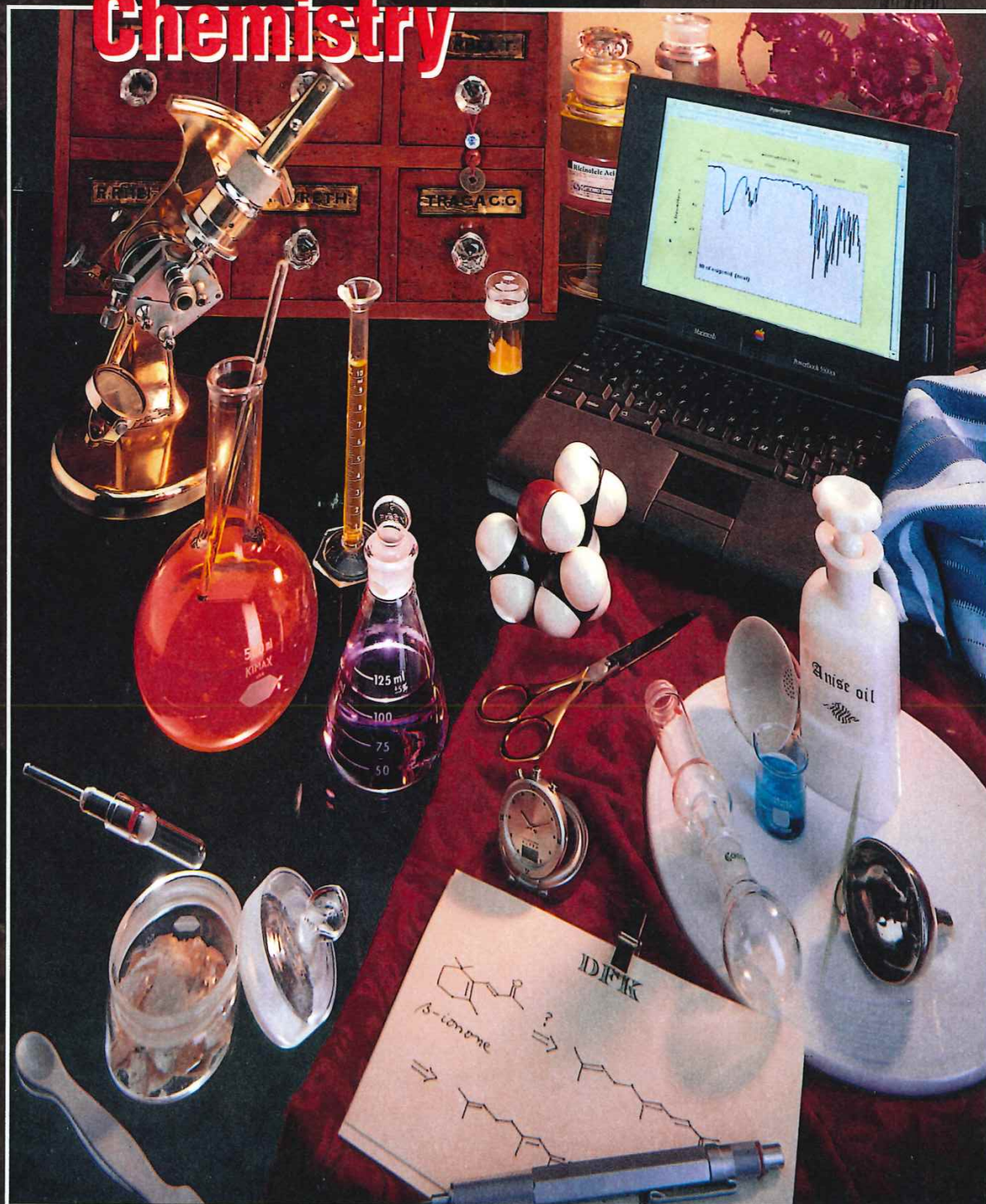


Experimental Organic Chemistry

Daniel R. Palleros



EXPERIMENTAL ORGANIC CHEMISTRY

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UNIT 2

Basic Concepts

In this unit we will discuss important concepts that are extensively used in the rest of the book. Some of them have been already introduced in general chemistry; some are new. In reviewing the old subjects (which include polarity, H-bonds, balancing chemical equations, and calculation of percentage yield) we will focus on their applications to organic chemistry. Among the new material you will find a description of organic solvents, searching for physical data, and the sources of chemical information including online services.

All these subjects are gathered here for easy reference. This unit is like a keepsake box. Take what you need, when you need it, and leave the rest. You will find references to this unit throughout the book.

2.1 POLARITY AND H-BONDS

The interaction between molecules, called **intermolecular interactions**, are responsible for their physical properties such as boiling point, melting point, and solubility. These intermolecular interactions are the result of the **polarity** of molecules and their tendency to form **hydrogen bonds**. In this section we will briefly review these two important concepts.

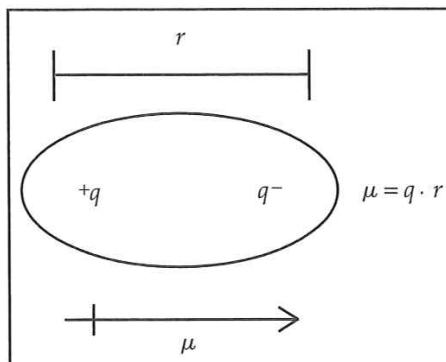
Dipole Moment and Dielectric Constant

Unlike density or melting point, which are easy to quantify, there is no universal agreement on how to measure the polarity of molecules. The **dipole moment** and the **dielectric constant** are two properties often used to describe polarity. We will discuss both of them here. Other polarity indices have also been defined in connection with chromatography, and are relevant where this separation technique is concerned (Units 7–10).

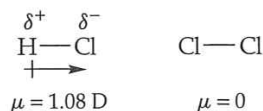
Molecules can be regarded as geometric entities with a core of positive charges surrounded by a negative electron cloud. For most molecules, the center of positive charge does not coincide with the negative charge center, and as a result, the molecule is a permanent dipole. If the charges, q , are separated by a distance r , the **dipole moment**, μ , is defined as the product between q and r . The dipole moment is a vector and, by convention, is represented as an arrow going from the positive to the negative end ($\leftrightarrow$). Two charges, one positive and one negative, equivalent to the electron charge (1.60×10^{-19} C) and separated by 1 Å (10^{-10} m) have a dipole moment of 1.60×10^{-29} C × m. A common unit for dipole moment is the debye (D); $1 \text{ D} = 3.336 \times 10^{-30}$ C × m. Thus, the dipole moment of an electron and a proton

separated by 1 Å is:

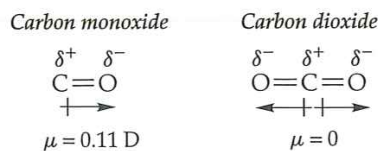
$$\mu = 1.60 \times 10^{-29} \text{ C} \times \text{m} \frac{1 \text{ D}}{3.336 \times 10^{-30} \text{ C} \times \text{m}} = 4.80 \text{ D}$$



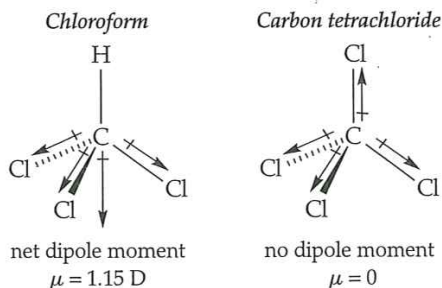
The dipole moment originates in the difference in electronegativity between atoms. For example, the HCl molecule has a permanent dipole moment because chlorine is more electronegative than hydrogen, and therefore it pulls the bond electrons toward itself creating a negative charge density, δ^- , on the chlorine atom, and leaving a positive charge density, δ^+ , on the hydrogen. In contrast, a chlorine molecule does not have a permanent dipole moment because both chlorine atoms have the same electronegativity.



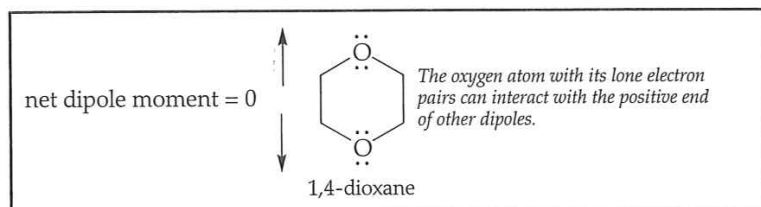
The dipole moment depends also on the molecular geometry. The dipole moment of a molecule is the vector addition of the dipole moments for individual bonds. For example, the dipole moment of carbon monoxide is 0.11 D, but the dipole moment of carbon dioxide is zero because the two opposite vectors cancel each other out.



By a similar argument it can be concluded that trichloromethane (CHCl_3 , most commonly known as chloroform) must have a finite dipole moment, whereas the dipole moment of tetrachloromethane (CCl_4 , carbon tetrachloride) is zero.



Molecules with no dipole moment because of symmetry, such as carbon dioxide and carbon tetrachloride, are not necessarily considered nonpolar. These molecules are made up of individual dipoles that are able to interact with other dipoles, and thus the molecule is considered polar. Let's consider yet another example: 1,4-dioxane. The molecule has no net dipole moment because of symmetry; however, each individual oxygen atom with its lone electron pairs can interact with the positive end of other dipoles, and thus 1,4-dioxane is a polar compound.



To describe the polarity of solvents the **dielectric constant** is often used. The dielectric constant of a substance, generally represented by ϵ , measures the effect of the substance on the transmission of an electric field. If two particles with charges, q_1 and q_2 , are separated by a distance, r , the force between them in a vacuum, F , is given by Coulomb's law:

$$F = k \frac{q_1 \times q_2}{r^2} \quad (1)$$

where k is a proportionality constant. If instead of a vacuum, the two charged particles are immersed in a liquid or solid, the force between them, F' , is diminished because the medium molecules can orient themselves and shield the net charge felt by the particles. The dielectric constant of the medium measures the decrease in this force.

