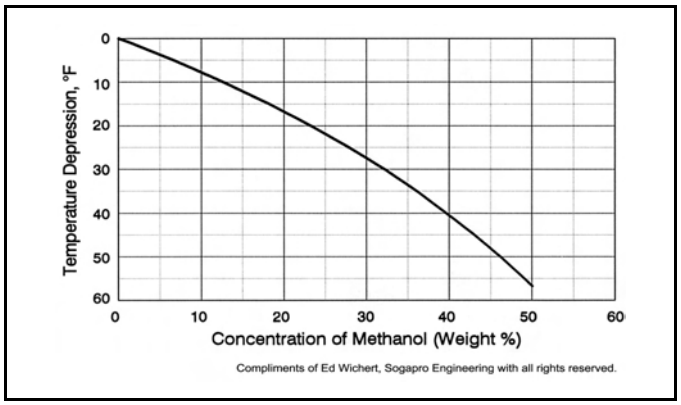
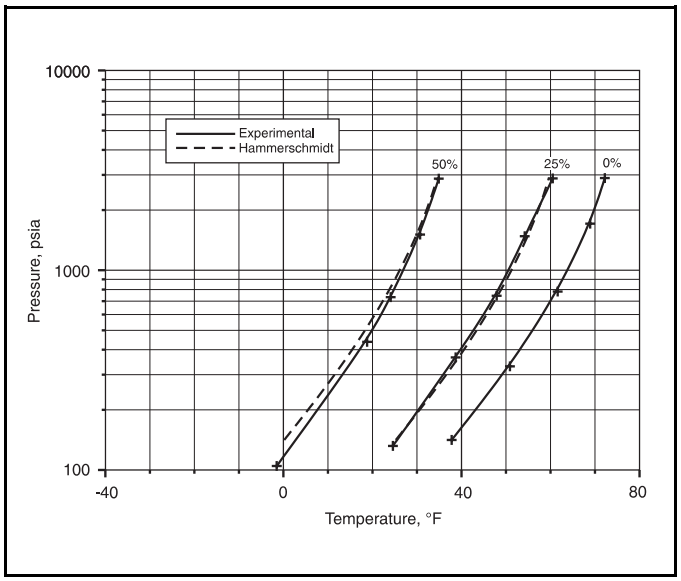


FIG. 20-60

Hydrate Inhibition with Ethylene Glycol: Hammerschmidt vs. Experimental Data[28]



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Example 20-11—30 MMscf/d of a 0.65 sp gr natural gas enters a TEG contactor at 600 psia and 100°F. Outlet water content specification is 7 lb H_2O/MMscf and the TEG circulation rate is 3 gal TEG/lb H_2O. Estimate the contactor diameter and number of bubble cap trays or height of structured packing required to meet this requirement. Assume z = 0.92.

Solutions Steps:

1. Estimate required TEG concentration from Fig. 20-68

   H_2O Dewpoint = 24°F, which from Fig. 20-4 is equivalent to a water content of 7 lb H_2O/MMscf @ 600 psia)

   Assume a 10°F approach to equilibrium

   @ T = 100°F, lean TEG concentration ≈ 98.8 wt%

2. Estimate number of theoretical stages.

   Calculate water removal efficiency

$$\frac{W_{in} - W_{out}}{W_{in}} = \frac{90 - 7}{90} = 0.922$$

From Fig. 20-70 (N = 1.5) at 3 gallon TEG/lb H_2O and 99.0 wt% TEG

$(W_{in} - W_{out})/W_{in} = 0.885$

From Fig. 20-71 (N = 2.0) at 3 gallon TEG/lb H_2O and 99.0 wt% TEG

$(W_{in} - W_{out})/W_{in} = 0.925$

use N = 2.0

2 theoretical stages ≅ 8 bubble cap trays @ 24 inch tray spacing

FIG. 20-61

Hydrate Inhibition with Methanol: Hammerschmidt vs. Experimental Data[28]

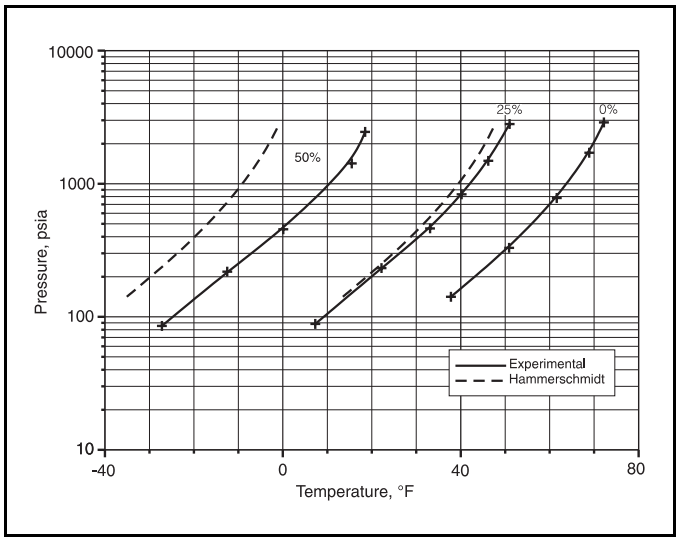


FIG. 20-62

Hydrate Inhibition with Methanol: Nielsen & Bucklin vs. Experimental Data[28]

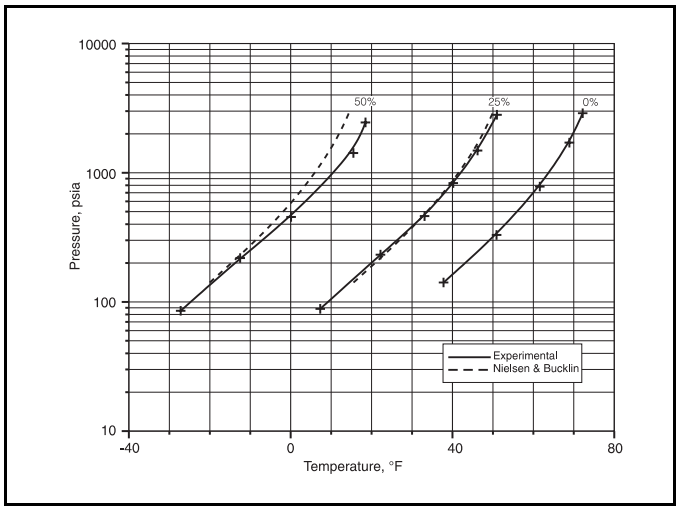


FIG. 20-63

Hydrate Inhibition with Methanol: Nielsen & Bucklin[26] vs. Experimental Data[28]

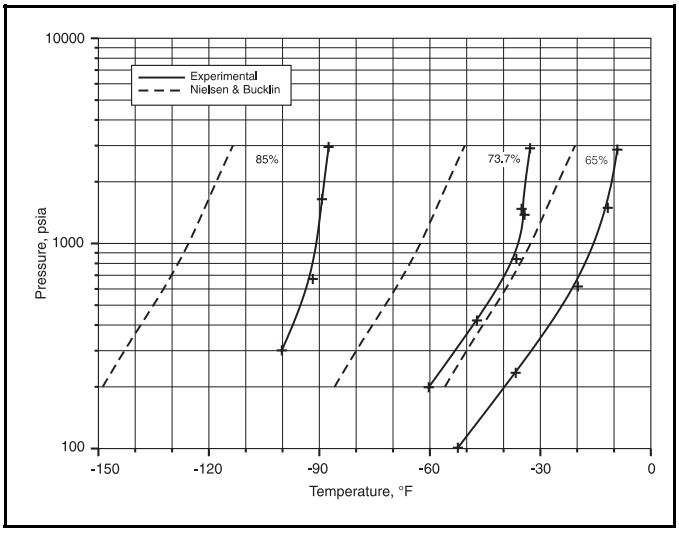
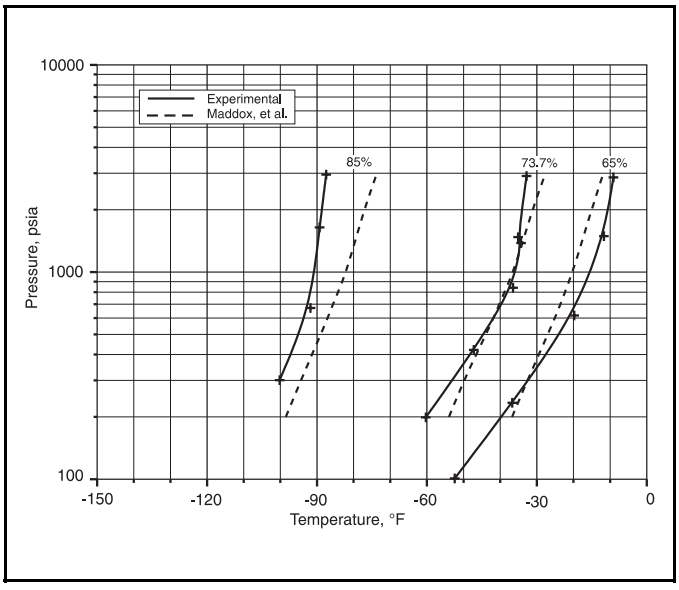


FIG. 20-64

Hydrate Inhibition with Methanol: Maddox et al.[27] vs. Experimental Data[28]



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2 theoretical stages ≅ 10 ft of structured packing

3. Size the contactor

Bubble caps, 24 inch tray spacing:

From Section 7

$$G = C\,[\rho_v(\rho_L - \rho_v)]^{0.5}$$

$$= 576\,[2.0(69.9 - 2.0)]^{0.5} = 6712 \text{ lb / ft}^2 \bullet \text{ hr}$$

$$\dot{m} = \left(\frac{30\,000\,000 \text{ scf}}{\text{d}}\right)\left(\frac{1 \text{ lb} \bullet \text{mol}}{379.5 \text{ scf}}\right)$$

$$\left(\frac{(0.65)(28.97) \text{ lb}}{\text{lb} \bullet \text{mol}}\right)\left(\frac{1 \text{ d}}{24 \text{ hr}}\right) = 62\,000 \text{ lb hr}$$

$$A = \frac{\dot{m}}{G} = \frac{62\,000}{6712} = 9.2 \text{ ft}^2$$

$$D = \left(\frac{4\,A}{\pi}\right)^{0.5} = \left(\frac{(4)(9.2)}{3.14}\right)^{0.5} = 3.4 \text{ ft}$$

For Structured packing:

$$D = \left(\frac{C_{\text{Bubble cap}}}{C_{\text{Structured packing}}}\right)^{0.5} (D_{\text{Bubble cap}})$$

$$= \left(\frac{576}{1200}\right)^{0.5} (3.4) = 2.4 \text{ ft}$$

TEG will typically absorb about 1 scf of sweet natural gas per gallon of glycol at 1000 psia and 100°F. Solubilities will be considerably higher if the gas contains significant amounts of CO_2 and H_2S.

The solubilities of pure H_2S and CO_2 in pure TEG are given in Fig. 20-76. These charts apply to pure TEG or to the lean TEG, which is essentially pure. For the rich-TEG solution leaving the bottom of a contactor, it is approximately correct to apply them to the TEG portion.

Heavier paraffin hydrocarbons are essentially insoluble in TEG. Aromatic hydrocarbons, however, are very soluble in TEG, and significant amounts of aromatic hydrocarbons may be absorbed in the TEG at contactor conditions. This may present an environmental or safety hazard when they are discharged from the top of the regenerator.

Vapor-liquid equilibrium constants (K-values) for benzene, toluene, ethylbenzene, and o-xylene in TEG solutions are presented in RR-131.[43] This data indicates that at typical contactor conditions approximately 10-30% of the aromatics in the gas stream may be absorbed in the TEG solution. Based on the data in RR-131 at 1000 psia, 100°F and a TEG circulation rate of 3 gal TEG/lb H_2O absorbed, the approximate percentage absorption of aromatics from the gas into the rich TEG are calculated as:

Benzene	10%
Toluene	14%
Ethylbenzene	19%
O-xylene	28%

Aromatic absorption increases with increasing pressure and decreasing temperature. Aromatic absorption is directly related to TEG circulation rate. Higher circulation rates result in increased absorption. Aromatic absorption is essentially independent of the number of contacts in the absorber so one method of minimizing aromatic absorption is to use taller contactors and minimize TEG circulation rates.

Most of the aromatic components will be stripped from the TEG solution in the regenerator.

Flash tank sizing should be sufficient to degas the glycol solution and skim entrained liquid hydrocarbons, if necessary. A minimum retention time of 3-5 minutes is required for degassing. If liquid hydrocarbons are to be removed as well, retention times of 20-30 minutes may be required for adequate separation. Flash tank pressures are typically less than 75 psia.

Regenerator sizing requires establishing the reboiler duty and, when high TEG concentrations are required, providing sufficient stripping gas.

FIG. 20-65

Ratio of Methanol Vapor Composition to Methanol Liquid Composition

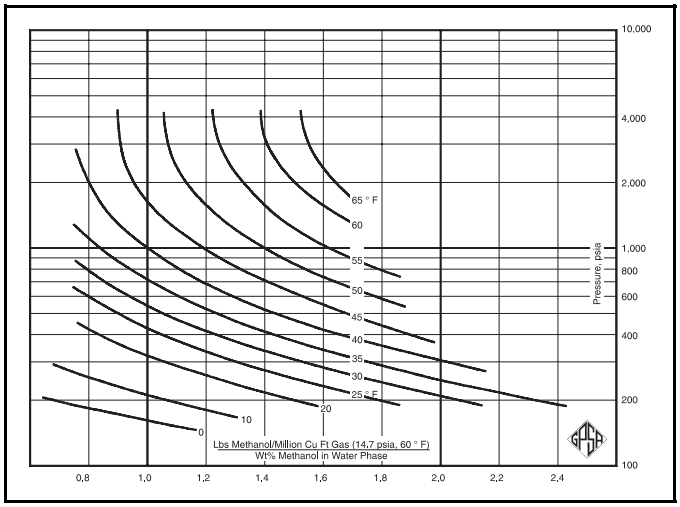
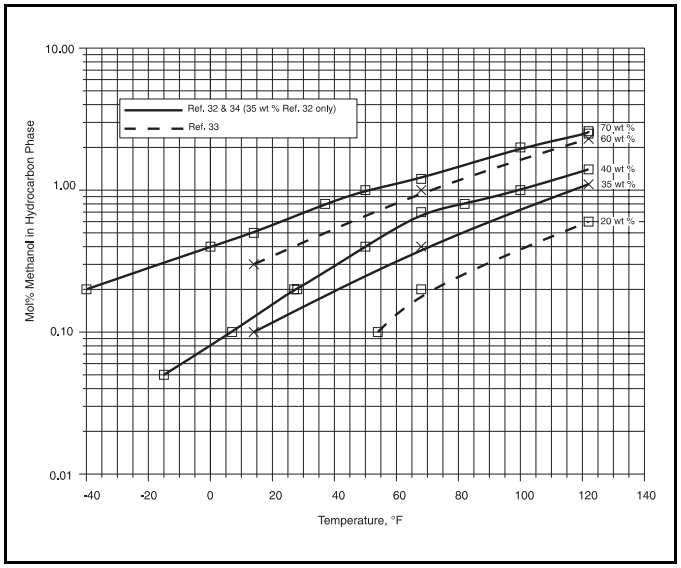


FIG. 20-66

Solubility of Methanol in Paraffinic Hydrocarbons[32, 33,34] vs. Temperature at Various Methanol Concentrations



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FIG. 20-67

Example Process Flow Diagram for Glycol Dehydration Unit

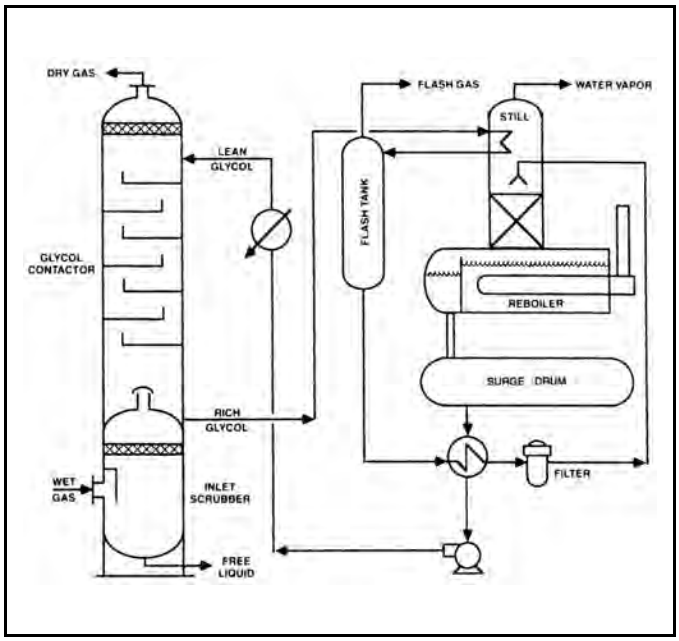
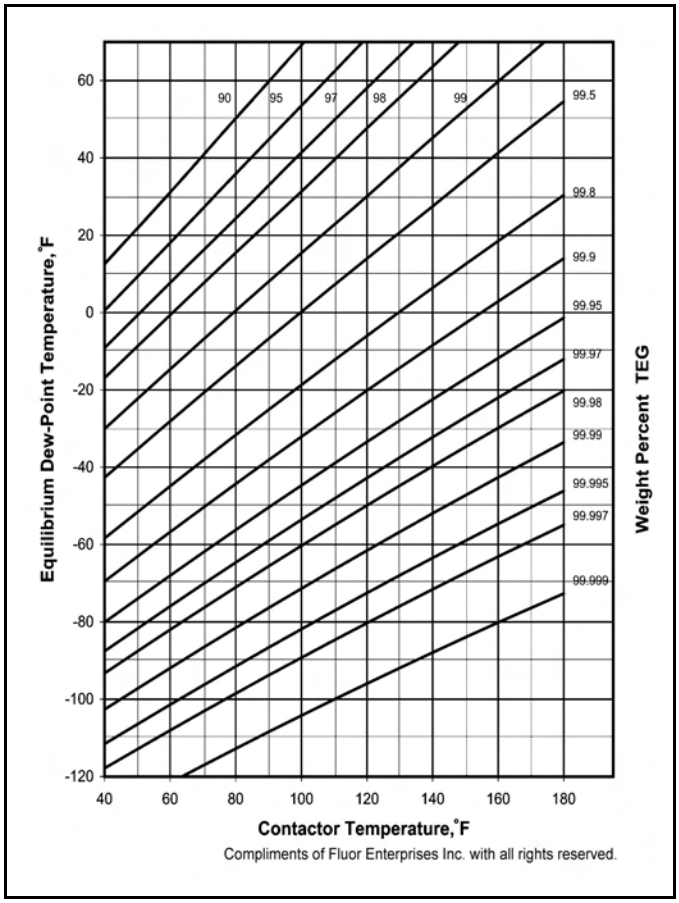


FIG. 20-68

Equilibrium H_2O Dewpoint vs. Temperature at Various TEG Concentrations



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A quick estimate of reboiler duty can be made using Eq 20-10.

$$Q = (1500)\,(L_g) \qquad \textbf{Eq 20-10}$$

Eq 20-10 is approximate and usually gives values which are higher than the actual duty. A more rigorous determination of reboiler duty is shown in Example 20-12.

Example 20-12 — Determine reboiler duty for conditions in the previous example. Assume the rich TEG temperature entering the regenerator is 300°F and the reboiler temperature is 400°F.

Glycol Reboiler Duty: Basis 1 gal. TEG

Sensible Heat:

$$Q_s = m\,C_p\,\Delta t$$

$$= \frac{(9.3\text{ lb})}{\text{gal.}}\left(\frac{0.665\text{ Btu}}{\text{lb}\bullet\,^\circ\text{F}}\right)(400^\circ\text{F} - 300^\circ\text{F})$$

$$= 618\text{ Btu /gal.}$$

Vaporization of Absorbed H_2O:

$$Q_v = (\Delta H_{vap})\,(\Delta W)$$

$$= \left(\frac{970\text{ Btu}}{\text{lb } H_2O}\right)\left(\frac{1\text{ lb } H_2O}{3\text{ gal. TEG}}\right)$$

$$= 323\text{ Btu /gal.}$$

Condenser Duty @ 25% Reflux Ratio:

$$Q_c = (0.25)\,(Q_v) = 81\text{ Btu /gal.}$$

Total Duty Including 10% Heat Loss:

$$Q_r = (618 + 323 + 81)\,(1.1) = 1124\text{ Btu /gal.}$$

Total Duty Based on 30 MMscfd of Gas:

Q = (1124 Btu/gal) (3 gal./lb) (30 MMscfd/24) ((90-7) lb/MMscf) = 350,000 Btu/hr

Boiling of TEG at 400°F and 1 atmosphere will provide about 98.6 wt% glycol. Regeneration at higher altitude will result in higher concentrations at 400°F or a reduced regeneration temperature at the same concentration.

ENHANCED GLYCOL CONCENTRATION PROCESSES

There are several principles and processes for obtaining higher TEG purity than 98.6 wt%, which is the TEG purity obtained by reboiling at 400°F and atmospheric pressure. All methods are based on the principle of reducing the effective partial pressure of H_2O in the vapor space of the glycol reboiler, and hence obtaining a higher glycol concentration at the same temperature.

The most common method for enhancement of the glycol concentration has been by use of stripping gas or by means of vacuum in the reboiler.

Other patented or proprietary processes in use to enhance the glycol purity and thereby achieve a more stringent water dew point depression are as described below based on information from the licensors.

The processes are illustrated on Fig. 20-77.

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DRIZO®

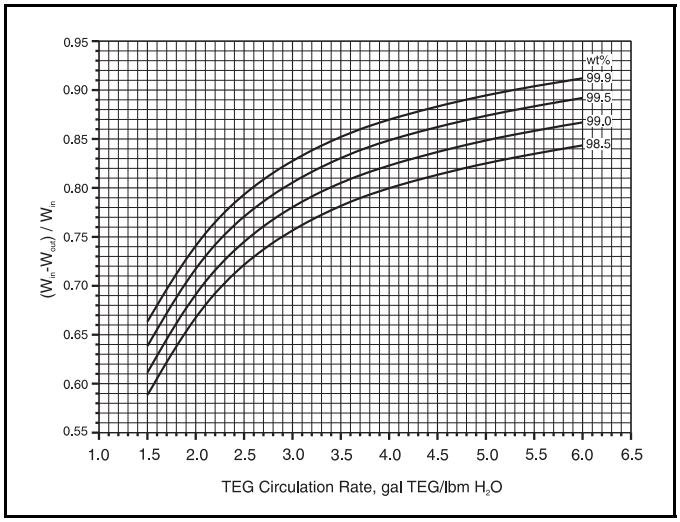
DRIZO® achieves glycol enrichment by means of its own internally generated stripping medium, a mixture of paraffinic and aromatic (BTEX) hydrocarbons of a C_5+ boiling range, which are absorbed by the glycol. The heavy hydrocarbons and water are condensed from the regenerator overhead while the non-condensables discharge to atmosphere essentially free of BTEX. The condensed hydrocarbons (with BTEX) are separated from the water, are vaporized and superheated, and flow to the lean-glycol stripping column to serve as the stripping medium, which results in TEG purities higher than 99.99 weight percent. As the liquid hydrocarbons build up, they are drawn off as an NGL product. Various options to further enhance the lean TEG purity are available, such as drying the hydrocarbon liquid solvent with solid desiccant, which achieves TEG purities as high as 99.999 weight percent. It is claimed that this high TEG purity level permits water dewpoint depressions in the range of 250°F.

COLDFINGER®

The COLDFINGER® process can be described as a trace-water exhauster for liquids, either hydrophilic (as with glycols) or hydrophobic (as with propane, butanes, etc.). With triethylene glycol (TEG), it is most effective at 400°F and corresponding water concentrations where the equilibrium vapor is water rich at approximately 40 to 45% by weight TEG and 55 to 60% water; and the water concentration of the liquid feed (lean TEG) is one and one-half percent (1-1/2%) or less. With the surge tank half full of hot-lean TEG, a condensing tube bundle ("cold finger") inserted in the surge tank's vapor space continuously condenses equilibrium vapor and discharges the condensate through a trough placed under the tube bundle. The liquid phase (lean TEG) seeks to restore the equilibrium vapor and in doing so, exhausts its trace water before it reaches the COLDFINGER® surge-tank outlet nozzle. With a limited residence time, the water in the liquid phase is exhausted, and the residual liquid (lean TEG) approaches better than 99.7% by weight TEG concentration. In the most common applications, dilute glycol (rich TEG) from the glycol contactor is used as the coolant in the COLDFINGER® tube bundle. The COLDFINGER® process does not use stripping gas.

FIG. 20-69

Water Removal vs. TEG Circulation Rate at Various TEG Concentrations (N = 1.0)



OTHER CONSIDERATIONS

Under conventional dehydration conditions, 40 to 60% of methanol in the feed gas to a glycol dehydrator will be absorbed by the TEG[44]. This will add additional heat duty on the reboiler and additional vapor load on the regenerator. High methanol injection rates and slug carryover can cause flooding.

Glycol losses can be defined as mechanical carryover from the contactor (normally 0.10 gallon/MMscf for standard mist eliminator) plus vaporization from the contactor and regenerator and spillage. Glycol losses, exclusive of spillage, range from 0.05 gallon/MMscf for high pressure low-temperature gases to as much as 0.30 gal/MMscf for low pressure, high temperature gases. Excessive losses usually result from foaming in the absorber and/or regenerator. Anti-foam agents are sometimes used.

FIG. 20-70

Water Removal vs. TEG Circulation Rate at Various TEG Concentrations (N = 1.5)

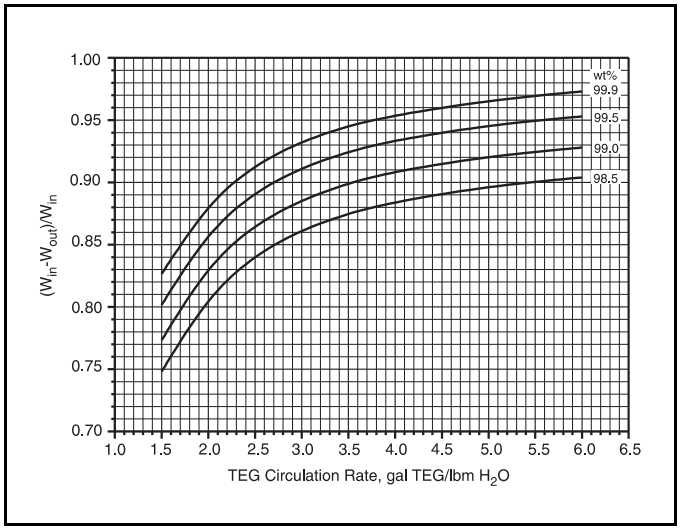
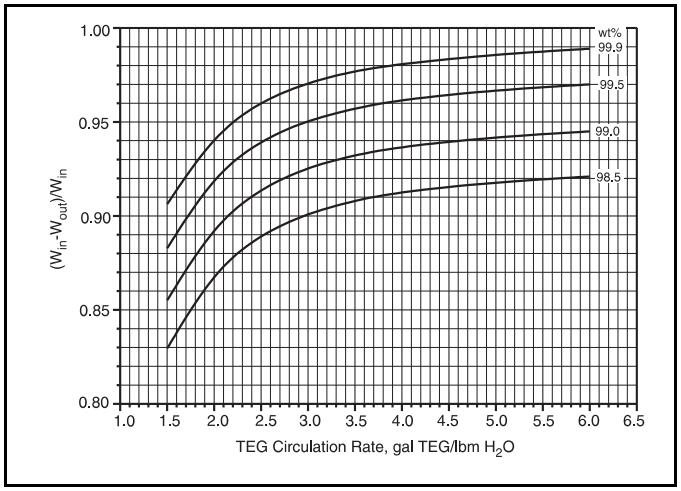


FIG. 20-71

Water Removal vs. TEG Circulation Rate at Various TEG Concentrations (N = 2.0)



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TEG vaporization losses at the contactor are minimal unless the gas temperature exceeds about 120°F. These losses are more significant at lower pressures. Tetraethylene glycol (TREG) has been used in some cases to minimize losses in high temperature, low pressure systems. Vaporization losses at the regenerator typically result from excessive stripping gas rates and/or inadequate reflux.

Glycol losses in CO_2 dehydration systems can be significantly higher than in natural gas systems particularly at pressures above about 900 psia. This is due to the solubility of TEG in dense phase CO_2. Glycerol[45] is much less soluble and has been used successfully as a desiccant in some CO_2 dehydration systems.

Glycol becomes corrosive with prolonged exposure to oxygen. A dry gas blanket on the glycol surge tank will help eliminate oxygen absorption. Special precautions should be taken if oxygen is in the gas to be dehydrated. Thermal decomposition of TEG can become a problem if TEG is heated to temperatures above 400°F.

A low pH accelerates decomposition of glycols. Bases such as triethanolamine, borax, or sodium mercaptobenzothiazole may be added to maintain pH, but they should be added sparingly.

FIG. 20-72

Water Removal vs. TEG Circulation Rate at Various TEG Concentrations (N = 2.5)

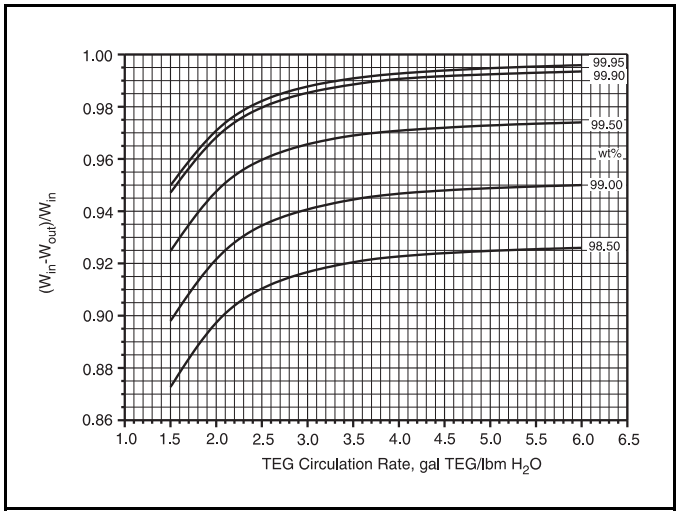
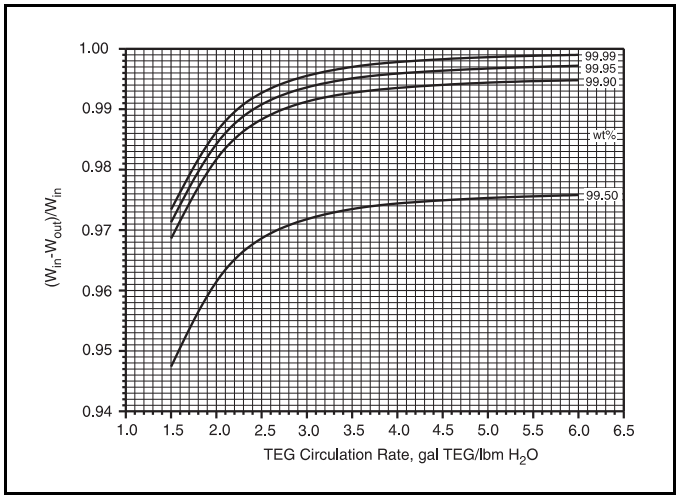


FIG. 20-73

Water Removal vs. TEG Circulation Rate at Various TEG Concentrations (N = 3.0)



SOLID DESICCANT DEHYDRATION

There are several solid desiccants which possess the physical characteristic to adsorb water from natural gas. These desiccants generally are used in dehydration systems consisting of two or more towers and associated regeneration equipment. See Fig. 20-80 for a simple two-tower system. One tower is onstream adsorbing water from the gas while the other tower is being regenerated and cooled. Hot gas is used to drive off the adsorbed water from the desiccant, after which the tower is cooled with an unheated gas stream. The towers are switched before the on-stream tower becomes water saturated. In this configuration, part of the dried gas is used for regeneration and cooling, and is recycled to the inlet separator. Other streams may be used if they are dry enough, such as part of the residue gas.

Solid desiccant units generally cost more to buy and operate than glycol units. Therefore, their use is typically limited to applications such as high H_2S content gases, very low water dewpoint requirements, simultaneous control of water and hydrocarbon dewpoints, and special cases such as oxygen containing gases, etc. In processes where cryogenic temperatures are encountered, solid desiccant dehydration usually is preferred over conventional methanol injection to prevent hydrate and ice formation. Solid desiccants are also often used for the drying and sweetening of NGL liquids.

Desiccants in common commercial use fall into one of three categories:

Gels – alumina or silica gels manufactured and conditioned to have an affinity for water.

Alumina – a manufactured or natural occurring form of aluminum oxide that is activated by heating.

Molecular Sieves – manufactured or naturally occurring aluminosilicates exhibiting a degree of selectivity based on crystalline structure in their adsorption of natural gas constituents.

Silica Gel is a generic name for a gel manufactured from sulfuric acid and sodium silicate. It is essentially pure silicon dioxide, SiO_2. It is used for gas and liquid dehydration and hydrocarbon (iC_5+) recovery from natural gas. When used for hydrocarbon removal, the units are often called HRUs (Hydrocarbon Recovery Units) or SCUs (Short Cycle Units). When used for dehydration, silica gel will give outlet dewpoints of approximately –60°F.

Alumina is a hydrated form of alumina oxide (Al_2O_3). It is used for gas and liquid dehydration and will give outlet dewpoints of about –90°F. Less heat is required to regenerate alumina and silica gel than for molecular sieve, and the regeneration temperature is lower. Molecular sieves give lower outlet water dewpoints.

Molecular sieves are a class of aluminosilicates. They produce the lowest water dewpoints, and can be used to simultaneously sweeten and dry gases and liquids. Their equilibrium

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water capacity is much less dependent on adsorption temperature and relative humidity. They are usually more expensive.

Molecular sieve dehydrators are commonly used ahead of NGL recovery plants designed to recover ethane. These plants operate at very cold temperatures and require very dry feed gas to prevent formation of hydrates. Dehydration to a –150°F dewpoint is possible with molecular sieves. Water dewpoints less than –150°F can be accomplished with special design and strict operating parameters.

Fig. 20-81 presents the important properties of commercial solid desiccants. Fig. 20-82[46] shows static equilibrium capacity vs. relative humidity for various new desiccants. This is for comparison only. Adsorption capacity depends on other parameters besides relative humidity, and design values should be obtained from desiccant suppliers. Figure 20-83 shows water-adsorption isotherms for 4A molecular sieve in contact with air. This gives the relationship of static-equilibrium water capacity to the operating temperature and gas dewpoint temperature. Although the chart is based on an air-water system, it also can be used for natural gas.

FIG. 20-74

Water Removal vs. TEG Circulation Rate at Various TEG Concentrations (N = 4.0)

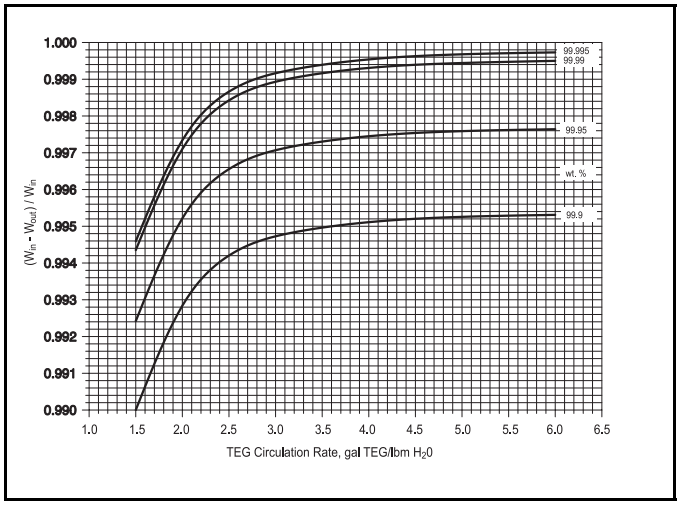


FIG. 20-75

Recommended Sizing Parameters for TEG Contactors

	K factor, ft/sec	C factor, ft/hr
Bubble Cap Trays		
20 inch spacing	0.14	504
24 inch spacing	0.16	576
30 inch spacing	0.17	612
Packing		
Structured	0.3 to 0.4*	1080-1440*
Random		
1 inch Pall rings	0.13 to 0.18	468-648
2 inch Pall rings	0.19 to 0.26	684-936
* Depending on packing density and vendor		

The continuous process requires two (or more) vessels with one on-line removing water while the other is being regenerated. Generally a bed is designed to be on-line in adsorption for 8 to 24 hours. When the bed is taken off-line, the water is removed by heating to 375°F-600°F, depending on the desiccant used and the performance specification (i.e., 375°F for silica gel and up to 600°F for molecular sieve, with alumina gel and activated alumina falling in between). The regeneration gas used to heat the bed is usually a slipstream of dry process gas. The regeneration gas is returned to the process after it has been cooled and the free water removed. Any heat source can be used including waste heat from engines and turbines. This is an important design consideration since heat is often a major operating cost.

Gas flow during adsorption is typically downflow. This allows higher gas velocities (thus smaller diameter towers) since bed fluidization is avoided. Regeneration gas flow is upflow during the heating period. In this way, any residual water left on the desiccant will be at the top of the bed and will not affect the effluent dewpoint when adsorption is resumed. In addition, upflow heating helps to strip any contaminants from the top of the bed extending desiccant life. Regeneration gas flow during the cooling period may be upflow if the gas is completely free of water, which saves two switching valves per tower. If the cooling gas contains water, cooling flow should be downflow to avoid preloading of the desiccant at the bottom of the bed with water.

Design

The first step is to determine the bed diameter, which depends on the superficial velocity. Too large a diameter will require a high regeneration gas rate to prevent channeling. Too small a diameter will cause too high a pressure drop and damage the sieve. The pressure drop is determined by a modified Ergun[47] equation, which relates pressure drop to superficial velocity as follows:

$$\frac{\Delta P}{L} = B\,\mu V + C\rho V^2 \qquad \textbf{Eq 20-11}$$

Constants for Eq 20-11 are:

Particle Type	B	C
1/8" bead (4x8 mesh)	0.0560	0.0000889
1/8" extrudate	0.0722	0.000124
1/16" bead (8x12 mesh)	0.152	0.000136
1/16" extrudate	0.238	0.000210

Fig. 20-87 was derived from Eq 20-11 by assuming a gas composition and temperature and setting the maximum allowable $\Delta P/L$ equal to 0.33 psi/ft. The design pressure drop through the bed should be about 5 psi. A design pressure drop higher than 8 psi is not recommended as the desiccant is fragile and can be crushed by the total bed weight and pressure drop forces. Remember to check the pressure drop after the bed height has been determined. Once the allowable superficial velocity is estimated, calculate the bed minimum diameter (i.e., $D_{minimum}$), and select the nearest standard diameter (i.e. $D_{selected}$):

$$D_{minimum} = \left(\frac{4q}{\pi V_{max}}\right)^{0.5} \qquad \textbf{Eq 20-12}$$

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$$q = \frac{\dot{m}}{60\rho} \qquad \textbf{Eq 20-13}$$

Obtain the corresponding superficial velocity, $V_{adjusted}$ as follows:

$$V_{adjusted} = V_{max}\left(\frac{D_{minimum}}{D_{selected}}\right)^2 \qquad \textbf{Eq 20-14}$$

An alternative and more exact method to using Fig. 20-11 is to calculate the maximum superficial velocity by solving Eq 20-11 algebraically, which gives Eq 20-15 below. The second term inside the square root of Eq 20-15 may be deleted since its value is insignificant compared to the first term, which gives Eq 20-16

$$V_{max} = \{(\Delta P/L)_{max}/(C\rho) + [(B/C)(\mu/\rho)/2]^2\}^{1/2} - [(B/C)(\mu/\rho)/2] \qquad \textbf{Eq 20-15}$$

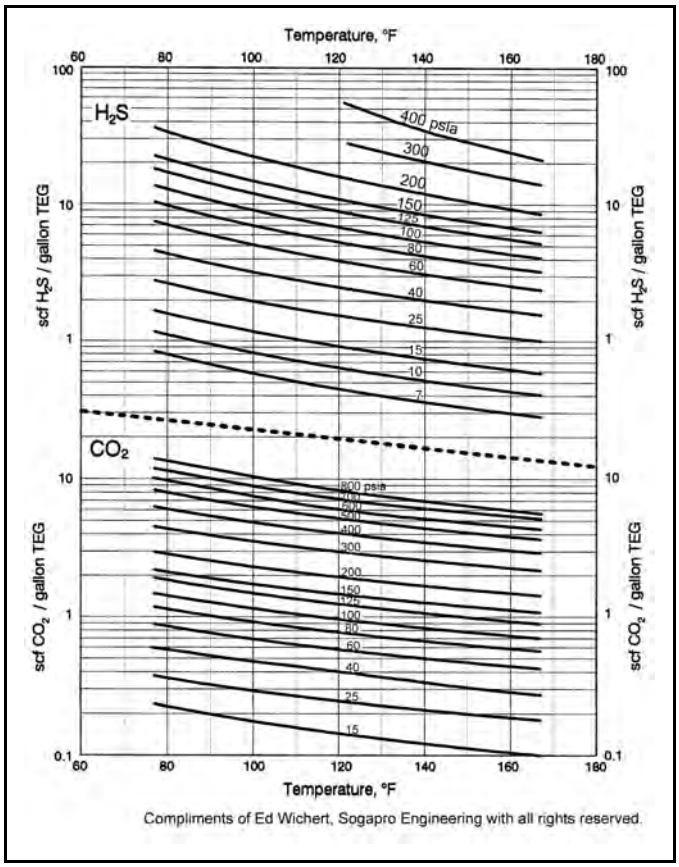
$$V_{max} = \{(\Delta P/L)_{max}/(C\rho)\}^{1/2} - [(B/C)(\mu/\rho)/2] \qquad \textbf{Eq 20-16}$$

The value of $(\Delta P/L)_{max}$ in these equations depends on the sieve type, size, and shape, but a typical value for design is 0.33 psi/ft.

The next step is to choose an adsorption period and calculate the mass of desiccant required. Eight to twelve hour adsorption periods are common. Periods of greater than 12 hours may be justified especially if the feed gas is not water saturated. Long adsorption periods mean less regenerations and longer sieve life, but larger beds and additional capital investment.

FIG. 20-76

Solubility of H_2S and CO_2 in Triethylene Glycol vs. Temperature and Partial Pressure



During the adsorption period, the bed can be thought of as operating with three zones. The top zone is called the saturation or equilibrium zone. The desiccant in this zone is in equilibrium with the wet inlet gas. The middle or mass transfer zone (MTZ) is where the water content of the gas is reduced from its inlet concentration to < 1 ppm. The bottom zone is unused desiccant and is often called the active zone. If the bed operates too long in adsorption, the mass transfer zone begins to move out the bottom of the bed causing a "breakthrough." At breakthrough, the water content of the outlet gas begins to increase and will eventually reach feed gas water content when the MTZ is completely displaced.

Both water capacity and the rate at which solid desiccants adsorb water decline as the material ages. The object of the design is to install enough desiccant such that after three to five years, the mass transfer zone will be at the bottom of the bed at the end of the adsorption period.

In the saturation zone, molecular sieve is expected to hold approximately 13 pounds of water per 100 pounds of sieve. New sieve will have an equilibrium capacity near 20%; 13% represents the approximate capacity of a 3-5 year old sieve. This capacity needs to be adjusted when the gas is not water saturated or the temperature is above 75°F. See Fig. 20-84 and 20-85 to find the correction factors for molecular sieve. To determine the mass of desiccant required in the saturation zone, calculate the amount of water to be removed during the cycle and divide by the effective capacity.

$$S_S = \frac{W_r}{(0.13)(C_{SS})(C_T)} \qquad \textbf{Eq 20-17}$$

$$L_S = \frac{(S_s)(4)}{\pi\,(D^2)(\text{bulk density})} \qquad \textbf{Eq 20-18}$$

Molecular sieve bulk density is 42 to 46 lb/ft^3 for spherical particles and 40 to 44 lb/ft^3 for extruded cylinders.

Even though the MTZ will contain some water (approximately 50% of the equilibrium capacity), the saturation zone is estimated assuming it will contain all the water to be removed.

The length of the mass transfer zone can be estimated as follows:

$$L_{MTZ} = (V_{adjusted} / 35)^{0.3}\,(Z) \qquad \textbf{Eq 20-19}$$

Where: Z = 1.70 ft for 1/8 inch sieve
0.85 ft for 1/16 inch sieve

The total bed height is the summation of the saturation zone and the mass transfer zone heights. It should be no less than the vessel inside diameter, or 6 feet, whichever is greater.

Now the total bed pressure drop is checked. The $\Delta P/L$ for the selected diameter, $D_{selected}$, is adjusted using Eq 20-11 or the following approximation:

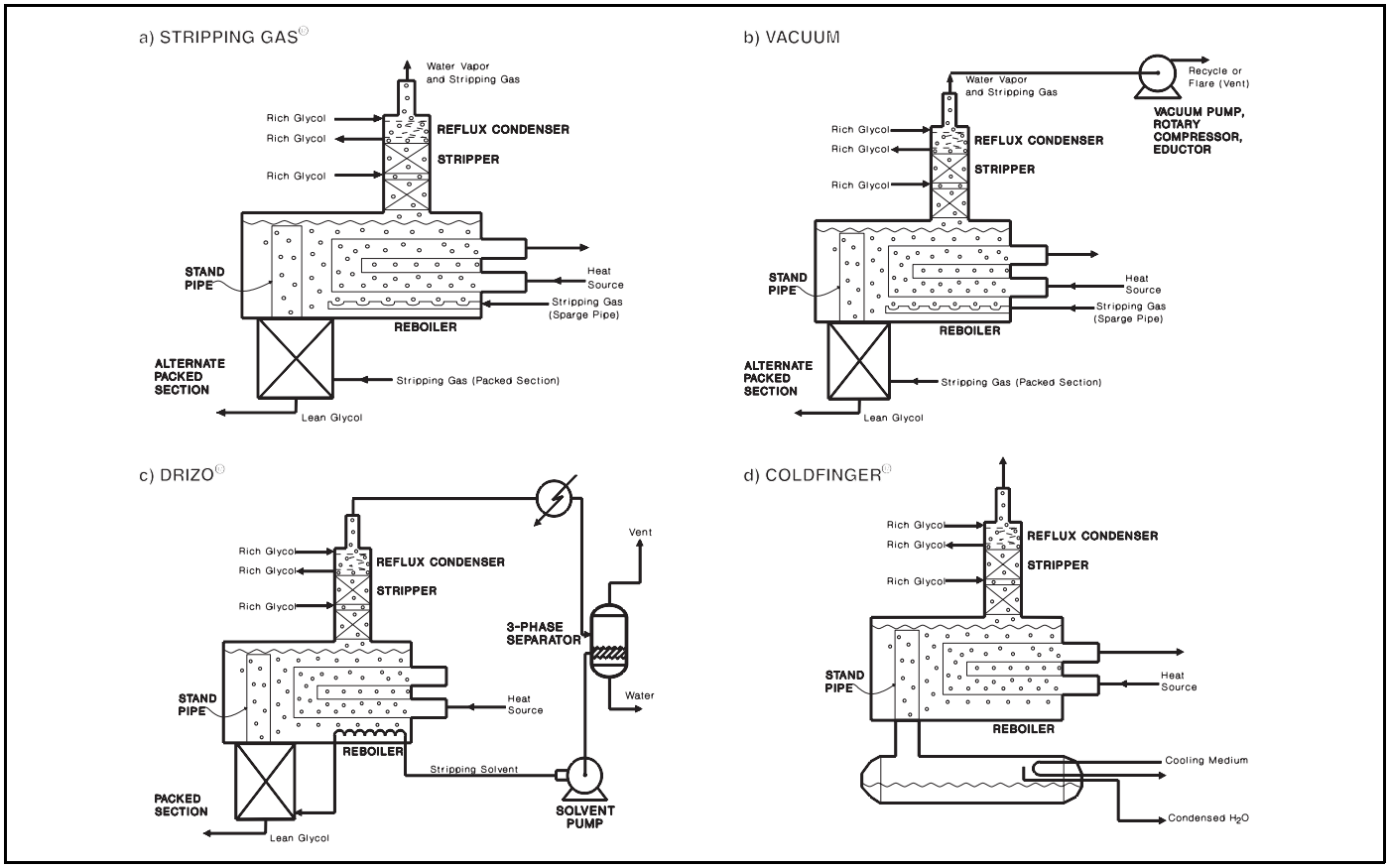
$$(\Delta P/L)_{adjusted} \cong (0.33\ \text{psi/ft})\left(\frac{V_{adjusted}}{V_{max}}\right)^2 \qquad \textbf{Eq 20-20}$$

The result is multiplied times the total bed height (L_S + L_{MTZ}) to get the total design pressure drop, which should be 5-8 psi. This is important, because the operating pressure drop can increase to as much as double the design value over three years. Too high a pressure drop plus the bed weight can crush the sieve. If the design pressure drop exceeds 8 psi, the bed diameter should be increased and the sieve amount and vessel dimensions recalculated.

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FIG. 20-77

Simplified Process Flow Diagrams of Enhanced TEG Regeneration Systems



A second method uses Eq 20-17, but replaces the saturation capacity of 13% with an "effective desiccant capacity" which includes the MTZ effect, temperature, and relative humidity corrections. When using this method, an effective capacity of 8-10% is typically assumed. This method is adequate for most planning and feasibility calculations.

To estimate the total cylindrical length of a tower, add 3 feet to the bed height, which provides the space for an inlet distributor and for bed support and hold-down balls under and on top of the sieve bed.

Regeneration Calculations

The first step is to calculate the total heat required to desorb the water and heat the desiccant and vessel. A 10% heat loss is assumed.

$$Q_w = \left(1800 \frac{Btu}{lb}\right)(\text{lbs of water on bed}) \qquad \textbf{Eq 20-21}$$

$$Q_{si} = (\text{lb of sieve})\left(\frac{0.24\ Btu}{lb\ °F}\right)(T_{rg} - T_i) \qquad \textbf{Eq 20-22}$$

$$Q_{st} = (\text{lb of steel})\left(\frac{0.12\ Btu}{lb\ °F}\right)(T_{rg} - T_i) \qquad \textbf{Eq 20-23}$$

$$Q_{hl} = (\text{heat loss}) = (Q_w + Q_{si} + Q_{st})(0.10) \qquad \textbf{Eq 20-24}$$

The temperature, T_{rg}, is the temperature to which the bed and vessel must be heated based on the vessel being externally insulated (i.e., no internal insulation which is usually the case). This is about 50°F below the temperature of the hot regeneration gas entering the tower.

The weight of the vessel steel is estimated from the equations below. Eq 20-25 is the ASME Section VIII equation in terms of the vessel inside diameter. It is based on a maximum tensile stress of 18,800 psi (i.e., the ASME 2001 maximum allowable tensile stress for SA516 Grade 70 steel at 650°F and a welded-joint efficiency of 1.0). This is 19,400 psi at 600°F. The design pressure, P_{design}, is usually set at 110% of the maximum operating pressure. The value of 0.125 in Eq 20-26 is the corrosion allowance in inches. The term $0.75D_{bed}$ is to account for the weight of the tower heads. The value of "3" provides the space for the inlet distributor and support and hold-down balls.

$$t(\text{inches}) = (12D_{bed}P_{design}) / ((2x18{,}800 = 37{,}600) - 1.2P_{design}) \qquad \textbf{Eq 20-25}$$

$$\text{Weight of steel (lb)} = 155(t + 0.125)(L_S + L_{MTZ} + 0.75D_{bed} + 3)D_{bed} \qquad \textbf{Eq 20-26}$$

For determination of the regeneration gas rate, calculate the total regeneration load from Eq 20-27.

$$Q_{tr} = (2.5)(Q_w + Q_{si} + Q_{st} + Q_{hl}) \qquad \textbf{Eq 20-27}$$

The 2.5 factor corrects for the change in temperature difference (in – out) across the bed with time during the regeneration period. It assumes that 40% of the heat in the gas transfers to the bed, vessel steel, and heat loss to atmosphere; and the balance leaves with the hot gas.

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FIG. 20-78

Effect of Stripping Gas on TEG Concentration

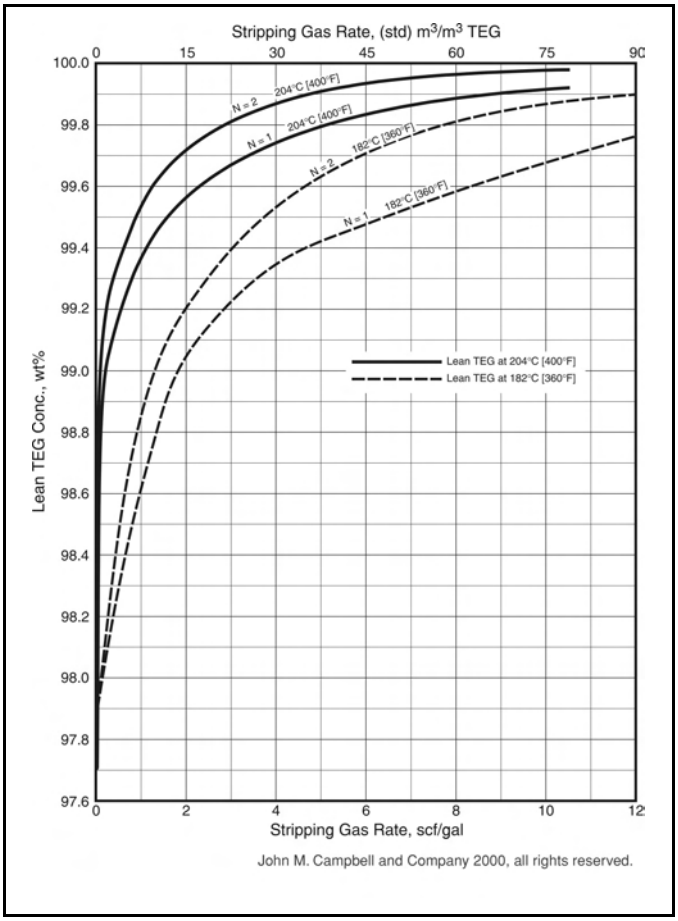


FIG. 20-79

Glycol Regeneration Processes

Process	TEG Conc. wt%	Water Dew Point Depression Possible, °F
Vacuum	99.2 to 99.9	100 to 150
COLDFINGER®	92.2 to 99.7	100 to 130
DRIZO®	99.99 to 99.999*	180 to 250*
Stripping Gas	99.2 to 99.9	100 to 150
*With Solvent Dryer		

The regeneration-gas flow rate is calculated from Eq 20-28 below. The heat capacity, C_p, is calculated with Eq 20-29, with the enthalpies obtained from the enthalpy vs. temperature plots for various pressures in Section 24. The temperature, T_{hot}, is 50°F above the temperature, T_{rg}, to which the bed must be heated. The temperature, T_b, is the bed temperature at the beginning of regeneration, which is the same as the dehydration-plant feed temperature.

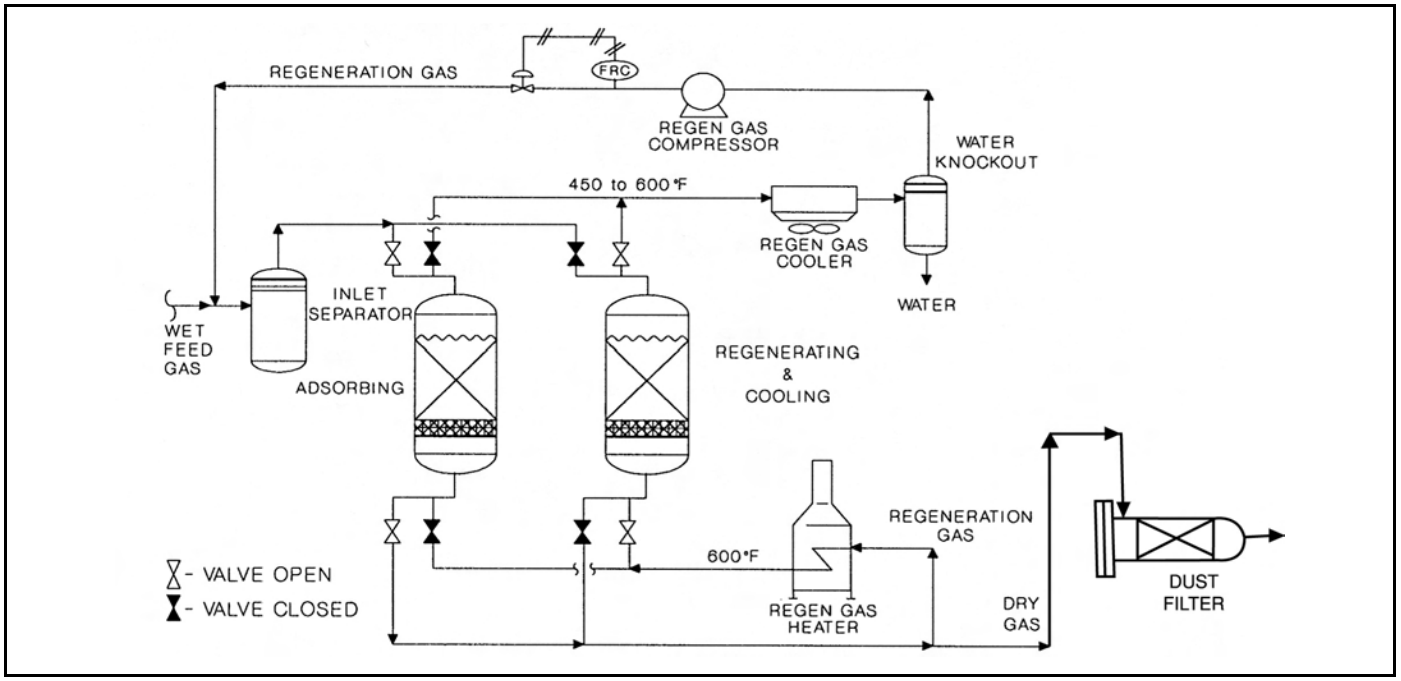
The heating time is usually 50% to 60% of the total regeneration time which must include a cooling period. Figure 20-87 shows a typical temperature profile for a regeneration period (heating and cooling). For 8 hour adsorption periods, the regeneration normally consists of 4 1/2 hours of heating, 3 hours of cooling and 1/2 hour for standby and switching. For longer periods the heating time can be lengthened as long as a minimum pressure drop of 0.01 psi/ft is maintained to ensure even flow distribution across the bed.

$$\dot{m}_{rg} = Q_{tr}/(C_p(T_{hot}—T_b)(\text{heating time})) \qquad \textbf{Eq 20-28}$$

$$C_p\ (\text{Btu/lb/°F}) = (H_{hot} — H_i)/(T_{hot} — T_b) \qquad \textbf{Eq 20-29}$$

FIG. 20-80

Example Solid Desiccant Dehydrator Twin Tower System



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The superficial velocity of the regeneration gas is calculated from Eq 20-30 for which q is calculated from Eq 20-13

$$V = 4q / (\pi D^2) \qquad \textbf{Eq 20-30}$$

The calculated superficial velocity can not be less than the value that corresponds with a minimum bed pressure drop of 0.01 psi/ft. This can be determined from Fig. 20-88, which was derived from Eq 20-11 by assuming a gas composition and temperature and setting ΔP/L equal to 0.01 psi / ft. If the calculated velocity is less than this, the regeneration gas rate, $\dot{m}_{rg}$, must be increased by multiplying it by the ratio V_{min} / V, and the period of regeneration should be decreased by multiplying it times the ratio V / V_{min}. A method more exact than Fig. 20-16 for calculating the minimum superficial velocity is to use Eq 20-16, but to consider it in terms of $(\Delta P/L)_{min}$ and V_{min} instead of $(\Delta P/L)_{max}$ and V_{max}.

General Comments

The regeneration cycle frequently includes depressuring/repressuring to match the regeneration gas pressure and/or to maximize the regeneration gas volume to meet the velocity criterion. In these applications, the rate of depressuring or repressuring should not exceed 50 psi/minute. Some applications, termed pressure swing adsorption, regenerate the bed only with depressurization and sweeping the bed with gas just above atmospheric pressure.

Moisture analyzers for very low water contents require care to prevent damage to the probes. When inserted into the beds, sample probes and temperature probes must be installed to reach the center of the gas phase.

Solid desiccant towers are insulated externally or possibly internally. Internal refractory requires careful installation and curing, usually before the desiccant is installed. It saves energy but the greatest benefit is it can dramatically reduce the required heating and cooling times. This is often an important benefit for systems where regeneration times are limited. The primary disadvantage is the potential for wet gas bypassing the desiccant through cracks and defects in the insulation during the adsorption cycle.

Example 20-13: 100 MMscfd of natural gas with a molecular weight of 18 is to be processed for ethane recovery in a turboexpander plant. It is water saturated at 600 psia and 100°F and must be dried to –150°F dew point. Determine the water content of the gas, and the amount of water that must be removed; and do a preliminary design of a molecular-sieve dehydration system consisting of two towers with down-flow dehydration in one tower and up-flow regeneration in the other. Use 4A molecular sieve of 1/8" beads (i.e., 4x8 mesh). The regeneration gas is part of the plant's residue gas, which is at 600 psia and 100°F and has a molecular weight of 17. The bed must be heated to 500°F for regeneration.

Solution Steps

1. Determine the bed diameter and the corresponding ΔP/L and V. First determine the maximum superficial velocity from Eq 20-16. Let the maximum ΔP/L be 0.33 psi/ft.

   z = 0.93 from Fig. 23-5 for 17.4 mole weight which is conservative

   ρ = (18 mole weight) (600 psia) / (10.73(560 °R)(0.93 z)) = 1.93 lb/ft^3 (Eq 23-2)

   μ = 0.015 centipoise (Fig. 23-23)

   $V_{max} = \{(0.33 \text{ psi/ft}) / (0.000089) / (1.93) \text{ lb/ft}^3)\}^{1/2} - [(0.056 / 0.000089) (0.015 \text{ centipoise}/1.93 \text{ lb/ft}^3)/2] = 41.4$ ft/min (Eq 20-16)

   $\dot{m}$ = (100 • 10^6 scf/day) / ((24 hr/day)(379.43 scf/lb mole)) (18 lb/lb mole) = 198,000 lb/hr of wet gas

   q = (198,000 lb/hr)/((60 min/hr)(1.93 lb/ft^3)) = 1710 ft^3/min of wet gas (Eq 20-13)

   $D_{minimum} = [(4(1710 \text{ ft}^3/\text{min}))/(\pi \bullet 41.4 \text{ ft/min})]^{1/2} = 7.25$ ft (Eq 20-12)

   Round off upward to 7.5 ft diameter, for which V and ΔP/L are adjusted as follows:

   $V_{adjusted} = (41.4)(7.25/7.5)^2 = 38.7$ ft/min (Eq 20-14)

   $(\Delta P/L)_{adjusted} = 0.33(38.7/41.4)^2 = 0.29$ psi/ft (Eq 20-20)

2. Estimate the amount of water to be removed from the feed per cycle for each bed. Base this on a 24-hour cycle

FIG 20-81

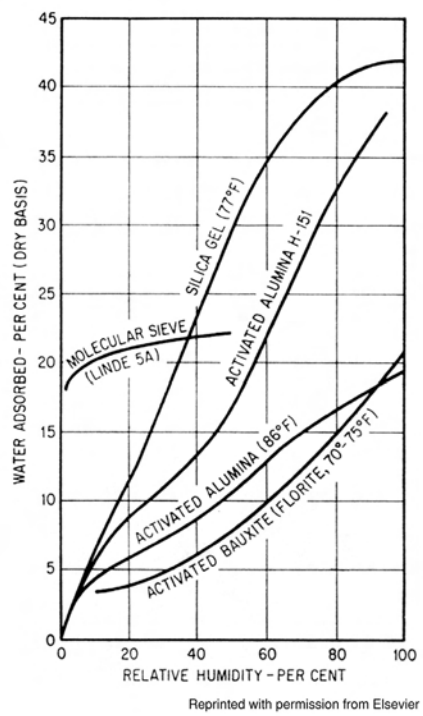
Typical Desiccant Properties

Desiccant	Shape	Bulk Density, lb/ft^3	Particle Size	Heat Capacity, Btu/(lb •°F)	Approx. Minimum Moisture Content of Effluent Gas
Alumina Alcoa F200	Beads	48	7x14 Tyler mesh 1/8" / 3/16" / 1/4"	0.24	–90°F dew point
Activated Alumina UOP A-201	Beads	46	3-6 mesh or 5-8 mesh	0.22	5-10 ppmv
Mole Sieve Grace – Davison 4A	Beads	42-45	4-8 mesh or 8-12 mesh	0.23	0.1 ppmv (–150°F)
Molecular Sieve UOP 4A-DG	Extrudate	40-44	1/8" or 1/16" pellets	0.24	0.1 ppmv
Mole Sieve Zeochem 4A	Beads	45-46	4-8 mesh or 8-12 mesh	0.24	0.1 ppmv
Silica Gel Sorbead® – R	Beads	49	5x8 mesh	0.25	–60°F dew point
Silica Gel Sorbead® – H	Beads	45	5x8 mesh	0.25	–60°F dew point
Silica Gel Sorbead®– WS	Beads	45	5x8 mesh	0.25	–60°F dew point

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FIG. 20-82

Static Equilibrium Capacity vs. Relative Humidity for Selected Solid Desiccants[46]



consisting of 12 hours adsorbing and 12 hours regenerating (heating, cooling, standby, and valve switching). From Fig. 20-4, the water content at 600 psia and 100°F is 88 pounds per million standard cubic feet (MMscf). The water content at a dew point of –150°F is essentially zero, so the water removed is the following:

$\dot{w}$ = (88-0 lb/MMscf)(100 MMscf/day) / (24 hr/day)
= 367 lb/hr of water removed

W_r = (367 lb/hr) (12 hr) = 4404 lb water removed per 12-hour drying period or 24-hour cycle per bed

3. Determine the amount of sieve required and the bed height based on a sieve bulk density of 45 lb/ft^3. Since the feed gas is water saturated, the relative humidity is 100%, so C_{SS} is 1.0 from Fig. 20-84. From Fig. 20-85, C_T is 0.93 at 100°F. Applying the equations:

   S_S = (4404) / ((0.13)(1.0)(0.93)) = 36,427 lb of sieve for each bed (Eq 20-17)

   L_S = (36,427)(4)/((3.1416) (7.5)^2 (45)) = 18.3 ft bed height (Eq 20-18)

   L_{MTZ} = (38.7/35)$^{0.3}$ (1.7) = 1.8 ft for mass-transfer zone (Eq 20-19)

   $L_S + L_{MTZ}$ = 18.3 + 1.8 = 20.1 ft of sieve for each bed

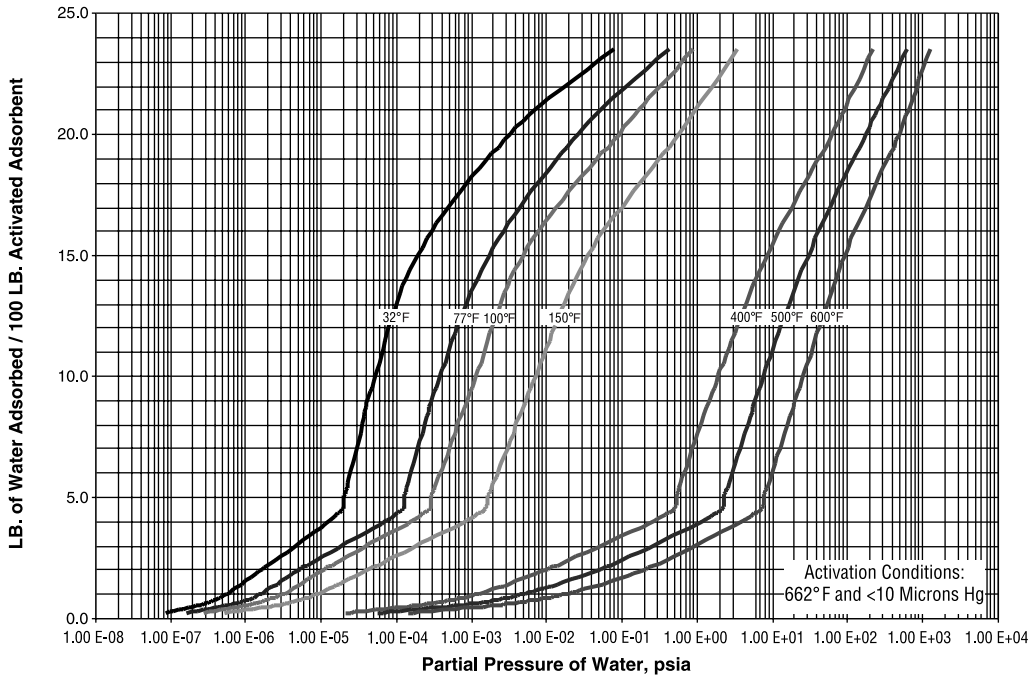
   The total sieve = (20.1/18.3)(36,427)
   = 40,010 lb for each bed

4. Check the bed design and pressure drop which is the $\Delta P/L$ calculated in Step 1 times the total bed height calculated in Step 3:

   (0.29 psi/ft)(20.1 ft) = 5.8 psi which meets the criteron of not exceeding 5–8 psi/ft

FIG. 20-83

UOP™ Adsorbents
4A-DG MOLSIV™ Pellets — Water Adsorption Isotherms



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FIG. 20-8

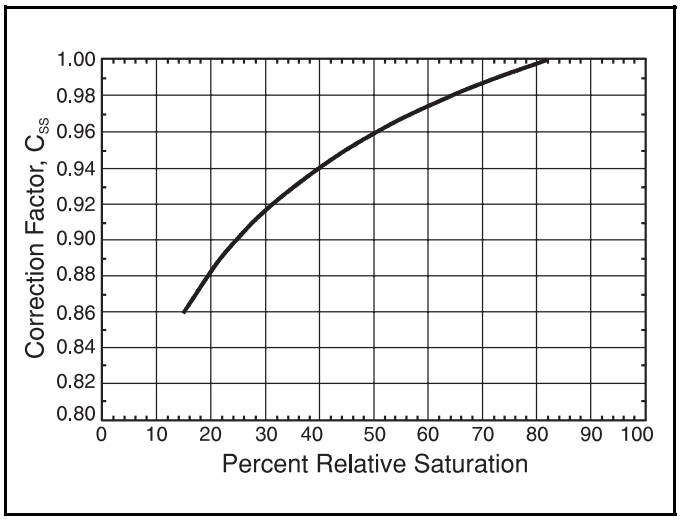


FIG. 20-85

Mole Sieve Capacity Correction for Temperature

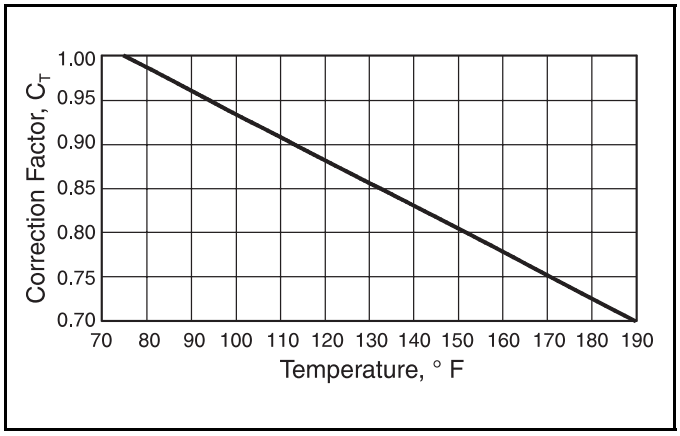
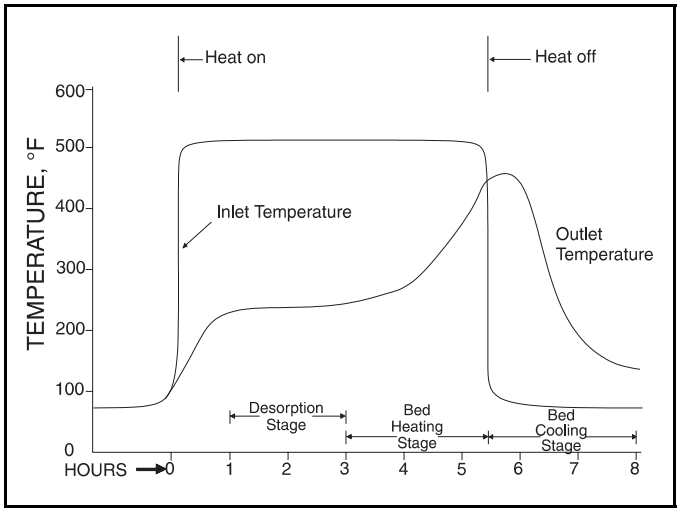


FIG. 20-86

Inlet and Outlet Temperatures During Typical Solid Desiccant Bed Regeneration Period



5. Calculate the total heat required to desorb the water based on heating the bed and vessel to 500°F. First calculate the weight of steel from Eq 20-25 and 20-26. Let the design pressure, P_{design}, be 110% of the operating pressure:

   P_{design} = (600)(1.1) = 660 psig

   t = (12)(7.5)(660) / (37,600 – (1.2)(660))
   = 1.614 inches (Eq 20-25)

   Weight of steel = (155) (1.614 + 0.125) (18.3 + 1.8 + (0.75) (7.5) + 3) (7.5) = 58,070 pounds (Eq 20-26)

   Q_{st} = (58,070 lb) (0.12 Btu/lb/°F) (500°F – 100°F) = 2,787,000 Btu (Eq 20-23)

   Q_w = (1800 Btu/lb (4404 lb water) = 7,927,000 Btu (Eq 20-21)

   Q_{si} = (40,010 lb) (0.24 Btu/lb/°F) (500°F – 100°F) = 3,841,000 Btu (Eq 20-22)

   Q_{hl} = (2,787,000 + 7,927,000 + 3,841,000) (0.10) = 1,455,000 Btu (Eq 20-24)

   Q_{tr} = (2.5) (2,787,000 + 7,927,000 + 3,841,000 + 1,455,000) = 40,025,000 Btu (Eq 20-27)

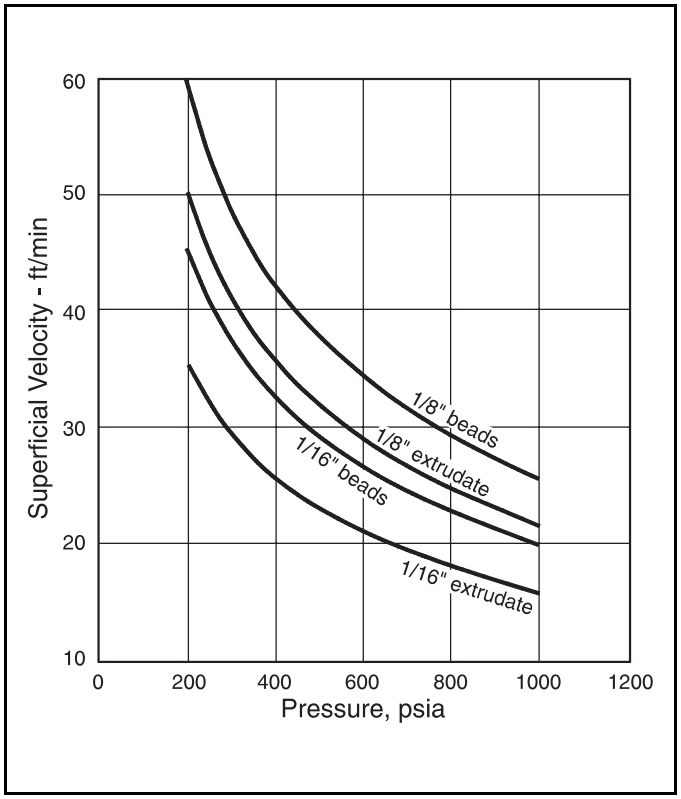
6. Calculate the flow rate of regeneration gas using Eq 20-28. Let the heating time be 60% of the total regeneration period, and calculate the gas heat capacity, C_p, from Eq 20-29:

   (60%) (12 hr) = 7.2 hours heating

   C_p (@ 600 psia from Fig. 24-12) = ((545 – 250) (Btu/lb))/((550 – 100) (°F)) = 0.66 Btu/lb/°F (Eq 20-29)

FIG. 20-87

Allowable Velocity for Mole Sieve Dehydrator



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$\dot{m}_{rg}$ = (40,025,000 Btu)/((0.66 Btu/lb/°F) (550 – 100) (°F) (7.2 hr)) = 18,717 lb/hr (Eq 20-28)

7. Check that the ΔP/L ≥ 0.01 psi/ft at 550°F.

   ρ = ((17 mole weight)(≈600 psi) /((10.73) (460 + 550)) = 0.94 lb/ft^3

FIG. 20-88

Minimum Regeneration Velocity for Mole Sieve Dehydrator

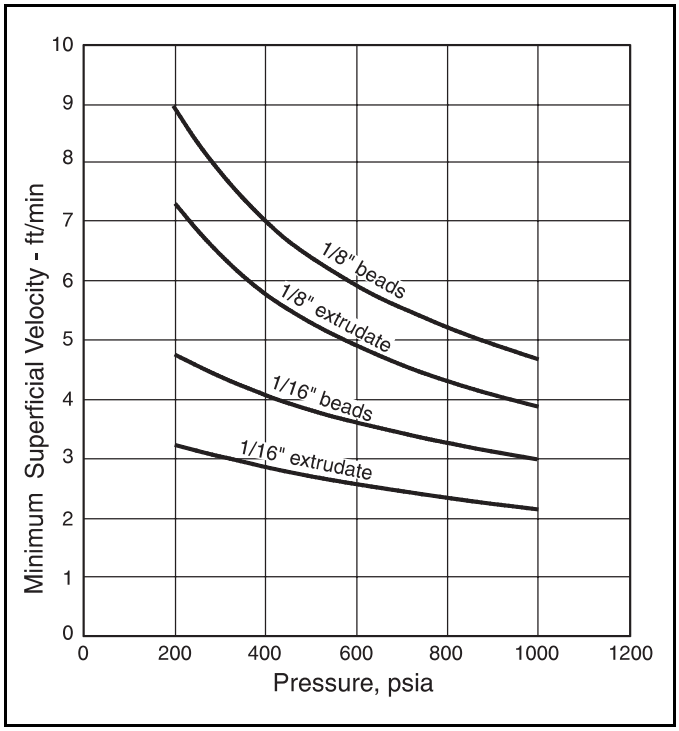
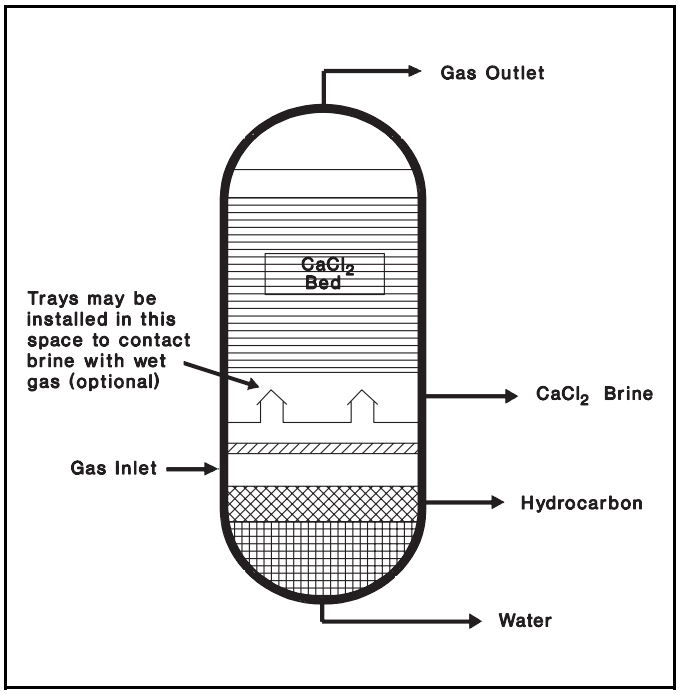


FIG. 20-89

Typical $CaCl_2$ Dehydrator



q = (18,717 lb/hr) / ((60 min/hr) (0.94 lb/ft^3)) = 331.9 ft^3/min of hot regeneration gas (Eq 20-13)

Rearranging Eq 20-12:

V = 4q/πD^2 = ((4)(331.9)/((3.414)(7.5)^2) = 6.91 ft/min

μ = 0.023 cP (Fig. 23-23)

ΔP/L = (0.056) (0.023) (6.91) + (0.000089) (0.94) (6.91)^2 = 0.013 psi/ft (Eq 20-11)

This is safely above the minimum value of 0.01 psi/ft needed to prevent channeling.

