

PLASTIC CRYSTALS: A HISTORICAL REVIEW

PROFESSOR J. TIMMERMANS

Sometime Professor of Physical Chemistry, Free University of Brussels

IN THIS short historical survey, I hope to give, to the best of my ability, the early experimental evidence concerning plastic crystals, and I apologize in advance if there remain some important gaps in my text, since I am a specialist in the study of physical properties of organic compounds, but am not so learned, either in inorganic chemistry or in theoretical physics.

Some twenty-five years ago, while collecting data for my book: *Les Constantes Physiques des Composés Organiques Cristallisés*, I saw directly, when I came to the chapter on the stoichiometry of the heat of melting, that the molecular heat of fusion and freezing temperature increase in ascending a homologous series. I tried to nullify this effect by dividing the values of the molecular heat by the absolute temperature of melting to obtain the molecular entropy of melting. There was, however, still no constancy of the melting entropy in a homologous series. However, some peculiar compounds, of usually relatively simple constitution, had a very low entropy of melting. These compounds were "globular", that is they were either symmetrical around their centre (CH_4 , CCl_4 , pentaerythritol, etc.); or would give a sphere by rotation around an axis (cyclohexane, camphor, etc.). All these compounds had an entropy of melting lower than 5 e.u. ($\text{cal deg}^{-1} \text{mole}^{-1}$), a quantity I represent by the symbol σ , and so far this arbitrary limit has not been exceeded. Thus cyclohexane with σ equal to 2.27, is globular, while methylcyclohexane with σ equal to 11.00 is non-globular; the reason seems to be that in methylcyclohexane, the lateral CH_3 -group would stop the rotation.

The comparative study of many other properties of organic crystals revealed that such compounds had many other remarkable values of their constants. Usually their melting point is relatively

high. While n-pentane melts at -141°C , tetramethylmethane melts at -16°C . However, they have a transition point lower down, with a high value of the entropy of transition (for $\text{C}(\text{CH}_3)_4$, this is at -133° with $\sigma = 4.40$).

Table 1 classifies certain organic compounds from this point of view as either globular (column 1) or non-globular (column 2).

With a high melting point goes a high saturated vapour pressure of the plastic crystals. The triple point ($V+L+S$) may be higher than atmospheric pressure, so that sometimes, under ordinary pressure, the crystals sublime directly—as C_2Cl_6 does—instead of melting first.

Between the melting and the transition points, they crystallize almost all in the cubic system, the system with the highest symmetry, and take another form below the transition points; (cyclopentane, although globular, is hexagonal). In some cases the transition takes place in two steps, as with hexachloroethane and hydrogen chloride. Fig. 1 illustrates this for a globular molecule $\text{C}(\text{CH}_3)_4$ (one transition) and a non-globular molecule, normal- C_5H_{12} , which has no transition in the crystal.

This similarity in the symmetry of globular compounds explains how it is possible that substances so different from the chemical point of view as methane and argon are able to give a continuous series of mixed crystals. It explains also that the two stereochemical antipodes of such compounds give, not a racemate, but a series of mixed crystals, with constant melting point, as has formerly been found for camphor (see Fig. 2). Prof. ASTON will tell us more about this question.

The American School of physical chemists has collected very numerous data on the change of specific heat of crystals on heating. And so one

finds that—in cyclopentane for example—the specific heat of the plastic crystals rises on lowering of the temperature, instead of falling as usual. This is shown in Fig. 3. where the heat capacity (C_p) of cyclopentane is plotted against the temperature.

In some cases, as with methyl alcohol, the transition from ordinary to plastic crystals by heating is preceded by a very high value of C_p just under the transition point as is shown in Fig. 4.

In another direction, SMYTH and his collaborators, in particular, have studied the change of

dielectric constant with temperature, and here also plastic crystals behave in a peculiar way. Usually when freezing, the dielectric constant of a substance falls markedly; but, with many plastic crystals the dielectric constant continues to rise on lowering the temperature, the curve for the plastic state being almost continuous with the curve for the liquid, and falling sharply only at the transition point. This is illustrated in Fig. 5 for methyl chloroform.