Two charged particles in a vacuum

Two charged particles in a dense medium

The force between charged particles is:

$$F = k \frac{q_1 \times q_2}{r^2}$$

The medium molecules are oriented and shield the charges. The force between charged particles is:

$$F' = k \frac{q_1 \times q_2}{\epsilon \times r^2}$$

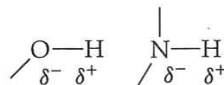
$$\frac{F}{F'} = \epsilon$$

The dielectric constant is the ratio between the two forces.

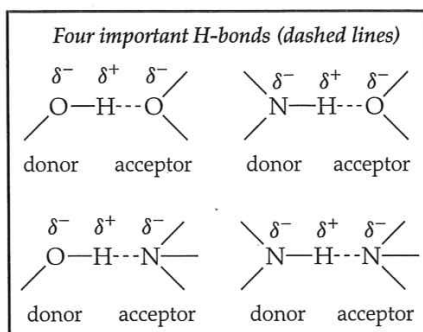
Polar compounds, with a high tendency to get oriented in an electric field, have large dielectric constants, whereas nonpolar compounds with little orientation in an electric field have very low dielectric constants. Water has one of the highest dielectric constant values ($\epsilon = 80.1$), while hydrocarbons (pentane, hexane, etc.) have the lowest value ($\epsilon = 1.89$). Because the dielectric constant is the ratio of two forces, it has no units. The dipole moment and the dielectric constant are related and, in general, compounds with high dipole moments also have high dielectric constants.

Hydrogen Bonding

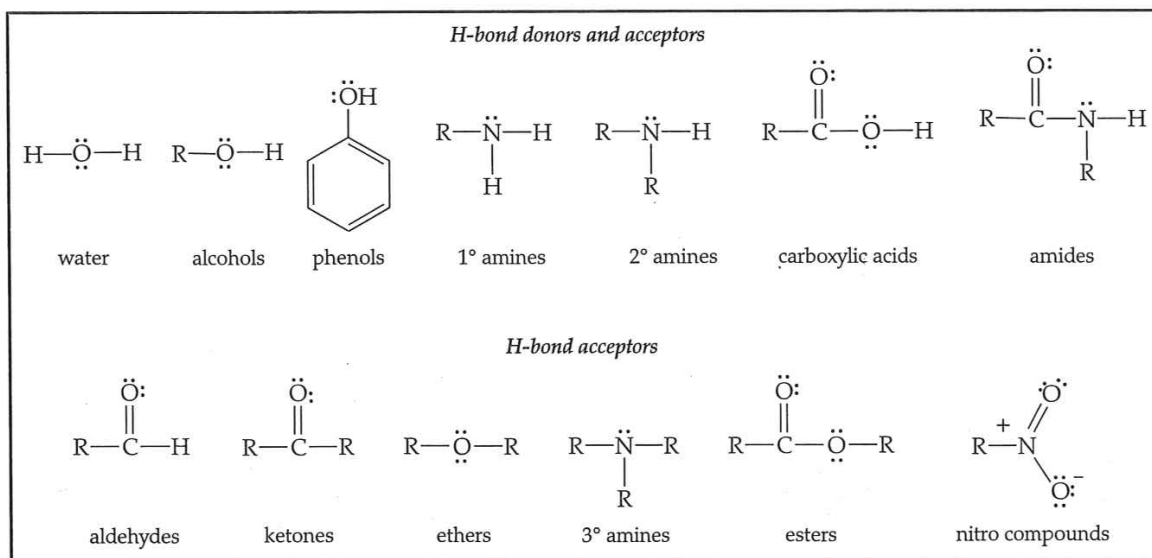
The covalent bond between a hydrogen and an electronegative element such as O or N is polarized with the positive charge density on the hydrogen.



The positive end of the O—H and N—H dipoles can interact with the negative end of other dipoles, especially with oxygen and nitrogen atoms, forming what is called a **hydrogen bond** or simply an **H-bond**.



The molecule that provides the hydrogen is called the **H-bond donor**, and the one that accepts the hydrogen is called the **acceptor**. Good hydrogen bond donors are compounds with O—H and N—H bonds such as water, alcohols, phenols, amines, carboxylic acids, and amides. Good hydrogen bond acceptors are compounds with oxygen or trivalent nitrogen. *All compounds that are good H-bond donors are also good H-bond acceptors* (with the exception of hydronium and ammonium cations, which are only H-bond donors). *However, not all H-bond acceptors are donors.* For example, there are molecules with oxygen or nitrogen but without O—H and N—H bonds, such as aldehydes, ketones, ethers, esters, nitrocompounds, and so on, which can accept H-bonds but cannot donate them. Hydrogens attached to carbon do not participate in H-bonds.

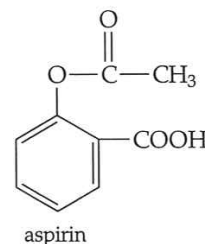


The formation of H-bonds has far-reaching consequences in organic chemistry. Compounds that can donate and accept H-bonds (compounds with O–H or N–H bonds) have higher boiling and melting points than compounds of similar molecular mass but without these bonds. Also, compounds with N–H and O–H bonds are, in general, more soluble in water than compounds lacking such groups.

We will come back to the subject of polarity and H-bonds when discussing specific topics such as boiling point (Unit 6), and chromatography (Units 7–10).

2.2 PHYSICAL DATA

It is very important to collect physical data about the compounds used in the laboratory *before* the beginning of the experiment. Knowing the density and boiling point of liquids, the melting point of solids, and the toxicity and hazards of all the chemicals is crucial to the success of the experiment. We can find all this information, and more, in handbooks available in libraries and laboratories, and also in the Material Safety Data Sheets (MSDS) supplied by the manufacturer. The most common and useful handbooks are the *Merck Index*, published by the Merck Company, the *CRC Handbook of Chemistry and Physics* published by the CRC Press, and the *Aldrich Catalog*, a list of chemicals sold by the Aldrich Company. The Merck Index is also available on CD ROM. In these handbooks, the chemicals are listed in alphabetical order, but they are often found under different names. For example, aspirin is found under the name *Aspirin* in the Merck Index, under the name *Acetylsalicylic acid* in the *Aldrich Catalog*, and under *Benzoic acid, 2-(acetyloxy)* in the *CRC Handbook* (76th edition). These handbooks also offer a list of synonyms that is useful in identifying the compounds. They also have useful molecular formula indexes. The molecular formula index has the names of all the compounds in the handbook with a given formula and gives the page where the compound can be found. For example the molecular formula for aspirin is $C_9H_8O_4$. The *CRC Handbook* (76th edition) has four compounds listed with this molecular formula, one of them under the name *Benzoic acid, 2-(acetyloxy)*, which corresponds to aspirin. When you are not sure under which name a chemical may be listed, first check the molecular formula index to find the name used in the handbook.



The information provided by these handbooks includes the molecular mass (MM), boiling point (bp), melting point (mp), density (d), refractive index (n_D), solubility, toxicity, and flammability. Depending on the scope of the experiment, different pieces of information must be gathered. For example, if we are performing a distillation experiment, we must collect the boiling points of the compounds, and may omit their solubility properties and refractive indexes. If we are doing a recrystallization instead, we would like to have solubility and melting point information.

Molecular Mass (MM), also called the Molecular Weight (MW) or Formula Weight (FW), is always given in grams per mole (g/mol).

Density (d or δ) is useful for liquids but of little use for solids except for plastics. It is given in grams per milliliter (g/mL), which for all practical purposes is equivalent to g/cm^3 . For example, the density listing for methanol in the Merck Index includes:

$$d_4^0 0.8100 \quad \text{and} \quad d_4^{20} 0.7915$$

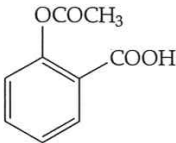
The superscript indicates the temperature at which the density was measured, and the subscript 4 indicates that the density of water at 4°C (1.000 g/mL) was used as a reference.

The **boiling point** (bp) is the temperature at which the vapor pressure of a liquid equals the applied pressure. The boiling point depends strongly on the applied pressure; the **normal boiling point** is determined at one atmosphere (760 Torr or 760 mm Hg). The pressure value at which the boiling point was determined is usually given as a subscript. For methanol, the Merck Index includes:

$$bp_{760} 64.7^\circ\text{C} \quad \text{and} \quad bp_{200} 34.8^\circ\text{C}$$

24 UNIT 2 • BASIC CONCEPTS

Table 2.1 Physical Data of Chemicals

Name	Structure	Molecular mass (g/mol)	Boiling point (°C)	Melting point (°C)	Density (g/mL)	Refractive index	Solubility	Toxicity and hazards
aspirin		180.15	—	138–140	—	—	1 g in 300 mL H ₂ O; 5 mL ethanol	LD ₅₀ 200 mg/kg (oral rat) toxic; irritant
methanol	CH ₃ OH	32.04	64.7	−98	d ₄ ²⁰ 0.7915	n _D ²⁰ 1.3292	∞ H ₂ O ∞ ethanol ∞ ether	highly toxic flammable

If the pressure is not indicated, it is understood that the number refers to the normal boiling point.

The **melting point** (mp) is the temperature at which solid coexists in equilibrium with liquid at normal atmospheric pressure. The melting point value is sometimes followed or preceded by the legend d. or dec., meaning that the solid decomposes during melting. Sometimes there are two melting points listed for the same compound. This may arise from different crystal forms, different recrystallization solvents, or just experimental error. Usually the melting point considered less reliable is given in parentheses. The recrystallization solvent is sometimes mentioned in parentheses next to the melting point.

The **refractive index** (n_D) is a useful property for the identification of liquids (discussed in Unit 11). The subscript D refers to the light source used (the D line of sodium). The temperature is normally indicated by a superscript. For example, the refractive index of methanol at 20°C is:

$$n_D^{20} 1.3292$$

The **solubility** of a chemical (called the **solute**) in a solvent is the maximum possible concentration of the chemical in that solvent at any given temperature. The solubility of organic and inorganic chemicals in water and organic solvents is a very important piece of information when reactions in solution are performed. The Merck Index usually expresses the solubility as the minimum volume of solvent necessary to dissolve 1 gram of compound. Ethanol, methanol, ether (diethyl ether), acetone, and chloroform are the solvents most frequently listed. The symbol ∞ means that the compound is soluble in all proportions in the solvent in question. When two liquids are soluble in all proportions they are said to be **miscible**.