8. The design results are summarized as follows:

   Number of vessels: two

   Vessel design pressure and temperature: 660 psig and 600°F

   Vessel dimensions: 90 inches (7.5 feet) ID by 23.1 feet tan to tan

   Weight of molecular sieve: 2x40,010 lb

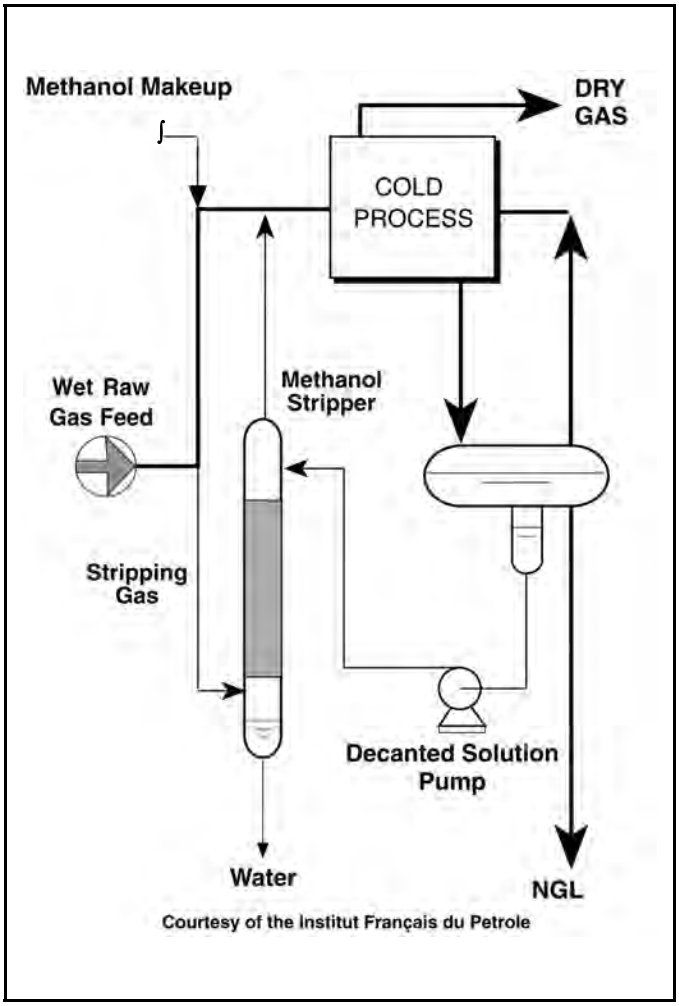
   Regeneration gas rate: 18,717 lb/hr (10.026 MMscfd)

   Regeneration gas temperature: 550°F

   Cycle time: 24 hours, 12 hours adsorption, 12 hours regeneration

FIG. 20-90

Example IFPEX-1 ® Dehydration Process Flow Diagram



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Heating time: 7.2 hours

This example is based on regeneration with a gas that is separate from the main stream that has been dehydrated. If a slip-stream of dehydrated gas is used as illustrated on Fig. 20-80, the amount of regeneration gas must be assumed and added to the inlet gas. In this case several trials must be performed until the amount calculated for regeneration is equal to the amount added to the plant feed. As illustrated by the above example, a good initial assumption is 10% of the plant feed.

Bottom bed support typically includes three to five layers of inert ceramic balls in graduated sizes (smallest on top). On top of the bed, a hold-down screen is provided, again covered with a layer of ceramic balls. In some cases, a layer of less expensive desiccant can be installed on the top of the bed to catch contaminants such as free water, glycol, hydrocarbons, amines, etc. This may extend the bed life. Good inlet separation of entrained contaminants is absolutely essential for long desiccant life.

Since solid desiccants can produce dust, 1µm filters are frequently installed at the outlet of the dehydration unit to protect downstream equipment.

Operating performance should be monitored periodically to adjust adsorption cycle length so that adequate dehydration is obtained. Performance tests are scheduled on a routine basis, ranging from monthly during early operations to six months or longer. The size of the unit and frequency of regeneration cycles also affect the timing of performance tests.

Calcium Chloride

Calcium chloride ($CaCl_2$) can be used as a consumable desiccant to dehydrate natural gas. Solid anhydrous $CaCl_2$ combines with water to form various $CaCl_2$ hydrates ($CaCl_2 \cdot XH_2O$). As water absorption continues, $CaCl_2$ is converted to successively higher states of hydration – eventually forming a $CaCl_2$ brine solution.

3/8 in. to 3/4 in. $CaCl_2$ pellets are installed in a fixed bed much like a dry desiccant tower. Gas flow is upflow. The more efficient designs utilize 3-4 trays below the solid bed to pre-contact the gas with the brine solution. This removes a portion of the water from the gas before contact with the solid $CaCl_2$ and increases unit capacity. One such unit is shown in Fig. 20-89.

The solid $CaCl_2$ near the bottom of the fixed bed will typically be $CaCl_2 \cdot 4H_2O$ or $CaCl_2 \cdot 6H_2O$ and the $CaCl_2$ at the top of the fixed bed will be anhydrous $CaCl_2$ or $CaCl_2 \cdot H_20$. In this way the gas contacts successively drier $CaCl_2$ as it flows upwards and in theory leaves the fixed bed in equilibrium with the $CaCl_2$ at the top of the bed.

Outlet water contents of 1 lb/MMscf have been achieved with $CaCl_2$ dehydrators. Typical $CaCl_2$ capacity is 0.3 lb $CaCl_2$ per lb H_20. Superficial bed velocities are 20-30 ft/min and length to diameter ratio for the bed should be at least 3 to 4:1.

$CaCl_2$ dehydrators may offer a viable alternative to glycol units on low rate, remote dry gas wells. The $CaCl_2$ must be changed out periodically. In low capacity – high rate units this may be as often as every 2-3 weeks. Brine disposal raises environmental issues. In addition, under certain conditions the $CaCl_2$ pellets can bond together to form a solid bridge in the fixed bed portion of the tower. This results in gas channeling and poor unit performance.

Dehydration by Refrigeration

The dehydration of natural gas can also be achieved by refrigeration and/or cryogenic processing down to – 150°F in the presence of methanol hydrate and freeze protection. The condensed water and methanol streams decanted in the cold process can be regenerated by conventional distillation or by a patented process called IFPEX-1®.

In the latter process illustrated in schematic form in Figure 20-90[48] a slip stream of water saturated feed gas strips essentially all the methanol in the cold decanted methanol water stream originating in the cold process at feed gas conditions to recirculate the methanol to the cold process. The water stream leaving the stripper contains generally less than 100 ppm wt of methanol. No heat is required for the process and no atmospheric venting takes place.

Dehydration By Membrane Permeation

Membranes can be used to separate gas stream components in natural gas such as water, CO_2 and hydrocarbons according to their permeabilities. Each gas component entering the separator has a characteristic permeation rate that is a function of its ability to dissolve in and diffuse through the membrane.

The driving force for separation of a gas component in a mixture is the difference between its partial pressure across the membrane. As pressurized feed gas flows into the metal shell of the separator, the fast gas component, such as water and CO_2, permeate through the membrane. This permeate is collected at a reduced pressure, while the non-permeate stream, i.e., the dry natural gas, leaves the separator at a slightly lower pressure than the feed.

The amount of methane and other natural gas components in the permeate stream is dependent on pressure drop and the surface area of the membranes. However, 5–10% of the feed stream is a realistic figure. Dehydration by membrane permeation is therefore normally only considered for plants that can make use of low pressure natural gas fuel.

LIQUID DEHYDRATION

Many liquid streams must be dehydrated to allow further processing or meet requirements of a handling chain to a direct consumer. Commercial propane must be dry before entering the fuel market to prevent freezing problems as the liquid vaporizes at temperatures below the hydrate point, or even below the freezing point of any free water that may be present.

The amount of water that can be in solution with light hydrocarbon liquid is very small, even at the saturation point. Effective drying to very low levels of moisture is usually required. The solubility of water in liquid hydrocarbons is presented in Fig. 20-2. The desired maximum moisture level for commercial propane is approximately 10 ppmw. However, liquids exposed to cryogenic temperatures require virtually all the moisture be removed.

The water content in light hydrocarbon liquids can be determined by using recommended methods in GPA Publication 2140 (Cobalt Bromide or Freeze Valve methods), or electronic instruments designed to indicate the moisture content directly.

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Gas Stripping

One simple method of dehydrating liquid hydrocarbons is counter current stripping with a dry gas. This method is currently used to dry condensate produced offshore prior to export from the production platform. The contactor is usually trayed. Stripping gas rates depend on the condensate rate, the amount of entrained water in the condensate, stripper temperature and pressure.

Advantages of this process are simplicity and low capital cost. Disadvantages include the requirement for a dry natural gas stream, and the coincidental stripping of some of the volatile hydrocarbons from the condensate. The stripping gas may be recycled to the gas dehydration unit or it can be used as fuel gas.

Solid Desiccant Dehydration

Several solid desiccant processes are available to dry liquid hydrocarbons.

Liquid velocity is usually 3-5 ft/minute through solid desiccant beds with a minimum travel of at least 5 feet to ensure good distribution. Direction of flow can be upflow or downflow in the adsorption cycle.

Special care must be taken in designing the bed supports in the liquid dehydrator vessels to prevent desiccant loss, desiccant damage, and to ensure proper distribution. Layers of ceramic balls are installed in decreasing size from the support screen. The support ball sizes may vary with the type and size of solid desiccant used but the layers of support balls should never be graduated in size more than twice the diameter of the balls being supported.

The regeneration of solid desiccant beds is very similar to gas dehydrators with the following exceptions:

- Liquid draining and filling time must be allowed.
- Pressuring and depressuring must be done carefully to avoid bed movement.
- Adequate bed cooling is required before liquid re-entry to minimize flashing.

It is important to prevent movement of the bed particles to prevent attrition that would require premature replacement. Also, desiccant dust particles can cause downstream plugging, equipment damage, and excessive filter maintenance. Liquid and vapor velocities must be controlled carefully and flashing of liquids or accelerated blow-down rates that would “lift” or “float” all or portions of the bed should be avoided.

Desiccant bed life can be extended by doing several or all of the following activities:

- Prevent the desiccant particles from moving.
- Keep contaminants out of the dehydrating portion of the bed by upstream conditioning or by providing a sacrificial layer of less expensive desiccant to act as a catcher of any compounds such as amine, glycol or oil.
- Prevent overheating the bed to reduce the formation of carbon during the regeneration cycle.
- Analyze the heating/cooling regeneration temperature cycles to minimize the time the bed is at elevated temperatures. This will also minimize energy requirements.

A typical heating/cooling regeneration temperature cycle plot is shown in Fig. 20-87, with a description of the stage activities. There are typically four (4) distinct stages in a normal cycle:

Stage 1—First bed-heating stage

Stage 2—Desorption stage

Stage 3—Second bed-heating stage

Stage 4—Bed-cooling stage

For a period of time after the heat source is introduced into a desiccant bed being dehydrated, the bed must be heated to a temperature where the water will start to be desorbed (Stage 1). As the water is desorbed (Stage 2), the bed temperature will usually rise only a few degrees because the regeneration gas heat is utilized to provide the heat of vaporization of the water being removed. The completion of the water desorption stage is characterized by a rapid increase in bed temperature measured as the outlet temperature. At this point the heating may be discontinued while bed heating will continue from residual heat in the heating cycle (Stage 3). As the unheated regeneration gas stream continues to pass through the bed, the bed will be cooled (Stage 4).

At near ambient pressures, regeneration of silica gel and alumina can be accomplished at 300°F. Molecular sieve requires 500-550°F to maintain the low dewpoint potential, and the higher temperatures may increase desiccant life by providing more complete removal of adsorbed hydrocarbons.

Capacity and performance data for new solid desiccants are usually presented based on a static test. Under operating conditions (dynamic) the performance data may be significantly different. Typically the effective capacity at operating conditions is about one-half of the capacity at equilibrium (static) conditions for most solid desiccants. This operating characteristic must be considered when designing a dehydration system and can be influenced by careful design and good control of operating parameters such as temperatures, contaminant levels, regeneration cycles, and desiccant selection. Solid desiccant manufacturers should be consulted for the most current product information and design criteria.

Molecular Sieve

Molecular sieve is not normally used for liquid dehydration because the required level of water removal is usually moderate and the cost of molecular sieve is considerably more than other types of suitable desiccants, such as activated alumina. However, in extreme cases where the moisture content of the liquid must be kept at an unusually low concentration, molecular sieve should be considered.

Molecular sieve may be used for removing other undesirable compounds, such as H_2S, COS, mercaptans, etc., from liquid streams. Dehydration may be a secondary benefit of using this type of treating method.

Refer to the discussion of molecular sieve for gas dehydration elsewhere in this Section for more information.

Activated Alumina

There are several types of alumina available for use as a solid desiccant. Alumina is widely used for drying liquid product streams following gas processing, treating, or fractionation. Most alumina desiccants will produce a dewpoint below –100°F if applied properly. Alumina tends to adsorb heavy hydrocarbons which are difficult to remove during regeneration. Alumina is alkaline and is subject to reaction with mineral acids which are found in some well treating fluids.

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The design of a solid desiccant liquid dehydration system is similar to a gas dehydration system. An effective desiccant capacity of 4-5% is typically used in liquid dehydrator design.

Calcium Chloride

Calcium chloride is used as a consumable desiccant. Solid calcium chloride combines with water to form a brine solution. From one to two pounds of water can be absorbed by a pound of calcium chloride. Large liquid $CaCl_2$ dehydrators are usually operated in a series that can be reversed with a moisture monitor located between the beds. In that way when the lead sacrificial bed is exhausted, no wet product is produced. The exhausted $CaCl_2$ bed is then recharged and the vessels reversed in service.

The bed size can be estimated using a superficial velocity of 3-5 ft/min and an L/D of 2.5 to 4:1.

Calcium chloride dehydration has become less popular because of the environmental problem of disposing of the produced brine.

Distillation

Wet NGLs can be dehydrated by distillation in specially designed fractionation columns. It will generally suffice to withdraw a sidestream liquid distillate three to four fractionation trays below the top of the distillation column to assure a dry product. Water in the NGL feed is passed overhead and is decanted in the overhead reflux drum while reflux is returned to the top of the column. Some extra costs will be required for the sidestream liquid withdrawal and cooling, but this can still be the most cost-effective manner to achieve the dehydration of propane and/or butane LPG products to adequate dryness specifications. The bottoms product of the distillation should be bone dry.

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SECTION 21

Hydrocarbon Treating

There are many methods that may be employed to remove acidic components (primarily H_2S and CO_2) and other impurities from hydrocarbon streams. The available methods may be broadly categorized as those depending on chemical reaction, absorption, adsorption or permeation. Processes employing each of these techniques are described and a general bibliography for additional reading is included. Because of the diversity of the processes available, and new processes introduced, all possible processes are not discussed. Fig. 21-1 contains the nomenclature and a glossary of terms used in this section.

FIG. 21-1

Nomenclature

Absorption: A separation process involving the transfer of a substance from a gaseous phase to a liquid phase through the phase boundary.

Acid Gases: Impurities in a gas stream usually consisting of CO_2, H_2S, COS, RSH, and SO_2. Most common in natural gas are CO_2, H_2S and COS.

Acid Gas Loading: The amount of acid gas, on a molar or volumetric basis, that will be picked up by a solvent.

Adsorption: The process by which gaseous components adhere to solids because of their molecular attraction to the solid surface.

Alkanolamine: An organic nitrogen bearing compound related to ammonia having at least one, if not two or three of its hydrogen atoms substituted with at least one, if not two or three linear or branched alkanol groups where only one or two could also be substituted with a linear or branched alkyl group (i.e. methyldiethanolamine MDEA). The number of hydrogen atoms substituted by alkanol or alkyl groups at the amino site determine whether the alkanolamine is primary, secondary or tertiary.

Antifoam: A substance, usually a silicone or a long-chain alcohol, added to the treating system to reduce the tendency to foam.

Chelate: An organic molecule in which a central metallic ion is held in a coordination compound.

Claus Process: The process in which one third of the H_2S is burned to SO_2 which is then reacted with the remaining H_2S to produce elemental sulfur.

Degradation Products: Impurities in a treating solution that are formed from both reversible and irreversible side reactions.

Doctor Sweet: Describes a hydrocarbon stream which has had mercaptans removed to a level that it passes the Doctor Test (GPA-1138).

Grain: A unit of mass where one pound is equivalent to 7,000 grains and a specification of 0.25 grain of H_2S per 100 SCF is equivalent to an H_2S concentration of 4.0 ppmv.

Mercaptan: Any of a homologous series of compounds of the general formula RSH. All of the materials possess a foul odor, e.g. methyl mercaptan.

Physical Solvent: A liquid capable of absorbing selected gas components by solubility alone without associated chemical reactions.

ppmv: A volume concentration of a species in a bulk fluid measured in parts per million.

Residence Time: The time period for which a fluid will be contained within a specified volume.

Selective Treating: Preferential removal of one acid gas component, leaving at least some of the other acid gas components in the treated stream.

Sour Gas: Gas containing undesirable quantities of hydrogen sulfide, mercaptans and/or carbon dioxide.

Sterically Hindered Amine: An alkanolamine containing a bulky substituent group close to the amino nitrogen site to lower the stability of the carbamate ion thus inhibiting reactions with CO_2 owing to the bulky nature of the CO_2 molecule. (i.e. diisopropanolamine DIPA).

SRU: Sulfur recovery unit.

Sweet Gas: Gas which has no more than the maximum sulfur content defined by: (1) the specifications for the sales gas from a plant; (2) the definition by a legal body such as the Texas Railroad Commission.

TGCU (Tail Gas Clean up Unit): a process unit that takes tail gas from a SRU and removes additional sulfur .

Threshold Limit Value: The amount of a contaminant to which a person can have repeated exposure for an eight hour day without adverse effects.

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SAFETY PRECAUTIONS

Hydrogen sulfide is a highly toxic gas. At concentrations as low as 10 ppmv irritation of the eyes, nose, and throat is possible. The human nose can detect hydrogen sulfide in concentrations as low as 0.02 ppmv. However, the human sense of smell cannot be relied on to detect hazardous concentrations of hydrogen sulfide. Higher concentrations and extended exposure to hydrogen sulfide will desensitize the sense of smell. The concentrations required for different reactions by the human body are:[1]

1. Threshold limit value (TLV) for prolonged exposure: 10 ppmv
2. Slight symptoms after several hours exposure: 10-100 ppmv
3. Maximum concentration that can be inhaled for one hour without serious effects such as significant eye and respiratory irritation: 200-300 ppmv
4. Dangerous after exposure of 30 minutes to one hour: 500-700 ppmv
5. Fatal in less than 30 minutes: 700-900 ppmv and above.
6. Death in minutes: greater than 1000 ppmv

Hydrogen sulfide is highly flammable and will combust in air at concentrations from 4.3 to 46.0 volume percent. Hydrogen sulfide vapors are heavier than air and may migrate considerable distances to a source of ignition.

Gaseous carbon dioxide is a naturally occurring gas that is 50% heavier than air and is colorless and odorless. It is also a principal by-product of combustion. CO_2 is inactive and therefore non-flammable. CO_2 will displace oxygen and can create an oxygen-deficient atmosphere resulting in suffocation. The principal hazard of CO_2 is exposure to elevated concentrations. The atmospheric concentration immediately hazardous to life is 10% (volume).[2] Because CO_2 is heavier than air, its hazard potential is increased, especially when entering tanks and vessels. "A common but erroneous belief is that CO_2 simply acts as an asphyxiant by lowering the oxygen level below the 16 percent minimum necessary to sustain life (at sea level). Although this is frequently the case in most serious accidents, CO_2 begins to have a noticeable effect on normal body functions at about two to three percent. The concentration of carbon dioxide in the blood affects the rate of breathing, a measurable increase resulting from a level of one percent in the inspired air."[2]

Anyone engaged in the design or operation of a facility in which H_2S and/or CO_2 are present should seek expert advice for detailed safety precautions and mechanical design considerations.

TYPES OF CONTAMINANTS

Ammonia (NH_3)
Hydrogen sulfide (H_2S)
Hydrogen cyanide (HCN)
Carbon dioxide (CO_2)
Carbonyl sulfide (COS)
Carbon disulfide (CS_2)
Mercaptans (RSH)
Nitrogen (N_2)
Water (H_2O)
Sulfur dioxide (SO_2)
Elemental sulfur
Mercury and arsenic
Oxygen

Removal of these contaminants is required for reasons of safety, corrosion control, gas and/or liquid product specifications, to prevent freeze-out at low temperatures, to decrease compression costs, to prevent poisoning of catalysts in downstream facilities and to meet environmental requirements. The removal of water (dehydration) is discussed in Section 20. The discussion in this section will deal with removal of some or all of the sulfur-containing compounds and carbon dioxide.

PRETREATMENT

All gas sweetening units should have well-designed pretreatment facilities. Carryover of brine or liquid hydrocarbon (as slugs or aerosol) from upstream production operations can cause problems for gas treating and downstream processing equipment. Also, field facilities are not typically designed to remove troublesome contaminants like gas-phase heavy hydrocarbons. These contaminants can likewise cause operational difficulties in the sweetening process.

Inlet Separation

If gross liquid carryover from an upstream facility is possible, a slug catcher is recommended. It should be sized not only for steady inlet fluid volumes, but for surge capacity to handle slugs of liquid hydrocarbons, water, and/ or well treatment chemicals. See Section 17 for options regarding slug catcher design.

If aerosols are a concern, an inlet filter separator is suggested. Selected filter elements can remove entrained droplets down to 0.3 microns in diameter. The detailed design of filter separators is described in Section 7. Note that the effectiveness of a filter separator may be enhanced by the injection of a small amount of polymer into the gas stream upstream of the filter [3].

In lieu of an inlet filter separator, a water wash column may be placed ahead of the sweetening unit. Water washing can be particularly effective for removing glycol mists or fogs. Of course, stainless steel or other corrosion-resistant alloy should be considered for water washing in a sour environment. In the case of fine iron sulfide blowing in a dry pipeline, a glycol wash column has been reported to be an effective means of solids removal[4].

For liquid hydrocarbon treatment, a filter coalescer may be used to remove suspended water or glycol prior to further processing.

Hydrocarbon Dewpoint Control

Heavy hydrocarbons (C6+) can be absorbed by solvents, which could lead to foaming in the sweetening unit. It is possible to reduce the heavy hydrocarbon content of the incoming gas through cooling (via Joule-Thomson expansion, propane refrigeration, or turbo-expansion as described in Section 16), and subsequent condensation of the heavy components. The condensed liquids are removed, and the gas is warmed above the saturation temperature before going to the sweetening unit.

An alternative means to remove gaseous heavy hydrocarbons is through adsorption. Either alumina or silica gel beds may be used in parallel such that one bed is regenerated while the other is in service. The beds are regenerated by heating

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and desorbing the hydrocarbons. The heavy hydrocarbons are recovered from the regeneration gas via condensation.

Rubbery membranes may have potential applications in heavy hydrocarbon dewpointing. However this technology has been tested only to a limited extent at this point of time. (See Section 16, Emerging Technologies).

Oxygen Contamination

Oxygen entry into a hydrocarbon system is often troublesome. If liquid water is present, severe corrosion may occur. If H_2S or sulfur is present, corrosion by a different mechanism or sulfur deposition and plugging may occur. Oxygen contamination may be addressed by several different approaches but the first step is to find and correct the source of oxygen entry into the system. This is often the simplest and most cost effective approach. Most oxygen leaks may be traced to compressor suctions or pipe fittings.

To eliminate oxygen contamination a number of possibilities exist:

- React the oxygen with chemicals.
  Chemicals such as amines, organics or inorganic compounds may be added to remove free oxygen. Oxygen scavengers are available from many suppliers such as Lubchem and Baker-Petrolite.
- Thermal oxidation reactions.
  Integrated processes such as the DeOxy by Optimized Process Designs can perform a very limited burn to consume the free oxygen.
- Remove other reactants that cause problems with the presence of oxygen. By removing offending components such as water or H_2S that react with oxygen, the presence of low amounts of oxygen may be tolerated.
- Treat the symptom.
  Corrosion inhibitors, filtration and / or alternate schemes may be utilized to stop or offset any adverse effects of oxygen contamination.

GAS TREATING – PROCESS OPTIONS

The gas treating process can affect the design of the entire gas processing facility including methods chosen for acid gas disposal and sulfur recovery, dehydration, liquids recovery, liquids fractionation and liquid product treating. Some of the factors to be considered in making a gas treating process selection are:

- Air pollution regulations regarding sulfur compound disposal and/or Tail Gas Clean Up (TGCU) requirements.
- Type and concentration of impurities in the sour gas.
- Specifications for the residue gas.
- Specifications for the acid gas.
- Temperature and pressure at which the sour gas is available and at which the sweet gas must be delivered.
- Volume of gas to be processed.
- Hydrocarbon composition of the gas.
- Selectivity required for acid gas removal.
- Capital cost and operating cost.
- Royalty cost for process.
- Liquid product specifications.
- Disposal of byproducts considered hazardous chemicals.

Any process which requires disposal of waste chemicals must determine if the chemical is considered "hazardous". The permitting requirements and economic impact of hazardous waste disposal on a project must not be overlooked.

The importance of having an accurate analysis of the inlet gas stream cannot be overstressed. Process selection and economics depend on knowing all components present in the gas. Impurities such as COS, CS_2 and mercaptans (even in very small concentrations) can have a significant impact on the process design of both the gas treating and downstream processing facilities.[5,6]

If the gas processing facility is to be used in conjunction with liquids recovery, the requirements for H_2S, CO_2, and mercaptan removal may be affected. In liquid recovery plants, varying amounts of H_2S, CO_2, and other sulfur compounds will end up in the liquid product. Failure to remove these components prior to liquids recovery may require liquid product treating in order to meet product specifications. In many instances, liquid treating may be required anyway.

When sulfur recovery is required, the composition of the acid gas stream feeding the sulfur plant must be considered. With CO_2 concentrations greater than 80% in the acid gas, the possibility of selective treating should be considered to raise the H_2S concentration to the sulfur recovery unit (SRU). This may involve a multi-stage gas treating system in which the gas exiting the first stage is enriched by passing it through another absorption solvent loop.

High concentrations of hydrocarbons can cause design and operating problems for the SRU. The effect of these components must be weighed when selecting the gas treating process to be used. Further discussion of this can be found in Section 22.

Decisions in selecting a gas treating process can many times be simplified by gas composition and operating conditions. High partial pressures (50 psi) of acid gases enhance the possibility of using a physical solvent. The presence of significant quantities of heavy hydrocarbons in the feed discourages using physical solvents. Low partial pressures of acid gases and low outlet specifications generally require the use of amines for adequate treating. Process selection is not easy and a number of variables must be weighed prior to making a process selection. Fig. 21-2 gives a summary for a number of processes.

Controlling pH is very important in most of the processes discussed in this section. The following is offered to assist in understanding electrolyte solutions and pH.

An electrolyte is a substance or material that will provide ionic conductivity when dissolved in water. Both bases and acids, if they ionize in water, can be electrolytes. In water, acids ionize or split, into H^+ and the anion. The H^+ combines with a water molecule to form H_3O^+ which is usually written as H^+ and is referred to as a hydrogen ion, or proton. Water-soluble bases, on the other hand, ionize in water to produce hydroxyl or OH^- ions and a cation. Pure water ionizes such that the concentration of H^+ (and OH^-) in the solution is 10^{-7} gram ions / liter.

The method used for measuring hydrogen and hydroxyl ion concentrations uses pH (from the French pouvoir hydrogene), where the pH of a solution is the logarithm (base 10) of the reciprocal of the hydrogen ion concentration (gram mole / liter). For pure water, then, the pH would be:

$$pH = \log (1/ [H^+]) = 7$$

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FIG. 21-2

Process Capabilities for Gas Treating

	Normally Capable of Meeting 4 ppmv H_2S	Removes Mercaptans and COS	Selective H_2S Removal	Solution Degraded (By)
Primary Amine	Yes	Partial	No	Yes (COS, CO_2, CS_2)
Secondary Amine	Yes	Partial	No	Some (COS, CO_2, CS_2)
Tertiary Amine	Yes	Partial	Yes*	No
Hybrid/Mixed	Yes	Partial	Yes*	Some (CO_2, CS_2)
Physical Solvent	Yes	Yes	Yes*	No
Solid Bed	Yes	Yes	Yes*	No
Liquid Redox	Yes	No	Yes	CO_2 at high conc.
Sacrificial	Yes	Partial	Yes	No

* Some selectivity exhibited

When a water molecule dissociates, one proton and one hydroxyl ion are formed. The concentration of OH^- in pure water, then, is also 10^{-7} mole / liter.

A strong acid (or strong base) is one which ionizes completely in water solution. Typical are HCl or NaOH. At an acid concentration of 0.1 mole / liter, the pH of a strong acid will be 1. The following table will be helpful in understanding the relative concentrations of H^+ and OH^- in solutions of different pH.

	pH	Concentration, mole/liter	
		H^+	OH^-
	1	$1.0 \cdot 10^{-1}$	$1.0 \cdot 10^{-13}$
Acid Side (Excess H^+)	2	$1.0 \cdot 10^{-2}$	$1.0 \cdot 10^{-12}$
	3	$1.0 \cdot 10^{-3}$	$1.0 \cdot 10^{-11}$
	4	$1.0 \cdot 10^{-4}$	$1.0 \cdot 10^{-10}$
	5	$1.0 \cdot 10^{-5}$	$1.0 \cdot 10^{-9}$
	6	$1.0 \cdot 10^{-6}$	$1.0 \cdot 10^{-8}$
Neutral Solution	7	$1.0 \cdot 10^{-7}$	$1.0 \cdot 10^{-7}$
	8	$1.0 \cdot 10^{-8}$	$1.0 \cdot 10^{-6}$
	9	$1.0 \cdot 10^{-9}$	$1.0 \cdot 10^{-5}$
	10	$1.0 \cdot 10^{-10}$	$1.0 \cdot 10^{-4}$
	11	$1.0 \cdot 10^{-11}$	$1.0 \cdot 10^{-3}$
Basic Side (excess OH-)	12	$1.0 \cdot 10^{-12}$	$1.0 \cdot 10^{-2}$
	13	$1.0 \cdot 10^{-13}$	$1.0 \cdot 10^{-1}$

Example 21-1 — 5,000 gallons of amine solution with a pH of 12 is to be neutralized by the addition of hydrochloric acid (HCl). How many pounds of pure HCl will be required?

Solution steps:

$$5{,}000 \text{ gal.} \cdot 3.79 \text{ (liter/gal)} = 1.9 \cdot 10^4 \text{ liters}$$

For each liter of solution the change in OH^- (H^+) required is

$$(10^{-2}) - (10^{-7}) = 1.0 \cdot 10^{-2} \text{ gram moles / liter}$$

The total requirement of HCl is

$$(1.9 \cdot 10^4) \text{ liter} \cdot (1.0 \cdot 10^{-2}) \text{ (g mole/liter)} = 190 \text{ g mole}$$

or

$$\frac{(190 \text{ g mole})(36.5 \text{ g/g mole})}{454 \text{ (gram/pound)}} = 15.3 \text{ pounds HCl}$$

Note that at a pH of 7, all of a weak acid (base) would probably not be neutralized. The pH required to have all of a weak acid (base) neutralized will vary with the acid but will usually be less (greater) than 7. In the example all of the HCl is neutralized because it is completely ionized in the water solution.

CHEMICAL SOLVENT PROCESSES

Chemical reaction processes remove the H_2S and/or CO_2 from the gas stream by chemical reaction with a material in the solvent solution. The reactions may be reversible or irreversible. In reversible reactions the reactive material removes CO_2 and/or H_2S in the contactor at high partial pressure and/or low temperature. The reaction is reversed by high temperature and/or low pressure in the stripper. In irreversible processes the chemical reaction is not reversed and removal of the H_2S and/or CO_2 requires continuous makeup of the reacting material. Fig. 21-4 shows the process flow for a typical reversible chemical reaction process. Figure 21-5 is a table of physical properties of gas treating chemicals. Figures 21-6 through 21-8 show vapor pressures at various temperatures, and freezing points and specific gravity for some of the treating chemicals.

Aqueous Alkanolamine Processes

Originally applied to gas treating in 1930 by Bottoms,[7] alkanolamines have become the most widely used solvents for the removal of acid gases from natural gas streams.[8] Triethanolamine (TEA) was the first used commercially for gas treating. It has been displaced for conventional applications by other alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA), diisopropanolamine (DIPA), diglycolamine® (DGA®) and methyldiethanolamine (MDEA).

Fig. 21-3 lists approximate guidelines for a number of alkanolamine processes.

The alkanolamine (hereafter amine) processes are particularly applicable where acid gas partial pressures are low and/or low levels of acid gas are desired in the residue gas. Because the water content of the solution minimizes heavy hydrocarbon absorption, these processes are well suited for gases rich in heavier hydrocarbons. Some amines can be used to selectively remove H_2S in the presence of CO_2.

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Chemistry — The overall equilibrium reactions applicable for H_2S and CO_2 and primary and secondary amines are shown below with a primary amine[9]. A qualitative estimation of the velocity of the reaction is given.

For hydrogen sulfide removal

$$RNH_2 + H_2S \leftrightarrow RNH_3^+ + HS^- \text{ Fast} \qquad \textbf{Eq. 21-1}$$

$$RNH_2 + HS^- \leftrightarrow RNH_3^+ + S^{--} \text{ Fast} \qquad \textbf{Eq. 21-2}$$

The overall reactions between H_2S and amines are simple since H_2S reacts directly and rapidly with all amines to form the bisulfide by Eq. 21-1 and the sulfide by Eq. 21-2.

For carbon dioxide removal

$$2\,RNH_2 + CO_2 \leftrightarrow RNH_3^+ + RNHCOO^- \text{ Fast} \qquad \textbf{Eq. 21-3}$$

$$RNH_2 + CO_2 + H_2O \leftrightarrow RNH_3^+ + HCO_3^- \text{ Slow} \qquad \textbf{Eq. 21-4}$$

$$RNH_2 + HCO_3^- \leftrightarrow RNH_3^+ + CO_3^{--} \text{ Slow} \qquad \textbf{Eq. 21-5}$$

FIG. 21-3

Approximate Guidelines for Amine Processes[1]

	MEA	DEA[9]	DGA®	Sulfinol	MDEA[9]
Acid gas pickup, scf/gal @ 100°F, normal range[2]	3.1–4.3	6.7– 7.5	4.7–7.3	4–17	3–7.5
Acid gas pickup, mols/mol amine, normal range[3]	0.33–0.40	0.20–0.80	0.25–0.38	NA	0.20–0.80
Lean solution residual acid gas, mol/mol amine, normal range[4]	0.12 ±	0.01 ±	0.06 ±	NA	0.005–0.01
Rich solution acid gas loading, mol/mol amine, normal range[3]	0.45–0.52	0.21–0.81	0.35–0.44	NA	0.20–0.81
Solution concentration, wt%, normal range	15–25	30–40	50–60	3 comps., varies	40–50
Approximate reboiler heat duty, Btu/gal lean solution[5]	1,000–1,200	840–1,000	1,100–1,300	350–750	800–900
Steam heated reboiler tube bundle, approx. average heat flux, Q/A = Btu/hr-ft^2 [6]	9,000–10,000	6,300–7,400	9,000–10,000	9,000–10,000	6,300–7,400
Direct fired reboiler fire tube, average heat flux, Q/A = Btu/hr-ft^2 [6]	8,000–10,000	6,300–7,400	8,000–10,000	8,000–10,000	6,300–7,400
Reclaimer, steam bundle or fire tube, average heat flux, Q/A = Btu/hr-ft^2 [6]	6–9	NA(7)	6–8	NA	NA[7]
Reboiler temperature, normal operating range, °F[8]	225–260	230–260	250–270	230–280	230–270
Heats of reaction;[10] approximate: Btu/lb H_2S	610	720	674	NA	690
Btu/lb CO_2	660	945	850	NA	790
NA — not applicable or not available					

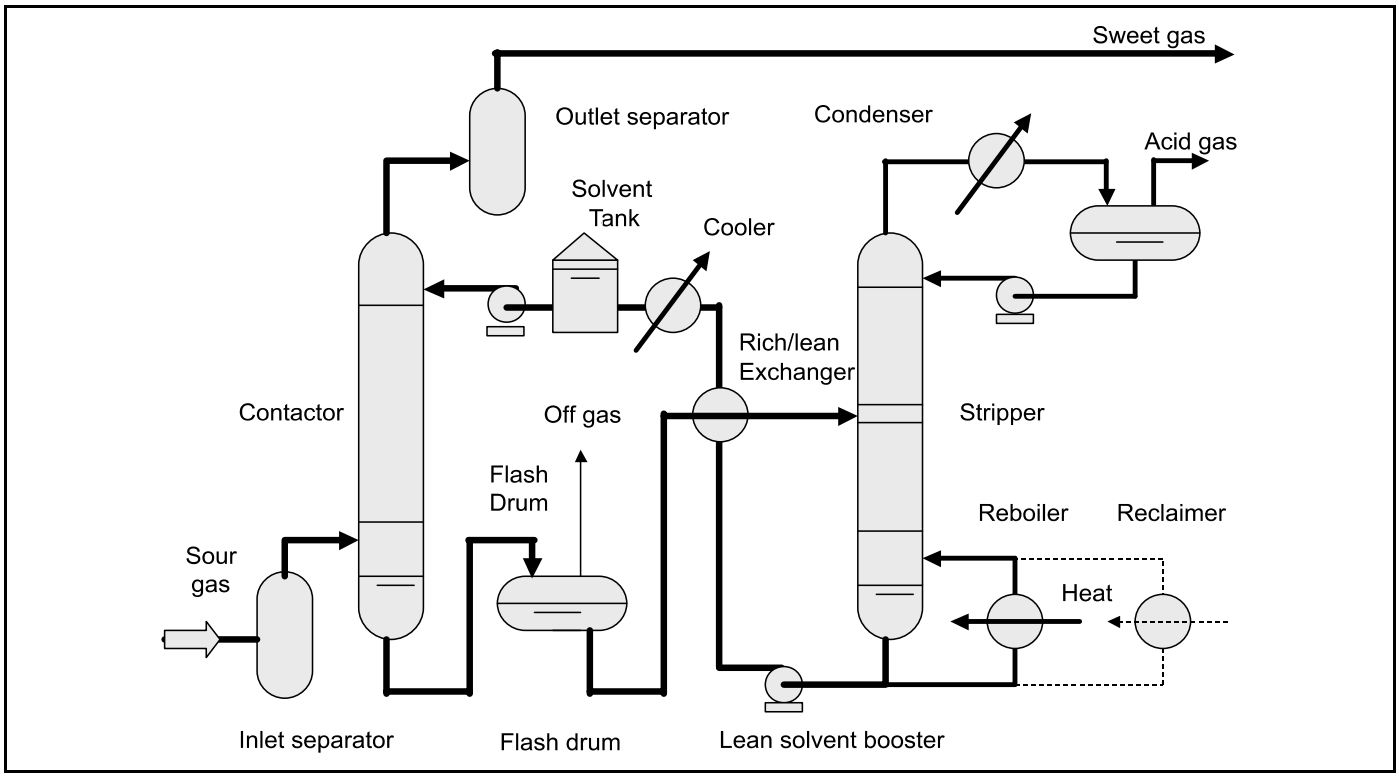
NOTES:

1. These data alone should not be used for specific design purposes. Many design factors must be considered for actual plant design.
2. Dependent upon acid gas partial pressures and solution concentrations.
3. Dependent upon acid gas partial pressures and corrosiveness of solution. Might be only 60% or less of value shown for corrosive systems.
4. Varies with stripper overhead reflux ratio. Low residual acid gas contents require more stripper trays and/or higher reflux ratios yielding larger reboiler duties.
5. Varies with stripper overhead reflux ratios, rich solution feed temperature to stripper and reboiler temperature.
6. Maximum point heat flux can reach 20,000–25,000 Btu/hr-ft^2 at highest flame temperature at the inlet of a direct fired fire tube. The most satisfactory design of firetube heating elements employs a zone by zone calculation based on thermal efficiency desired and limiting the maximum tube wall temperature as required by the solution to prevent thermal degradation. The average heat flux, Q/A, is a result of these calculations.
7. Reclaimers are not used in DEA and MDEA systems.
8. Reboiler temperatures are dependent on solution conc. flare/vent line back pressure and/or residual CO_2 content required. It is good practice to operate the reboiler at as low a temperature as possible.
9. According to Total.
10. B.L. Crynes and R.N. Maddox, Oil Gas J., p. 65-67, Dec. 15 (1969). The heats of reaction vary with acid gas loading and solution concentration. The values shown are average[10].

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FIG. 21-4

Typical Gas Sweetening by Chemical Reaction



Concerning the chemical reactions with CO_2, primary amines (**RNH_2**) such as MEA and DGA® agent, and secondary amines (**RR'NH**) such as DEA and DIPA, differ from tertiary amines (**RR'R"N**) such as TEA and MDEA.

Primary and Secondary Amines

With the primary and secondary amines, the predominant overall reaction (Eq. 21-3) rapidly leads to the formation of a stable carbamate which is slow to further hydrolyze to bicarbonate.

The other overall reactions leading to bicarbonate (Eq. 21-4) and to carbonate (Eq. 21-5) are slow because they have to proceed through the hydration of CO_2.

Therefore, according to Eq. 21-3 there is a theoretical limit to the chemical loading capacity of the primary and secondary amine solutions to 0.5 mole CO_2 per mole of amine, even at relatively high partial pressures of CO_2 in the gas to be treated.

Tertiary Amines

Unlike primary and secondary amines, the nitrogen (**N**) in tertiary amines (**RR'R"N**) has no free hydrogen (**H**) to rapidly form carbamate as per overall Eq. 21-3. As a consequence, the removal of CO_2 by tertiary amines can only follow the slow route to bicarbonate by Eq. 21-4 and carbonate by Eq. 21-5.

The slowness of the reaction leading to bicarbonate is the underlying reason why tertiary amines can be considered selective for H_2S removal, by playing with absorption contact time, and this attribute can be used to full advantage when complete CO_2 removal is not necessary.

However, the slow route to bicarbonates theoretically allows at equilibrium a chemical loading ratio of one mole of CO_2 per mole of amine. Furthermore, at high partial pressure, the solubility of CO_2 in tertiary amines is far greater than in the primary and secondary amines thus further enhancing the CO_2 loading by physical solubility at high partial pressure.

Therefore, in case of gases to be treated for bulk CO_2 removal, large amounts of CO_2 can be liberated from the rich solvent by simple flash alleviating the thermal regeneration duty with consequent energy savings.

Activated Tertiary Amines

The use of activators mitigates the slowness of the reaction to bicarbonate for tertiary amines. Activators are generally primary or secondary amines; they are tailored to increase both the hydrolysis of the carbamate and the rate of hydration of dissolved CO_2 thus making the activated-tertiary amines specially suitable for efficient and economical bulk CO_2 removal when selectivity is not required (see section on MDEA).

Process Flow — The general process flow for an alkanolamine treating plant is shown in Fig. 21-4. The basic flow varies little for different solutions though some designs incorporate multiple feeds and contactor sections.

Sour natural gas enters through an inlet separator for the removal of liquids and/or solids. From the separator, the gas stream enters the bottom of the contactor where it contacts the amine solution flowing down from the top of the column. The acid gas components in the gas react with the amine to form a regenerable salt. As the gas continues to pass up the contactor, more acid gases chemically react with the amine. The sweetened gas leaves the top of the contactor and passes through an outlet separator to catch any solution which may

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FIG. 21-5

Physical Properties of Gas Treating Chemicals

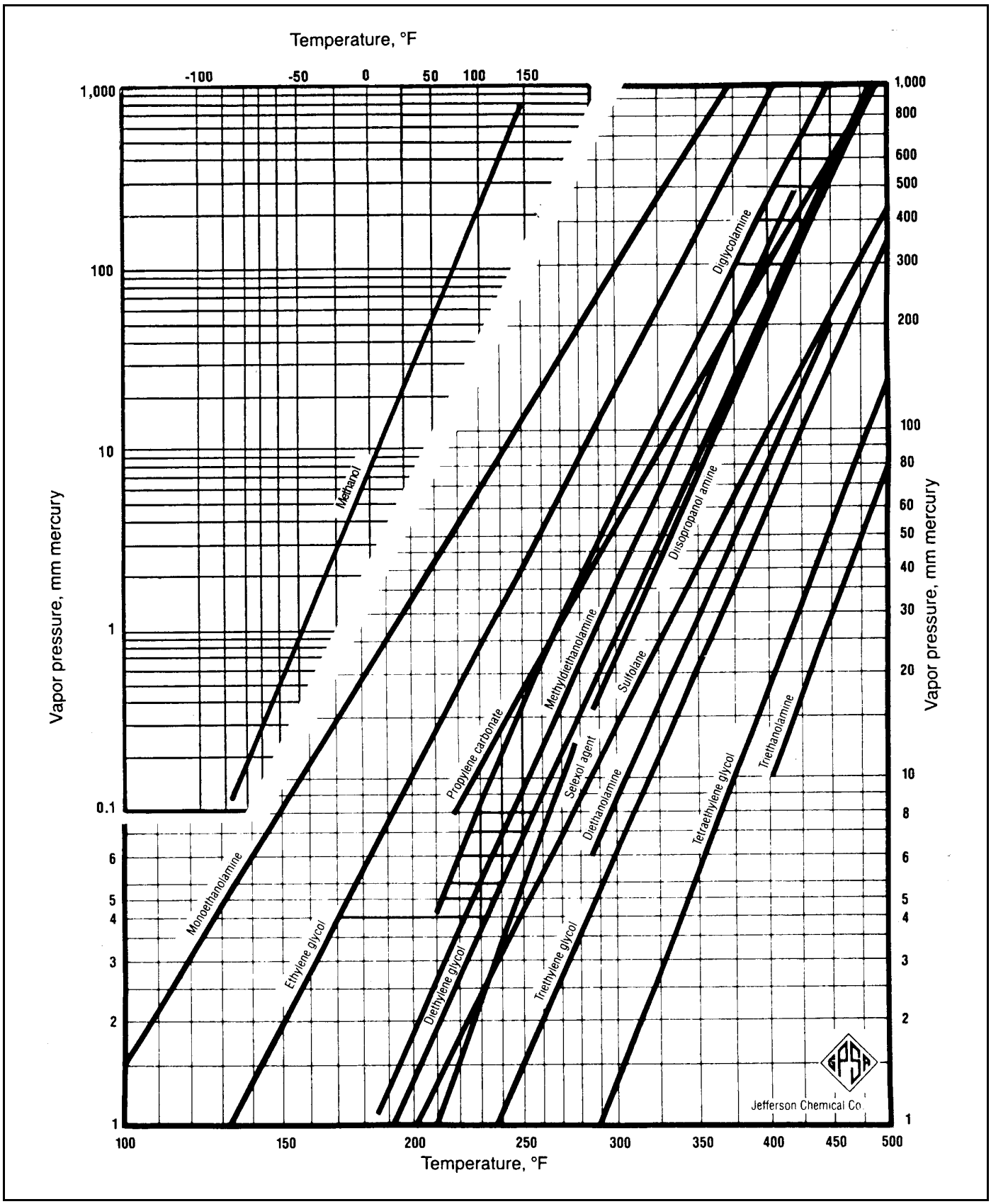
	Monoethanol-amine	Diethanol-amine	Triethanol-amine	Diglycol® -amine	Diisopropanol-amine	Selexol®
Formula	$HOC_2H_4NH_2$	$(HOC_2H_4)_2NH$	$(HOC_2H_4)_3N$	$H(OC_2H_4)_2NH_2$	$(HOC_3H_6)_2NH$	Polyethylene glycol derivative
Molecular Wt	61.08	105.14	148.19	105.14	133.19	280
Boiling point @ 760 mm Hg, °F	338.9	516.2 (decomposes)	680 (decomposes)	430	479.7	518
Freezing point, °F	50.9	82.4	72.3	9.5	107.6	–20
Critical constants						
Pressure, psia	868	474.7	355	547.11	546.8	–
Temperature, °F	662	827.8	957.7	756.6	750.6	–
Density @ 20°C, gm/cc.	1.018	1.095	1.124	1.058 @ 60°F	0.999 @ 30°C	1.031 @ 77°F
Weight, lb/gal	8.48 @ 60°F	9.09 @ 60°F	9.37 @ 68°F	8.82 @ 60°F		8.60 @ 77°F
Specific gravity 20°C/20°C	1.0179	1.0919 (30/20°C)	1.1258	1.0572	0.989 @ 45°C/20°C	–
Specific heat @ 60°F, Btu/lb/°F	0.608 @ 68°F	0.600	0.70	0.571	0.69 @ 30°C	0.49 @ 41°F
Thermal conductivity						
Btu/[(hr • sq ft • °F)/ft] @ 68°F	0.148	0.127	–	0.121	–	0.11 @ 77°F
Latent heat of vaporization, Btu/lb	180 @ 760 mmHg	288 @ 73 mmHg	230 @ 73 mmHg	219 @ 760 mmHg	185 @ 760 mmHg	–
Heat of reaction, Btu/lb of Acid Gas						
H_2S			–400	–674	–	–190 @ 77°F
CO_2			–630	–850	–	–160 @ 77°F
Viscosity, cp	24.1 @ 68°F	350 @ 68°F (at 90% wt. solution)	1013 @ 68°F (at 95% wt. solution)	40 @ 60°F	870 @ 86°F 198 @ 113°F 86 @ 129°F	5.8 @ 77°F
Refractive index, N_d 68°F	1.4539	1.4776	1.4852	1.4598	1.4542 @ 113°F	–
Flash point, COC, °F	200	298	365	260	255	304

	Propylene Carbonate	Methyldiethanol-amine	Sulfolane®	Methanol	10% Sodium Hydroxide
Formula	$C_3H_6CO_3$	$(HOC_2H_4)_2NCH_3$	$C_4H_8SO_2$	CH_3OH	
Molecular Wt	102.09	119.16	120.17	32.04	19.05
Boiling point @ 760 mm Hg, °F	467	477	545	148.1	217
Freezing point, °F	–56.6	–9.3	81.7	–143.8	14
Critical constants					
Pressure, psia	–		767.3	1153.9	
Temperature, °F	–		1013.8	464	
Density @ 20°C, gm/cc.	1.2057				
Weight, lb/gal		8.68	10.623 @ 30°C/30°C		9.254
Specific gravity 20°C/20°C	1.203	1.0418	1.268	0.7917	1.110
Specific heat @ 60°F, Btu/lb/°F	0.335	0.535	0.35 @ 30°C	0.59 @ 5°-10°C	0.897
Thermal conductivity					
Btu/[(hr • sq ft • °F)/ft] @ 68°F	0.12 @ 50°F	0.159	0.114 @ 100°F	0.124	
Latent heat of vaporization, Btu/lb	208 @ 760 mmHg	204	225.7 @ 212°F	474 @ 760 mmHg	
Heat of reaction, Btu/lb of Acid Gas					
H_2S	–				
CO_2					
Viscosity, cp	1.67 @ 100°F 19.4 cs @ –40°F 1.79 cs @ 100°F 0.827 cs @ 210°F	1.3 cs @ 50°F 0.68 cs @ 100°F 0.28 cs @ 212°F	10.3 @ 86°F 6.1 @ 122°F 2.5 @ 212°F 1.4 @ 302°F 0.97 @ 392°F	0.6 @ 68°F	1.83 @ 68°F 0.97 @ 122°F 0.40 @ 212°F
Refractive index, N_d 68°F	1.4209	1.469	1.481 @ 86°F	1.3286	
Flash point, COC, °F	270	265	350	58	

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FIG. 21-6

Vapor Pressures of Gas Treating Chemicals



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FIG. 21-7

Freezing Points of Aqueous Amine Solutions

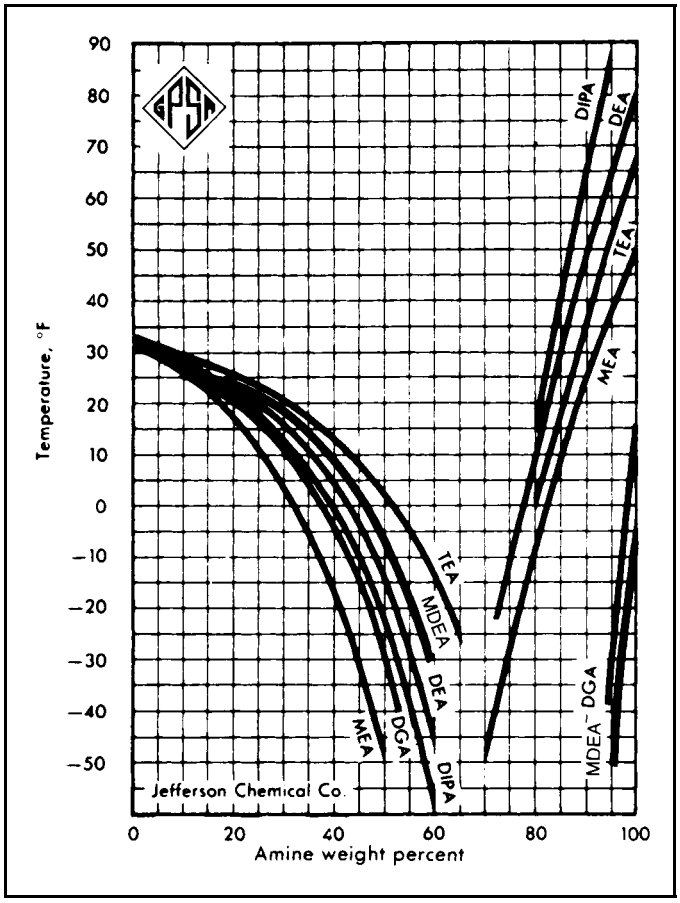
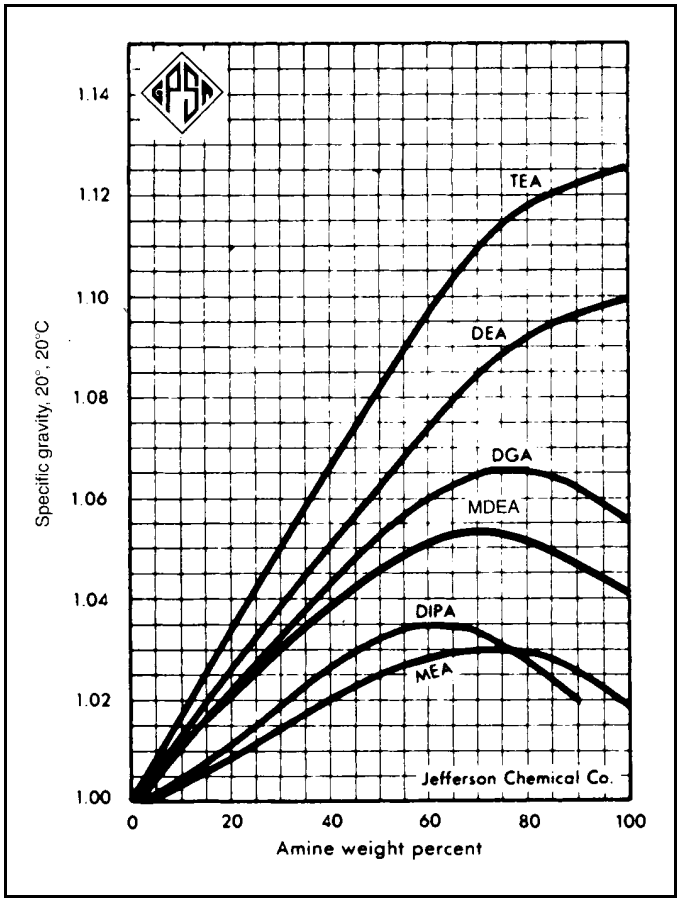


FIG. 21-8

Specific Gravity of Aqueous Amine Solutions



be carried over. The sweet gas leaving the contactor is saturated with water so dehydration, discussed in Section 20, is normally required prior to sale. If MEA is the sweetening agent, or the contactor is operating at unusually high temperature, a water wash may be used to attempt to recover some of the vaporized and/or entrained amine from the gas leaving the contactor. If a water wash is used it generally will consist of three or four trays at the top of the contactor, with makeup water to the unit being used as the wash liquid. Rich amine solution leaving the contactor flows through a flash drum to remove absorbed hydrocarbons or skim off. From the flash drum, the rich solution passes through the rich/lean exchanger where heat is absorbed from the lean solution. The heated rich amine goes to the mid portion of the stripper. As the solution flows down the column to the reboiler, it is stripped of H_2S and CO_2. The amine solution leaves the bottom of the stripper as lean solution. This lean solution is then passed through the rich/lean exchanger and a lean cooler to reduce the lean solution temperature to approximately 10°F warmer than the inlet gas temperature, to stay above the hydrocarbon dew point. At this point, the lean solution is returned to the contactor to repeat the cycle.

Acid gas stripped from the amine passes out of the top of the stripper. It goes through a condenser and separator to cool the stream and recover water. The recovered water is usually returned to the stripper as reflux. The acid gas from the reflux separator is either vented, incinerated, sent to sulfur recovery facilities, or compressed for sale or reinjected into a suitable reservoir for enhanced (see acid gas injection) oil recovery projects or for sequestration.

Reclaimer — A reclaimer is usually required for MEA and DGA® amine-based systems. The reclaimer helps remove degradation products from the solution and also aids in the removal of heat stable salts, suspended solids, acids and iron compounds. The reclaimers in MEA and DGA® systems differ. For MEA, a basic solution helps reverse the reactions. Soda ash and/or caustic soda is added to the MEA reclaimer to provide a pH of approximately 8-9; no addition is required for the DGA® reclaimer system. Reclaimers generally operate on a side stream of 1-3% of the total amine circulation rate.[11] Reclaimer sizing depends on the total inventory of the plant and the rate of degradation expected.

Reclaimer operation is a semi-continuous batch operation. The reclaimer is filled with hot amine solution and, if necessary, soda ash is added. As the temperature in the reclaimer increases, the liquid will begin to distill. Overhead vapors can be condensed and pumped back into the amine system, but generally the reclaimer is operated at slightly above stripper column pressure and the vapors are returned to the stripper. The initial vapor composition is essentially water. Continued distillation will cause the solution to become more and more concentrated with amine. This raises the boiling point of the solution and amine will begin to distill overhead. Fresh feed is continually added until the boiling point of the material in the reclaimer reboiler reaches 280° to 300°F. At this point, distillation is continued for a short time adding only water to

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help recover residual amine in the reclaimer reboiler. The reclaimer is then cleaned, recharged, and the cycle is repeated.[12]

Reclaimer "sludge" removed during cleaning must be handled with care. Disposal of the "sludge" must be in accordance with the governing regulations.

If needed a reclaiming company may be contracted to remove degradation products or heat stable salts from the amine. One type of reclaimer performs vacuum distillation on batches of spent amine mixed with sufficient caustic to neutralize the excess acidity. Another type of reclaimer uses ion exchange resin beds to remove heat stable salts.

Amines Used

Monoethanolamine — Gas sweetening with monoethanolamine (MEA) is used where there are low contactor pressures and/or stringent acid gas specifications. MEA removes both H_2S and CO_2 from gas streams. H_2S concentrations well below 4.0 ppmv can be achieved. CO_2 concentrations as low as 100 ppmv can be obtained at low to moderate pressures. COS and CS_2 are removed by MEA, but the reactions are irreversible unless a reclaimer is used. Even with a reclaimer, complete reversal of the reactions may not be achieved. The result is solution loss and build-up of degradation products in the system. Total acid gas pick up is traditionally limited to 0.3-0.35 moles of acid gas/mole of MEA and solution concentration is usually limited to 10-20 wt%. Inhibitors can be used to allow much higher solution strengths and acid gas loadings. Because MEA has the highest vapor pressure of the amines used for gas treating, solution losses through vaporization from the contactor and stripper can be high. This problem can be minimized by using a water wash.

Diethanolamine — This process employs an aqueous solution of diethanolamine (DEA). DEA will not treat to pipeline quality gas specifications at as low a pressure as will MEA.

Among the processes using DEA is the SNPA-DEA process developed by Societe Nationale des Petroles d'Aquitaine (today Total) to treat the very sour gas which was discovered in Lacq France in the 1950s. The original patents covered very high acid gas loading of 0.9 to 1.3 moles per mole of amine. This process is used for high pressure, high acid gas content streams having a relatively high ratio of H_2S/CO_2. The original process has been progressively improved and Total through Prosernat is now proposing high DEA solution concentrations up to 40 wt% with the high acid gas loading together with corrosion control by appropriate design and operating procedures.

Maximum attainable loading is limited by the equilibrium solubility of H_2S and CO_2 at the absorber bottoms conditions. Below are equilibrium solubility values for 40 wt% DEA solutions at 190°F

H_2S partial pressure (psia)	45	145	220
mole H_2S / mole amine	0.66	0.80	0.97
CO_2 partial pressure (psia)	45	90	145
mole CO_2 / mole amine	0.49	0.55	0.60

Although mole/mole loadings as high as 0.8-0.9 have been reported, most conventional DEA plants still operate at significantly lower loadings.

The process flow scheme for conventional DEA plants resembles the MEA process. The advantages and disadvantages of DEA as compared to MEA are:

- The mole/mole loadings typically used with DEA (0.35-0.82 mole/mole) are much higher than those normally used (0.3-0.4) for MEA.
- Because DEA does not form a significant amount of nonregenerable degradation products, a reclaimer is not required. Also, DEA cannot be reclaimed at reboiler temperature as MEA can.
- DEA is a secondary amine and is chemically weaker than MEA, and less heat is required to strip the amine solution.
- DEA forms a regenerable compound with COS and CS_2 and can be used for the partial removal of COS and CS_2 without significant solution losses.

Diglycolamine® — This process uses Diglycolamine® brand [2-(2-aminoethoxy)] ethanol in an aqueous solution. DGA® is a primary amine capable of removing not only H_2S and CO_2, but also COS and mercaptans from gas and liquid streams. Because of this, DGA® has been used in both natural and refinery gas applications. DGA® has been used to treat natural gas to 4.0 ppmv at pressures as low as 125 psig.[13] DGA® has a greater affinity for the absorption of aromatics, olefins, and heavy hydrocarbons than the MEA and DEA systems. Therefore, adequate carbon filtration should be included in the design of a DGA® treating unit.

The process flow for the DGA® treating process is similar to that of the MEA treating process. The three major differences are:

- Higher acid gas pick-up per gallon of amine can be obtained by using 50-60% solution strength rather than 15-20% for MEA (more moles of amine per volume of solution).
- The required treating circulation rate is lower. This is a direct function of higher amine concentration.
- Reduced reboiler steam consumption.

Typical concentrations of DGA® range from 50% to 60% DGA® by weight while in some cases as high as 70 wt% has been used. DGA® has an advantage for plants operating in cold climates where freezing of the solution could occur. The freezing point for 50% DGA® solution is –30°F. Because of the high amine degradation rate DGA® systems require reclaiming to remove the degradation product. DGA® reacts with both CO_2 and COS to form N, N′, bis (hydroxyethoxyethyl) urea, generally referred to as BHEEU.[14] DEA is recovered by reversing the BHEEU reaction in the reclaimer.

Methyldiethanolamine—Methyldiethanolamine (MDEA) is a tertiary amine which can be used to selectively remove H_2S to pipeline specifications at moderate to high pressure. If increased concentration of CO_2 in the residue gas does cause a problem with contract specifications or downstream processing, further treatment will be required. The H_2S/CO_2 ratio in the acid gas can be 10-15 times as great as the H_2S/CO_2 ratio in the sour gas. Some of the benefits of selective removal of H_2S include:

- Reduced solution flow rates resulting from a reduction in the amount of acid gas removed.
- Smaller amine regeneration unit.
- Higher H_2S concentrations in the acid gas resulting in reduced problems in sulfur recovery.

CO_2 hydrolyzes much slower than H_2S. This makes possible significant selectivity of tertiary amines for H_2S. This fact is used by several companies who provide process designs using

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MDEA for selective removal of H_2S from gases containing both H_2S and CO_2.

A feature of MDEA is that it can be partially regenerated in a simple flash. As a consequence the removal of bulk H_2S and CO_2 may be achieved with a modest heat input for regeneration. However as MDEA solutions react only slowly with CO_2 (see chemistry) activators must be added to the MDEA solution to enhance CO_2 absorption and the solvent is then called activated MDEA.

Triethanolamine — Triethanolamine (TEA) is a tertiary amine and has exhibited selectivity for H_2S over CO_2 at low pressures. TEA was the first amine commercially used for gas sweetening. It was replaced by MEA and DEA because of its inability to remove H_2S and CO_2 to low outlet specifications. TEA has potential for the bulk removal of CO_2 from gas streams. It has been used in many ammonia plants for CO_2 removal.

Diisopropanolamine — Diisopropanolamine (DIPA) is a secondary amine which exhibits, though not as great as tertiary amines, selectivity for H_2S. This selectivity is attributed to the steric hindrance of the chemical.

Formulated Solvents and Mixed Amines — Formulated Solvents is the name given to a new family of amine-based solvents. Their popularity is primarily due to equipment size reduction and energy savings over most of the other amines. All the advantages of MDEA are valid for the Formulated Solvents, usually to a greater degree. Some formulations are capable of slipping larger portions of inlet CO_2 (than MDEA) to the outlet gas and at the same time removing H_2S to less than 4 ppmv. For example, under conditions of low absorber pressure and high CO_2 /H_2S ratios, such as Claus tail gas clean-up units, certain solvent formulations can slip upwards to 90 percent of the incoming CO_2 to the incinerator. While at the other extreme, certain formulations remove CO_2 to a level suitable for cryogenic plant feed. Formulations are also available for CO_2 removal in ammonia plants. Finally, there are solvent formulations which produce H_2S to 4 ppmv pipeline specifications, while reducing high inlet CO_2 concentrations to 2% for delivery to a pipeline. This case is sometimes referred to as bulk CO_2 removal.

This need for a wide performance spectrum has led Formulated Solvent suppliers to develop a large stable of different MDEA-based solvent formulations. Most Formulated Solvents are enhancements to MDEA discussed above. Thus, they are referred to as MDEA-based solvents or formulations.

Benefits claimed by suppliers are:

For New Plants

- reduced corrosion
- reduced circulation rate
- lower energy requirements
- smaller equipment due to reduced circulation rates

For Existing Plants

- increase in capacity, i.e., gas through-put or higher inlet acid gas composition
- reduced corrosion
- lower energy requirements and reduced circulation rates

Formulated solvents are proprietary to the specific supplier offering the product. Companies offering these products and/or processes include INEOS, Huntsman Corporation, Dow Chemical Company, UOP, BASF, Shell Global Solutions and TotalFinaElf via Prosernat .

Sterically Hindered Amines — Other amines have been used to treat sour gas[15]. One specialty amine has been constructed by a process defined as steric hindrance (see the nomenclature for a definition). The actual structure of the amine has been formed to accommodate a specific process requirement. This type of amine and the associated technology is different than Formulated Solvents, which create the desired formulations by blending different components with a standard amine such as MDEA. An example of this technology is FLEXSORB® solvents, marketed by Exxon Mobil Research and Engineering Company.[16,17]

Simplified Design Calculations — A simplified procedure for making rough estimates of the principal parameters for conventional MEA, DEA and DGA® amine treating facilities when both H_2S and CO_2 are present in the gas is given below. It is based on excerpts from Jones and Pearce,[18] modified and extended by the Section 21 Subcommittee[19] in 2002. The procedure involves estimating the amine circulation rate and using it as the principal variable in estimating other parameters. For estimating amine circulation rate, the following equations are suggested:

For MEA:

$$GPM = 41 \cdot (Qy/x) \qquad \textbf{Eq 21-6}$$

(0.33 mol acid gas pick-up per mole MEA assumed)

For DEA (conventional):

$$GPM = 45 \cdot (Qy/x) \qquad \textbf{Eq 21-7}$$

(0.5 mol acid gas pick-up per mole DEA assumed)

For DEA (high loading):

$$GPM = 32 \cdot (Qy/x) \qquad \textbf{Eq 21-8}$$

(0.7 mol acid gas pick-up per mole DEA assumed)

For DGA®

$$GPM = 55.8 * (Qy/x) \qquad \textbf{Eq 21-9}$$

(0.39 mol acid gas pick-up per mole DGA® assumed)

(DGA® concentrations are normally 50-60% by weight)

Where:

Q = Sour gas to be processed, MMscfd
y = Acid gas concentration in sour gas, mole%
x = Amine concentration in liquid solution, wt%

After the amine circulation has been estimated, heat and heat exchange requirements can be estimated from the information in Fig. 21-9. Pump power requirements can be estimated from Fig. 21-10.

Eqs 21-6 to 21-9 normally provide conservative (high) estimates of required circulation rate. They should not be used if the combined H_2S plus CO_2 concentration in the gas is above 5 mole%. They also are limited to a maximum amine concentration of about 30% by weight.

The diameter of an amine plant contactor, can be estimated using the following equation:

$$D_c = 44 * \sqrt{Q / \sqrt{P}} \qquad \textbf{Eq 21-10}$$

Where:

Q = MMscfd gas to contactor

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P = Contactor pressure is psia

D_c = Contactor diameter in inches before rounding up to nearest 6 inches.

Similarly, the diameter of the regenerator below the feed point can be estimated using the following equation:

$$D_r = 3.0 * \sqrt{GPM} \qquad \textbf{Eq 21-11}$$

Where:

GPM = Amine circulation rate in gallons per minute

D_r = Regenerator bottom diameter in inches

The diameter of the section of the still above the feed point can be estimated at 0.67 times the bottom diameter.

Example 21-2 — 30.0 MMscfd of gas available at 850 psig and containing 0.6% H_2S and 2.8% CO_2 is to be sweetened using 20%, by weight, DEA solution. If a conventional DEA system is to be used, what amine circulation rate is required, and what will be the principal parameters for the DEA treating system?

Solution:

Using Eq 21-7, the required solution circulation is:

GPM = 45(Qy/x) = 45(30 • 3.4/20) = 230 gallons of

20% DEA solution per minute.

Heat exchange requirements (from Fig. 21-9)

Reboiler

$H = 72{,}000 \cdot 230 = 16.6 \cdot 10^6$ Btu/hr

$A = 11.3 \cdot 230 = 2600$ ft^2

Rich-Lean amine exchanger

$H = 45{,}000 \cdot 230 = 10.4 \cdot 10^6$ Btu/hr

$A = 11.25 \cdot 230 = 2590$ ft^2

Amine cooler

$H = 15{,}000 \cdot 230 = 3.45 \cdot 10^6$ Btu/hr

$A = 10.2 \cdot 230 = 2350$ ft^2

Reflux condenser

$H = 30{,}000 \cdot 230 = 6.9 \cdot 10^6$ Btu/hr

$A = 5.2 \cdot 230 = 1200$ ft^2

Power requirements (Fig. 21-10)

Main amine pumps

$HP = 230 \cdot 850 \cdot 0.00065 = 127$

Amine booster pumps

$HP = 230 \cdot 0.06 = 14$

Reflux pumps

$HP = 230 \cdot 0.06 = 14$

Aerial cooler

$HP = 230 \cdot 0.36 = 83$

Contactor diameter

$D_c = 44 * \sqrt{30 \diagup \sqrt{865}} = 44.4$ inches or 48 inches rounded up.

Regenerator diameter below feed point:

$Dr = 3.0 * \sqrt{230} = 45.5$ inches or 48 inches (bottom) rounded up to nearest 6 inches.

Regenerator diameter above feed point:

$D_{ra} = 0.67 * 48 = 32.2$ inches or 36 inches (top) rounded up to nearest 6 inches.

FIG. 21-9

Estimated Heat Exchange Requirements

	Duty, Btu/hr	Area, Sq ft.
Reboiler (Direct fired)	72,000 • GPM	11.30 • GPM
Rich-Lean Amine HEX	45,000 • GPM	11.25 • GPM
Amine cooler (air cooled)	15,000 • GPM	10.20 • GPM
Reflux condenser	30,000 • GPM	5.20 • GPM

FIG. 21-10

Estimated Power Requirements

Main Amine Solution Pumps	GPM • PSIG • 0.00065	= HP
Amine Booster Pumps	GPM • 0.06	= HP
Reflux Pumps	GPM • 0.06	= HP
Aerial Cooler	GPM • 0.36	= HP

EQUILIBRIUM DATA FOR AMINE-SOUR GAS SYSTEMS

One of the peculiarities of amine treating systems is the interactive effects of one acid gas constituent with amine upon the equilibrium partial pressure of the other constituent. The most commonly encountered sour gas constituents are H_2S and CO_2. The capacity of a given amine for either one of the acid gas constituents alone is much greater than when the two occur together.

Jones et al.[20] have presented data to confirm the interactive effect of H_2S and CO_2 in monethanolamine solutions. Lee et al.[10,21] have presented similar data for diethanolamine solutions. Dingman et al.[22] have presented data for H_2S and CO_2 in equilibrium with commercially used concentrations of DGA®. These data provide the basis for predicting the equilibrium concentrations of MEA, DEA, and DGA® solutions when in contact with sour gases containing both H_2S and CO_2.

Jou, Otto, and Mather investigated the solubility of H_2S and CO_2 in MDEA and published data in 1981.[23] More recently they investigated the solubility of mixtures of H_2S and CO_2 in MDEA, and published data in 1986.[24] The first paper presents solubilities H_2S in MDEA and solubility of CO_2 in MDEA, whereas the second paper presents the results of varying mixtures of H_2S and CO_2 and their solubility in MDEA.

Kent and Eisenberg[25] proposed a reaction equilibrium model to correlate/predict the vapor-liquid equilibrium be-

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tween H_2S and CO_2 and primary or secondary ethanolamines. They tested the model extensively against data for MEA and DEA with good results. This model allows for interpolation/extrapolation of equilibrium data to compositions and temperatures where no measurements have been made.

GPA reports on amine enthalpies of solution and acid gas equilibrium solubility are listed at the end of this chapter.

CAUSTIC WASH

Caustic (NaOH) scrubbing systems can be used to treat natural gas streams to remove CO_2, CS_2, H_2S, and mercaptans.[26]

The process employs countercurrent contacting of the gas stream with a caustic solution in a packed or trayed column. The column may contain one stage or several stages depending on the required degree of removal. The multi-stage systems generally have different caustic concentrations ranging from 4-6 weight percent in the first stage to 8-10 weight percent in the latter stages. Multiple stages increase the caustic efficiency while maintaining a sufficient driving force to achieve absorption.[27]

The spent solution is either regenerated or discarded depending on what acid gas components are present in the gas stream. If only mercaptans are present, the caustic solution is regenerated with steam in a stripping still. If CO_2 is present, a nonregenerable product (Na_2CO_3) is formed and the solution must be discarded. As a result, the presence of CO_2 in caustic systems leads to high caustic consumption. This is a serious disadvantage of the caustic scrubbing process. The spent caustic solutions are considered hazardous wastes.

Natural gas is usually water washed after a caustic wash to remove any caustic entrained in the gas prior to dehydration.

1. Chemistry

   The chemical reactions involved are as follows:

$$H_2S + NaOH \rightarrow NaSH + H_2O \qquad \textbf{Eq 21-12}$$

$$NaSH + NaOH \rightarrow Na_2S + H_2O \qquad \textbf{Eq 21-13}$$

$$H_2S + 2\,NaOH \rightarrow Na_2S + 2H_2O \qquad \textbf{Eq 21-14}$$

$$RSH + NaOH \rightarrow RSNa + H_2O \qquad \textbf{Eq 21-15}$$

$$CO_2 + 2\,NaOH \rightarrow Na_2CO_3 + H_2O \qquad \textbf{Eq 21-16}$$

$$CS_2 + 2\,NaOH \rightarrow 2\,NaHS + CO_2 \qquad \textbf{Eq 21-17}$$

2. Important physical properties including density, specific heat, solid/liquid phases, viscosity, and heat content are given in Figs. 21-11 through 21-13 A typical process flow diagram for a regenerative caustic treating process is shown in Fig. 21-14.

Although caustic soda dissolves in water to form solutions of high concentration, due account must be taken of the temperature at which these solutions separate solid hydrates. A number of these hydrates are formed which separate from solutions at definite temperatures and concentrations from –28°C to 64.3°C (–18.4°F to 147.7°F) and from 19% NaOH to about 74% NaOH. A detailed diagram of solid and liquid phases showing the temperature and concentration relations of NaOH and water is given in Fig. 21-11.

PHYSICAL SOLVENT PROCESSES

These processes are based on physical absorption and operate with a flow scheme as shown in Fig. 21-15. In general, a physical solvent process should be considered when:[28]

- The partial pressure of the acid gas in the feed is greater than 50 psi.
- The heavy hydrocarbon concentration in the feed gas is low.
- Bulk removal of the acid gas is desired.
- Selective removal of H_2S is desired.

These processes are economically attractive because little energy is required for regeneration. The solvents are regenerated by:

- Multi-stage flashing to low pressures.
- Regeneration at low temperatures with an inert stripping gas.
- Heating and stripping of solution with steam/solvent vapors.

In general, physical solvents are capable of removing COS, CS_2, and mercaptans.

In certain instances, physical absorption processes are capable of simultaneously dehydrating and treating the gas although additional equipment and higher energy requirements may be needed to dry the solvent. The processes operate at ambient or subambient temperature to enhance the solubility of the acid gases. The solvents are relatively noncorrosive so carbon steel can be used. Chemical losses are low due to low solvent vapor pressure or refrigerated conditions. Physical solvents will absorb heavy hydrocarbons from the gas stream resulting in high hydrocarbon content in the acid gas stream as well as possibly significant hydrocarbon losses.

Some of the physical absorption processes are summarized below.

Selexol®

This process developed by Allied Chemical Corp.[29,30] uses a polyethylene glycol derivative as a solvent. The solvent is selective for RSH, CS_2, H_2S, and other sulfur compounds. The process can be used to selectively or simultaneously remove sulfur compounds, carbon dioxide, water, as well as paraffinic, olefinic, aromatic and chlorinated hydrocarbons from a gas or air stream. Because water and heavy hydrocarbons are highly soluble in Selexol®, the treated gas from a Selexol® unit normally meets both water and hydrocarbon dew point specifications. The vendor states that the solvent is very stable, no degradation products are formed or disposed of, and no solvent reclaiming is required. Depending on the applications, the operating pressure could be as low as ambient though higher pressure is preferred. Operating temperature varies from 0°F to ambient. Selexol® is a Dow Chemical solvent and a UOP technology.