And finally, Dr. MICHILS, for his doctoral dissertation, has made comparative measurements

Table 1. Classification of Molecules

Globular compounds		Non-globular compounds	
Inorganic Substances			
A, Xe HCl H ₂ S H ₃ P H ₄ Si CO DCl SF ₆		— HF H ₂ O H ₃ N Cl ₄ Si CO ₂ D ₂ O —	
Organic Substances: Fatty Series			
CH ₄ , CD ₄ , CH ₃ D C ₂ H ₂ C(CH ₃) ₄ CF ₄ , CCl ₄ , CBr ₄ CCl(CH ₃) ₃ , CCl ₂ (CH ₃) ₂ CCl ₃ CH ₃ , CClF ₂ CH ₃ CCl(CH ₃) ₂ NO ₂ C(NO ₂) ₄ C(SCH ₃) ₄ C ₂ Cl ₆ , C ₂ F ₆ , C ₂ F ₅ Cl C ₂ (CH ₃) ₆ , C ₂ Cl(CH ₃) ₅ C(CH ₃) ₃ C ₂ H ₅ , CH(CH ₃) ₂ CH(CH ₃) ₂ CH(CH ₃) ₂ C(CH ₃) ₂ C ₂ H ₅ C(CH ₃) ₃ C(CH ₃) ₂ C ₂ H ₅ C(CH ₃) ₃ CH(CH ₃)CH(CH ₃) ₂ C(CH ₃) ₃ CH = CH ₂ CH ₃ CH = CHCH = CHCH ₃ CH ₃ OH, CH ₃ OD (CH ₃) ₃ COH, (CH ₃) ₃ CSH CH ₃ CH(OH) ₂ (CH ₃) ₂ C ₂ H ₅ COH C(CH ₃) ₃ CO ₂ H, CCl ₃ CO ₂ H CCl ₃ C ₆ H ₅ (CNCH ₂) ₂		C ₂ H ₆ CH = CH C(C ₂ H ₅) ₄ CH ₂ Cl ₂ CHCl ₃ CClH ₃ CCl ₂ HCH ₂ Cl CH(NO ₂) ₃ C(SC ₂ H ₅) ₄ C ₂ HCl ₅ — — — C(CH ₃) ₃ CH(CH ₃)C ₂ H ₅ — CH ₃ CH ₂ CH = CHCH ₂ CH ₃ — C ₂ H ₅ OH — — CH(CH ₃) ₂ CH ₂ CO ₂ H CH ₂ ClCO ₂ H CH ₂ ClC ₆ H ₅ Malonitrile, Glutaronitrile.	

Table 1 (continued)

Globular compounds	Non-globular compounds
Heterocyclics	
Azocyclohexane Endomethylene piperazine Tropinone Camphor anhydride Tetrahydrofuran Thiocyclohexane	Piperidine Piperazine Thiophene Cineol Furane Dioxane
CYCLIC SERIES	
Polymethylenes	
In C ₄ : Perfluorocyclobutane In C ₅ : 1,1 and 1,2- <i>cis</i> -Dimethylcyclopentane 1,1,2- <i>trans</i> -Trimethylcyclopentane Cyclopentanol, Cyclopentadienol Cyclopentyl chloride, Perfluorocyclopentane In C ₆ : Cyclohexane, Cyclohexylchloride Cyclohexanol, Cyclohexanone, α -Hexachlorocyclohexane, Cyclohexene 1,3-Cyclohexadiene, 1,4-Cyclohexadiene Cyclohexylfluoroform, 1,1 and 1,2- <i>cis</i> Dimethylcyclohexane In C ₈ and C ₉ : Ketone	Cyclobutanone Methylcyclopentane, 1,3 and 1,2- <i>trans</i> Dimethylcyclopentane Cyclopentene, Cyclopentanone, Cyclopentylamine, Cyclopentyl nitrile, Cyclopentanone, Methylcyclopentanol Methylcyclohexane, 1,3, 1,4 and 1,2- <i>trans</i> - Dimethylcyclohexane β -Hexachlorocyclohexane, Cyclohexylamine Cyclohexanoxime Menthane
Condensed Cyclics	
Decahydronaphthalene Dicyclopentadiene Dihydro and tetrahydrodicyclopentadiene- α : Alcohol, Ketone, Oxide and Bioxide Tetrahydrohydrindane	Tricyclopentadiene
Bridged Cyclics	
Endomethylenecyclohexane, Camphene Camphenilane, Isocamphane, Camphenilone Norcamphor, Norpinane, Pinane, Tricyclene Endoethylenecyclohexane	Fenchane : Alcohol and Ketone
Camphor Group	
Camphane, Isobornylane, Bornylene, Bornyl and Isobornyl chloride, 2,6 and 2,10 Dichlorcamphane, Borneol and Isoborneol, Bornylamine, Camphor, Thiocamphor, 2,3- Camphanedione, 3-Cyanocamphor, Camphoroxime and Camphorquinone.	3-Camphor : Chloride, Bromide, Sulfone, Sulfonamide, Sulfoxide, and Sulfochloride