You should always research the **toxicity** and **hazards** of the chemicals before you use them. This information may prevent complications and headaches (real and figurative). The LD₅₀ can be used as a rough guide for the acute toxicity of chemicals and can be found in the Merck Index and the MSDS (Unit 1). A detailed hazards profile of the chemical is found in the MSDS.

The best way to organize the physical data information is in a table format. Table 2.1 gathers the physical data for two of the chemicals that we have considered in this section: aspirin and methanol.

2.3 SOLVENTS

Solvents play a pivotal role in organic chemistry. They provide the environment where reactions occur. They are used to extract chemicals from complex mixtures, and also

to separate and purify all types of compounds. In this section we will discuss some of the most frequently used solvents and stress their important characteristics. In order of decreasing polarity they are:

Water. When possible, it is the solvent of choice. It is cheap, readily available, nonflammable, and nontoxic. An H-bond donor and acceptor. Very polar. Dissolves polar compounds such as inorganic and organic salts (especially salts of sodium and potassium), organic molecules with five carbon atoms or fewer, small sugars, and proteins. Does not dissolve nonpolar compounds. Difficult to evaporate.

Dimethyl sulfoxide. (CH_3SOCH_3 ; DMSO) Very polar. Excellent solvent for nonpolar and polar compounds including salts. An H-bond acceptor. Useful in organic synthesis. Totally miscible with water. Very difficult to evaporate. Irritant. Low flammability.

Methanol. (CH_3OH ; MeOH) Less polar than water and DMSO but more polar than most organic solvents. Because of the $-\text{OH}$ group, it is a good H-bond donor and acceptor. Dissolves organic compounds of medium polarity, especially at high temperatures. It is a good recrystallization solvent (Unit 4). Totally miscible with water. Toxic and flammable. Easy to evaporate.

Ethanol. ($\text{CH}_3\text{CH}_2\text{OH}$; EtOH) Also called simply "alcohol." Less polar than methanol. Because of the $-\text{OH}$ group, it is a good H-bond donor and acceptor. Dissolves organic compounds of medium polarity, especially at high temperatures. It is a good recrystallization solvent (Unit 4). Totally miscible with water. It is available as a 95% solution in water (190 proof) and as absolute ethanol (100%; 200 proof). Less toxic than methanol. It is often rendered unfit for human consumption, and called **denatured alcohol**, by addition of small amounts of methanol, acetone, or toluene. Flammable. Easy to evaporate.

Acetone. (CH_3COCH_3) An excellent solvent for polar and nonpolar compounds alike. It does not dissolve salts. Because of the carbonyl group it is a good H-bond acceptor. Totally miscible with water. Toxic and flammable. Easy to evaporate.

Acetic acid. (CH_3COOH ; AcOH) Polar. Acidic. Dissolves polar and medium polarity compounds. Totally miscible with water. An H-bond donor and acceptor. Difficult to evaporate. Corrosive. Flammable.

Ethyl acetate. ($\text{CH}_3\text{COOCH}_2\text{CH}_3$; AcOEt) Medium polarity. Partially miscible with water. Lighter than water. Because of the carbonyl group it is an H-bond acceptor. Moderately easy to evaporate. Irritant. Flammable.

Methylene chloride. (CH_2Cl_2) Also known as dichloromethane. Medium polarity. Dissolves nonpolar and medium polarity compounds. Immiscible with water. Denser than water. Easy to evaporate. Nonflammable. A possible carcinogen. When possible it should be replaced by other solvents. Toxic. Irritant.

Tetrahydrofuran. (THF) Dissolves nonpolar and medium polarity compounds. Miscible with water. Very useful in organic synthesis. Limited shelf life because it forms explosive peroxides on exposure to air. Irritant. Flammable.

Chloroform. (CHCl_3) Dissolves nonpolar and medium polarity compounds. Immiscible with water. Denser than water. A possible carcinogen with very low P.E.L. Used for specific applications (for example, the deuterated form (CDCl_3) is used as an NMR solvent) but largely replaced by other solvents with higher P.E.L.

Diethyl ether. ($\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$; Et_2O) Also called simply "ether." Excellent solvent for nonpolar and low polarity compounds. Less polar than THF. Immiscible with water. Limited shelf life because it forms explosive peroxides on exposure to air. Lighter than water. Very easy to evaporate. Toxic. Flammable.

tert-Butyl methyl ether. ($(\text{CH}_3)_3\text{C}-\text{OCH}_3$; BME) Same uses as diethyl ether but with less tendency to form explosive peroxides. Immiscible with water. Lighter than water. Flammable. Very easy to evaporate. Excellent solvent for liquid-liquid extractions. Irritant.

Toluene. ($\text{C}_6\text{H}_5\text{CH}_3$) Low polarity. A good solvent for nonpolar compounds. Does not form H-bonds. Immiscible with water. Lighter than water. Moderately easy to evaporate. Toxic. Flammable.

Carbon tetrachloride. (CCl_4) Dissolves nonpolar compounds. Immiscible with water. Denser than water. A possible carcinogen with very low P.E.L. It has been largely replaced by other solvents with higher P.E.L.

Benzene. (C_6H_6) Low polarity. Dissolves nonpolar compounds. Does not form H-bonds. Immiscible with water. Lighter than water. A known carcinogen. It should be avoided in the laboratory. It has been largely replaced by toluene and other solvents with higher P.E.L. Flammable.

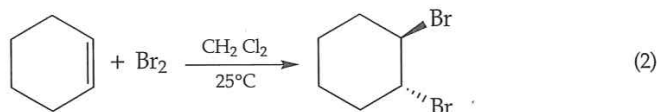
Hexane(s). A mixture of isomeric hexanes. Among the least polar organic solvents. Does not form H-bonds. Dissolves only nonpolar compounds. Immiscible with water. Lighter than water. Easy to evaporate. Flammable. Irritant.

Petroleum ether. It is not an ether in the chemical sense of the word. It is a mixture of low-boiling point hydrocarbons. Available in different boiling point ranges ($40\text{--}60^\circ\text{C}$; $60\text{--}80^\circ\text{C}$; and so on; fractions with boiling points higher than 60°C are often called **ligroin**). Among the least polar organic solvents. Does not form H-bonds. Dissolves only nonpolar compounds. Immiscible in water. Lighter than water. Very easy to evaporate. Toxic. Flammable.

Table 2.2 summarizes the most important properties of some common solvents.

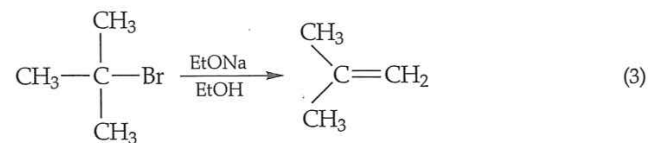
2.4 BALANCING CHEMICAL EQUATIONS

The communication of chemical information is essentially visual; chemical ideas are conveyed in the form of detailed equations showing the structures of reactants and products. Without a pictorial description of chemical transformations there would be no organic chemistry. Often, the chemical equation includes not only the reactants and products, but also the reaction conditions such as solvent, temperature, and catalyst. The latter are generally written on the arrow, for example:



Here, CH_2Cl_2 is the solvent and the reaction is performed at 25°C .

It is also common to write on the arrow the reagents that do not contribute with carbon atoms to the final product. This includes inorganic compounds such as Br_2 , HBr , HCl , H_2 , and so on, and organic reagents acting as acids or bases. For example, the elimination reaction of *tert*-butyl bromide with sodium ethoxide (EtONa) in ethanol as a solvent (EtOH) can be represented as:



In this representation, the other reaction products, which in this case are ethanol and NaBr , are omitted. A balanced equation showing all the products is given below:

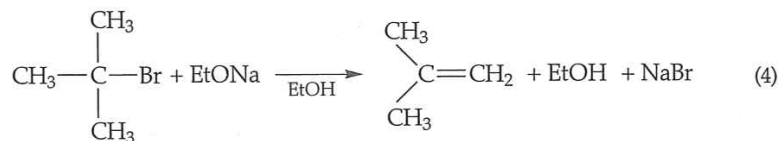


Table 2.2 Useful Solvents

Solvent	M.M.	b.p.	dens.	f.p.	flam.	ϵ	P.I.	μ	n	S.W.	W.S.	Az.bp	%W	P.E.L.	Structure
acetic acid	60.05	118.0	1.049	16.7	x	6.15	6.2	1.70	1.3718	M	M	N	N	10	CH ₃ COOH
acetone	58.08	56.3	0.790	-94.7	xx	20.7 ^a	5.1	2.69 ^b	1.3587	M	M	N	N	750	CH ₃ COCH ₃
acetonitrile	41.05	81.6	0.782	-43.8	xx	37.5	5.8	3.44 ^b	1.3441	M	M	76.0	14.2	40	CH ₃ CN
benzene	78.11	80.1	0.879	5.5	xxx	2.28	2.7	0 ^b	1.5011	0.18 ^a	0.063 ^a	69.3	8.8	1	C ₆ H ₆
<i>n</i> -butanol	74.12	117.7	0.810	-88.6	x	15.8	3.9	1.75	1.3993	7.81	20.07	92.7	42.5	50	CH ₃ (CH ₂) ₂ CH ₂ OH
butanone	72.10	80.1	0.805	-86.7	xx	18.51	4.7	2.76	1.3788	24.0	10.0	73.4	11.3	200	CH ₃ COCH ₂ CH ₃
<i>t</i> -butyl methyl ether	88.15	55.2	0.741	-108.6	xxx	—	2.5	1.32	1.3689	4.8	1.5	52.6	4.0	40 ^d	CH ₃ OC(CH ₃) ₃
carbon tetrachloride	153.84	76.8	1.594	-23.0	0	2.24	1.6	0 ^b	1.4601	0.08	0.008	66.0	4.1	2 ^e	CCl ₄
chloroform	119.39	61.2	1.489	-63.6	0	4.81	4.1	1.15	1.4458	0.82	0.056	56.1	2.8	2 ^f	CHCl ₃
cyclohexane	84.16	80.7	0.779	6.5	xxx	2.02	0.2	0	1.4262	0.01	0.01	69.0	9.0	300	C ₆ H ₁₂
diethyl ether	74.12	34.6	0.713	-117.4	xxx	4.34	2.8	1.15	1.3524	6.89	1.26	34.1	1.26	400	(CH ₃ CH ₂) ₂ O
dimethylformamide (DMF)	73.09	153.0	0.949	-60.4	x/0	36.7	6.4	3.86	1.4305	M	M	—	—	10	HCON(CH ₃) ₂
dimethylsulfoxide (DMSO)	78.13	189.0	1.100	18.5	x/0	46.7	7.2	3.9	1.4783	M	M	—	—	N.L.	CH ₃ SOCH ₃
1,4-dioxane	88.10	101.3	1.034	11.8	x	2.25	4.8	0.45	1.4224	M	M	87.8	18.0	25	C ₄ H ₈ O ₂
ethanol	46.07	78.5	0.789	-114.1	x	26.0	5.2	1.70	1.3610	M	M	78.2	4.0	1000	CH ₃ CH ₂ OH
ethyl acetate	88.10	77.1	0.901	-84.0	xx	6.02 ^a	4.4	1.88	1.3724	8.7	3.3	70.4	8.5	400	CH ₃ CH ₂ OCOCH ₃
<i>n</i> -hexane	86.17	68.7	0.659	-95.3	xxx	1.89	0.1	0.08	1.3749	0.001 ^a	0.01	61.5	—	50	CH ₃ (CH ₂) ₄ CH ₃
isopropanol	60.09	82.3	0.785	-88.0	x	19.92 ^a	3.9	1.66 ^c	1.3772	M	M	80.3	12.6	400	CH ₃ CH(OH)CH ₃
methanol	32.04	64.7	0.791	-98.0	x	32.7 ^a	5.1	1.70	1.3290	M	M	N	N	200	CH ₃ OH
methylene chloride	84.94	39.8	1.326	-95.1	0	8.93 ^a	3.1	1.14	1.4241	1.6	0.24	38.1	1.5	50	CH ₂ Cl ₂
petroleum ether	U	30–60	0.64–0.67	-49	xxx	—	0.1	—	1.36–1.38	—	—	—	—	N.L.	5–6-Carbon Hydroc.
tetrahydrofuran (THF)	72.10	66.0	0.888	-108.5	xx	7.6	4.0	1.75	1.4072	M	M	—	—	200	C ₄ H ₈ O
toluene	92.13	110.6	0.867	-95.0	xx	2.38 ^a	2.4	0.31 ^b	1.4969	0.074	0.03 ^a	84.1	13.5	50	Ph-CH ₃
water	18.02	100.0	0.998	0.0	0	80.1	10.2	1.87	1.3330	—	—	—	—	N.L.	H ₂ O

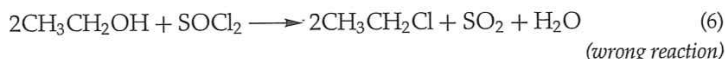
M.M.: molecular mass (g/mol); b.p.: boiling point (°C); dens.: density (g/mL) at 20°C referenced to water at 4°C; f.p.: freezing point (°C); flam.: flammability, 0: nonflammable; x/0: nonflammable but combustible; x: flammable; xx: very flammable; xxx: highly flammable; ϵ : dielectric constant at 20°C; P.I.: polarity index (L.R. Snyder, *J. Chromat. Sci.*, **16**, 223 (1978)); μ : dipole moment (D) at 25°C; n : index of refraction at 20°C; S.W.: solubility in water (%w/w) at 20°C; M: miscible in all proportions; Az. bp: boiling point of azeotrope with water (°C); N: nonazeotropic mixture; %W: % water in azeotrope; P.E.L.: permissible exposure limit: the maximum permitted average concentration of airborne solvent in ppm (volume) for workers exposed 8 hours daily, according to the California Code of Regulations, Title 8, Section 5155, 1998; these are also the threshold-limit values, time-weighted average (TLV-TWA), recommended by the American Conference of Governmental Industrial Hygienists (ACGIH), except where noted; N.L.: not listed; ^a at 25°C; ^b at 20°C; ^c at 30°C; ^d not listed, the given value is the TLV-TWA suggested by ACGIH; ^e TLV-TWA (ACGIH): 5 ppm; ^f TLV-TWA (ACGIH): 10 ppm; U: undetermined.

In general, we adopt a minimalist approach to the representation of chemical reactions, and we usually prefer Equation 3 to Equation 4. However, there are instances when we need as detailed a picture of the reaction as possible. This is particularly true in the laboratory where we need to mix the reactants in the right molar amounts in order to carry out the reaction successfully. To figure out the amounts of material needed we must have a full description of the reaction including all reactants and products with their stoichiometric coefficients. In other words, we need a **balanced equation**.

The first step in balancing a chemical equation is to find out all the chemicals used or produced in the reaction. If one of them is missing, our final balanced equation would be incorrect. Let us consider, for example, the synthesis of ethyl chloride by the reaction of ethanol with thionyl chloride (SOCl_2). SO_2 and HCl are also reaction products. A balanced equation is shown below:

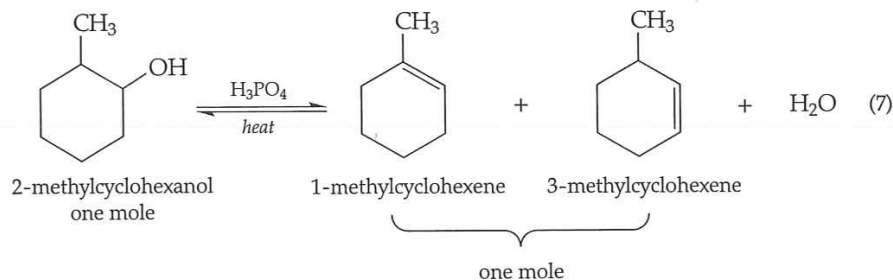


If we did not know, for example, that HCl was a byproduct, we would have balanced the equation as:



Equation 6 implies that two molecules of ethanol react with one molecule of thionyl chloride, which is not the case experimentally. The correct stoichiometry for the reaction is given by Equation 5.

A question frequently asked by students is how to balance a chemical reaction that affords two or more products with the same molecular formula but different structures (these compounds are called isomers). For example, the dehydration of 2-methylcyclohexanol with phosphoric acid as a catalyst gives a mixture of 1-methyl and 3-methylcyclohexene. A balanced equation for the transformation is given below:



Notice that there are two rings on the right side of the equation (representing the two products), and only one on the left side (the starting material). However, the equation is correctly balanced because it is understood that only *one mole of the mixture* of methylcyclohexenes forms per *each mole* of 2-methylcyclohexanol that reacted.

2.5 CONCENTRATION UNITS

There are many ways to express the concentration of solutions. Molarity, mass per volume, and percentage are commonly used in organic chemistry.

The concentration expressed in molarity units gives the *number of moles of solute per liter of solution*. To calculate the molarity of a solution the number of moles of

solute is divided by the volume of the solution (in liters) in which it is contained.

$$\text{molarity} = \frac{\text{number of moles solute}}{\text{volume of solution(L)}} \quad (8)$$

Another useful way to express concentration is as the mass of solute (in grams or milligrams) per volume of solution (usually 1 mL, 100 mL, or 1 L). For example, if 50 g of sodium chloride is dissolved in water and the final volume of the solution is 1000 mL, the concentration in different mass/volume units is:

$$[\text{NaCl}] = \frac{50 \text{ g}}{1000 \text{ mL}} = 50 \frac{\text{g}}{\text{L}} = 0.050 \frac{\text{g}}{\text{mL}} = 50 \frac{\text{mg}}{\text{mL}} \quad (9)$$

Another way of calculating concentrations is as the percentage of solute in solution. This can be expressed as a weight or volume percentage.

The *weight percentage expresses the mass of solute as a percentage of the mass of the solution*. It is represented by the symbol w/w, which means **weight in weight**. For example, if 100 grams of sodium chloride is dissolved in water to make 1000 g of solution, the concentration of sodium chloride is:

$$[\text{NaCl}] = \frac{100 \text{ g}}{1000 \text{ g}} \times 100 = 10\%(\text{w/w}) \quad (10)$$

The *volume percentage expresses the volume of solute as a percentage of the volume of the solution*. For instance, if 25 mL of methanol (MeOH) is mixed with water and the final solution volume is 100 mL, the concentration of methanol is:

$$[\text{MeOH}] = \frac{25 \text{ mL}}{100 \text{ mL}} \times 100 = 25\%(\text{v/v}) \quad (11)$$

The **v/v** symbol means **volume in volume**. This concentration notation is particularly useful for liquid solutes.

Sometimes the concentration is expressed as the *mass of solute per 100 mL of solution*. This is called **weight in volume (w/v)** percentage. For example, if 12 g of sodium chloride is dissolved in water to make 200 mL of solution, the concentration as weight in volume (w/v) percentage is:

$$[\text{NaCl}] = \frac{12 \text{ g}}{200 \text{ mL}} \times 100 = 6\%(\text{w/v}) \quad (12)$$

It should be noted that in all the cases discussed here including w/w, v/v, and w/v, the solute percentage is always *with respect to the whole solution and not just the solvent*.

Finally, there is another concentration notation that is particularly useful for mixtures of liquids. It describes a solution of liquids by the volume of each individual component in the mixture. For example, a mixture of 30 mL of water, 20 mL of methanol, and 10 mL of acetone is described as water: methanol: acetone (30 : 20 : 10 or 3 : 2 : 1).