Fluor Solvent

This process patented by the Fluor Corporation, is based on the use of anhydrous propylene carbonate.[31] The temperature of the lean solution to the absorber is usually well below ambient, and some method of refrigerating the solvent is usually necessary.[32]

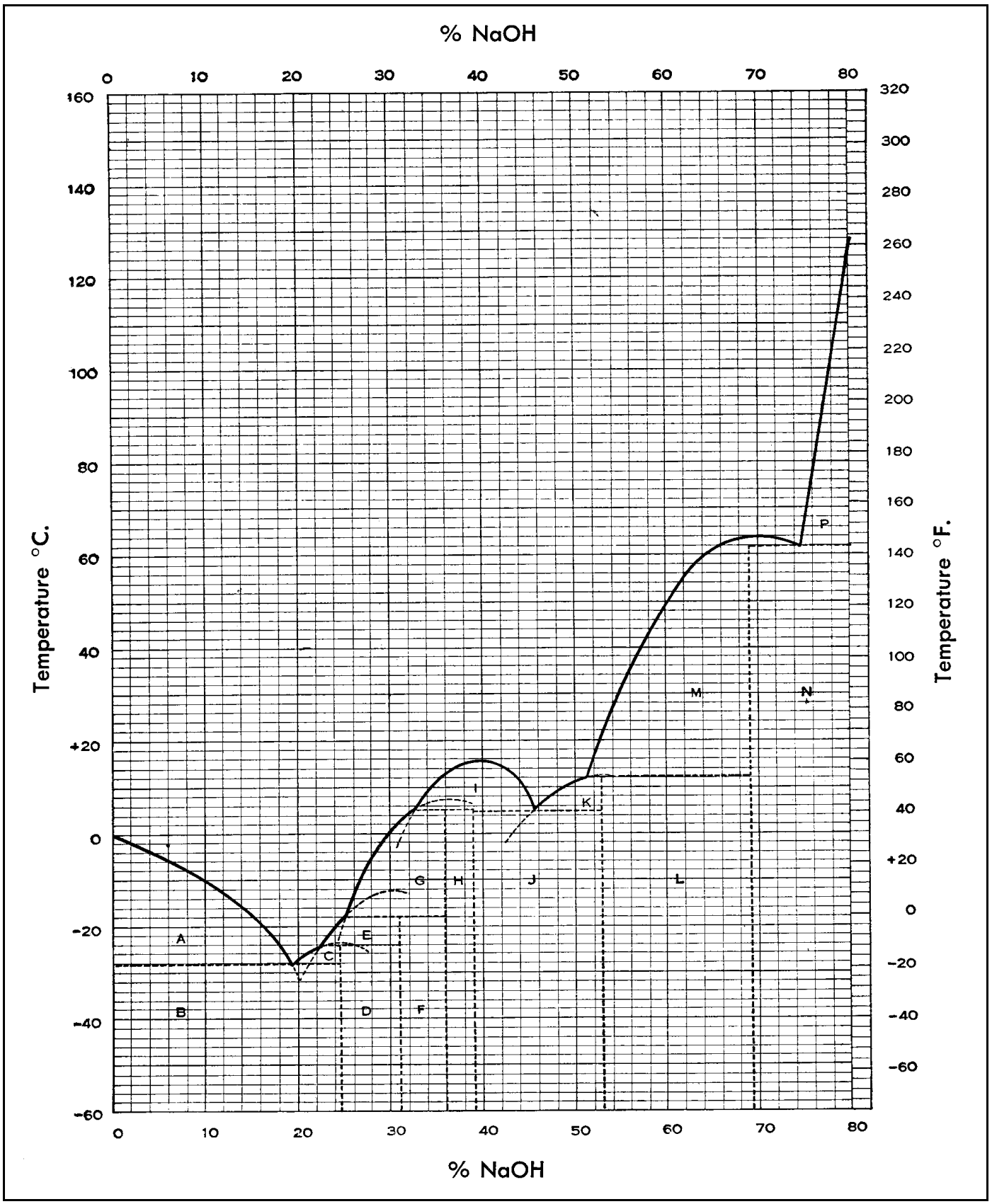
Rectisol Process®

This process uses pure refrigerated methanol as a solvent and has been developed and licensed by Lurgi Oel Gas Chemie

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FIG. 21-11

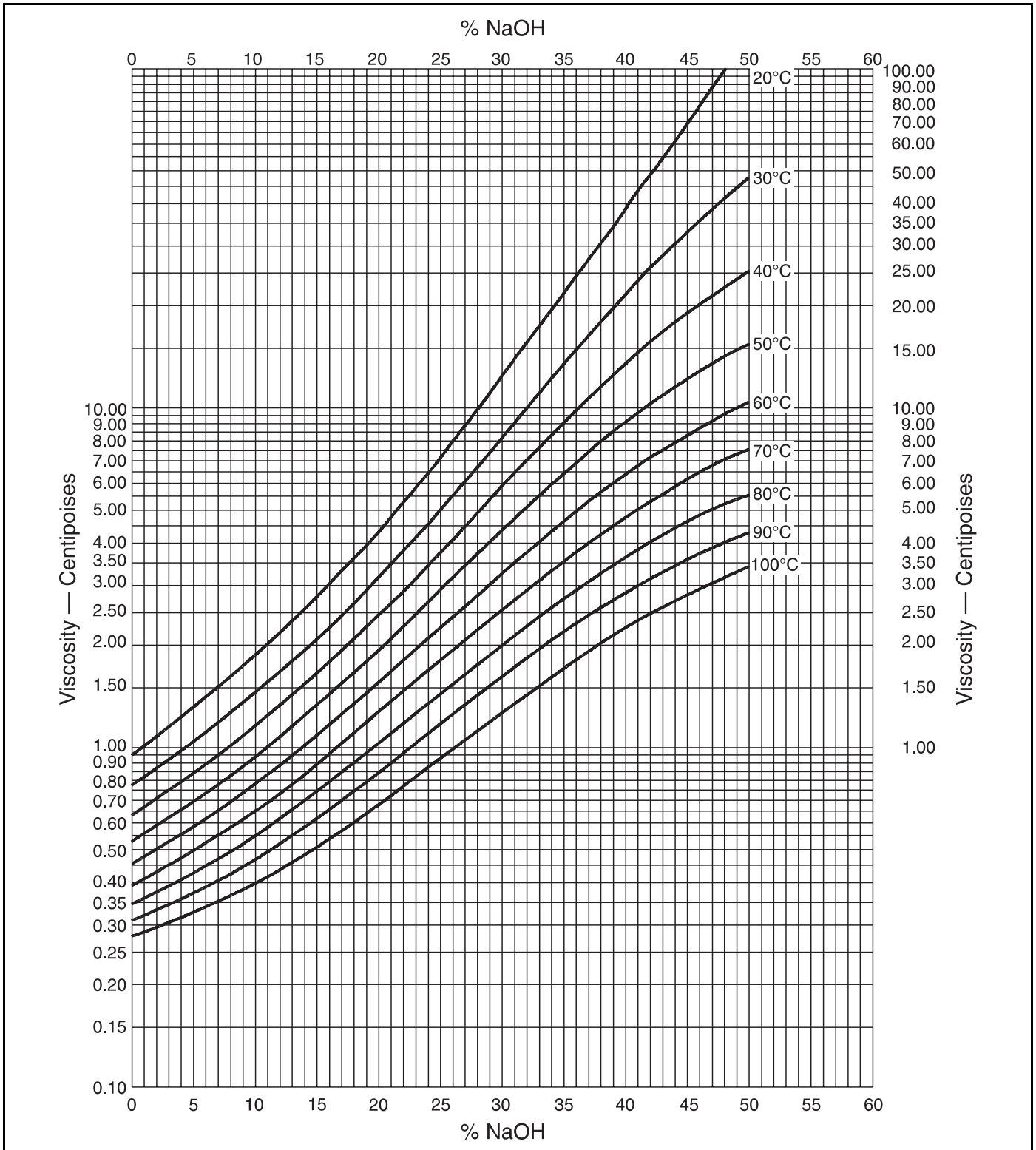
Solubility of Pure NaOH in Water and Freezing Points of the Solutions



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FIG. 21-12

Viscosity of Caustic Soda Solutions at Various Temperatures and Concentrations

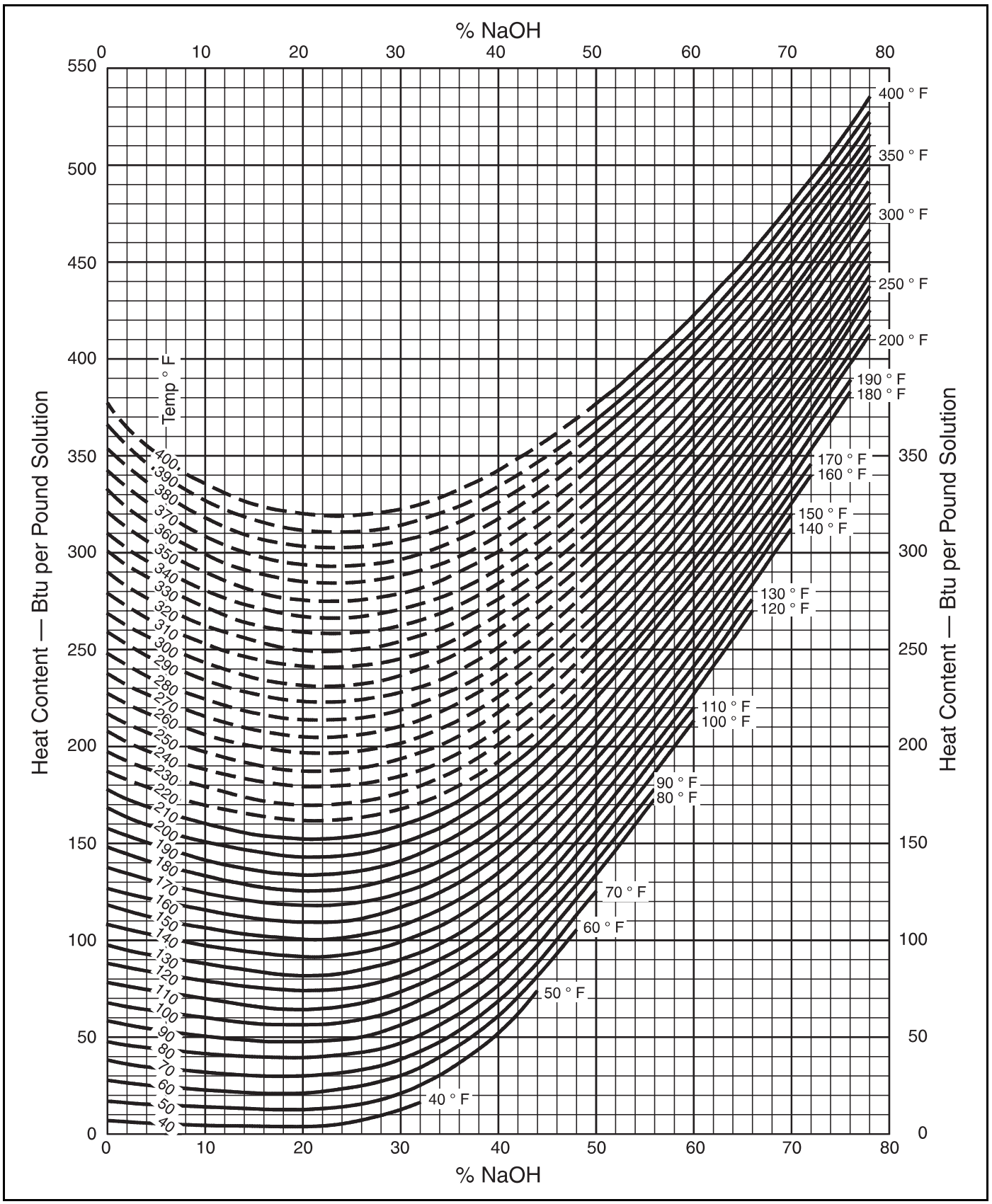


Data developed in the laboratory of The Solvay Process Division; the viscosities at 20°, 30° and 40° C, are from Hitchcock and McIlhemy, Ind. Eng. Chem. 27, 461 (1935) with which the Solvay determinations agree closely.

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FIG. 21-13

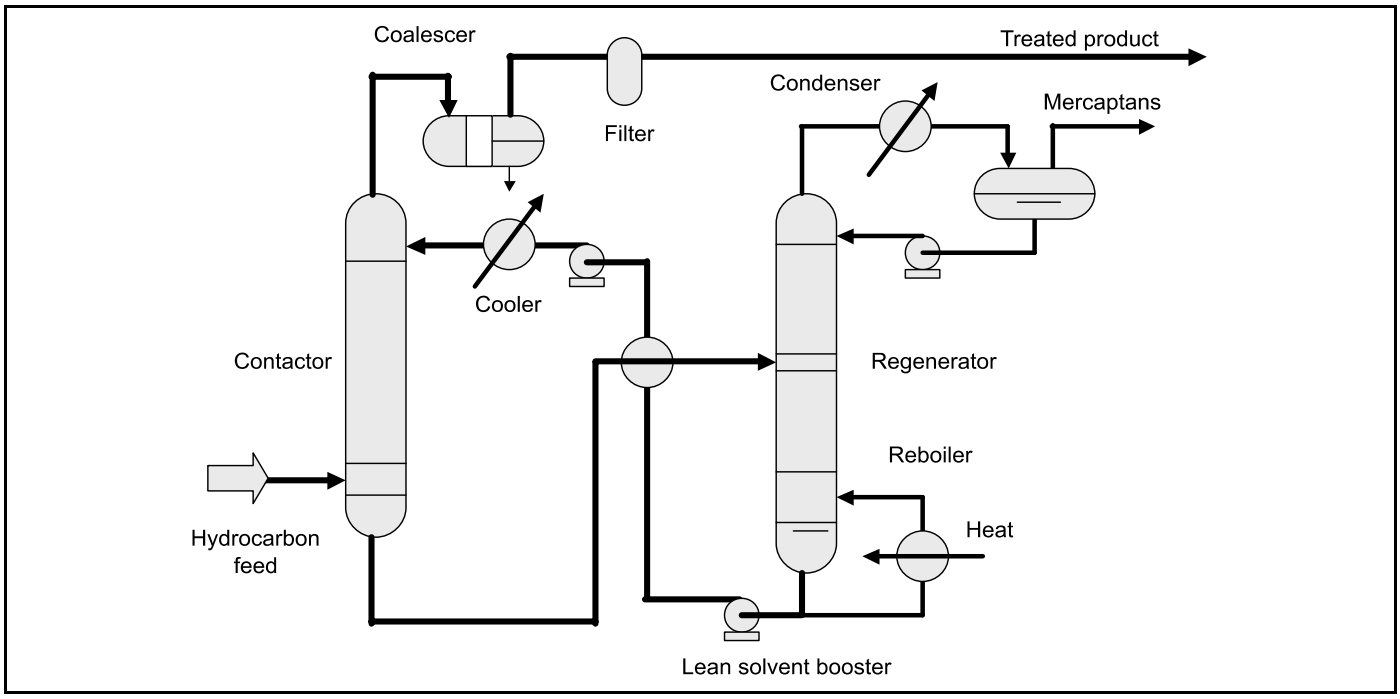
Heat Content-Concentration Diagram for Caustic Soda Solutions



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FIG. 21-14

Regenerative Caustic



and Linde. The process is often applied for syngas purification and operates at temperatures as low as minus 30 to minus 100°F. Applications include selective or bulk removal of sour components. However the extremely low total sulfur impurities achievable with this process, down to less than 0.1 ppmv. are normally not required in natural gas service. Here the process is best suited where there are very high amounts of CO_2 to be removed.

The process has been applied for the purification of natural gas for LNG production. However as pure cold methanol exhibits a certain co-absorption of higher hydrocarbons, implementation of the process in natural gas service has been limited to applications where only low concentrations of ethane and heavier components are present.

Ifpexol Process®

This process developed by IFP licensed by Prosernat uses refrigerated methanol solutions containing water in order to reduce hydrocarbon co-absorption. It is generally associated downstream of the Ifpex-1 dehydration process (see Section 20) which simultaneously extracts heavier hydrocarbons. The Ifpex-2 process attains equivalent acid gas and mercaptans removal performance of the Rectisol process but at a slightly higher solvent rate due to the lower solvent purity.

Purisol®

This process has been developed and licensed by Lurgi Oel Gas Chemie[33]. The solvent used is N-methyl-2-pyrrolidone (NMP or N-Pyrol), a high boiling point liquid. Purisol exhibits a selectivity for H_2S, like Selexol, and features equivalent process possibilities.

As Purisol is also well suited for the selective removal of mercaptans; it can be used for the recovery of mercaptans from regeneration off gases from adsorptive mercaptan removal units.

Catasol®

This process is licensed by Eickmeyer and Associates. Catasol solvents are reported to have selectivity for H_2S/CO_2, CO_2/propane, and COS/CO_2.[34]

Morphysorb®

A physical solvent process developed by Krupp Uhde called Morphysorb[76], uses N-formyl morpholine (NFM) as a physical solvent. The process claims lower investment and operating costs when processing gases heavily loaded with acid components.

HYBRID SOLVENT PROCESSES

There are several gas treating processes which use the effects of both physical and chemical solvents. One of the earlier hybrid solvent processes developed by Lurgi was the Amisol process combining amines with methanol[35]. There are many hybrid solvent processes in the development stage (see Hybrisol in Emerging Technologies for example). Among the successfully proven technologies the most widely used is Sulfinol.

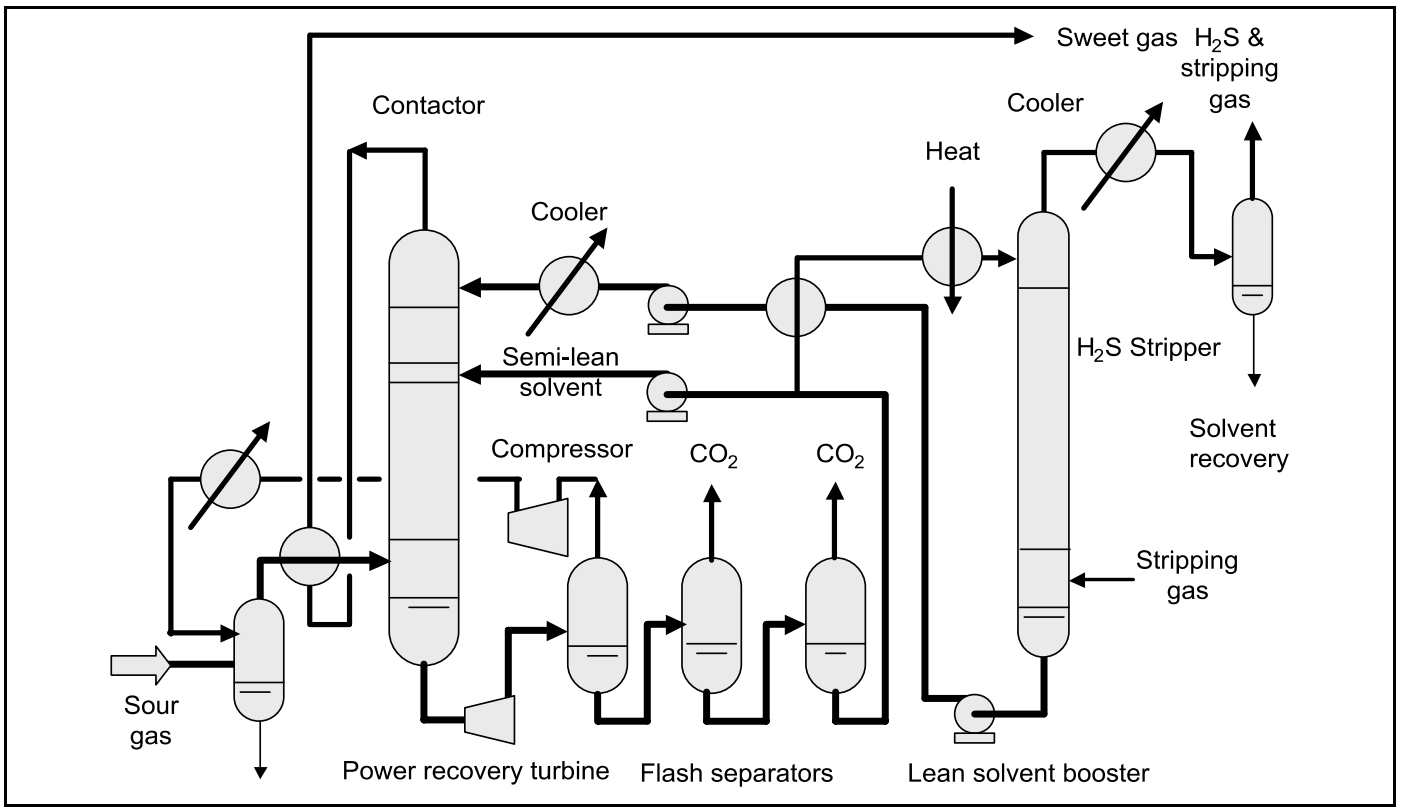
Sulfinol® Process

The Sulfinol® Process, licensed by Shell Global Solutions, is used to remove H_2S, CO_2, COS, CS_2, mercaptans and polysulfides from natural and synthetic gases. Sulfinol is a mixture of Sulfolane (a physical solvent), water and either DIPA or MDEA (both chemical solvents). It is this dual capacity as both a physical and a chemical solvent that gives Sulfinol its advantages. Sulfinol with DIPA (Sulfinol-D) is used when complete removal of H_2S, CO_2, and COS is desired. Sulfinol with MDEA (Sulfinol-M) is used for the selective removal of H_2S in the presence of CO_2, with partial removal of COS. Both Sulfinols can reduce the total sulfur content of treated gas down to low ppm levels. Some disadvantages are: a higher heavy hy-

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FIG. 21-15

Typical Gas Sweetening by Physical Absorption



drocarbon co-absorption,[36] and a reclaimer is sometimes required for Sulfinol D when removing CO_2.

Selefining Process

This process developed by Snamprogetti uses tertiary amines such as dimethyl ethanol amine (DMEA) dissolved in an organic solvent with limited amounts of water. The process is very selective to H_2S as CO_2 hydration is almost completely avoided. It also removes other sulfur species such as mercaptans, COS and CS_2. It has a tendency to co-absorb hydrocarbons which can to some extent be controlled by increasing the water content of the solvent.

ALKALINE SALT PROCESS (HOT CARBONATE)

The basic process was developed by the U.S. Bureau of Mines and employs an aqueous solution of potassium carbonate (K_2CO_3). The contactor and stripper both operate at temperatures in the range of 230-240°F. The process is not suitable for gas streams containing only H_2S.[9] If H_2S is to be removed to pipeline specification or there are low CO_2 outlet specifications, special designs or a two-stage system may have to be used. Potassium carbonate processes are somewhat effective in removing carbonyl sulfide and carbon disulfide.

The overall reactions for CO_2 and H_2S with potassium carbonate can be represented by:

$$K_2CO_3 + CO_2 + H_2O \leftrightarrow 2\ KHCO_3 \qquad \textbf{Eq 21-18}$$

$$K_2CO_3 + H_2S \leftrightarrow KHS + KHCO_3 \qquad \textbf{Eq 21-19}$$

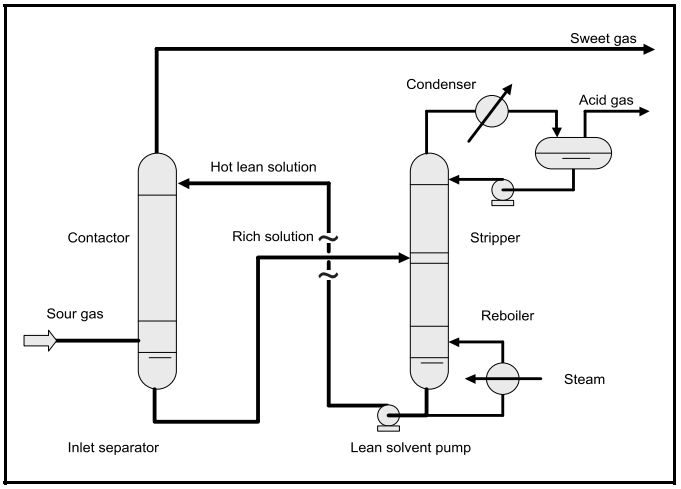
There are three basic process flow variations for the potassium carbonate process. The flow scheme required depends on the outlet specification of the natural gas. These are:

Single Stage Process

The single stage process is shown in Fig. 21-16. Potassium carbonate is pumped to the top of a packed or trayed contactor where it contacts the gas stream. The rich solution flows to the stripper where the acid gases are stripped with steam. The

FIG. 21-16

Alkaline Salt: Single-Stage Process



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lean solution is then pumped back to the contactor to complete the cycle.

Split Flow Process

In this process scheme (Fig. 21-17) the lean solution stream is split. Hot solution is fed to the middle of the contactor for bulk removal. The remainder is cooled to improve equilibrium and is fed to the top of the contactor for trim acid gas removal.

Two Stage Process

In this process scheme (Fig. 21-18) the contactor is like that of the split flow process. In addition, the stripper is in two sections. A major portion of the solution is removed at the midpoint of the stripper and pumped to the lower section of the contactor. The remainder is further stripped with steam and then cooled prior to entering the top of the contactor.

Numerous improvements have been made to the potassium carbonate process resulting in significant reduction in capital and operating costs. At the same time, lower acid gas concentration in the treated gas can now be achieved. The most popular of the carbonate processes are:

FIG. 21-17

Alkaline Salt: Split-Flow Process

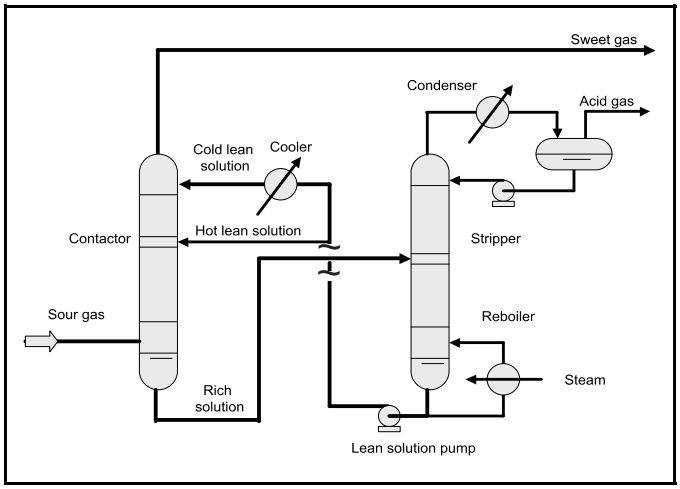
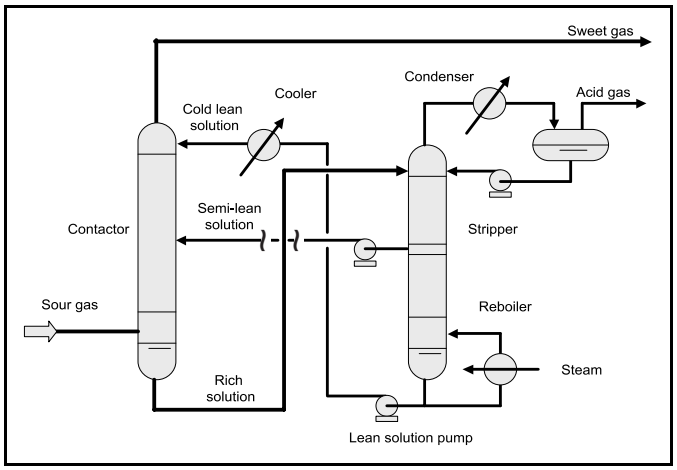


FIG. 21-18

Alkaline Salt: Two-Stage Process



Benfield Process

The Benfield Process is licensed by UOP. Several activators are used to enhance the performance of the potassium carbonate solution.

Hi-Pure Process

The Hi-Pure process is a combination conventional Benfield potassium carbonate process and alkanolamine process. The gas stream is first contacted with potassium carbonate followed by contacting with an amine. The process can achieve outlet CO_2 concentrations as low as 30 ppmv and H_2S concentrations of 1 ppmv.[37]

Catacarb Process

The Catacarb Process is licensed by Eickmeyer and Associates. Activators, corrosion inhibitors, potassium salts, and water are contained in the solution. This process is mostly used in the ammonia industry.

GENERAL CONSIDERATIONS FOR SOLVENT PROCESS

Solution Filtration

Filtration of the treating solution to remove entrained solids is essential to the successful operation of a gas treating plant. Filtration rates should be as high as practical and may range from 5 per cent of circulation to full stream. Removing particles down to 5 microns in size is recommended. In order to do this efficiently, two stages of filtration may be required. The first stage, typically a cartridge-type or precoat filter, is designed to remove particles down to the 10 micron or less range. The second stage of filtration, typically an activated carbon filter, removes hydrocarbons and other contaminants. This is accomplished by adsorption. The carbon filter can also remove smaller particles from the amine stream. The carbon granule size can be selected to remove particles down to the 5 micron range. The activated carbon filter should always be located downstream of the first stage filter because the deposition of solids would plug the carbon filter.[38]

The carryover of carbon fines can be controlled by either locating a second cartridge-type filter immediately downstream of the carbon filter or using a graded carbon bed. In a graded bed, larger granules are placed at the outlet of the filter to trap fines. Large carbon granules produce fewer fines but are less efficient for adsorption.

Basic degradation products are identified by gas chromatography and mass spectrometry. Acidic degradation products are identified by ion chromatography exclusion. These tests are recommended when the amine solution appears to lose its ability to pick up acid gas. Degradation products affect the results of the conventional estimation of amine concentration by titration. This may cause artificially high or low apparent amine concentrations Also, the carbon bed will adsorb very little strong acid degradation products. In this case, purging or reclamation of the solution is recommended.

Carbon filters can be partially regenerated with steam, which removes hydrocarbons and other adsorbed contaminants. Regeneration or bed change out is recommended when foam tests on the inlet and outlet streams show no improvement. This indicates carbon bed saturation.

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Filters may be located on the lean or rich solution side. Filtration on the rich side seeks to remove particles that are more insoluble under the rich solution conditions. It also prevents solids accumulation in the hot environment of the stripper. However, proper design and operating procedures for personnel protection during filter maintenance is mandatory when H_2S may be present.

Filtration equipment should be used continuously beginning with the first day of plant operations. When starting up the plant, the full flow filter, even if temporary, may prove its worth by removing the scale and other solid particles and allowing much quicker and easier start-up of the plant.

Flash Tank

Rich solution leaving the contactor may pass through a flash tank. A flash tank is more important when treating high pressure gas. Gases entrained in the rich solution will be separated. In addition, the amount of absorbed gas will be decreased because of the lower operating pressure of the flash tank. Using a flash tank will:

- Reduce erosion in rich/lean exchangers.
- Minimize the hydrocarbon content in the acid gas.
- Reduce the vapor load on the stripper.
- Possibly allow the off-gas from the flash tank to be used as fuel (may require sweetening).

When heavy hydrocarbons are present in the natural gas, the flash tank can also be used to skim off the heavy hydrocarbons that were absorbed by the solution. Residence times for flash tanks in amine service vary from 3-10 minutes depending on separation requirements. Inlet gas streams containing only methane and ethane require shorter residence times. Rich gas streams require longer time for the dissociation of gas from solution and/or the separation of liquid phases.

Corrosion

Corrosion is an operating concern in nearly all sweetening installations. The combination of H_2S and CO_2 with water practically ensures that corrosive conditions will exist in portions of the plant. In general, gas streams with high H_2S to CO_2 ratios are less corrosive than those having low H_2S to CO_2 ratios. H_2S concentrations in the ppmv range with CO_2 concentrations of 2 percent or more tend to be particularly corrosive. Because the corrosion in sweetening plants tends to be chemical in nature, it is strongly a function of temperature and liquid velocity. The type of sweetening solution being used and the concentration of that solution has a strong impact on the corrosion rate. Increased corrosion can be expected with stronger solutions and higher gas loadings.

Hydrogen sulfide dissociates in water to form a weak acid. The acid attacks iron and forms insoluble iron sulfide. The iron sulfide will adhere to the base metal and may provide some protection from further corrosion, but it can be eroded away easily, exposing fresh metal for further attack.

CO_2 in the presence of free water will form carbonic acid. The carbonic acid will attack iron to form a soluble iron bicarbonate which, upon heating, will release CO_2 and an insoluble iron carbonate or hydrolize to iron oxide. If H_2S is present, it will react with the iron oxide to form iron sulfide.

High liquid velocities can erode the protective iron sulfide film with resulting high corrosion rates. In general, design velocities in rich solution piping should be 50% of those that would be used in sweet service. Because of the temperature relationship to corrosion, the reboiler, the rich side of the amine-amine exchanger, tend to experience high corrosion rates. Because of the low pH the stripper overhead condensing loop also tends to experience high corrosion rates.

Acid degradation products also contribute to corrosion. A suggested mechanism for corrosion is that degradation products act as chelating agents for iron when hot. When cooled, the iron chelates become unstable, releasing the iron to form iron sulfide in the presence of H_2S. Primary amines are thought to be more corrosive than secondary amines because the degradation products of the primary amines act as stronger chelating agents.

Several forms of stress corrosion cracking are possible in amine sweetening systems. Amine stress corrosion cracking can occur and is worst in hot solutions, but cracking can occur in cooler lines and both rich and lean streams. Post-weld heat treatment (PWHT) can prevent this type of cracking.[39] Wet sulfide cracking and blistering can occur due to hydrogen generated in corrosion reactions. The hydrogen can collect at small inclusions in the steel which delaminate and then link in a step-wise pattern to create blisters. This is called HIC or hydrogen induced cracking. Sometimes stress influences the cracking to cause SOHIC or stress oriented hydrogen induced cracking. PWHT helps, but does not prevent HIC and SOHIC. HIC resistant steels are available. Seamless pipe is less prone to HIC than plate steels.

Corrosion in alkaline salt processes, such as the hot carbonate process, has been reported to range from none to severe. Corrosion can be expected where CO_2 and steam are released through flashing. Severe erosion can take place when carbonate solution strengths exceed 40% because of the tendency to form bicarbonate crystals when the solution cools.

Many corrosion problems may be solved using corrosion inhibitors in combination with operating practices which reduce corrosion. Following are some guidelines to minimize corrosion.

- Maintain the lowest possible reboiler temperature.
- If available, use low temperature heat medium rather than a high temperature heat medium or direct firing. When a high temperature heat medium or direct firing for the reboiler is used, caution should be taken to add only enough heat for stripping the solution.
- Minimize solids and degradation products in the system through reclaimer operation and effective filtration.
- Keep oxygen out of the system by providing a gas blanket on all storage tanks and maintain a positive pressure on the suction of all pumps.
- Ensure deionized water or oxygen/chemical-free boiler condensate is used for make up water. If available, steam can be used to replace water loss.
- Limit solution strengths to minimum levels required for treating.
- Pipe solution exchangers for upflow operation with the rich solution on the tube side.
- Monitor corrosion rates with coupons or suitable corrosion probes.
- Maintain adequate solution level above reboiler tube bundles and fire tubes; a minimum tube submergence of 12" is recommended.

Corrosion inhibitors used include high molecular weight amines and heavy metal salts. The compositions are generally proprietary. Certain inhibitors are available when only H_2S or CO_2 is in the gas which allow increased solution strengths and acid gas loadings. These inhibitors offer potential savings in

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both capital and operating costs for these special cases. An example of this type inhibitor use is in ammonia plants.

Foaming

A sudden increase in differential pressure across a contactor or a sudden liquid level variation at the bottom of the contactor often indicates severe foaming. When foaming occurs, there is poor contact between the gas and the chemical solution. The result is reduced treating capacity and sweetening efficiency, possibly to the point that outlet specification cannot be met.

Some reasons for foaming are:[11]

- Suspended solids
- Organic acids
- Corrosion inhibitors
- Condensed hydrocarbons
- Soap-based valve greases
- Makeup water impurities
- Degradation products
- Lube Oil

Foaming problems can usually be traced to plant operational problems. Contaminants from upstream operations can be minimized through adequate inlet separation. Condensation of hydrocarbons in the contactor can usually be avoided by maintaining the lean solution temperature at least 10°F above the hydrocarbon dew point temperature of the outlet gas.

Temporary upsets can be controlled by the addition of antifoam chemicals. These antifoams are usually of the silicone or long-chain alcohol type.

The following test for foaming should be run with the various types of inhibitors being considered for a given application.[40] This test should give the operator an indication of which antifoam will be the most effective for the particular case. Place several drops of antifoam in 200 ml of treating solution contained in a 1000 ml cylinder. Bubble oil-free air through the solution at a constant rate. After five minutes have elapsed shut off the air and start a timer. Note the height of foam at the time the air was shut off and the amount of time required for the foam to break. The foam height is the difference between the height of the foam and the initial height of the liquid. The time for the foam to break is an indication of the stability of the foam. A comparison of antifoams will let the operator select which inhibitor will best solve his foaming problems. Between antifoam tests, care should be taken to clean the test cylinder thoroughly because a very small amount of inhibitor may affect the test.

Materials

Treating plants normally use carbon steel as the principal material of construction. Vessels and piping should be stress relieved in order to minimize stress corrosion along weld seams. Corrosion allowance for equipment ranges from 1/16" to 1/4", typically 1/8". In some instances, when corrosion is known to be a problem, or high solution loadings are required, stainless steel or clad stainless steel may be used in the following critical areas:

1. Reflux condenser
2. Reboiler tube bundle
3. Rich/lean exchanger tubes
4. Bubbling area of the contactor and/or stripper trays.
5. Rich solution piping from the rich/lean exchanger to the stripper.
6. Bottom 5 trays of the contactor and top 5 trays of stripper, if not all.

Usually 304, 316, or 410 stainless steel will be used in these areas, even through corrosion has been experienced with 410 stainless in DEA service for CO_2 removal in the absence of H_2S. L grades are recommended if the alloys are to be welded.

Controlling oxygen content to less than 0.2 ppmw is effective in preventing chloride SCC in waters with up to 1000 ppmw chloride content, at temperatures up to 570°F. There has been an increased use of duplex stainless steels, and they have been successfully used in the water treatment industry to prevent chloride SCC in high chloride waters. This suggests duplex stainless steels could be utilized in amine plant service where high chloride content is expected. As with any specialty steel, proper fabrication techniques and welding procedures are required.

BATCH AND CYCLIC PROCESSES

In this section, processes having chemical reactions and/or physical adsorption are discussed. They all have the common requirement that the process be operated as a batch or cyclic system. At the end of the cycle the operator must either change solution or regenerate in order to continue treating.

Under this heading the following process classification is considered:

- Scavenger or sacrificial processes with liquid or solid sacrificial scavenging agents
- Adsorption processes, including cyclically regenerated adsorbents such as molecular sieves and non-regenerated impregnated activated carbon.

Scavenger Processes

Scavengers are chemicals which react with H_2S and sometimes other sulfur compounds like COS or mercaptans. Generally the spent product is not or cannot be regenerated so the use of scavengers is limited to the removal of small quantities of sulfur impurities.

Liquid scavengers can be applied on a continuous or batch mode while solid scavengers are used in a batch mode. In the continuous mode the liquid scavenger is injected into the gas stream after separation of liquid hydrocarbons and water. After mixing, usually through a static mixer or an atomizing device, a few seconds contact time is provided by a length of pipe for the chemical reaction to occur. The mixture is then separated in a coalescing filter and the resultant liquid product is discarded.

In the batch mode the gas is passed through a vessel filled with liquid or solid scavenger agent. The batch mode has a higher scavenger utilization efficiency but a much higher capital cost.

Numerous liquid chemicals, typically triazines, and solid scavengers are commercially available. Some of these are described below, starting with liquid scavengers.

Sulfa-check—Sulfa-Check is a product of ExxonMobil Chemicals which selectively removes H_2S and mercaptans from natural gas in the presence of CO_2. The original process was developed and marketed by NL Treating Chemicals / NL Industries Inc. The patented process converts the sour gas directly to sulfur. This is accomplished by sparging the gas in a buffered , water based oxidizing solution containing sodium nitrite ($NaNO_2$).The sodium nitrite is reduced to ammonia

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(NH_3) which remains in solution. The spent product is classified as non-hazardous.

The sparging vessel is similar to the vessel used in other batch processes such as Iron Sponge etc. Dozens of field applications include gas rates ranging from 15 Mscf/d to 3.0 MMscf/d and inlet H_2S concentrations ranging from 10 to 3000 ppmv.[41]

A number of variables, including some associated risks must be considered prior to determining if the Sulfa-Check process is applicable. For example, low levels of ammonia may appear in the treated gas. Also, the reduction of NO_2 may result in the formation of nitric oxide (NO). If air is present in the raw gas, it will react with nitric oxide to form nitrogen dioxide (NO_2). NO_2 is a strong oxidizing agent that will react with elastomers and odorants and cause corrosion in a moist environment. It is recommended that ExxonMobil be consulted for further information.

Sulfa-Scrub—Sulfa-Scrub from Baker-Petrolite is a product that uses triazine compound to selectively react with H_2S. The raw gas can be sparged into a vessel containing the liquid scavenging agent. Alternatively the liquid may be injected to the gas stream as an H_2S scavenger. The spent material is considered as non-hazardous and is claimed to be an excellent corrosion inhibitor[42].

Iron-Sponge Process—The iron sponge process selectively removes H_2S from gas or liquid streams. The process is limited to treating streams containing low concentrations of H_2S at pressures ranging from 25 to 1200 psig. The process employs hydrated iron oxide, impregnated on wood chips.

Care must be taken with the iron sponge bed to maintain pH, gas temperature, and moisture content to prevent loss of bed activity. Consequently, injections of water and sodium carbonate are sometimes needed. H_2S reacts with iron oxide to form iron sulfide and water. When the iron oxide is consumed, the bed must be changed out or regenerated. The bed can be regenerated with air; however, only about 60% of the previous bed life can be expected.[43] The bed life of the batch process is dependent upon the quantity of H_2S, the amount of iron oxide in the bed, residence time, pH, moisture content, and temperature.

The change-out of the spent sponge beds is hazardous. Iron sulfide is pyrophoric when exposed to air will rapidly oxidize and can result in spontaneous combustion of the spent bed. To prevent this, the entire bed should be wetted before beginning the change-out operation. Regulations on sponge disposal vary with location; therefore, local regulations on allowable methods of disposal should be checked.

Chemsweet®—Chemsweet® is the name for another batch process for the removal of H_2S from natural gas. Chemicals used are a mixture of zinc oxide, zinc acetate, water, and a dispersant to keep solid particles in suspension. Natural gas is bubbled through the solution where H_2S reacts with zinc oxide.

Though several reactions take place in solution, the net result is that zinc oxide reacts with H_2S to form zinc sulfide and water.

Chemsweet® can treat gas streams with H_2S concentration up to 400 ppmv. and has been operated between pressures of 75 and 1,400 psig.[44] Mercaptan concentrations in excess of 10% of the H_2S concentration in the gas stream can cause a problem. Some of the mercaptans will react with the zinc oxide and be removed from the gas. The resulting zinc mercaptides [Zn(OH)RH] will form a sludge and possibly cause foaming problems.

SulfaTreat™—SulfaTreat™ is a patented process of the SulfaTreat Company which has been licensed to GSA Technologies, Inc. The material is a dry, free-flowing granular substance used for selective removal of H_2S and mercaptans from natural gas in the presence of CO_2. It is not affected by CO_2, and it does not produce sulfur or nitric oxide (NO_x). Also SulfaTreat will not ignite or "cement up" in the vessel. Other advantages include longer bed life and lower cost.

SulfaTreat's particle size varies from 4 to 30 mesh and has a bulk density of 70 lb/ft^3. These physical properties give uniform porosity and permeability, which offers small resistance to flow and resistance to bed compression at normal velocities.

Applications for SulfaTreat include: natural gas treating, amine treater off gas, high concentration CO_2 streams, geothermal noncondensible gas, and any other H_2S-containing system.

PuraSpec™—Johnson Matthey Catalysts supplies the PuraSpec range of processes and products for desulfurisation of hydrocarbon gases and liquids. The processes use fixed beds of granular, metal oxide-based chemical absorbents which are developments of the 'high temperature zinc oxide' used for purification of hydrocarbon feedstocks to steam reformers in ammonia, hydrogen, and methanol plants. PuraSpec absorbents are effective at temperatures down to 32°F, so no added heat is necessary, and are in service at pressures from atmospheric, treating vent gases, to 1800 psi treating dense phase gas feed to a gas processing plant.

PuraSpec units are in service treating natural gas to pipeline or petrochemical specifications.[45,46] Because the absorbents remove H_2S and COS irreversibly, they are best suited to polishing duties. In large scale applications this can be removal of up to 50 ppmv or 200-400 lbs per day of sulfur. Liquid treating applications include removal of H_2S/COS from propane/LPG to meet copper strip test specifications. Spent absorbents are normally sent to metals refineries where they can be treated as high-grade ores for metals recovery. PuraSpec™ is a trademark of Synetix, a Johnson Matthey company.

Adsorption Processes

Adsorption is also used to remove H_2S, CO_2 and other sulfur contaminants from natural gases. Adsorbents used are either regenerated such as molecular sieves or not regenerated such as impregnated activated carbon.

Molecular Sieve—Molecular sieves can be used for removal of sulfur compounds from gas streams (Fig. 21-19). Hydrogen sulfide can be selectively removed to meet 0.25 grain/100 scf specification. The sieve bed can be designed to dehydrate and sweeten simultaneously. In addition, molecular sieve processes can be used for CO_2 removal.

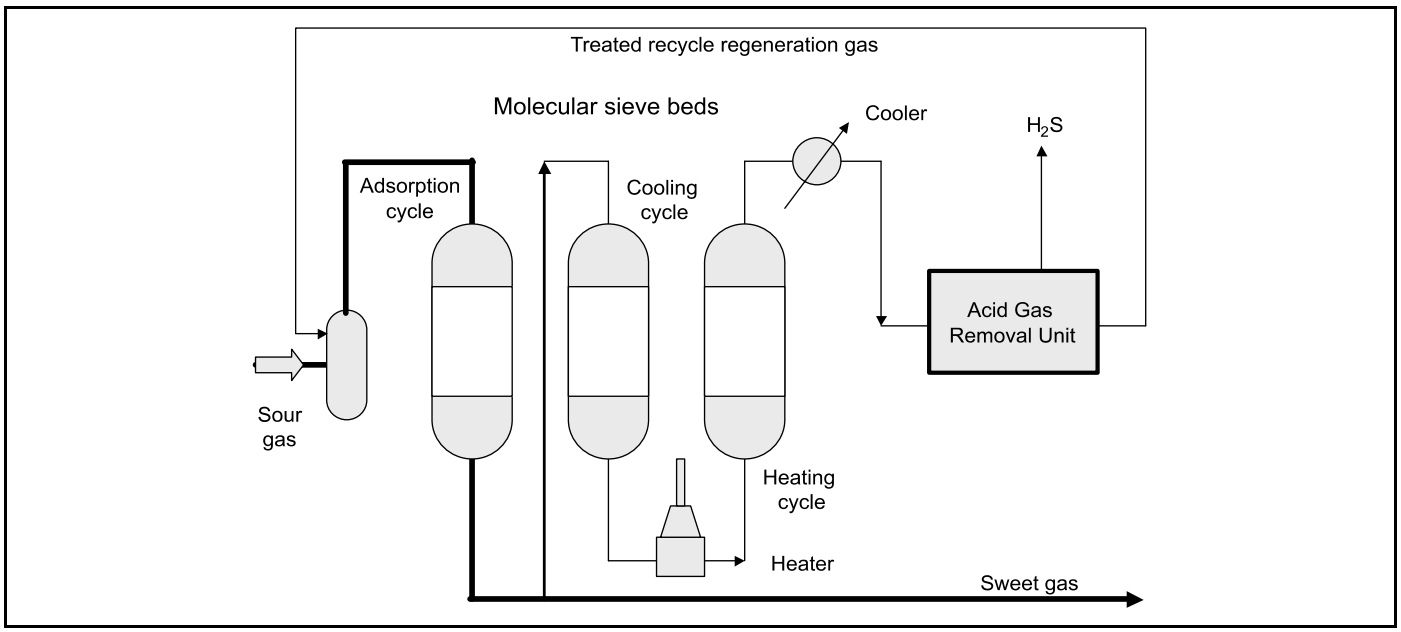
In general, the concentrations of acid gas are such that cycle times are in the order of 6-8 hours. To operate properly the sieves must be regenerated at a temperature close to 600°F for a long enough period of time to remove all adsorbed materials, usually one hour or more. Exact arrangement of the regeneration cycle depends upon process conditions.

Regeneration of a molecular sieve bed concentrates the H_2S into a small regeneration stream which must be treated or disposed of. During the regeneration cycle, the H_2S will exhibit a peak concentration in the regeneration gas. The peak is ap-

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FIG. 21-19

Integrated Natural Gas Desulfurization Plant



proximately 30 times the concentration of the H_2S in the inlet stream. Knowing the concentration of this stream is essential for the design of a gas treater for the regeneration gas.

The problem of COS formation during processing according to the reaction:

$$H_2S + CO_2 \leftrightarrow COS + H_2O \qquad \textbf{Eq 21-20}$$

has been extensively studied. Molecular sieve products have been developed that do not catalyze COS formation.[47] The central zone in the regeneration cycle is most favorable to COS formation.

Operation of adsorbent plants is simple, but design is complex. For example a dust filter is generally required downstream of the beds to ensure that fine solid particles are not entrained into the treated gas. Manufacturers must be consulted for potential applications. Refer to Dehydration (Section 20) and the gasoline and LP-gas treating portion of this section for additional details.

Oxorbon—Oxorbon is an alternative solid bed material which consists of activated carbon impregnated with potassium iodide (KI). Donau Carbon markets such a carbon for the removal of H_2S and mercaptans. The adsorbed H_2S is converted to elemental sulfur by catalytic reaction under the presence of oxygen. The resulting sulfur is fixed on the pores of the activated carbon. Sulfur loadings as high as 60% of the carbon mass have been reported and sulfide concentrations below 1 ppmv are claimed.

LIQUID REDOX PROCESSES

Processes in this group absorb H_2S from gas streams and produce elemental sulfur by reacting oxidizing/reducing agents with the H_2S to form elemental sulfur and water.[48]

The redox agent is then regenerated by reaction with air in an oxidizer vessel.

Liquid redox sulfur recovery processes all share the following major steps:[49]

- Sour gas cleaning by absorption of H_2S into a circulating alkaline solution.
- Conversion of the formed HS to elemental sulfur via the action of an auxiliary redox reagent (ARR).
- Separation and recovery of solid sulfur.
- Regeneration of the spent auxiliary reagent via reaction with oxygen dissolved in the solution.

The processes share the general chemistry shown below.[49]

- H_2S absorption using an alkaline solution:

$$H_2S_{(g)} \leftrightarrow H_2S_{(sol'n)} \qquad \textbf{Eq 21-21}$$

$$H_2S_{(sol'n)} \leftrightarrow H^+ + HS^- \qquad \textbf{Eq 21-22}$$

Note that this is a non-selective, basic scrubbing solution; thus, additional acidic components (CO_2 , HCN) of the sour gas will be soluble in the scrubbing solution. While CO_2 is partially absorbed in the alkaline solution, it does not participate in the redox reactions. CO_2 may however increase the rate of consumption of caustic or buffering compounds. The fate of other reduced sulfur species (COS, CS_2, RSH, RSR) depends on the particular process being considered.

- Conversion to Elemental Sulfur:

$$HS^- + H^+ + \tfrac{1}{2} O_{2\,(sol'n)} \rightarrow H_2O_{(l)} + \tfrac{1}{8} S_8 \qquad \textbf{Eq 21-23}$$

Note that in the absence of an ARR the reaction shown as Eq 21-24 is slow and nonspecific. The addition of an auxiliary redox reagent (ARR) increases the rate of reaction and directs the oxidation to elemental sulfur. The reaction shown as Eq 21-25 is common to all processes considered.

$$HS^- + ARR_{(OX)} \rightarrow \tfrac{1}{8} S_8 + H^+ + ARR_{(RED)} \qquad \textbf{Eq 21-24}$$

where (OX) denotes the oxidized form and (RED) denotes the reduced form of the ARR.

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- Regeneration of the Spent ARR Using Air:

$$O_{2\,(g)} \leftrightarrow O_{2\,(sol'n)} \qquad \textbf{Eq 21-25}$$

$$ARR_{(RED)} + \tfrac{1}{2}\,O_{2\,(sol'n)} + 2\,H^{+} \rightarrow ARR_{(OX)} + H_2O_{(l)} \qquad \textbf{Eq 21-26}$$

The overall simplified chemistry of liquid redox processes is thus:

$$H_2S_{(g)} + \tfrac{1}{2}\,O_{2\,(g)} \rightarrow H_2O_{(l)} + \tfrac{1}{8}\,S_8 \qquad \textbf{Eq 21-27}$$

Because they share major process operations and are based on similar process chemistries, the process flow sheets and equipment requirements for liquid redox systems are rather similar.

Stretford Process

The Stretford process was developed by British Gas PLC. It involves the use of vanadium salts as the ARR. The process has been extensively used in Europe[48]. However environmental concerns around the discharge of vanadium compounds has limited its use.

IRON CHELATE PROCESSES

Chelates are the most commonly used auxiliary redox reagents. A chelating agent is generally an organic molecule which is able to bind with a metallic cation in such a way that the cation is sequestered from the solution. To illustrate, consider the case of iron compunds. Fe(III) is capable of oxidizing H_2S to sulfur, with subsequent formation of Fe(II). Fe(II) is easily oxidized by air back to Fe(III). However, both forms of unsequestered iron will form precipitates with the sulfides or oxides in solution, thereby rendering it ineffective. By chelating the iron with a compound like ethylenediaminetetraacetic acid EDTA, the iron will not precipitate, but is still able to transfer an electron in the redox process. The process solutions are monitored regularly, with occasional addition of buffering agents and sometimes defoamers

A common problem with chelate-based processes is the degradation of the chelating agent[50]. Another problem is sulfur plugging in the contact tower. For this reason, these processes were usually limited to low pressures (below 300 psig), unless combined with a high pressure amine absorber. Today direct applications to high pressure sour gases have been developed and these are mentioned hereafter.

Because they share major process operations and are based on similar process chemistries, the process flow sheets and equipment requirements for liquid redox systems are rather similar. Lo-Cat, SulFerox, and Sulfint-HP are chelated iron liquid redox processes.

Lo-Cat II®

The Lo-Cat II® process[51,52,53], licensed by Merichem, is an improvement over the earlier Lo-Cat ® process. The process can be applied directly to natural gas sweetening or treatment of low-H_2S acid gas for conversion of H_2S to sulfur (see Section 22). The process uses a solution of iron which is held in solution by organic chelating agents. The iron in the solution oxidizes the hydrogen sulfide to sulfur. The iron chelate is then circulated to an oxidizer and regenerated for reuse in the process.

The process will not remove CO_2, COS, CS_2 nor RSH. If desired, some CO_2 can be removed from the feed gas by strong buffering of the solution.

Lo-Cat II utilizes special additives to reduce the rate of chelant degradation. For acid gas applications, an auto-circulation design is offered. Here, sparging of air in the oxidizer box causes solution to flow to the next compartment, obviating the need for a pump. Under proper conditions, the sulfur derived in the process is suitable for sale.

SulFerox®

The Shell SulFerox® process, developed by Shell Development Company and the Dow Chemical Company, is an iron chelate redox technology that removes hydrogen sulfide and converts it directly to salable sulfur in one step. The process offers low capital and operating costs through the use of a high concentration iron chelate solution and effective control of chelate degradation. The process also offers a patented contactor design to improve the overall efficiency of the process which further reduces capital costs. The optimum application for SulFerox is in the one to twenty tons per day range of recovered sulfur.

Sulfint-HP

The Sulfint-HP is an iron chelate based liquid redox technology licensed by Prosernat an IFP group company. It is claimed that it can be directly applied to high pressure sour gas streams. To avoid the problem of sulfur plugging which have plagued other redox technologies at elevated pressure, Sulfint-HP applies direct filtration of the sulfur containing solution which exits the high pressure absorber[54]. After filtration the clarified high pressure solution can then be partly recycled back to the absorber thus minimizing pumping cost and partly be letdown in pressure to be regenerated with air in an oxidizer vessel. The expansion of the aqueous based redox solution yields extremely low amounts of flashed gas. Sulfint-HP operation has proved easy and reliable in field operation[55].

BIOLOGICAL PROCESSES

Among biological processes worthy to mention is the Shell-Pacques process for removal of hydrogen sulfide from gas streams. The process can be considered attractive for quantities of hydrogen sulfide in the range of 0.5 to 30 long tons per day.

In this process a gas stream containing H_2S contacts an aqueous soda solution containing sulfur bacteria in an absorber. The soda absorbs the H_2S and then transfers to a regenerator. The regenerator consists of an aerated atmospheric tank where hydrogen sulfide is biologically converted to sulfur. The sulfur may be recovered as a moist filter cake or as a liquid product.

MEMBRANE SEPARATION PROCESS

Membranes are thin polymer-based barriers that allow preferential passage of certain substances over others. Gas separation through membranes relies on the principle that gases dissolve in and diffuse through the membrane polymers. Certain gases like H_2O, H_2S and CO_2, will permeate through a membrane at a faster rate than hydrocarbons due to a difference in the solubility and diffusion ability of those gases through the membrane. The difference in gas permeability rates through the membrane provides the basis for the sepa-

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ration. The separation is actually driven by the component partial pressure differences across the polymer membrane. The technology is therefore not applicable for very stringent sour gas specifications.

In design of membrane systems for these purposes it is important to focus on achieving high selectivity of CO_2 vs. natural gas in order to avoid natural gas losses, avoiding plastification of membrane materials due to high CO_2 partial pressures, and ensuring sufficient lifetime of the membrane material.

Recently, several very large membrane systems including some treating in excess of 300MMSCFD of gas containing over 30% CO_2 have been successfully implemented as a result of advances in pretreatment technology. Membrane system suppliers include Grace, Kvaerner Process Systems, Natco-Cynara, UOP, and Ube.

Pressure drop through the membrane is high, so the gas which permeates is available only at lower pressure. For the natural gas not permeating the membrane, the pressure drop will be similar to that through any other process unit.[56.]

Natural gas sweetening and dehydration using membranes often offers significant advantages over the more conventional methods such as amine treating, physical solvents, and solid adsorbents. Membranes can be used by themselves or in conjunction with amine units to maximize the benefits of both technologies. Membranes are particularly attractive when the pressure of the feed gas is high (over 500 psig) and/or the CO_2 content of the gas to be treated is high (over 10%). However membrane materials are not suitable for high hydrogen sulfide partial pressures and applications for bulk H_2S removal is not practical. According to Kvaerner Process Systems the maximum permissible H_2S partial pressure is around 20 psia for present membrane materials.

Other benefits of membrane systems are: a lower capital investment than amine plants in most cases (especially small capacities), reduced maintenance and labor costs, no moving parts and no chemicals used, excellent flexibility in adjusting to variations in feed flow and feed composition, and a significant space and weight advantage over amine plants. The last benefit is particularly significant in offshore applications. In all membrane systems care should be taken in order to have a proper pre-conditioning of the gas, and to avoid prohibitive natural gas losses.

PROCESS SELECTION

Selection of the best technology to apply to a given gas stream depends on many factors, and should be done by experienced personnel. Among the factors to be considered are: feed temperature and pressure, type and concentration of impurities, desired gas specification, flow rate, location, operating expense, and overall cost. Despite the large number of parameters involved, it is possible to give some general guidelines as to which process is most appropriate. For example, physical solvents will generally be more attractive than chemical solvents when the partial pressure of acidic components is high, owing to the higher loading and lower regeneration energy requirements associated with a physical solvent. If heavy hydrocarbons are present, however, physical solvents may be less attractive due to their tendency to co-adsorb these contaminants.

Figure 21-20 shows an example process selection chart for the case where both H_2S and CO_2 are to be removed from the gas stream. This is a modified version of a graph taken from Tennyson and Schaaf,[28] who also presented cases for removal of only H_2S, only CO_2 , and selective H_2S removal. Note that specific conditions may dictate the use of a process different from what is presented in this type of chart.[57]

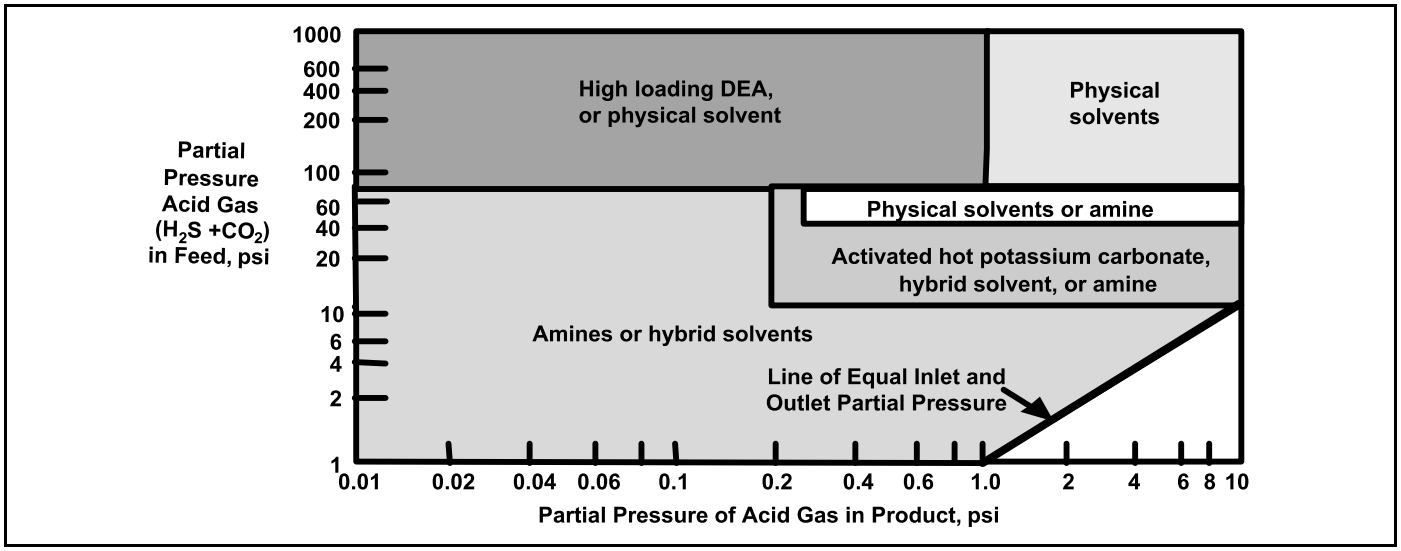
MERCURY REMOVAL

Calgon

Solid adsorbents can remove mercury from gas to produce residuals in the range of 0.01–0.001 μg/Nm^3. Calgon sulfur impregnated HGR® (4 x 10 mesh) and HGR®-P (4 mm dia.) carbons are used for mercury removal and indicate designs removing mercury down to very low levels. Removal of both inorganic and organic mercury is achieved. By first drying the gas the degree of mercury removal increases. The sulfur im-

FIG. 21-20

Process Selection Chart for Simultaneous Removal of H_2S and CO_2[28].



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pregnate reacts with the mercury to produce a mercury sulfide that is fixed in the carbon microstructure.

Merespec™

Johnson Matthey Catalysts supplies MereSpec™ fixed bed absorbents for removal of traces, elemental and organic, of mercury from hydrocarbon liquids and gases. The absorbents have been shown to be capable of providing the outlet mercury concentration normally specified for LNG production and are in service in several European locations including an offshore oil/gas production platform. Merespec™ is a trademark of Synetix.

Desorex

Activated carbon provides only a limited storage capacity for the strictly physical adsorption of mercury. Desorex HGD2S and HGD4S from Donau Carbon can be employed to bind mercury through the process of chemical adsorption involving oxidation and adsorption in the form of stable compound or fixation in metallic form as an amalgam. Many reference installations of these Desorex products for the purification of natural gases to levels as low as 10 ng/m^3 of mercury have been realized over a long period of time.

HgSIV

UOP supplies HgSIV adsorbents which are molecular sieves coated with elemental silver. Mercury in the gas is trapped by amalgamation with the silver. The adsorbent also serves the dual function of dehydrating the gas. HgSIV is regenerated thermally, just like molecular sieves for dehydration. This material can be added as a layer to existing molecular sieve dryers[58]. However, one must take care to appropriately handle the regeneration gas in this case, as it will contain mercury.

CMG 275 and 273

Another mercury trapping material labeled CMG 275 was developed by IFP and Procatalyse (today Axens) which is sulfur supported onto mesoporous alumina. The advantage of mesoporous alumina based product is its resistance to capillary condensation[59]. The larger pore size of this material, compared to carbon based trapping materials permits utilization under near dew point conditions. In another material from Axens labeled CMG 273 the trapping component is anchored on the alumina carrier making it completely insoluble in liquid hydrocarbons and water. The material has been subjected at gas plant sites to both DEA and liquid hydrocarbon carry-over with no active phase leaching. This same material has been used to eliminate elemental mercury from LPG and full range condensates.

Organic Mercury Removal

Removal of all forms of organic mercury compounds from natural gases and liquids requires firstly the conversion of the compounds to elemental metallic mercury followed by trapping materials to remove the metallic mercury formed. This requires in the first stage some hydrogen for the organo-mercury hydrogenolysis with a suitable catalyst. The first stage catalyst such as MEP 841 also traps arsenic and lead impurities in the feed. The two stage impurities removal process is called RAM and is available from Axens.

ACID GAS INJECTION

In some cases, it is possible to compress the acid gas as generated from a chemical or a physical solvent process and inject it into a depleted, non-producing, or even a producing reservoir[60]. A key consideration is the phase behavior of the acid gas mixture. Depending on temperature, pressure, and composition, the acid gas may be injected as a liquid or gas; or as a dense phase. Dehydration is usually necessary to avoid corrosion or hydrate formation. However, in many cases, a minimum in water-holding capacity occurs with respect to pressure. Thus, it may be possible to compress the gas to a given level, cool it, and drop out the liquid water. Further compression increases the capacity of acid gas to hold water, so that water drop out should not occur in the downstream piping or well. The phase behavior of acid gas mixtures is complex, and careful consideration must be given to the design of the project.[61,62.]

There have been a number of successful acid gas injection projects, with sulfur contents of 1 to more than 70 tons per day[63].

LIQUID HYDROCARBON TREATING

As a guide in the selection of the method of treating to be used, the following characteristics of each are given:

Regenerated Caustic

1. Can handle large volumes of hydrocarbon.
2. Primarily for removing methyl and ethyl mercaptans.
3. Capable of producing a doctor-sweet product.
4. Reduces the total sulfur content of treated product.

Perco Solid Copper Chloride

1. Can treat gasoline streams with relatively high mercaptan content.
2. Suited for small flow rate.
3. Sulfur content not reduced.
4. Water content must be only that of saturation.
5. Hydrogen sulfide must be removed ahead of contact with bed.
6. Excess regeneration oxygen may cause corrosion downstream of bed. Gasoline with components that may be affected by oxygen, such as olefins, should not be treated with this process.
7. Capable of producing doctor-sweet product.

Batch Caustic Wash

1. Can use a single wash.
2. Best suited for streams with low mercaptan content (if mercaptan removal is important).
3. Primarily for removing trace amounts of hydrogen sulfide and methyl and ethyl mercaptans.
4. Disposing of spent caustic can be a major consideration.
5. Relatively high caustic consumption per gallon of product.

Solid Potassium Hydroxide

1. Low installation and operation costs.
2. Acts as a desiccant as well as removing the sulfur compounds.
3. Suitable for removing trace amounts of H_2S.

Molecular Sieve

1. Can handle large or small streams.
2. Reduces total sulfur content by removing hydrogen sulfide, mercaptans, and partially removing organic sulfur in the same adsorber vessel.

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3. Will produce 1A copper-strip, doctor-sweet product.
4. Will dry in the same step with additional equipment.
5. Requires that the regeneration gas be made slightly sour by use of this stream to strip sulfur compounds from the molecular sieve.

Merox

1. Can handle large or small streams.
2. Eliminates problem of disposal of spent caustic.
3. Product is sweet when it leaves unit; no holding period is required.
4. Adds problems of sulfur compounds in regeneration air leaving the regenerator.

Merichem

1. Can handle large or small streams of light hydrocarbon liquids.
2. Removes mercaptans and organic acids.
3. Uses a bundle of fibers to increase interfacial area between caustic and hydrocarbon.
4. Sulfur compounds are present in regeneration air

GENERAL NOTES ON LIQUID HYDROCARBON TREATING

Mixing (Liquid/Liquid Treating Systems)

Good mixing of gasoline and treating solution may be accomplished by means of a low efficiency (40%) centrifugal pump. The gasoline stream and solution recycle stream join just ahead of the pump and are discharged to the solution settling tank.

Treaters may use static in-line mixers to obtain good gasoline-caustic contact. A properly designed in-line static mixer will create a controlled droplet size with a narrow size distribution. Continuous renewal of the dispersed phase surface area accelerates mass transfer. The static mixer accomplishes this uniform dispersion with less energy than most other devices. As the velocity through the static mixer increases, the pressure drop increases and the mean droplet diameter decreases. A homogeneous mix is usually achieved in a mixer which is a few pipe diameters in length.[64]

Treated Product Clean-up

Sand towers may be placed downstream of a liquid wash of gasoline or LPG to remove any entrained water or solution. The gasoline flows downward through the tower. The design of the tower is based on a space velocity of (4 volumes of gasoline)/(volume of sand)/hour.

A downstream water wash of the treated hydrocarbon liquid is also a good way to remove entrained water-based treating solutions such as caustic and amine. The process is identical to the caustic wash shown in Fig. 21-21. A water circulation rate of 10 to 30 percent of the hydrocarbon rate should be adequate, if good liquid-liquid contact is obtained. The solution concentration in the wash water should not build up to more than 3 weight percent.

Counterflow Contact Towers

In the liquid/liquid contact tower, the hydrocarbon feed is introduced through a distributor at the bottom of the tower and becomes the dispersed phase. The treating solution is introduced countercurrently at the top of the tower and becomes the continuous phase. The dispersed phase migrates upward through the packing due to the difference in densities of the two liquids. The sweetened product is removed from the top of the tower where 8 to 10 feet of open column are provided for disengagement of the heavy phase.

Counterflow contact towers can either be packed or trayed. A sieve (perforated) tray with downcomers is probably the most effective for use in liquid-liquid contact devices. The light liquid flows through the perforations of each plate and is thereby dispersed into drops which rise through the continuous phase. The continuous liquid flows horizontally across each plate and passes to the plate beneath it through the downcomer. If the heavy liquid is the dispersed phase, the same design may be used but turned upside down. Extraction rates are enhanced by the repeated coalescence and re-formation of droplets of the dispersed phase.

For best tray efficiency, the dispersed phase must issue cleanly from the perforations. This requires that the material of the plates be preferentially wetted by the continuous phase or that the dispersed phase issues from nozzles projecting beyond the plate's surface. This may be formed by punching the holes and leaving the burr in place, or otherwise forming the jets. The liquid flowing at the larger volume rate should be the dispersed phase.

Perforations are usually 1/8" to 1/4" diameter with a total hole area equal to 15 to 25 percent of the column cross-sectional area. The tray has no outlet weir. Perry provides a calculation procedure for designing liquid-liquid contact sieve trays.[65]

Metal or plastic ring packing also provides good solution contact in counterflow towers. One theoretical stage can generally be obtained in 6 to 8 feet of packed bed height. Ceramic or steel packing should not be preferentially wetted by the dispersed (hydrocarbon) phase. Previous investigations of wetting properties in liquid extraction applications generally indicate that where the dispersed phase wets the packing, mass transfer efficiency is reduced.[66]

The packing diameter should be no larger than one-eighth of the tower diameter, but normally no smaller than one-half inch. The hydrocarbon velocity should be about 15 GPM per square foot of open tower cross sectional area.[65] The hydrocarbon distribution nozzles should be designed with an orifice velocity in the range of one ft/sec. Higher velocities result in the formation of small droplets which can form a hydrocarbon emulsion in the treating solution leaving the bottom of the tower.[66]

For caustic treaters, the packing material is usually carbon raschig rings, which offer better resistance to attack by the caustic solution.

GASOLINE AND LP-GAS TREATING

Most gasoline and LP-gas streams contain sulfur in various forms and LP-gas and raw NGL streams also can contain carbon dioxide. Especially objectionable are hydrogen sulfide, mercaptans, and elemental sulfur. Gasoline containing hydrogen sulfide has objectionable odor and is corrosive. Mercaptans give an objectionable odor to gasoline and elemental sulfur makes the gasoline corrosive. Carbonyl sulfide in the LP-gas can hydrolyze and cause the product to become corrosive. A product containing the objectionable materials can be treated to remove the hydrogen sulfide, carbonyl sulfide, and elemental sulfur and to either remove the mercaptans or convert them to less objectionable compounds.

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Hydrogen Sulfide and Carbon Dioxide Removal

Hydrogen sulfide and carbon dioxide can be removed from LP-gas and gasoline by liquid-liquid contacting processes using a caustic solution, aqueous alkanolamines, or solid KOH. The caustic wash processes are described later. The alkanolamine processes were described earlier in the gas treating section. For application, both a coalescer and a full flow carbon filter should be used to minimize the introduction of hydrocarbons into the regeneration section of the amine unit.

When treating hydrocarbon liquids with amine, contacting is generally accomplished in a liquid-liquid contactor, though stirred reactors can be used. The tower should have a minimum of 20 feet of packing. The design flow rates for packed towers should not exceed 20 gpm liquid per square foot of cross sectional area.

Sulfur Removal

Elemental sulfur is removed from the gasoline by contacting it with a polysulfide wash solution. The solution is made up by using the following amounts of chemicals per 1,000 gallons of water: 1,000 lb. of caustic (NaOH), 800 lb. of commercial Na_2S, and 20 lb. of sulfur. The sodium sulfide (Na_2S) is melted in a vat by use of a steam lance. Add the sulfur to the melted Na_2S. The sulfur must be completely dissolved in the liquid sulfide, and then this mixture is added to the 10% (1,000 gal. water and 1,000 lb. NaOH) caustic solution. Protective clothing and goggles should be worn when handling these chemicals.

Mercaptan Treating

Mercaptans can be converted to disulfides or removed from liquid hydrocarbons by several methods. The method or combination of methods that can be used depends on the mercaptan content of the product to be treated and the specification that must be met. Some of the common treating methods are discussed below.

Carbonyl Sulfide Removal

Because carbonyl sulfide (COS) can hydrolyze and cause sweet LP-gas to become corrosive, and as the concern for minimizing total sulfur emissions has increased, there has been a growth of interest in removing COS from propane and LP-gas streams. Several alternative processes can be used. COS can, of course, be removed sacrificially by MEA. Mick[67] has reported successful use of a combination of potassium hydroxide and methanol. This process is also sacrificial. The Malaprop[68,69] process uses diglycolamine® and requires little or no modifications in the process flow from that used for gas treating. The ADIP[70] process utilizes aqueous diisopropanolamine. Molecular sieves can be used for removing COS. The Malaprop, ADIP and molecular sieve processes are regenerative.

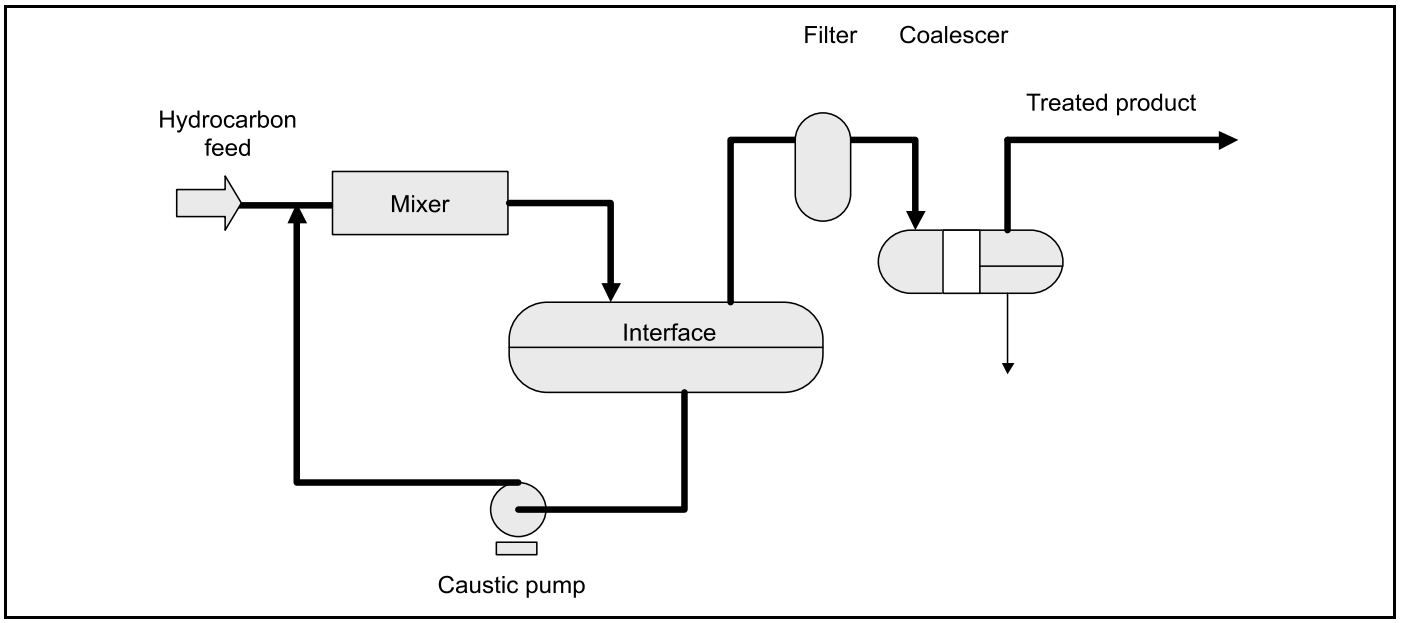
CONTINUOUS LIQUID PROCESSES

Regenerative Caustic

The regenerated caustic method of removing methyl and ethyl mercaptans from LP-gas or butane employs countercurrent contacting of the liquid with 10% sodium hydroxide solution in a packed column. A typical flow scheme is illustrated in Fig. 21-14. The caustic is regenerated in a stripping column by the addition of open steam or by steam internally generated by a column heating element. A condenser may be used to condense water vapors that go overhead with the liberated mercaptan vapors. The condensate is returned to the stripping column to maintain caustic concentration. An LP-gas stream containing 0.03% mercaptan sulfur can be treated doctor sweet with volume ratios of hydrocarbon to caustic as high as 33 to 1. Approximately six pounds of process steam per gallon of caustic are required for regeneration at this hydrocarbon/caustic volume ratio. The following ratios may be used to determine optimum plant design:

FIG. 21-21

Non-Regenerative Caustic



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lb steam / gal. NaOH	4	5	6	7	8	10	12	14.5	17
gal. hydrocarbon / gal. NaOH	15	25	33	39	43	50	55	60	62

Highly corrosive conditions that can exist in a unit for this process are minimized by careful attention to operation conditions, specifically by minimizing the contamination of the regenerated caustic system with sodium sulfide and by operating the rectifying column at low pressure and temperature. The maximum desired steam temperature to the reboiler is 260°F. The sulfide contamination is controlled by caustic washing of the LP-gas ahead of the mercaptan extractor and by blowdown of the circulating solution. A maximum Na_2S content of 0.2% is suggested.

The diameter of the extractor is based upon the hydrocarbon throughput. A typical design uses flow rates of 10-15 GPM/sq ft of cross-sectional area for a column packed with 1-1/4 in. raschig rings. Other tower packing may be used and, if so, the above throughput would be changed. The packed height is normally about 30 feet in two or three packed sections to optimize dispersion of the hydrocarbon phase. An additional 8 - 10 feet of column height is required for distribution and settling areas.

Merox®

A variation of regenerated caustic process has been developed by UOP Process Division. Sour product is treated with caustic containing Merox catalyst to extract the mercaptans. The Merox solution is regenerated by mixing with air and oxidizing. Disulfides and excess air are removed overhead. Existing extraction equipment with steam regeneration can be adapted to the Merox process.

The Merox solution gives a very high degree of removal of mercaptans in a liquid stream. If more complete removal is desired, Merox also provides a fixed-bed catalytic conversion of mercaptans to disulfides. These disulfides will not be removed from the liquid stream, but will remain with the liquids. However, the sulfur leaves as disulfide (no odor) rather than mercaptans.

Merichem®

Merichem®[71] offers several processes for the removal of Na_2S and/or mercaptans from light hydrocarbon liquids. In all of these the key technology is use of a patented Fiber Film® bundle to achieve intimate contact between the hydrocarbon feed and the caustic solution. The bundle is comprised of long continuous small diameter fibers placed in a pipe. The caustic solution preferentially wets the fibers, creating a large interfacial area for contact with the hydrocarbon liquid. The fiber bundles can be installed easily into existing systems.

1. Merifining uses caustic to extract organic acids, mercaptans, and other sulfur compounds from catalytic cracked hydrocarbons.
2. Napfining extracts naphthenic and other organic acids from petroleum distillates that produce kerosene and jet fuel.
3. Mericat uses an oxidation catalyst bearing caustic solution and air to oxidize gasoline and kerosene mercaptans to disulfides.
4. Thiolex uses caustic to extract hydrogen sulfide and mercaptans from fuel gas, propane, butane, alkylation feed and straight run gasolines.
5. Regen uses air to regenerate Thiolex caustic solutions for reuse.

Perco Solid Copper Chloride Sweetening

The copper chloride sweetening process can be used to sweeten natural gasoline. It is a continuous process in which the mercaptan sulfur in the gasoline is converted to disulfides in a reaction with copper chloride.

The copper chloride reagent is impregnated on a stationary bed of Fullers earth. As manufactured, this material contains approximately 16% water and loses its reactivity below 7%. To maintain the reactivity of the Perco bed, water should be added by (a) injecting a small quantity of steam into the gasoline feed stream to the treater, or (b) bubbling a sidestream of gasoline through a small pot containing water and returning it to the main stream. Above 30% water content, the copper chloride tends to be extracted from the Fullers earth. Because water is formed in the overall Perco sweetening reaction, it is often necessary to heat the gasoline feed to prevent the formation of free water which would tend to dissolve copper chloride from the Fullers earth. Any hydrogen sulfide in the gasoline must be removed by a caustic wash before contact with the Perco bed.

In the sweetening reaction mercaptans are oxidized to the disulfide and copper is reduced from cupric to cuprous:

$$4\,RHS + 4\,CuCl_2 \rightarrow 2\,RSSR + 4\,CuCl + 4\,HCl \qquad \textbf{Eq 21-28}$$

The cuprous chloride is regenerated simultaneously by adding air to the inlet gasoline stream:

$$4\,CuCl + 4\,HCl + O_2 \rightarrow 4\,CuCl_2 + 2\,H_2O \qquad \textbf{Eq 21-29}$$

The "standard" bed depth is 7 feet with a maximum of 9 feet and a minimum of 4 feet.

FIG. 21-22

Standard Solid Copper Reagent Towers

Charge Rate, bbl/day	Tower size, ft.	Bed Volume, cu ft.	Reagent, lb.
187	2 x 10	21.9	1,090
424	3 x 10	49.5	2,475
752	4 x 10	88.0	4,400
1,177	5 x 10	137.5	6,870
1,500	5 x 12	176.5	8,830

The charge rate in Fig. 21-22 is based on two volumes of gasoline/volume of reagent. If the mercaptan content of the gasoline is low, this charge rate can be exceeded.

Air is added to the sour charge by means of a diffusing disc at the rate of 1 cu ft of air (STP)/bbl of charge for each 0.01% mercaptan sulfur. If the mercaptan content of the gasoline is high, the operating pressure must be increased to hold the additional air in solution. The rate of air injection should be maintained as near to this figure as practical since insufficient air will prevent complete reactivation of the reagent and excess air may result in airbinding of the treater vessel — an extremely hazardous condition.

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BATCH PROCESSES

Caustic Wash

Caustic wash can be used to remove hydrogen sulfide and/or lighter mercaptans from LP-gas and gasoline. Liquid hydrocarbon and recirculated caustic (Ratio 1:0.5) are mixed by means of a pump or static mixer and discharged to a settling tank where the liquids separate. The size of the tank required is based on the retention time necessary for complete separation of the gasoline-caustic emulsion. The retention time varies from 1-1/2 hours for heavy gasolines to 30 minutes or less for propane. A coalescing element on the settling tank inlet can reduce the required retention time. Since the separating tank is one-third full of caustic, the liquid hydrocarbon retention time is based on two-thirds of the tank volume. A typical caustic wash system utilizing a static mixer is given in Fig. 21-21.

Any discussion on materials of construction for caustic must take personnel safety into consideration for every application. Caustic solutions, especially when hot, are extremely damaging to the human body. The materials selection decision must take into account potential personnel exposure and may dictate a more costly but more reliable material.

Mild steel remains the most utilized material. It is effective in caustic solutions up to 50 percent concentration and at temperatures up to 150°F. Corrosion rates in the range of 15-25 MPY (depending on agitation, etc.) can be expected. Austenitic Ni-Cr stainless steels, primarily type 304 and 316, are very resistant to caustic in concentrations up to 50 percent and temperatures to about 200°F.