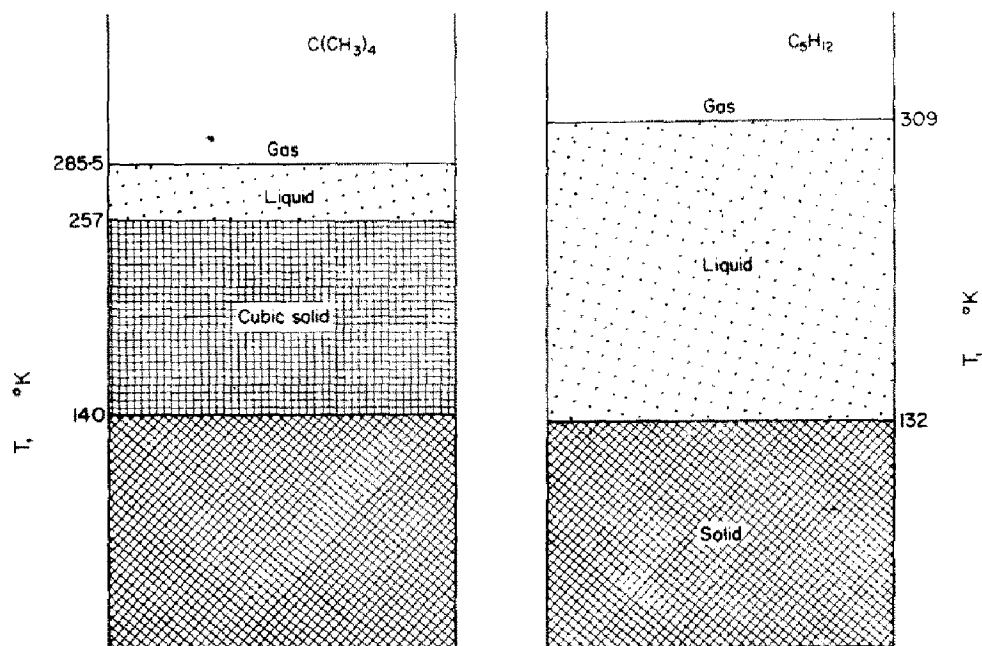


FIG. 1. Phases for neopentane (globular) compared with those for normal pentane (non-globular).