2.6 MOLES AND MILLIMOLES

When performing a synthesis the reagents must be mixed in the correct molar proportions. Failure to do so may result in side reactions, unwanted products, and loss of time and money. To calculate the number of moles of a given compound, the mass (grams) is divided by the molecular mass (g/mol).

$$\boxed{\text{\#moles} = \frac{\text{mass(g)}}{\text{MM(g/mol)}}} \quad (13)$$

30 UNIT 2 • BASIC CONCEPTS

For example, 0.25 g of aspirin (MM 180.15, Table 2.1) is equivalent to 0.00139 mol, Equation 14:

$$\text{\#moles} = \frac{\text{mass(g)}}{\text{MM(g/mol)}} = \frac{0.25 \text{ g}}{180.15 \text{ g/mol}} = 0.00139 \text{ mol} \quad (14)$$

In organic chemistry we frequently handle amounts much smaller than a mole. This is especially true in microscale experiments, where only milligram amounts of material are used. In such cases, instead of moles a smaller unit, the **millimole**, is preferred. One millimole, represented by **mmol**, is one thousandth of the mole, or in other words there are 1000 mmol in one mol:

$$1 \text{ mmol} = 10^{-3} \text{ mol}; \quad 1000 \text{ mmol} = 1 \text{ mol} \quad (15)$$

To convert moles into mmoles the number is multiplied by 1000. Thus, for the previous calculation, 0.00139 moles of aspirin is equivalent to 1.39 mmol:

$$0.00139 \text{ mol} \times 1000 \frac{\text{mmol}}{\text{mol}} = 1.39 \text{ mmol} \quad (16)$$

To calculate the number of moles in a *volume of pure liquid*, the volume is first converted into mass using the density, *d*, Equation 17.

$$\text{mass(g)} = d(\text{g/mL}) \times \text{Volume(mL)} \quad (17)$$

The number of moles is then calculated using Equation 13. For example, 2.5 mL of methanol (*d* 0.7915 g/mL; MM 32.04 g/mol, Table 2.1) corresponds to 1.98 g or 0.0618 mol:

$$\text{mass(g)} = d(\text{g/mL}) \times \text{Volume(mL)} = 0.7915 \frac{\text{g}}{\text{mL}} \times 2.5 \text{ mL} = 1.98 \text{ g} \quad (18)$$

$$\text{\#moles} = \frac{\text{mass(g)}}{\text{MM(g/mol)}} = \frac{1.98 \text{ g}}{32.04 \text{ g/mol}} = 0.0618 \text{ mol} = 61.8 \text{ mmol} \quad (19)$$

In using these equations you should be aware of the units and make sure that they cancel out properly.

To calculate the number of moles of a chemical in solution, the concentration and volume are needed. If the concentration is given in g/mL, the mass of solute is obtained by multiplying the concentration by the volume of the solution:

$$\text{mass(g)} = \text{concentration (g/mL)} \times \text{Volume (mL)} \quad (20)$$

For example, 1.3 mL of a solution of sodium chloride in water with a concentration of 0.5 g/mL has 0.65 g of NaCl:

$$\text{mass} = 0.5 \frac{\text{g}}{\text{mL}} \times 1.3 \text{ mL} = 0.65 \text{ g} \quad (21)$$

The mass of sodium chloride can then be converted into moles with the help of Equation 13 and the molecular mass for sodium chloride.

If the concentration of the solution is given in molarity, the calculation of the number of moles is even simpler. Multiplication of the solution volume (in L) by the molarity gives the number of moles, Equation 22:

$$\text{\#moles} = \text{concentration (mol/L)} \times \text{Volume(L)} \quad (22)$$

If the concentration is given as weight percentage, as is often the case with concentrated inorganic acids, also called **mineral acids**, the calculation of number of moles involves the density of the acid solution, and is explained in the next section.

2.7 MINERAL ACIDS

In the organic chemistry laboratory we often use concentrated (c) mineral acids such as hydrochloric acid, HCl (c), hydrobromic acid, HBr (c), nitric acid, HNO₃ (c), sulfuric acid, H₂SO₄ (c), and phosphoric acid, H₃PO₄ (c). All these concentrated acids are solutions of the acid in water. The concentration of commercial concentrated mineral acids is usually shown on the bottle's label as % **weight in weight** (w/w). As you may recall from section 2.5, % weight in weight means the mass of solute, pure acid in this case, per 100 g of solution. For example, the concentration of HCl (c) is typically 37% w/w, which means that there are 37 g of HCl per 100 g of solution.

To calculate the number of moles of acid in a given volume of the concentrated solution, you need its concentration (in % w/w), the density of the concentrated solution (also shown on the bottle's label), and the molecular mass of the acid. Let's calculate as an example the number of moles of HCl in one liter of its concentrated solution. All the information needed is gathered in Table 2.3, which also contains the typical concentration and density values for other mineral acids.

Table 2.3 Typical Concentrated Mineral Acids

Acid	Concentration (%w/w)	Density (g/mL)	Molecular Mass (g/mol)	Concentration (mol /L)
HBr	48	1.490	80.92	8.84
HCl	37	1.200	36.46	12.2
HNO ₃	70	1.420	63.01	15.8
H ₂ SO ₄	98	1.840	98.08	18.4
H ₃ PO ₄	85	1.685	98.00	14.6

The first step in the calculation is to figure out the mass of the solution. To do this the solution density is used. For concentrated HCl, the density is 1.200 g/mL, thus the mass in one liter is:

$$\text{mass solution (g)} = d \text{ (g/mL)} \times \text{Volume (mL)} = 1.200 \frac{\text{g}}{\text{mL}} \times 1000 \text{ mL} = 1,200 \text{ g (23)}$$

The next step is to calculate how much of this total mass is pure HCl. Since the concentrated solution has 37 g of pure HCl per 100 g of solution, multiplying the mass of the solution by the concentration of HCl (37 g HCl/100 g solution) the mass of HCl is obtained:

$$\begin{aligned} \text{mass HCl (g)} &= \text{mass solution} \times \% \text{HCl (w/w)} \\ &= 1,200 \text{ g sol.} \times 37 \text{ g HCl/100 g sol.} = 444 \text{ g HCl} \end{aligned}$$

Finally, to calculate the number of moles, the mass of HCl is divided by its molecular mass:

$$\# \text{moles} = \frac{\text{mass(g)}}{\text{MM(g/mol)}} = \frac{444 \text{ g}}{36.46 \text{ g/mol}} = 12.2 \text{ mol} \quad (24)$$

This number corresponds to the molarity of the acid given in the last column of Table 2.3.

2.8 CALCULATION OF YIELDS

To advance in the laboratory we must assess the progress of our experimental work at every step. Whether we are isolating a chemical from a natural source or synthesizing it from scratch, the calculation of the percentage yield is a simple way of measuring our achievements.

Yield of an Isolation

In the isolation of a product from a complex mixture, the **percentage yield** is calculated as the ratio of the mass of the product over the mass of the whole mixture multiplied by 100. For example, if we extract the fat from milk cream and obtain 2.1 g of fat from 10 g of cream, the percentage yield is:

$$\% \text{yield} = \frac{\text{mass of product}}{\text{mass of mixture}} \times 100 \quad (25)$$

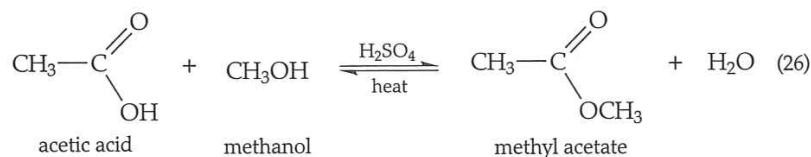
$$\% \text{yield} = \frac{2.1 \text{ g}}{10 \text{ g}} \times 100 = 21\%$$

Yield of an Organic Synthesis

The percentage yield for an organic synthesis has a different meaning. To calculate the percentage yield of a chemical reaction you must first calculate the number of moles of reactants and products, and use the balanced equation to determine what is *the maximum amount of product that the reaction can yield*. This amount is called the **theoretical yield**.

When chemicals are mixed to carry out a reaction, the mixture is usually nonstoichiometric. This means that there is often a molar deficit of one of the reactants and an excess of others. At the end of the reaction, the chemicals in excess will still be present, while the one present in a molar deficit would be completely consumed. This compound is called the **limiting reagent** because it is used up in the reaction. The limiting reagent determines the theoretical yield. Let's further clarify these concepts with the calculation of percentage yield for a chemical reaction.

In the transformation shown below, acetic acid reacts with methanol in the presence of sulfuric acid, a catalyst, to give methyl acetate (an ester) and water. This type of reaction, called esterification, is very useful for making esters in the laboratory. We will postpone discussing its chemistry until Unit 22; for now we will consider it as a prototype for any reaction of the form: $A + B \longrightarrow C + D$:



Let's assume that in the laboratory we mix 1.0 mL of acetic acid with 5 mL methanol in the presence of a catalytic amount of sulfuric acid (100 μL). After heating for about one hour we obtain 770 mg of methyl acetate. What is the percentage yield in the synthesis of the ester?

To answer this question we must first calculate number of millimoles of reagents and products. The volumes of reactants used and mass of product obtained are summarized in Table 2.4. This table also gathers the density and molecular mass of reactants and products that are needed to calculate the number of mmols. The figures above the double line are the data, and the question marks indicate those quantities that must be calculated.

Table 2.4 Table of Reagents for the Synthesis of Methyl Acetate

	Acetic acid	Methanol	Sulfuric acid	Methyl acetate
volume	1.0 mL	5.0 mL	100 μ L	—
density (g/mL)	1.049	0.7915	1.84 for 98% w/w	0.9342
MM (g/mol)	60.05	32.04	98.08	74.08
mass (g)	?	?	?	0.770
mmol	?	?	?	?

The mass for each chemical is calculated using Equation 17, and then the number of mmoles is calculated with Equation 13. The volume of sulfuric acid is given in **microliters** (μ L), which is a useful unit for small volumes. The conversion between microliters and milliliters is as follows: $1 \mu\text{L} = 10^{-6} \text{ L} = 10^{-3} \text{ mL}$. Thus, $100 \mu\text{L} = 0.100 \text{ mL}$. (To give you an idea of the size of a microliter, remember that a drop of water contains about $30 \mu\text{L}$).