Stress corrosion cracking (caustic embrittlement) has been reported in laboratory testing at concentrations as low as 10 percent with temperatures of 210°F.[72] Stress relieving of carbon steel is recommended for most applications.

Centrifugal pumps used in caustic circulation may experience premature seal failure which results from crystallization of sodium hydroxide on the seal face. Using an API Plan 62 (external fluid quench) system with a fresh water seal flush fluid or a Plan 52 (tandem seal) system with a buffer fluid are good solutions. Glandless pumps (such as magnetic drive and canned motor) are also used in this application.

A method for calculating the acid (H_2S and RSH) removal efficiency in a batch caustic wash system was published by Beychok in 1973.[73] and is covered in detail in the previous 11th edition GPSA Engineering Databook as Example 21-3 starting on page 21-22.

OFFSHORE DESIGN CONSIDERATIONS

Hydrocarbon Treating in the offshore industry encompasses many of the same processes as can be seen in the onshore industry. However, much more emphasis is given to minimize size and weight of the equipment. For floating production certain precautions also need to be taken in order to mitigate the negative influences of the vessel movements. Of particular importance is the constant tilt of the contacting and regeneration towers, which will seriously deteriorate the performance of the towers due to mal-distribution. References are made to Sections 7 and 19, where the separators and fractionators /absorbers face similar challenges.

Some key considerations of importance for a sound design of a hydrocarbon treating system on an offshore installation are:

Extensive use of sophisticated high tensile strength metallurgy, since this will both reduce equipment weight and allow for less maintenance. The reduced equipment weight is due to reduced wall thickness when using high tensile steels. Less maintenance will be required since less corrosion particles will be expected and therefore less filtration and less chemical consumption.

Compact contacting technology in order to save weight and space.

Compact module-based units with great emphasis on optimized piping lay-outs and integrated solutions in order to save weight and space.

Great emphasis on keeping a clean operating plant by starting with a clean plant and degreasing before first fill and after large revamps. Keeping the feed gas clean by proper pre-treatment of the gas. Maintaining a clean solvent by proper solvent filtration with both charcoal and mechanical filters and minimizing use of additives like anti foam agents. Keeping a clean system by avoiding hydrocarbon condensation in the absorber by introducing superheat if retrograde properties exist, insulating the contactor and/or keeping a safe differential temperature between liquid inlet and gas inlet (typically 20°F higher on liquid side).

Keeping a clean operating plant is much more important offshore, because of the great difficulties of "trucking" in huge reclaiming equipment and other rescue matters[74].

Well equipped offshore laboratory with skilled personnel is very important, since more of the problems need troubleshooting and to be solved on-site.

Special considerations for floating production units should include:

- avoiding greater constant tilt than 1 degree.
- keeping vessel movements to a minimum with full dampening often required.
- careful level measurements, see also Section 7.
- internals selection; for example pressurized liquid distribution in absorber and regeneration towers.

EMERGING TECHNOLOGIES

This sub-section of Section 21 is intended to mention recently developed technologies in hydrocarbon treating some of which have not yet seen full scale industrial applications but have been subject of past GPA and Laurance Reid Gas Conditioning conferences and/or publications worldwide. In future evolving editions of this "living" GPSA Engineering Databook, some of these emerging technologies will be placed along with the industrial ones already described in the main text while yet newer technologies emerge to find their mention here.

The text which follows is in the order of subject appearance in the main text, starting with chemical reaction processes and ending with batch processes. Understandably, it is beyond the scope and intent of this data book to cover every emerging technology worthy of mention.

Alkanolamine Processes

A compact alkanolamine process (CAP) based on the ProPure[75] co-current contacting technology is being developed by ProPure Purification, a subsidiary of Statoil. It is a continuous selective trace H_2S removal process. It relies on the rapid and selective tertiary alkanolamine chemistry with H_2S used

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in a novel co-current short residence time contactor, further enhancing the H_2S selectivity. The process is ideally suited for offshore applications where low weight and foot print is a premium. It competes well with conventional scavenging processes as the H_2S containing solvent is regenerated and thus scavenger chemical consumption is avoided.

Hybrid Solvent Processes

A modern version of the Amisol process has been developed by IFP together with Total called Hybrisol[77]**.** This process combines the physical solvency attributes of methanol with the chemical reactivity of alkanolamines (DEA or MDEA)**.** It is integrated upstream with the Ifpex-1 dehydration technique (see Section 20 dehydration) and when coupled with a downstream cold process achieves simultaneous dehydration, complete acid gas and mercaptan removal together with sweet NGL extraction. Furthermore it produces dry acid gas at some pressure.

Highly Sour Gas Pretreatment Processes

Among processes destined for acid gas re-injection when treating very highly sour lean natural gases are the following pretreatment processes. Each can be followed by a complete acid gas removal process to make pipeline gas specification:

In the Sprex process developed by IFP together with Total[77] a substantial part of the acid gases; notably the H_2S, from the inlet gas is pre-extracted in a cyclone or column by cold reflux as a bottoms pumpable liquid at line pressure and ambient temperature. The extracted liquid also contains essentially all the water of saturation of feed gas so no further dehydration nor inhibition is required for the downstream cold condensing process. The liquid also contains some limited amount of hydrocarbons.

An Acid Gas Fractionation process developed by Kvaerner Process Systems[78] utilizes refrigeration and a downstream fractionation column to liquefy the acid gas components as a bottoms product for disposal. The process claims high extraction levels of H_2S and CO_2 with limited hydrocarbon losses with use of the fractionation column.

Claus Reaction Processes

An alternative to liquid redox processes has recently been developed.[79,80] CrystaSulf, marketed by CrystaTech, Inc., is a technology that utilizes a non-aqueous solution to absorb H_2S from the process stream, and react it with dissolved SO_2 to form dissolved elemental sulfur in the absorber via the modified Claus reaction. The proprietary non-aqueous solution does not absorb CO_2, and therefore is not affected by high partial pressures of CO_2.

After contact with the process stream, the solution is flashed to lower pressure. The flash gas may be vented to fuel gas or to a flare, or may be compressed and returned to the inlet, if desired. The solution keeps elemental sulfur dissolved until the temperature is reduced from the absorber temperature of 150F-160F to the crystallizer temperature of 90F-120F. There, elemental sulfur precipitates from solution. Since the elemental sulfur is kept dissolved in the absorber and other pressurized portions of the plant, the problem of sulfur plugging in high-pressure equipment is thus avoided, and the process can be applied to high-pressure gas streams.

Molecular Sieves

Engelhard has developed the Molecular Gate™ technology using titanium silicate materials whose pore size can be adjusted to +/- 0.1 Angstrom. These materials can be used to preferentially adsorb molecules on a size exclusion basis. For example, a material with 3.7 Angstrom pore diameter will adsorb nitrogen with a molecular diameter of 3.6 Angstrom but pass methane with a molecular diameter of around 3.8 Angstroms.

The Molecular Gate™ system utilizes a pressure swing adsorption (PSA) process. It can also be designed for the simultaneous removal of CO_2 and nitrogen from natural gases containing both impurities[81].

Gas/Liquid Membranes

Kvaerner Process Systems and its joint industry partners are in the final stages of commercializing a novel membrane contactor technology based on highly resistant inert PTFE materials from WL Gore and Associates[82].

The contactor can be applied in a range of gas processing applications with amines including both low pressure removal of CO_2 from exhaust gases and high pressure natural gas sweetening. Benefits include substantial reduction of volume and weight of contactor and reduced energy requirements.

Membranes for CO_2 Removal from Liquid Ethane

It has been verified in a pilot facility utilizing a full scale membrane element, that membranes can be used to remove CO_2 from a liquid ethane stream. The membrane module constitute of an assymetric hollow fiber made of cellulose-acetate. Tests have shown acceptable ethane losses, while providing a secondary benefit of removing some methane from the ethane product[83].

Batch Scavenging Processes

The Gas Research Institute (GRI) have sponsored an evaluation program for H_2S scavenging technologies[84]. Among the novel / emerging scavengers tested are the following:

- Sulfa-Scrub HSW-700L from Baker-Petrolite
- GasTreat 136 from Champion Technologies
- GasTreat 155 from Champion Technologies
- Swan MSS-58 from Swan Industries Inc.
- Sulfarid 8411 from Edmunds and Associates Inc.
- Quaker Enviro-Tek from Quaker Chemicals Corp.
- DM-5927 from BetzDearborn
- Nalco/Exxon EC-5492A from Nalco/Exxon Energy Chemical L.P.
- Dynea and Statoil have patented and developed an H_2S scavenger called Dyno HR 2707 which is reported to be very efficient at low temperatures and very low levels of H_2S.[85]

Controlled-Freeze Zone (CFZ) Process

This ExxonMobil process removes CO_2, H_2S, and other impurities from natural gas. The unique aspect of the process is that it induces CO_2 freezing in an open area of a cryogenic fractionation column.[86] (The Ryan Holmes process, described in Section 16, adds a hydrocarbon stream to suppress CO_2 freezing in the distillation column.) The solid CO_2 melts in the stripping section of the CFZ column, and flows out as a liquid along with the other contaminants. The liquid stream can then be easily pumped for downhole disposal. Methane, nitrogen, and helium come out overhead.

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GPA RESEARCH REPORTS

Listed below are GPA Research Reports that deal with amine enthalpies and acid gas equilibrium.

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Report No.	Report Title
RR-85	Enthalpies of Solutions of CO_2 in Aqueous Diglycolamine® Solutions - Scott P. Christensen, James J. Christensen and Reed M. Izatt, Brigham Young University, Provo, Utah. Project 821-84.
RR-102	Enthalpies of Solution of CO_2 in Aqueous Methyldiethanolamine Solutions - Keith E. Markley, James J. Christensen and Reed M. Izatt, Brigham Young University, Provo, Utah. Project 821.
RR-104	Equilibrium Solubility of Carbon Dioxide or Hydrogen Sulfide in Aqueous Solutions of Monoethanolamine, Diglycolamine, Diethanolamine and Methyldiethanolamine - R.N. Maddox, A.H. Bhairi, James R. Diers and P.A. Thomas, Oklahoma State University, Stillwater, Oklahoma. Project 841.
RR-108	Enthalpies of Solution of CO_2 in Aqueous Diethanolamine Solutions - Rebecca Helton, James J. Christensen and Reed M. Izatt, Brigham Young University, Provo, Utah, Project 821-86.
RR-114	Enthalpies of Solution of H_2S in Aqueous Diethanolamine Solutions - Rebecca Van Dam, James J. Christensen, Reed M. Izatt, and John L. Oscarson, Brigham Young University, Provo, Utah. Project 821.
RR-124	Equilibrium Solubility of CO_2 or H_2S in Protonated Solutions of DEA at Low Partial Pressures - R. N. Maddox and E. M. Elizondo, Oklahoma State University, Stillwater, Oklahoma. Project 841.
RR-125	Equilibrium Solubility of CO_2 or H_2S in Protonated Solutions of DEA - R. N. Maddox, M. Abu-Arabi and E. M. Elizondo, Oklahoma State University, Stillwater, Oklahoma. Project 841.
RR-127	Enthalpies of Solution of H_2S in Aqueous Methyldiethanolamine Solutions - J. L. Oscarson, and R. M.Izatt, Brigham Young University, Provo, Utah. Project 821.
RR 151	Reaction Kinetics of CO_2 with MEA, DEA, and MDEA and in MDEA Based Blends - Ralph W. Weiland, Optimized gas Treating Inc. Houston, Texas. Project 911.
RR 152	Physical Properties of MEA, DEA, MDEA and MDEA Based Blends - Ralph W. Weiland, Optimized gas Treating Inc. Houston, Texas. Project 911.
RR 153	Enhanced Factors for Acid Gas Removal with Single and Mixed Amines - Ralph W. Weiland, Optimized gas Treating Inc. Houston, Texas. Project 911.

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SECTION 22

Sulfur Recovery

Sulfur is present in natural gas principally as hydrogen sulfide (H_2S) and, in other fossil fuels, as sulfur-containing compounds which are converted to hydrogen sulfide during processing. The H_2S, together with some or all of any carbon dioxide (CO_2) present, is removed from the natural gas or refinery gas by means of one of the gas treating processes described in Section 21. The resulting H_2S-containing acid gas stream is flared, incinerated, or fed to a sulfur recovery unit. This section is concerned with recovery of sulfur by means of the modified Claus and Claus tail gas clean-up processes. Redox processes are touched upon. For a discussion and description of other sulfur recovery processes, see Maddox[1].

THE CLAUS PROCESS

The Claus process as used today is a modification of a process first used in 1883 in which H_2S was reacted over a catalyst with air (oxygen) to form elemental sulfur and water.

$$H_2S + \tfrac{1}{2}\,O_2 \rightarrow S + H_2O \qquad \textbf{Eq 22-1}$$

Control of this highly exothermic reaction was difficult and sulfur recovery efficiencies were low. In order to overcome these process deficiencies, a modification of the Claus process was developed and introduced in 1936 in which the overall reaction was separated into (1) a highly exothermic thermal or combustion reaction section in which most of the overall heat of reaction (from burning one-third of the H_2S and essentially 100% of any hydrocarbons and other combustibles in the feed) is released and removed, and (2) a moderately exothermic catalytic reaction section in which sulfur dioxide (SO_2) formed in the combustion section reacts with unburned H_2S to form elemental sulfur. The principal reactions taking place (neglecting those of the hydrocarbons and other combustibles) can then be written as follows:

Thermal or Combustion Reaction Section

$$H_2S + 1\tfrac{1}{2}\,O_2 \rightarrow SO_2 + H_2O \qquad \textbf{Eq 22-2}$$

ΔH @ 77°F ≈ –223 100 Btu

Combustion and Catalytic Reaction Sections

$$2\,H_2S + SO_2 \rightarrow \frac{3}{x}\,S_x + 2\,H_2O \qquad \textbf{Eq 22-3}$$

ΔH @ 77°F ≈ – 41 300 Btu

Overall Reaction

$$3\,H_2S + 1\tfrac{1}{2}\,O_2 \rightarrow \frac{3}{x}\,S_x + 3\,H_2O \qquad \textbf{Eq 22-4}$$

ΔH @ 77°F ≈ –264 400 Btu

This is a simplified interpretation of the reaction actually taking place in a Claus unit. The reaction equilibrium is complicated by the existence of various species of gaseous sulfur (S_2, S_3, S_4, S_5, S_6, S_7, and S_8) whose equilibrium concentrations in relation to each other are not precisely known for the entire range of process conditions. Furthermore, side reactions involving hydrocarbons, H_2S, and CO_2 present in the acid gas feed can result in the formation of carbonyl sulfide (COS), carbon disulfide (CS_2), carbon monoxide (CO), and hydrogen (H_2). Gamson and Elkins[2] cover the basic theory involved in the Claus process; however, they ignore the many potential side reactions and also the existence of S_3, S_4, S_5, and S_7.

For the usual Claus plant feed gas composition (water-saturated with 30-80 mol % H_2S, 0.5-1.5 mol % hydrocarbons, the remainder CO_2), the modified Claus process arrangement results in thermal section (burner) temperatures of about 1800 to 2500°F. The principal molecular species in this temperature range is S_2 (Fig. 22-20) and conditions appear favorable for the

FIG. 22-1

Nomenclature

H = heat content or enthalpy, Btu/lb or Btu/lb-mole

K_p = equilibrium constant

For the low pressure, vapor phase Claus reaction

$$2\,H_2S + SO_2 \rightarrow 2\,H_2O + \frac{3}{x}\,S_x$$

$$K_p = \frac{(P_{H_2O})^2\,(P_{S_x})^{3/x}}{(P_{H_2S})^2\,(P_{SO_2})}$$

$$= \frac{[\text{Mols } H_2O]^2\,[\text{Mols } S_x]^{3/x}}{[\text{Mols } H_2S]^2\,[\text{Mols } SO_2]}\left[\frac{\pi}{\text{Total Mols}}\right]^{\frac{3}{x}-1}$$

LT/D = long ton per day. A long ton is 2240 pounds.

P = partial pressure, atmospheres

π = total pressure, atmospheres

Acid Gas: feed stream to sulfur recovery plant consisting of H_2S, CO_2, H_2O, and usually less than 2 mol % hydrocarbons.

Claus Process: a process in which ⅓ of the H_2S in the acid gas feed is burned to SO_2 which is then reacted with the remaining H_2S to produce sulfur. This is also referred to as the modified Claus process.

Residence Time: the period of time in which a process stream will be contained within a certain volume or piece of equipment, seconds.

Tail Gas Cleanup Unit: a process unit designed to take tail gas from a Claus sulfur recovery plant and remove additional sulfur with the goal of meeting environmental sulfur emission standards.

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formation of elemental sulfur by direct oxidation of H_2S (Eq 22-5) rather than by the Claus reaction (Eq 22-6).

$$2\ H_2S + O_2 \rightarrow 2\ H_2O + S_2 \qquad \textbf{Eq 22-5}$$

ΔH @ 77°F = −135 200 Btu

$$2\ H_2S + SO_2 \rightarrow 2\ H_2O + \frac{3}{2}\ S_2 \qquad \textbf{Eq 22-6}$$

ΔH @ 77°F = +20 400 Btu

However, both laboratory and plant measurements indicate the more highly exothermic oxidation of H_2S to SO_2 (Eq 22-2) predominates and the composition of the equilibrium mixture therefore is determined by the slightly endothermic Claus reaction (Eq 22-6).

Fig. 22-2 is a representation of theoretical equilibrium conversion as a function of temperature for

- An acid gas from a wellhead-type treater, with about 3.5 mol % hydrocarbons (Curve 1)
- An acid gas from a refinery treater, with about 7 mol % hydrocarbons and 1 mol % mercaptans (Curve 2)
- Pure H_2S (Curve 3)

These curves indicate:

- Sulfur recovery would be expected to be lower for a feed gas from a refinery than for a wellhead treater because of higher hydrocarbon content
- The calculated equilibrium conversion for both acid gas feeds follows closely the idealized curve for pure H_2S
- Conversion of H_2S to elemental sulfur is favored in the reaction furnace by higher operating temperatures of 1800°F and in the catalytic converters by lower operating temperatures of less than 700°F.

To attain an overall sulfur recovery level above about 70%, the thermal, or combustion, section of the plant is followed by one or more catalytic reaction stages. Sulfur is condensed and separated from the process gases after the combustion section and after each catalytic reaction stage in order to improve equilibrium conversion. Although Fig. 22-2 indicates that the Claus reaction is favored by lower temperatures, the process gases must be reheated prior to being fed to the catalytic reaction stage in order to maintain acceptable reaction rates and to ensure that the process gases remain above the sulfur dewpoint as additional sulfur is formed. Fig. 22-3 is the flow sheet of an example three-stage Claus sulfur recovery plant; Fig. 22-4 shows the mechanical arrangement of an example small, package-type, two-stage Claus plant.

Gases leaving the final sulfur condensation and separation stage may require further processing. These requirements are established by local, state, or national regulatory agencies. These requirements can be affected by the size of the sulfur recovery plant, the H_2S content of the plant feed gas, and the geographical location of the plant.

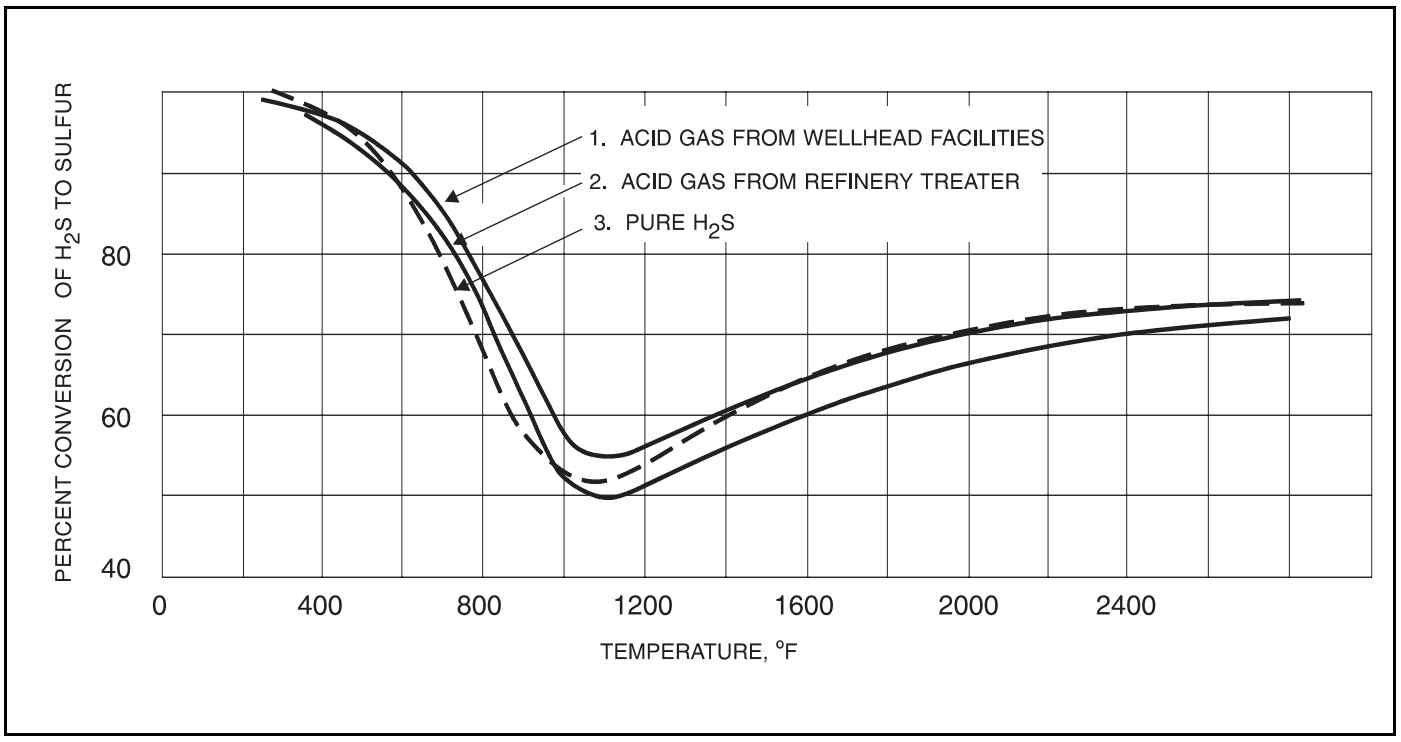
CLAUS PROCESS CONSIDERATIONS

The Claus sulfur recovery process includes the following process operations:

- Combustion — burn hydrocarbons and other combustibles and 1/3 of the H_2S in the feed.
- Waste Heat Recovery — cool combustion products. Because most Claus plants produce 150-500 psig steam (365-470°F), the temperature of the cooled process gas stream is usually about 600-700°F.
- Sulfur Condensing — cool outlet streams from waste heat recovery unit and from catalytic converters. Low

FIG. 22-2

Theoretical Equilibrium Percent Conversion of Hydrogen Sulfide to Sulfur[3]



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FIG. 22-3

Example Three-Stage Sulfur Plant
(Straight-Through Operating with Acid Gas-Fueled Inline Burners for Reheating)

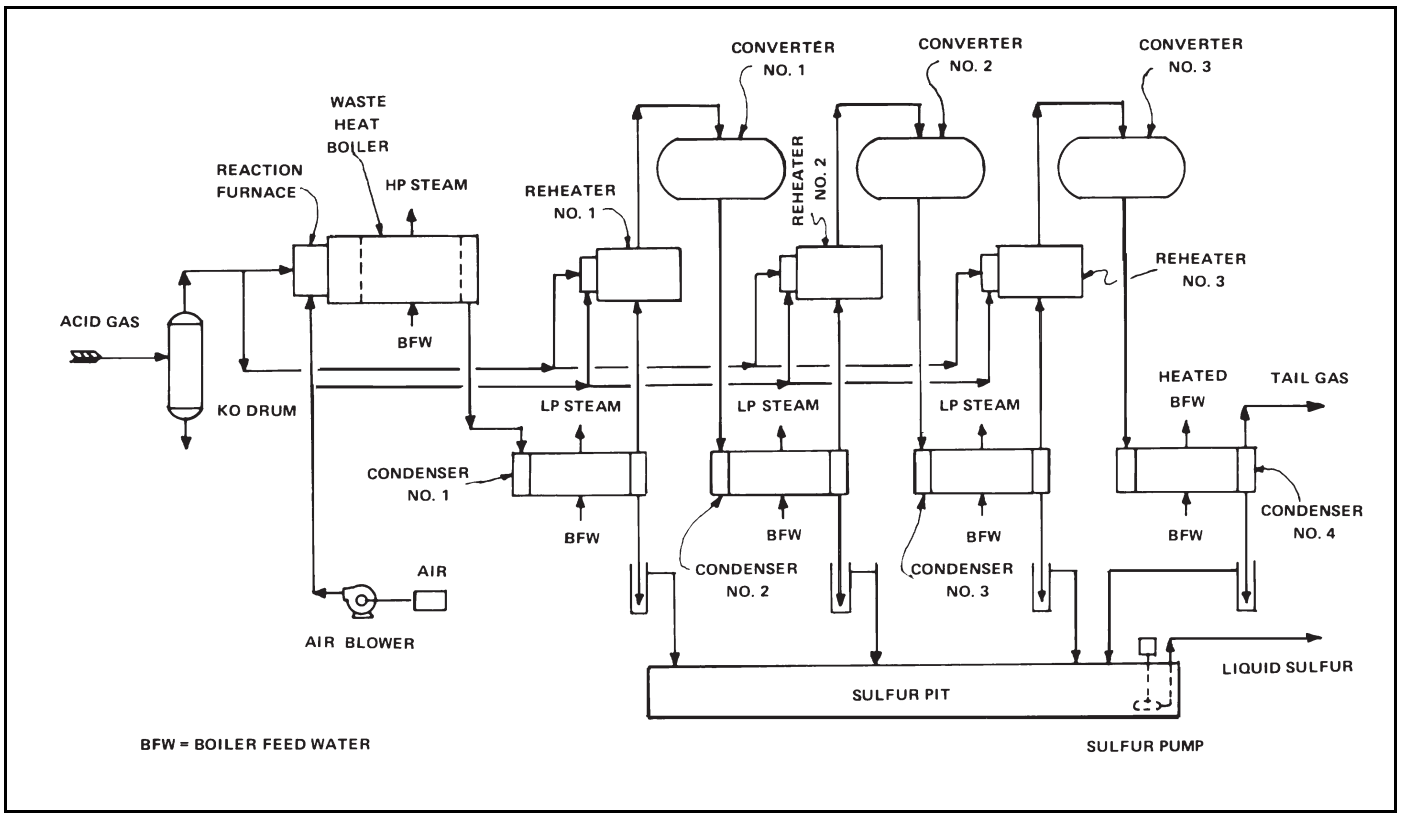
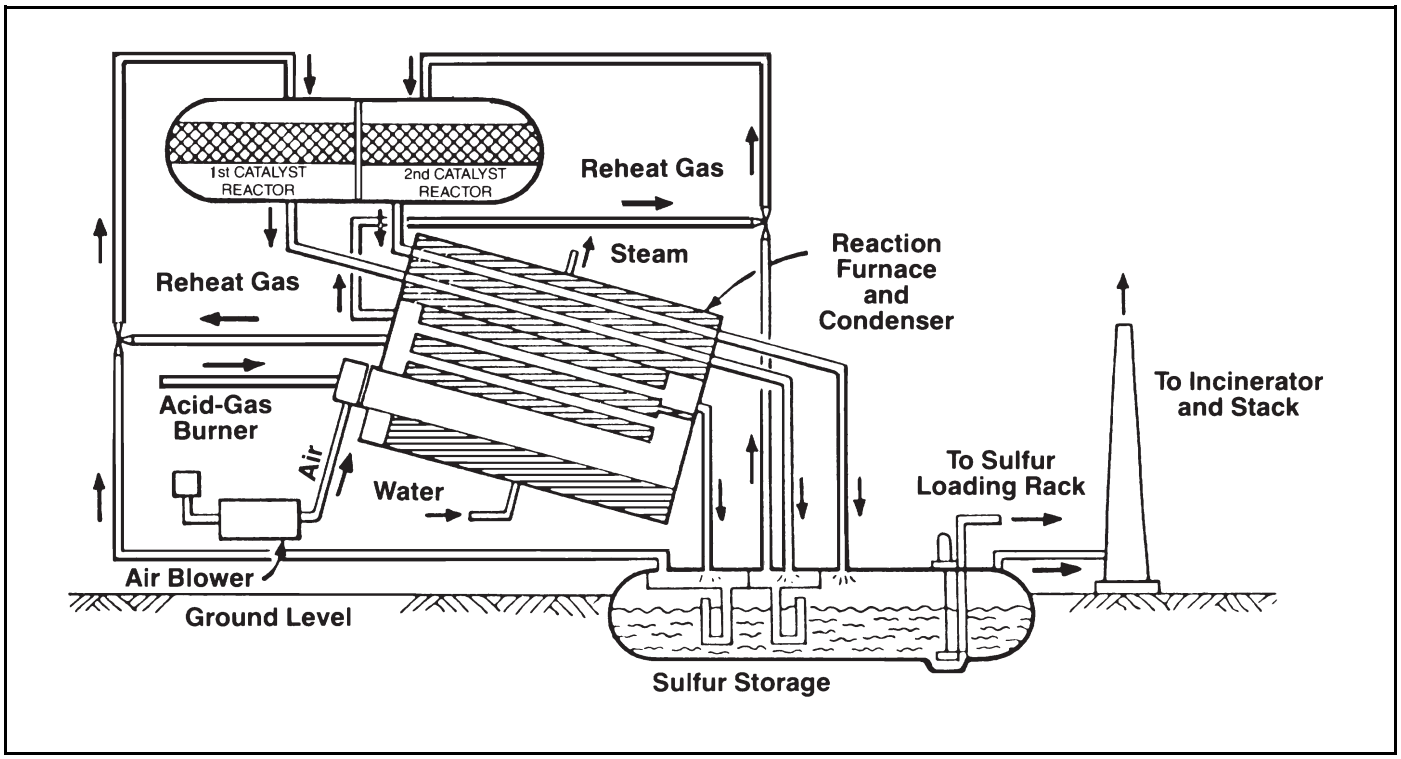


FIG. 22-4

Example Package-Type Sulfur Plant



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pressure steam at 50-70 psig is often produced and the temperature of the cooled gas stream is usually about 350°F or 260-300°F for the last condenser.

- Reheating — Reheat process stream, after sulfur condensation and separation, to a temperature high enough to remain sufficiently above the sulfur dewpoint, and generally, for the first converter, high enough to promote hydrolysis of COS and CS_2 to H_2S and CO_2.

$$COS + H_2O \rightarrow CO_2 + H_2S \qquad \textbf{Eq 22-7}$$

$$CS_2 + 2\,H_2O \rightarrow CO_2 + 2\,H_2S \qquad \textbf{Eq 22-8}$$

- Catalytic Conversion — Promote reaction of H_2S and SO_2 to form elemental sulfur (Eq 22-3)

Process Variations

Several variations of the basic Claus process have been developed to handle a wide range of feed gas compositions. Some of these are shown in Fig. 22-5. Straight-through operation results in the highest overall sulfur recovery efficiency and is chosen whenever feasible.

Fig. 22-6 can be used as a guide in Claus process selection.

Combustion Operation

Most Claus plants operate in the "straight-through" mode. The combustion is carried out in a reducing atmosphere with only enough air (1) to oxidize one-third of the H_2S to SO_2, (2) to burn hydrocarbons and mercaptans, and (3) for many refinery Claus units, to oxidize ammonia and cyanides. Air is supplied by a blower and the combustion is carried out at 3-14 psig, depending on the number of converters and whether a tail gas unit is installed downstream of the Claus plant.

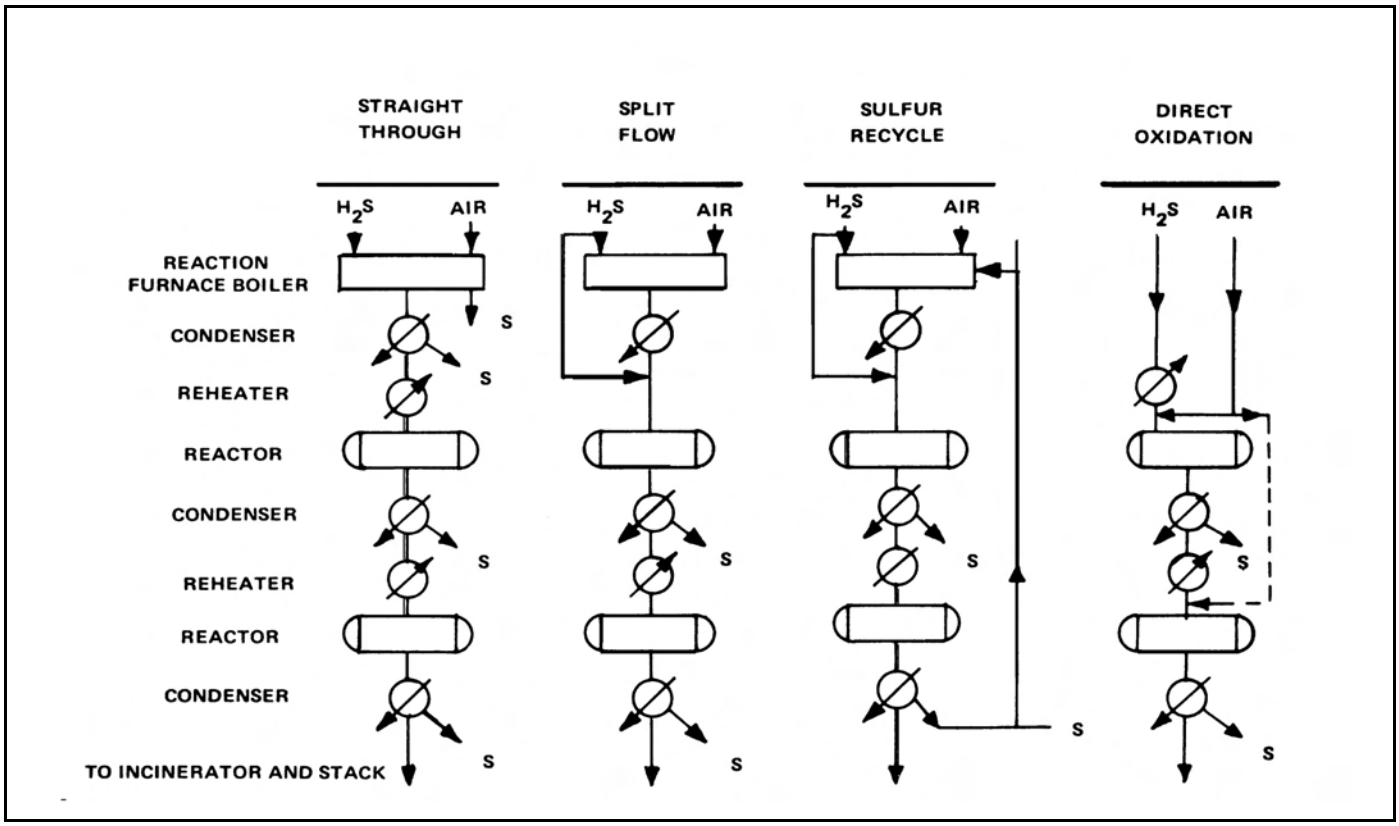
Numerous side reactions can also take place during the combustion operation, resulting in such products as hydrogen (H_2), carbon monoxide (CO), carbonyl sulfide (COS), and carbon disulfide (CS_2). Thermal decomposition of H_2S appears to be the most likely source of hydrogen since the concentration of H_2 in the product gas is roughly proportional to the concentration of H_2S in the feed gas. Formation of CO, COS, and CS_2 is related to the amounts of CO_2 and/or hydrocarbons present in the feed gas. Plant tests indicate concentrations of H_2 and CO in the product gas to be approximately at equilibrium at reaction furnace temperatures; Fig. 22-7 indicates potential COS and CS_2 formation in the Claus furnace.

Heavy hydrocarbons, ammonia, and cyanides are difficult to burn completely in a reducing atmosphere. Heavy hydrocarbons may burn partially and form carbon which can cause deactivation of the Claus catalyst and the production of off-color sulfur. Ammonia and cyanides can burn to form nitric oxide (NO) which catalyzes the oxidation of sulfur dioxide (SO_2) to sulfur trioxide (SO_3); SO_3 causes sulfation of the catalyst and can also cause severe corrosion in cooler parts of the unit. Unburned ammonia may form ammonium salts which can plug the catalytic converters, sulfur condensers, liquid sulfur drain legs, etc. Feed streams containing ammonia and cyanides are sometimes handled in a special two-combustion stage burner or in a separate burner to ensure satisfactory combustion.

Flame stability can be a problem with low H_2S content feeds (a flame temperature of about 1800°F appears to be the mini-

FIG. 22-5

Claus Process Variations



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mum for stable operation). The split flow, sulfur recycle, or direct oxidation process variations often are utilized to handle these H_2S-lean feeds; but in these process schemes, any hydrocarbons, ammonia, cyanides, etc. in all or part of the feed gas are fed unburned to the first catalytic converter. This can result in the cracking of heavy hydrocarbons to form carbon or carbonaceous deposits and the formation of ammonium salts, resulting in deactivation of the catalyst and/or plugging of equipment. A method of avoiding these problems while still improving flame stability is to preheat the combustion air and/or acid gas, and to operate "straight-through". An example of such an arrangement is shown in Fig. 22-8. Steam-, hot oil-, or hot gas-heated exchangers and direct fired heaters have been used. The air and acid gas are usually heated to about 450-500°F. Sometimes split flow is combined with acid-gas preheat. Other methods of improving flame stability are to use a high intensity burner, to add fuel gas to the feed gas, or to use oxygen or oxygen-enriched air for combustion.

Fig. 22-33 gives the theoretical flame temperature for a straight-through operation and for a split-flow operation with two-thirds of the acid gas bypassing the combustion section. For each operation there are isotherms, which represent the temperature of the acid gas feeding the combustion section. The isotherms for temperatures above 110°F represent acid-gas preheat. For the split-flow operation, the part of the acid gas that bypasses the combustion section is not preheated. This figure can also be used for combinations of straight through and split flow. In this case, the split flow (i.e., the amount of acid-gas bypass) should be minimized, which will maximize the overall sulfur recovery and minimize the problems associated with acid-gas bypass that are mentioned in the foregoing paragraph. For acid-gas temperatures different than the isotherm values, and for acid-gas bypasses less than two thirds, corresponding flame temperatures can be estimated by linear extrapolation/interpolation of the curves.

Waste Heat Recovery Operation

Most Claus plants cool the process gases leaving the combustion section by generating steam in a fire-tube waste heat boiler. Steam pressures usually range between 150 psig and 500 psig. The waste heat boiler outlet temperature is therefore normally above the sulfur dewpoint of the process gases; however, some sulfur may condense, especially during partial loads, and provision should be made to drain this sulfur from the process stream (or the piping should be arranged so the sulfur will drain through downstream equipment).

Other methods of cooling the hot combustion gases include the use of glycol-water mixtures, amine solutions, circulating cooling water (no boiling), and oil baths. The utilization of one of these alternate cooling fluids can be especially advantageous at locations where good quality boiler feed water is not available, or where steam generation is not desired.

Some small Claus units use a closed steam system. Steam is generated at 20-30 psig, condensed with air in an elevated condenser, and the steam condensate returned by gravity to the boiler as feed water.

Sulfur Condenser Operation

Sulfur is condensed ahead of the first catalytic converter (except in the case of split-flow operation) and following each catalytic converter in order to promote the Claus reaction. These condensers (other than the one following the last catalytic converter) are typically designed for outlet temperatures of 330-360°F which results in a condensed liquid sulfur of reasonably low viscosity and a metal skin temperature (on the

FIG. 22-6

Claus Plant Configurations

Feed H_2S Concentration, Mol%	Claus Variation Suggested
55 - 100	Straight-through
30 - 55	Straight-through or straight-through with acid gas and/or air preheat
15 - 30	Split-flow or straight-through with feed and/or air preheat
10 - 15	Split-flow with acid gas and/or air preheat
5 - 10	Split-flow with fuel added or with acid gas and air preheat, or direct oxidation or sulfur recycle
< 5	Sulfur recycle or variations of direct oxidation or other sulfur recovery processes.

FIG. 22-7

Potential COS and CS_2 Formation in Claus Furnaces[19]

Feed composition, mol%				COS, CS_2 formation, % of sulfur in feed[a,b]
Hydrocarbon (as C_3H_8)	Water	CO_2	H_2S	
0	6	4	90	0.5
0	6	14	80	1.5
0	6	24	70	2.5
0	6	34	60	3.5
0	6	44	50	4.5
0	6	54	40	5.5
0	6	64	30	6.5
0	6	74	20	7.5
2	6	4	88	2.0
2	6	14	78	3.0
2	6	24	68	4.5
2	6	34	58	6.0
2	6	44	48	7.0
2	6	54	38	9.0
2	6	64	28	11.0
2	6	74	18	14.0
4	6	4	86	3.5
4	6	14	76	5.0
4	6	24	66	6.0
4	6	34	56	8.0
4	6	44	46	10.0
4	6	54	36	12.0
4	6	64	26	14.0
4	6	74	16	18.0

[a] Maximum. Actual production varies with operating temperature and pressure, residence time, burner mixing and burner efficiency.

[b] Units feeding <30% H_2S may operate other than "straight through," causing reduced COS and CS_2 production proportional to amount fed to main burner.

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process gas side) above the sulfurous/sulfuric acid dewpoint. The final sulfur condenser outlet temperature can be as low as 260°F, depending on the cooling medium available. A large temperature difference between process gases and cooling medium should be avoided, however, because of the possible formation of sulfur fog; this is especially important for the final sulfur condenser.

Reheating Operation

The temperature of the process gas at the inlet of the catalytic converters should be such that the effluent gas temperature is

- Higher (25-30°F) than the expected outlet sulfur dewpoint
- As low as possible to maximize H_2S conversion but high enough to obtain a satisfactory Claus reaction rate
- High enough for hydrolysis of COS and CS_2 (for the first catalytic converter only)

Fig. 22-9 shows the methods of reheat commonly used.

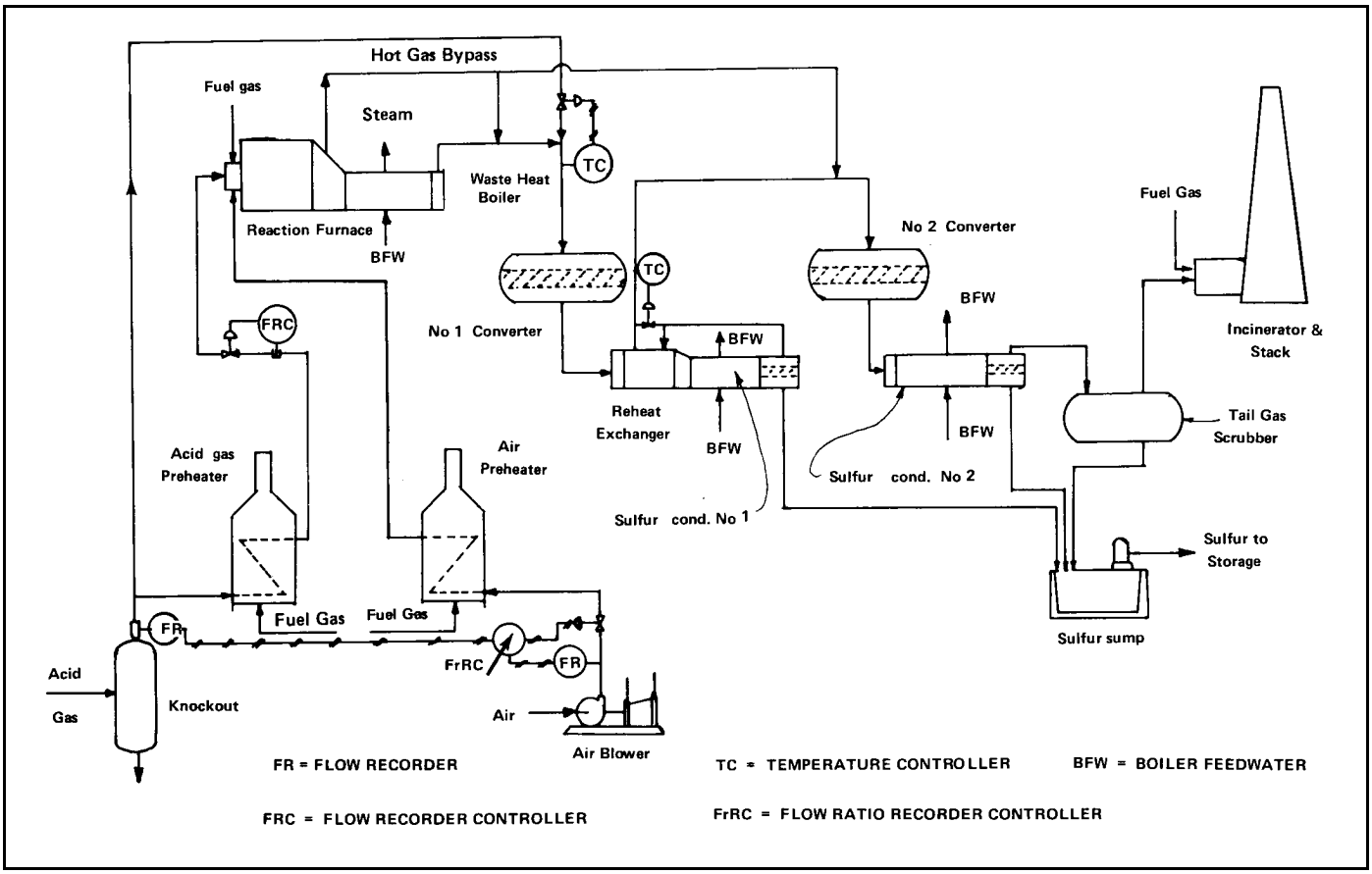
- The hot gas bypass method takes a slip-stream of hot process gases from the waste heat recovery unit, usually at 900°F to 1200°F, and mixes this stream with the sulfur condenser outlet gases upstream of the catalytic converter.
- The direct fired method of reheating uses inline burners burning either fuel gas or acid gas, with the combustion products being mixed with the sulfur condenser outlet gases.
- The indirect reheat methods use direct fired heaters or heat exchangers to heat the sulfur condenser outlet gases; high pressure steam, hot oil, and hot process gases have been used. Electrical reheating has also been used.

Hot gas bypass reheating is normally the lowest cost alternative, is relatively simple to control, and results in low pressure drop. Its disadvantage is lower overall sulfur recovery, particularly at reduced throughput. The hot gas bypass method is sometimes used for the first two catalytic converters and an indirect method of reheat used for the third converter.

Direct fired reheating uses an inline burner which usually burns a portion of the Claus plant feed gas but which sometimes burns fuel gas. This reheating method can be designed to heat the process gases to any desired temperature level. Pressure drop is also relatively low. Potential disadvantages of inline burners are the possible formation of SO_3, if acid gas is burned (sulfates deactivate the catalyst) and of soot, if fuel gas is burned (soot can plug and also deactivate the catalyst). A well-mixed, high-intensity burner capable of operating substoichiometrically without producing soot should be utilized for burning fuel gas. Burner requirements are less stringent for burning acid gas; the H_2S:SO_2 ratio in the inline burner outlet gases is usually maintained at about 1:2 to 1:3. Precautions must be taken, however, to avoid oxygen breakthrough from the inline burners. Oxygen in as low a concentration as 30 ppmv can rapidly sulfate the catalyst.

FIG. 22-8

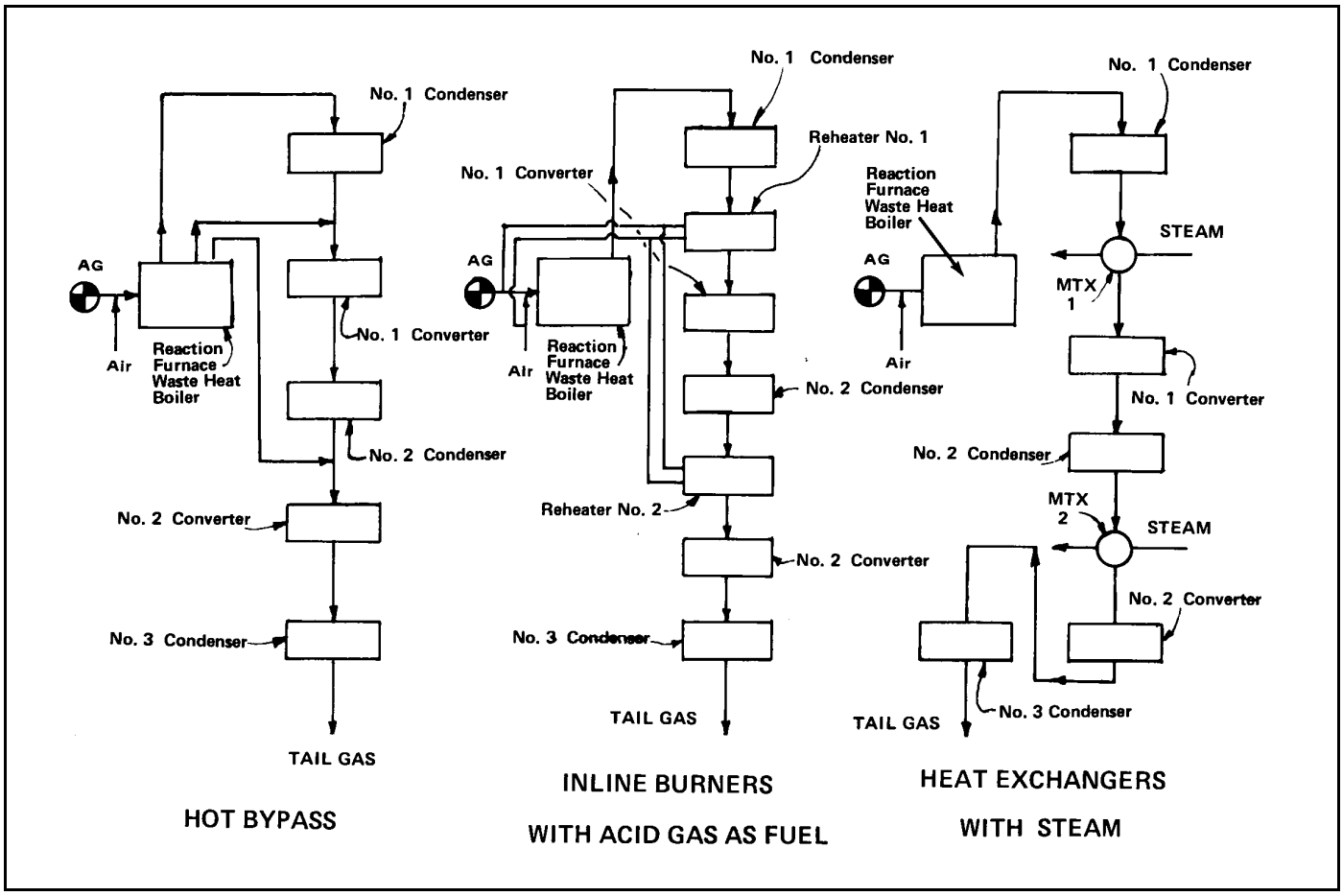
Sulfur Recovery Process with Acid Gas and Air Preheat



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FIG. 22-9

Alternate Methods of Reheating[3]



Indirect reheating, which involves a heat exchanger ahead of each catalytic converter, is the most expensive alternative and results in the highest pressure drop. In addition, converter inlet temperatures are limited by the temperature of the heating medium. For example, the use of 600 psig steam (489°F) as the heat source would limit the converter inlet temperature to a maximum of about 470°F. Thus, catalyst rejuvenation is usually not possible and COS and CS_2 hydrolysis may be more difficult. However, indirect reheating usually results in the highest overall sulfur recovery, and deactivation of the catalyst (because of sulfation, carbon deposits, etc.) is less likely to occur.

Catalyst Converter Operation

The Claus reaction is exothermic at converter temperatures, and the reaction equilibrium is favored by lower temperatures. However, carbonyl sulfide (COS) and carbon disulfide (CS_2) hydrolyze more completely at higher temperatures as shown by Fig. 22-10. The first catalytic converter is therefore frequently operated at temperatures high enough to promote the hydrolysis of COS and CS_2; the second and third catalytic converters are operated at temperatures only high enough to obtain acceptable reaction rates and to avoid liquid sulfur deposition and associated catalyst deactivation. A three converter Claus unit will utilize inlet temperatures in the following range: (1) first converter, 450-480°F; (2) second converter, 390-430°F; (3) third converter, 370-410°F.

A temperature rise occurs across each catalytic converter because both the Claus and COS/CS_2 hydrolysis reactions are exothermic. The temperature rise will generally be 80-180°F for the first converter, 25-60°F for the second converter, and 5-15°F for the third converter. Because of heat losses, measured temperatures for the third converter will often show a small temperature drop.

The foregoing is based on using the regular Claus catalyst in all of the converters. Regular catalyst is made of activated alumina (Al_2O_3). The primary function of activated alumina is to increase the rate of the Claus reaction (Eq 22-3) and ensure full equilibrium conversion to sulfur. It also helps hydrolyze the carbon sulfides, COS and CS_2, to H_2S and CO_2 in the first converter (Eq 22-7 and Eq 22-8); but it achieves reasonable hydrolysis only at high temperatures of 600 to 650°F (Fig. 22-10), which reduces the equilibrium conversion to sulfur in the Claus reaction (Fig. 22-2). A catalyst made of activated titania (i.e., titanium dioxide TiO_2) can achieve greater than 90% hydrolysis of the carbon sulfides at temperatures of 600-650°F, and reasonable hydrolysis at lower temperatures where Claus conversion is enhanced. Up to 50% of the sulfur in the plant tail gas can be in the form of carbon sulfides, and therefore titania in the first converter can be a way to achieve higher sulfur recovery. However, titania is very expensive, and can be 10-15 times the cost of activated alumina. Sometimes a combination such as 50-50% activated alumina and titania is used.

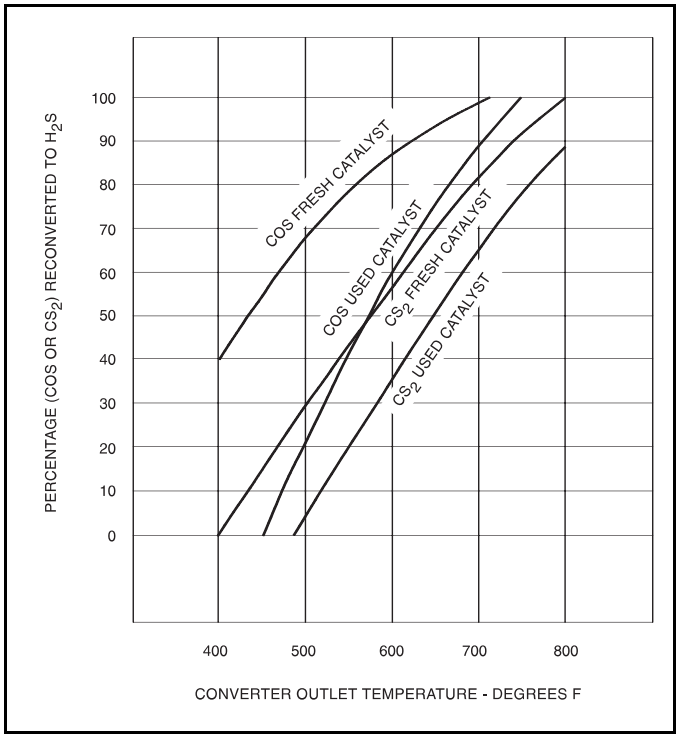
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FIG. 22-10

Hydrolysis of COS and CS_2 with Activated Alumina Catalyst in Sulfur Converter

$COS + H_2O = H_2S + CO_2$

$CS_2 + 2\ H_2O = 2\ H_2S + CO_2$



When this is done, the titania should be placed in the bottom of the bed to protect it from contamination.

MECHANICAL CONSIDERATIONS

Combustion Operation

Combustion is carried out in the reaction furnace which may be either external (separate from waste heat recovery facility) or internal (combined with waste heat recovery facility). At the normal operating temperature of 1800-2500°F, external furnaces require a refractory lining to protect the steel shell, but with internal furnaces, the burner is surrounded by the cooling medium and refractory is not required. For small Claus units, an internal furnace is less expensive. For units larger than about 30 LTD, an external furnace is usually more economical.

Reaction furnaces are designed for a residence time of at least 0.5 seconds; plant tests indicate this is adequate to reach equilibrium. Feed gases richer in H_2S generally require less residence time than leaner feeds.

The refractory in the external reaction furnace serves to resist the high flame temperatures and to protect the steel shell. Refractories capable of withstanding high temperatures normally have a high alumina content, e.g., 85-90% alumina. However, these refractories have relatively poor insulating properties and will not provide adequate protection for the steel shell. Therefore, an insulating refractory layer is normally placed against the steel shell, and a layer of high alumina refractory covers the insulating refractory. Occasionally, three different refractories have been used in reaction furnaces. (See Section 8 for additional information regarding refractories.)

Refractory selection and design is important because the steel shell can be overheated (above 650°F) resulting in direct sulfide (H_2S) attack, or can be cooled below the dewpoint of SO_2 and SO_3, resulting in acid condensation and rapid corrosion. External insulation or shrouding for personal protection is often installed to allow metal temperatures above about 400°F, which is generally safely above the acid dewpoint.

Interior refractory checker walls are sometimes installed in external-type reaction furnaces to improve mixing and to serve as a heat buffer. This is of greater importance if ammonia or cyanides or high concentrations of hydrocarbons are present in the feed gas.

Waste Heat Recovery Operation

For most internal reaction furnace-type waste heat recovery units, the acid gas burner is installed inside a single, large, first-pass firetube (radiant section) and the process gas then flows through one or more additional tube passes (convection section). The first pass firetube is cooled externally and therefore does not require refractory protection; however, pass plates and other uncooled metal surfaces exposed to the process gases at temperatures above about 650°F should be protected with refractory. Tube sizes for the convection section passes range from 1" to 6" with a tube mass velocity of 2-5 lb/(sec • ft^2).

External reaction furnace-type waste heat recovery units are usually single pass exchangers with small tubes (2"-3"). The inlet ends of these tubes are exposed to the hot combustion gases (and possibly to the flame). To ensure a reasonable tube life, the inlet end of each tube is protected by inserting a ceramic ferrule that extends about 3"-6" beyond the inside of, and about 3" outside of the tube sheet. This prevents the hot gases from directly contacting the tube at the critical junction of tube and tubesheet. These ceramic ferrules should also be wrapped with a thin layer of insulation (1/8"-3/8" thick). The inlet tube sheet should be protected by a refractory overlay, usually about 3" thick.

Waste heat recovery units are usually designed to meet pressure containment requirements according to Section I of the ASME Code rather than to TEMA standards. A two-pass tube welding procedure is normally used. Conventional practice is to apply the first-pass weld before tube rolling (or after a light rolling), which allows venting to eliminate gas traps. The first-pass weld is usually pressure tested to locate all weld pinholes for repairing prior to subsequent tube rolling and final welding. After final welding, the completed tube attachment is lightly rolled. During the final hydrotest, the tube weld surfaces should be inspected with a dye-penetrant test.

Tube sizes range between 2" and 6". Tube spacing is based on a minimum ligament (distance between outer edge of each tube) dimension of 0.75"-1.0". The design mass velocity in these tubes ranges between 1.0 lb/(sec • ft^2) and 8.0 lb/(sec • ft^2). For most installations, the tube mass velocity will be 2 to 5 lb/(sec • ft^2). Allowable tube side pressure drop often determines tube velocity.

Both kettle-type and natural circulation-type waste heat boilers are used as horizontal units to ensure total submergence of the tubes.

The advantages of the natural circulation-type unit which has a separate elevated steam disengaging drum, include:

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- Improved steam quality because of surface blowdown capability and more sophisticated steam/water separation devices.
- More water holdup above the hot process tubes which provides additional time to react to emergency conditions and lessens the chance of tube failure from overheating.
- Better steam/water circulation at the critical tube/tubesheet junction.

The advantages of the kettle-type boilers include:

- Lower installed cost
- Ability to handle a much wider range of load conditions

Both kettle-and natural circulation-type waste heat boilers should be considered as severe-service applications. Some early boilers were designed to TEMA standards and the resulting thick tubesheets together with the high heat flux resulted in failures at the tube-tubesheet juncture.

The tubesheet design is based upon the thermal, mechanical stresses at the tube-tubesheet attachment. Tubesheets are usually thin (3/4" to 1-1/2") resulting in acceptable temperature profiles at the tube weld, the ligaments between tubes, and the portion of tubesheet not cooled by water. The deflection of these thin tubesheets during operation reduces the stress transmitted to the tube-tubesheet attachment. Natural circulation-type units have tube patterns arranged to accommodate the bending stress at the pattern's outer boundaries, while kettle-type units have stayrods to stiffen the portions of the tubesheet without tubes. Waste heat boilers utilizing flexible, thin tubesheets have extremely good service histories.

Sulfur Condenser Operation

Sulfur condensers may be single pass or multi-pass units. Both natural circulation- and kettle-type condensers are used; horizontal units are recommended. Condensers are designed with a minimum tube diameter of 1". Normally 12 BWG steel tubes are used, installed with a 1/2" to 3/4" ligament between tubes.

Sulfur condensers operate at much lower heat fluxes than waste heat boilers and usually operate at lower shell side pressures. Both of these factors significantly reduce the mechanical design requirements for tubesheets and tube attachments. Sulfur condensers are designed to meet either ASME Section I or Section VIII Codes. Tubes are typically rolled, seal welded, and re-rolled.

The design mass velocity for the sulfur condenser tubes varies from 3.0 lb/(sec • ft^2) to 8.0 lb/(sec • ft^2) with a typical minimum mass velocity at design conditions of 5.0 lb/(sec • ft^2). The design mass velocity should be sufficiently high to prevent sulfur fogging from occurring during turndown conditions.[21] If sulfur fogging does occur, the liquid sulfur will not adequately separate from the process gas in the separator downstream of the condenser. The tube velocity is also limited by the allowable tube side pressure drop, which is usually about 0.3 to 0.5 psi.

Sulfur condensers are subject to plugging with solid sulfur. In the design of the plant piping system, the condensers should be the low points in the system and should also slope toward the outlet end. This allows any liquid sulfur present upstream of the condenser, as well as that formed in the condenser, to drain into the liquid-vapor separator chamber and out through the sulfur drain.

To allow access to the tubes for cleaning and inspection, sulfur condensers should have inspection ports and manways at both ends. Additional access to the tubes should be provided by using bolted cover (end) plates.

Vapor-liquid separator chambers are installed downstream of the sulfur condensers to separate the liquid sulfur from the process gases and to allow the liquid sulfur to drain from the system. These separator chambers can be integral parts of the condenser or separate vessels and may be provided with wire-mesh type mist eliminators or impingement plates to reduce liquid sulfur entrainment. A superficial gas velocity of 20-30 ft/sec is commonly used as a basis for sizing the separator chambers.

Sulfur condensers are usually designed to generate low pressure (20-100 psig) steam on the shell side. The final sulfur condenser is often used to heat boiler feed water, but care must be taken not to over cool the stream and solidify sulfur. Sometimes 15 psig steam is generated, condensed and returned in a closed circuit.

Reheating Operation

Hot Gas Bypass Method — Piping and valves are usually of stainless steel (although sometimes refractory-lined piping is used) in order to handle the hot (900-1200°F) corrosive process gas. An additional valve is sometimes installed in the process stream downstream of the hot gas bypass extraction point in order to improve turndown capability.

Direct (Inline Burner) Method — Inline burners are usually designed to raise the temperature of the process gas at least 50°F above the normal operating inlet temperature of the catalytic converter. This extra heat release capacity is useful during a "heat soak" or catalyst rejuvenation operation. Usually, a portion of the acid gas is burned in the inline burner; however, other fuels, such as natural gas, can be used. The burner is installed in a refractory lined combustion chamber and the hot combustion gases are mixed with the process gas to reach the reactor inlet temperature. The retention time in the mixing chamber is usually between 0.1 and 0.3 seconds.

Indirect (Heating Exchanger) Method — Heat exchangers used for reheating are normally constructed to the same mechanical requirements as sulfur condensers. These exchangers should slope toward the inlet end so any liquid sulfur present can drain back into the liquid-vapor separator located downstream of the upstream sulfur condenser.

Catalyst Converter Operation

Catalytic converters are usually designed for a flow at operating conditions of 700 to 1400 standard ft^3/hr of process gas per cu ft of catalyst bed. Because of pressure drop considerations, this usually results in a bed depth of 3-5 feet. The catalyst is activated alumina (Al_2O_3) or promoted activated alumina which is installed on top of a 3"-6" thick layer of more dense support material. Catalyst density is about 45-53 lb/ft^3; the support medium, which usually has a density of 84-100 lb/ft^3, reduces migration of catalyst and/or catalyst fines from the reactor bed to the sulfur condenser downstream. These catalyst fines can plug the sulfur drain legs and condenser tubes. The catalyst and support material are installed on top of stainless steel wire screens which are tied to carbon steel grating. A minimum of 3" of the support material may be placed on top of the catalyst bed to serve as a gas flow distributor.

For Claus units smaller than about 100 LT/D, the catalyst beds are frequently installed in a single horizontal vessel, with internal partition plates. For larger units, individual catalyst bed vessels are used. Vertical (stacked) beds are sometimes

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used but this is usually not economical for units smaller than about 800 LT/D. Internal refractory lining of these vessels is not necessary unless it is planned to regenerate the catalyst in place; in this case the grating floor design must also be adequate for the expected elevated temperatures. If internal refractory is not used, a minimum of 3" external insulation is recommended. If a refractory lining is installed, the outside insulation thickness can be reduced to 1"-2". Most converters have internal refractory from the bottom to about 6" above the top of the catalyst bed, which protects against high-temperature upsets.

Nozzles in the bottom of the catalyst bed vessels should be installed flush with the vessel interior.29

Piping

The piping systems in Claus plants which require special attention are liquid sulfur lines and vapor process lines. Since sulfur freezes at about 245°F, liquid sulfur lines must be adequately heated and insulated. Process lines are also insulated to prevent sulfur from condensing and/or desubliming to the solid form and to keep the metal temperature above the dewpoints of sulfurous/sulfuric acids. Process lines operating at temperatures above 650°F are often lined with refractory or, especially in smaller units, are of stainless steel. Vapor process piping must also have proper allowance for thermal expansion. Either convoluted expansion joints or expansion "loops" are used. Convoluted joints should be constructed of series 300 stainless steel, and insulated to prevent either water and/or sulfur condensation. The expansion joints should be installed in vertical pipe runs so, if condensation does occur, the liquid can drain freely. If liquid sulfur does not drain, it could solidify, causing the convolutes to be inoperable. Undrained water results in corrosion because of the acids formed.

Carbon steel process piping is normally adequate. Because a Claus plant operates below 15 psig pressure, schedule 40 pipe is normally used for small lines. For 14" or larger lines, standard weight pipe is adequate. For process lines over 30" in diameter, the piping thickness can be the same as the catalyst bed vessel walls.

Valves should be steel and fully jacketed. Smaller valves usually have integral jackets; large valves may have fabricated jackets. Valves in liquid sulfur service should be full-opening gate or plug type to permit rodding out. Liquid sulfur normally drains by gravity from the condensers into a sulfur collection pit or storage vessel with a liquid sulfur seal on each drain line to prevent gases from escaping to atmosphere. Sulfur drain lines often include both horizontal and vertical sections of piping. Because of potential plugging of these lines, facilities should be installed to clean-out (usually by rodding) these lines to prevent a plugged sulfur drain from causing premature unit shutdown. As shown in Fig. 22-11, these "rodding-out" facilities usually include both horizontal and vertical crosses at each change in piping direction. The crosses are often equipped with external valves. Valves are also often placed in the horizontal sections of the sulfur drain lines to allow easy cleaning of these segments, either mechanically or with steam, while the unit continues to operate.

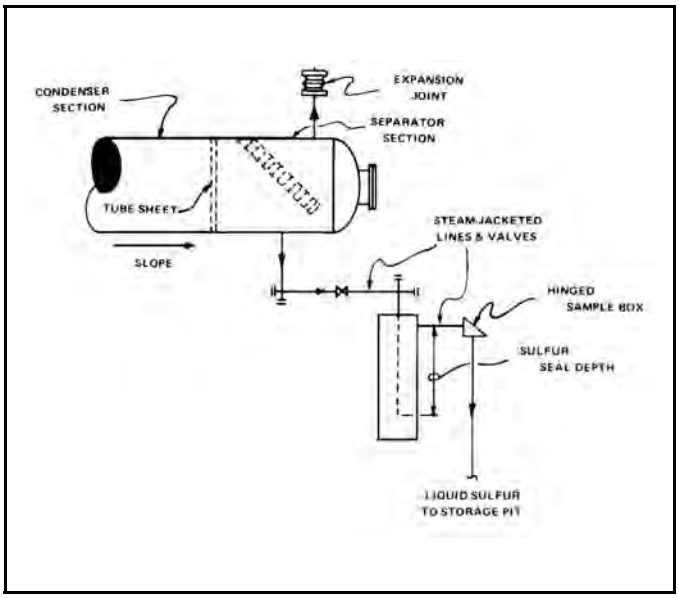
Each sulfur liquid/vapor separator should have a separate drain line and sulfur seal to facilitate detection of plugging. Each sulfur seal should be equipped with a sight port (oriented away from sidewalks, etc.) so the sulfur draining into the storage pit can be observed. When the flow of liquid sulfur stops, remedial action can be taken to eliminate the restriction or plug so as not to cause additional damage to the plant.

Steam-jacketing is the preferred method of heating liquid sulfur lines. Internal (gut) steam lines are sometimes used, especially for longer lines. Skin Effect Current Tracing (SECT) which utilizes the skin effect phenomenon exhibited when an alternating current passes through a steel pipe has also been used to heat long pipelines. For short lines, steam tracing may be satisfactory. Steam is the most common heating medium, but hot oil can also be used. The liquid sulfur lines should be designed to maintain the sulfur at a minimum temperature of 280°F which corresponds to a steam pressure of at least 50 psig. High pressure steam (above 100 psig) or superheated steam should normally not be used because of the possibility of heating the sulfur into the highly viscous region. (Fig. 22-15)

Since the liquid sulfur is used as a seal to prevent process vapors from being vented to the atmosphere, the "net" liquid column head must be large enough to withstand the maximum expected operating pressure. For most plants this maximum operating pressure is the same as the air blower maximum discharge pressure. The density of liquid sulfur is about 112 lb/ft^3, so for a 10 psi seal, the required "net" sulfur seal depth is 12.8 ft. Minimum safety factors would require at least a 13.0 ft. seal depth, and often an extra 6"-12" is added to the calculated depth to allow for upsets, lower sulfur density, etc.

FIG. 22-11

Typical Relationship of Sulfur Seal and Drain



CLAUS UNIT TAIL GAS HANDLING

The tail gas from a Claus unit contains N_2, CO_2, H_2O, CO, H_2, unreacted H_2S and SO_2, COS, CS_2, sulfur vapor, and entrained liquid sulfur. Because of equilibrium limitations and other sulfur losses, overall sulfur recovery efficiency in a Claus unit usually does not exceed 96-97%. Venting of this tail gas stream without further processing is seldom permitted; the minimum requirement is normally incineration, the principal purposes of which are to reduce H_2S concentrations to a low level (which value will depend on the local regulations) and to provide the thermal lift for dispersion of SO_2 upon release to atmosphere through a stack. Depending upon the size of the Claus unit, the H_2S content of the feed gas, and the geographi-

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cal location, a tail gas cleanup process may be required in order to reduce emissions to the atmosphere.

Incineration

Incineration of the H_2S (as well as the other forms of sulfur) in the Claus plant tail gas to SO_2 can be done thermally or catalytically. Thermal oxidation normally is carried out at temperatures between 900°F and 1500°F in the presence of excess oxygen. Most thermal incinerators are natural draft operating at sub-atmospheric pressure with air flow controlled with dampeners; the excess oxygen level varies between 20% and 100%. A typical concentration of oxygen in the stack effluent is 2.0%. Although the Claus unit tail gas contains some combustibles — for example, H_2S, COS, CO, CS_2, H_2, and elemental sulfur (in the case of "split-flow" plants, some hydrocarbons) — these combustibles are at too low a concentration to burn since they generally amount to less than 3% of the total tail gas stream. The entire tail gas stream must therefore be incinerated at a high enough temperature for oxidation of sulfur and sulfur compounds to SO_2.

Incinerator fuel consumption can be reduced significantly by utilizing catalytic incineration. This involves heating the tail gas stream to about 600-800°F with fuel gas and then passing the heated gas along with a controlled amount of air through a catalyst bed. Catalytic incinerators are normally forced draft, operating at a positive pressure in order to maintain closer control of excess air. Catalytic incineration is a proprietary process which should be considered where fuel costs for conventional (thermal) incineration are high.

Another method of improving overall fuel economy involves recovering heat from the incinerator outlet gases. Saturated steam at pressures ranging between 50 psig and 450 psig has been produced, and saturated steam has been superheated, using waste heat from the incinerator outlet gases. The effect of lower emission temperature upon dispersion of the outlet stream, and therefore upon the required stack height, must be considered in evaluating this alternative. Incinerators with waste heat recovery are normally forced draft operating at a positive pressure.

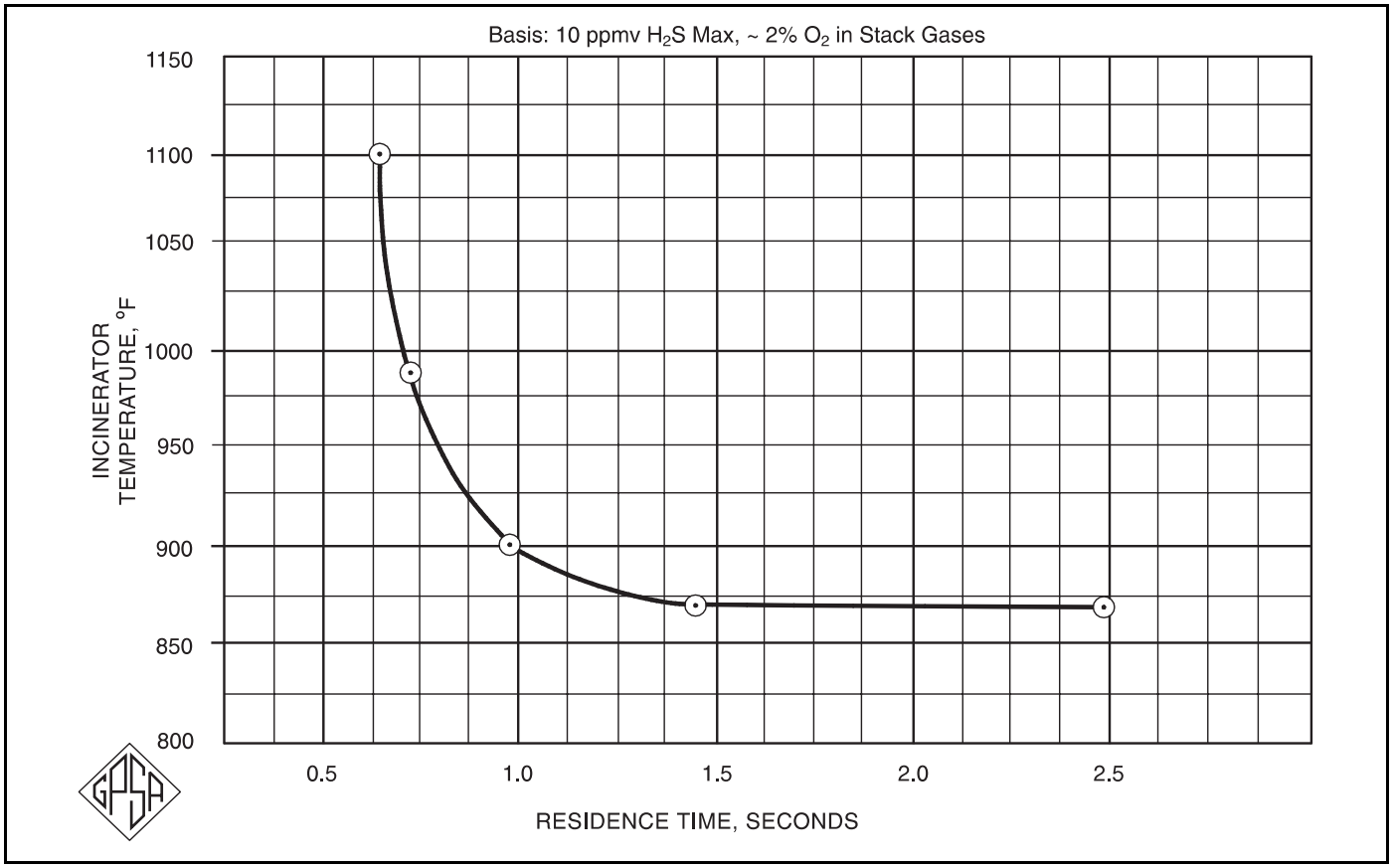
Fuel required for thermal incineration is determined by the amount of heat needed to heat the Claus tail gas, air, and fuel to the required temperature. Normally the incinerator is sized for at least 0.5 second residence time, and sometimes for as much as 1.5 seconds residence time. Generally, the longer the residence time, the lower the incinerator temperature needed to meet the environmental requirements. This is illustrated by Fig. 22-12 which shows the relationship between residence time and temperature for a typical installation to meet a maximum H_2S requirement of 10 ppmv.

The incinerator and stack can sometimes be combined into a single vessel. The incinerator is the enlarged base, and the smaller diameter stack is mounted on top of the incinerator. The burner is normally mounted horizontally in the side of the incinerator. The tail gas is sometimes fed through the burner, but it can also be fed into the incinerator adjacent to the burner.

Both the incinerator and stack are refractory lined to protect the steel from the high temperatures. This refractory is not as

FIG. 22-12

Typical Relationship Between Incinerator Residence Time and Required Temperature



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elaborate as that used for the reaction furnace at the front of the Claus unit, because of lower operating temperatures. The incinerator is normally designed for a maximum operating temperature of 2000°F. Refractories rated as low as 2200°F have been used in incinerator-stack installations; one layer of refractory is generally sufficient. The refractory is usually an insulating castable rated for service conditions of 2200°F or above, except where flame impingement is anticipated. A high alumina castable (above 60% alumina) is used in the area of flame impingement.

For vertical incinerators installed at the base of the stack, protection for the incinerator steel floor is important. The best method to protect the floor is to allow for ambient (cooling) air circulation below the floor even though the floor is refractory lined. If there is no cooling below the floor, or if the space is too restricted (too close to grade), the floor refractory usually will not provide adequate protection.

The steel components (floor, walls, stack shell) should be kept below 650-700°F and above 300°F. This requires careful design of both the inside refractory lining and outside insulation. Normally the refractory thickness to protect the incinerator shell (either vertical or horizontal type) will be between 2" and 4", with an average of about 3". The incinerator floor on the vertical style units normally has refractory thicknesses ranging between 4" and 6".

The incinerator and stack should be insulated on the outside to prevent low shell temperatures. This insulation can be in the form of an air gap (usually 3"-4") with either a stainless steel or aluminum sheathing, or can be a thin (1" thick) layer of blanket type insulation covered with either an aluminum or a stainless steel overlay. Care should be taken not to over-insulate because overheating of the steel shell can then result.

Another method of handling potential corrosion of the outside shell of the stack is to make the most critical section of the stack (say the top 15 ft) of unlined and uninsulated stainless steel.

Stacks can be designed as free-standing, guyed, or derrick-supported structures. Selection of the type of stack is dictated by the required stack height diameter and by windload and/or seismic criteria for the particular installation site. A guyed stack is often the most economical design; however, this requires plot space for guy anchors and cables. A free standing steel stack is a common design for heights not exceeding 250 ft. Stacks taller than about 350 feet are usually derrick-supported steel stacks or are free-standing, reinforced concrete stacks. Typical design stack velocities are between 40 ft/sec and 100 ft/sec with allowable pressure drop generally determining the design stack velocity.

Most governmental air control bodies (federal, state, and/or local) require that the emissions from the incinerator-stack system be monitored on a periodic basis. In some areas, stack emissions must be monitored and recorded continuously. The stack should therefore be equipped with platforms, sample nozzles, and utilities located at an appropriate elevation. These design details are specified in current state or Environmental Protection Agency regulations. This equipment permits a periodic measurement of the stack flow rate and stack gas composition, which can be used to determine a reasonably accurate emission rate. Atmospheric emissions usually are expressed in total lb/hr of sulfur dioxide, or expressed as SO_2 concentration in ppmv reported on a water and oxygen free basis. The detailed stack sampling procedures are covered in EPA or state and/or local regulations and procedures.

Where continuous monitoring is required, stack gas analyzers (which measure the amount of SO_2 in the stack gas) are installed on the stack. These instruments are often coupled with a flow measuring instrument so there is a continuous record of both the flow and SO_2 content of the stack gas. This allows the total daily emission level to be determined.