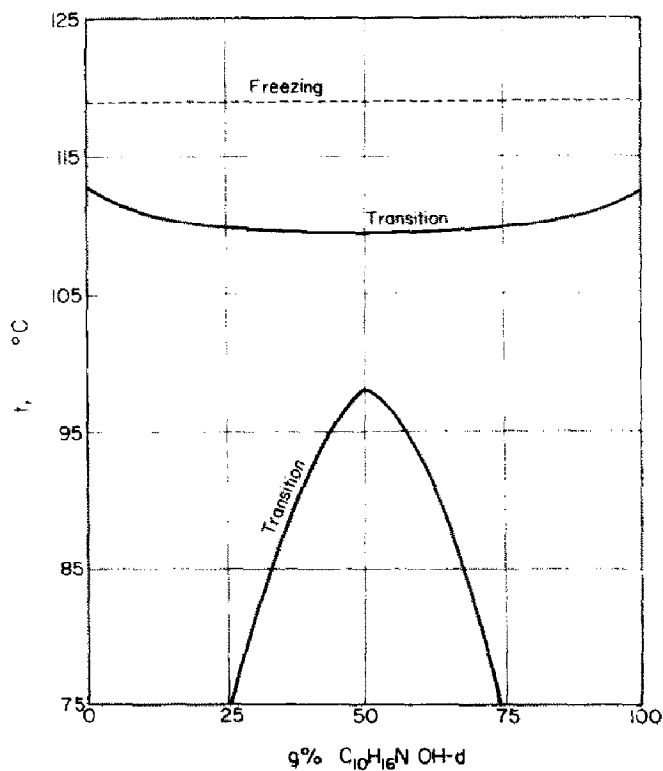


FIG. 2. Freezing-point-composition diagram for solid solutions of D- and L- camphoroxime.

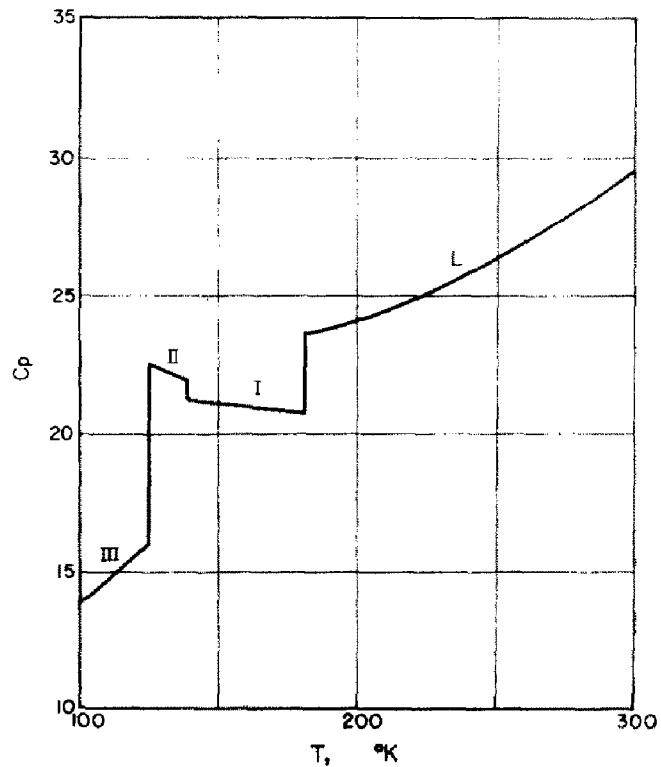


FIG. 3. Heat capacity-temperature curve for cyclopentane (a globular molecule).

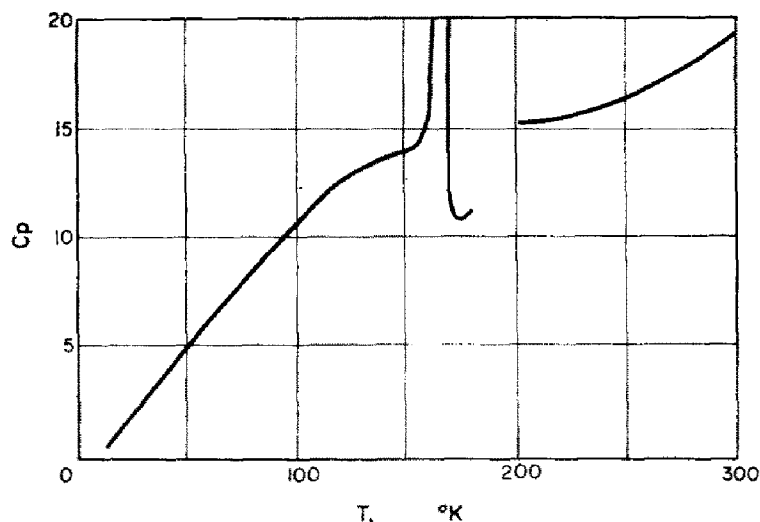


FIG. 4. Heat capacity-temperature curve for methyl alcohol (a globular molecule)

of the plasticity of these unusual substances, a few degrees higher and lower than their transition point, and has found that, for example with C_2Cl_6 , they flow through a hole under a pressure which is more than ten times smaller in the plastic state than below the transition temperature.