The last two rows of Table 2.4, with the calculated figures, are shown below:

	Acetic acid	Methanol	Sulfuric acid	Methyl acetate
mass (g)	1.05	3.96	0.180	0.770
mmol	17.5	123.6	1.83	10.4

Our calculations indicate that 17.5 mmol of acetic acid, 123.6 mmol of methanol, and 1.83 mmol of sulfuric acid were mixed. According to the balanced equation, Equation 26, the reaction between acetic acid and methanol is 1 to 1, or in other words, one mole of methanol is required per each mole of acetic acid. Since the number of mmol for methanol is larger than the number of mmol for acetic acid, an excess of methanol remains unreacted at the end of the reaction, while all the acetic acid reacts. Therefore, **acetic acid is the limiting reagent**.

If acetic acid is totally consumed and transformed into methyl acetate, the maximum number of mmol of methyl acetate that can be obtained must be equal to the number of mmol of acetic acid, because according to the reaction stoichiometry, one mole of ester is formed per each mole of acetic acid reacted. Thus, the theoretical yield for this reaction is 17.5 mmol of methyl acetate. *The **theoretical yield** is the maximum amount of product that a reaction can afford, assuming that it goes to completion and ignoring experimental losses.*

$$\text{theoretical yield} = 17.5 \text{ mmoles}$$

The esterification reaction is an equilibrium reaction. This means that at the end of the reaction there is always some reactant left. However, for the calculation of the theoretical yield it is normally assumed that the reaction is irreversible and goes to completion.

The **actual yield** of the reaction is the amount obtained experimentally, in this case, 10.4 mmol. The **percentage yield** is the ratio between the actual and theoretical yields, times 100:

$$\% \text{yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100 \quad (27)$$

In our example the percentage yield is:

$$\% \text{yield} = \frac{10.4 \text{ mmol}}{17.5 \text{ mmol}} \times 100 = 59.4\%$$

The student may wonder why in this reaction sulfuric acid isn't the limiting reagent if it contributes the lowest number of mmol of all three "reagents" (1.83 mmol). The answer is simple. Sulfuric acid is the *catalyst* of the reaction and not a true reagent. It is *consumed* and *regenerated* during the reaction where it is needed just to speed up the reaction rate.

2.9 SCALING UP, SCALING DOWN

Often in the organic chemistry lab you will need to scale up or down experimental procedures regarding the synthesis or isolation of chemicals. If you want to scale up a synthesis by a factor of 2, masses and volumes should be multiplied by this factor, but concentrations, temperatures, and times should remain the same. Glassware should be changed accordingly. As an example, the following procedure is shown at two different scales.

In a 25-mL Erlenmeyer flask mix 1.0 g of A with 3.0 mL of a 5% solution of B in water. Let the system react for 15 minutes at 35°C. Collect the precipitate by vacuum filtration and recrystallize it from about 10 mL of ethanol using a 25-mL Erlenmeyer flask.

Here is the same procedure scaled up by a factor of 2.5:

In a 25-mL Erlenmeyer flask mix 2.5 g of A with 7.5 mL of a 5% solution of B in water. Let the system react for 15 minutes at 35°C. Collect the precipitate by vacuum filtration and recrystallize it from about 25 mL of ethanol using a 50-mL Erlenmeyer flask.

2.10 KEEPING LAB BOOKS AND WRITING LAB REPORTS

Documentation of scientific information is the keystone in the building of science. You should keep a record of your experiments in a concise, precise, and thorough manner. To this end you should always use a laboratory notebook and never loose sheets of paper that can be easily misplaced. The lab book should be bound and have numbered pages. Spiral notebooks do not make good lab books because the pages can be easily removed.

You should prepare before each experiment by reviewing the theory and finding information about the chemicals involved. You should document this work in your lab book. If your lab book is well organized before you start the experiment, you will save time and effort. Having an organized lab book will also help you write a good lab report. To assist you in this task, pre-lab and in-lab questions are included at the end of each experiment.

Laboratory work is training in meaningful observation. When you are performing an experiment you should always write all the data and pertinent information in your lab book. This includes casual observations such as color changes, formation of a precipitate, evolution of a gas, or the malfunctioning of an instrument. To help you collect and analyze the data, in-lab questions are provided at the end of the experiments. Refer to them as you are performing the experiment.

It is very important that you do a preliminary analysis of your results as they are generated. Do not wait until you get home or until the next day to interpret your data. It may be too late. By then, some results may be meaningless and the experiment, or part of it, must be repeated. This is easy to do on the spot, but it takes more time and effort after completion of the experiment when chemicals and instrumentation have been put away.

At the end of the experiment you will normally be asked to write a lab report. Consult with your instructor regarding the format and the extent of the lab report. The following guidelines will help you in this endeavor.

The lab report should include the following parts:

1. Experiment # and title.
2. Your name, your instructor's name, the lab section.
3. The date.
4. An **INTRODUCTION** including:
 - Purpose of the experiment. Mention the techniques introduced by the experiment. If there is a hypothesis to prove, it should be included here. For example, "Does the dehydration of alcohols follow Zaitsev's rule?"
 - Theoretical background. A brief discussion of the theory behind the experiment. Answering the pre-lab questions will help you build up this part. If the experiment involves a chemical reaction, balanced chemical equations should be shown in this part. If requested, a reaction mechanism should be included.
5. An **EXPERIMENTAL PART** including:
 - A table with the physical properties of reagents, solvents, and products. The table should contain: molecular mass, structure, melting point, boiling point, density, solubility, flammability (for solvents), toxicity and hazards, as required. For synthesis experiments, the table should also include mass, volume, and mmoles used in the reaction.
 - A flowchart outlining the experimental procedure.
 - Observations such as color change, precipitation, solubilization of a solid, gas evolution, and so on.
 - Equipment used. For example, if you are performing a gas chromatography experiment, mention the instrument model, the type of column used, and the experimental conditions. Some of the in-lab questions will help you write this part.
 - Data. This includes melting points, boiling points, retention times, gas chromatography traces, IR spectra, and so on. To avoid repetition, present the data in a table format whenever possible.
 - If the experiment involves the isolation of a compound you should include the yield. In synthesis experiments, the theoretical, actual, and %yields should be included.
6. A **DISCUSSION** including:
 - Interpretation of your data, comparison with previously reported results, and brief comment on sources of error in your determinations. Some of the in-lab questions will help you write the discussion. Avoid colloquial comments such as "overall, the experiment went smoothly." Instead, let your data and your conclusions speak for themselves.
7. Include **REFERENCES** (*Merck Index*, *CRC Handbook*, etc.) at the end.

A sample of a lab report for selected parts of Experiment 1 (recrystallization of acetanilide and the identification of an unknown) is shown in Figure 2.1.

2.11 CHEMICAL LITERATURE

Before we engage in experimental work we must research the chemical literature to make sure, on one hand, that we have all the pertinent information to make our work successful, and on the other hand, that we are not repeating work and mistakes made by somebody else. A few hours spent in the library may save us days or weeks of frustration.

Student: Synton X. Plosiff
Instructor: Krystal de Rocca

Date: 1/5/2000
Lab section: Tue 1-5; room 2-71

Experiment 1

Recrystallization of acetanilide and identification of an unknown by melting point

Introduction

Learning objectives: (In-lab #1) In this experiment we will purify acetanilide by recrystallization from water. We will also identify an unknown solid by the mixture melting point technique.

Recrystallization: (Pre-lab #1-3; 5c) Recrystallization is a purification technique for solids. It consists of the following steps: 1) selection of the solvent; 2) dissolving the sample in the minimum volume of boiling solvent; 3) doing a hot filtration (if necessary) to remove insoluble impurities; 4) allowing the system to cool down to crystallize the solid; 5) separating the solid from the liquid (mother liquor) by vacuum filtration (this removes soluble impurities); 6) washing the solid on the filter with a small volume of cold solvent; 7) drying the solid.

A good recrystallization solvent (Pre-lab #4; 9d) should dissolve the sample very well at high temperatures, and sparingly at low temperatures. It should dissolve impurities very well or not at all (the nature of the impurities is usually unknown). The bp of the solvent should be in the range 50-120°C. The solvent should not react with the sample. Other things being equal, we should choose the solvent with the lowest toxicity. The bp of the solvent should be lower than the mp of the solid.

If the solubilities in the hot (S^H) and cold (S^C) solvent are known, the theoretical % Recovery (% R) of the recrystallization can be calculated (Pre-lab #10):

$$\% R = 100 \times (S^H - S^C) / S^H$$

In principle, theoretical % R doesn't depend on the total amount of material to be recrystallized. If $S^H = 1 \text{ g/100 mL}$ and $S^C = 0.03 \text{ g/100 mL}$, the % R is:

$$\% R = 100 \times (1 - 0.03) / 1 = 97 \%, \text{ regardless of the amount of solid.}$$

Melting point. (Pre-lab #5a,b; 6; 9a-c) The melting of a pure organic compound occurs in a very narrow temperature range, called the melting point range, which is normally less than 2°C. Most impurities have a dual effect on the mp: They lower the mp and extend the mp range. If the melting range is narrow it doesn't necessarily mean that the compound is pure. For example, the melting point of eutectic mixtures is sharp. Also, some impurities, especially inorganic compounds (NaCl, chalk, sand, etc.) do not change the mp of organic solids.

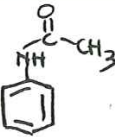
Figure 2.1 A sample lab report.

Mixture melting point is a technique for the identification of organic solids. We mix two compounds (A and B) with the same mp. If the mp of the mixture is identical to the mp of the individual components, then A and B are the same. If the mp is different, then A and B are different compounds.