Tail Gas Clean-up Processes

Fig. 22-13 is a summary of some of the available Claus tail gas cleanup (TGCU) processes, not all of which are proven commercially. All of these processes fit roughly into four categories:

- Processes based primarily on the continuation of the Claus reaction to produce additional sulfur under more favorable equilibrium conditions than normally found in the Claus units, either through operation at temperatures below the sulfur dewpoint or in the liquid phase at a temperature above the melting point of sulfur.
- Processes based on converting all the sulfur components in the tail gas to SO_2 and recovering the SO_2 for further processing.
- Processes based on converting all the sulfur in the Claus unit tail gas to H_2S, then recovering sulfur from this H_2S.
- Processes that directly oxidize the tail-gas H_2S to sulphur.

Continuation Processes

The dry-bed subdewpoint processes include CBA (Cold Bed Adsorption) of the United States, Clinsulf of Germany, MCRC (Maximum Claus Recovery Conversion) of Canada, and Sulfreen of France. Generally, the licensors of these processes report sulfur recoveries of 99-99.5%. The processes have not been widely used in the U.S. because the attainable sulfur recovery level will seldom meet local air quality requirements. Incineration of the residue gas is still required and the stack gases from tail gas treaters of this type generally contain 1200-2000 ppmv SO_2.

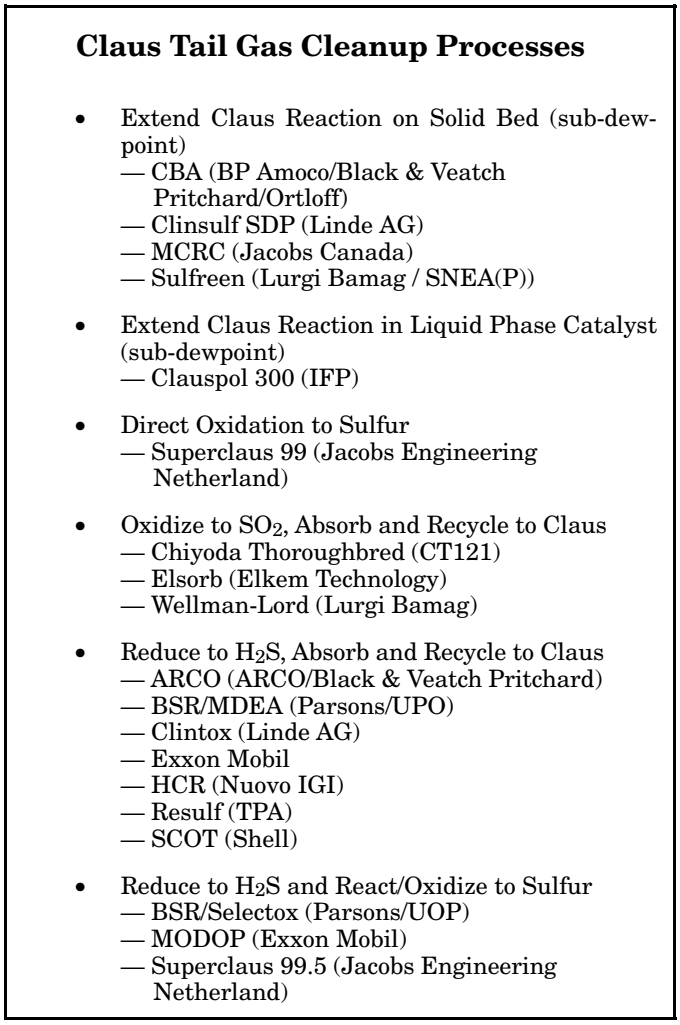
The IFP process Clauspol II continues the Claus reaction also at subdewpoint, but in the presence of a catalyst containing liquid solvent, which is fed counter-currently with the incoming Claus tail gas in a packed tower. The process operates above the melting point of sulfur so the product sulfur is recovered as a liquid. Any liquid and vapor sulfur present in the Claus tail gas is also recovered. IFP reports sulfur recoveries to 99.8%.

A typical subdewpoint sulfur plant will resemble a conventional Claus plant in the process flow through the waste heat boiler, the first catalytic converter, the first condenser, and the first reheat unit. At this point in the process flow, the subdewpoint plant differs significantly from the conventional Claus plant and the different subdewpoint processes (CBA, Clinsulf, MCRC, and Sulfreen) differ in the downstream process sequencing. Generally one converter in the subdewpoint plants is operating below the dewpoint temperature of sulfur. Other converters may be operating in a cooling or in a regeneration mode. Bed switching is a common feature of these plants so the subdewpoint bed is regenerated periodically. The subdewpoint catalytic converter temperature means a significantly higher equilibrium constant for the Claus reaction, thus resulting in less unreacted H_2S and SO_2 in the tail gas. Like the IFP process, close control of the H_2S:SO_2 ratio is essential for effective subdewpoint operation; and any COS and CS_2 present in process gas pass through to the plant tail gas incinerator.

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FIG. 22-13

Claus Tail Gas Clean Up Processes



Although the principles of the dry-bed subdewpoint processes are similar, each process claims to have unique and desirable features. The licensors of these processes should be consulted for details.

SO_2 Recovery Processes

The SO_2 recovery processes involve incineration of the Claus tail gas as the first step. This converts essentially all the forms of sulfur to SO_2.

- The Wellman-Lord Process involves using a basic solution to absorb the SO_2 which is generally recovered from the solution as essentially pure SO_2. This SO_2 is available as a liquid or a vapor.
- For small Claus units, a solution of NaOH may be used to scrub SO_2 from the incinerator outlet stream; the resulting sulfite solution after further oxidation to sulfate with air (or another oxidizing agent such as hydrogen peroxide) can be disposed of underground or at an approved disposal facility.

H_2S Recovery Processes

In these processes, essentially all forms of sulfur in the Claus tail gas are converted to H_2S by hydrogenation and hydrolysis. The Beavon-Stretford process then recovers elemental sulfur directly from the H_2S in this tail gas stream in a Stretford unit. The ARCO (Atlantic Richfield), BSR (Beavon Sulfur Removal)-MDEA, Exxon, Resulf and SCOT processes remove the H_2S using an amine solution that is selective for H_2S over CO_2. The H_2S and any coabsorbed CO_2 from the regenerated solution are recycled to the front end of the Claus unit.

BSR-Stretford can reduce the H_2S content in the absorber off gas to 10 ppmv. Generally the amine-based processes (i.e., SCOT et al.), using generic amines such as MDEA without additives, are limited to about 100-150 ppmv. However, using proprietary amines (such as Dow's GAS/SPEC, Exxon's FLEXSORB SE, Shell's SCOT-LSS or Union Carbide's UCARSOL HS 102), these processes can also achieve 10 ppmv H_2S. All of these processes result in overall sulfur recovery in excess of 99.9%. BSR-MDEA was developed by Parsons and Unocal (Unocal's version sold to UOP), SCOT by Shell, and Resulf by TPA.

Direct Oxidation Processes

MODOP (Mobil Oil Direct Oxidation Processes[27]) and SUPERCLAUS 99 and 99.5[28] are Claus TGCU processes that include air oxidation of tail gas H_2S to sulfur using special catalysts. In MODOP, all forms of sulfur in the Claus tail gas are converted to H_2S in a sulfur-reduction (i.e., hydrogenation/hydrolysis) unit. Cooling of the reduction-unit effluent includes direct contact with recirculating water which reduces the water vapor in the effluent to about 5-9%. The effluent combines with air, and enters a MODOP reactor where the H_2S is selectively oxidized to sulfur with the aid of titanium-dioxide catalyst. The prior removal of water vapor in the reduction unit increases the conversion to sulfur. MODOP can achieve 99.5% overall recovery by using three Claus stages followed by sulfur reduction and one MODOP stage, or by using two Claus stages followed by sulfur reduction and two MODOP stages.

SUPERCLAUS 99 does not include a sulfur-reduction unit. Claus tail gas is reheated and mixed with Claus-blower air, and is processed in a SUPERCLAUS reactor employing a proprietary catalyst. SUPERCLAUS 99 achieves up to 99% recovery depending upon the quality of the acid gas and whether there are two or three Claus converters. SUPERCLAUS 99.5 does include a sulfur-reduction unit, and can achieve an overall sulfur recovery of 99.5%. Its description is similar to the MODOP description; however, direct-contact cooling of reduction-unit effluent, with the associated water-vapor removal, is unnecessary because water does not impede SUPERCLAUS catalysis.

Final selection of a tail gas treating process should consider the applicable pollution regulations, initial investment, long term (continuing) operating costs, and the operating advantages and disadvantages of each process. Since these tail gas treating processes are proprietary, the process developer or a contractor authorized to design and install these systems should be consulted for more definitive information.

Liquid Redox

Liquid redox sulfur recovery processes all share the following major operations:

- Removal of the acid gas, H_2S, from a gas stream by absorption into an alkaline solution to form the ions S^{--} and $2H^{+}$;

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- Conversion (i.e. oxidation) of the S^{--} to elemental sulfur (S°) by the action of a redox reagent (i.e. catalyst) such as iron attached to a legend (also called chelant)(i.e. $Fe^{+++}L$) which keeps the iron in solution:

$$S^{--} + 2H^{+} + 2Fe^{+++}L \rightarrow S^{\circ} + 2H^{+} + 2Fe^{++}L$$

The reagent is said to be "spent" and the iron "reduced."

- Separation and recovery of solid sulfur. Depending on the regeneration process, this may precede or succeed the next step.
- Regeneration of the spent redox reagent (i.e. $Fe^{++}L$) by reacting it with oxygen dissolved in the solution:

$$^{1}/_{2}O_2 + 2H^{+} + 2Fe^{++}L \rightarrow H_2O + 2Fe^{+++}L$$

The iron is said to be "oxidized."

Thus the reagent is reduced as it converts H_2S to sulfur and is oxidized as it is regenerated with oxygen/air, and hence the term "redox."

Redox processes can remove and convert to sulfur up to 99.9% of the H_2S in sour natural gas and acid gas. Their turndown capabilities are very good, and they can be designed for large variations in H_2S concentrations. However, the sulfur color is a brown/tan yellow rather than the bright yellow produced in Claus plants. The redox solutions are corrosive, and much of the equipment must be alloy or coated. Also, chemical consumption can be high, and disposal of spent chemicals can be a problem. The solution must usually be analyzed daily with addition of chemicals.

Nevertheless, redox can be considered for various combinations of the following:

- Natural gas or acid gas containing less than 20 t/d of sulfur.
- Sour natural gas for which CO_2 does not have to be removed.
- Acid gas with very low concentrations of H_2S.

Established redox processes include the following:

- Stretford licensed by British Gas, uses a vanadiam redox reagent.
- ARI-LO-CAT II licensed by Wheelabrator Clean Air Systems, SulFerox licensed by Dow, and Sulfint licensed by IFP. All employ iron redox reagents.

Oxygen Enrichment in Claus Plants

Oxygen enrichment refers to enrichment of the oxygen in a Claus furnace reaction. The objective is to increase the sulfur processing capacity of an existing Claus train (or trains), and thereby avoid having to build an additional train. The concept is to use oxygen-enriched air to a Claus reaction furnace instead of regular air as the carrier of the reactant, oxygen. This reduces the amount of inert nitrogen and therefore the process gas, and increases the acid-gas processing capacity. It also reduces the tail gas rate and therefore the incinerator fuel-gas requirements. If the concentration of H_2S in the acid gas is high, however, the design temperatures of an existing reaction furnace and waste-heat boiler can limit the degree of oxygen enrichment, and this has to be designed for. As well, any part of the plant that must handle an increased sulfur rate must be checked for adequacy. Reference 29 presents a comprehensive checklist for this purpose.

Oxygen enrichment is achieved by injecting oxygen into the regular air stream or into a burner of special design. The oxygen can be from pressurized-gas storage, an air-separation plant, a pressure-swing adsorption (PSA) process, or liquid storage with a vaporizer. Following is a list of commercial oxygen-enrichment processes and their licensors. The unique feature of each of these processes is the method of limiting the furnace operating temperature. The licensors should be contacted for details.

- COPE (Claus Oxygen-based Process Expansion) by Air Products
- OxyClause by Lurgi
- OxyMax by TPA
- SURE/DCP (Double Combustion Process) by Parsons/BOC

Emerging Processes

The following processes are in the development stage. For details, please refer to the references given.

- PROClaus (Parsons) — A Claus tail gas treatment process employs selective reduction followed by selective oxidation to achieve up to 99.5% overall sulfur recovery.[30]
- CrystaSulf (Radian International) — High-pressure sour gas containing H_2S in the range of 0.2 to 25 LTPD is contacted with a regenerable nonaqueous scrubbing liquid that absorbs the H_2S and converts it to sulfur, which is recovered by solvent cooling and crystalization, and is separated by slurry thickening and filtration. The overall sulfur recovery is 99.9+%.[31]
- CANSOLV (Cansolv Technologies Inc.) — A tail gas cleanup process oxidizes the sulfur compounds to SO_2, absorbs the SO_2 from the tail gas with an aqueous solvent, regenerates the solvent, and returns stripped SO_2 to the Claus reactor. The overall sulfur recovery is 99.9+%.[32]
- SUPER (Calabrian Corporation) — Pure SO_2 or oxygen enhanced SO_2 is injected into the acid-gas burner instead of air to eliminate nitrogen and reduce the gas handling capacity of a Claus plant.[33]

PROPERTIES OF SULFUR

Sulfur is a solid at ambient temperatures; it exists in two octatomic crystalline forms (rhombic and monoclinic) and an amorphous form. Up to about 204°F, rhombic crystals are the stable form; above this temperature and up to its melting point, monoclinic sulfur is the stable variety. Both crystalline forms consist basically of eight-membered rings, but the arrangement of the rings and the interatomic distances are different. Amorphous sulfur is prepared by rapidly chilling liquid sulfur which has been heated to near its boiling point. Amorphous sulfur, which slowly changes to the rhombic crystalline form at ambient temperatures, is also referred to as "rubber" sulfur and its presence is not desired. The approximate density of each solid sulfur form is as follows:

Rhombic	129 pounds/cubic foot
Monoclinic	122 pounds/cubic foot
Amorphous	120 pounds/cubic foot

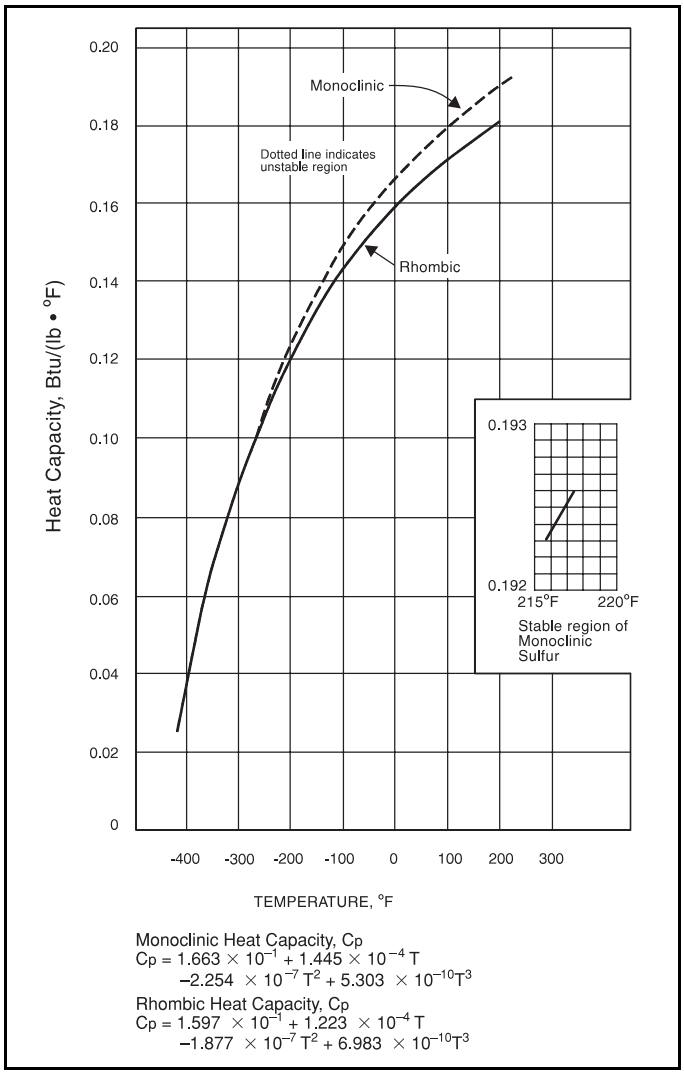
The heat capacity of solid sulfur is shown in Fig. 22-14.

The melting points of solid sulfur range from 235°F for rhombic sulfur to 248°F for amorphous sulfur. Pure crystals of monoclinic sulfur melt at 239.4°F. When melted, sulfur becomes a brownish-yellow, transparent liquid (lambda sulfur),

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FIG. 22-14

Heat Capacity of Solid Sulfur at Constant Pressure[4, 36]



whose molecular structure is also octatomic. As liquid sulfur is heated to about 320°F, the structure of the liquid undergoes an abrupt change; its color becomes a dark reddish brown and its viscosity increases significantly. Long chain polymers, (μ sulfur), exist in equilibrium with octatomic sulfur molecules. Fig. 22-15 shows how the viscosity of pure liquid sulfur changes with temperature and Fig. 22-16 shows how dissolved H_2S affects the viscosity of liquid sulfur. As the temperature is increased above 320°F, the color of liquid sulfur darkens and turns to a brownish-black above 482°F and remains dark up to the boiling point of 832°F. Fig. 22-17 and Fig. 22-18 show how the density and heat capacity, respectively, of liquid sulfur change with temperature. Fig. 22-19 shows the thermal conductivity of liquid sulfur.

Several sulfur molecules are present in the vapor phase, but the principal sulfur species are S_2, S_6, and S_8. Fig. 22-20 shows the distribution of sulfur species as a function of temperature. In sulfur plant vapors, the distribution of sulfur species is similar but not identical to that shown in Fig. 22-20 because of the presence of components other than sulfur. This sulfur species distribution was used to calculate (1) the equivalent vapor pressure of sulfur shown in Fig. 22-21 and (2) the latent heat of condensing sulfur vapors shown in Fig. 22-22. The S_1 equivalent vapor pressure and latent heat curves are convenient to use in process calculations although they may not be rigorous when components other than sulfur are present. The viscosity of sulfur vapors is shown in Fig. 22-23; the heat capacity of sulfur vapors is shown in Fig. 22-24.

SULFUR STORAGE AND HANDLING

Sulfur can be stored and handled as a liquid (at about 280°F) or as a solid (at ambient temperature). A Claus sulfur recovery plant will usually be provided with a rundown tank or pit (which may be either of steel or of acid-resistant concrete) sized for 3-5 days' production. If the sulfur is handled as a liquid, it can be pumped from the rundown tank either directly to tank truck or railroad tank car or to intermediate liquid sulfur storage. If the sulfur is handled as a solid, it is pumped to storage block (where the sulfur is allowed to cool and solidify) or to sulfur-forming facilities such as a flaker, a prilling tower, etc.

Serious environmental and/or safety problems can occur in the handling of liquid sulfur produced in Claus units. As shown in Fig. 22-25, the total solubility of H_2S in liquid sulfur increases with temperature because of the formation of hydrogen polysulfides (H_2S_x). Sulfur is produced in Claus units at temperatures of 280°F to 310°F but in storage, or during transportation, the temperature of the sulfur may drop as low as 260°F. Under these conditions, H_2S is emitted and accumulates in the vapor space above the liquid sulfur.

Concentrations of H_2S exceeding its lower explosive or flammability limit of 3.5 mol % (in air) have been measured in the vapor space of railroad tank cars. Emission of H_2S from liquid sulfur during solid sulfur forming operations can also present serious operating and/or environmental problems.

The H_2S/H_2S_x content of Claus sulfur is dependent on the partial pressure of H_2S in the process stream and the operating temperature. Typical measured concentrations (as H_2S) are as follows:

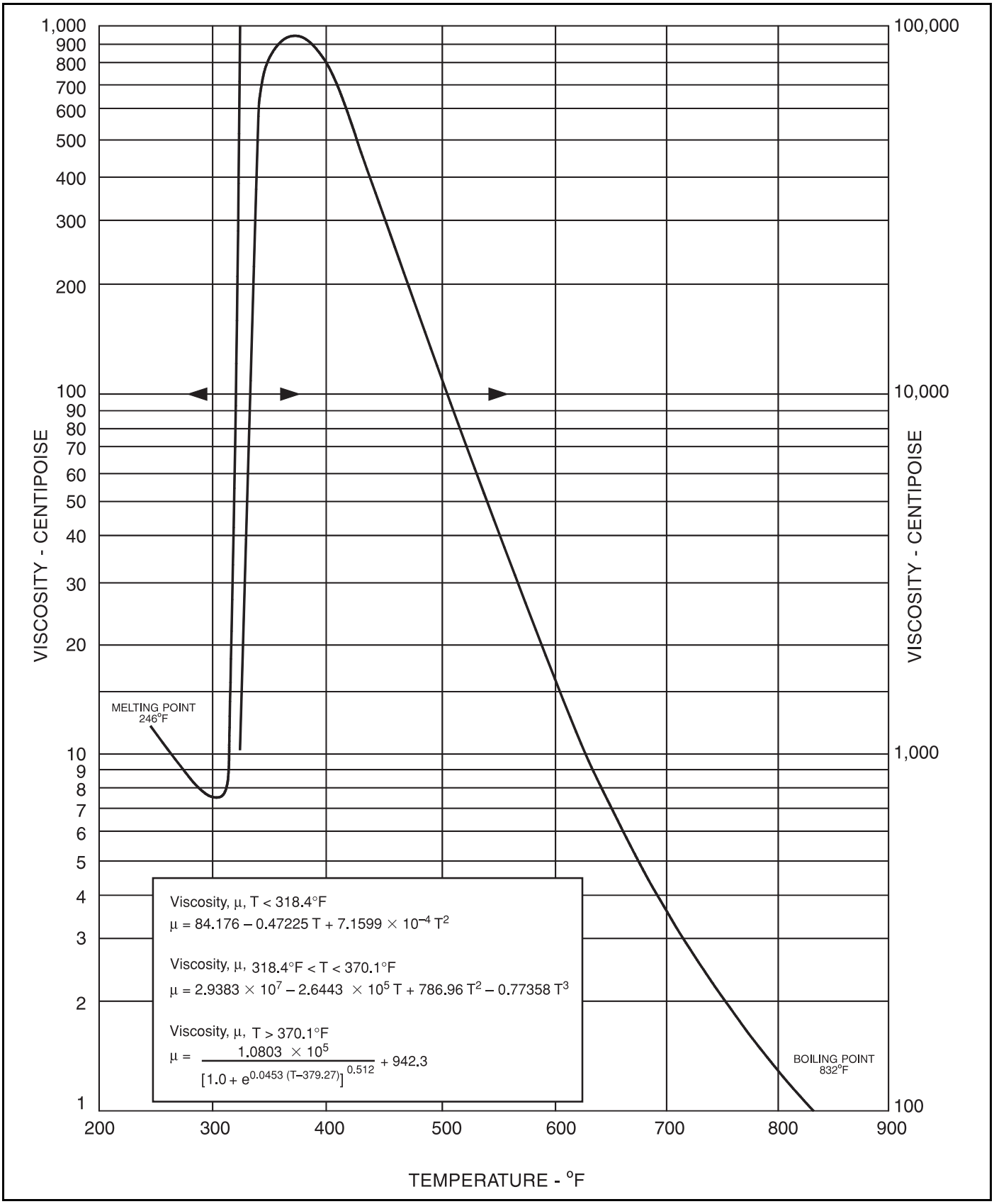
Reference	Ref. 17	Ref. 34
From thermal condenser	500-700	280-630
From first conv. condenser	180-280	90-220
From second conv. condenser	70-110	10-80
From tail-gas coalescer	5-10	NA

These H_2S concentrations are well above values that would be predicted from laboratory chemical-equilibrium and solubility data applied to corresponding temperatures and H_2S partial pressures at condenser outlets.[34] This is particularly true for the thermal condenser (i.e., 200-300%), and to a lesser extent for the first converter condenser. It is believed[35] that this is caused by a combination of two factors. One is sulfur condensation in the waste-heat boiler at temperatures higher than the condenser-outlet temperature, which increases the formation of H_2S_x and therefore the amount of dissolved H_2S. This is feasible because temperatures inside the flow-boundary layers of the waste-heat boiler tubes can be below the sulfur dewpoint temperature. The second factor is a combination of chemical equilibrium, reaction kinetics, and transport phenomena in the condenser tubes, which results in residual H_2S and H_2S_x higher than predicted at the condenser outlet. Thus it is not feasible to predict the amount of residual H_2S and H_2S_x in the sulfur product.

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FIG. 22-15

Viscosity of Liquid Sulfur[12, 36]



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FIG. 22-16

Effects of Hydrogen Sulfide on the Viscosity of Molten Sulfur[12, 18]

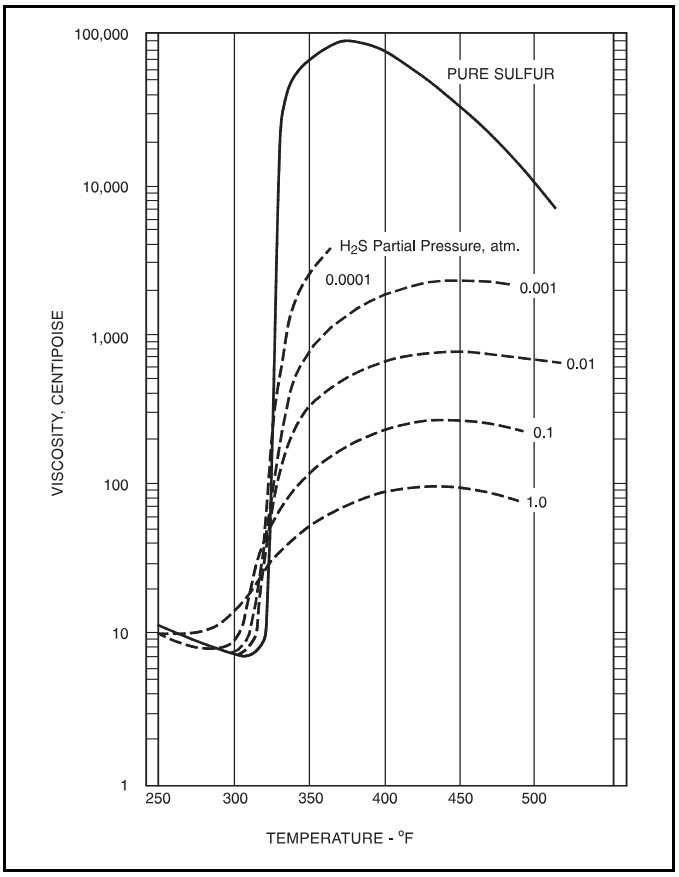
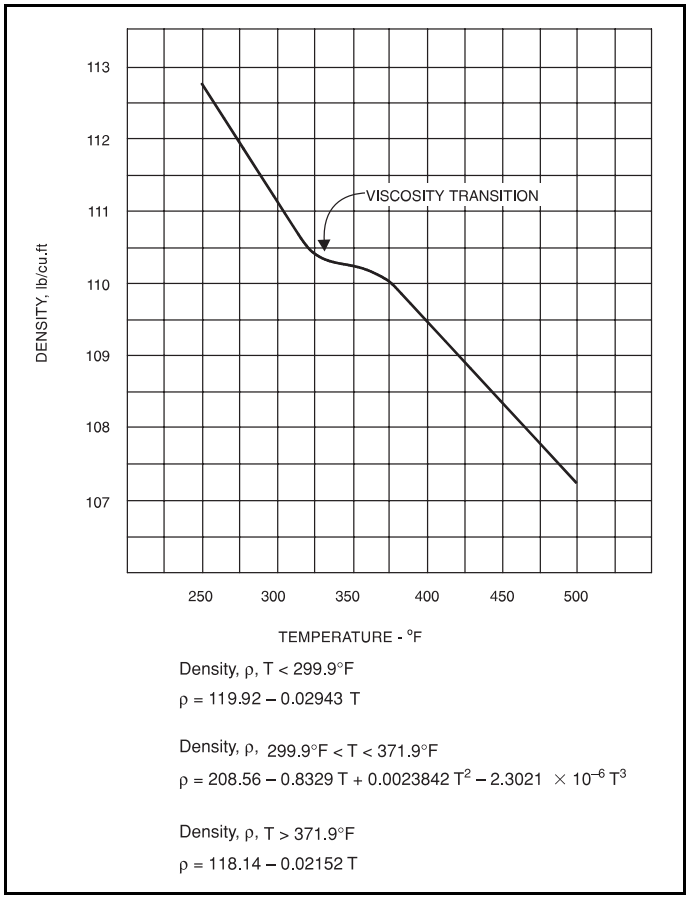


FIG. 22-17

Density of Liquid Sulfur[26, 36]



Degasification facilities handling Claus sulfur are normally designed on the basis of an average value of 250 to 300 ppmw total H_2S.

Tests using railroad tank cars with liquid sulfur containing 7 ppmw, 15 ppmw, and 100 ppmw of total H_2S indicated that 15 ppmw H_2S is the upper limit for safe handling of liquid sulfur and, therefore, degasification facilities should be designed for a maximum of 10 ppmw H_2S.[17, 24] Commercial degasification processes are available from BP Amoco, Elf Aquitaine, Exxon Mobil, Enersul, Shell, and Goar Allison and Associates.

CLAUS PLANT STARTUP AND SHUTDOWN PROCEDURES

Initial Startup

For the initial startup, three important procedures must be followed before putting a Claus sulfur recovery plant in service. These are:

- Curing of all refractory (in combustion chamber, piping, inline burners, incinerator, stack, etc.)
- Cleaning of the waste heat boiler and other steam-producing equipment
- Heating of the catalyst beds and all other equipment to proper operating temperatures

Curing of the refractory, which involves carefully controlled heating, is necessary because, if wet refractory is heated too quickly, the contained water will vaporize too rapidly, damaging the refractory. The manufacturer of the refractory (or refractories) should be consulted regarding suitable curing procedures.

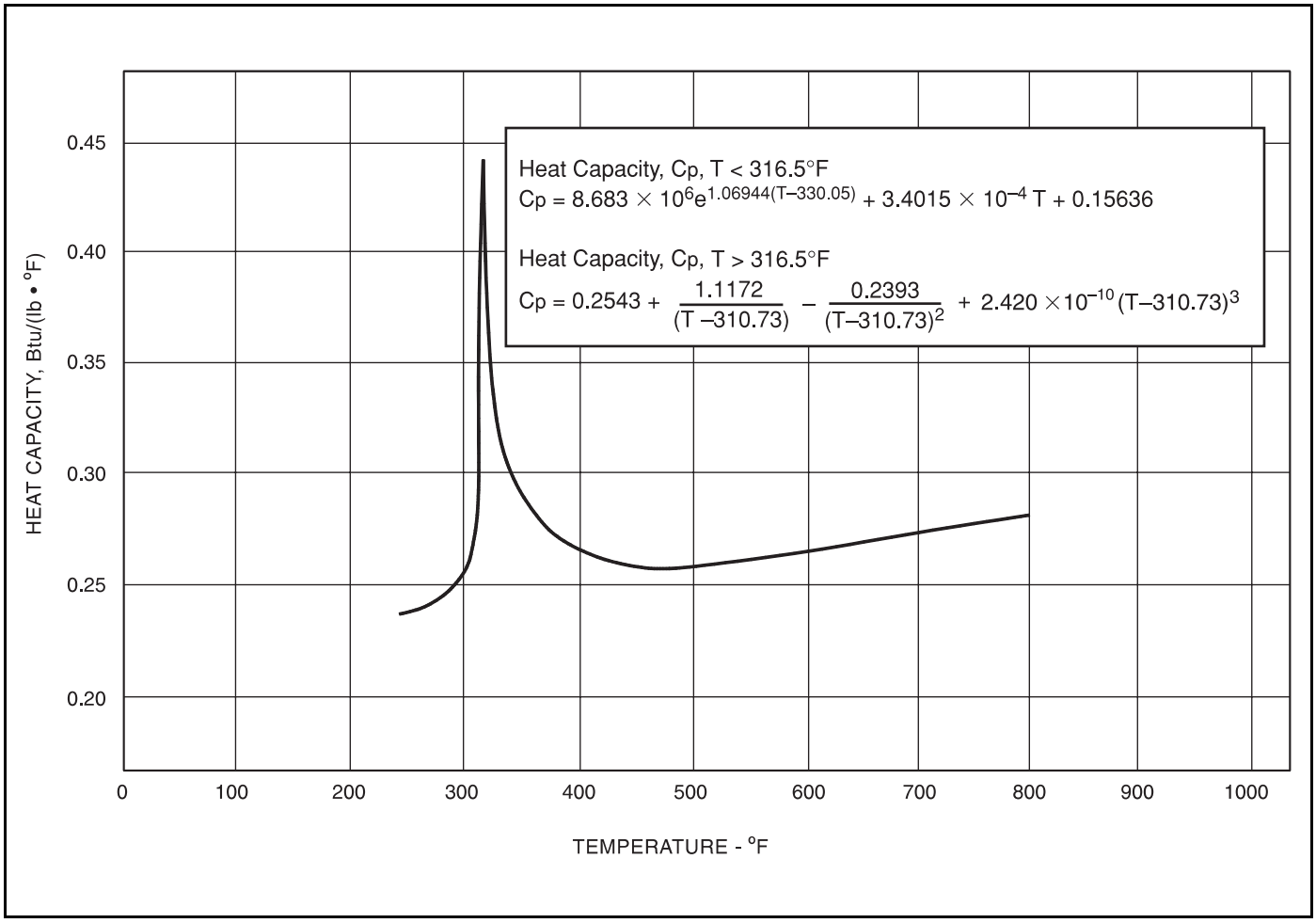
Cleaning of the waste heat boiler and other steam-producing equipment is necessary to remove oil and grease. The equipment can be boiled out with water plus boil-out chemicals (such as sodium hydroxide and sodium carbonate) or it can be cleaned chemically. If a chemical cleaning procedure is chosen, any steam produced during the refractory curing can be fed to the plant steam headers; if a boil-out procedure is followed, any steam produced should be vented to atmosphere. Under either procedure, the steam-producing equipment should be filled with water to prevent tube damage before refractory curing and/or boiling-out are commenced and either the pilot burners or the main gas burners are lit.

Heating the catalytic converters and all other equipment to near normal operating temperatures by burning fuel gas is necessary to prevent condensation of liquid sulfur on the catalyst beds when acid gas is fed to the unit. The pilot burners are lit first and after about 30 minutes, the main burners are used to gradually raise the temperatures of the refractory and all the equipment. Each catalytic converter should be heated until the outlet temperature is about 400°F. Usually the Claus plant is ready for startup when the catalytic converters are

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FIG. 22-18

Heat Capacity of Liquid Sulfur[5, 36]



hot. Acid gas is then fed to the plant while continuing to burn fuel gas. When combustion of the acid gas is assured, the fuel gas rate is gradually reduced to zero. The air rate is then adjusted to give optimum sulfur recovery.

Subsequent Startups

Claus plant startups after the plant has been in operation are either hot startups or cold startups. A hot startup is when the catalyst bed temperatures have not dropped below about 400°F and other temperatures in the unit have not dropped below about 300°F; a cold startup is when the unit temperatures have dropped below these values.

A hot startup does not require that the plant be heated with fuel gas. The fuel gas pilots are lit and acid gas is fed to the plant. When stable acid gas combustion has been established, the pilots are turned off and the air rate adjusted for optimum sulfur recovery. Excess air should not be used.

A cold startup requires that the plant be heated with fuel gas as in the initial startup procedure with two exceptions. The refractory need not be cured (unless refractory repairs have been made) nor the steam-producing equipment boiled out. Second, excess air should normally not be used during the heating procedure, unless the unit has been completely purged of all sulfur and sulfur compounds as part of a planned shutdown.

Shutdowns

The procedures to be followed during a planned shutdown of a Claus sulfur recovery unit are an important part of plant operations.

If the plant is being shutdown for only a few hours (for example, for reasons unrelated to the sulfur plant operation) the procedure may only involve

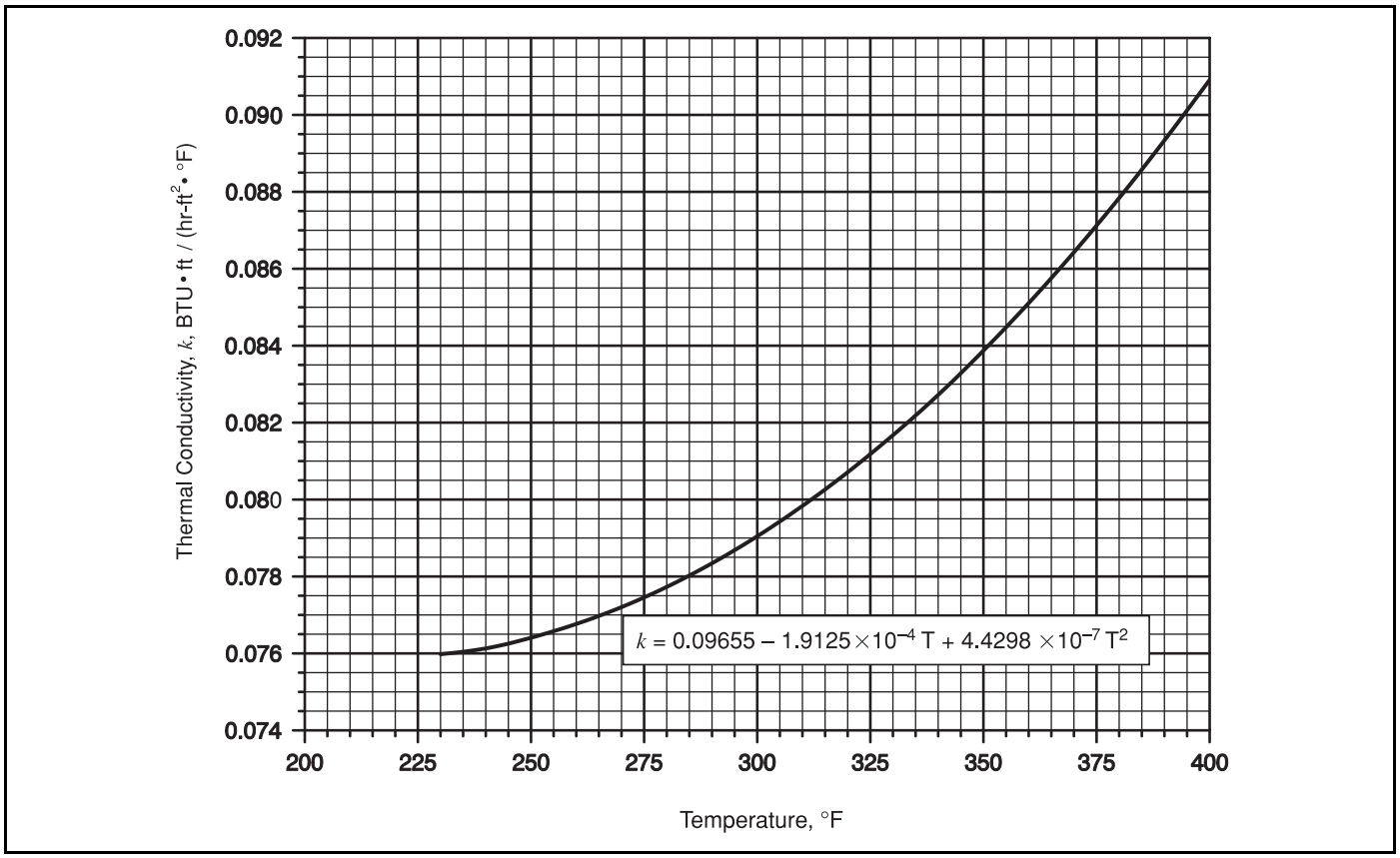
- Raising the catalyst bed temperatures by 30-40°F, in order to provide added assurance that sulfur condensation will not occur during the shutdown period
- Shutting off the air and acid gas
- Blocking in (isolating) the plant to prevent the entrance of air.

If a longer shutdown period is planned, the air rate is reduced (after the catalyst bed temperatures have been raised) to give an H_2S/SO_2 ratio at the front end of 2.5/1 to 3/1 and the plant is operated in this manner for several hours to rejuvenate the catalyst beds. Fuel gas is then added to the burner and as soon as the fuel gas flame is established, the acid gas is gradually shut off. The air rate is then adjusted to provide (as close as possible) the stoichiometric requirement for combustion of the fuel gas. Insufficient air, which can result in carbon formation and fouling of the unit, should be avoided; excess air is more acceptable but because sulfur fires within

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FIG. 22-19

Thermal Conductivity of Liquid Sulfur[36]



the unit are possible even with a small amount of excess air, temperatures should be closely monitored and the combustion products should be analyzed regularly. Control of the combustion temperature (to prevent damaging the refractory) is obtained by injecting an inert gas (usually steam, although nitrogen and carbon dioxide can be used). This purging of the plant by combustion of fuel gas should be continued at least until sulfur stops draining from the unit. If it is planned to enter the unit for maintenance or other work, the fuel gas is then shut off, but the flow of air is continued until the unit is sufficiently cooled and thoroughly purged of hazardous materials; if entry to the unit is not scheduled, both air and fuel gas are shut off, and the unit is blocked in.

Emergency shutdowns can cause serious problems if proper precautions are not taken. If the plant cannot be placed in operation soon after an emergency shutdown, an inert gas should be fed to purge the plant. Otherwise, sulfur in the unit may solidify and damage the plant, or require replacement of the catalyst beds, and manual cleaning of the waste heat boiler and sulfur condenser tubes.

CLAUS PROCESS CALCULATION

Process calculations for a Claus sulfur recovery unit are complicated by the existence of various species of gaseous sulfur (S_2, S_3, S_4, S_5, S_6, S_7, and S_8) whose equilibrium concentrations in relation to each other are often not precisely known, and by the number of side reactions involving other feed gas components such as CO_2, hydrocarbons, ammonia, etc., which take place simultaneously. These calculations are usually carried out by computer with equilibrium conditions and compositions. A data base which is often utilized for these Claus plant calculations is the JANAF (Joint Army Navy Air Force) tables.[8]

Reasonably accurate process calculations can be carried out manually, however, if side reactions are ignored. The following example illustrates a simplified method of calculating the significant process parameters for a 100 LT/D (feed) Claus plant.

Example 22-1 —

Feed Gas @ 110°F & 20.7 psia		
	mol %	mols/hr
H_2S	60.65	291.06
CO_2	32.17	154.39
H_2O	6.20	29.75
Hydrocarbons (as C_1)	0.98	4.71
	100.00	479.91

Ambient Conditions	
Dry Bulb Temperature	100°F
Wet Bulb Temperature	75°F
Air Blower Discharge Temperature	180°F

Step 1 Combustion/Reaction Section

Calculate air required to burn ⅓ of the H_2S in the feed and for total combustion of hydrocarbons

$$H_2S + 1½O_2 \rightarrow H_2O + SO_2$$ From Eq 22-2

$$\Delta H @ 77°F = -223\,100 \text{ Btu}$$

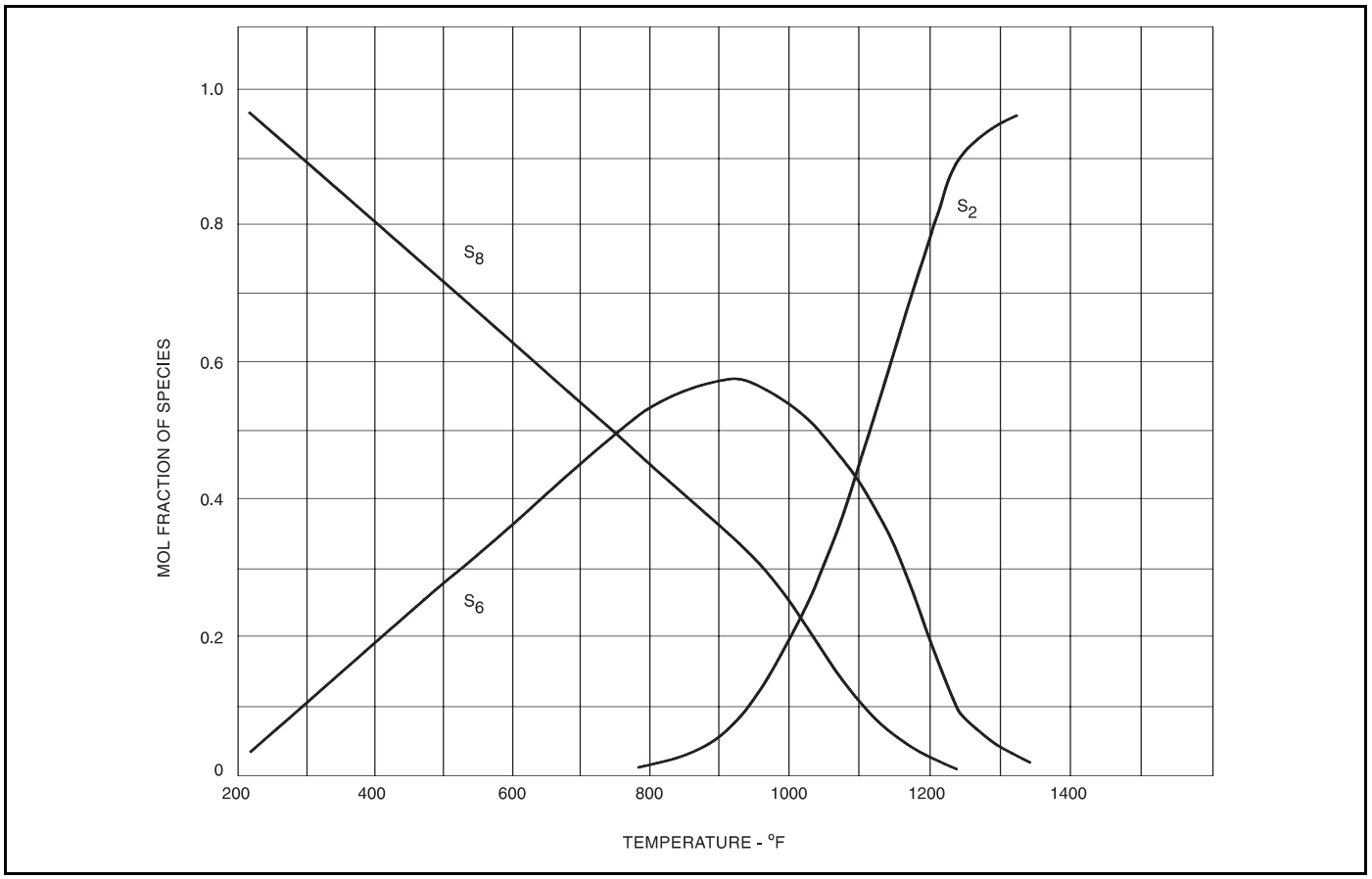
$$CH_4 + 2O_2 \rightarrow CO_2 + 2\,H_2O$$ **Eq 22-9**

$$\Delta H @ 77°F = -345\,170 \text{ Btu}$$

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FIG. 22-20

Distribution of Sulfur Vapor Species[2]



Find oxygen required:

$H_2S \rightarrow SO_2$ (⅓) (3/2) (291.06) = 145.53 mols / hr O_2

Hydrocarbons (as C_1) 2 (4.71) = 9.42 mols / hr O_2

Total = 154.95 mols/ hr O_2

Assume x = mols of H_2S reacting

$$2\ H_2S + SO_2 \rightarrow 2\ H_2O + \tfrac{3}{2}\ S_2$$
$$x \qquad \tfrac{1}{2}\ x \qquad x \qquad \tfrac{3}{4}\ x$$

From Eq 22-6

ΔH @ 77°F = +20 400 Btu

Material Balance (Combustion/Reaction Section)

	Feed Gas Mols/hr	Air Mols/hr
H_2S	291.06	—
CO_2	154.39	—
H_2O	29.75	21.91
SO_2	—	—
N_2	—	582.65
O_2	—	154.95
S_2	—	—
S_6	—	—
S_8	—	—
Hydrocarbons (as C_1)	4.71	—
	479.91	759.51

	Combustion Products Mols/hr	Reaction Products Mols/hr
H_2S	194.04	194.04 – x
CO_2	159.10	159.10
H_2O	158.10	158.10 + x
SO_2	97.02	97.02 – ½x
N_2	582.65	582.65
S_2	—	¾x
S_6	—	—
S_8	—	—
Hydrocarbons (as C_1)	—	—
	1190.91	1190.91 + ¼x

Assume ΔP through the burner and furnace is 1.6 psi. Then P = 19.1 psia or 1.3 atmospheres

At equilibrium,

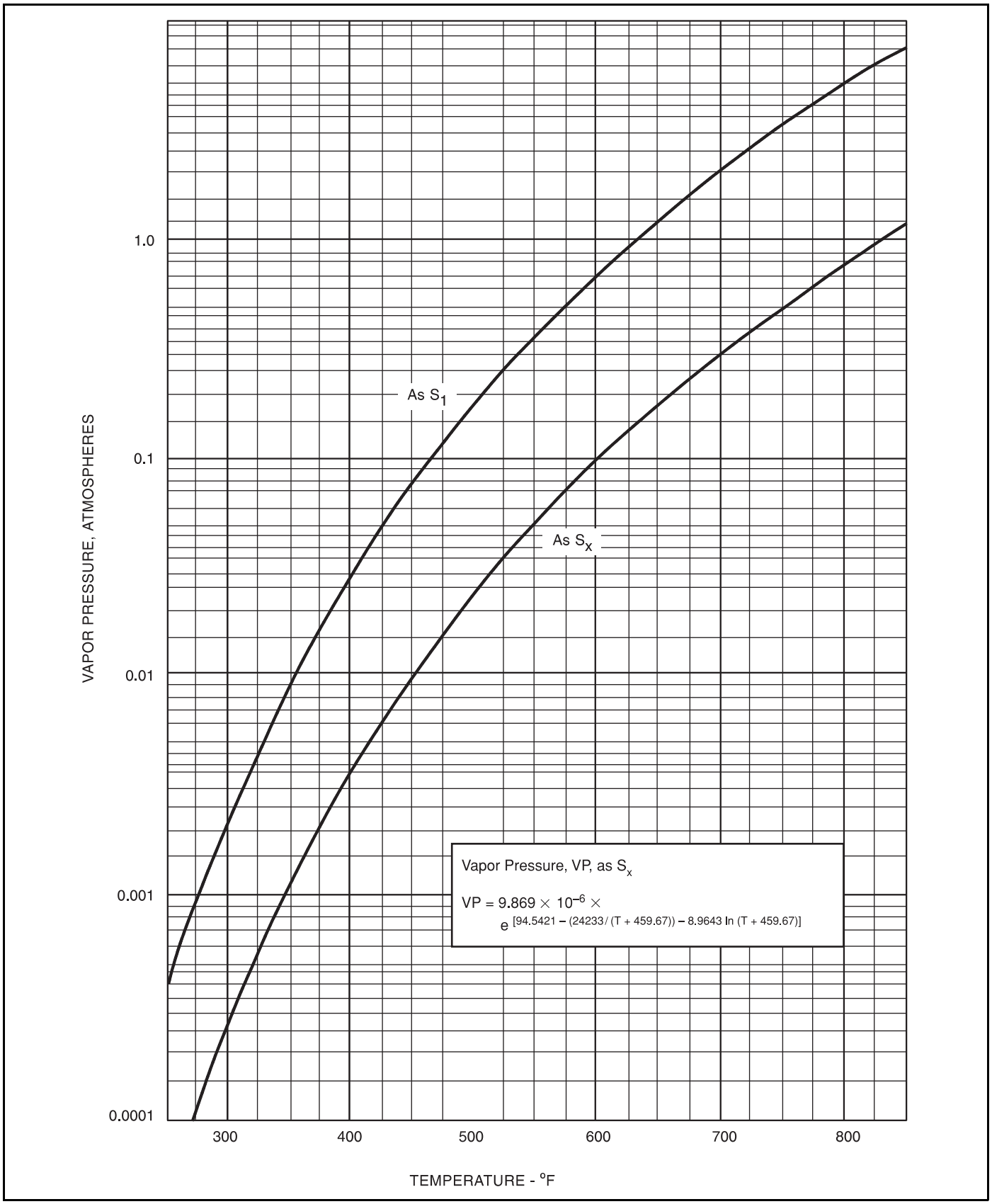
$$K_p = \frac{[H_2O]^2\,[S_2]^{3/2}}{[H_2S]^2\,[SO_2]}\left[\frac{\pi}{\text{total mols}}\right]^{\frac{3}{2}-1}$$

$$= \frac{[158.10 + x]^2\,[\tfrac{3}{4}\,x]^{3/2}}{[194.04 - x]^2\,[97.02 - \tfrac{1}{2}x]}\left[\frac{[1.3]}{[1190.91 + \tfrac{1}{4}x]}\right]^{1/2}$$

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FIG. 22-21

Vapor Pressure of Sulfur[9, 20, 36]



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FIG. 22-22

Heat of Vaporization of Sulfur

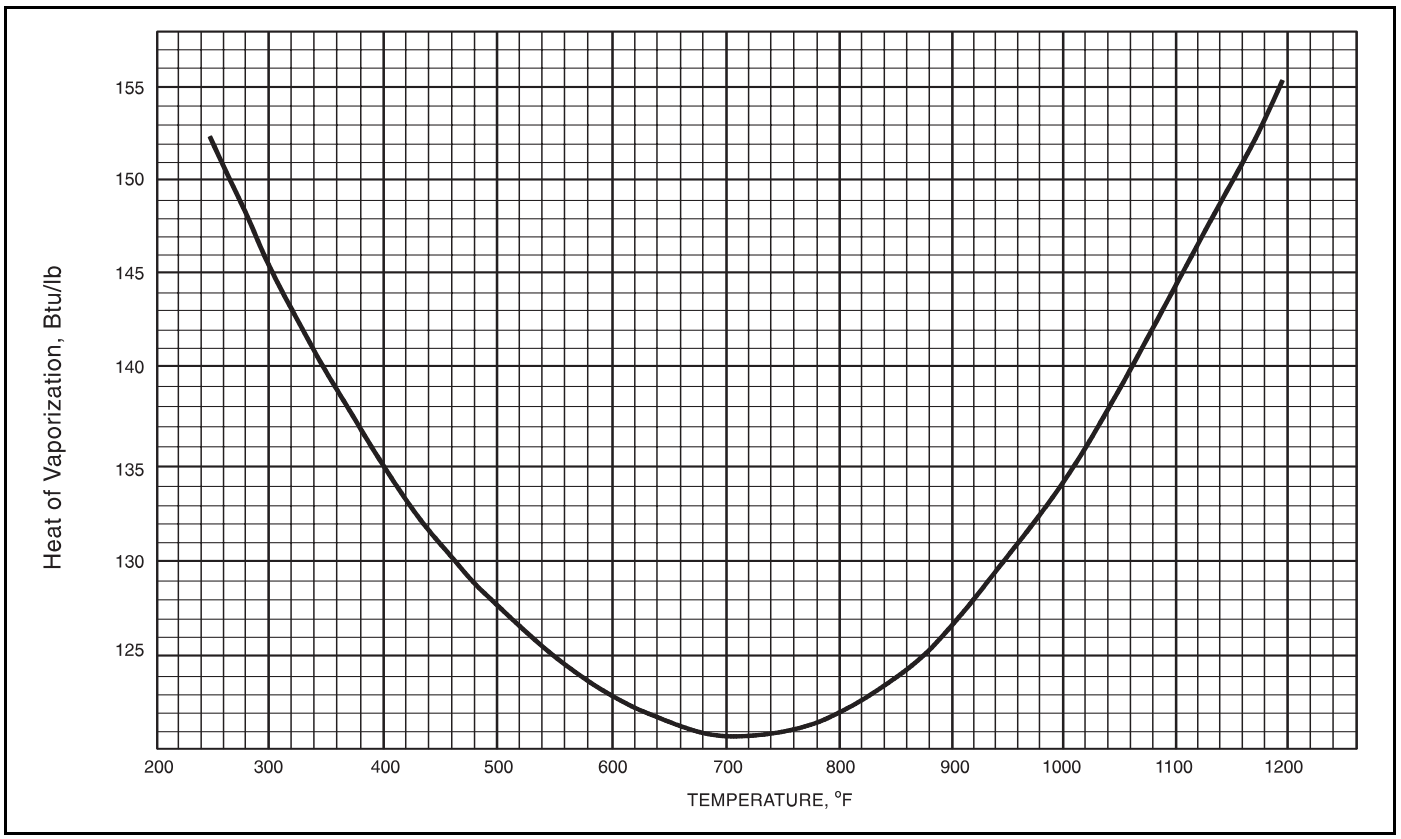
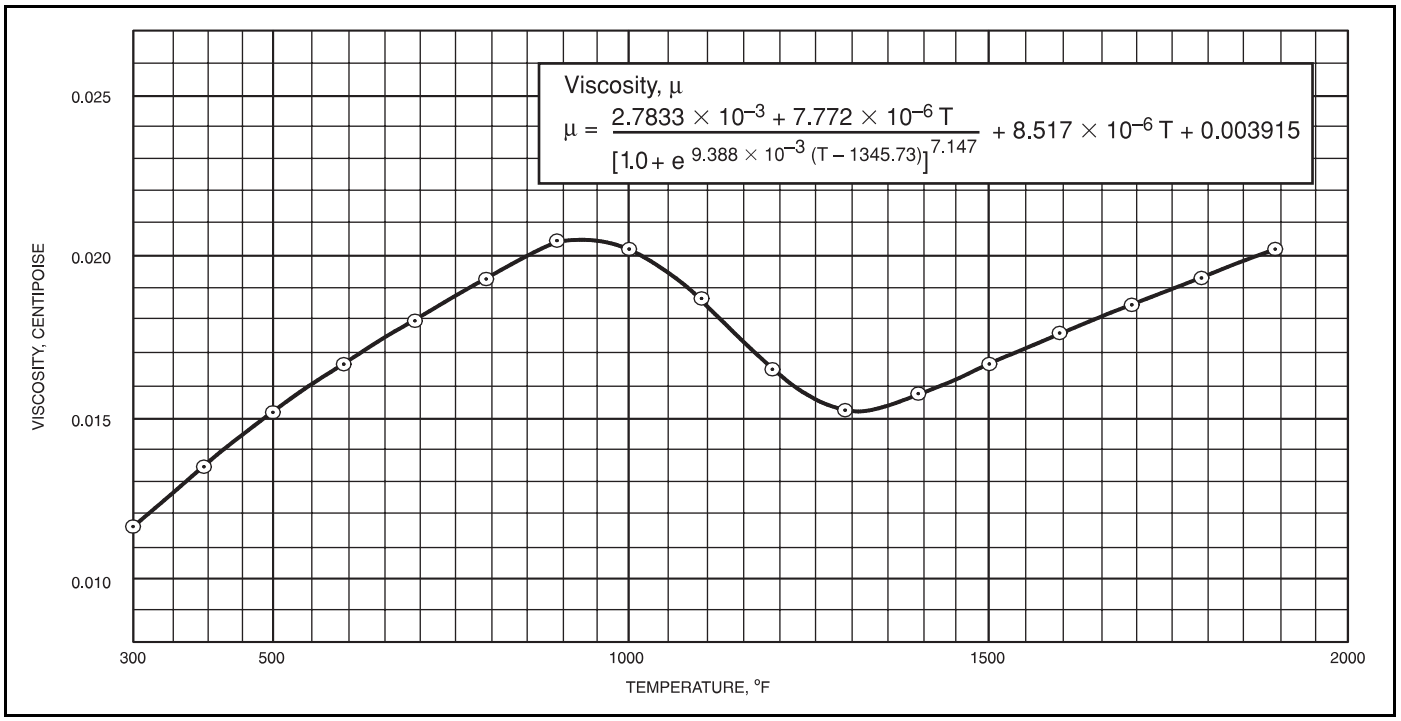


FIG. 22-23

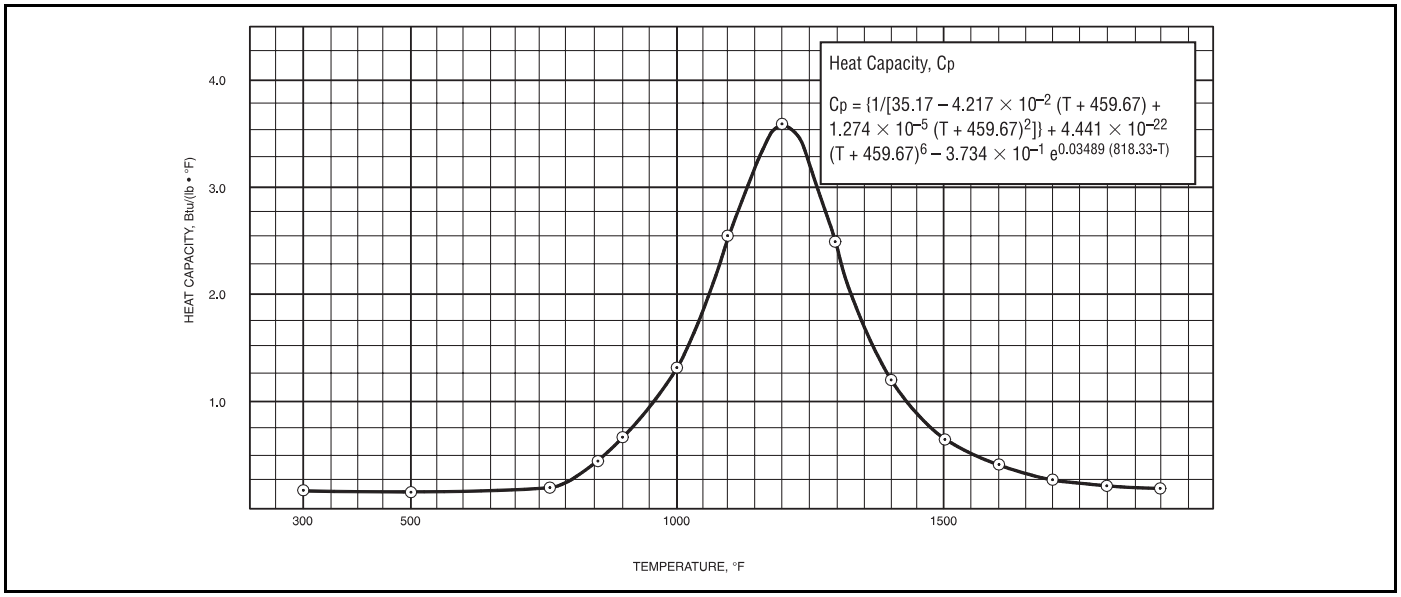
Viscosity of Sulfur Vapor[12, 36]



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FIG. 22-24

Heat Capacity of Equilibrium Sulfur Vapors[7, 10, 16, 36]



x, mols/hr (assumed)	K_p (calculated)	Equilibrium Temperature (from Fig. 22-26)
130	19.8	1880°F
135	27.7	2090°F
140	39.5	2390°F

Determine flame temperature by heat balance for each value of x using the thermodynamic data in Fig. 22-27. For example, at x = 130 mols/hr

	Feed Gas H @ 110°F		
	mols/hr	Btu/lb-mol	Btu/hr
H_2S	291.06	633.9	184 500
CO_2	154.39	690.8	106 650
H_2O	29.75	626.1	18 630
Hydrocarbons (as C_1)	4.71	666.1	3 140
	479.91		312 920

	Combustion Air H @ 180°F		
	mols/hr	Btu/lb-mol	Btu/hr
O_2	154.95	1043.3	161 660
N_2	582.65	1030.7	600 540
H_2O	21.91	1191.5	26 110
	759.51		788 310

	Reaction Products H @ 2100°F		
	mols/hr	Btu/lb-mol	Btu/hr
H_2S	64.04	21 020	1 346 120
CO_2	159.10	25 010	3 979 090
H_2O	288.10	19 470	5 609 310
SO_2	32.02	25 190	806 580
N_2	582.65	15 670	9 130 130
S_2	97.50	17 840	1 739 400
	1223.41		22 610 630

	Reaction Products H @ 2200°F	
	Btu/lb-mol	Btu/hr
H_2S	22 220	1 422 970
CO_2	26 400	4 200 240
H_2O	20 570	5 926 220
SO_2	26 520	849 170
N_2	16 490	9 607 900
S_2	18 730	1 826 180
		23 832 680

Heat in, Btu/hr:

Feed Gas		=	312 920
Combustion Air		=	788 310
H_2S Combustion	(97.02 mols/hr) (223 100)	=	21 645 160
HC Combustion	(4.71 mols/hr) (345 170)	=	1 625 750
Claus Reaction	(130/2 mols/hr) (–20 400)	=	–1 326 000
			23 046 140

By interpolation, flame temperature is approximately 2135°F.

Similarly for x = 135 mols/hr, the calculated flame temperature is 2131°F, and for x = 140 mols/hr, 2127°F. Plotting the assumed values of x versus calculated equilibrium temperature and flame temperatures (Fig. 22-28) gives a value of x = 136 mols/hr (equivalent to 70.1% conversion) and a temperature of 2130°F which meet both thermodynamic equilibrium and heat balance conditions.

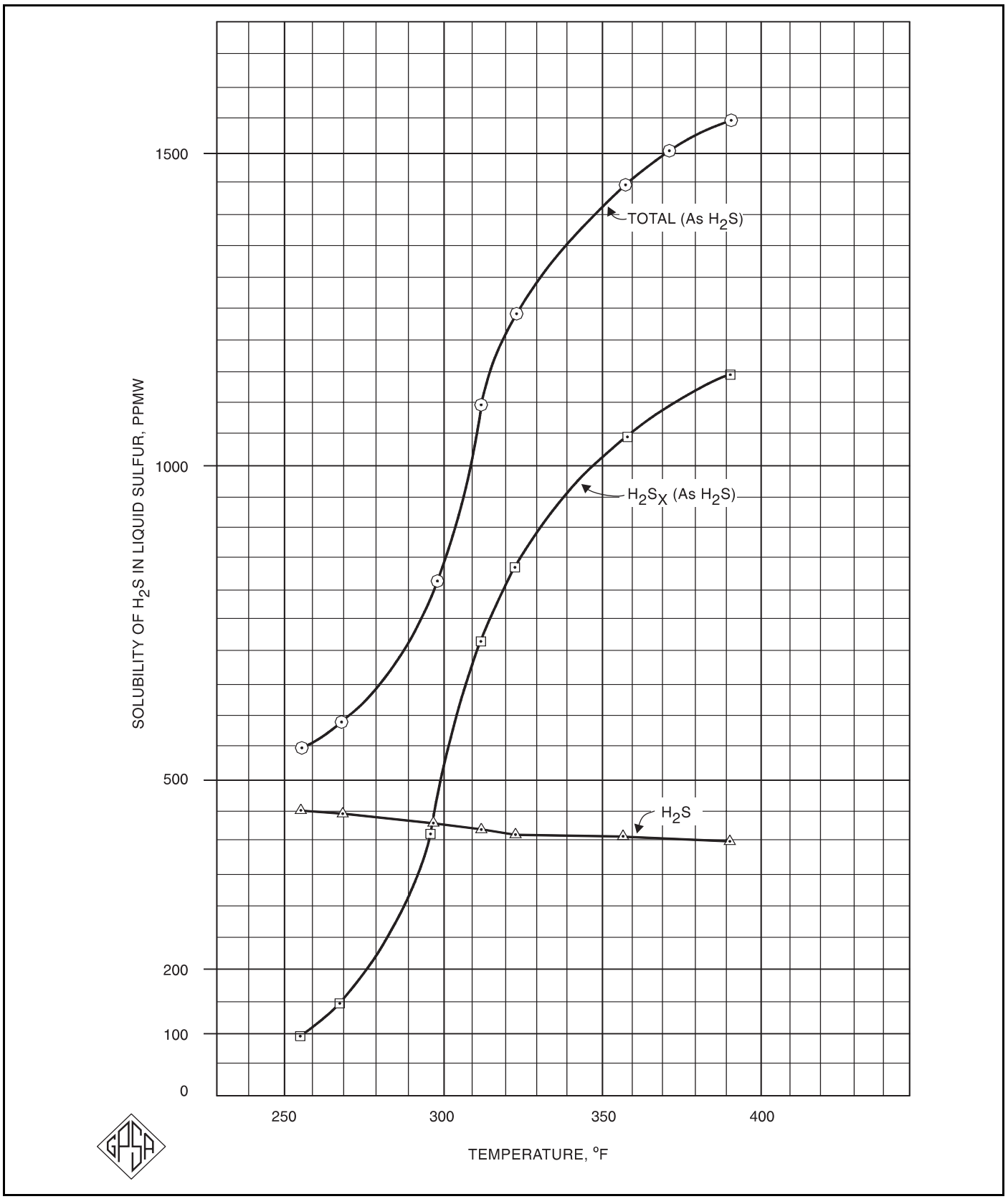
Step 2 Waste Heat Boiler Duty

Assume that 250 psig steam is generated in the waste heat boiler and therefore that the temperature of the cooled combustion products is 700°F. From Fig. 22-20, the distribution of sulfur vapor species at 700°F is approximately 0.5 mol % S_2, 45 mol % S_6, and 54.5 mol % S_8. The cooled combustion product composition and waste heat boiler heat balance are therefore as follows:

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FIG. 22-25

H_2S and H_2S_x to Total H_2S Solubility
(at 1 bar H_2S vapor pressure)



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	Reaction Products H @ 2130°F		
	mols/hr	Btu/lb-mol	Btu/hr
H_2S	58.04	21 380	1 240 900
CO_2	159.10	25 427	4 045 440
H_2O	294.10	19 800	5 823 180
SO_2	29.02	25 589	742 590
N_2	582.65	15 916	9 273 460
S_2	102.00	18 107	1 846 910
S_6	—	—	—
S_8	—	—	—
	1224.91		22 972 480

	Cooled Reaction Products H @ 700°F		
	mols/hr	Btu/lb-mol	Btu/hr
H_2S	58.04	5 796	336 400
CO_2	159.10	6 855	1 090 630
H_2O	294.10	5 572	1 638 730
SO_2	29.02	7 181	208 390
N_2	582.65	4 713	2 746 030
S_2	0.14	5 498	770
S_6	12.98	14 005	181 780
S_8	15.73	18 228	286 730
	1151.76		6 489 460

ΔH: 22 972 480 – 6 489 460 = 16 483 020 Btu/hr

From Fig. 22-29

S_2 (vapor) $\rightarrow$ S_6 (vapor) (12.98) (120 000) = 1 557 600 Btu/hr

From Fig. 22-29

S_2 (vapor) $\rightarrow$ S_8 (vapor) (15.73) (178 316) = 2 804 910 Btu/hr

Total heat duty

16 483 020 + 1 557 600 + 2 804 910 = 20 845 530 Btu/hr

Note: Partial pressure of sulfur vapor

$$= \frac{S_2 + S_6 + S_8}{\text{Total Mols}} (\text{Total Pressure})$$

$$= \frac{0.14 + 12.98 + 15.73}{1151.76} (1.3) = 0.033 \text{ atmospheres}$$

From Fig. 22-21, the vapor pressure of sulfur at 700°F is approximately 0.3 atmosphere, so no sulfur is condensed.

Step 3 1st Sulfur Condenser

Assume a pressure drop through the condenser of 0.5 psi, with the process stream further cooled to 350°F. From Fig. 22-21, the vapor pressure of sulfur at 350°F is 0.0011 atmospheres so the stream is below the sulfur dewpoint. From Fig. 22-20, the distribution of sulfur species is 14.5 mol % S_6 and 85.5 mol % S_8. If no condensation took place, there would be 3.84 mols/hr of S_6 and 22.62 mols/hr of S_8. [Note: (6)(3.84) + (8)(22.62) ≅ (2)(102.0)]

Uncondensed sulfur

$$= \left[\frac{(0.0011)(14.7)}{18.6 - (0.0011)(14.7)}\right][1151.76 - (3.84 + 22.62)]$$

= 0.98 mols/hr

S_6: 0.145 (0.98) = 0.14 mols/hr uncondensed
3.84 – 0.14 = 3.70 mols/hr condensed
S_8: 0.853 (0.98) = 0.84 mols/hr uncondensed
22.62 – 0.84 = 21.78 mols/hr condensed

		Condenser Outlet Conditions H @ 350°F	
	mols/hr	Btu/lb-mol	Btu/hr
H_2S	58.04	2646.5	153 600
CO_2	159.10	3023	480 960
H_2O	294.10	2586	760 540
SO_2	29.02	3205	93 010
N_2	582.65	2219	1 292 900
S_2 (vapor)	—	—	—
S_6 (vapor)	3.84	6506	24 980
S_8 (vapor)	22.62	8463	191 430
	1149.37		2 997 420

DH: 6 489 460 – 2 997 420 = 3 492 040 Btu/hr

Fig. 22-30 DH:

S_6 (vapor) $\rightarrow$ S_{liq} (3.70) (39 690) = 146 850 Btu/hr

Fig. 22-30 DH:

S_8 (vapor) $\rightarrow$ S_{liq} (21.78) (34 830) = 758 600 Btu/hr

Fig. 22-29 DH:

S_2 (vapor) $\rightarrow$ S_6 (vapor) (0.005) (118 600) = 590 Btu / hr

Fig. 22-29 DH:

S_2 (vapor) $\rightarrow$ S_8 (vapor) (0.031) (176 216) = 5460 Btu / hr

Total Duty

3 492 040 + 146 850 + 758 600 + 590 + 5460
= 4 403 540 Btu/hr

Step 4 1st Reheater

One of the principal purposes of reheating is to maintain the process gas above the sulfur dewpoint throughout the catalyst bed. To estimate the dewpoint temperature at the bed outlet, assume that 20% of the H_2S in the feed will be converted to sulfur in the first catalyst bed. Total sulfur (as S_1) at the bed outlet will then be

0.14 (6) + 0.84 (8) + 0.20 (291.06) = 65.77 mols/hr vapor as S_1 assuming a pressure drop for the reheater and catalyst bed of 1.0 psi,

Sulfur vapor pressure (as S_1) then is:

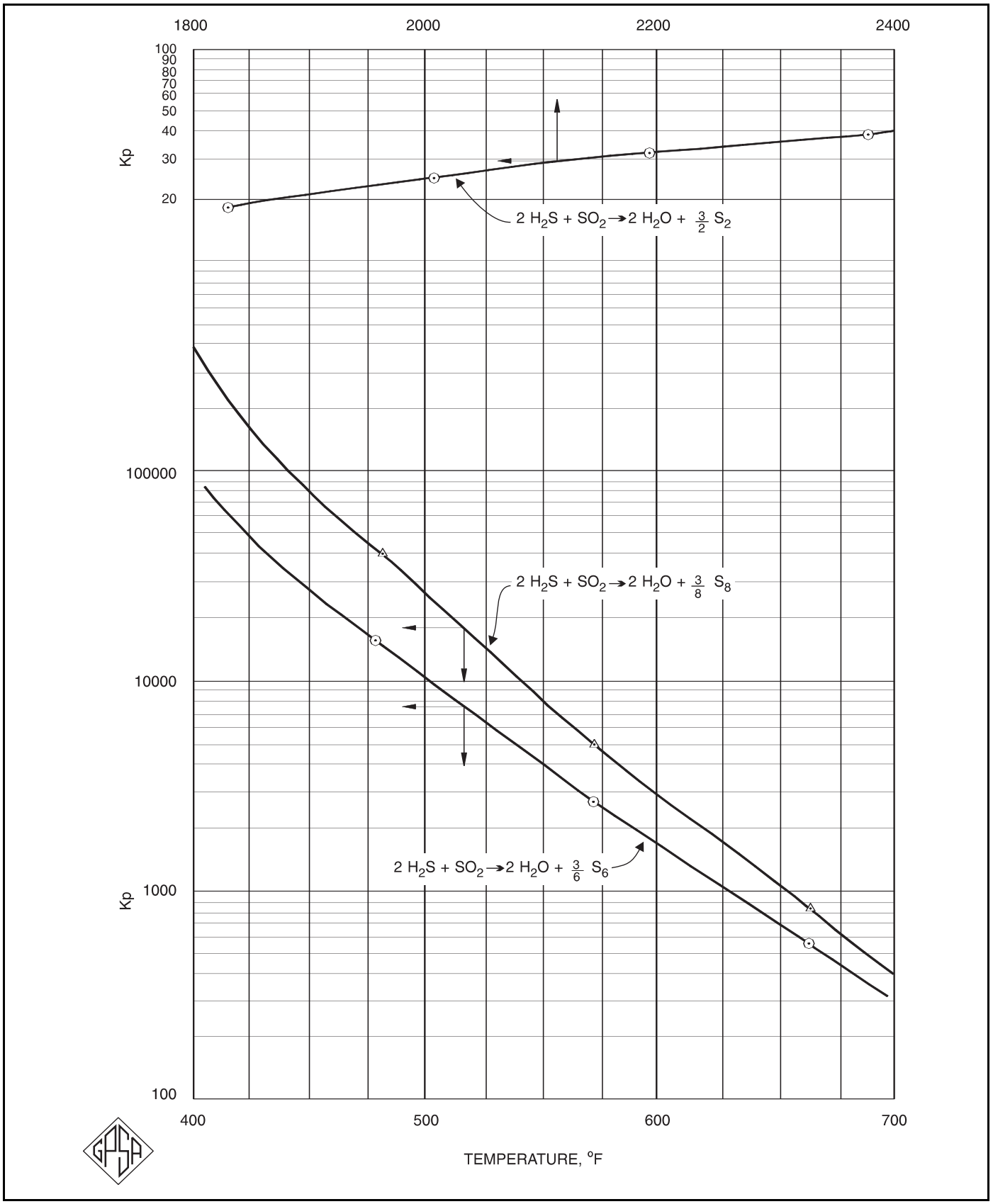
$$\frac{65.77}{1129.35}(17.6) = 1.03 \text{ psi or } 0.07 \text{ atmospheres}$$

From Fig. 22-21, the vapor pressure of sulfur at 445°F is about 0.070 atm. The preheater outlet temperature is therefore set 30°F higher or 475°F.

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FIG. 22-26

Equilibrium Constant for Claus Reaction



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FIG. 22-27

Enthalpies of Paraffin Hydrocarbons, Combustion Products and Sulfur Compounds[11]

Enthalpies of Paraffin Hydrocarbons, C_1-C_6 Btu/lb-mole

°F	C_1	C_2	C_3	nC_4	iC_4	nC_5	nC_6
32	0.0	0.0	0.0	0.0	0.0	0.0	0.0
60	234.3	338.2	467.8	633.4	614.2	787.6	943.6
77	378.6	549.8	762.3	1030	1001	1280	1533
100	576.3	843.7	1174	1582	1544	1966	2353
200	1474	2225	3114	4184	4086	5201	6227
300	2430	3775	5340	7128	7032	8851	10579
400	3470	5492	7827	10395	10315	12890	15396
500	4590	7366	10539	13070	13910	17310	20653
600	5790	9401	13470	17830	17780	22060	26323
700	7065	11584	16620	21940	21910	27130	32353
800	8416	13900	19940	26290	26270	32490	38720
900	9827	16330	23450	30850	30860	38100	45400
1000	11330	18880	27110	35600	35640	43950	52350
1100	12880	21540	30920	40540	40610	50020	59540
1200	14490	24290	34870	45640	45750	56310	66990
1300	16170	27130	38940	50900	51030	62780	74670
1400	17890	30050	43110	56310	56470	69430	82570
1500	19660	33090	47430	61890	62050	76280	90670
1600	21470	36190	51840	67590	67800	83280	98930
1700	23350	39340	56340	73400	73670	90350	107390
1800	25260	42560	60930	79330	79600	97640	116000
1900	27210	45870	65560	85370	85590	105000	124760
2000	29190	49210	70320	91470	91690	112480	133650
2100	31210	52600	75080	97630	97910	120200	142680
2200	33210	56060	79970	103910	104190	127800	151750
2400	37420						
2800	46050						
3000	50480						
3500	61870						
4000	73440						

Enthalpies of Combustion Gases Btu/lb-mole

°F	N_2	O_2	Air	H_2	CO	CO_2	H_2O
32	0.0	0.0	0.0	0.0	0.0	0.0	0.0
60	194.9	195.9	194.6	191.9	194.9	243.1	224.2
77	312.2	315.1	312.7	308.9	313.3	392.2	360.5
100	473.3	476.7	472.7	467.6	473.5	597.9	545.3
200	1170	1185	1170	1160	1171	1527	1353
300	1868	1903	1870	1861	1872	2509	2171
400	2570	2634	2576	2560	2578	3537	3001
500	3277	3379	3289	3258	3292	4607	3842
600	3991	4137	4010	3940	4013	5714	4700
700	4713	4908	4740	4653	4744	6855	5572
800	5443	5690	5479	5350	5484	8026	6460
900	6182	6484	6227	6058	6234	9224	7364
1000	6929	7288	6984	6771	6993	10447	8284
1100	7686	8100	7750	7469	7762	11692	9222
1200	8152	8921	8524	8181	8540	12960	10176
1300	9227	9748	9308	8892	9326	14240	11147
1400	10009	10582	10098	9620	10120	15540	12130
1500	10799	11422	10895	10352	10921	16860	13140
1600	11600	12270	11703	11072	11729	18190	14160
1700	12400	13120	12510	11799	12540	19530	15190
1800	13210	13970	13330	12520	13360	20890	16240
1900	14020	14830	14150	13250	14190	22250	17300
2000	14840	15700	14970	14000	15020	23630	18380
2100	15670	16560	15800	14780	15850	25010	19470
2200	16490	17430	16640	15570	16690	26400	20570
2300	17340	18310	17480	16360	17530	27800	21690
2400	18180	19190	18320	17140	18380	29210	22810
2500	19020	20070	19170	17940	19230	30620	23950
3000	23280	24520	23460	21880	23520	37750	29780
3500	27600	29050	27810	26020	27860	45020	35820
4000	31950	33660	32190	30280	32240	52400	42020
4500	36340	38340	36620	34560	36660	59820	48340
5000	40760	43100	41090	39010	41100	67300	54770
5500	45210	47910	45590	43480	45560	74820	61270
6000	49670	52780	50120	48010	50040	82400	67840
6500	54150	57700	54680	52630	54530	90020	74440

Enthalpies of Sulfur Compounds Btu/lb-mole

°F	S_2	SO_2	SO_3	H_2S	CS_2	COS	S_6	S_8
32	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
60	215.2	262.6	330	226	300.4	217.7	560.5	728.7
77	346.3	423.9	530	363.8	484.4	440.6	902	1173
100	526	644.6	825	551.6	738.6	675.2	1365	1775
200	1318	1633	2115	1375	1873	1711	3398	4419
300	2129	2667	3500	2216	3054	2799	5460	7102
400	2955	3743	4995	3077	4275	3933	7552	9824
500	3793	4858	6560	3960	5530	5091	9674	12586
600	4642	6004	8200	4866	6814	6293	11825	15383
700	5498	7181	9915	5796	8121	7531	14005	18228
800	6359	8386	11680	6751	9449	8784	16216	21109
900	7227	9609	13480	7730	10790	10060	18455	24029
1000	8099	10840	15330	8732	12150	11350	20725	26988
1100	8974	12100	17210	9757	13530	12660	23024	29987
1200	9851	13370	19140	10800	14910	13990	25353	33025
1300	10730	14660	21090	11870	16310	15230	27711	36103
1400	11610	15950	23070	12960	17710	16680	30099	39221
1500	12500	17250	25070	14060	19120	18040	32516	42377
1600	13390	18550	27100	15180	20540	19410		
1700	14270	19860	29140	16320	21960	20790		
1800	15160	21180	31220	17470	23390	22180		
1900	16050	22510		18640	24830	23560		
2000	16940	23850		19820	26270	24980		
2100	17840	25190		21020	27710	26380		
2200	18730	26520		22220	29150	27800		
2500	21410	30550		25890	33510	32060		
3000	25900	37340						
3500	30400	44180						
4000	34920	51030						
4500	39440	57910						
5000	43980	64780						

Note: Values are based upon datum of 0.0 Btu/lb-mole @ 32°F

		H @ 475°F		H @ 350°F
	mols/hr	Btu/lb-mol	Btu/hr	Btu/hr
H_2S	58.04	3 739.3	217 030	153 600
CO_2	159.10	4 339.5	690 410	480 960
H_2O	294.10	3 631.8	1 068 110	760 540
SO_2	29.02	4 579.3	132 890	93 010
N_2	582.65	3 100.3	1 806 390	1 292 900
S_6	0.26	9 143	2 380	910
S_8	0.75	11 896	8 920	7 110
	1123.92		3 926 130	2 789 030

Reheater Heat Duty = 3 926 130 – 2 789 030

= 1 137 100 Btu/hr

NOTE: At 475°F, the molecular distribution of sulfur vapor species (Fig. 22-20) is 0.255 S6 and 0.745 S8.