Examples are given in Table 2 for the substances shown in column 1 along with entropy of fusion shown in column 2. The third and fourth columns

give, respectively, the crystal form for the crystals stable above (I) and below (II) the transition. The fifth and sixth columns give the pressure to produce flow through a hole of forms I and II respectively. The example of 1,4-dichlorobenzene is of a case where evidently the form above the transition is not a plastic crystal as indicated by the high entropy of fusion, 13.4 e.u. In this case there is little difference between the two pressures. In all cases, where the entropy of fusion is lower than 5 e.u., the form stable above the transition flows at a pressure at most one half of that required for the form stable below.

Later on, I did find that formerly a few authors had observed some of the characteristics of plastic crystals, without realizing the importance of the subject, or at least in considering them as very special phenomena.

BRUNI and his co-workers have measured the molecular lowering of the freezing point of cyclohexane as a solvent, and I remember how struck we were, both my colleague at Brussels the late Professor CHAVANNE, and myself, when a student prepared pure cyclohexane from benzene, by the catalytic method of hydrogenation of Sabatier, and confirmed BRUNI's high value of the molecular lowering of the freezing point. Some

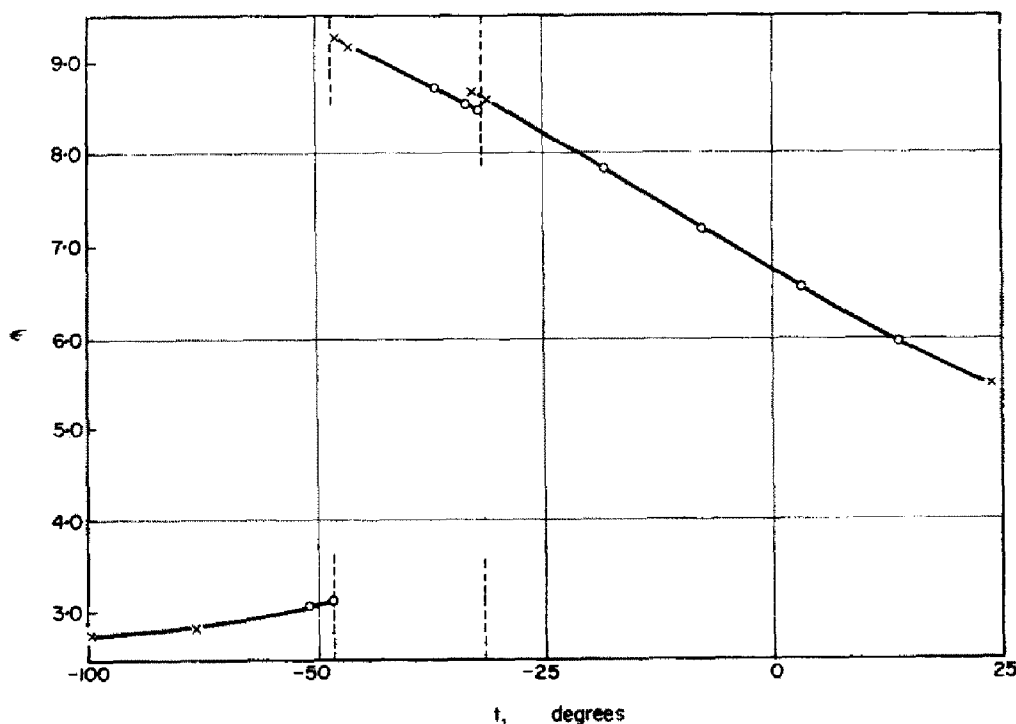


FIG. 5. Dielectric constant-temperature curve for methyl chloroform (a globular molecule).

Table 2. Comparison of flow properties of plastic and non-plastic crystals.