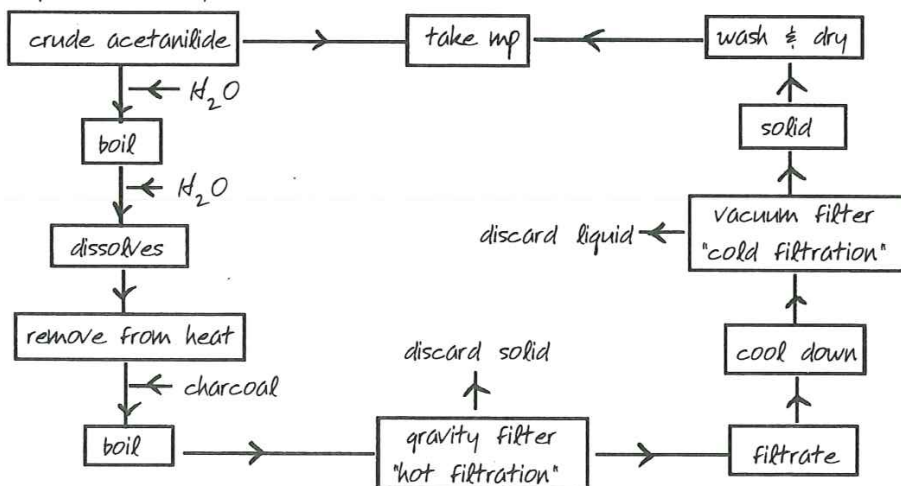
We should heat the sample slowly in the vicinity of the mp to make sure that the thermometer and the sample are at the same temperature (Pre-lab #7). A resolidified sample should not be reused to take a second mp because the sample may contain decomposition products that act as impurities and lower the mp. (Pre-lab #8)

Experimental

Table of reagents (Pre-lab #11)

compound	MM (g/mol)	structure	mp (°C)	bp (°C)	density (g/mL)	flamm.	solubility	toxicity/ hazards
acetanilide	135.17		113- 115	304- 305	-	-	1 g/15 mL H ₂ O (room temp) 1 g/20 mL H ₂ O (100°C)	LD ₅₀ 800 mg/kg (oral rat) Toxic Irritant
water	18.02	H ₂ O	0	100	1.00	0	-	nontoxic

Flowchart: (Pre-lab #12) Experimental procedure according to "Experimental Organic Chemistry"



Glassware and equipment: (Pre-lab #13) spatula; 2 Erlenmeyer flasks (125 mL); glass rod; hot plate; short-stem funnel; filter paper; boiling chips; ice-water bath; filter flask (125 mL); Buchner funnel; watch-glass; oven; mp apparatus; capillary tubes.

Figure 2.1 (Continued)

Data (In-lab #2; 3; 10-13)

Recrystallization of acetanilide

	mass (g)	mp (°C)
before recrystallization	3.0	105-109
after recrystallization	1.3	110-112

Recrystallization solvent: water

Observations: Some acetanilide crystallized on the filter paper during the hot filtration and was lost. Crude acetanilide was beige. Acetanilide recrystallized as white flakes. The recrystallized product was dried in an oven (70°C) for 1 hour before weighing and determining the mp.

% Recovery:

$$\%R = 100 \times \text{mass after recryst} / \text{mass before recryst}$$

$$\%R = 100 \times 1.3 \text{ g} / 3.0 \text{ g} = 43\%$$

Identification of an unknown

Unknown number: 501; white solid.

mp (fast): 150-152°C; mp (slow): 155-157°C.

According to the table of unknowns, the possible compounds are: m-tromobenzoic acid (mp 155-157°C) and salicylic acid (mp 156-158°C).

Mixture mp

unknown + m-tromobenzoic acid: 120-135°C

unknown + salicylic acid: 155-157°C

Discussion and conclusions

The recrystallization of acetanilide gave a % Recovery of 43%. Loss of product during the hot filtration accounts, in part, for this low recovery. The melting point of the recrystallized product (110-112°C) is higher than the mp of the crude material (105-109°C). This indicates that the recrystallization was effective in removing impurities. However, the mp of the recrystallized product is lower than the literature value (113-115°C). Presence of residual water (recrystallization solvent) and error in determining the mp may account for this.

Based on the mixture mp, I can conclude that the unknown # 501 was salicylic acid, because there was no depression in the mp of the mixture.

Bibliography

Experimental Organic Chemistry, D. Palleros.

Merck Index, 12th edition. Aldrich Catalog, 1998-1999.

Figure 2.1 (Continued)

The wealth of chemical information could be overwhelming. More than 700,000 articles related to chemistry were published in 1996 alone. However, with the widespread use of computers the search for chemical information is becoming easier and faster every day. The primary source of chemical information is peer-reviewed scientific journals. Some journals publish original results in all fields of chemistry and others offer comprehensive reviews on specific subjects. The reviews are written by authorities in the field and comment on the most important and recent bibliography. Physical and spectroscopic data can be found in handbooks, catalogs, and special collections. The information contained in journals is compiled, sorted out, and catalogued by different services, among them the *Chemical Abstracts*, the *Beilstein Handbook of Organic Chemistry*, and the *Current Contents*.

Let's consider the most important sources of chemical information separately.

Journals

Some general journals for all areas of chemistry include:

- *Journal of the American Chemical Society*, also known as JACS, is arguably the most important and prestigious journal in chemistry. There is free Internet access to the table of contents of the current issue (<http://www.ChemCenter.org>).
- *Journal of Chemical Education*. Published by the Division of Chemical Education of the American Chemical Society. Articles with emphasis on chemistry education. Many good ideas for teachers and students. There is substantial free access on the Internet. Some articles and abstracts are available online free of charge. Index also available online (<http://jchemed.chem.wisc.edu/>).
- *Chemical Reviews*. Also published by the American Chemical Society. Comprehensive reviews on different subjects written by authorities in the field. The Internet access is <http://www.ChemCenter.org>.
- *Angewandte Chemie. International Edition in English*. A German journal translated into English. It publishes original articles and reviews. There is free Internet access to the table of contents and the abstracts to some "hot" papers (<http://www.vchgroup.de/home/angewandte>).

Important journals in the field of organic chemistry include:

- *The Journal of Organic Chemistry*. Published by the American Chemical Society. Covers all areas of organic chemistry. There is free Internet access to the table of contents of current issue (<http://www.ChemCenter.org>).
- *Tetrahedron* and *Tetrahedron Letters*. The first publishes full articles in all areas of organic chemistry, and the second is for the fast publication of short communications, most of them dealing with organic synthesis.
- *Synthesis*. A journal devoted to synthetic organic chemistry. There is free Internet access to the table of contents of recent issues (<http://www.thieme.com/chem.htm>).
- *Journal of the Chemical Society. Perkin Transactions I*. Published by the Royal Society of Chemistry (UK). Mainly devoted to organic synthesis. There is free Internet access to the table of contents (<http://chemistry.rsc.org/rsc/>).
- *Journal of the Chemical Society. Perkin Transactions II*. Published by the Royal Society of Chemistry (UK). Specializes in physical organic chemistry (reaction mechanisms, kinetics, spectroscopy, quantum mechanics). There is free Internet access to table of contents (<http://chemistry.rsc.org/rsc/>).

Other publications important in organic chemistry are:

- *Organic Syntheses*. Published annually by Wiley (New York). It describes the synthesis of diverse organic compounds. The syntheses are checked by independent chemists for accuracy. There are eight **Collective Volumes**.

- *Fieser and Fieser's Reagents for Organic Synthesis*. Published by Wiley (New York). Written by the legendary couple Louis and Mary Fieser from Harvard University. Describes the uses and applications of the most important reagents in organic chemistry. Started in 1967 and is periodically upgraded.
- *Encyclopedia of Reagents for Organic Synthesis*. Leo A. Paquette, editor. Wiley (Chichester, New York; 1995). A description of 3000 reagents with examples of use and references.
- *Advanced Organic Chemistry. Reactions, Mechanisms and Structure*. J. March. 4th ed. Wiley, New York, 1992. An excellent compilation of the most important reactions in organic chemistry with references.
- *Vogel's Textbook of Practical Organic Chemistry*. A. I. Vogel, B. S. Furniss, A. J. Hannaford, P. W. G. Smith, and A. R. Tatchell. Longman, Harlow, 5th ed., 1989. A classic laboratory textbook with many macroscale syntheses. Complete and thorough.

Laboratory Handbooks

- *Aldrich Catalog of Fine Chemicals*. Published by the Aldrich Company. Updated annually. It contains more than 27,000 chemical products. It cross-references to Beilstein (see below) and the Merck Index. Lists physical properties, and references spectroscopic information. Gives the Chemical Abstract Service (CAS) registry number (see below). Has molecular formula index. Also available on CD-ROM.
- *Merck Index. An Encyclopedia of Chemicals, Drugs, and Biologicals*. Published by the Merck Company (Whitehouse Station, NJ). S. Budavari, editor. Listing of about 10,000 chemicals; includes physical data, uses, toxicity, and hazards. References synthesis. Gives CAS registry number. Has molecular formula index. Upgraded periodically. Also available on CD ROM.
- *CRC Handbook of Chemistry and Physics*. Published by the CRC Press (Boca Raton, FL). D.R. Lide, editor. Contains a table of organic compounds with physical properties; cross-references Beilstein. Upgraded annually. Has molecular formula index.
- *Lange's Handbook of Chemistry*. Published by McGraw-Hill (New York). J. A. Dean, editor. Physical data for most important organic chemicals. Upgraded periodically.

Other Reference Handbooks

- *Dictionary of Organic Compounds*. Published by Chapman and Hall, 6th ed., 1996 (nine volumes). It contains physical data, references on synthesis, derivatives, applications, toxicity, and hazards of about 150,000 compounds. Has molecular formula index. Gives CAS registry number. Also available on CD ROM and online. For more information: <http://www.chapmanhall.com>.
- *CRC Handbook of Data on Organic Compounds*. Published by the CRC Press (Boca Raton, FL), 3rd ed., 1994. Physical data, extensive spectral data information. Molecular formula index. CAS registry numbers. Beilstein references. Also available on CD ROM.
- *Handbook of Natural Products Data*. Atta-ur-Rahman and Viqar Uddin Ahmad. Elsevier (Amsterdam, 1994). Contains spectral data. Has molecular formula and molecular mass indexes.
- *Physicians' Desk Reference*. Published annually by the Medical Economics Co. (Montvale, NJ), contains information about prescription and nonprescription drugs.