Step 5 1st Catalytic Converter

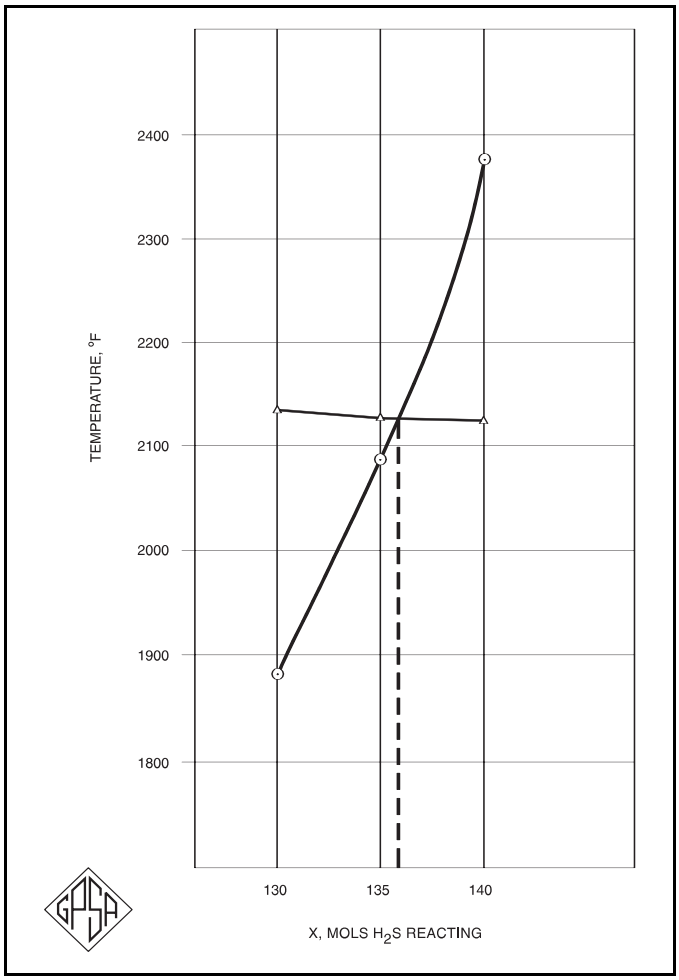
In the temperature range of 400°F-700°F prevailing in the catalytic reactors, the Claus reaction equilibrium involving formation of S_2, S_6, and S_8 should all be used in equilibrium calculations. However, a good approximation is obtained (usually within 1% total overall conversion) if only the reaction to form S_8 is considered.

Assume y mols of H_2S react.

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FIG. 22-28

Calculation of Reaction Furnace Temperature



$$2\ H_2S + SO_2 \rightarrow 2\ H_2O + \tfrac{3}{8}\ S_8$$
$$y \quad \tfrac{1}{2}\ y \quad y \quad \tfrac{3}{16}\ y$$

ΔH @ 77°F = –45 060 Btu

	Feed Gas @ 475°F mols/hr	Outlet Conditions mols/hr
H_2S	58.04	58.04 – y
CO_2	159.10	159.10
H_2O	294.10	294.10 + y
SO_2	29.02	29.02 – y/2
N_2	582.65	582.65
S_6	0.26	—
S_8	0.75	0.95 + (3/16)y
	1123.86	1123.86 – 0.3125y

at equilibrium

$$K_p = \frac{[H_2O]^2\,[S_8]^{3/8}}{[H_2S]^2\,[SO_2]}\left[\frac{\pi}{\text{total mols}}\right]^{\frac{3}{8}-1}$$

$$= \frac{[294.10+y]^2\,[0.95+(3/16)\,y]^{3/8}}{[58.04-y]^2\,[29.02-y/2]}\left[\frac{[1.2]}{[1123.86-0.3125y]}\right]^{-5/8}$$

y, mols/hr (assumed)	K_p (calculated)	Equilibrium Temperature (from Fig. 22-26)
36	3130	597°F
38	4299	580°F
40	6051	566°F

For each assumed value of y, calculate the total outlet stream enthalpy (using the data in Fig. 22-27) and the overall converter heat balance. For example, for y = 38 mols/hr

	Outlet Stream mols/hr	H @ 580°F Btu/lb-mol	H @ 580°F Btu/hr
H_2S	20.04	4 685	93 890
CO_2	159.10	5 493	873 940
H_2O	332.10	4 528	1 503 750
SO_2	10.02	5 775	57 870
N_2	582.65	3 848	2 242 040
S_6	3.10	11 395	35 320
S_8	5.75	14 825	85 240
	1112.76		4 892 050

Heat Balance

Heat In (from Step 4)		=	3 926 130 Btu/hr
Claus Reaction	(38/2) (45 060)	=	856 140 Btu/hr
Total Heat Out		=	4 782 270 Btu/hr

NOTE: At 580°F, the molecular distribution of sulfur species (Fig. 22-20) is 0.35 S_6 and 0.65 S_8.

These calculated values are plotted in Fig. 22-31. By interpolation, a value of y = 38.7 mols/hr meets both equilibrium and thermodynamic conditions and the converter outlet temperature is 575°F ($K_p \cong 4790$). [NOTE: At 575°F, the molecular distribution of sulfur species is 0.345 S_6 and 0.655 S_8.]

	Converter Outlet mols/hr	H@ 575°F Btu/lb-mol	H@ 575°F Btu/hr
H_2S	19.34	4 640	89 740
CO_2	159.10	5 437	865 030
H_2O	332.80	4 486	1 492 940
SO_2	9.67	5 718	55 290
N_2	582.65	3 813	2 221 640
S_6	3.05	11 287	34 430
S_8	5.79	14 688	85 040
	1112.40		4 844 110

Step 6 2nd Sulfur Condenser

Repeat procedure of Step 3.

Step 7 2nd Reheater

Repeat procedure of Step 4.

Step 8 2nd Catalyst Converter

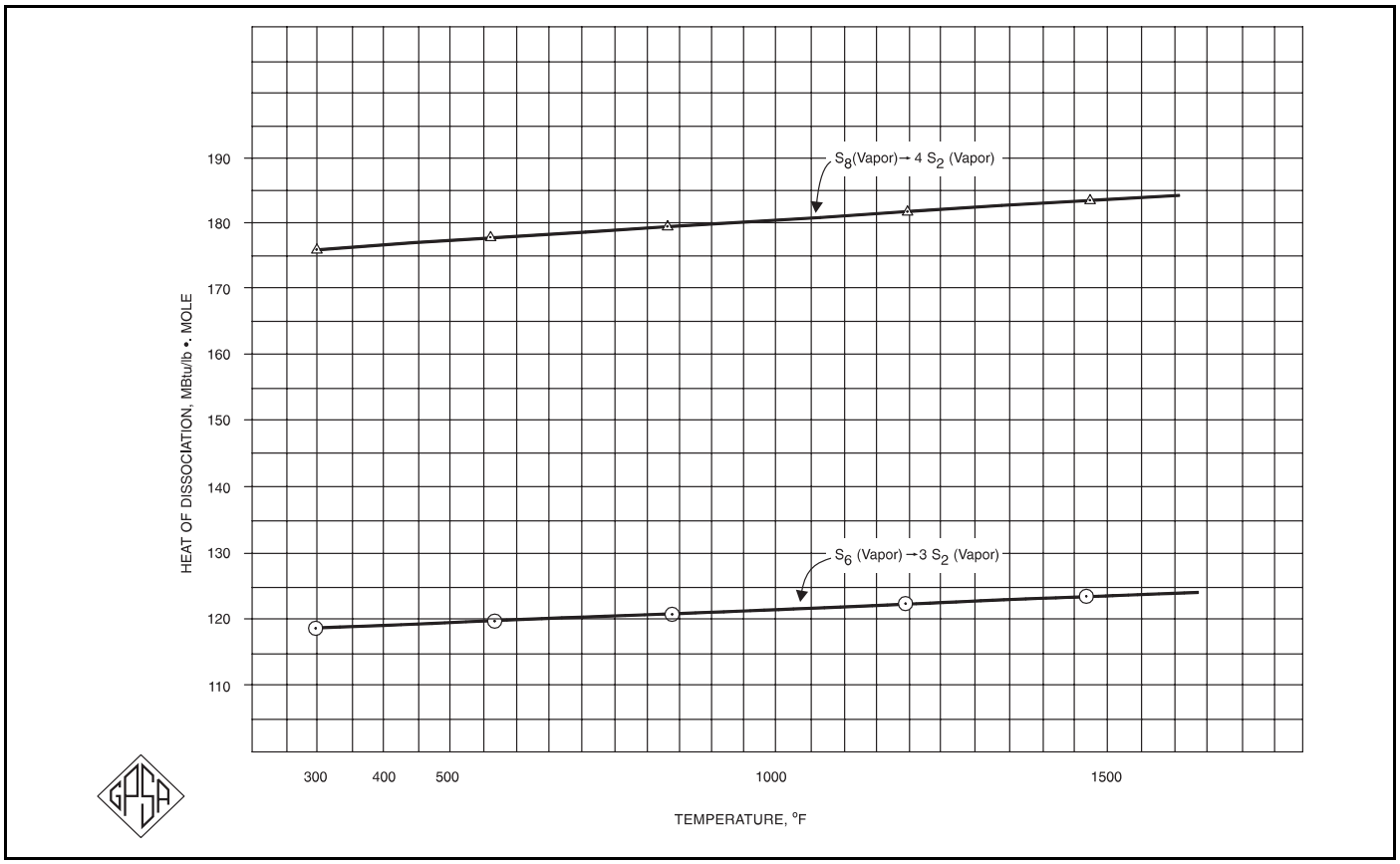
Repeat procedure of Step 5.

These calculation steps are continued for the number of catalytic converter stages being utilized. For this example, a three-stage plant is assumed and the total calculated **conversion** efficiency is about 98%. Total **recovery** efficiency, after allowing for sulfur vapor losses and about ½% for liquid sulfur entrainment, is about 97% and the tail gas composition is approximately as follows:

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FIG. 22-29

Heat of Dissociation of Sulfur Vapor Species



	mols/hr	H @ 300°F Btu/lb-mol	H @ 300°F Btu/hr
H_2S	3.88	2216	8 600
CO_2	159.10	2509	399 180
H_2O	348.26	2171	756 070
SO_2	1.94	2667	5 170
N_2	582.65	1868	1 088 390
S_6 (vapor)	0.02	5460	110
S_8 (vapor)	0.22	7102	1 560
S_{liq} (as S_1)	1.40	–3815	–5 340
	1097.47		2 253 740

	Feed	Air		
			H @ 100°F	
	mols/hr	mols/hr	Btu/lb-mol	Btu/hr
H_2S	3.88	—	—	—
CO_2	159.10	—	—	—
H_2O	348.26	1.93	545.3	1 050
SO_2	1.94	—	—	—
N_2	582.65	51.33	473.3	24 290
S (as S_1)	3.28	—	—	—
O_2	—	13.65	476.7	6 510
	1099.11	66.91		31 850

This is the feed to the incinerator. Assuming 50% excess air (based upon combustibles) and an outlet temperature of 1000°F, the fuel gas requirement and stack gas volume can be calculated as follows:

Step 1. Calculate oxygen required for combustibles in feed gas

$H_2S + 3/2\ O_2 \rightarrow H_2O + SO_2$ from Eq 22-2

ΔH @ 77°F = –223 100 Btu

$S_1 + O_2 \rightarrow SO_2$ **Eq 22-10**

ΔH @ 77°F = –256 100 Btu

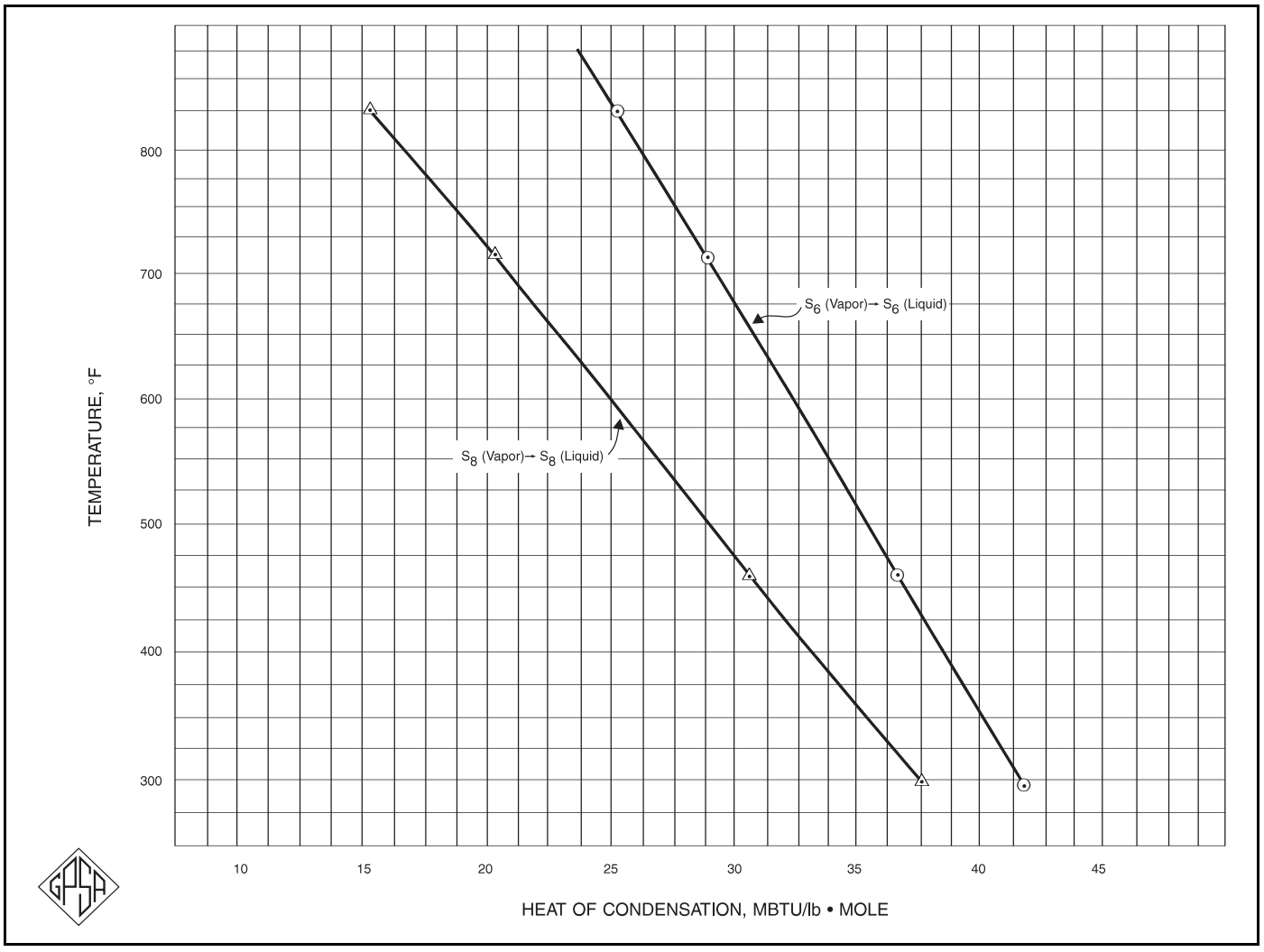
H_2S:	1.5 (3.88)	=	5.82 mols/hr O_2
S_1:	1.0 (3.28)	=	3.28 mols/hr O_2
			9.10 mols/hr O_2
	+ 50%	=	13.65 mols/hr O_2

	Products		
		H @ 1000°F	
	mols/hr	Btu/lb-mol	Btu/hr
H_2S	—	—	—
CO_2	159.10	10 447	1 662 120
H_2O	354.07	8 284	2 933 120
SO_2	9.10	10 840	98 640
N_2	633.98	6 929	4 392 850
S (as S_1)	—	—	—
O_2	4.55	7 288	33 160
	1160.80	—	9 119 890

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FIG. 22-30

Molar Heat of Condensation of S_6 and S_8



Heat Balance

Heat Out		9 119 890 Btu/hr
Heat In		
Feed @ 300°F		2 253 740 Btu/hr
Air @ 100°F		31 850 Btu/hr
H_2S Combustion 3.88 (223 100)	=	865 630 Btu/hr
S_1 Combustion 3.28 (256 100)	=	840 010 Btu/hr
		3 991 230 Btu/hr
Heat Gained by Feed Gas		5 128 660 Btu/hr

Step 2. Calculate net heat release for fuel (assumed to be methane) at 50% excess air, using 10 mols/hr as the base rate.

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$$

$$\Delta H\ @\ 77°F = -345\,170\ \text{Btu}$$

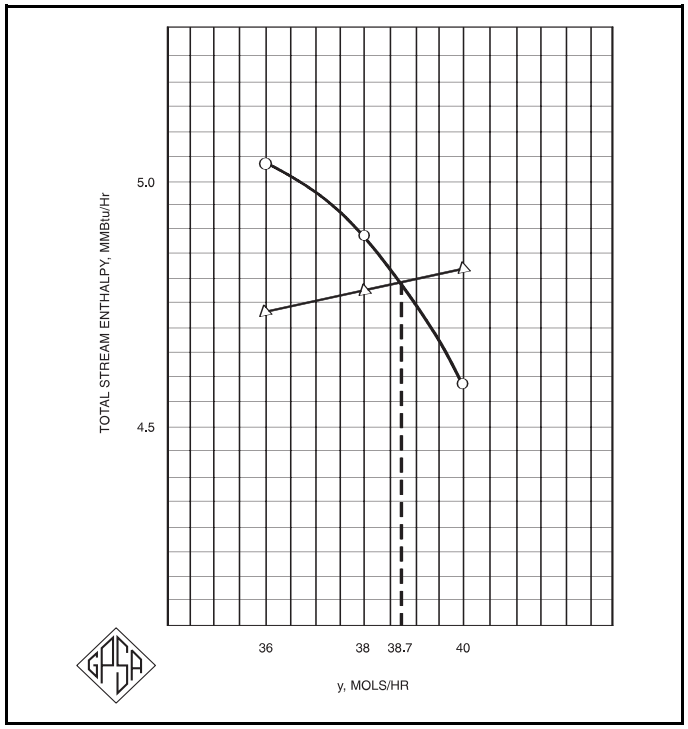
Fuel			
		H @ 100°F	
	mols/hr	Btu/lb-mol	Btu/hr
CH_4	10.0	576.3	5760
CO_2	—	—	—
O_2	—	—	—
N_2	—	—	—
H_2O	—	—	—
	10.0		5760

Air			
		H @ 100°F	
	mols/hr	Btu/lb-mol	Btu/hr
CH_4	—	—	—
CO_2	—	—	—
O_2	30.0	476.7	14 300
N_2	112.81	473.3	53 390
H_2O	4.24	545.3	2 310
	147.05		70 000

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FIG. 22-31

Calculation of Converter Outlet Temperature



	Combustion Products		
		H @ 1000°F	
	mols/hr	Btu/lb-mol	Btu/hr
CH_4	—	—	—
CO_2	10	10 447	104 470
O_2	10	7 288	72 880
N_2	112.81	6 929	781 660
H_2O	24.24	8 284	200 800
	157.05		1 159 810

Heat Balance

Heat In	
Fuel	5 760 Btu/hr
Air	70 000 Btu/hr
C_1 Combustion 10 x 345170	3 451 700 Btu/hr
	3 527 460 Btu/hr
Heat Out	1 159 810 Btu/hr
Net Heat Release of Fuel	2 367 650 Btu/hr

Step 3. Calculate fuel requirement and stack gas rate and composition

$$\text{Fuel required} = \frac{\text{Heat gained by feed gas}}{\text{Net Heat Release of Fuel}} (10 \text{ mols/hr})$$

$$= \frac{5\,128\,660}{2\,367\,650} (10) = 21.66 \text{ mols/ hr}$$

	Stack Gas	
	mols/hr	mol %
CO_2	180.76	12.04
H_2O	406.57	27.09
SO_2	9.10	0.61
N_2	878.33	58.51
O_2	26.21	1.75
	1500.97	100.00

Total Heat Release

Fuel =	21.66 (345 170)	=	7 476 380 Btu/hr
H_2S (From Step 1)			865 630 Btu/hr
S (From Step 1)			840 010 Btu/hr
			9 182 020 Btu/hr

SULFUR PRODUCT SPECIFICATIONS

A sulfur product meeting the following specifications will normally satisfy the requirements of the major consumers of sulfur such as manufacturers of sulfuric acid, chemicals, fertilizers, etc.:

Purity	99.5%-99.9% by weight (dry basis)
Acidity (as H_2SO_4)	Less than 0.01% by weight
Moisture	Less than 1.0% by weight
Ash	Less than 0.05% by weight
Carbonaceous Matter	Less than 0.025% by weight
Arsenic, Tellurium, Selenium	Commercially Free*
Color (see Note below)	Bright yellow at ambient temperature

*Contents of less than 0.25 ppmw of arsenic and 2.0 ppmw of selenium and tellurium are usually considered as "commercially free."

NOTE: The color of sulfur is an important property because it gives an immediate indication of product purity. The sulfur is a bright yellow if the impurity content is less than about 0.02% by weight. Small amounts of carbon (soot) change the bright yellow color to dull yellow or green; "dark" sulfur in which the yellow color has a shade of gray or brown usually contains 0.1%-0.5% by weight of carbon. For sulfuric acid manufacturers, however, sulfur color is usually less important than ash and heavy metal contents.

INSTRUMENTATION

Since the quantity of acid gas being handled by the sulfur recovery unit is determined by upstream sweetening facilities, the sulfur plant feed gas rate is normally not controlled. However, during startup or in an emergency, part or all of the feed gas can be directed to flare.

For the main burner, the volume of feed gas is measured and the amount of air is controlled in ratio with the amount of acid gas. Both feed-forward[25], in which the measured feed gas flow rate and assumed composition are used, and feed-back, in which the measured ratio of H_2S:SO_2 in the plant tail gas is used, can be utilized to adjust the air/feed gas ratio for maximum sulfur recovery. A combination feed-forward/feed-back

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control system, in which the feed gas flow rate is used to control a main air valve and to set an approximate air/feed gas ratio and the ratio of H_2S:SO_2 in the tail gas is used to control a trim air valve, is often utilized.

For inline burners, the process stream temperature is normally used to adjust the combustion air rate and the amount of fuel (either acid gas or fuel gas) is controlled in ratio with the amount of air. Because these burners normally operate with a near substoichiometric air, this control system will result in a more rapid response to changes in process requirements.

Although conventional orifice meters can be used for acid gas and air measurement, the venturi meter is often more suitable. Thermocouples are used for most temperature measurements and a multipoint strip chart temperature recorder can be useful to operations by indicating trends. Tail gas analyzers (for H_2S and SO_2) are usually of the ultraviolet type although chromatographic analyzers have been utilized successfully. Except at the front of the plant and on air, acid gas or fuel gas systems, pressure gauges are not normally installed. Sample connections should be as short as possible; sample valves should be plug valves. Sample connections and valves should be fully steam-jacketed.

Measurement of reaction furnace temperature is sometimes used as an indication of satisfactory air/acid gas control. Both thermocouples and infra-red type instruments have been utilized; however, thermocouple life is short (6-9 months reported) and the response time for infra-red instruments can be poor.

Conventional infra-red instruments often can be utilized as flame monitoring devices for both the main burner and the inline burners; combination infra-red/ultraviolet (flicker-type) instruments have also been used successfully.

FIG. 22-32

Plot Showing That a Slight Change in Air to Acid Gas Ratio at the Head End of the Plant Will Make a Significant Change in the Tail Gas Ratio, H_2S:SO_2

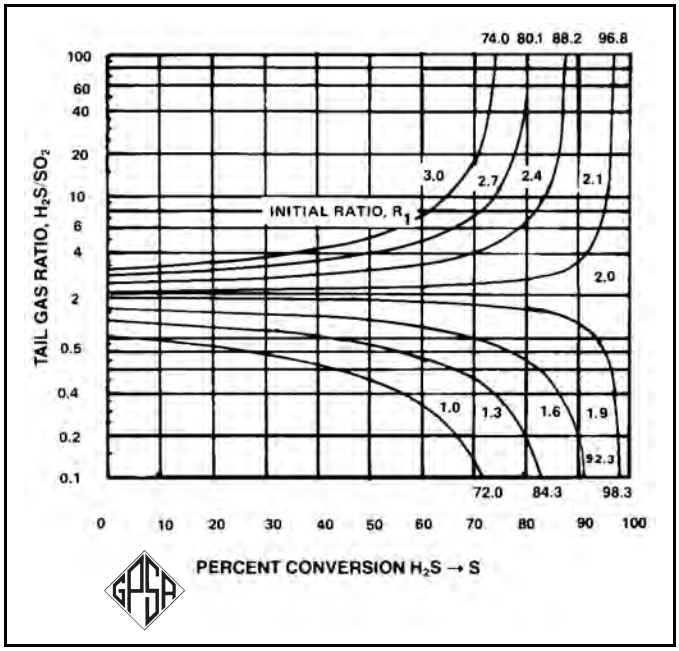
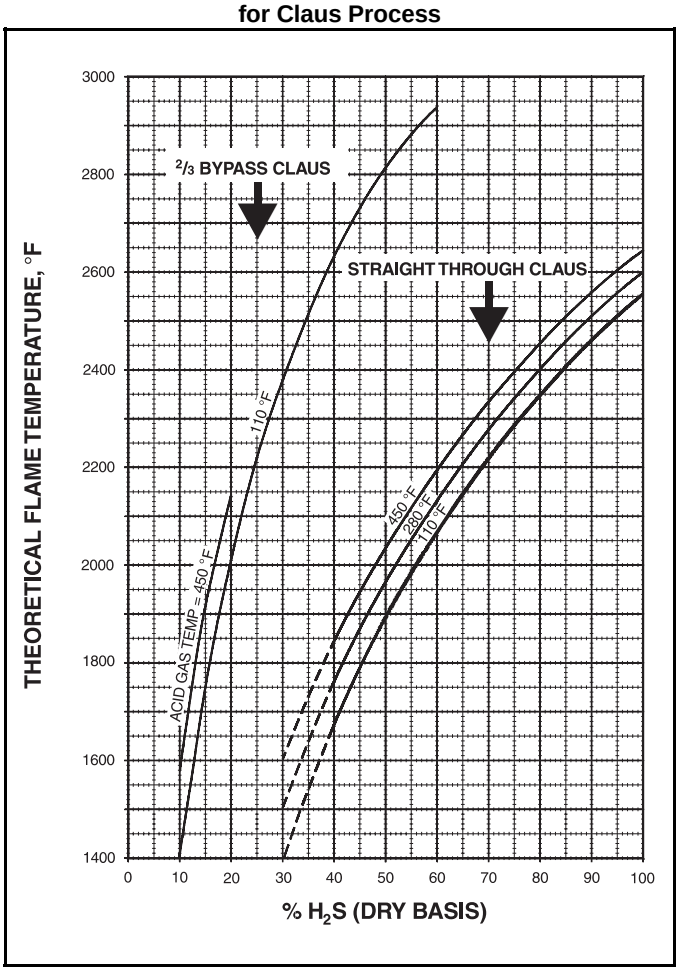


FIG. 22-33

Theoretical Flame Temperatures for Claus Process



OPERATIONAL ASPECTS

Overall Claus plant conversion efficiency is maximized by maintaining the stoichiometric H_2S:SO_2 ratio of 2:1 in the process gas to the catalytic converters. The most suitable point for this determination is at the outlet of the last sulfur condenser because a slight change in the air:acid gas ratio at the front of the plant will result in a significant change in the H_2S:SO_2 ratio in the tail gas and in the theoretical overall sulfur recovery (Fig. 22-32). An H_2S:SO_2 ratio in the tail gas of between 1:1 and 3:1 can be considered normal although the desired goal should be a 2:1 ratio.

A simple method of determining the H_2S:SO_2 ratio is by the use of stain tubes. This determination should be done at least once every 8 hours during startup, plant test runs, and whenever significant changes in plant operating variables are observed. Other analytical procedures involving wet chemistry, chromatography, or UV photometry are also suitable for adjusting plant operations.

Because of the effect of temperature upon the Claus reaction equilibrium, control of temperatures at various points in the process sequence is important. Unexpected changes in operating temperatures usually denote changes in conversion efficiency. For example, a decrease in the temperature rise across a catalytic converter bed is an indication of declining catalyst activity which may be caused by adsorption of elemental sulfur

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on the active surface area of the catalyst. Operating the catalyst bed at a temperature 50-100°F higher than normal for 24-48 hours will remove this sulfur from the catalyst and can restore its activity.

CLAUS PLANT MAINTENANCE

Maintenance and repair of Claus plant equipment requires special precautions because of the physical properties of sulfur and the potential hazards and/or toxicity of many plant process streams. Equipment handling liquid sulfur should be drained completely and other equipment should be purged of all hazardous materials (see shutdown portion of this section). A satisfactory welding procedure can involve sandblasting and/or grinding to a bare metal surface, extensive preheating, and the use of Type 309 stainless steel rod.

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SECTION 23

Physical Properties

This section contains charts, correlations, tables and procedures for predicting physical properties of hydrocarbons and other components of interest to the natural gas industry. Figure 23-1 contains the nomenclature used in this section.

Figure 23-2 is a listing of the physical properties for a number of hydrocarbons and other selected compounds. Following the property values are detailed footnotes and references for the entries in Fig. 23-2. After Fig. 23-2, this Section contains procedures for estimating the Z-factor for gases and material relating to hydrocarbon fluid densities, boiling points, ASTM distillation, critical properties, acentric factors, vapor pressures, viscosity, thermal conductivity, surface tension, and gross heating value.

FIG. 23-1

Nomenclature

B = second virial coefficient for a gas mixture, $(psia)^{-1}$
B′ = mole fraction of H_2S in a sour gas stream, Eq 23-6
B_{ii} = second virial coefficient for component i
B_{ij} = second cross virial coefficient for components i and j
$b_i^{1/2}$ = summation factor for component i
c = cost of gas
CABP = cubic average boiling point, °F
d = density, g/cc
gal = gallons
G = specific gravity or relative density (gas density)
G_i = specific gravity (gas gravity) of ideal gas, MW/MW_a
G_i^{id} = molecular weight ratio of component i in mixture
Hv^{id} = gross heating value per unit volume of ideal gas, Btu/cu ft
K_W = Watson characterization factor, Fig. 23-12
k = thermal conductivity, Btu/[(hr ft^2 °F)/ft]
k_A = thermal conductivity at one atmosphere, Btu/[(hr ft^2 °F)/ft]
lbm = pounds mass
M = mass fraction
m = mass, lbm
MW = Molecular weight, lbm/lbmol
MABP = molal average boiling point, °F or °R
MeABP = Mean average boiling point, °F or °R
n = number of moles, (mass/*MW*)
p = price of real gas
p^{id} = price of ideal gas
P = pressure, psia
P_c' = pseudo-critical pressure adjusted for acid gas composition, psia
P_{vp} = vapor pressure at a reduced temperature of 0.7
$P_w^{\bullet}$ = vapor pressure of water, 0.25636 psia at 60°F
R = gas constant, 10.73 (psia ft^3)/(°R lbmol) for all gases (Section 1 has *R* in other units)
S = specific gravity at 60°/60°F
T = absolute temperature, °R
t = ASTM D-86 distillation temperature for a volumetric fraction, °F or °R, Eq 23-11
T_c' = pseudo-critical temperature adjusted for acid gas composition, °R
V = volume, cu ft
v = volume fraction
$\dot{V}$ = volumetric flow rate, real gas
$\dot{V}^{id}$ = volumetric flow rate, ideal gas
VABP = volumetric average boiling point, °F
W = mass, lbm
WARP = weight average boiling point, °F
y_i = mole fraction of component i from analysis on dry basis, Eq 23-38
x = mole fraction in liquid phase
$y_i(cor)$ = mole fraction of component i adjusted for water content
y = mole fraction in gas phase
Z = Z-factor = PV/nRT

Greek

ε = pseudo-critical temperature adjustment factor, Eq 23-6
θ = MeABP/T_{pc}
ρ = density, lbm/ ft^3
μ = viscosity at operating temperature and pressure, centi poise
μ_A = viscosity at 14.7 psia (1 atm) and operating temperature, centipoise
ξ = factor defined by Eq 23-20
σ = surface tension, dynes/cm
ω = acentric factor
η = kinematic viscosity, centistokes
Δt = accounting period

Subscripts

a = air
b = boiling
c = critical
i = component i
L = liquid
m = mixture
pc = pseudo-critical
r = reduced state
V = vapor
v = volume
w = water

Superscripts

id = ideal gas
w = water
° = reference state

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FIG. 23-2

Physical Constants

Note: Numbers in this table do not have accuracies greater than 1 part in 1000. In some cases extra digits have been added to achieve internal consistency or to permit recalculation of experimental values.

	See Note No. →		A.	B.		C.	D.				
								Critical Constants			
Number	Compound	Formula	Molar Mass (Molecular Weight)	Boiling Point, °F 14.696 psia	Vapor Pressure, psia, 100 °F	Freezing Point, °F 14.696 psia(abs)	Refractive Index 60 °F	Pressure, psia (abs)	Temperature, °F	Volume, ft³/lb	Number
1	Methane	CH_4	16.042	-258.67	(5000)*	-296.45	1.00041	667.0	-116.66	0.0985	1
2	Ethane	C_2H_6	30.069	-127.48	(800)*	-297.04	1.21241	706.6	89.92	0.0775	2
3	Propane	C_3H_8	44.096	-43.72	188.7	-305.73	1.29506	615.5	205.92	0.0728	3
4	Isobutane	C_4H_{10}	58.122	11.08	72.48	-255.30	1.32469	527.9	274.41	0.0715	4
5	n-Butane	C_4H_{10}	58.122	31.09	51.68	-217.05	1.33593	550.9	305.55	0.0703	5
6	Isopentane	C_5H_{12}	72.149	82.11	20.46	-255.80	1.35626	490.4	369.0	0.0685	6
7	n-Pentane	C_5H_{12}	72.149	96.98	15.76	-201.50	1.35993	488.8	385.8	0.0676	7
8	Neopentane	C_5H_{12}	72.149	49.12	36.70	2.17	1.34167	463.5	321.0	0.0690	8
9	n-Hexane	C_6H_{14}	86.175	155.72	4.961	-139.56	1.37717	436.9	453.8	0.0688	9
10	2-Methylpentane	C_6H_{14}	86.175	140.44	6.773	-244.60	1.37387	436.6	435.8	0.0682	10
11	3-Methylpentane	C_6H_{14}	86.175	145.84	6.103	-261.20	1.37888	452.5	448.3	0.0682	11
12	Neohexane	C_6H_{14}	86.175	121.49	9.865	-147.69	1.37126	446.7	420.0	0.0667	12
13	2,3-Dimethylbutane	C_6H_{14}	86.175	136.34	7.410	-199.35	1.37730	454.0	440.2	0.0665	13
14	n-Heptane	C_7H_{16}	100.202	209.13	1.6203	-131.01	1.38987	396.8	512.9	0.0682	14
15	2-Methylhexane	C_7H_{16}	100.202	194.05	2.273	-180.87	1.38717	396.0	494.5	0.0673	15
16	3-Methylhexane	C_7H_{16}	100.202	197.33	2.130	-	1.39091	407.6	503.7	0.0646	16
17	3-Ethylpentane	C_7H_{16}	100.202	200.25	2.012	-181.44	1.39568	419.2	513.2	0.0665	17
18	2,2-Dimethylpentane	C_7H_{16}	100.202	174.50	3.494	-190.80	1.38447	401.8	477.1	0.0665	18
19	2,4-Dimethylpentane	C_7H_{16}	100.202	176.85	3.294	-182.59	1.38383	397.4	475.8	0.0667	19
20	3,3-Dimethylpentane	C_7H_{16}	100.202	186.87	2.775	-209.99	1.39314	427.9	505.7	0.0662	20
21	Triptane	C_7H_{16}	100.202	177.54	3.376	-12.21	1.39167	427.9	496.3	0.0636	21
22	n-Octane	C_8H_{18}	114.229	258.21	0.5366	-70.17	1.39962	360.7	564.2	0.0673	22
23	Diisobutyl	C_8H_{18}	114.229	228.39	1.102	-132.09	1.39461	361.1	530.3	0.0676	23
24	Isooctane	C_8H_{18}	114.229	210.62	1.709	-161.23	1.39365	372.7	519.4	0.0656	24
25	n-Nonane	C_9H_{20}	128.255	303.40	0.17003	-64.28	1.40747	330.7	610.8	0.0693	25
26	n-Decane	$C_{10}H_{22}$	142.282	345.40	0.06160	-21.39	1.41386	304.6	652.2	0.0703	26
27	Cyclopentane	C_5H_{10}	70.133	120.61	9.917	-136.96	1.40896	653.8	461.2	0.0594	27
28	Methylcyclopentane	C_6H_{12}	84.159	161.29	4.491	-224.38	1.41210	548.8	499.4	0.0607	28
29	Cyclohexane	C_6H_{12}	84.159	177.40	3.267	44.03	1.42863	590.7	536.6	0.0586	29
30	Methylcyclohexane	C_7H_{14}	98.186	213.69	1.609	-195.81	1.42534	503.4	570.3	0.0600	30
31	Ethene(Ethylene)	C_2H_4	28.053	-154.72	–	-272.50	1.24100	731.0	48.5	0.0746	31
32	Propene(Propylene)	C_3H_6	42.080	-53.85	227.9	-301.47	1.31256	676.6	198.4	0.0717	32
33	1-Butene(Butylene)	C_4H_8	56.106	20.79	62.07	-301.65	1.35056	586.4	296.2	0.0683	33
34	cis-2-Butene	C_4H_8	56.106	38.70	45.93	-218.02	1.36656	615.4	324.4	0.0667	34
35	trans-2-Butene	C_4H_8	56.106	33.59	49.84	-158.03	1.35867	574.9	311.9	0.0679	35
36	Isobutene	C_4H_8	56.106	19.56	63.17	-220.61	1.35390	580.2	292.6	0.0681	36
37	1-Pentene	C_5H_{10}	70.133	85.93	19.12	-265.40	1.37426	509.5	376.9	0.0674	37
38	1,2-Butadiene	C_4H_6	54.090	51.14	37.23	-213.14	-	655.6	354.3	0.0696	38
39	1,3-Butadiene	C_4H_6	54.090	23.85	59.46	-164.05	-	620.3	305.6	0.0654	39
40	Isoprene	C_5H_8	68.117	93.30	16.68	-230.71	1.42498	581.6	402.9	0.0665	40
41	Acetylene	C_2H_2	26.037	-118.87	-	-113.44	-	890.4	95.3	0.0693	41
42	Benzene	C_6H_6	78.112	176.10	3.222	41.96	1.50393	710.4	552.2	0.0531	42
43	Toluene	C_7H_8	92.138	231.10	1.0322	-138.89	1.49946	595.5	605.6	0.0549	43
44	Ethylbenzene	C_8H_{10}	106.165	277.09	0.3705	-138.93	1.49827	523.0	651.3	0.0564	44
45	o-Xylene	C_8H_{10}	106.165	291.96	0.2632	-13.30	1.50767	541.6	674.9	0.0557	45
46	m-Xylene	C_8H_{10}	106.165	282.35	0.3291	-54.12	1.49951	512.9	651.0	0.0567	46
47	p-Xylene	C_8H_{10}	106.165	280.99	0.3422	55.86	1.49810	509.2	649.5	0.0572	47
48	Styrene	C_8H_8	104.149	293.47	0.2467	-23.15	1.54937	587.8	703.0	0.0534	48
49	Isopropylbenzene	C_9H_{12}	120.192	306.27	0.1884	-140.81	1.49372	465.4	676.3	0.0568	49
50	Methyl alcohol	CH_4O	32.042	148.17	4.631	-143.79	1.33012	1174	463.1	0.0590	50
51	Ethyl alcohol	C_2H_6O	46.068	172.91	2.313	-173.29	1.36309	891.7	465.4	0.0581	51
52	Carbon monoxide	CO	28.010	-312.73	-	-337.04	1.00036	506.7	-220.63	0.0527	52
53	Carbon dioxide	CO_2	44.010	-109.12	-	-69.81	1.00048	1070.0	87.76	0.0343	53
54	Hydrogen sulfide	H_2S	34.082	-76.52	395.5	-121.81	1.00060	1306.5	212.81	0.0462	54
55	Sulfur dioxide	SO_2	64.065	14.04	85.31	-103.81	1.00062	1143	315.48	0.0305	55
56	Ammonia	NH_3	17.0306	-27.99	212.0	-107.77	1.00036	1644	270.1	0.0712	56
57	Air		28.9586	-317.64	-	-	1.00028	551.9	-220.97	0.0458	57
58	Hydrogen	H_2	2.0159	-422.97	-	-434.55	1.00013	190.7	-399.9	0.5319	58
59	Oxygen	O_2	31.9988	-297.332	-	-361.82	1.00027	731.4	-181.43	0.0367	59
60	Nitrogen	N_2	28.0135	-320.431	-	-346.00	1.00028	492.5	-232.53	0.0511	60
61	Chlorine	Cl_2	70.9054	-29.25	157.3	-149.73	1.38729	1117	290.93	0.0280	61
62	Water	H_2O	18.0153	211.953	0.95051	32.00	1.33342	3200.1	705.10	0.04975	62
63	Helium	He	4.0026	-452.06	-	-455.75	1.00003	33.0	-450.32	0.2300	63
64	Hydrogen chloride	HCl	36.4606	-121.00	921	-173.52	1.00042	1205	124.77	0.0356	64

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FIG. 23-2 (Cont'd)

Physical Constants

Note: Numbers in this table do not have accuracies greater than 1 part in 1000. In some cases extra digits have been added to achieve internal consistency or to permit recalculation of experimental values.

	E. Density of Liquid 14.696 psia, 60 °F			F.	G.	H.	I. Ideal Gas 14.696 psia, 60 °F			J. Specific Heat 60 °F & 14.696 psia		
Number	Relative Density (specific gravity) 60 °F / 60 °F	lb/gal (wt in vacuum)	gal/lb mol	Tempearture coefficient of density, 1/T(K)	Acentric Factor, ω	Summation Factor, psia^{-1} 60 °F	Relative Density (specific gravity) Air = 1	ft^3 gas/lb	Volume Ratio ft^3 gas/gal liquid	C_p, Ideal Gas Btu/(lb °F)	C_p, liquid Btu/(lb °F)	Number
1	(0.3)*	(2.5)*	(6.4172)	-	0.0115	0.0116	0.5540	23.655	(59.138)*	0.52725	-	1
2	0.35643	2.9716	10.119	-	0.0994	0.0238	1.0383	12.620	37.503	0.40880	1.0900	2
3	0.50738	4.2301	10.424	-0.00156	0.1529	0.0349	1.5227	8.6060	36.404	0.38970	0.6253	3
4	0.56295	4.6934	12.384	-0.00120	0.1865	0.0444	2.0071	6.5291	30.644	0.38798	0.5633	4
5	0.58408	4.8696	11.936	-0.00108	0.2003	0.0471	2.0071	6.5291	31.794	0.39649	0.5679	5
6	0.62460	5.2074	13.855	-0.00089	0.2284	0.0572	2.4914	5.2598	27.390	0.38311	0.5370	6
7	0.63113	5.2618	13.712	-0.00086	0.2515	0.0603	2.4914	5.2598	27.676	0.38882	0.5439	7
8	0.59624	4.9710	14.514	-0.00104	0.1966	0.0516	2.4914	5.2598	26.146	0.39126	0.5534	8
9	0.66404	5.5363	15.566	-0.00075	0.2993	0.0792	2.9758	4.4036	24.380	0.38696	0.5335	9
10	0.65794	5.4853	15.710	-0.00078	0.2777	0.0743	2.9758	4.4036	24.155	0.38391	0.5268	10
11	0.66902	5.5777	15.450	-0.00075	0.2726	0.0718	2.9758	4.4036	24.562	0.37782	0.5188	11
12	0.65371	5.4501	15.812	-0.00077	0.2331	0.0673	2.9758	4.4036	24.000	0.38202	0.5141	12
13	0.66603	5.5528	15.519	-0.00073	0.2481	0.0685	2.9758	4.4036	24.453	0.37465	0.5141	13
14	0.68819	5.7375	17.464	-0.00068	0.3483	0.0953	3.4602	3.7872	21.729	0.38566	0.5279	14
15	0.68327	5.6966	17.590	-0.00070	0.3312	0.0899	3.4602	3.7872	21.574	0.38225	0.5216	15
16	0.69170	5.7668	17.376	-0.00069	0.3231	0.0899	3.4602	3.7872	21.840	0.37957	0.5137	16
17	0.70291	5.8603	17.099	-0.00069	0.3111	0.0898	3.4602	3.7872	22.194	0.38669	0.5141	17
18	0.67828	5.6550	17.719	-0.00070	0.2870	0.0832	3.4602	3.7872	21.417	0.38687	0.5167	18
19	0.67714	5.6455	17.749	-0.00072	0.3035	0.0844	3.4602	3.7872	21.381	0.39524	0.5241	19
20	0.69720	5.8127	17.239	-0.00059	0.2687	0.0846	3.4602	3.7872	22.014	0.38385	0.5023	20
21	0.69433	5.7887	17.310	-0.00068	0.2501	0.0817	3.4602	3.7872	21.923	0.37797	0.4991	21
22	0.70698	5.8942	19.380	-0.00063	0.3977	0.1214	3.9445	3.3222	19.582	0.38446	0.5250	22
23	0.69806	5.8199	19.627	-0.00066	0.3571	0.1041	3.9445	3.3222	19.334	0.37652	0.5103	23
24	0.69628	5.8050	19.678	-0.00065	0.3043	0.0960	3.9445	3.3222	19.285	0.38154	0.5172	24
25	0.72186	6.0183	21.311	-0.00060	0.4421	0.1350	4.4289	2.9588	17.807	0.38358	0.5221	25
26	0.73406	6.1200	23.249	-0.00058	0.4875	0.1516	4.9133	2.6671	16.323	0.38294	0.5207	26
27	0.74985	6.2516	11.218	-0.00073	0.1950	0.0589	2.4218	5.4109	33.827	0.27199	0.4214	27
28	0.75353	6.2823	13.396	-0.00069	0.2267	0.0712	2.9062	4.5091	28.328	0.30142	0.4406	28
29	0.78349	6.5321	12.884	-0.00066	0.2105	0.0729	2.9062	4.5091	29.454	0.29084	0.4331	29
30	0.77394	6.4525	15.217	-0.00062	0.2352	0.0866	3.3906	3.8650	24.939	0.31989	0.4403	30
31	-	-	-	-	0.0865	0.0208	0.9687	13.527	-	0.35897	-	31
32	0.52265	4.3574	9.6570	-0.00169	0.1407	0.0324	1.4531	9.0182	39.296	0.35759	0.5729	32
33	0.60046	5.0062	11.207	-0.00112	0.1923	0.0442	1.9375	6.7637	33.860	0.35613	0.5370	33
34	0.62754	5.2319	10.724	-0.00102	0.2056	0.0461	1.9375	6.7637	35.387	0.33368	0.5280	34
35	0.61017	5.0871	11.029	-0.00106	0.2035	0.0464	1.9375	6.7637	34.408	0.36630	0.5293	35
36	0.60066	5.0078	11.204	-0.00113	0.1995	0.0442	1.9375	6.7637	33.871	0.36689	0.5480	36
37	0.64600	5.3859	13.022	-0.00092	0.2314	0.0575	2.4218	5.4109	29.143	0.36017	0.5191	37
38	0.65773	5.4836	9.8640	-0.00094	0.1715	0.0468	1.8679	7.0158	38.472	0.34433	0.5411	38
39	0.62718	5.2289	10.345	-0.00109	0.1887	0.0438	1.8679	7.0158	36.685	0.34316	0.5356	39
40	0.68606	5.7199	11.909	-0.00083	0.2149	0.0563	2.3522	5.5711	31.866	0.35092	0.5193	40
41	-	-	-	-	0.1976	0.0218	0.8991	14.575	-	0.39647	-	41
42	0.88458	7.3749	10.592	-0.00067	0.2092	0.0685	2.6974	4.8582	35.829	0.24266	0.4098	42
43	0.87182	7.2686	12.676	-0.00059	0.2637	0.0883	3.1817	4.1186	29.937	0.26014	0.4006	43
44	0.87169	7.2674	14.608	-0.00056	0.3026	0.1084	3.6661	3.5745	25.977	0.27833	0.4113	44
45	0.88453	7.3745	14.396	-0.00052	0.3118	0.1135	3.6661	3.5745	26.360	0.29052	0.4163	45
46	0.86882	7.2435	14.657	-0.00055	0.3255	0.1121	3.6661	3.5745	25.892	0.27480	0.4040	46
47	0.86557	7.2164	14.712	-0.00055	0.3211	0.1116	3.6661	3.5745	25.795	0.27506	0.4023	47
48	0.91088	7.5942	13.714	-0.00056	0.2453	0.1071	3.5965	3.6437	27.671	0.26320	0.4119	48
49	0.86655	7.2246	16.636	-0.00055	0.3256	0.1247	4.1505	3.1573	22.811	0.30697	0.4204	49
50	0.79626	6.6386	4.8266	-0.00066	0.5649	0.0807	1.1065	11.843	78.624	0.32504	0.5918	50
51	0.79402	6.6199	6.9590	-0.00060	0.6446	0.1000	1.5908	8.2374	54.531	0.33176	0.5640	51
52	0.79265	6.6085	4.2385	-	0.0510	0.0052	0.9672	13.548	89.533	0.24738	-	52
53	0.82203	6.8534	6.4216	-0.00801	0.2239	0.0195	1.5197	8.6228	59.095	0.19875	-	53
54	0.80269	6.6922	5.0928	-0.00170	0.1010	0.0242	1.1769	11.135	74.514	0.23811	0.5191	54
55	1.39241	11.609	5.5186	-0.00110	0.2570	0.0358	2.2123	5.9235	68.764	0.14735	0.3293	55
56	0.61730	5.1466	3.3091	-0.00132	0.2560	0.0284	0.5881	22.283	114.68	0.49679	1.1256	56
57	0.87603	7.3036	3.9649	-	-	0.00523	1.00000	13.104	95.710	0.23992	-	57
58	0.07087	0.5908	3.4120	-	-0.2140	-	0.06961	188.25	111.22	3.4027	-	58
59	1.14230	9.5236	3.3599	-	0.0222	0.0072	1.1050	11.859	112.94	0.21894	-	59
60	0.80687	6.7270	4.1643	-	0.0372	0.00442	0.9674	13.547	91.128	0.24829	-	60
61	1.4241	11.873	5.9720	-	0.0722	0.0300	2.4485	5.3520	63.544	0.11365	-	61
62	1.00000	8.3372	2.1608	-0.00009	0.3443	0.05557	0.62210	21.0646	175.620	0.44476	1.0003	62
63	0.12486	1.0409	3.8452	-	-0.3820	-	0.1382	94.810	98.692	1.2404	-	63
64	0.8512	7.097	5.1375	-0.00169	0.1269	0.0202	1.259	10.41	73.9	0.19033	-	64

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FIG. 23-2 (Cont'd)

Physical Constants

Note: Numbers in this table do not have accuracies greater than 1 part in 1000. In some cases extra digits have been added to achieve internal consistency or to permit recalculation of experimental values.

	K. Heating Value, 60 °F					L.	M.	Flammability Limits, vol% in air mixture		ASTM octane number		
	Net		Gross									
Number	Btu/ft³ Ideal gas 14.696 psia	Btu/lb Liquid (wt in vacuum)	Btu/ft³ Ideal gas 14.696 psia	Btu/lb Liquid (wt in vacuum)	Btu/gal Liquid	Heat of vaporization 14.696 psia at boiling point, Btu/lb	Air required for combustion of ideal gas ft³(air)/ft³(gas)	Lower	Higher	Motor Method D-357	Research Method D-908	Number
1	909.4	-	1010.0	-	-	219.8	9.542	5	15	-	-	1
2	1618.7	20277	1769.7	22182	65916	210.3	16.698	2.9	13	+0.05	+1.6*	2
3	2314.9	19758	2516.2	21490	90905	182.9	23.855	2	9.5	97.1	+1.8*	3
4	3000.4	19437	3252.0	21080	98935	157.2	31.011	1.8	8.5	97.6	+0.1*	4
5	3010.8	19494	3262.4	21136	102926	166.3	31.011	1.5	9	89.6	93.8	5
6	3699.0	19303	4000.9	20891	108789	147.7	38.168	1.3	8	90.3	92.3	6
7	3706.9	19335	4008.7	20923	110094	154.4	38.168	1.4	8.3	62.6*	61.7*	7
8	3682.9	19235	3984.8	20823	103509	135.8	38.168	1.3	7.5	80.2	85.5	8
9	4403.8	19232	4756.0	20783	115060	144.1	45.324	1.1	7.7	26	24.8	9
10	4395.2	19202	4747.4	20753	113838	138.8	45.324	1.18	7	73.5	73.4	10
11	4398.1	19214	4750.3	20765	115819	140.2	45.324	1.2	7.7	74.3	74.5	11
12	4383.7	19162	4735.9	20713	112890	131.3	45.324	1.2	7	93.4	91.8	12
13	4392.7	19195	4744.9	20746	115198	136.0	45.324	1.2	7	94.3	0.3	13
14	5100.0	19156	5502.5	20680	118654	136.7	52.481	1	7	-	-	14
15	5092.1	19133	5494.7	20658	117678	132.2	52.481	1	7	46.4	42.4	15
16	5096.0	19147	5498.5	20671	119206	132.9	52.481	(1.01)	6.6	55.8	52	16
17	5098.2	19155	5500.8	20679	121185	133.5	52.481	(1.00)	6.5	69.3	65	17
18	5079.6	19096	5482.1	20620	116607	125.6	52.481	(1.09)	6.8	95.6	92.8	18
19	5084.2	19111	5486.7	20636	116499	126.9	52.481	(1.08)	6.8	83.8	83.1	19
20	5086.4	19119	5488.9	20644	119996	127.4	52.481	(1.04)	7	86.6	80.8	20
21	5081.2	19104	5483.7	20628	119410	124.5	52.481	(1.08)	6.8	+0.1	+1.8	21
22	5796.0	19097	6248.9	20601	121428	130.0	59.637	0.8	6.5	-	-	22
23	5780.5	19059	6233.3	20563	119675	122.0	59.637	(0.92)	6.3	55.7	55.2	23
24	5778.8	19063	6231.6	20568	119396	115.8	59.637	0.95	6	100	100	24
25	6493.2	19054	6996.4	20543	123634	124.7	66.794	0.7	5.6	-	-	25
26	7189.5	19018	7743.0	20494	125424	119.6	73.950	0.7	5.4	-	-	26
27	3512.0	18825	3763.6	20186	126195	167.9	35.782	(1.48)	8.3	84.9*	+0.1	27
28	4199.0	18769	4500.9	20130	126465	149.9	42.939	1.0	8.35	80	91.3	28
29	4179.7	18675	4481.6	20036	130880	153.0	42.939	1.2	8.35	77.2	83	29
30	4863.7	18641	5215.9	20002	129063	137.1	50.095	1.1	6.7	71.1	74.8	30
31	1499.1	-	1599.8	-	-	208.2	14.313	2.7	36	75.6	+0.03	31
32	2182.1	19512	2333.0	20873	90951	189.2	21.469	2.0	11.7	84.9	+0.2	32
33	2878.6	19308	3079.9	20669	103472	168.7	28.626	1.6	10	80.8	97.4	33
34	2871.0	19243	3072.3	20604	107798	178.9	28.626	1.6	10	83.5	100	34
35	2866.8	19219	3068.1	20580	104694	174.8	28.626	1.6	10	-	-	35
36	2859.9	19179	3061.2	20540	102861	166.4	28.626	1.6	10	-	-	36
37	3575.0	19184	3826.5	20545	110652	154.9	35.782	1.3	10	77.1	90.9	37
38	2789.0	19379	2940.0	20438	112072	193.6	26.240	(1.62)	10.3	-	-	38
39	2730.0	18980	2880.9	20039	104780	178.4	26.240	2.0	12.5	-	-	39
40	3410.8	18832	3612.1	19953	114131	163.6	33.397	(1.12)	8.5	81	99.1	40
41	1423.9	-	1474.3	-	-	353.3	11.927	1.5	100	-	-	41
42	3590.9	17256	3741.9	17989	132671	169.5	35.782	1.2	8	+2.8	-	42
43	4273.7	17422	4474.9	18251	132658	155.5	42.939	1.2	7.1	+0.3	+5.8	43
44	4970.4	17594	5222.0	18493	134394	144.7	50.095	1.0	8	97.9	+0.8	44
45	4958.1	17545	5209.7	18444	136016	148.5	50.095	1.0	7.6	100	+0	45
46	4956.1	17541	5207.7	18440	133572	146.5	50.095	1.0	7	+2.8	+4	46
47	4957.1	17545	5208.6	18444	133102	145.6	50.095	1.0	7	+1.2	+3.4	47
48	4830.5	17415	5031.8	18148	137819	153.5	47.710	1.1	8	+0.2	>+*3	48
49	5660.8	17710	5962.7	18663	134831	132.9	57.252	0.8	6.5	99.3	+2.1	49
50	766.2	8561	866.9	9753	64744	482.4	7.156	5.5	44	-	-	50
51	1447.5	11523	1598.5	12766	84511	364.0	14.313	3.28	19	-	-	51
52	320.5	-	320.5	-	-	92.5	2.385	12.5	74.2	-	-	52
53	0	-	0	-	-	246.5	-	-	-	-	-	53
54	586.8	6337	637.1	6897	46156	234.4	7.156	4.3	45.5	-	-	54
55	0	-	0	-	-	167.2	-	-	-	-	-	55
56	358.7	-	434.2	-	-	588.8	3.578	15.5	27	-	-	56
57	0	-	0	-	-	86.8	-	-	-	-	-	57
58	273.8	-	324.2	-	-	191.5	2.385	4	74.2	-	-	58
59	0	-	0	-	-	91.6	-	-	-	-	-	59
60	0	-	0	-	-	85.6	-	-	-	-	-	60
61	-	-	-	-	-	123.6	-	-	-	-	-	61
62	-	-	#VALUE!	-	0	970.12	-	-	-	-	-	62
63	-	-	0	-	-	8.9	-	-	-	-	-	63
64	-	-	-	-	-	192.3	-	-	-	-	-	64

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FIG. 23-2 (Cont'd)

Notes and References for the Table of Physical Constants

Note: Numbers in this table do not have accuracies greater than 1 part in 1000. In some cases extra digits have been added to achieve internal consistency or to permit recalculation of experimental values.

	See Note No. →		A.	B.		C.	D.				
								Critical Constants			
Number	Compound	Formula	Molar Mass (Molecular Weight)	Boiling Point, °F 14.696 psia	Vapor Pressure, psia, 100 °F	Freezing Point, °F 14.696 psia(abs)	Refractive Index 60 °F	Pressure, psia (abs)	Temperature, °F	Volume, ft³/lb	Number
1	Methane	CH_4	1	b	e, f	2, g	2, h	2	2	2	1
2	Ethane	C_2H_6	1	b	e, f	2, g	2, g	2	2	2	2
3	Propane	C_3H_8	1	b	b	2, g	2, g	2	2	2	3
4	Isobutane	C_4H_{10}	1	b	b	2	2, g	2	2	2	4
5	n-Butane	C_4H_{10}	1	b	b	2	2, g	2	2	2	5
6	Isopentane	C_5H_{12}	1	b	b	2	2	2	2	2	6
7	n-Pentane	C_5H_{12}	1	b	b	2	2	2	2	2	7
8	Neopentane	C_5H_{12}	1	b	b	2	2, g	2	2	2	8
9	n-Hexane	C_6H_{14}	1	b	b	2	2	2	2	2	9
10	2-Methylpentane	C_6H_{14}	1	b	b	2	2	2	2	2	10
11	3-Methylpentane	C_6H_{14}	1	b	b	2	2	2	2	2	11
12	Neohexane	C_6H_{14}	1	b	b	2	2	2	2	2	12
13	2,3-Dimethylbutane	C_6H_{14}	1	b	b	2	2	2	2	2	13
14	n-Heptane	C_7H_{16}	1	b	b	2	2	2	2	2	14
15	2-Methylhexane	C_7H_{16}	1	b	b	2	2	2	2	2	15
16	3-Methylhexane	C_7H_{16}	1	b	b	2	2	2	2	2	16
17	3-Ethylpentane	C_7H_{16}	1	b	b	2	2	2	2	2	17
18	2,2-Dimethylpentane	C_7H_{16}	1	b	b	2	2	2	2	2	18
19	2,4-Dimethylpentane	C_7H_{16}	1	b	b	2	2	2	2	2	19
20	3,3-Dimethylpentane	C_7H_{16}	1	b	b	2	2	2	2	2	20
21	Triptane	C_7H_{16}	1	b	b	2	2	2	2	2	21
22	n-Octane	C_8H_{18}	1	b	b	2	2	2	2	2	22
23	Diisobutyl	C_8H_{18}	1	b	b	2	2	2	2	2	23
24	Isooctane	C_8H_{18}	1	b	b	2	2	2	2	2	24
25	n-Nonane	C_9H_{20}	1	b	b	2	2	2	2	2	25
26	n-Decane	$C_{10}H_{22}$	1	b	b	2	2	2	2	2	26
27	Cyclopentane	C_5H_{10}	1	b	b	2	2	2	2	2	27
28	Methylcyclopentane	C_6H_{12}	1	b	b	2	2	2	2	2	28
29	Cyclohexane	C_6H_{12}	1	b	b	2	2	2	2	2	29
30	Methylcyclohexane	C_7H_{14}	1	b	b	2	2	2	2	2	30
31	Ethene(Ethylene)	C_2H_4	1	b	e, f	2	7, g	2	2	2	31
32	Propene(Propylene)	C_3H_6	1	b	b	2	2, g	2	2	2	32
33	1-Butene(Butylene)	C_4H_8	1	b	b	2	2, g	2	2	2	33
34	cis-2-Butene	C_4H_8	1	b	b	2	2, g	2	2	2	34
35	trans-2-Butene	C_4H_8	1	b	b	2	2, g	2	2	2	35
36	Isobutene	C_4H_8	1	b	b	2	2, g	2	2	2	36
37	1-Pentene	C_5H_{10}	1	b	b	2	2	2	2	2	37
38	1,2-Butadiene	C_4H_6	1	b	b	2	2	2	2	2	38
39	1,3-Butadiene	C_4H_6	1	b	b	2	2	2	2	2	39
40	Isoprene	C_5H_8	1	b	b	2	2	2	2	2	40
41	Acetylene	C_2H_2	1	b	f	2		2	2	2	41
42	Benzene	C_6H_6	1	b	b	2	2	2	2	2	42
43	Toluene	C_7H_8	1	b	b	2	2	2	2	2	43
44	Ethylbenzene	C_8H_{10}	1	b	b	2	2	2	2	2	44
45	o-Xylene	C_8H_{10}	1	b	b	2	2	2	2	2	45
46	m-Xylene	C_8H_{10}	1	b	b	2	2	2	2	2	46
47	p-Xylene	C_8H_{10}	1	b	b	2	2	2	2	2	47
48	Styrene	C_8H_8	1	b	b	2	2	i	i	i	48
49	Isopropylbenzene	C_9H_{12}	1	b	b	2	2	2	2	2	49
50	Methyl alcohol	CH_4O	1	b	b	2	2	2	2	2	50
51	Ethyl alcohol	C_2H_6O	1	b	b	2	2	2	2	2	51
52	Carbon monoxide	CO	1	c	f	c, g	2, h	c	c	c	52
53	Carbon dioxide	CO_2	1	c,d	f	c, g	2, h	c	c	c	53
54	Hydrogen sulfide	H_2S	1	c	c	c, g	2, h	c	c	c	54
55	Sulfur dioxide	SO_2	1	c	c	c, g	2, h	c	c	c	55
56	Ammonia	NH_3	1	c	c	c, g	2, h	c	c	c	56
57	Air		1	c	f		2, h	c	c	c	57
58	Hydrogen	H_2	1	c	f	c, g	2, h	c	c	c	58
59	Oxygen	O_2	1	c	f	c, g	2, h	c	c	c	59
60	Nitrogen	N_2	1	c	f	c, g	2, h	c	c	c	60
61	Chlorine	Cl_2	1	4	4	2	2, g	2	2	2	61
62	Water	H_2O	1	5	5	5	2	5	5	5	62
63	Helium	He	1	c	f	c, g	2, h	c	c	c	63
64	Hydrogen chloride	HCl	1	b	6	2	2, h	2	2	2	64

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FIG. 23-2 (Cont'd)

Notes and References for the Table of Physical Constants

Note: Numbers in this table do not have accuracies greater than 1 part in 1000. In some cases extra digits have been added to achieve internal consistency or to permit recalculation of experimental values.

	E. Density of Liquid 14.696 psia, 60 °F			F.	G.	H.	I. Ideal Gas 14.696 psia, 60 °F			J. Specific Heat 60 °F & 14.696 psia		
Number	Relative Density (specific gravity) 60 °F / 60 °F	lb/gal (wt in vacuum)	gal/lb mol	Tempearture coefficient of density, 1/T(K)	Acentric Factor, w	Summation Factor, psia^{-1} 60 °F	Relative Density (specific gravity) Air = 1	ft^3 gas/lb	Volume Ratio ft^3 gas/gal liquid	C_p, Ideal Gas Btu/(lb °F)	C_p, liquid Btu/(lb °F)	Number
1	e, f	e, f	e, f	e, f	2	9			e, f	10		1
2	8, g	8, g	8, g	8, g	2	9			g	10	11	2
3	8, g	8, g	8, g	8, g	2	9			g	10	11	3
4	8, g	8, g	8, g	8, g	2	9			g	10	11	4
5	8, g	8, g	8, g	8, g	2	9			g	10	11	5
6	8	8	8	8	2	9				10	11	6
7	8	8	8	8	2	9				10	11	7
8	8, g	8, g	8, g	8, g	2	9			g	10	11	8
9	8	8	8	8	2	9				10	11	9
10	8	8	8	8	2	9				10	11	10
11	8	8	8	8	2	9				10	11	11
12	8	8	8	8	2	k				10	11	12
13	8	8	8	8	2	9				10	11	13
14	8	8	8	8	2	9				10	11	14
15	8	8	8	8	2	k				10	11	15
16	8	8	8	8	2	k				10	11	16
17	8	8	8	8	2	k				10	11	17
18	8	8	8	8	2	k				10	11	18
19	8	8	8	8	2	k				10	11	19
20	8	8	8	8	2	k				10	11	20
21	8	8	8	8	2	k				10	11	21
22	8	8	8	8	2	9				10	11	22
23	8	8	8	8	2	k				10	11	23
24	8	8	8	8	2	k				10	11	24
25	8	8	8	8	2	c				10	11	25
26	8	8	8	8	2	c				10	11	26
27	8	8	8	8	2	k				10	11	27
28	8	8	8	8	2	k				10	11	28
29	8	8	8	8	2	k				10	11	29
30	8	8	8	8	2	k				10	11	30
31					2	k			f	10		31
32	8	8	8	8	2	k				10	11	32
33	8	8	8	8	2	k				10	11	33
34	8	8	8	8	2	k				10	11	34
35	8	8	8	8	2	k				10	11	35
36	8	8	8	8	2	k				10	11	36
37	8	8	8	8	2	k				10	11	37
38	8	8	8	8	2	k				10	11	38
39	8	8	8	8	2	k				10	11	39
40	8	8	8	8	2	k				10	11	40
41					2	k				10		41
42	8	8	8	8	2	k				10	11	42
43	8	8	8	8	2	k				10	11	43
44	8	8	8	8	2	k				10	11	44
45	8	8	8	8	2	k				10	11	45
46	8	8	8	8	2	k				10	11	46
47	8	8	8	8	2	k				10	11	47
48	8	8	8	8	2	k				i	11	48
49	8	8	8	8	2	k				10	11	49
50	8	8	8	8	2	9				10	11	50
51	8	8	8	8	2	9				10	11	51
52	c	c	c	c	c	c			j	10		52
53	c	c	c	c	c	c			g	10		53
54	c	c	c	c	c	c			g	10	c	54
55	c	c	c	c	c	c			g	c	c	55
56	c	c	c	c	c	c			g	c	c	56
57	c	c	c	c	c	c			j	c		57
58	c, j	c, j	c, j	c, j	c	c			j	10		58
59	c, j	c, j	c, j	c, j	c	c			j	c		59
60	c, j	c, j	c, j	c, j	c	c			j	c		60
61	2, g	2, g	2, g	2, g	2	k			g	10		61
62	5	5	5	5	5	5				5	c	62
63	c, j	c, j	c, j	c, j	c	c			j	c		63
64	2, g	2, g	2, g	2, g	2	9			g	10		64

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FIG. 23-2 (Cont'd)

Notes and References for the Table of Physical Constants

Note: Numbers in this table do not have accuracies greater than 1 part in 1000. In some cases extra digits have been added to achieve internal consistency or to permit recalculation of experimental values.

	K.					L.	M.	Flammability Limits, vol% in air mixture		ASTM octane number		
	Heating Value, 60 °F											
	Net		Gross									
Number	Btu/ft³ Ideal gas 14.696 psia	Btu/lb Liquid (wt in vacuum)	Btu/ft³ Ideal gas 14.696 psia	Btu/lb Liquid (wt in vacuum)	Btu/gal Liquid	Heat of vaporization 14.696 psia at boiling point, Btu/lb	Air required for combustion of ideal gas ft³(air)/ft³(gas)	Lower	Higher	Motor Method D-357	Research Method D-908	Number
1	2	f	2	f	f	b, 8, 9		I	I	–	–	1
2	2	2, g	2	2, g	2, g	b, 8, 9		I	I	13	13	2
3	2	2, g	2	2, g	2, g	b, 8, 9		I	I	13	13	3
4	2	2, g	2	2, g	2, g	b, 8, 9		I	I	13	13	4
5	2	2, g	2	2, g	2, g	b, 8, 9		I	I	13	13	5
6	2	2	2	2	2	b, 8, 9		I	I	13	13	6
7	2	2	2	2	2	b, 8, 9		I	I	13	13	7
8	2	2, g	2	2, g	2, g	b, 8, 9		I	I	13	13	8
9	2	2	2	2	2	b, 8, 9		I	I	13	13	9
10	2	2	2	2	2	b, 8, 9		I	I	13	13	10
11	2	2	2	2	2	b, 8, 9		I	I	13	13	11
12	2	2	2	2	2	b, 8, k		I	I	13	13	12
13	2	2	2	2	2	b, 8, 9		I	I	13	13	13
14	2	2	2	2	2	b, 8, 9		I	I	–	–	14
15	2	2	2	2	2	b, 8, k		I	I	13	13	15
16	2	2	2	2	2	b, 8, k		I, i	I, i	13	13	16
17	2	2	2	2	2	b, 8, k		I, i	I, i	13	13	17
18	2	2	2	2	2	b, 8, k		I, i	I, i	13	13	18
19	2	2	2	2	2	b, 8, k		I, i	I, i	13	13	19
20	2	2	2	2	2	b, 8, k		I, i	I, i	13	13	20
21	2	2	2	2	2	b, 8, k		I, i	I, i	13	13	21
22	2	2	2	2	2	b, 8, 9		I	I	–	–	22
23	2	2	2	2	2	b, 8, k		I, i	I, i	13	13	23
24	2	2	2	2	2	b, 8, k		I	I	13	13	24
25	2	2	2	2	2	b, 8, c		I	I	–	–	25
26	2	2	2	2	2	b, 8, c		I	I	–	–	26
27	2	2	2	2	2	b, 8, k		I, i	I, i	13	13	27
28	2	2	2	2	2	b, 8, k		I	I	13	13	28
29	2	2	2	2	2	b, 8, k		I	I	13	13	29
30	2	2	2	2	2	b, 8, k		I	I	13	13	30
31	2	f	2	f	f	b, 8, k		I	I	13	13	31
32	2	2, g	2	2, g	2, g	b, 8, k		I	I	13	13	32
33	2	2, g	2	2, g	2, g	b, 8, k		I	I	13	13	33
34	2	2, g	2	2, g	2, g	b, 8, k		I	I	13	13	34
35	2	2, g	2	2, g	2, g	b, 8, k		I	I	–	–	35
36	2	2, g	2	2, g	2, g	b, 8, k		I	I	–	–	36
37	2	2	2	2	2	b, 8, k		I	I	13	13	37
38	2	2, g	2	2, g	2, g	b, 8, k		I, i	I, i	–	–	38
39	2	2, g	2	2, g	2, g	b, 8, k		I	I	–	–	39
40	2	2	2	2	2	b, 8, k		I, i	I, i	13	13	40
41	2	f	2	f	f	b, 8, k		I	I	–	–	41
42	2	2	2	2	2	b, 8, k		I	I	13	–	42
43	2	2	2	2	2	b, 8, k		I	I	13	13	43
44	2	2	2	2	2	b, 8, k		I	I	13	13	44
45	2	2	2	2	2	b, 8, k		I	I	13	13	45
46	2	2	2	2	2	b, 8, k		I	I	13	13	46
47	2	2	2	2	2	b, 8, k		I	I	13	13	47
48	2	2	2	2	2	b, 8, k		I	I	13	13	48
49	2	2	2	2	2	b, 8, k		I	I	13	13	49
50	2	2	2	2	2	b, 8, 9		I	I	–	–	50
51	2	2	2	2	2	b, 8, 9		I	I	–	–	51
52	2	2, g	2	2, g	2, g	c		I	I	–	–	52
53						b, d				–	–	53
54	2	2	2	2	2	c		I	I	–	–	54
55						c				–	–	55
56						c		I	I	–	–	56
57						c				–	–	57
58						c		I	I	–	–	58
59						c				–	–	59
60						c				–	–	60
61						b, 8, k				–	–	61
62			5			5				–	–	62
63						c				–	–	63
64						b, 8, 9				–	–	64

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FIG. 23-2 (Cont'd)

Notes for the Table of Physical Constants

a The molar mass for air is based upon the following composition expressed in mole fraction: N2(g), 0.7812; O2(g), 0.2096; Ar(g), 0.0092.

b Calculated with the evaluated vapor-pressure equation in the TRC Table Database (Reference 2)

c NIST REFPROP Database: Reference Fluid Thermodynamic and Transport Properties (Reference 3)

d Sublimation point

e Estimated for the hypothetical liquid state

f Temperature is above the critical temperature

g At saturation pressure

h Refractive index of the gas

i Estimated value

j Densities of the liquid at the normal boiling temperature

k Estimated 2nd virial coefficients with a corresponding-states correlation

l Extreme values of those reported in reference 12

Column definitions and general notes

A Molar mass (molecular weight) is based upon the following atomic weights: C =12.0107; H = 1.00794; O = 15.9994; N = 14.00674; S = 32.066; Cl = 35.4527; He = 4.002602; and Ar = 39.948.

B Boiling point: the temperature corresponding to equilibrium between the liquid and vapor phases at 101.325 kPa (or 14.696 psia).

C Freezing point: the temperature corresponding to equilibrium between the crystal phase and the air-saturated liquid at 101.325 kPa (or 14.696 psia).

D The refractive index values represent those determined with light of wavelength corresponding to the sodium D-line (589.26 nm).

E The specific gravities of water used in the relative density calculations were 8.3372 lb/gal at 60 °F and 999.103 $kg \cdot m^{-3}$ at 15 °C. These values are included in the FPS and SI tables.

F The temperature coefficient of densityis related to the expansion coefficient by: $(\partial r/\partial T)_p/r = -(\partial V/\partial T)_p/V$ in units of 1/T.

G Pitzer acentric factor: $w = -\log_{10}(p/p_c)^{-1}$, where p is at T = 0.7 T_c.

H The summation factor is $(-B/RT)^{0.5}$ where B is the second virial coefficient evaluated at temperature T and R is the gas constant. T = 15 °C for SI units and T = 60 °F for FPS units.

I The density of an ideal gas relative to air is calculated by dividing the molar mass of the gas by the average molar mass of air given in the table. The specific volume of an ideal gas is calculated from the ideal-gas equation.

J The heat capacity values for the liquid phase are not rigorously C_p, but rather are along the saturation line C_{sat} defined by: $C_{sat} = C_p - T(\partial V/\partial T)_p(\partial p/\partial T)_s$. For liquids far from the critical temperature, C_{sat} and C_p are nearly equal.

K The heating value is the negative of the enthalpy of combustion at 15 °C (or 60 °F) and 101.325 kPa (or 14.696 psia) in an ideal reaction (one where all of the gasses are ideal). For an arbitrary organic compound, the combustion reaction is:

$C_nH_mO_hS_jN_k(s, l, or g) + (n + m/4 - h/2 + j)\ O_2(g) \rightarrow n\ CO_2(g) + m/2\ H_2O(g or l) + k/2\ N_2(g) + j\ SO_2(g)$,

where s, l, and g denote the phase of compound. For "gross" heating values, the water formed is liquid; for "net" heating values, the water formed is ideal gas. Values reported are on a dry basis. To account for water in the heating value, see GPA 2172. The phase of the material combusted is indicated in the column headings.

L The heat of vaporization is the enthalpy of the saturated vapor minus the enthalpy of the saturated liquid at the boiling temperature.

M Air required for the combustion of ideal gas for compounds of formula $C_nH_mO_hS_jN_k$ is: V(air)/V(gas) = (n + m/4 -h/2 +j) / 0.2096.

Units and conversion factors

- Reported units are based upon the following units (SI) with their equivalent corresponding FPS units:
- mass: 453.59237 g = 1 Pound(avdp), lbm
- length: 0.3048 meters = 1 foot, ft
- temperature: 1.8(t / °C) = (t / °F) - 32; 0 °C = 273.15 K. All temperatures are defined by the International Temperature Scales of 1990 (ITS-90).
- volume: 0.02831685 m^3 = 1 cubic foot, ft^3
- pressure: 6.894757 kPa = 1 pound per square inch absolute, psia
- energy: 1055.056 J = 1 British thermal unit, Btu
- Gas constant R = 8.314472 $J \cdot K^{-1} \cdot mol^{-1}$ or 10.7316 psia $ft^3/(lbmol \cdot °R)$
- 1 gal = 231 in^3
- 1 atm = 14.69595 psia = 760 torr = 101.325 kPa

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FIG. 23-2 (Cont'd)

References for the Table of Physical Constants

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Physical properties for compounds of interest for the natural gas industry appear in GPA Standard 2145, "Table of Physical Properties for Hyrdocarbons and Other Compounds of Interest to the Natural Gas Industry."