Substance	Q/T , cal deg ⁻¹ mole ⁻¹	Crystall. form I	Crystall. form II	P , Kg/cm ²	
				Form I	Form II
CBr ₄	2.4	Cubic	Monocl.	247	1,500
C ₂ Cl ₆	4.3	Cubic	Triclin.	about 250	3,600
C ₂ (CH ₃) ₆	4.5	Cubic	—	—	—
Camphor-D	2.8	Cubic	Rhomb.	247	454
Borneol-D	4.1	—	—	240	864
Camphor anhydride	4.0	—	Orthor.	760	1,500
Camphoroxime	1.3	—	—	—	1,940
D-Bromcamphor- α	27.6	Cubic	Monocl.	1,960	—
Fenchylic alc. D	5.8	—	—	650	—
Naphthalene	13.3	Monocl.	—	2,240	—
Hexamethylbenzene	11.0	Triclin.	—	2,800	—
1-4-Dichlorbenzene	13.4	Monocl. I	Monocl. II	740	1,150
Dotriacontane	55.7	Orthor.	—	1,200	—
Stearic acid	39	Monocl.	Monocl.	1,120	—

years later, camphor was also used as a solvent by organic chemists, because the high value of that lowering has made possible the measurement of molecular weights with ordinary thermometers.

During the thirties, PAULING and later BERNAL explained some anomalies of ammonium salts by making the assumption of rotation of the molecules inside the crystal.

Our colleague PIRSCH, some 25 years ago, in a systematic survey of cyclic polymethylenes and their derivatives has discovered many other compounds of the plastic crystals series.

And just before the war, some of our Japanese colleagues had begun the study of this same kind of crystals by electronic microscopy, the last paper of this group of research workers being that of Professor NITTA, of Osaka: they found by this method that in the plastic state crystals give diagrams similar to those of liquids and not to those of real crystals.

And finally, a few years ago, my collaborator Dr. TRAPPENIERS, who is now Professor of Physical Chemistry in Gröningen (Netherlands), made a very interesting contribution to the problem, in combining the views of my colleague at Brussels, Professor PRIGOGINE, with my own notions about plastic crystals. Accepting the freezing diagram, under high pressure, of BRIDGMAN for CCl₄ as standard, he applied the idea of corresponding states to the similar diagram for CBr₄, taking

their triple points as corresponding states: I had myself compared these two diagrams of BRIDGMAN many times, thinking that it was impossible that two such isomorphous compounds would not be similar also under high pressure, but without avail. With his theory, TRAPPENIERS found that in the diagram of BRIDGMAN there was a gap, in which there was a transition curve that this author was unable to detect fifty years ago because the difference of volume of the two phases was too small. TRAPPENIERS was able to detect it, almost exactly in the region where it was expected, by using a sensitive method of piezometric analysis developed in my own laboratory. The phase diagrams for CCl₄ and CBr₄ are compared in Fig. 6. This is, to my knowledge, the first time that the theory of corresponding states has been quantitatively applied, with success, to crystals.

In considering this large domain, I think that we are able to make certain general conclusions. The phenomenon of melting is not very easy to understand because our theoretical knowledge of the inner state of liquids is much more superficial than for crystals and gases. At the end of the last century, the discovery of liquid crystals had proved that the melting process is a superposition of two different effects, although both result from the thermal movements of molecules. When the temperature is high enough, the thermal energy becomes so great that the crystal boundaries