Toxicity and Hazards Handbooks

- *Hazardous Materials Handbook*. R.P. Pohanish and S.A. Greene. Published by Van Nostrand Reinhold (New York, 1996). It contains a brief description of fire, exposure, and health hazards, chemical reactivity, water pollution, and emergency response for most important chemicals.
- *The Sigma-Aldrich Library of Regulatory and Safety Data*. R.E. Lenga, and K.L. Votoupal, 1st ed., 1992. A compilation on the toxicity, safety, and hazards of more than 20,000 chemicals.

Spectral Collections

- *Aldrich Library of ^{13}C and ^1H FT-NMR Spectra*. C.J. Pouchert, and J. Behnke. 1st Edition, 1993. A collection of ^1H and ^{13}C -NMR spectra. The ^1H - and the ^{13}C -NMR spectra were obtained at 300 and 75 MHz, respectively.
- *Aldrich Library of NMR Spectra*. C.J. Pouchert. 2nd ed., 1983. A collection of ^1H -NMR spectra obtained with a 60 MHz instrument.
- *Aldrich Library of FT-IR Spectra*. C.J. Pouchert. 1st ed., 1985. A collection of more than 17,000 IR spectra.
- *Sadtler Standard Spectra*. Published by Sadtler Research Laboratories, Inc. (Philadelphia, PA). There are different collections containing IR, UV, ^1H - and ^{13}C -NMR spectra.

Compilation Services

The journals listed here are only a small fraction of all the chemistry journals published worldwide. The information contained in them is compiled, sorted out, and catalogued by different services, among them the *Chemical Abstracts*, the *Beilstein Handbook of Organic Chemistry*, and the *Current Contents*.

The *Chemical Abstracts*, published by the American Chemical Society, is the most complete chemical information resource. It has more than 16 million compounds on record. It gives a short abstract in English of articles on chemistry published anywhere in the world and in any language beginning in 1907. There are thirteen cumulative indexes, one every 10 years until 1957 (1917; 1927; 1937; 1947 and 1957), and one every 5 years thereafter (1957–61; 1962–66; 1967–71; 1972–76; 1977–81; 1982–86; 1987–91 and 1992–97). The cumulative indexes include formula, general subjects, chemical substances, authors, and patents. There is also an index by the **registry number**, which is a unique number that the Chemical Abstracts Service (CAS) assigns to every compound. For example, the CAS registry number for aspirin is 50-78-2. This number is extremely useful for carrying out searches, especially by computer. Searches on the *Chemical Abstract* can also be performed (for a fee) online. Information about the CAS can be obtained at <http://www.cas.org>.

The *Beilstein Handbook of Organic Chemistry* is everything but a handbook. Its latest edition (1995) has 480 volumes. It is the most complete database for organic chemistry. It contains more than 6 million compounds. It is also the oldest compilation, starting in 1881 and reaching as far back as 1779. It was originally published in German, but it is now published in English. More than 350 properties are listed for some chemicals. The search can also be done online. Its Internet site is <http://www.beilstein.com>.

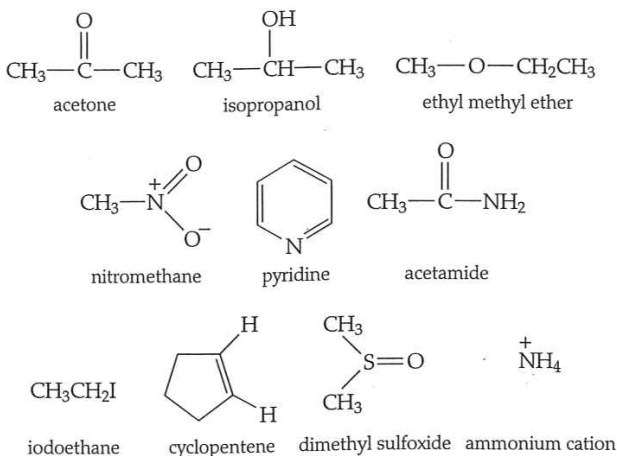
The *Current Contents* article database is very useful to find titles and authors of current articles published by the most important journals. Most college libraries subscribe to this service. The online database contains almost 7 million citations from 6500 journals in many different fields (not only chemistry) and goes back as far as July 1989. Retrieval of information is done by title words or authors.

Online Resources

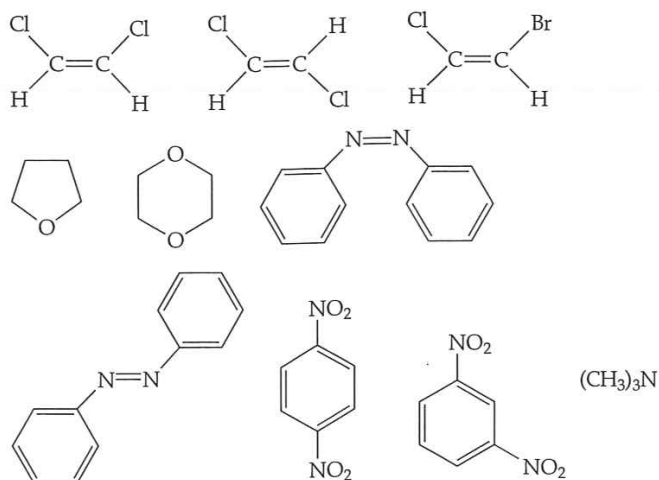
Other online resources include **MEDLINE** and **MEDLINE PLUS**, which are databases with citations and abstracts from more than 8,000 journals in medicine, life science, and health administration. The database contains almost 2 million citations from 1992. Medline backfiles from 1966 to 1991 are also available as separate databases. Many libraries subscribe to this service.

EXERCISES**Problem 1**

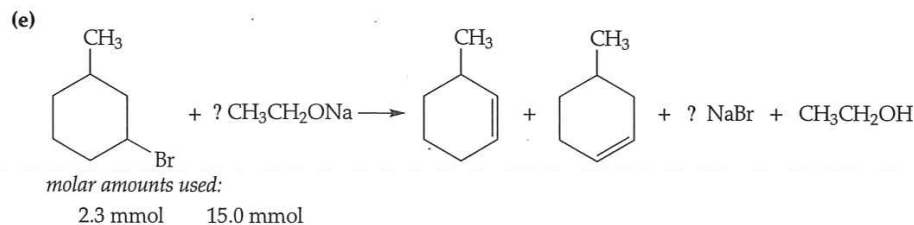
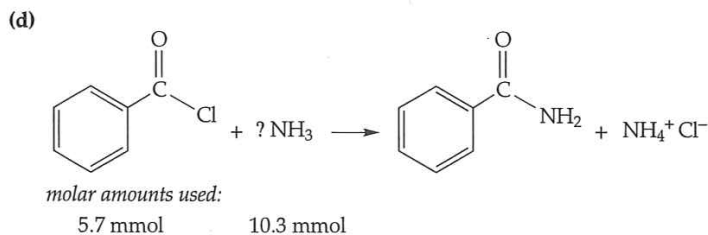
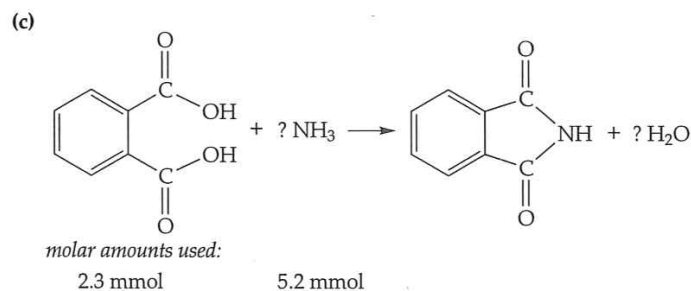
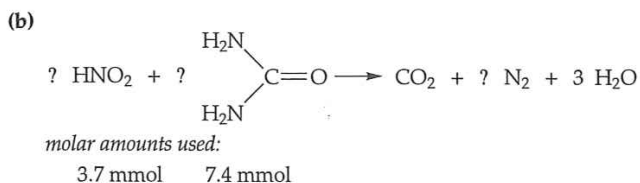
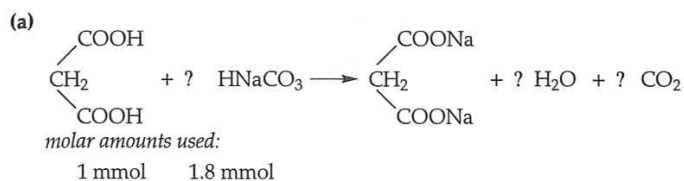
Circle the H-bond donors, and box the H-bond acceptors.

**Problem 2**

Based on geometric considerations, predict which of the following molecules have a permanent dipole moment.

**Problem 3**

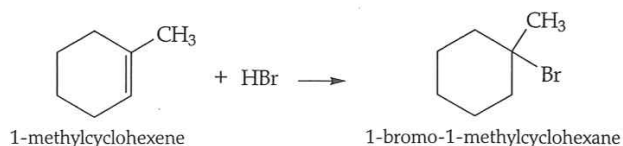
Balance the following equations by replacing the question mark with the appropriate stoichiometric coefficient. In each case determine the limiting reagent and the theoretical yield for each product when the molar amounts indicated under the reagents are mixed.

**Problem 4**

Calculate the concentration of an aqueous solution of hydroiodic acid (56% w/w, density = 1.70 g/mL; MM HI = 127.91 g/mol) in molarity, g/L and %w/v.

Problem 5

When 970 μL of 1-methylcyclohexene (MM = 96.17 g/mol; $d = 0.809 \text{ g/mL}$) was reacted with 3.0 mL of concentrated HBr (48% w/w; $d = 1.49 \text{ g/mL}$; MM HBr = 80.92 g/mol) it gave 1.10 g of 1-bromo-1-methylcyclohexane (MM = 177.09). Calculate the number of mmoles for each compound. Determine the limiting reagent. Calculate the theoretical yield of the product and the percentage yield. The balanced equation is shown below.



Problem 6

When benzil reacts with periodic acid, benzoic acid is obtained. The balanced equation is shown below. Calculate the percentage yield of the synthesis if 1.05 g of benzoic acid (MM = 122.12 g/mol) was obtained from 1.05 g of benzil (MM = 210.23 g/mol) and 3.3 mL of a 1.6 M solution of periodic acid was used.