Figure 23-2 contains several fictitious entries: the vapor pressures of methane, ethane and ethene at 100 °F, the refractive indicies of methane and ethane at 60 °F, and the liquid densities of methane at 60°F (their use in calculating a few other properties propagate through the figure). The reason they are fictitious is that 60 or 100 °F is above the critical temperatures of these compounds and the liquid state does not exist under such conditions. In no instance is it necessary to use these entries from a technical perspective, but they have worked their ways into contractual agreements. Rather than cause opening of contracts, the GPSA includes these unphysical values in the figure, but users should not rely upon calculations using these values outside of contractual agreements

Liquid Volume Fraction Calculation

Component	x	MW	x•MW	M	lbm	lbm/gal	gal	v
Carbon Dioxide	0.0011	44.010	0.0484	0.0011	914	6.8199	134	0.0007
Methane	0.0214	16.043	0.3433	0.0079	6,480	2.5	2,592	0.0127
Ethane	0.3897	30.070	11.7183	0.2680	221,192	2.9696	74,485	0.3643
Propane	0.3648	44.097	16.0866	0.3679	303,647	4.2268	71,839	0.3514
Iso-butane	0.0294	58.123	1.7088	0.0391	32,255	4.6927	6,873	0.0336
Normal-butane	0.0877	58.123	5.0974	0.1166	96,217	4.8691	19,761	0.0967
Iso-pentane	0.0171	72.150	1.2338	0.0282	23,288	5.2058	4,474	0.0219
Normal-pentane	0.0182	72.150	1.3131	0.0300	24,786	5.2614	4,711	0.0230
Hexanes +	0.0706	87.436	6.1730	0.1412	116,520	5.5910	19,580	0.0958
TOTAL	1.0000		43.7227	1.0000	825,300		204,449	1.0000

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and defined specifications. An example would be calculation of the liquid volume fractions for the components of a liquid mixture. The table above comes from GPA Standard 8173:

The liquid volume fraction for methane is fictitious, but experience has shown that using this calculation procedure provides a reliable specification for the maximum liquid volume fraction for methane.

COMPUTER PREDICTION METHODS

Computer methods that predict physical and thermodynamic properties for light hydrocarbons and natural gas constituents are widely available. People involved in the design and operation of natural gas processing facilities use them routinely. This section emphasizes hand calculation methods that provide reliable estimate for thermophysical properties. These methods provide quick, order-of-magnitude checks to evaluate more detailed procedures or when a computer is not available.

Some computer results appear in the section. Using equations of state to predict properties is convenient and easy, but such methods do not apply equally well for all properties. Accurate and reliable values result for gas phase densities, volumes and Z-factors, while liquid volumes and densities are less accurate but still as reliable as predictions using hand-calculation methods. Equations of state are not suitable to predict thermal conductivities, viscosities and surface tensions. Computer programs cited in this section are representative of those widely available for prediction of physical and thermodynamic properties. Inclusion of commercial products in the recommendations of this section does not constitute GPA and/or GPSA endorsement of the program(s). An accurate, reliable equation of state is always the most convenient method for obtaining engineering accuracy gas phase properties. Unfortunately, widespread availability and ease of use are not suitable criteria for choosing an equation of state program.

Z-FACTOR FOR GASES

Pure Gases

The ideal gas equation of state is a convenient and often satisfactory tool when dealing with gases at pressures that do not exceed one atmosphere. The errors associated with this equation are about 2-3% in this pressure range. However, the errors can escalate to hundreds of per cents at higher pressures.

Section 25 presents many equations of state that represent the pressure-volume-temperature relationships for gases. Use of these equations for engineering calculations is complicated and requires a computer or a programmable calculator to complete the calculations in a reasonable amount of time. A generalized, corresponding states plot of Z-factors is reasonably convenient and sufficiently accurate for normal engineering requirements. The Z-factor provides the ratio of the real gas volume to that of the ideal gas.

$$PV = ZnRT = ZmRT/MW \qquad \textbf{Eq 23-1}$$

The Z-factor is a dimensionless parameter, independent of the quantity of gas, determined by the characteristics of the gas, the temperature, and the pressure. Knowing Z, calculation of PVT relationships are as easy at high pressure as at low pressure.

The equation used to calculate gas density is:

$$\rho = \frac{(MW) \cdot P}{10.73\ RT} \qquad \textbf{Eq 23-2}$$

The value for R is 10.73 when pressure is psia, volume is cubic feet, quantity of gas is pound moles, and temperature is °R. Values of R for other combinations of units appear in Section 1.

The theorem of corresponding states that fluids that have the same value of reduced temperature and reduced pressure have the same reduced volume. The reduced property is the property divided by the value of the property at the critical point. Thus, according to the theorem, different fluids that have the same reduced temperature and reduced pressure have the same Z-factor.

$$\text{Reduced Temperature, } T_r = T/T_c \qquad \textbf{Eq 23-3}$$

$$\text{Reduced Pressure, } P_r = P/P_c \qquad \textbf{Eq 23-4}$$

For gas mixtures, the reduced conditions can be determined using pseudo-critical values instead of the true critical values:

$$\text{pseudo-reduced Temperature, } T_r = T/\sum_i (y_i T_{ci}) = T/T_{pc} \qquad \textbf{Eq 23-3a}$$

$$\text{pseudo-reduced Pressure, } P_r = P/\sum_i (y_i P_{ci}) = P/P_{pc} \qquad \textbf{Eq 23-4a}$$

Any units of temperature or pressure are acceptable provided that the same absolute units are used for T as for T_c (T_{pc}) and for P as for P_c (P_{pc}). The "average molecular weight" for a gas mixture is

$$MW_{avg} = \sum_i y_i MW_i \qquad \textbf{Eq 23-5}$$

Figure 23-3 illustrates calculation of pseudo-critical properties and MW_{avg} for a typical natural gas. Estimation techniques to calculate the critical temperature and pressure for hexanes and heavier or heptanes and heavier fractions using molecular weight and specific gravity or average boiling point and relative density are presented in this section.

Attempts to prepare a generalized plot suitable for application to the low molecular weight hydrocarbons, including methane, ethane, and propane, indicate that an error frequently in excess of 2 to 3% is unavoidable because they deviate from the theorem of corresponding states. Figure 23-4, prepared using pure component and gas mixture data, can estimate Z (2-3% error) for pure hydrocarbon gases. Use reduced temperature and pressure instead of pseudo-reduced values for pure components. At low pressures, the different compounds more nearly conform to corresponding states. The Z-factor is approximately 1.0 at pressures below 1 atmosphere. Errors generally are 2-3% for pressures ≤300 psia if the gas is 50 °F or more above its saturation temperature at the pressure of concern.

It is possible to determine gas volumes, densities and Z-factors for pure hydrocarbon and non-hydrocarbon vapors using P-H diagrams like those in Section 24, Thermodynamic Properties. Interpolation between specific volume curves on a P-H diagram does not yield results of high accuracy. An equation of state provides more accurate pure component PVT properties, particularly if that equation has been fit to volumetric data for the specific component. Tabulations of properties obtained in this way appear in the literature.[12]

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Example 23-1 — Pure component properties

Using Fig. 24-27, the P- H diagram for propane, calculate the density of propane vapor at 200°F and 100 psia.

Solution Steps

On the P-H diagram at the intersection of the T = 200°F, P = 100 psia lines read v = 1.5 ft^3/lbm. Then: ρ = 1/1.5 = 0.667 lbm ft^{-3}

Using the EZ*THERMO[90] version of the SRK[91] equation of state, ρ is 0.662 lb/ft^3, from which v = (1/0.662) = 1.51 ft^3/lbm.

For propane at 200°F and 100 psia using data from Fig. 24-27.

$$Z = \frac{MW \bullet P}{R\,T\rho} = \frac{(44.10)\,(100)}{(10.73)\,(458.67 + 200)\,(0.667)} = 0.936$$

The SRK calculation gives ρ = 0.662 lb/ft3, and Z = 0.941.

Gas Mixtures

GPA Standard 2172, "Calculation of Gross H Value, Relative Density and Compressibility Factor for N Gas Mixtures from Compositional Analysis" contains additional information regarding the calculation of Z-factors for mixtures at pressures below 150 psia.

Minor Amounts of Non-hydrocarbons — Fig 23-4[1] shows Z-factors for typical sweet natural gases. Using Z-factors from Fig. 23-4 should yield mixture volumes (densities) within 2% to 3% of the true values for reduced temperatures from slightly greater than 1.0 to the limits of the chart for both temperature and pressure. The chart has been prepared from data for binary mixtures of methane with ethane, propane and butane and data for natural gas mixtures. All mixtures have average molecular weights less than 40, and all gases contain less than 10% nitrogen and less than 2% combined hydrogen sulfide and carbon dioxide. Fig. 23-4 applies for temperatures 20 °F or more above saturation up to pressures of 10,000 psia.

Appreciable Amount of Non-Hydrocarbons — Figure 23-4 does not apply for gases or vapors with more than 2% H_2S and/or CO_2 or more than 20% nitrogen. Use other methods for vapors that have compositions atypical of natural gases mixtures or for mixtures containing significant amounts of water and/or acid gases, and for all mixtures as saturated fluids, other methods should be employed.

Figure 23-4 provides reasonably accurate gas Z-factors for natural gases with high nitrogen content, up to 50% (or even higher) when using the molar average pseudo-criticals from Eqs 23-3a and 23-4a. The same approach applies to gas condensate fluids containing appreciable amounts of heptanes and heavier components. Critical temperatures and pressures for heptane and heavier fractions can be estimated from molecular weight and relative density, or average boiling point and relative density, using correlations presented in this section.

Figs. 23-5, 23-6 and 23-7 provide Z-factors for low molecular weight natural gases. These figures cover a wide range of molecular weights (15.95 to 26.10), temperatures (-100 to l000 °F) and pressures (up to 5,000 psia). For gases with molecular weights between those shown in Figs. 23-5 through 23-7, linear interpolation between adjacent charts is sufficient to compute the Z-factors.

In general, Z-factors for gases with less than 5% noncondensable non-hydrocarbons, such as nitrogen, carbon dioxide, and hydrogen sulfide, result with less than 5% error. When the molecular weight is above 20 and the Z-factor is below 0.6, errors as large as 10% may occur.

Effect of Acid Gas Content — Natural gases containing H_2S and/or CO_2 exhibit different Z-factor behavior than do sweet gases. Wichert and Aziz[3] present a calculation procedure to account for these differences. Their method uses the standard gas Z-factor chart (Fig. 23-3) and provides accurate sour gas Z-factors that contain as much as 85% total acid gas. Wichert and Aziz define a "critical temperature adjustment factor," ε, that is a function of the concentrations of CO_2 and H_2S in the sour gas. This correction factor adjusts the pseudocritical temperature and pressure of the sour gas according to the equations:

$$T_c' = T_c - \varepsilon \qquad \textbf{Eq 23-6}$$

FIG. 23-3

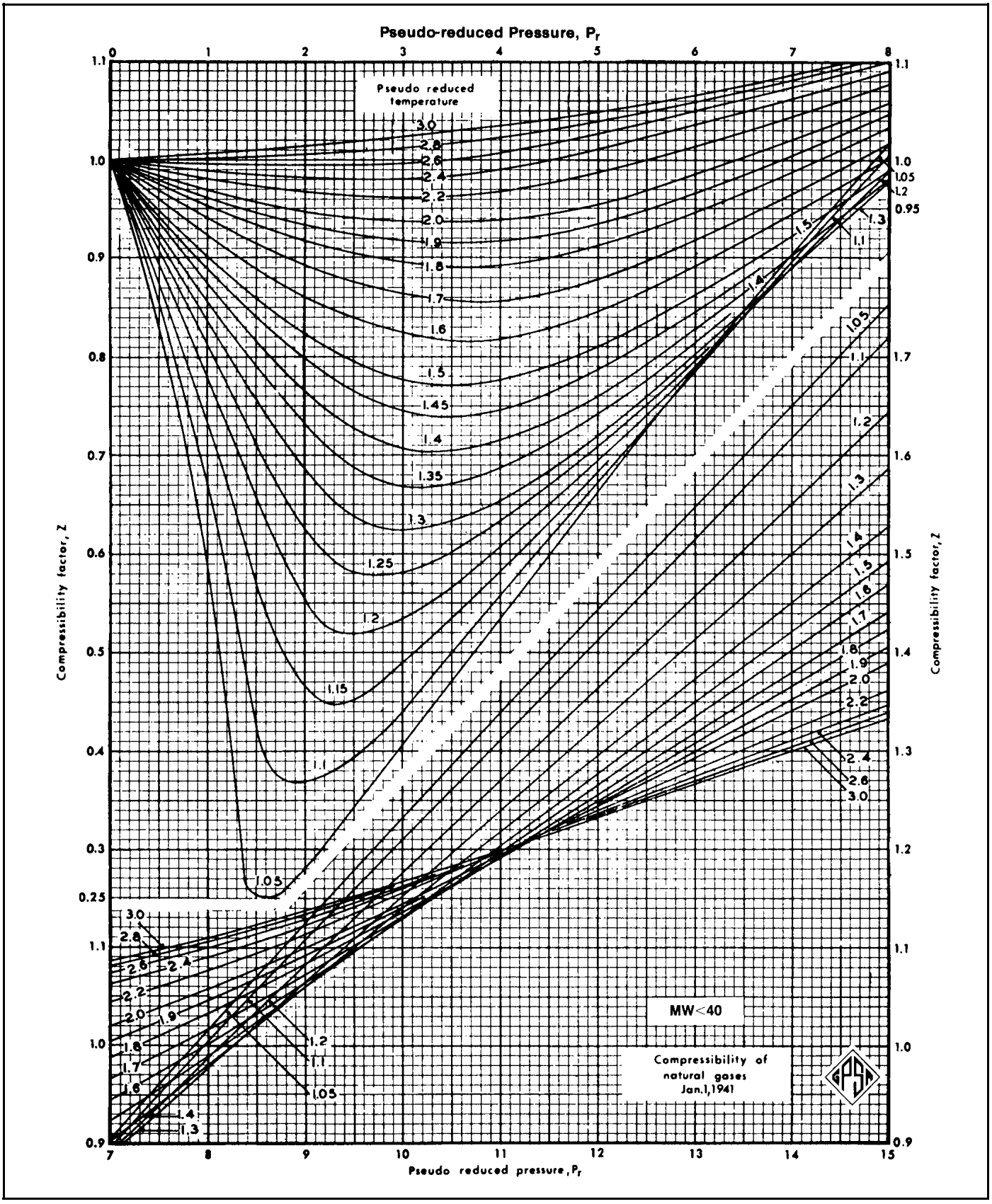
Calculation of Pseudo-critical Temperature and Pressure for a Natural Gas Mixture

Component	Mole Fraction, y_i	Component Critical Temperature, T_{ci}, °R	Pseudocritical Temperature, T_{pc}, °R	Component Critical Pressure, P_{ci}, psia	Pseudocritical Pressure, P_{pc}, psia	Component Molecular Weight, MW	Mixture Molecular Weight, $y_i \bullet MW$
CH_4	0.8319	343.0	285.3	666.4	554.4	16.043	13.346
C_2H_6	0.0848	549.6	46.6	706.5	59.9	30.070	2.550
C_3H_8	0.0437	665.7	29.1	616.0	26.9	44.097	1.927
iC_4H_{10}	0.0076	734.1	5.58	527.9	4.01	58.123	0.442
nC_4H_{10}	0.0168	765.3	12.86	550.6	9.25	58.123	0.976
iC_5H_{12}	0.0057	828.8	4.72	490.4	2.80	72.150	0.411
nC_5H_{12}	0.0032	845.5	2.71	488.6	1.56	72.150	0.231
nC_6H_{14}	0.0063	913.3	5.75	436.9	2.75	86.177	0.543
			T_{pc} = 392.62		P_{pc} = 661.57		MW_m = 20.426
				G = 20.426/28.9625 = 0.705			

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FIG. 23-4

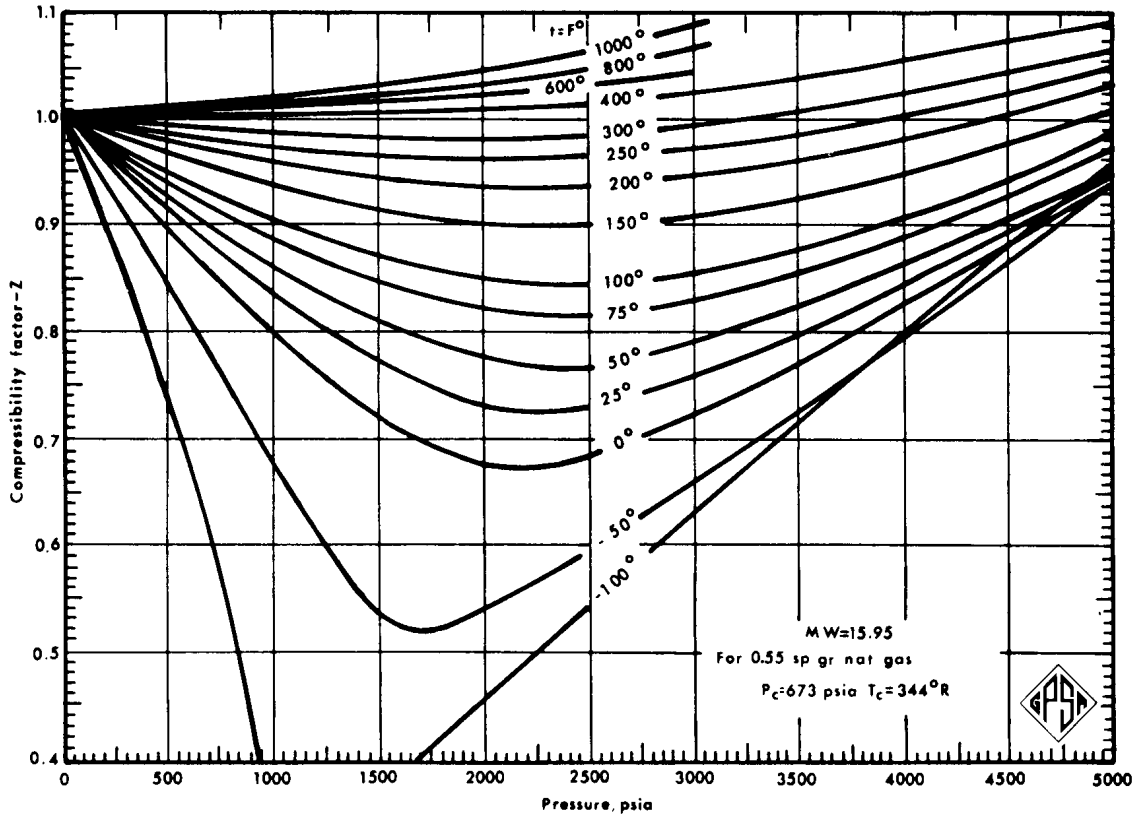
Compressibility Factors for Natural Gas[1]

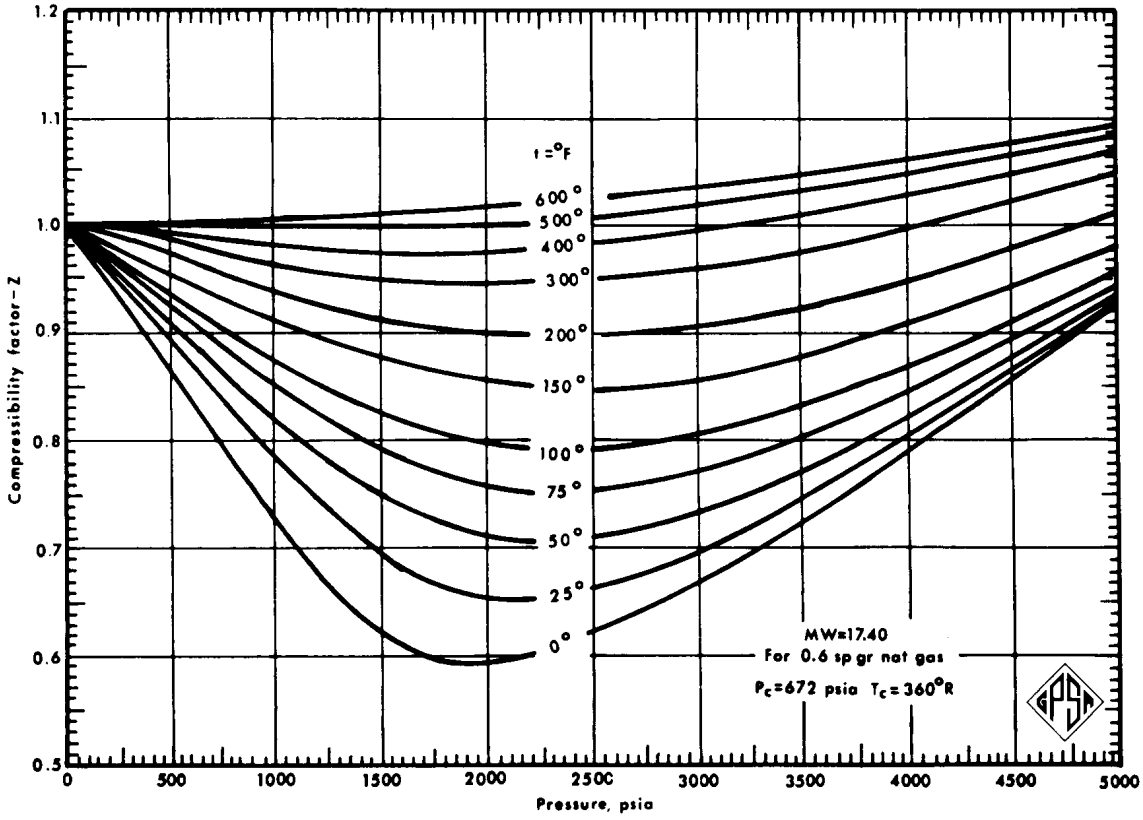


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FIG. 23-5

Compressibility of Low-Molecular-Weight Natural Gases[11]

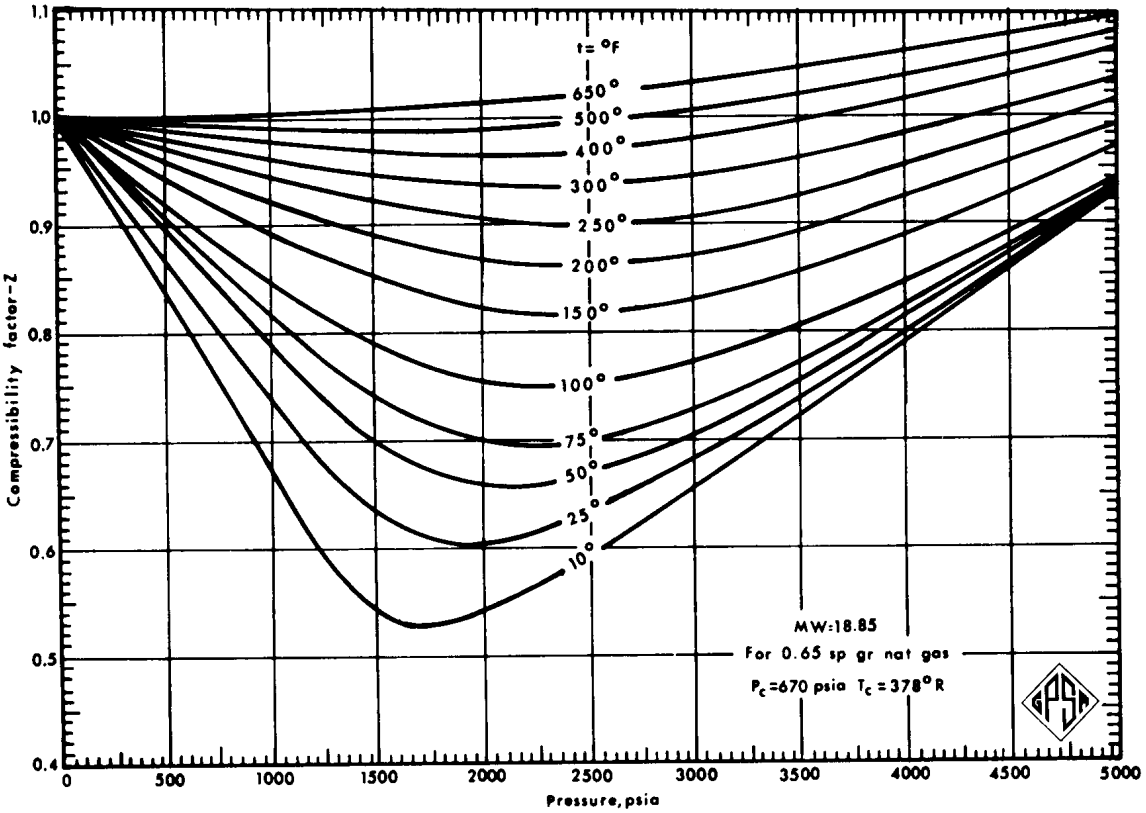


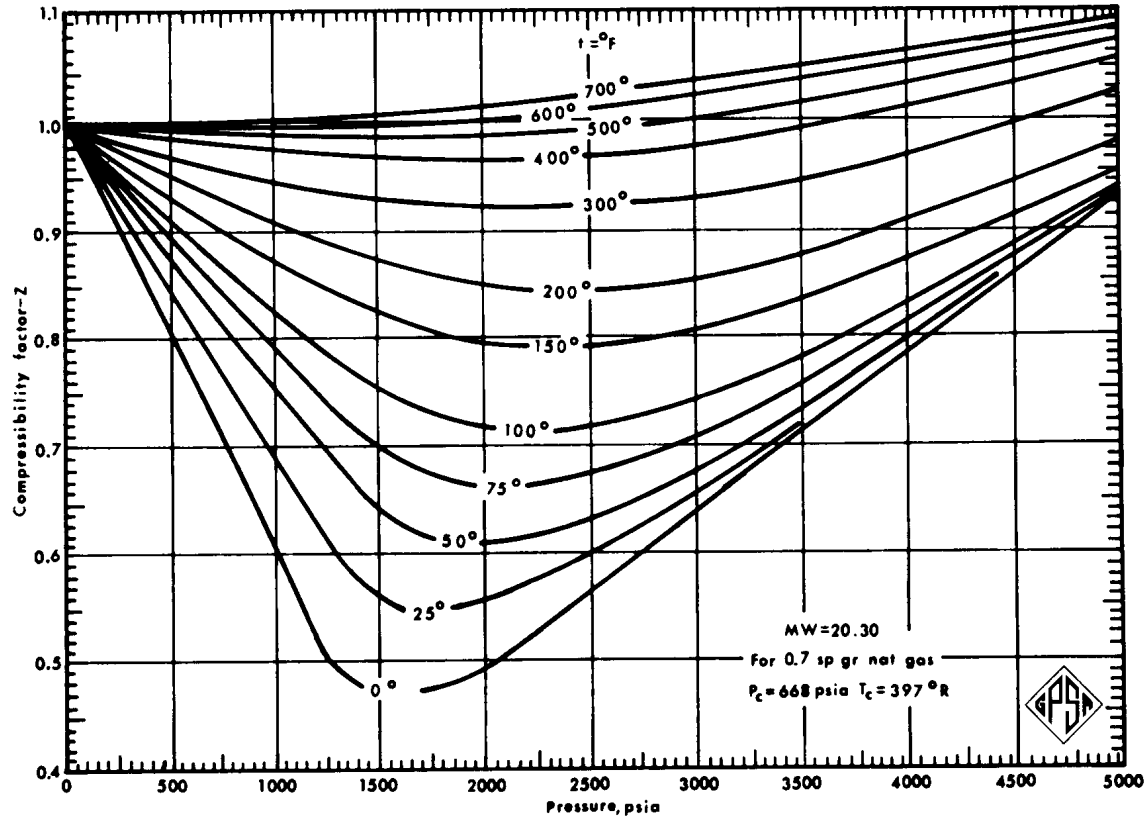


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FIG. 23-6

Compressibility of Low-Molecular-Weight Natural Gases[11]

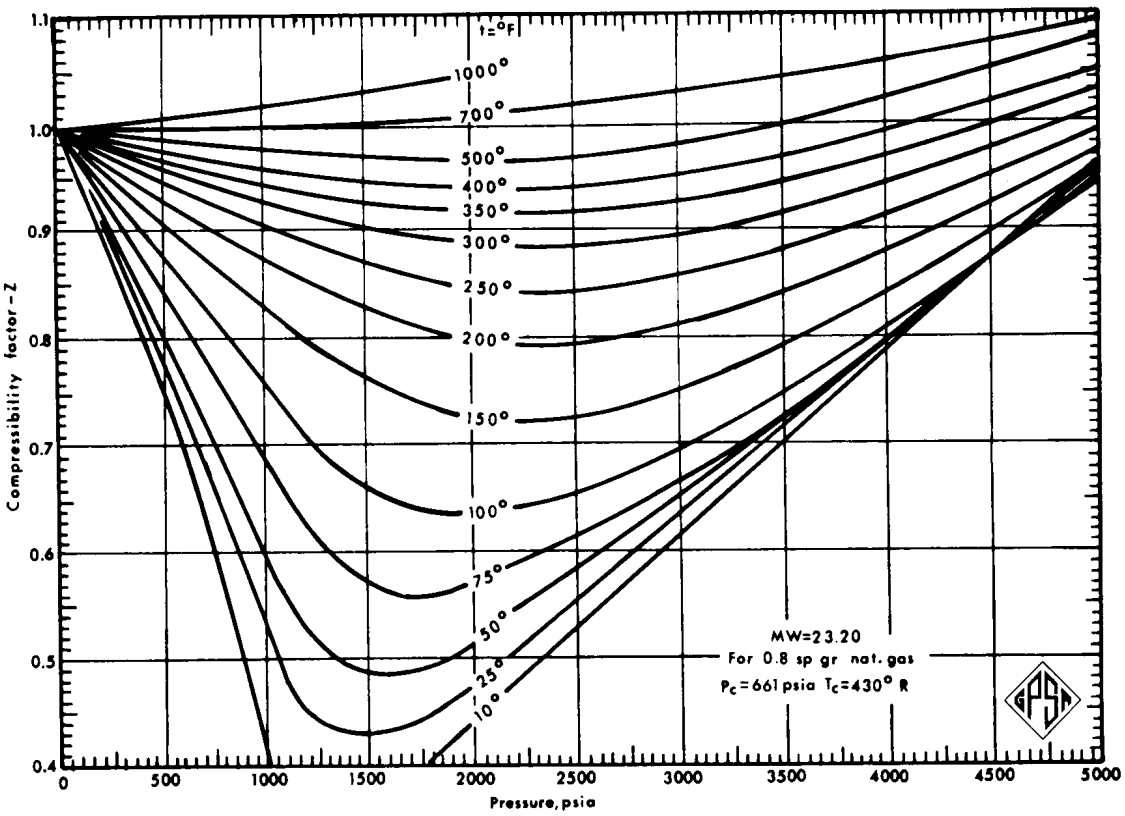


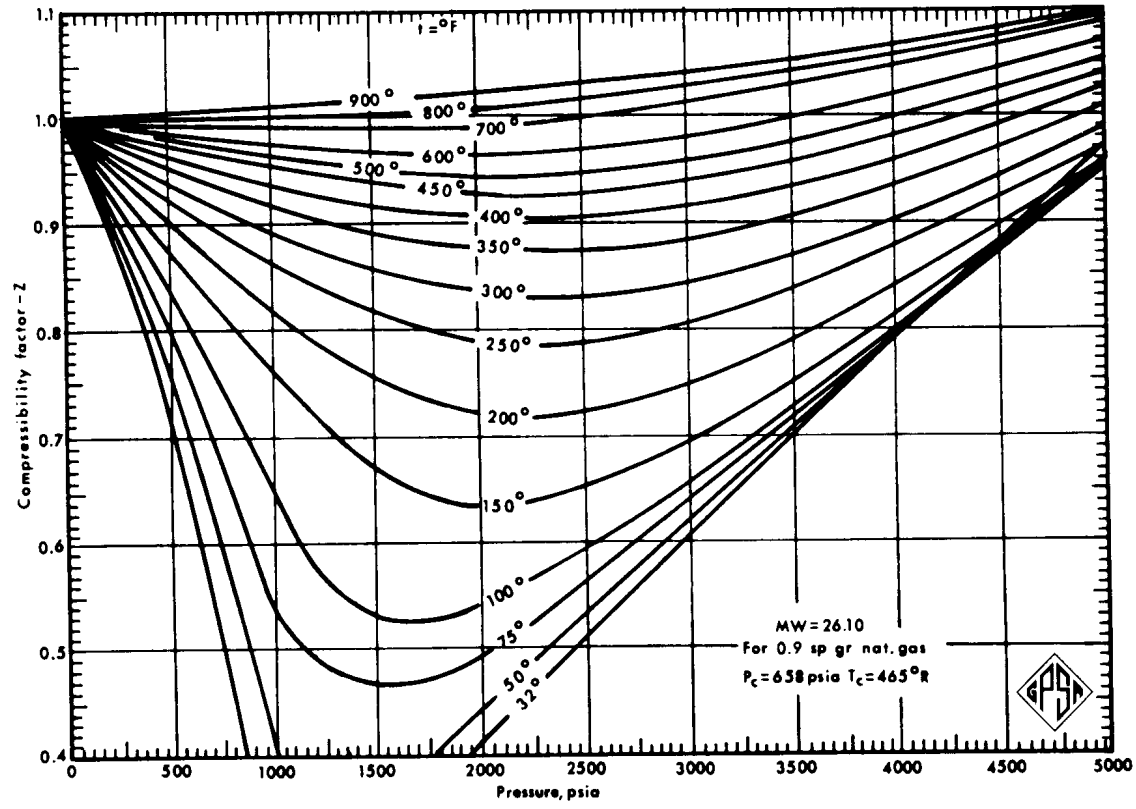


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FIG. 23-7

Compressibility of Low-Molecular-Weight Natural Gases[11]





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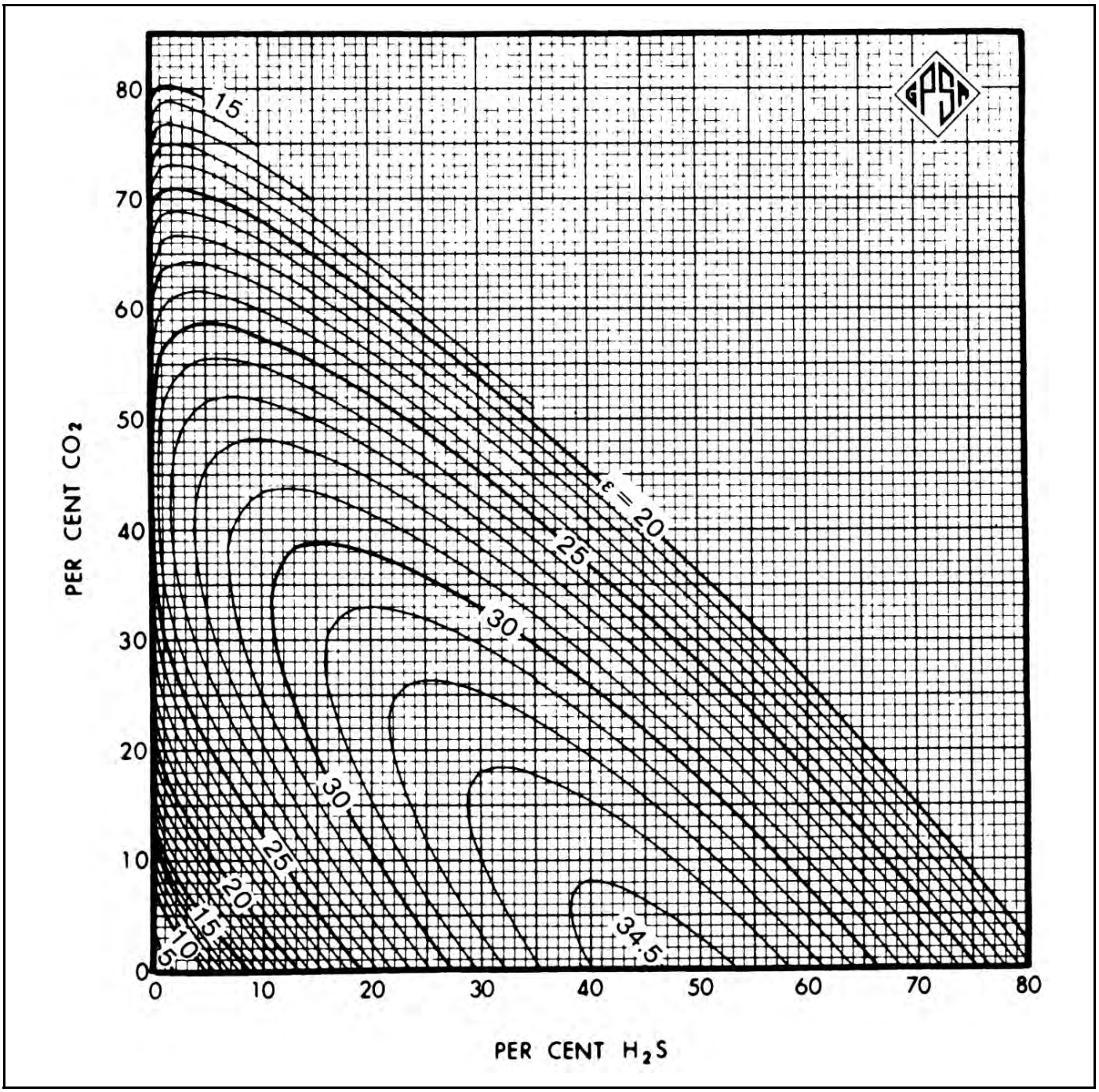
$$P_c' = \frac{P_c T_c'}{T_c + B'(1 - B')\varepsilon} \qquad \textbf{Eq 23-7}$$

Figure 23-8 presents the pseudo-critical temperature adjustment factor. To use the factor, calculate the pseudo-critical temperature and pressure using the procedure outlined earlier. Include the H_2S and CO_2 in this calculation as well as hydrocarbon and other non-hydrocarbon constituents. Read the pseudo-critical temperature adjustment factor from Fig. 23-8 and use it to adjust the values of critical temperature and pressure. The reduced temperature and reduced pressure are calculated using the adjusted values. The Z-factor is then available from Fig. 23-4.

Example 23-2 — A sour natural gas has the composition shown in the following table. Determine the Z-factor for the gas at 100°F and 1000 psia.

FIG. 23-8

Pseudocritical Temperature Adjustment Factor[3], ε, °F



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Solution Steps

The first step is to calculate the pseudo-critical temperature and pseudo-critical pressure for the sour gas. Read the pseudo-critical temperature adjustment factor from Fig. 23-8 as 29.8°F. The adjusted pseudo-critical temperature is:

$$T_c' = 433.9 - 29.8 = 404.1\ °R$$

The adjusted pseudo-critical pressure is:

$$P_c' = \frac{(826.9)\,(404.1)}{433.9 + 0.2\,(1 - 0.2)\,(29.8)} = 761.7\ \text{psia}$$

The pseudo-reduced temperature and pseudo-reduced pressure are:

$$T_r' = \frac{100 + 459.67}{404.1} = 1.385$$

$$P_r' = \frac{1000}{761.7} = 1.313$$

$$Z = 0.831 \quad \text{(Fig. 23-4)}$$

(The EZ*THERMO[90] version of the SRK gives Z = 0.838.)

HYDROCARBON FLUID DENSITIES

Data and Correlations

Fig. 23-9 presents saturated fluid densities (liquid and vapor) for hydrocarbons and liquid densities for some mixtures. Fig. 23-10 is a plot of relative density as a function of temperature for petroleum fractions.

Figure 23-11 contains subcooled liquid hydrocarbon densities from –50 °F to +140 °F. Corrections to liquid hydrocarbon densities caused by high pressure appear in Fig. 23-15.

Figure 23-12 presents *specific gravities* for petroleum fractions with temperature ranging from 0 °F to 1000 °F and with pressures from atmospheric to 1500 psia. The petroleum fraction is identified within the center grid by two of three characteristics — API gravity at 60 °F, the Watson characterization factor, K_W, or the mean average boiling point. Fig. 23-18 contains the mean average boiling point, the API gravity and an ASTM D-86 distillation of the petroleum fraction. The characterization factor, K_W, is defined in the inset example that illustrates use of Fig. 23-12.

Fig. 23-13 contains the specific gravity of paraffinic hydrocarbons at their boiling points or bubble points. The nomograph applies to mixtures as well as to single components. Alignment points for paraffinic mixtures and pure components vary according to molecular weight.

Fig. 23-13 generally predicts specific gravities within 3% of measured values for paraffinic mixtures. However, the accuracy is somewhat less for mixtures having:

- Reduced temperatures above 0.9.
- Molecular weights less than 30 (low temperature region) and where methane is a significant part of the liquid.

Density of Saturated and Subcooled Liquid Mixtures — Standing and Katz[1] proposed a versatile, manual procedure to calculate the density of gas-saturated and subcooled hydrocarbon liquid mixtures. The basic method proposed uses the additive volume approach for propane and heavier components at standard conditions, then corrected this ideal volume using apparent densities for the gaseous components ethane and methane. Then they corrected the resulting pseudo-density at 60°F and 14.7 psia for pressure using a hydrocarbon liquid compressibility chart and for temperature using a thermal expansion chart (Fig. 23-17). Experience with crude oils and rich absorber oils showed this correlation could predict densities within 1 to 4% of experimental data.

The original correlation did not have a procedure for handling significant amounts of non-hydrocarbons and had a fairly narrow applicable temperature range of 60°F to 240°F. The following procedures and charts are generally applicable to liquids containing components heavier than pentanes (gas saturated or subcooled) at pressures up to 10,000 psia and temperatures from –100°F to 600°F. This procedure can handle significant amounts of non-hydrocarbons (up to 20% N_2, 80% CO_2, and 30% H_2S).

1. Set up a calculation table as shown in the example in Fig. 23-16.
2. Calculate the density of propane and heavier (C_3+) or, if H_2S is present, of H_2S and heavier (H_2S+) components, assuming additive volumes.

$$\text{Density of } CO_2 \text{ and } (N_2S+) = \frac{\text{Weight } C_3 + (\text{or } H_2S+) \text{ components}}{\text{Vol } C_3 + (\text{or } H_2S+) \text{ components}} \qquad \textbf{Eq 23-8}$$

3. Determine the weight percent of (N_2 + C_2) in the (N_2 + C_2+) fraction.

$$\text{Wt \% } (N_2 + C_2) = \frac{100\,[\text{Wt } (N_2 + C_2)]}{\text{Wt } (N_2 + C_2+)} \qquad \textbf{Eq 23-9}$$

4. Use Fig. 23-14 to determine the pseudo-density of the (N_2 + C_2+) fraction. Enter with the C_3+ (or H_2S plus) density from Step 2 in the upper left of the chart and go horizontally to the line (interpolate if necessary) representing the weight % (N_2 + C_2) , then look up and read the pseudo-density of the (N_2 + C_2+ along the top of the chart.

At temperatures below –20°F, ethane can be included in Step 2 and only N_2 used in Steps 3 and 4.

5. If CO_2 is not present, go to Step 6. If it is present, then account for it on an additive volume basis:

$$\text{Density of } CO_2 \text{ and } (N_2 + C_2+) = \frac{\text{Wt } CO_2 + \text{Wt } (N_2 + C_2+)}{\text{Vol } CO_2 + \text{Vol } (N_2 + C_2+)} \qquad \textbf{Eq 23-10}$$

where

$$\text{Vol } (N_2 + C_2+) = \frac{\text{Wt } (N_2 + C_2+)}{\text{Density } (N_2 + C_2+)}$$

6. Calculate the weight percent methane Wt methane

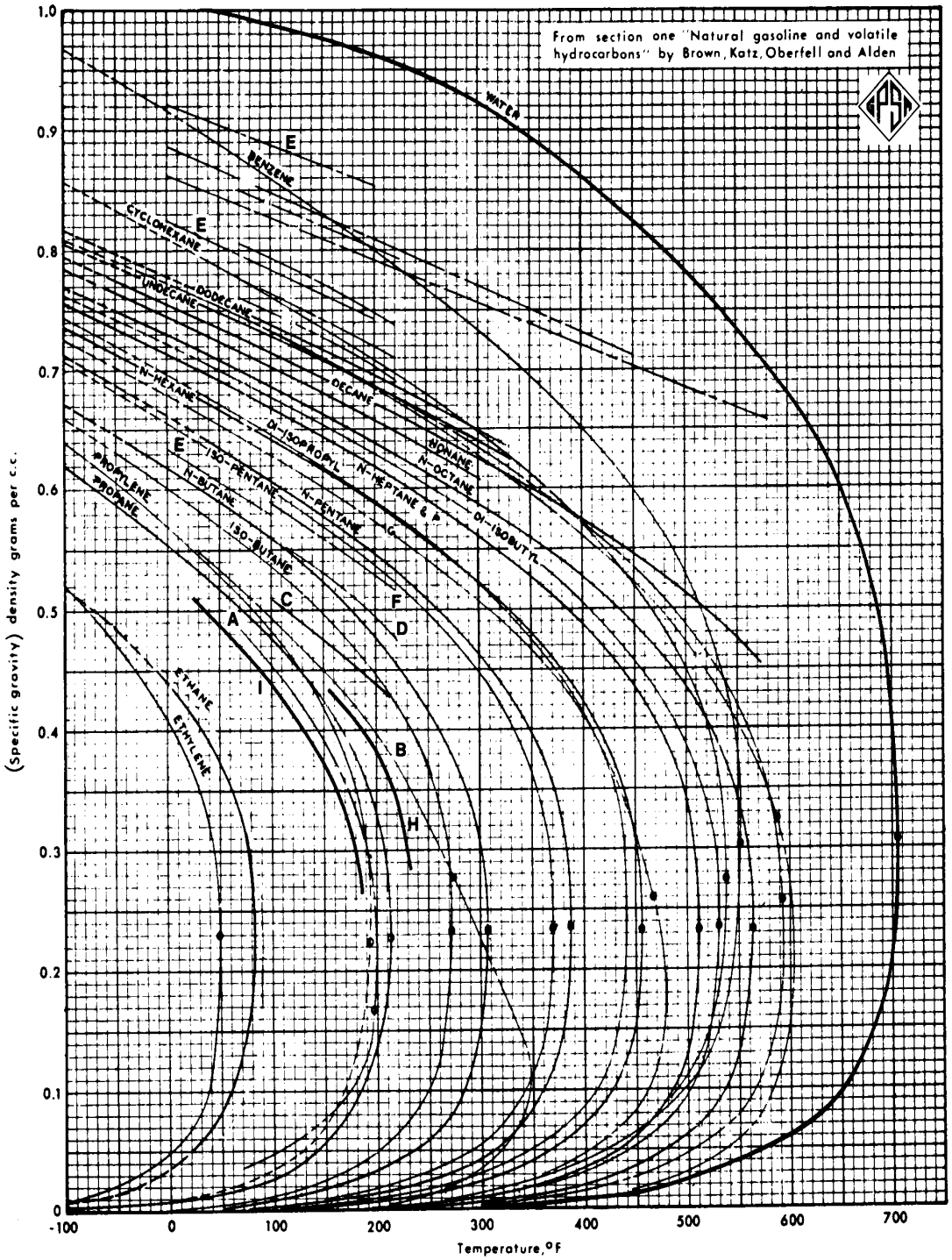
$$\text{Wt \% methane} = \frac{100\ (\text{Wt methane})}{\text{total Wt}} \qquad \textbf{Eq 23-11}$$

7. Enter the top of Fig. 23-14 with the pseudo-density from Step 4 or 5 as appropriate, and drop vertically to the line (interpolation may be required) representing the weight percent methane. Read the pseudo-density of the mixture (60°F and 14.7 psia) on the right side of the chart.
8. Correct the pseudo-density to the actual pressure using Fig. 23-15. Add the correction to the pseudo-density from Step 7.

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FIG. 23-9

Hydrocarbon Fluid Densities[2, 3, 19]



Identification

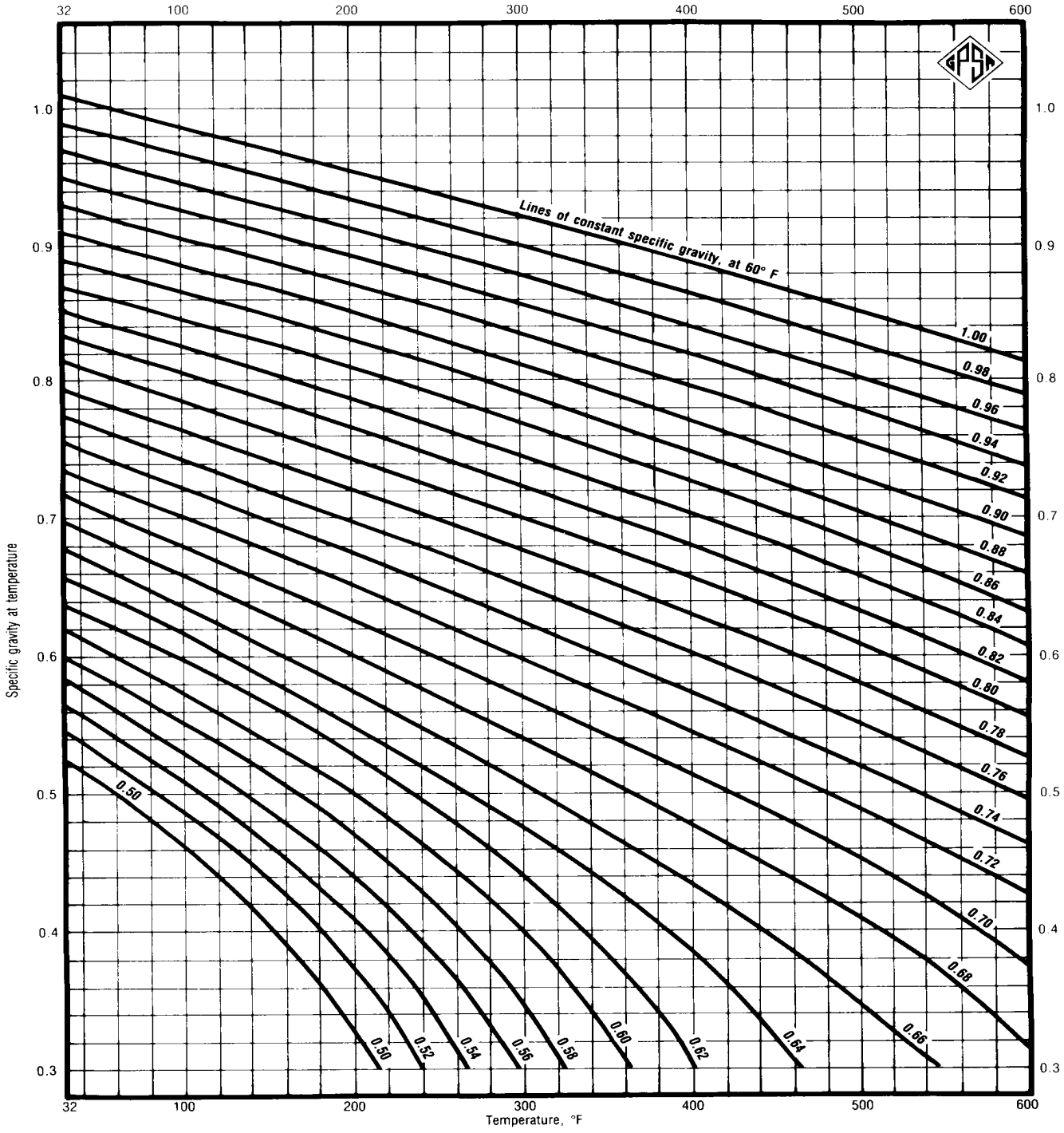
A 8 mol % CH_4—92 mol % C_3H_8 (370-739 lbs.)
B 50.25 wt. % C_2H_6—49.75 wt. % n-C_7H_{16}
C 19.2 wt. % CH_4—80.8 wt. % C_6H_{14} (2412-2506 lbs.)
D 7.15 wt. % CH_4—92.85 wt. % n-C_5H_{12} (854-1043 lbs.)
E National Standard Petroleum Oil Tables
F 7.15 wt. % CH_4—92.85 wt. % n % C_5H_{12} (at 3000 lbs.)
G 9.78 wt. % C_2H_6—90.22 wt. % n-C_7H_{16}
H 75.45 mole % C_3H_8—24.55 % nC_4H_{10} (ref 4)
I 65.77 mole % C_2H_6—34.23 % nC_4H_{10} (ref 3)

(Note: Reference for streams A-G see ref. 19)

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FIG. 23-10

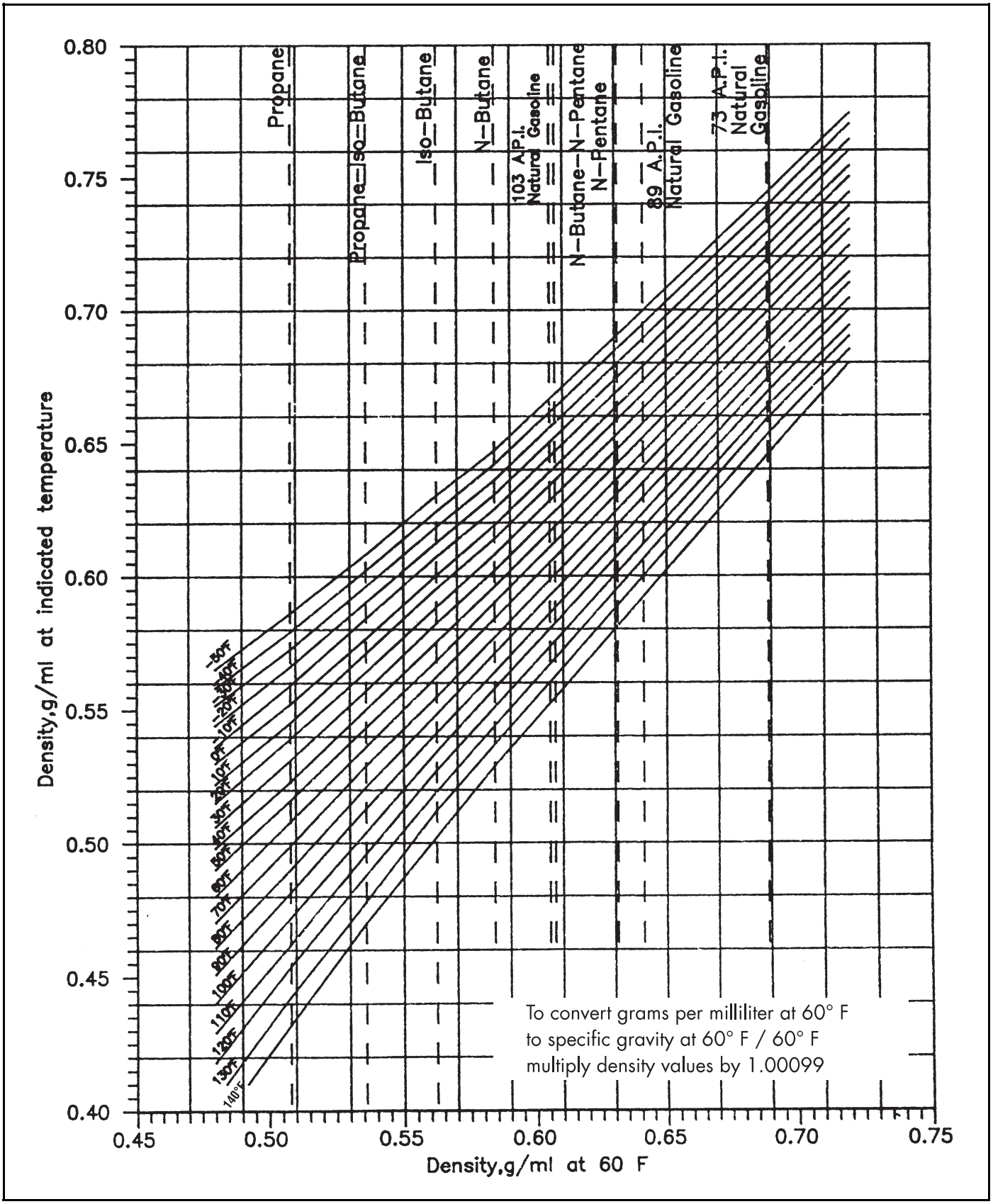
Approximate Specific Gravity of Petroleum Fractions



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FIG. 23-11

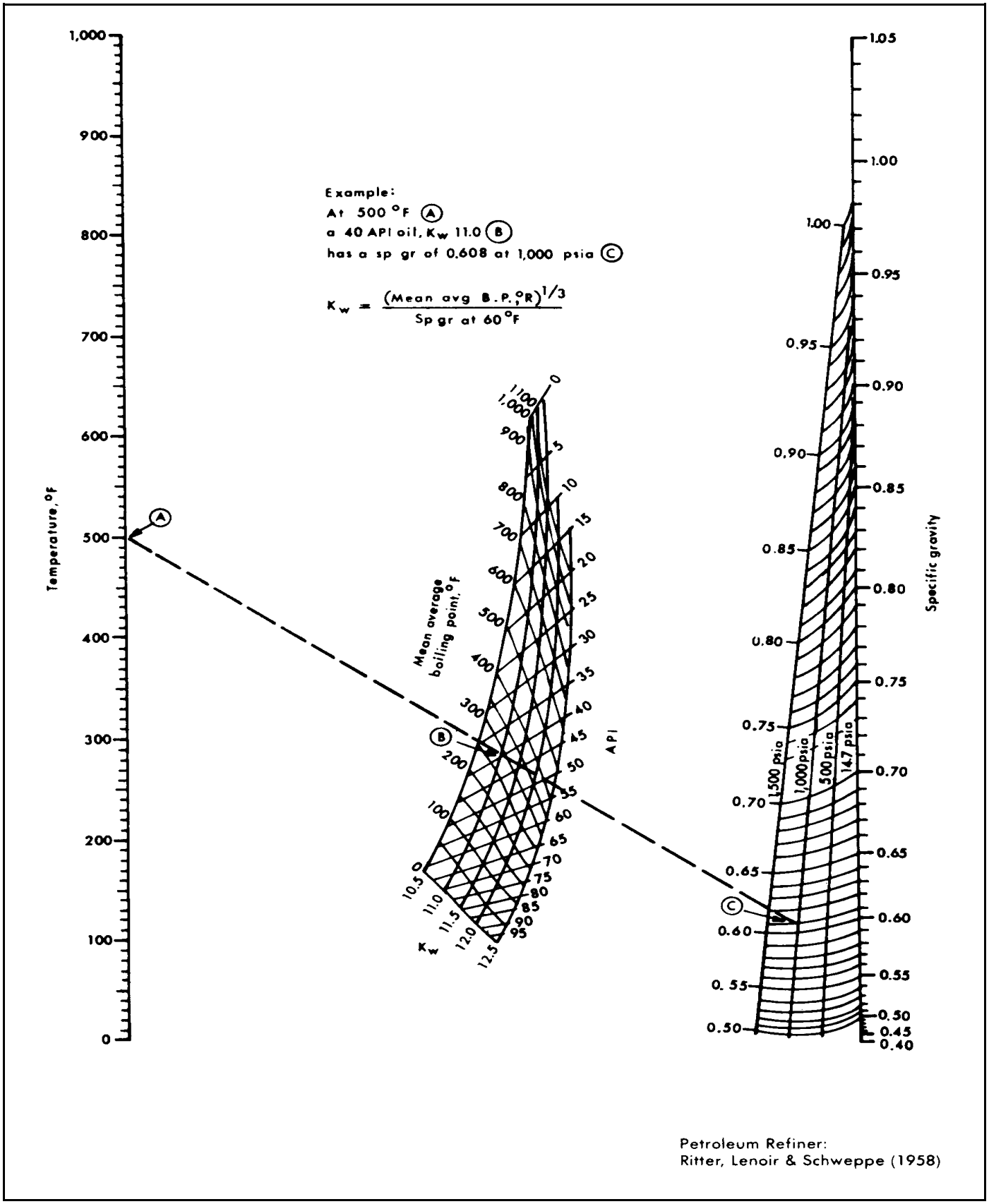
Effect of Temperature on Hydrocarbon Liquid Densities[19]



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FIG. 23-12

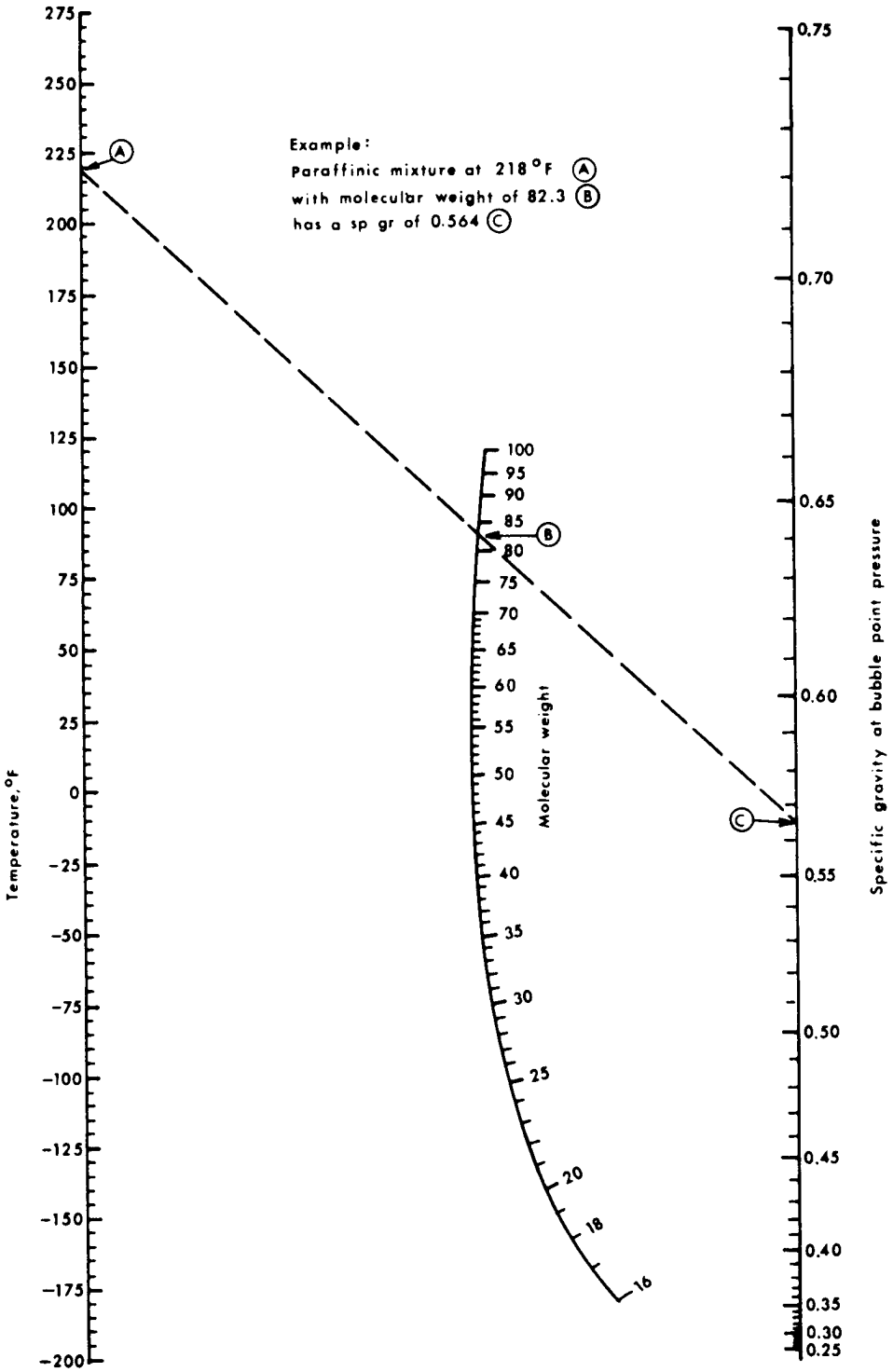
Specific Gravity of Petroleum Fractions



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FIG. 23-13

Specific Gravity of Paraffinic Hydrocarbon Mixtures

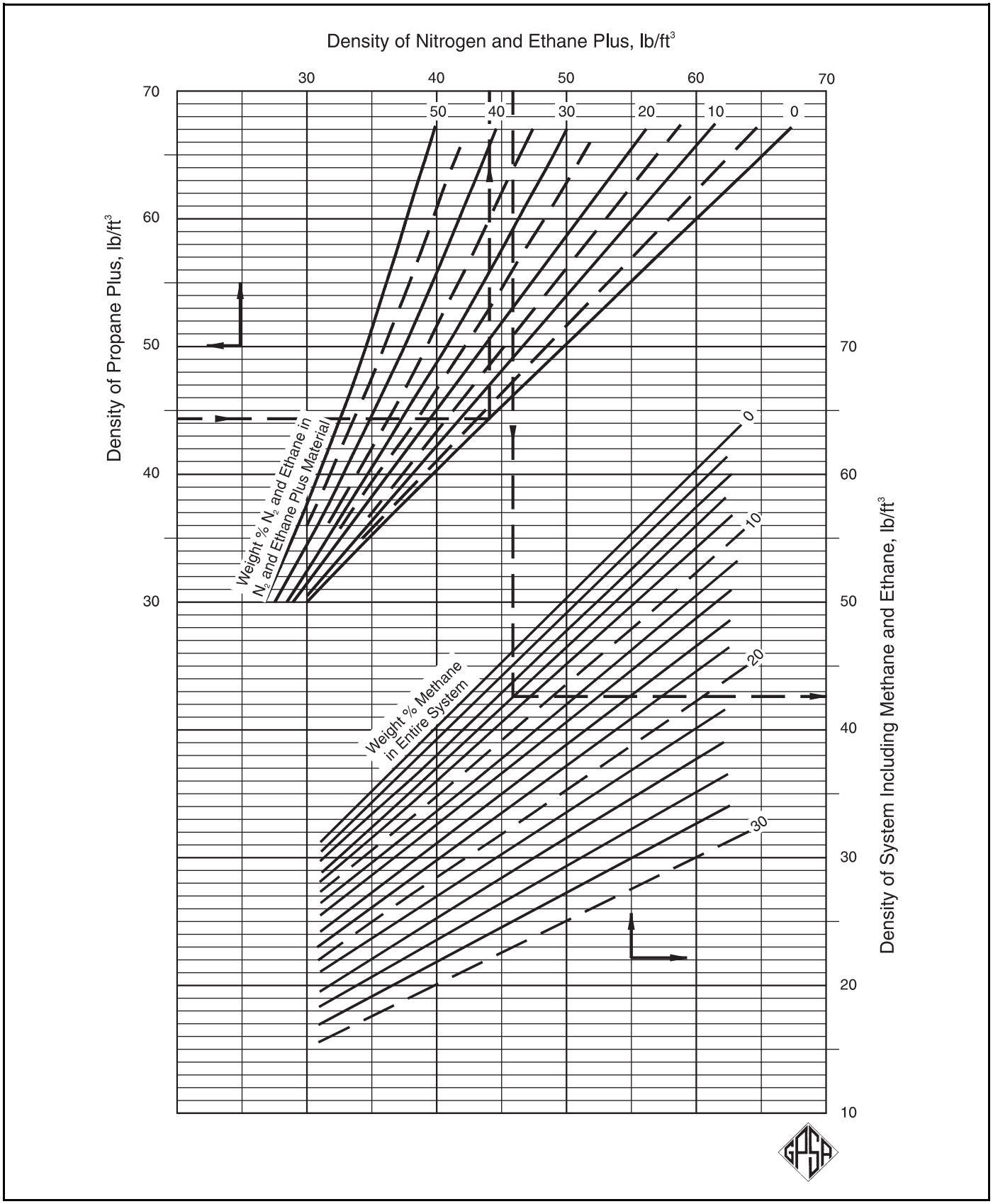


Modified from Petroleum Refiner:
Ritter, Lenoir & Schweppe (1958)

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FIG. 23-14

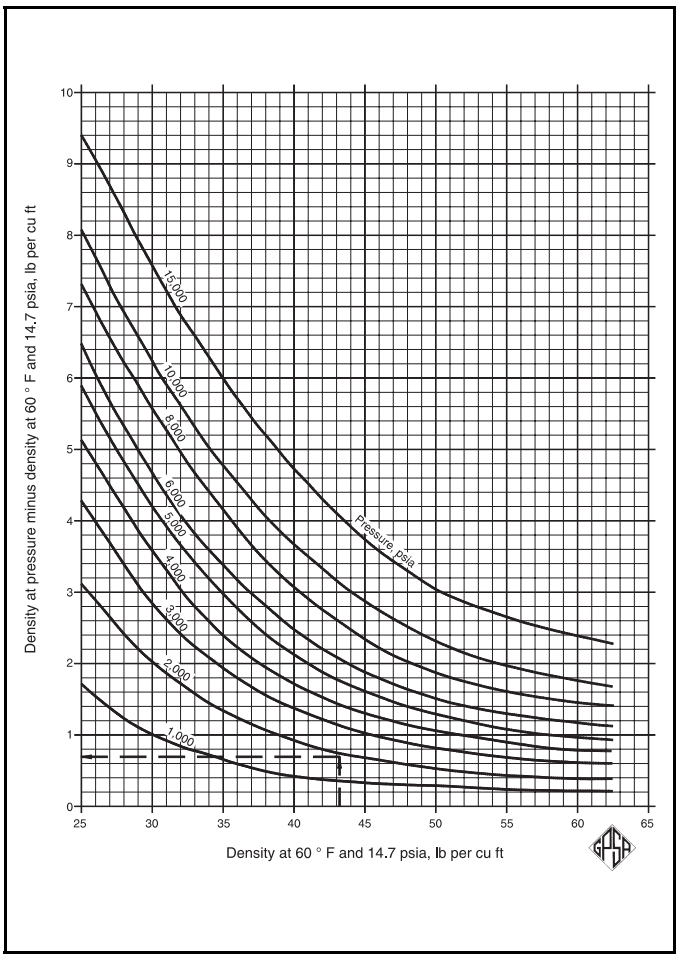
Pseudo Liquid Density of Systems Containing Methane and Ethane



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FIG. 23-15

Density Correction for Compressibility of Hydrocarbon Liquids



9. Correct the density at 60°F and pressure to the actual temperature using Fig. 23-17. Add the correction to the density from Step 8.

This procedure is not valid in the critical region. Mixtures at temperatures greater than 150 °F that contain more than 60 mol% methane or more than 80 mol% CO2 are problem areas. Outside the near-critical region, calculated densities usually are within 5% of experimental data[35] and errors are rarely greater than 8%. The best accuracy occurs for mixtures containing mostly C_5+ with relatively small amounts of dissolved gaseous components (errors are usually less than 3%). Note that densities of C_2+, C_3+, CO_2+, or C_4+ mixtures can be calculated by this procedure at various temperatures and pressures, and that the gaseous components need not be present.

Example 23-3 — Fig. 23-16 illustrates the procedure outlined above.

$$\text{Density of } C_3+ = \frac{\text{Wt of } C_3+}{\text{Vol of } C_3+} = \frac{44.836 \text{ lbm}}{1.0128 \text{ ft}^3}$$

$$= 44.275 \text{ lbm/ft}^3$$

$$\text{Wt \% } C_2 \text{ in } C_2+ = \left(\frac{100\ (0.567)}{0.567 + 44.836}\right) = 1.25\%$$

$$\text{Density of } CO_2+ = \frac{45.403 + 17.485}{(45.403/44.0) + 0.3427} = 45.75 \text{ lbm/ft}^3$$

Wt% of CH_4 in Total = 100(3.352)/66.241 = 5.1%

Pseudo-density of mixture at 60°F and 14.7 psia from Fig. 23-14 = 42.9 1bm/ft^3

Pressure correction to 1760 psia from Fig. 23-15 = +0.7

Density at 60°F and 1760 psia = 42.9 + 0.7 = 43.6 lb/ft^3

Temperature correction to 120 °F from Fig. 23-17 = -1.8

Density at 120 °F and 1760 psia = 43.6- 1.8 = 41.8 lb/ft^3

FIG. 23-16

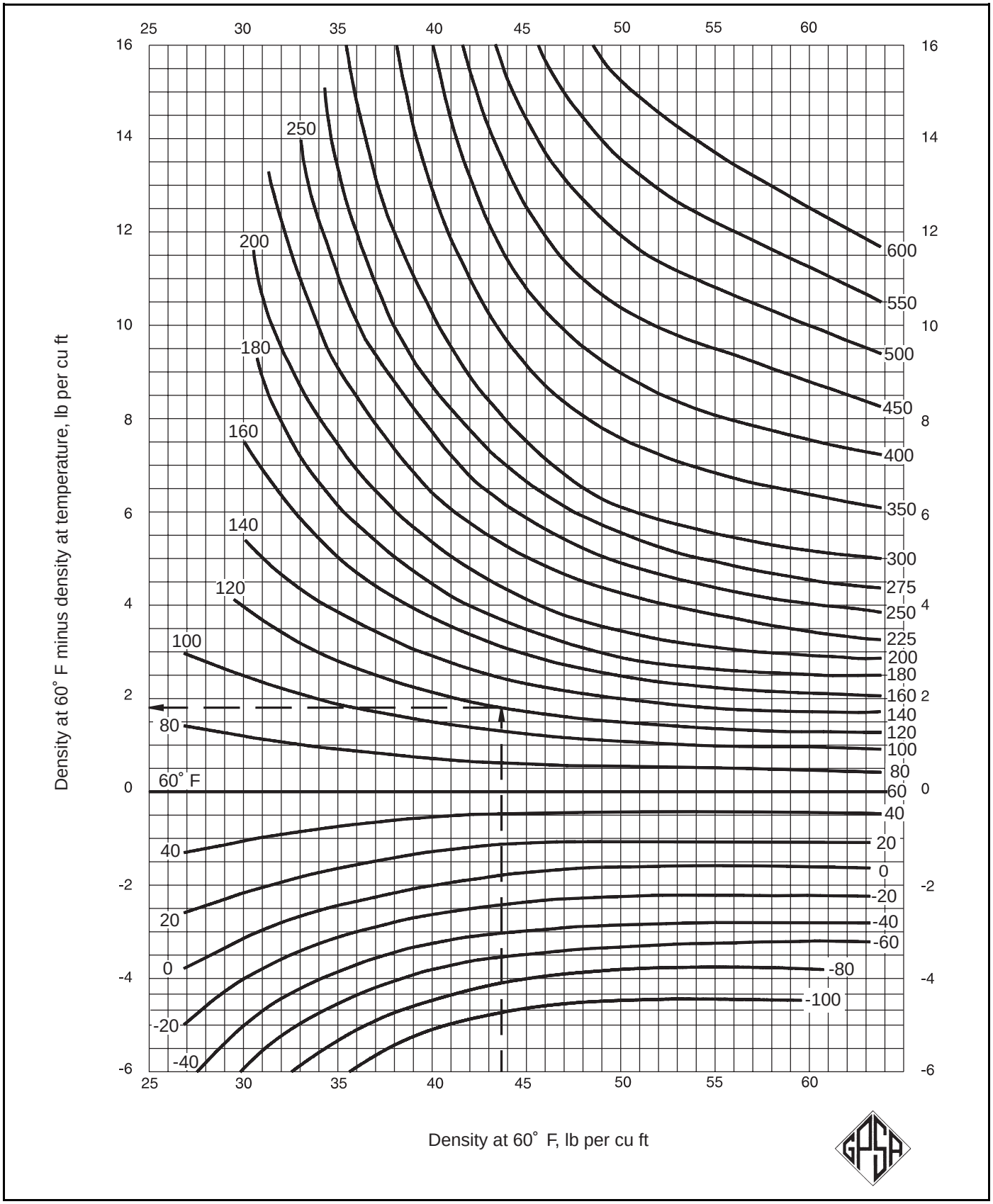
Calculation of Liquid Density of a Mixture at 120°F and 1760 psia

(1)	(2)	(3)	(4)=(2).(3)	(5)	(6)=(4)/(5)
Component	**Mole Fraction**	**Molecular Weight**	**Weight, lb**	**Density (60°F), lb/cu ft**	**Volume, cu ft**
Methane	0.20896	16.043	3.352	–	–
Carbon Dioxide	0.39730	44.010	17.485	51.016	0.3427
Ethane	0.01886	30.070	0.567	–	–
Propane	0.02387	44.097	1.053	31.619	0.0333
n-Butane	0.03586	58.123	2.084	36.423	0.0572
n-Pentane	0.02447	72.150	1.766	39.360	0.0449
n-Hexane	0.01844	86.177	1.589	41.400	0.0384
n-Heptane	0.02983	100.204	2.989	42.920	0.0696
n-Octane	0.02995	114.231	3.421	44.090	0.0776
n-Decane	0.18208	142.285	25.907	45.790	0.5658
n-Tetradecane	0.03038	198.394	6.027	47.815	0.1260

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FIG. 23-17

Density Correction for Thermal Expansion of Hydrocarbon Liquids



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Density from EZ*THERMO version of SRK using Costald[92] = 41.815 lb/ft^3.

Experimental density[35] at 120°F and 1760 psia = 41.2 lb/ft^3

Error = (41.8 - 41.2)/41.2 = 0.015, or 1.5%

BOILING POINTS, CRITICAL PROPERTIES, ACENTRIC FACTOR, VAPOR PRESSURE

Boiling Points

Fig. 23-18 shows the interconversion between ASTM D-86 distillation 10% to 90% slope and the different boiling points used to characterize fractions of crude oil to determine the properties; VARP, WARP, CARP, MeARP, and MABP. On the basis of ASTM D-86 distillation data, the volumetric average boiling (VARP) point is:

$$VARP = (t_{10} + t_{30} + t_{50} + t_{70} + t_{90})/5 \qquad \textbf{Eq 23-12}$$

where the subscripts 10, 30, 50, 70, and 90 refer to the volume percent recovered during the distillation. The 10% to 90% slope used as the abscissa in Fig. 23-18 is:

$$slope = (t_{90} - t_{10})/(90 - 10) \qquad \textbf{Eq 23-13}$$

To use the graph, locate the curve for the distillation VARP in the appropriate set for the type of boiling point desired. For the known 10-90% slope, read a correction for the VABP from the selected VABP curve.

Example 23-4 — Determine the mean average boiling point (MeABP) and the molecular weight for a 56.8° API petroleum fraction with the following ASTM distillation data.

% Over	Temperature, °F
IBP	100
5	130
10	153
20	191
30	217
40	244
50	280
60	319
70	384
80	464
90	592
EP	640

IBP = initialboiling point EP = endpoint

Slope = (592 – 153)/80 = 5.49

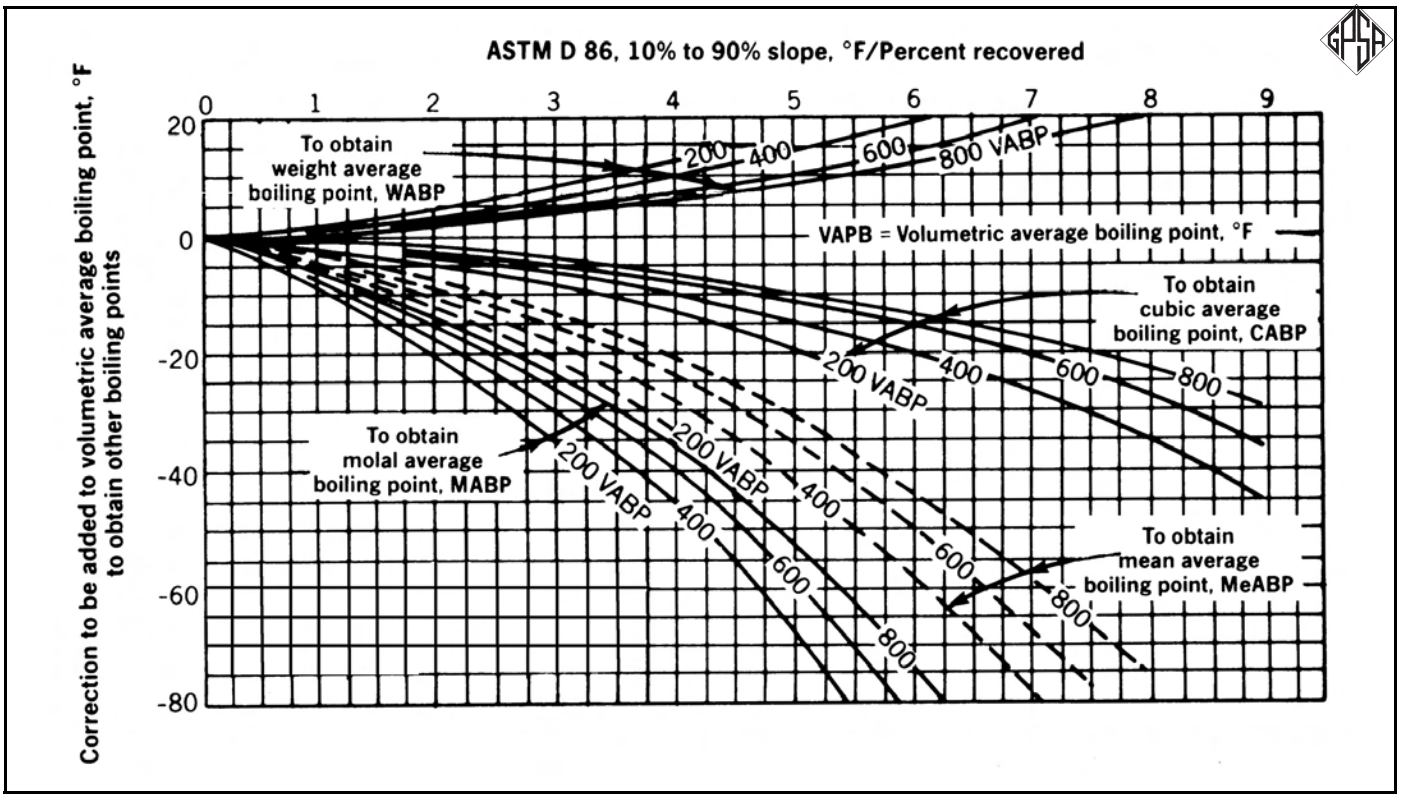
VABP = (153 + 217 + 280 + 384 + 592)/5 = 325°F

Refer to Fig. 23-18. Read down from a slope of 5.49 to the interpolated curve to 325 °F in the set drawn with dashed lines (MeABP). Read a correction value of –54 on the ordinate. Then

MeABP = 325 – 54 = 271°F

FIG. 23-18

Characterizing Boiling Points of Petroleum Fractions (From API Technical Data Book)



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The significance of the various average boiling points, interconversion of D-86 and D-1160 A8TM distillations, and the calculation of true-boiling point and atmospheric flash curves from A8TM distillation data are in Chapters 3 and 4 of the API Technical Data Book.[36]

Molecular weight can be calculated from Eq 23-14 using MeABP in °R and S (specific gravity at 60°F):

$$MW = 204.38\,(T^{0.118})(S^{1.88})\,e^{(0.00218T\,-\,3.075\,S)} \qquad \textbf{Eq 23-14}$$

This relationship is valid in the molecular weight range of 70 to 720; the MeABP range of 97 to 1040 °F; and the API range of 14° to 93°. The average error is about 7%. Eq. 23-14 works best for molecular weights above 115; it tends to over-predict below this value.