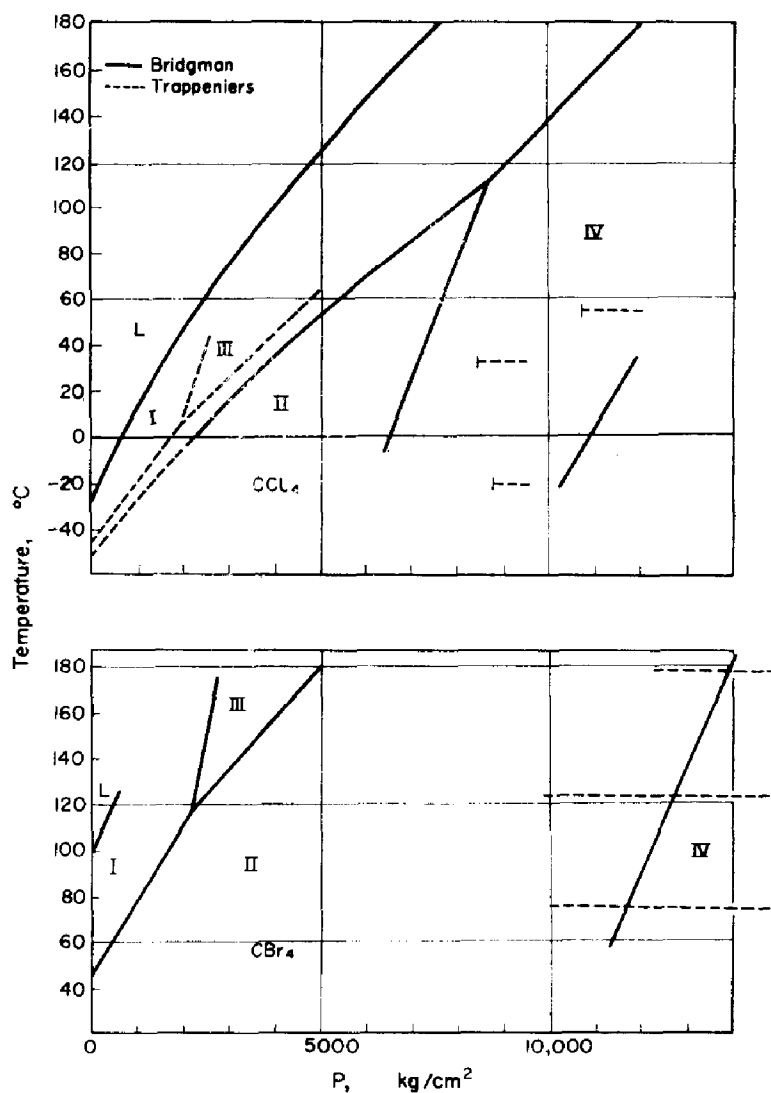


FIG. 6. Temperature-pressure equilibrium diagrams for CCl_4 and CBr_4 .

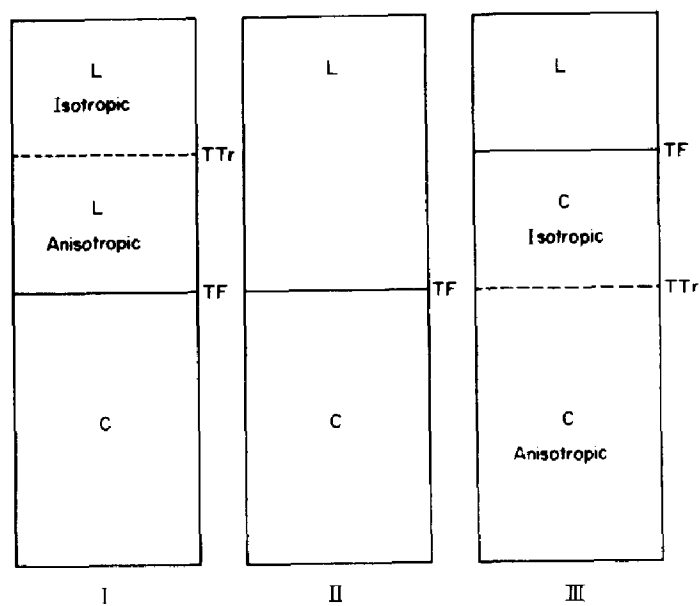


FIG. 7. Phases for systems giving: I. crystal, anisotropic liquid and isotropic liquid; II. crystal and liquid; III. anisotropic crystal, isotropic crystal and liquid (C = crystal; L = liquid).

are broken and the substance liquefies; if there is room, the free molecules then begin to turn in all directions, giving an isotropic liquid, as usual. The compounds which give anisotropic liquids are generally very long molecules which, because of double bonds, are unable to bend, having the shape of a string, and which need much space to rotate freely. Therefore, some directions in the liquids are privileged and it remains anisotropic, till the higher transition point where, by expansion, it becomes isotropic.

In the plastic crystals, on the contrary, the

freedom to rotate exists already in the crystal state, because they are globular in shape, but the coherence of the crystal is broken only at a higher temperature, the melting point. In the two cases, the liquefaction and the isotropy do not happen at the same temperature. In liquid crystals, by heating, the fluidity comes first, but in plastic crystals, the isotropy comes first. This is illustrated in Fig. 7. They are complementary from this point of view, as I pointed out, in my first paper on the subject, in forging the nomenclature of the globular compounds, or plastic crystals.