Example 23-5 — Calculation of molecular weight.

From Example 23-4:

S = 0.7515 for 56.8° API

MeABP = 271 + 460 = 731°R

Using Eq 23-14,

$$MW = 204.38(731)^{0.118}\,(0.7515)^{1.88}\,e^{[(0.00218)(731)\,-\,(3.075)(0.7515)]} = 127.0$$

Critical Properties

Critical properties are of interest because they are used to find reduced conditions of temperature and pressure as required for corresponding states correlations. Pseudo-critical properties are used in many corresponding states correlations for mixtures.

The following equations taken from the API Technical Data Book[36a,b] estimate pseudo-critical temperature and pressure for petroleum fractions (pseudo, or undefined components):

$$P_{pc} = 3.12281(10^9)\,T^{-2.3125}\,S^{2.3201} \qquad \textbf{Eq 23-15}$$

$$T_{pc} = 24.2787\,T^{0.58848}\,S^{0.3596} \qquad \textbf{Eq 23-16}$$

These equations are in terms of T = MeABP (°R) and specific gravity, S, at 60 °F. Both of these correlations are valid over the range of 80 to 690 molecular weight; 70 to 295°F normal boiling point; and 6.6° to 95° API.

Example 23-6 — Pseudo-critical temperature and pressure.

Take the previous mixture (from Example 23-4) with:

VABP = 325 °F
MeABP = 271°F
API = 56.8°
MW = 127 (Ex. 23-5)
ASTM D-86, 10% to 90% Slope = 5.49

Find its pseudo-critical temperature.

Solution Steps

From Fig. 23-18 with ASTM D-86 slope = 5.49 find a VABP correction of about –85°F (extrapolated from the left-hand group).

MABP = 325- 85 = 240°F

Use Eq 23-16 to calculate the pseudo-critical temperature:

$$T_{pc} = 24.2787\,(271 + 460)^{0.58848}\,(0.7515)^{0.3596} = 1062\ °R \text{ or } 602\ °F$$

For this 56.8° **API** fluid, estimate the pseudo-critical pressure, using Eq 23-15 and MeABP = 271°F:

$$P_{pc} = 3.12281(10^9)\,(271 + 460^{)-2.3125}\,(0.7515)^{2.3021} = 386 \text{ psia}$$

Acentric Factor

The acentric factor, ω, is often a third parameter in corresponding states correlations. Figure 23-2 tabulates it for pure hydrocarbons. The acentric factor is a function of P_{vp}, P_c, and T_c. It is arbitrarily defined as

$$\omega = -\log(P_{vp}/P_c)_{Tr=0.7} - 1.0 \qquad \textbf{Eq 23-17}$$

This definition requires knowledge of the critical (pseudo-critical) temperature, vapor pressure, and critical (pseudo-critical) pressure.

For a hydrocarbon mixture of known composition that contains similar components, a reasonably good estimate for the acentric factor is the molar average of the individual pure component acentric factors:

$$\omega = \sum_i y_i \omega_i \qquad \textbf{Eq 23-18}$$

If the vapor pressure is not known, ω can be estimated[38] for pure hydrocarbons or for fractions with boiling point ranges of 50°F or less using:

$$\omega = \frac{3}{7}\left[\frac{\log P_c - \log 14.7}{(T_c/T_b) - 1}\right] - 1.0 \qquad \textbf{Eq 23-19}$$

Example 23-7 — Acentric factor.

A narrow-boiling petroleum fraction has a VABP of 418°F, an ASTM slope of 0.75 and an API gravity of 41°. Estimate its acentric factor. To use Eq 23-19 we need the average boiling point (MeABP); the pseudo-critical temperature (a function of MABP); and the pseudo-critical pressure (a function of MeABP).

From Fig. 23-18, the correction to VABP for mean average is –3°F; the correction for MABP is –5°F. Note that for narrow-boiling fractions, all boiling points approach the volumetric average. Then, MeABP = 415°F and MABP is 413°F.

From Eq. 23-15, the pseudo-critical pressure is:

T = 415 + 460 = 875 °R

S for 41° API = 141.5/(131.5 + 41) = 0.871

$$P_{pc} = 3.12281(10^9)\,(875)^{-2.3125}(0.871)^{2.3201} = 356 \text{ psia}$$

From Eq 23-16, the pseudo-critical temperature is:

$$T_{pc} = 24.2787(875)^{0.58848}(0.871)^{0.3596} = 1244\ °R$$

$$\omega = \frac{3}{7}\left[\frac{\log (356) - \log (14.7)}{(1244/875) - 1.0}\right] - 1.0 = 0.407$$

Vapor Pressure

The vapor pressures of light hydrocarbons and some common inorganics in the temperature range below 100°F appear in Fig. 23-19. Vapor pressures at higher temperatures, up to 600°F, are in Fig. 23-20 for the same compounds. Note that, except for ethylene and propylene, the hydrocarbons are all normal paraffins.

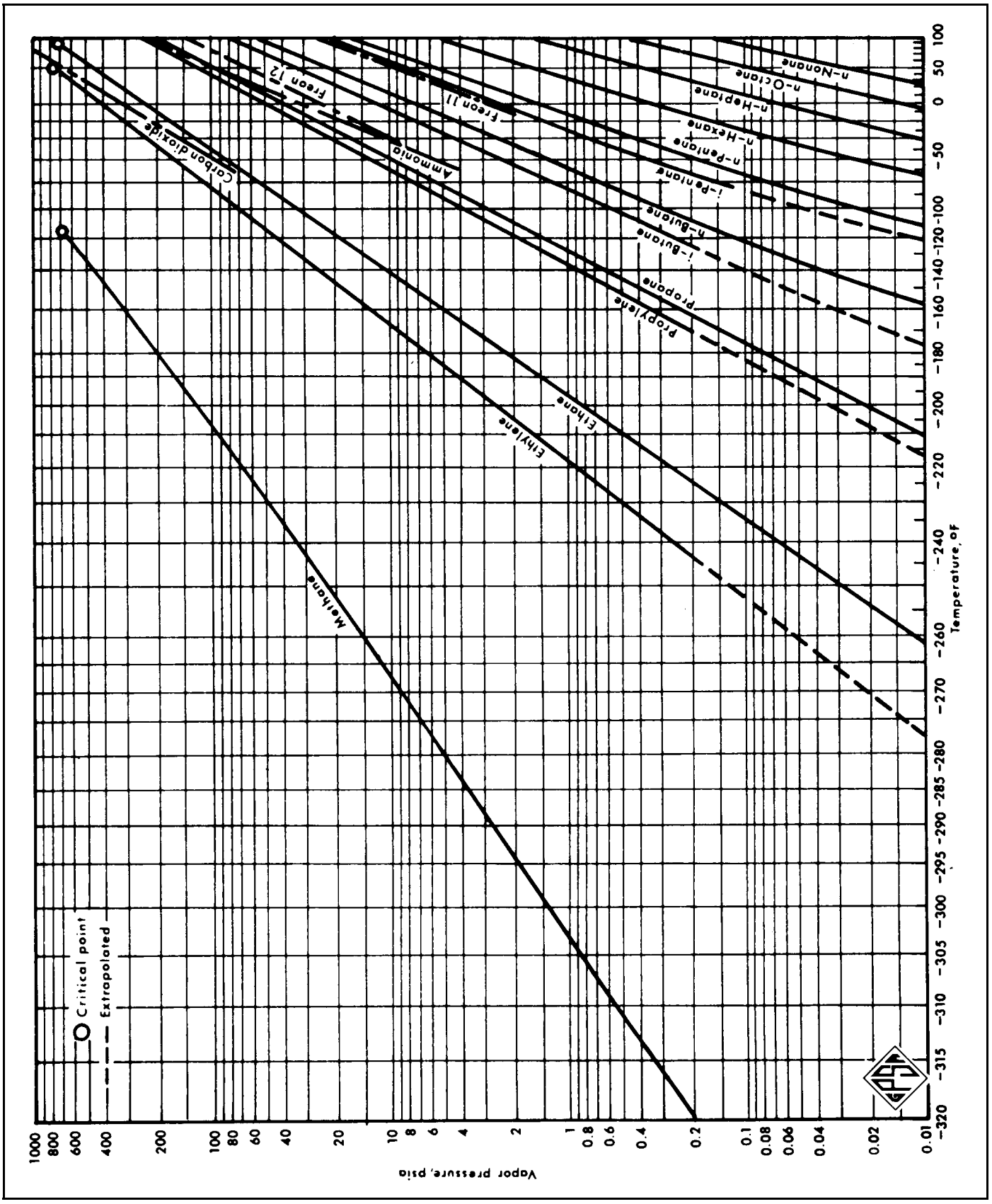
VISCOSITY

Figures 23-21 through 23-29 give the viscosity of hydrocarbon liquids and vapors, water, steam, and miscellaneous gases. Figure 23-21 gives data on hydrocarbon liquids. Figures 23-22, 23-23 and 23-24 present data on hydrocarbon gases. To correct for pressure, adjust the gas viscosity from Fig. 23-22 from atmospheric pressure using Fig. 23-24, or read directly

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FIG. 23-19

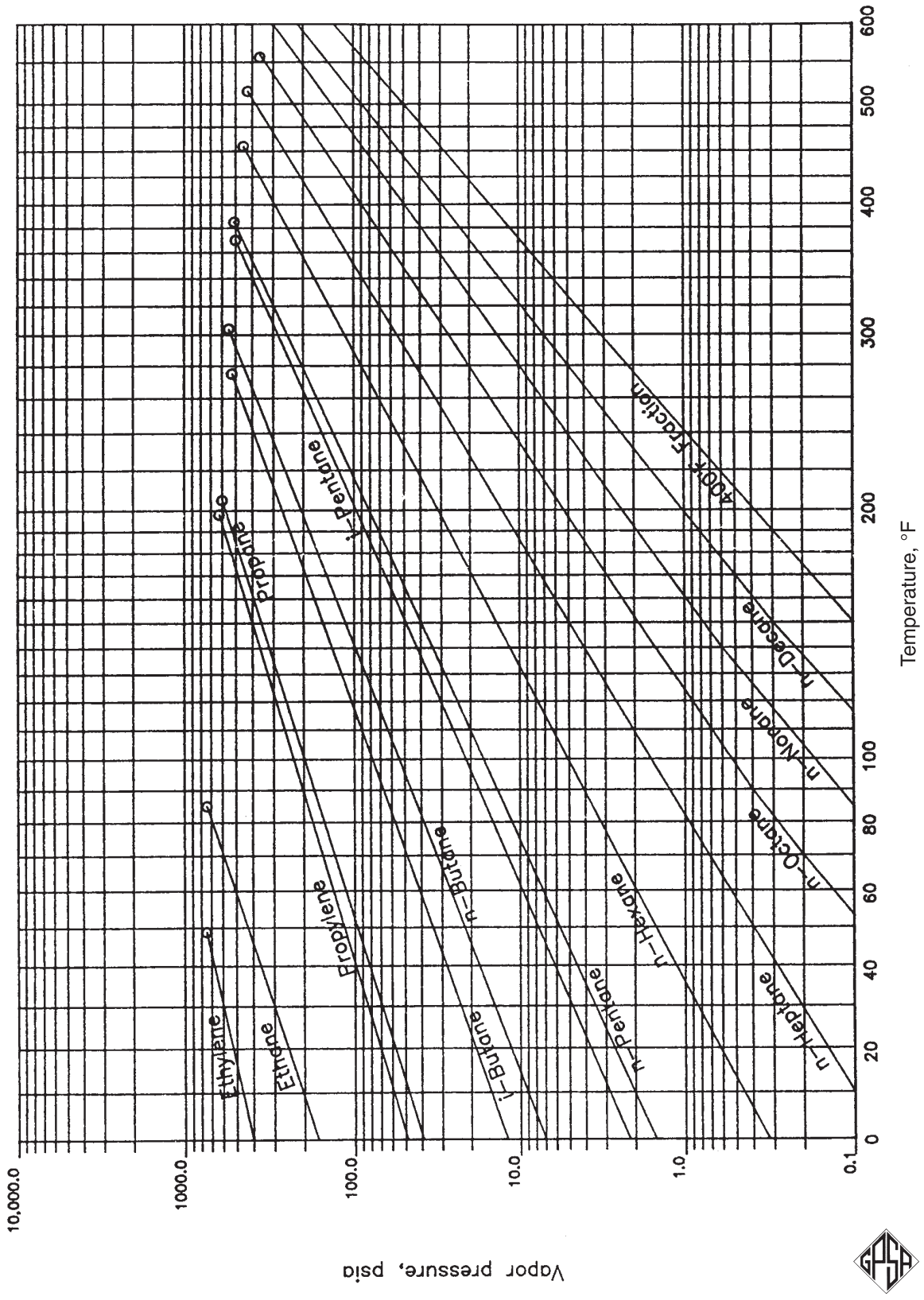
Low-Temperature Vapor Pressures for Light Hydrocarbons



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FIG. 23-20

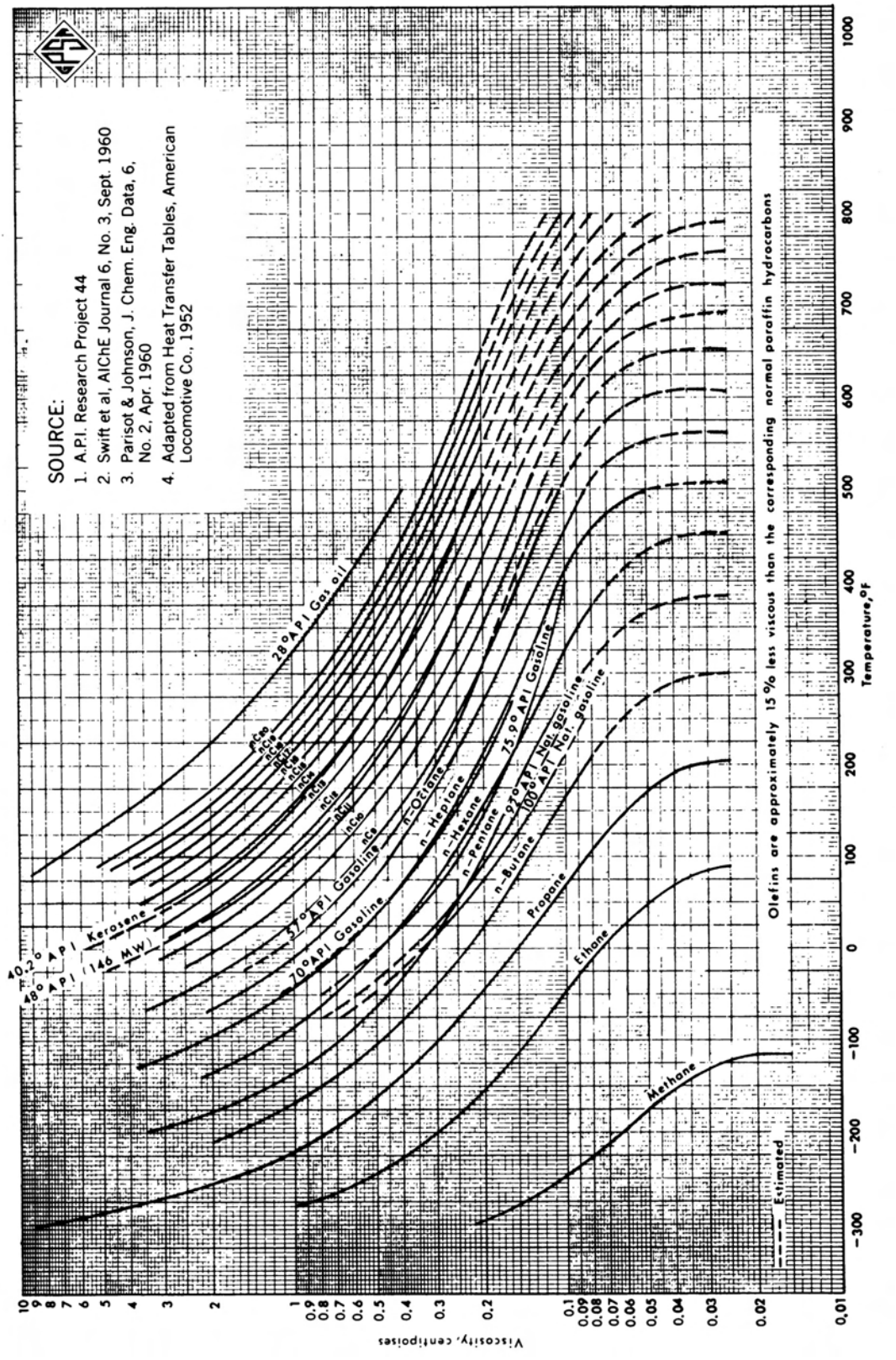
High-Temperature Vapor Pressures for Light Hydrocarbons



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FIG. 23-21

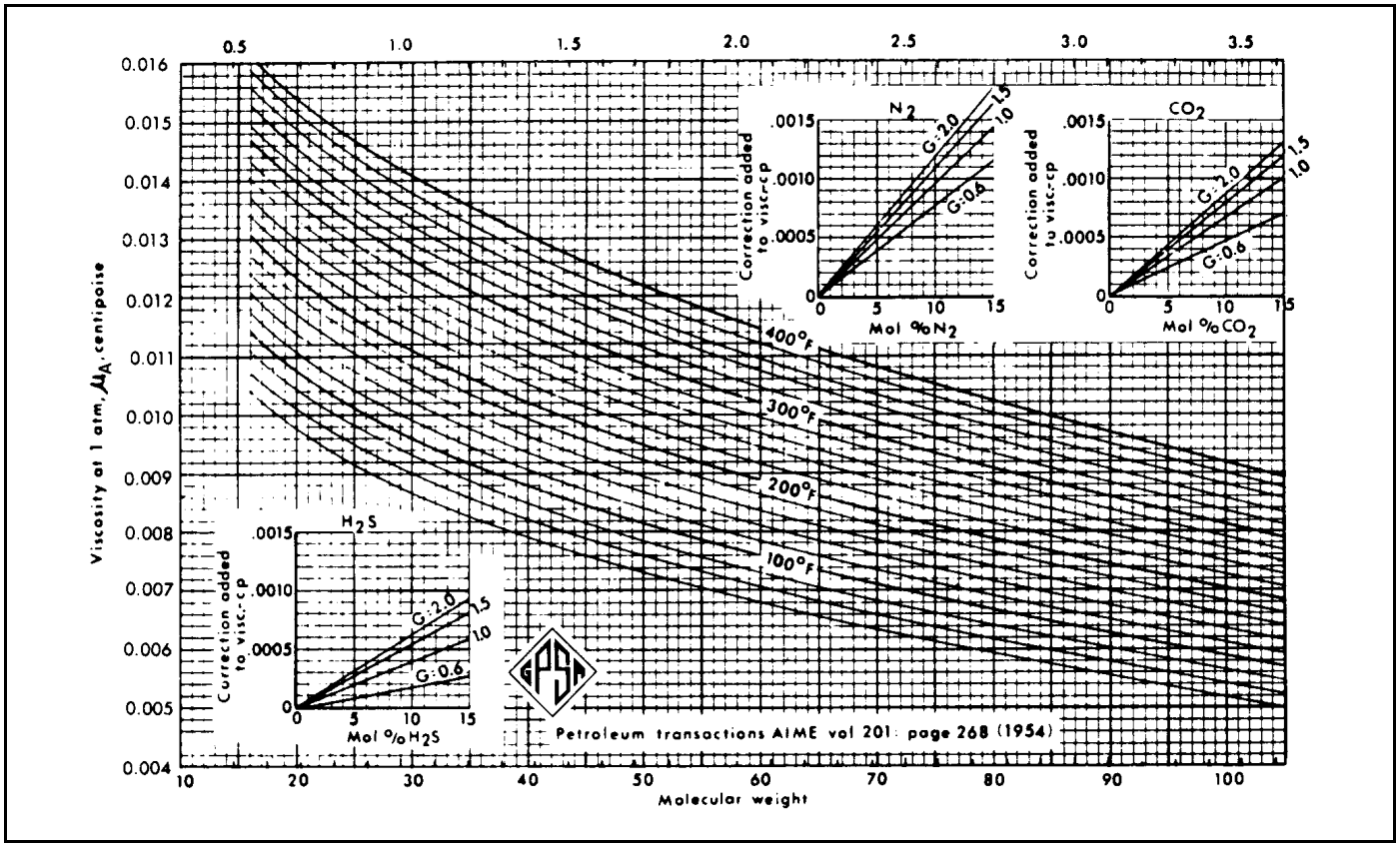
Viscosities of Hydrocarbon Liquids



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FIG. 23-22

Viscosity of Paraffin Hydrocarbon Gases at One Atmosphere



from Fig. 23-23. Figure 23-24 is better when the reduced temperature is greater than 1.0. Figure 23-28 gives the viscosity of hydrocarbon liquids containing dissolved gases. Note that Fig. 1-7 gives conversion factors for viscosity.

Calculation of Gas Mixture Viscosity

Example 23-8 — Determine the viscosity of a gas at 1,000 psia and 100 °F with the properties: MW = 22, T_c = 409°R, P_c = 665 psia.

Solution Steps

$G^{id} = 22/28.9625 = 0.760$

From Fig. 23-22 at 100 °F:

$\mu_A = 0.0105$ centipoise

Then:

$$T_r = \frac{100 + 459.67}{409} = 1.37 \qquad P_r = \frac{1000}{665} = 1.50$$

Note: If the composition of the gas is available, calculate the pseudo-critical temperatures and pressures as outlined in this section.

Because $T_r > 1.0$, Fig. 23-24 is better than Fig. 23-23 to obtain the correction for elevated pressure to the viscosity at one atmosphere.

From Fig. 23-24:

$\mu/\mu_A = 1.21$

Hence, the viscosity at 1000 psia and 100°F is:

$\mu = (1.21)\,(0.0105) = 0.0127$ centipoise

The method of Dean and Stiel[41] is best for calculating the viscosity of a gaseous mixture with large amounts of non-hydrocarbons. This method is particularly useful for handling natural gas with high CO_2 content. Compared to 30 CO_2-N_2 mixtures, this method has an average deviation of 1.21% at pressures up to 3525 psia. The method uses a factor, ξ, defined as:

$$\xi = 5.4402\left[\frac{T_{cm}^{1/6}}{P_{cm}^{2/3}\left(\sum_i y_i MW_i\right)^{1/2}}\right] \qquad \textbf{Eq 23-20}$$

If $T_r > 1.5$, then

$$\xi\mu_A = 166.8(10^{-5})(0.1338\,T_r - 0.0932)^{5/9} \qquad \textbf{Eq 23-21}$$

If $T_r \geq 1.5$,

$$\xi\mu_A = 34.0(10^{-5})\,(T_r^{8/9}) \qquad \textbf{Eq 23-22}$$

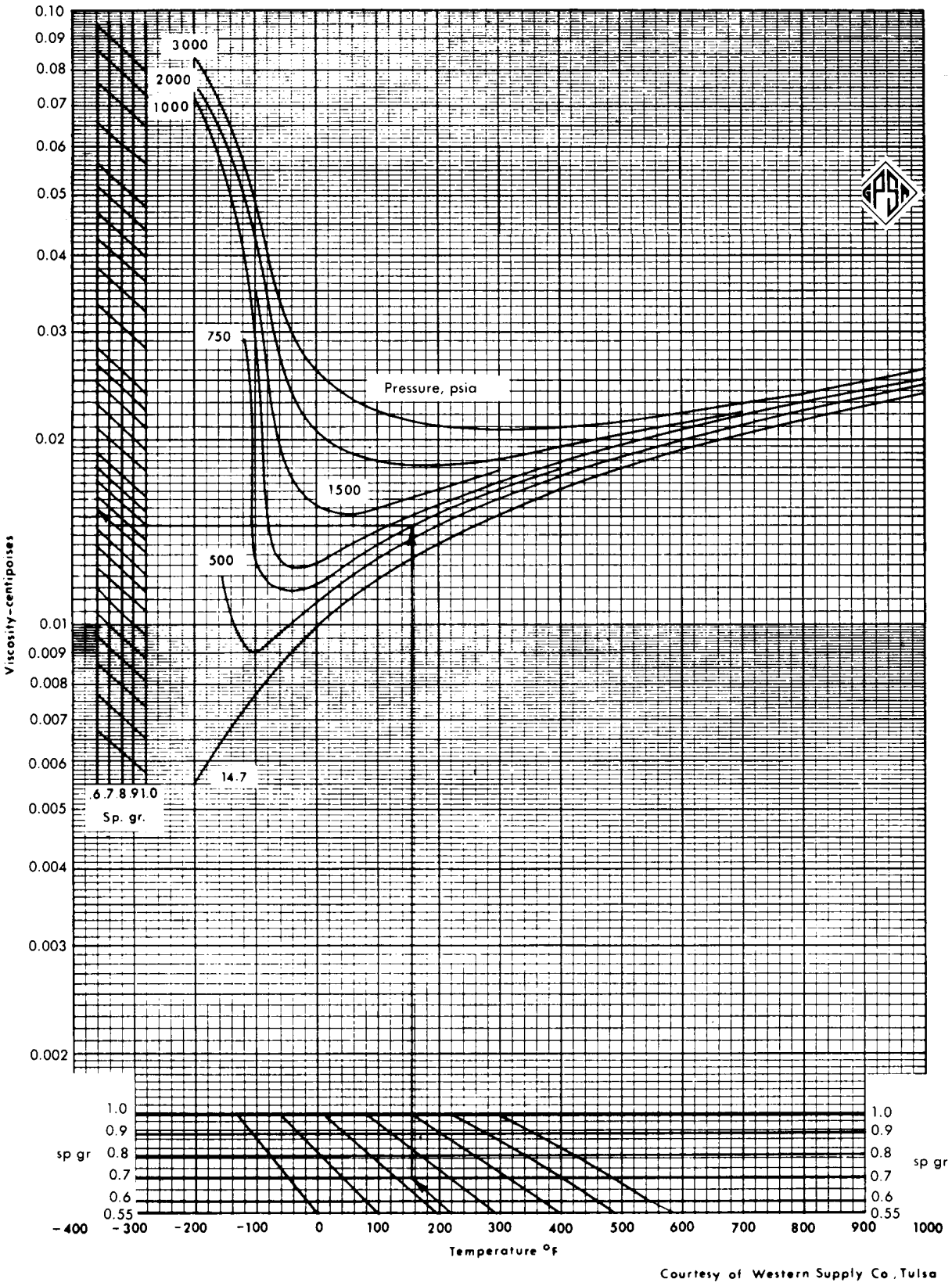
In either case, μ_A is $\xi\mu_A$ divided by ξ.

Equations 23-20 through 23-22 predict the viscosity of pure gases as well as mixtures. To apply the Dean and Stiel[41] method to mixtures, calculate the pseudo-critical volumes, Z-

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FIG. 23-23

Hydrocarbon Gas Viscosity



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FIG. 23-24

Viscosity Ratio vs. Pseudoreduced Temperature

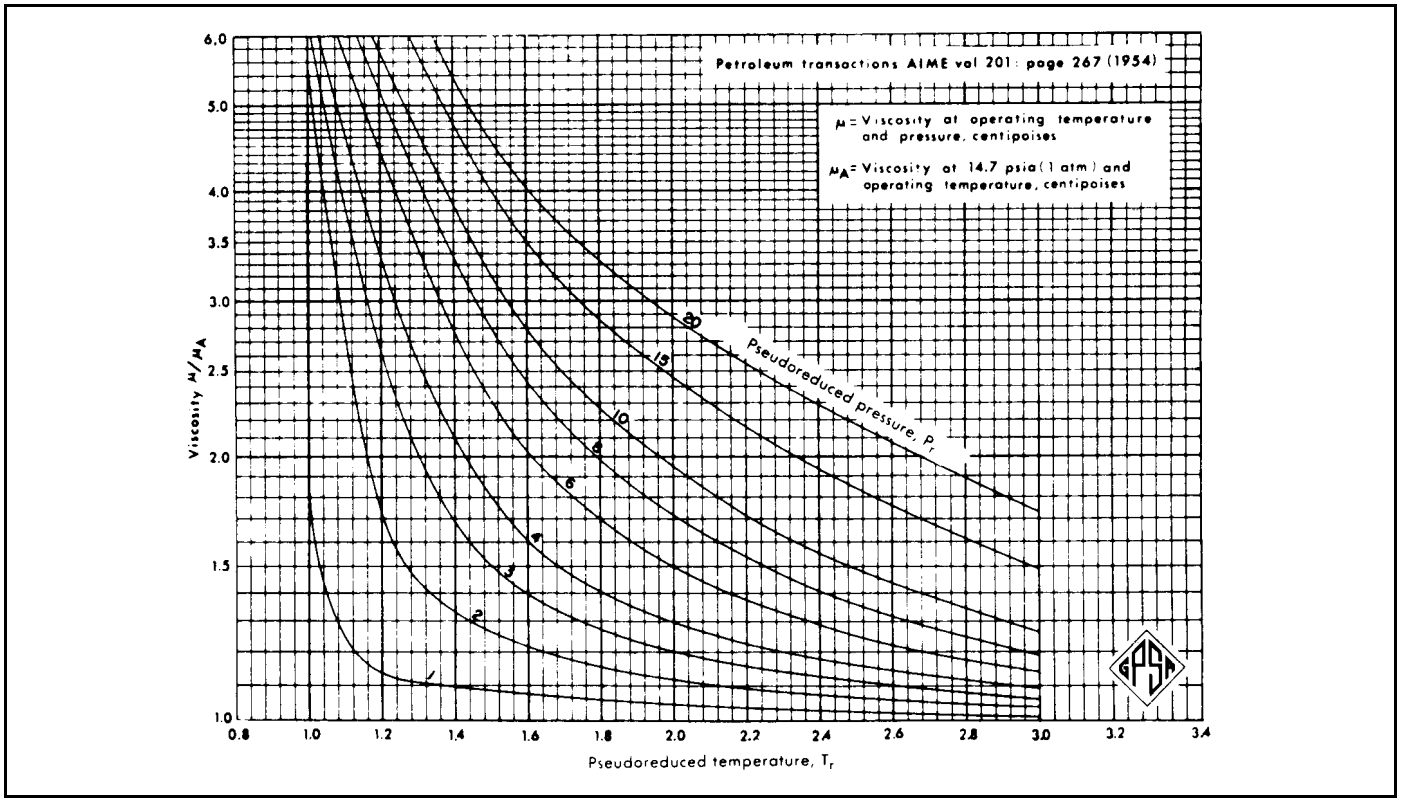


FIG. 23-25

Viscosity of Miscellaneous Gases – One Atmosphere

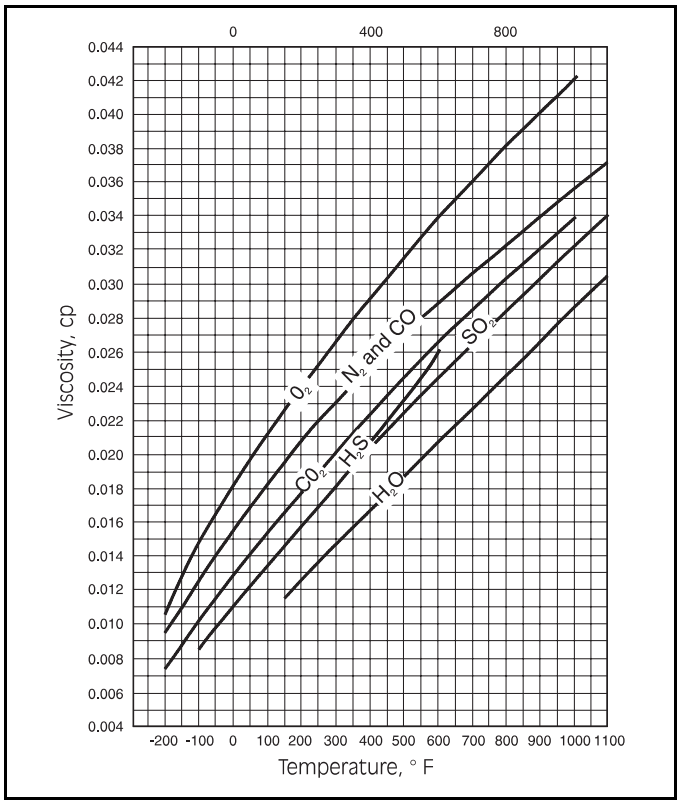
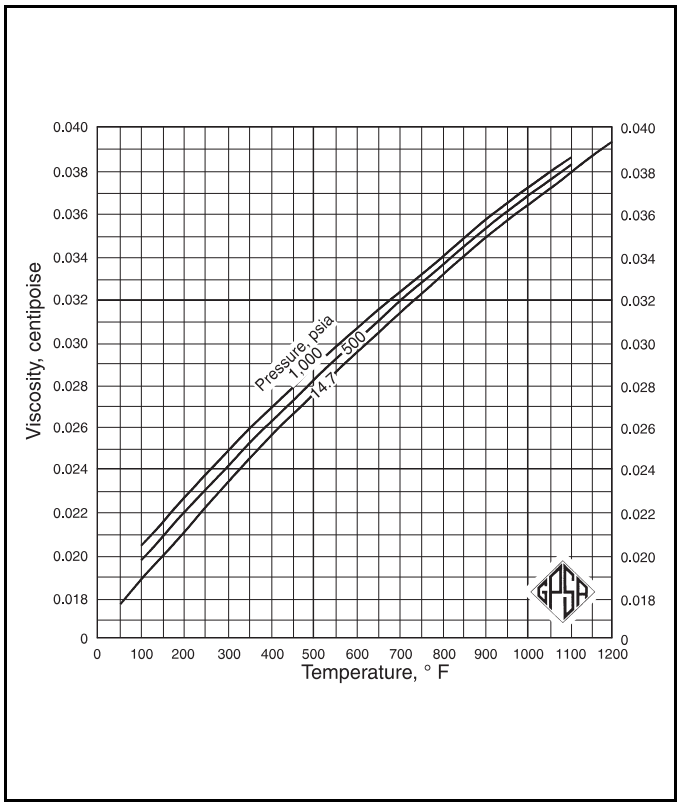


FIG. 23-26

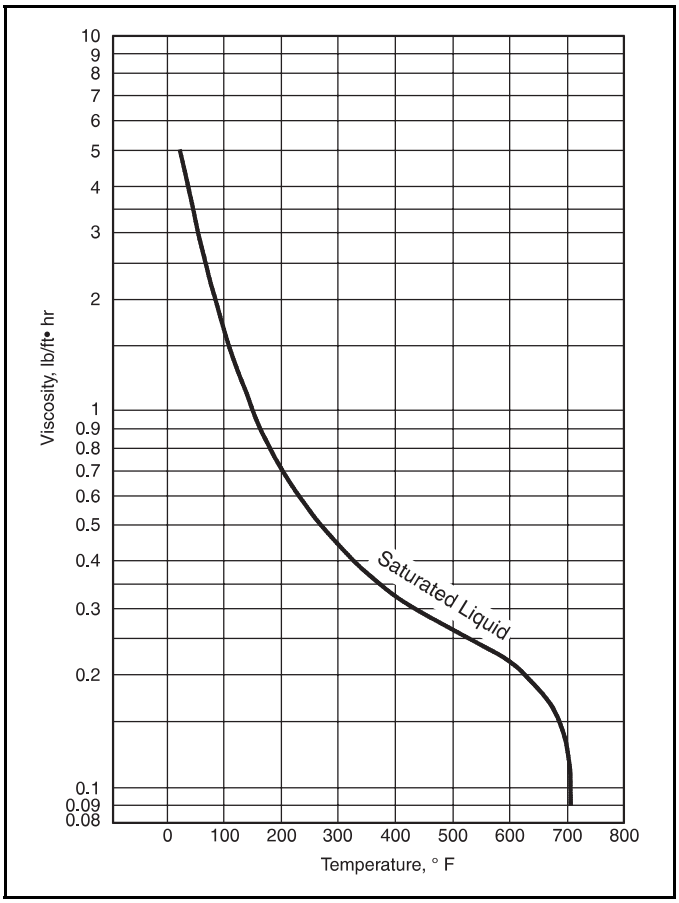
Viscosity of Air[43, 44, 45]



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FIG. 23-27

Water Viscosity at Saturated Conditions



factors, and temperatures using the Prausnitz and Gunn[42] mixing rules:

$$V_{cm} = \sum_i y_i V_{ci} \qquad \textbf{Eq 23-23}$$

$$Z_{cm} = \sum_i y_i Z_{ci} \qquad \textbf{Eq 23-24}$$

$$T_{cm} = \sum_i y_i T_{ci} \qquad \textbf{Eq 23-25}$$

$$P_{cm} = \frac{Z_{cm} R T_{cm}}{V_{cm}} \qquad \textbf{Eq 23-26}$$

Example 23-9 — For a temperature of 50 °F and a pressure of 300 psia, estimate the viscosity of a mixture of 80 mol% methane, 15 mol% nitrogen, and 5 mol% carbon dioxide. Fig. 23-30 summarizes the calculations:

$P_{cm} = Z_{cm}RT_{cm}/V_{cm} = (0.2877)(10.73)(335.9)/1.562 =$ 663.4 psia

Substituting from the calculation table in Fig. 23-30 into Eq 23-20:

$\xi = (5.4402)(335.9)^{1/6}/[(19.237)^{1/2}(663.4)^{2/3} = 0.043$

$T_r = T/T_{cm} = 509.7/335.9 = 1.517$

Because $T_r > 1.5$, the expression for $\xi\mu_A$ is Eq 23-21.

$$\xi\mu_A = 166.8(10^{-5})(0.1338\ T_r - 0.0932)^{5/9}$$
$$= 166.8(10^{-5})\ [(0.1338)\ (1.517) - 0.0932]^{5/9}$$
$$= 48.91(10^{-5})$$

$\mu_A = 0.01138$ centipoise

Using Fig. 23-22 and correcting for the nitrogen and carbon dioxide content of this mixture gives $\mu_a = 0.0116$ cp. This is a good check. Had this example contained a 20% N_2 content, the N_2 range of Fig. 23-22 would be exceeded and dictate use of the Dean and Stiel method. When conditions fall within the limits of Fig. 23-23, use this figure and not the Dean and Stiel correlation.

Viscosity of Petroleum Fractions

Mid-Boiling Point Method — The viscosity of a crude oil or crude oil fraction can be estimated if the mid-boiling point and gravity are known:

Mid-boiling point is defined as the boiling point at 50% volume distilled.

$$\eta = A \bullet e^{(1.8B/T)} \qquad \textbf{Eq 23-27}$$

$$A = (101.78T_b^{-0.175} - 29.263)K_W/B \qquad \textbf{Eq 23-28}$$

$$\text{In}\ (B) = 4.717 + 0.00292\ T_b \qquad \textbf{Eq 23-29}$$

Example 23-10 — At l00°F and 210°F find the viscosity of a heavy condensate having a mid-boiling point of 325°F and a specific gravity of 0.7688.

Solution Steps

$$K_W = \frac{\sqrt[3]{325 + 459.67}}{0.7688} = 11.99$$

$\ln(B) = 4.717 + 0.00292(325 + 459.67) = 7.01$

$B = 1105.7$

$A = [\ 101.78(325 + 459.67)^{-0.175} - 29.263](11.99/1105.3)$
$= 0.02645$

The same constants apply at 100°F and at 210°F.

$h = 0.02645 \bullet e^{[1.8(1105.7)/559.67\ ]} = 0.926$ cs at 100°F

$h = 0.02645 \bullet e^{[1.8(1105.7)/669.67\ ]} = 0.517$ cs at 210°F

The reported experimental values are 0.93 and 0.52 centistokes, respectively.

THERMAL CONDUCTIVITY

Thermal conductivity for natural gas mixtures at elevated pressure can be calculated from an atmospheric value and a pressure correction. Figs. 23-31 through 23-36 present low pressure thermal conductivity data for gases developed from published data[51,54]. The pressure correction of Lenoir *et al*.[52] shown in Fig. 23-32 applies to these low pressure data. The thermal conductivity of liquid paraffin hydrocarbons appears in Fig. 23-35 and the thermal conductivity of liquid petroleum fractions appears in Fig. 23-36.

Example 23-11 — Find the thermal conductivity of a natural gas at 700 psia and 300 °F with properties MW = 25, T_c = 440 °R and P_c = 660 psia.

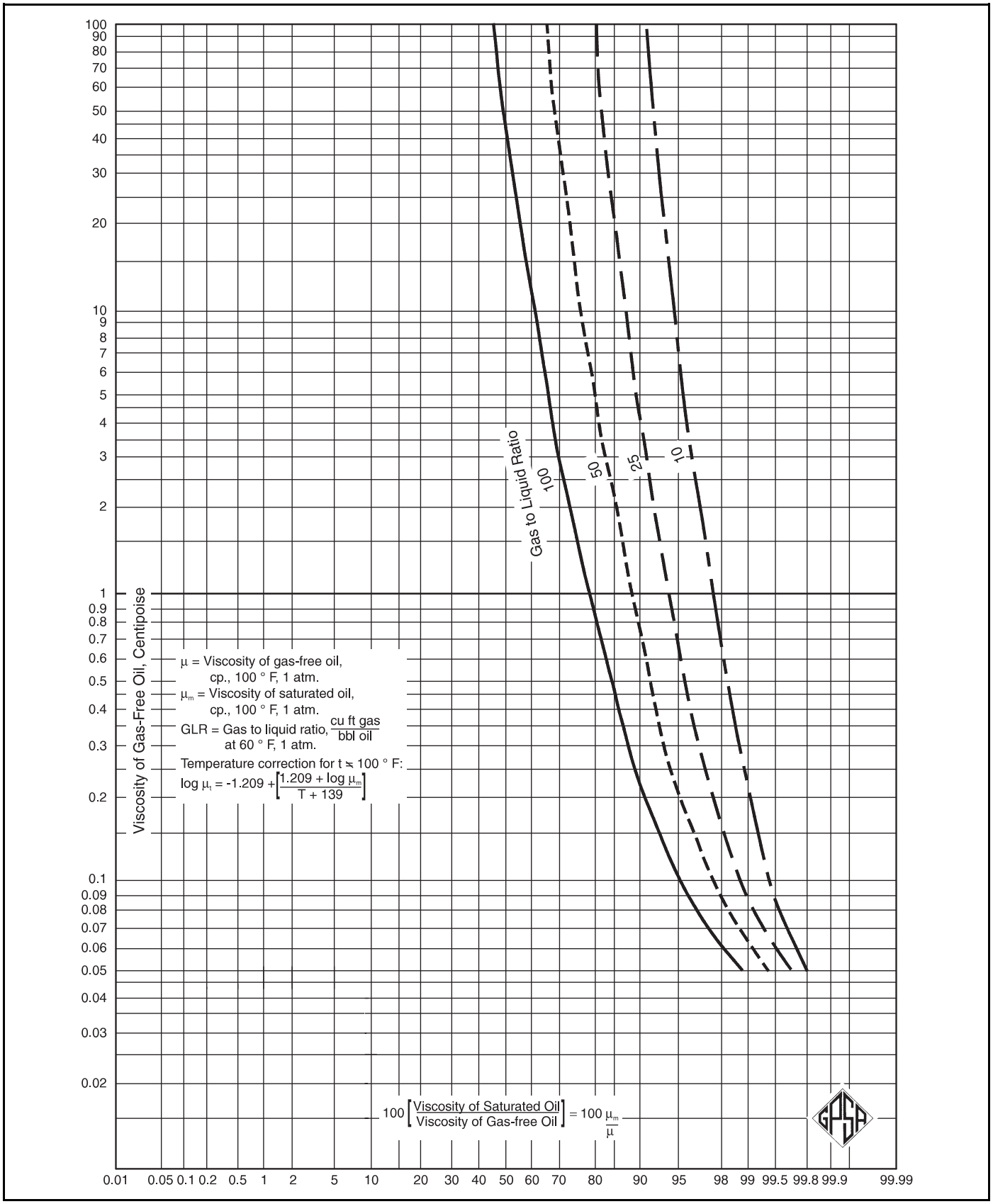
Solution Steps

From Fig. 23-31, at 300°F:

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FIG. 23-28

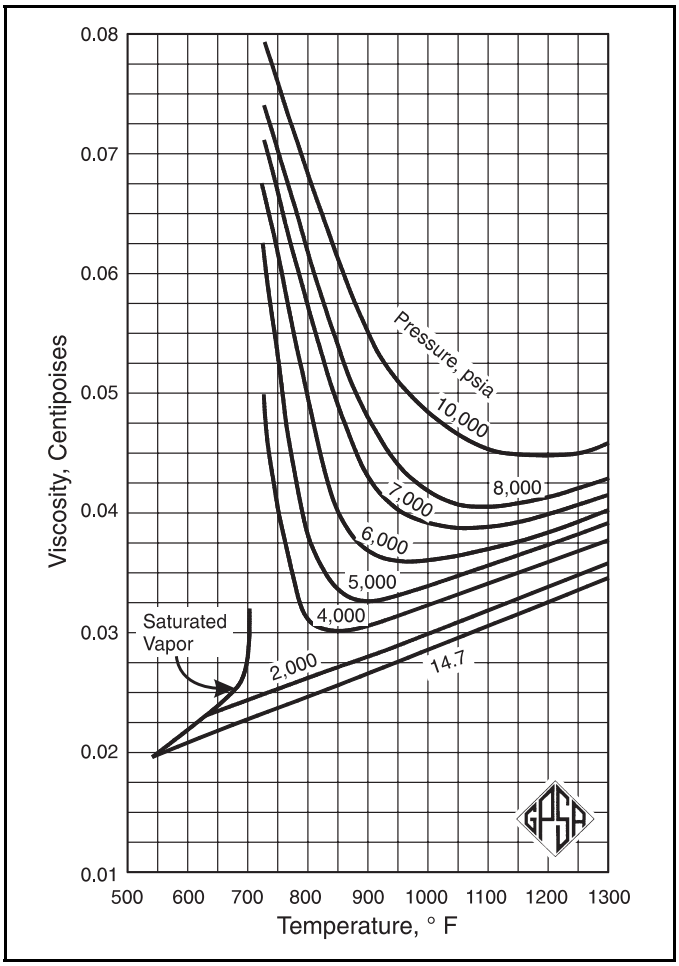
Liquid Viscosity of Pure and Mixed Hydrocarbons Containing Dissolved Gases at 100°F and One Atmosphere



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FIG. 23-29

Viscosity of Steam[46, 47]



k_A = 0.0248 Btu/[(hr ft^2 °F)/ft]

T_r= (300 + 459.67)/440 = 1.73

P_r = 700/660 = 1.06

From Fig. 23-32:

k/k_A = 1.15

k = (1.15) (0.0248) = 0.0285 Btu/[(hr ft^2 °F)/ft]

Stiel and Thodos[53] present another method for estimating thermal conductivity. To determine the thermal conductivity of a gaseous mixture of defined components, the thermal conductivity of each component at the given temperature is read from the charts provided and the thermal conductivity of the mixture is determined by the "cube root rule[56]." This rule is applicable to mixtures of simple gases; it does not apply to mixtures containing CO_2 because its thermal conductivity goes through a maximum.

$$k_m = \frac{\sum_i y_i k_i \sqrt[3]{MW_i}}{\sum_i y_i \sqrt[3]{MW_i}} \qquad \textbf{Eq 23-30}$$

Compared to 17 systems[56], the cube root rule has an average deviation of 2.7%. The method of Li[55] based upon volume fractions works best for the thermal conductivity of a liquid mixture.

Example 23-12 — Find the thermal conductivity of the gaseous mixture shown in Fig. 23-37 at 200 °F and one atmosphere.

k_m = 0.05774/2.822 = 0.0205 Btu/[(hr ft^2 °F)/ft]

TRANSPORT PROPERTY REFERENCES

No simple correlations exist for the transport properties of viscosity and thermal conductivity. For pure components, the best approach is a complicated equation with many constants that must be fit to experimental data, or extensive tables. Vargaftik[62] and Touloukian[65] each have extensive collections of experimental data.

SURFACE TENSION

The interior molecules of a liquid exert an inward force of attraction upon the surface molecules that tends to minimize the surface area of the liquid. The work required to enlarge the surface area by one square centimeter is the surface free energy. The perpendicular force in the liquid surface, called surface tension, exerts a force parallel to the plane of the surface. Surface tension is an important property for wetting, foaming, emulsification, and droplet formation and is used in the design of fractionators, absorbers, two-phase pipelines, and in reservoir calculations.

Pure Components

Figure 23-38 provides the surface tension of pure hydrocarbons as a function of temperature.

Mixtures

Surface tension for binaries of known composition at or near amospheric pressure may be calculated[78] using:

FIG. 23-30

Calculation of Viscosity of a Gas Mixture

	Mole Fraction, y_i	Molecular Weight, MW_i	Pci, psia	T_{ci}, °R	V_{ci}, ft^3/lb	$V_{ci} = MW_i \cdot v_{ci}$ ft^3/lb mole	$Z_{ci} = \frac{P_{ci} \cdot V_{ci}}{10.73 \cdot T_{ci}}$
CH_4	0.80	16.043	667.0	343.0	0.0988	1.59	0.2882
N_2	0.15	28.013	492.8	227.2	0.0510	1.43	0.2891
CO_2	0.05	44.010	1069.5	547.4	0.0342	1.51	0.2749
Mixture	1.00	19.237	—	335.9	—	1.562	0.2877
	Σ	$MW_{cm} = \Sigma y_i \cdot MW_i$		$T_{cm} = \Sigma y_i \cdot T_{ci}$		$V_{cm} = \Sigma y_i \cdot V_{ci}$	$Z_{cm} = \Sigma y_i \cdot Z_{ci}$

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FIG. 23-31

Thermal Conductivity of Natural and Hydrocarbon Gases at One Atmosphere (14.696 psia)

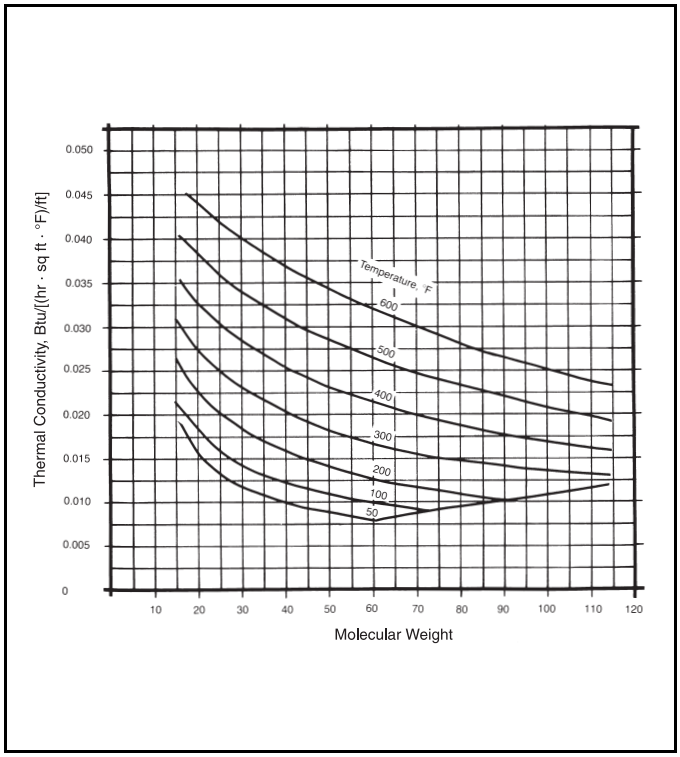


FIG. 23-32

Thermal Conductivity Ratio for Gases

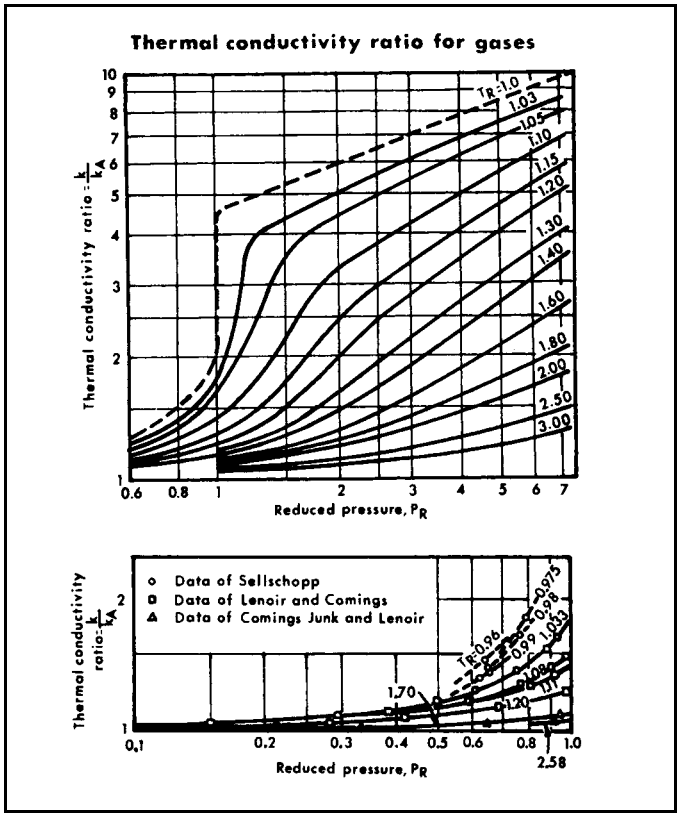


FIG. 23-33

Thermal Conductivity of Miscellaneous Gases at One Atmosphere[59, 60, 61, 62]

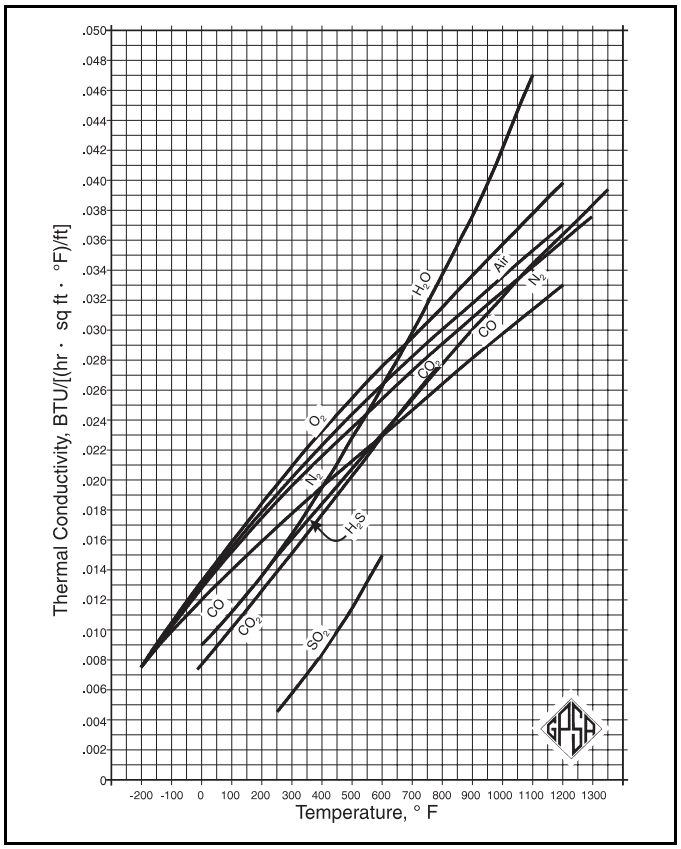
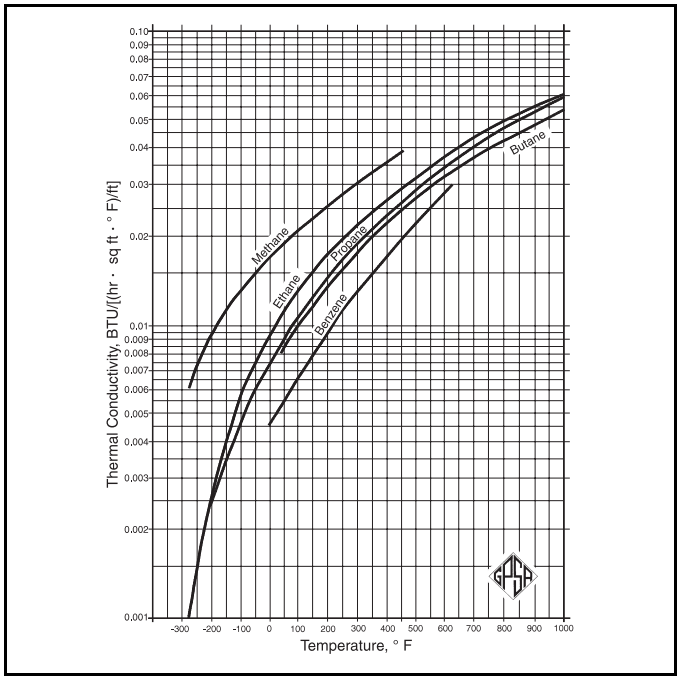


FIG. 23-34

Thermal Conductivity of Hydrocarbon Gases at One Atmosphere[67, 68, 69]



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FIG. 23-35

Thermal Conductivity of Liquid Paraffin Hydrocarbons

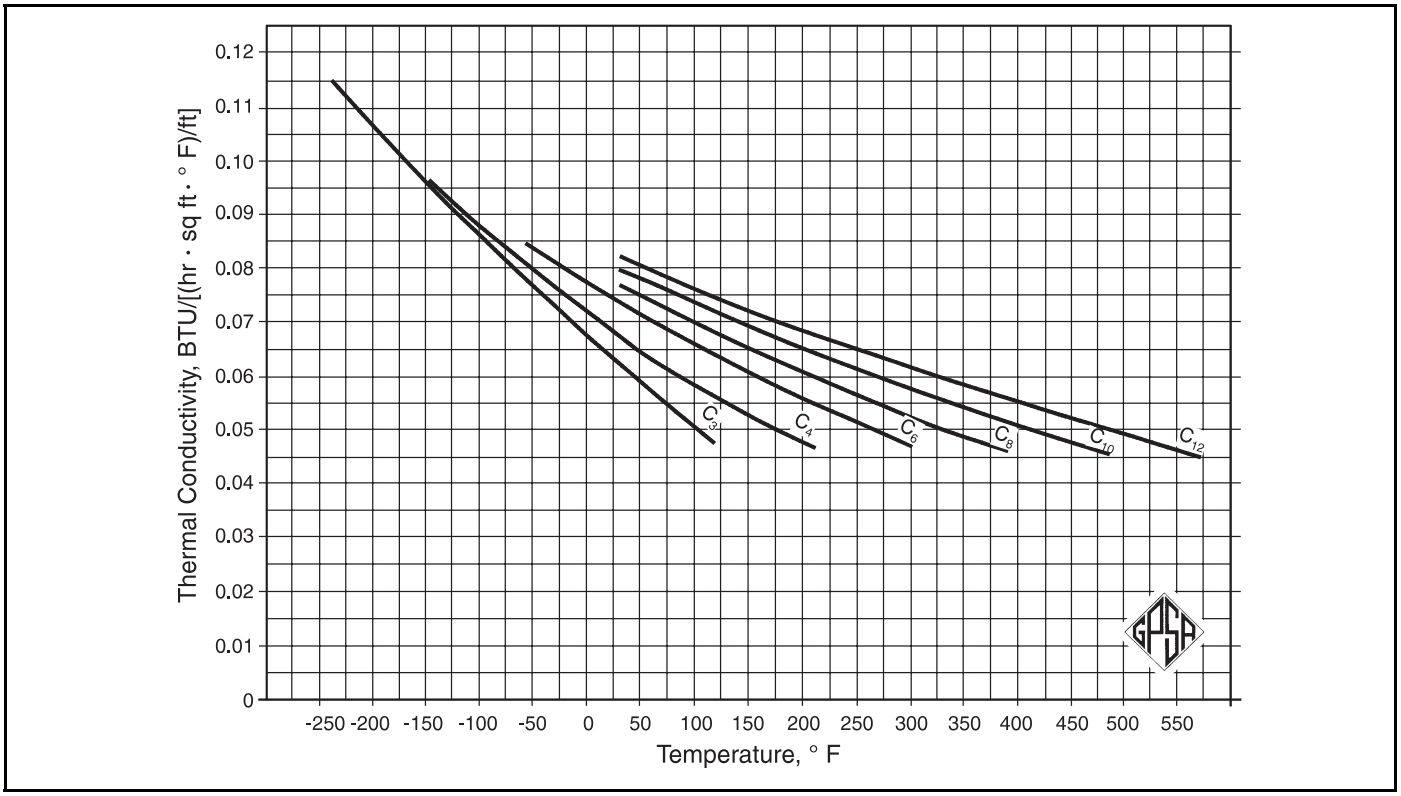
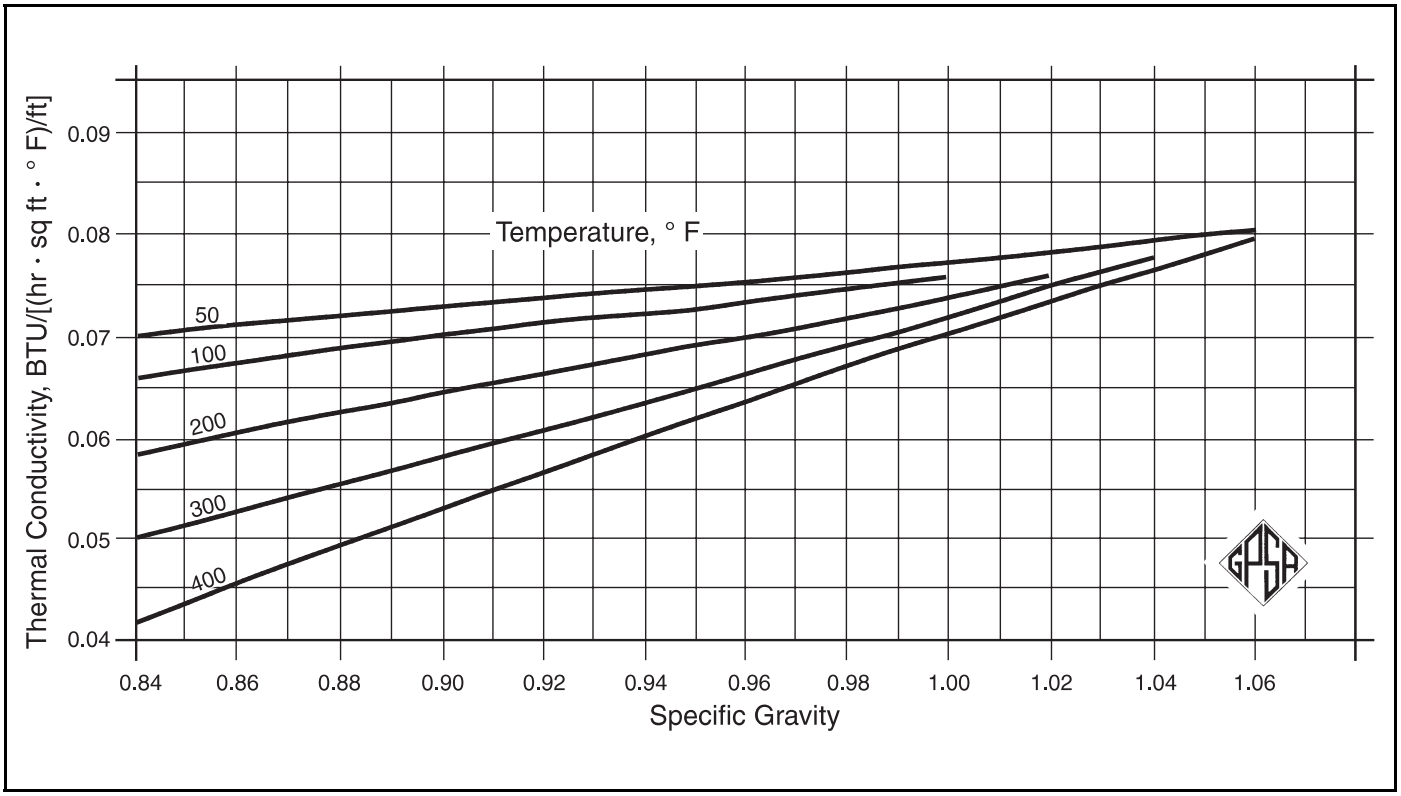


FIG. 23-36

Thermal Conductivity of Liquid Petroleum Fractions[58]



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$$\sigma_m = (\sigma_1\sigma_2)/(\sigma_1 x_2 + \sigma_2 x_1) \quad \textbf{Eq 23-31}$$

The presence of inert gases, such as N_2 and CO_2, in the liquid phase tends to lower the surface tension of the liquid. When the concentration of inert gases in the liquid exceeds 1.0 mol%, estimated values of surface tension may be 5 to 20% higher than actual values for the mixture.

GROSS HEATING VALUE OF NATURAL GASES

A complete compositional analysis of the mixture permits calculation of the gross heating value, specific gravity, and Z-factor of a natural gas mixture. Some definitions are in order before starting this discussion. It is necessary to understand the concepts: real gas, ideal gas, gross heating value (higher heating value, higher calorific value), net heating value (lower heating value, lower calorific value), hypothetical state.

Real Gas — refers to an actual fluid in its vapor phase. It is possible to collect samples of these fluids and to measure their thermophysical properties.

Hypothetical State — refers to a definition of a fluid in a state that cannot actually exist, e.g. methane as a liquid at 60 °F and 14.696 psia. Methane cannot be in its liquid phase at this temperature and pressure, but such a state, when defined, can be used in calculations. Unfortunately, it is not possible to find an unambiguously suitable numerical value for methane properties at these conditions.

Ideal Gas — refers to a hypothetical state in which a fluid behaves in a particularly simple manner. A simple equation of state describes an ideal gas exactly. The ideal gas is a useful concept even if the state cannot be achieved because an unambiguous path exists to reach the state starting with a real fluid.

Gross Heating Value — by definition is the total energy transferred as heat in an ideal combustion reaction at a standard temperature and pressure in which all water formed appears as liquid. The gross heating is an ideal gas property in a hypothetical state (the water cannot all condense to liquid because some of the water would saturate the CO_2 in the products):

$$Hv^{id} = \sum_i y_i Hv_i^{id} \quad \textbf{Eq 23-32}$$

Values for Hv^{id} and MW_i are in Fig. 23-2.

Calculation of the ideal energy flow requires multiplication of the gross heating value by the ideal gas volumetric flow rate of gas for the time period. To employ a real gas flow to calculate the ideal energy flow requires converting the real gas flow rate to the ideal gas flow rate by dividing by the Z-factor. Often the heating value Hv^{id} appears in tables divided by the Z-factor in preparation for multiplying by the real gas flow rate. Thus, Hv^{id}/Z is the ideal gross heating value per unit volume of real gas. Note that the Z-factor must be determined for the natural gas mixture and then divided into the gross heating value of the mixture. It is not correct to divide each pure component gross heating value by the pure component Z-factor and then take the molar average.

Net Heating Value — by definition is the total energy transferred as heat in an ideal combustion reaction at a standard temperature and pressure in which all water formed appears as vapor. The net heating is an ideal gas property in a hypothetical state (the water cannot all remain vapor because, after the water saturates the CO_2 in the products, the rest would condense). It is a common misconception that the net heating value applies to industrial operations such as fired heaters and boilers. While the flue gases from these operations do not condense, the net heating value does not apply directly because the gases are not at 60°F. Were the gases to cool to 60°F, some of the water would condense while the remainder would saturate the gases. It is possible to use either the gross or net heating value in such situations taking care to utilize the hypothetical state properly.

Cost of Gas — comes from a simple accounting equation

$$c = \dot{V}^{id} Hv^{id} p^{id} \Delta t = \dot{V} Hv p \Delta t \quad \textbf{Eq 23-33}$$

This equation shows that for custody transfer it is not necessary to use real gas heating values (real gas heating values could be calculated from the ideal gas values using well known, but computationally intense methods). If the price is set by contract, it is possible to set either a real gas price or an ideal gas price. For the former, it is necessary to use real gas values; for the latter, the ideal gas values are correct. Because it is much simpler to obtain the ideal gas values, it is preferable to establish contracts based upon the ideal gas values. The ideal gas flow rate comes from the real gas flow rate

$$\dot{V}^{id} = \dot{V}/Z \quad \textbf{Eq 23-34}$$

because the Z-Factor is the ratio of the real gas volume to the ideal gas volume.

This paragraph represents the justification for using the GPA property tables for custody transfer. The GPA tables present ideal gas properties that are more accurate to use in mixture calculations and easier to present in tables than real gas properties.

Z-Factor — when dealing with custody transfer of natural gas, it is common to use a simple equation of state for calculations because the base pressure (at which transfer occurs by definition) is near atmospheric. The equation is

$$Z = 1 + BP / RT \quad \textbf{Eq 23-35}$$

It is common to assume that

$$-B/RT = \left[\sum_{i=1}^{N} x_i b_i\right]^2 \quad \textbf{Eq 23-36}$$

and

$$b_i = \sqrt{-B / RT} \quad \textbf{Eq 23-37}$$

This Z-Factor is sufficiently accurate at low pressure for calculations involving natural gas mixtures.

Specific gravity (also termed relative density or gas gravity) – by definition is the ratio of gas density (at the temperature and pressure of the gas) to the density of dry air (at the air temperature and pressure).

$$G = \rho / \rho_a = (PT_aZ_a / P_aTZ)\,(MW / MW_a) \quad \textbf{Eq 23-38}$$

The ideal gas specific gravity is the ratio of the molecular weight of the gas to the molecular weight of dry air.

$$G^{id} = MW/MW_a$$

For a mixture

$$G^{id} = \sum_i y_i G_i^{id} \quad \textbf{Eq 23-39}$$

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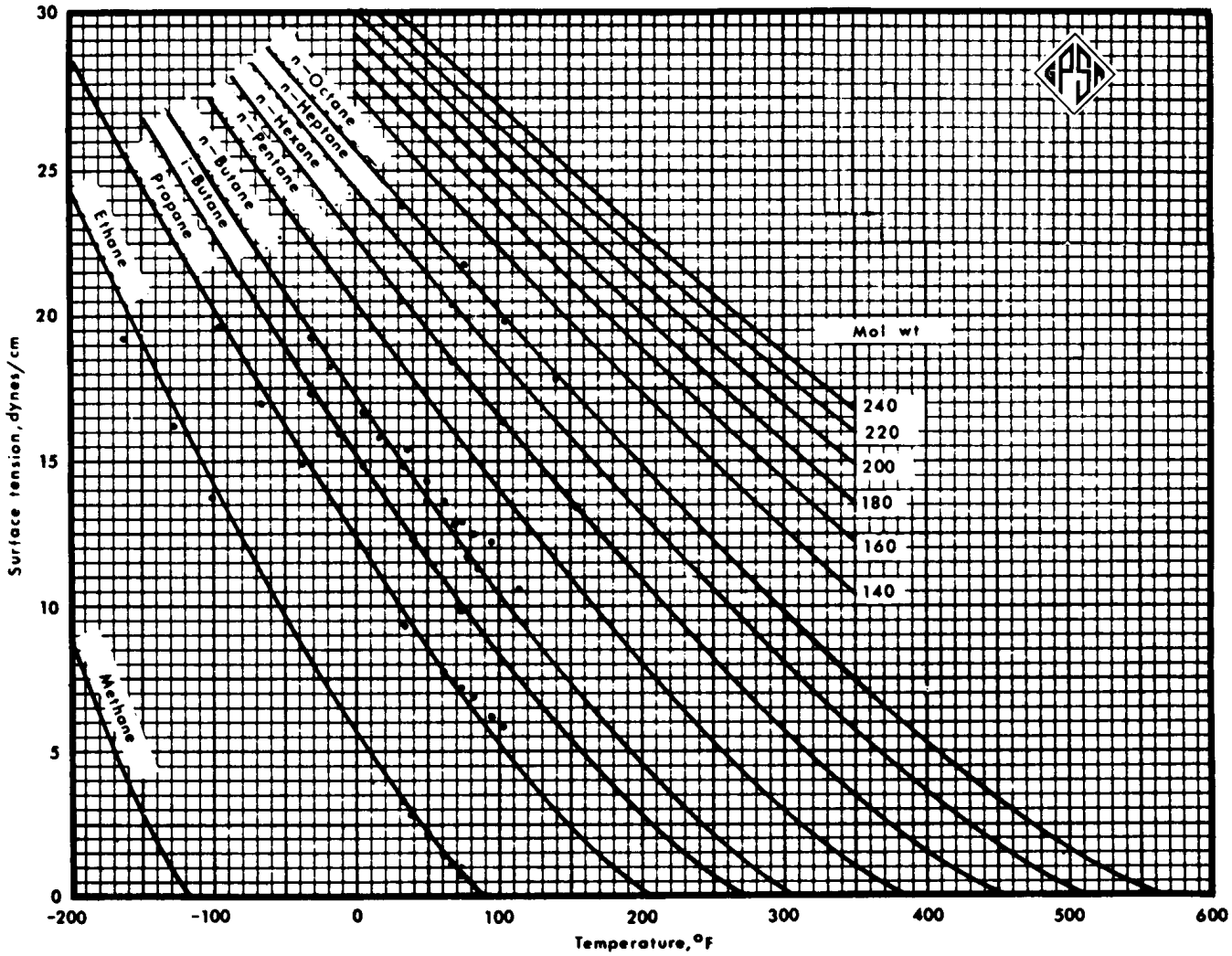
FIG. 23-37

Calculation of Thermal Conductivity

Component	Mole Fraction	Thermal Conductivity Btu/[(hr • sq ft • °F)/ft]	Molecular Weight	$\sqrt[3]{MW_i}$	$(y_i \sqrt[3]{MW_i})$	$(y_i k_i \sqrt[3]{MW_i})$
CO_2	0.10	0.0127	44.010	3.530	0.3530	0.00448
H_2S	0.20	0.0136	34.076	3.242	0.6484	0.00882
N_2	0.05	0.0175	28.013	3.037	0.1519	0.00266
CH_4	0.60	0.0258	16.043	2.522	1.5132	0.03904
C_2H_6	0.05	0.0176	30.070	3.109	0.1555	0.00274
Total	1.00				2.8220	0.05774

FIG. 23-38

Surface Tension of Paraffin Hydrocarbons[85]



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The specific gravity G is measured and is generally used to calculate the molecular weight ratio G^{id} when the gas composition is not available.

$$G^{id} = MW/MW_a = GP_aTZ / PT_aZ_a \qquad \textbf{Eq 23-40}$$

The temperatures and pressures used must correspond to actual measurement conditions or serious errors in G^{id} can occur.

Corrections for Water Content — When the gas contains water, but the component analysis is on a dry basis, the component analysis must be adjusted to reflect the presence of water. The mole fraction of water in the mixture is estimated from the definition of relative humidity:

$$y_w = h^g P_w^\sigma / P = n_w / (1 + n_w) \quad \text{(on a one mole basis)} \qquad \textbf{Eq 23-41}$$

where h^g is the relative humidity of the gas (h^g = 1 for saturated gas). Rearranging Eq 23-41 for the moles of water:

$$n_w = y_w / (1 + y_w) \qquad \textbf{Eq 23-42}$$

Then, the corrected mole fractions of the gas become:

$$y_i(cor) = y_i \left[\frac{1}{1 + n_w}\right] = y_i \left[\frac{1}{1 + y_w/(1\ y_w)}\right] = (1 - y_w)y_i \qquad \textbf{Eq 23-43}$$

and the gross heating value becomes:

$$Hv^{id} = (1 - y_w) \sum_i y_i Hv_i^{id} \qquad \textbf{Eq 23-44}$$

If the compositional analysis determines water as a component, and the summation contains the water term, the heating value becomes:

$$Hv^{id} = \sum_i y_i Hv_i^{id} - y_w\, Hv_w^{id} \qquad \textbf{Eq 23-45}$$

We remove the effect of water because, although water has a heating value (the ideal enthalpy of condensation), we assume that the water carried by wet gas (spectator water) does not condense while we assume that the water formed by the reaction does condense.

Accounting for water using Eqs 23-41 through Eq 23-45 is sufficient for custody transfer purposes because the contracting parties can agree to accept the hypothetical state for the gross heating value. When trying to model actual situations, the question becomes more complex. It is obvious that all the water formed in a reaction cannot condense because in a situation in which both air and gas are dry, some of the reaction water must saturate the product gases while the remainder condenses. It is possible to account for these effects, but those interested should consult GPA Standard 2172, "Calculation of Gross Heating Value, Relative Density and Compressibility Factor for Natural Gas Mixtures from Compositional Analysis," for the analysis. This standard contains additional details and examples covering all these calculation methods. GPA 2172 contains a listing of the Basic source code for a computer program to perform the calculations.

FIG. 23-39

Specific Heat for 0.58 Specific gravity gas (16.7 MW)

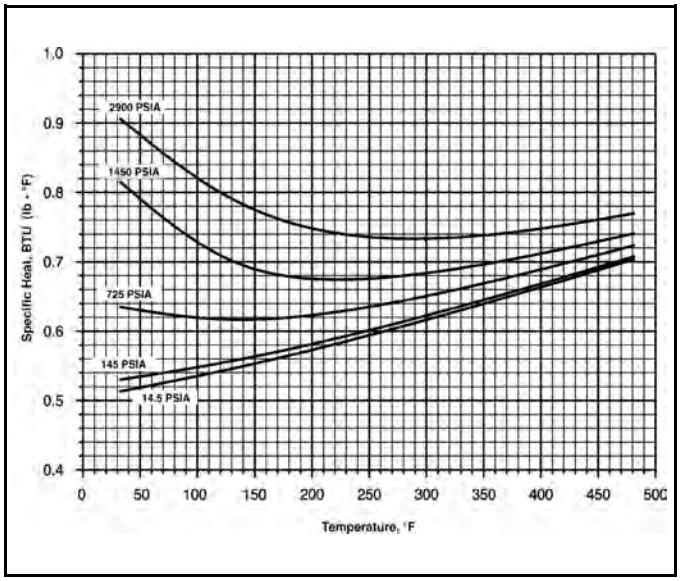
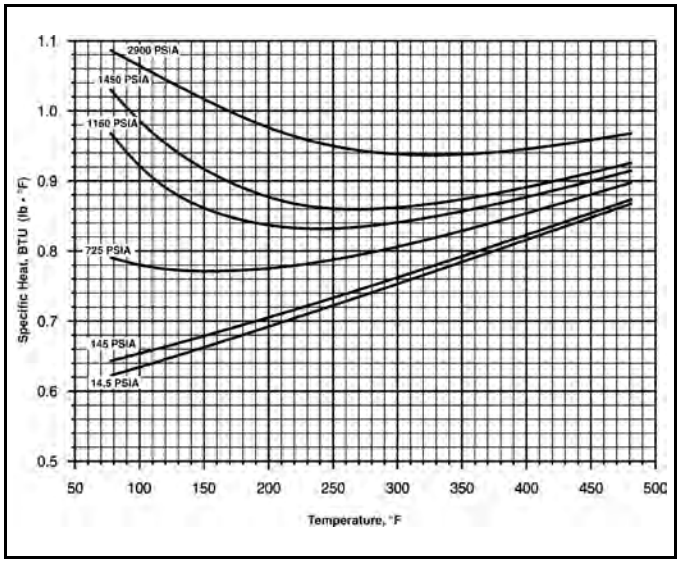


FIG. 23-40

Specific Heat for 0.75 Specific gravity gas (21.6 MW)



SPECIFIC HEAT

Figs. 23-39 and 23-40 present specific heat curves for two different gas mixtures. These curves are not based on experimental data but were developed using calculated values from a process simulator. These charts should give reasonable results for quick calculations of sensible heating/cooling.

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