MELTING AND CRYSTAL STRUCTURE

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Sir Humphry Davy's original suggestion that melting involves some kind of increase in the heat motion of the molecules has been greatly clarified by the discovery that, unlike liquids, solids normally consist of long regular arrays of molecules, and by the development of thermodynamical and other methods of studying the nature of "increases in heat motion".

1. Thermodynamical Studies on Melting

1.1 Entropy Changes on Fusion.—For different solids, the phenomenon of melting can occur at very different temperatures and can involve very different heats of fusion. For example, solid hydrogen melts at 14·0° K., with a heat of fusion of 28·2 kcals./g.-mol., whereas solid platinum melts at 2028° K., with a heat of fusion of 5310 kcals./g.-atom. However, the respective entropies of fusion are closely similar (2·01 and 2·62) and indicate that the melting process is very similar for the two solids. The Clausius–Clapeyron equation for phase changes

$$\mathrm{d}P_f/\mathrm{d}T_f = \Delta S_f/\Delta V_f \quad . \quad . \quad . \quad . \quad (1.1)$$

relates the temperature T_f and the pressure P_f at which the phase change occurs, with ΔS_f and ΔV_f, the entropy and volume changes respectively per unit mass (conveniently per g.-mol. of substance). The equation indicates that these two thermodynamic parameters might give significant information about the nature of the phase change. This is supported by Boltzmann's statistical relationship between (*a*) the entropy of fusion and (*b*) W_S and W_L the number of ways of realising the solid and the liquid state respectively:

$$\Delta S_f = \boldsymbol{R} \ln W_L/W_S \text{ per mole} \quad . \quad . \quad . \quad (1.2)$$

though no corresponding generalisation has been proposed with regard to the volume change on melting. The statistical interpretation of melting is discussed in greater detail in Section 4.

Empirical correlation of entropies of melting with crystal structure suggests that the entropy of fusion is approximately constant and ranges between 1·5 and 3 entropy units for the following types of compound: crystals composed of simple units, *e.g.*, single atoms or ionic crystals such as NaCl (Table I), metals (Table II), and crystals of certain polyatomic molecules (Table III).

Even quite large molecules can have comparatively low entropies of fusion when the molecular shape is compact so that intermolecular attractions depend essentially on van der Waals forces acting at the molecular surface (cf. the data in Table IV from ref. 2*a*). However, other polyatomic molecules, even when fairly similar in character, have very much larger

TABLE I

Entropies of fusion of crystals composed of simple (spherically symmetrical) units

(V_s = molar volume of crystal just below the m.p.)

Substance.	Ref.	ΔS_f.	T_f(° K.).	$\Delta V_f/V_s$.
Ne . . .	1, 1*a*	3·26	24·6	0·151
Ar . . .	1, 1*a*	3·35	83·6	0·144
Kr . . .	1	3·36	115·95	0·151
Xe . . .	1	3·4	161·3	0·151
NaCl . . .	1	3·35	1073	0·30
KCl . . .	1	3·08	1042	0·23

TABLE II

Melting parameters of metals (cf. ref. 1*b*)

C_p = specific heat at constant pressure. V_s = specific volume of solid.
α = coefficient of expansion.

Metal.	Co-ordination no. in solid.	ΔS_f.	$\Delta V_f/V_s$.	$C_{p\text{ solid}}/T_f$, cals. deg.$^{-2}$, $\times 10^3$.	$C_{p\text{ liquid}}/T_f$, cals. deg.$^{-2}$, $\times 10^3$.	α_{solid}, deg.$^{-1}$, $\times 10^3$.	α_{liquid}, deg.$^{-1}$, $\times 10^3$.
Li .	8	1·53	0·0165	15·3	15·4	0·18	—
Na .	8	1·70	0·025	19·0	20·2	0·22	0·275
K .	8	1·70	0·0255	20·8	22·8	0·25	0·29
Rb .	8	1·68	0·025	23·0	25·2	0·27	0·34
Cs .	8	1·65	0·026	24·4	26·4	0·29	0·37
Cu .	12	2·29	0·0415	5·5	5·7	0·070	0·095
Ag .	12	2·22	0·038	6·05	6·7	0·081	0·105
Au .	12	2·29	0·051	5·5	5·2	0·058	0·069
Mg .	12	2·25	0·041	8·2	8·8	0·110	0·125
Zn .	6 + 6	2·48	0·042	10·2	11·1	0·113	0·154
Cd .	6 + 6	2·57	0·047	11·6	12·0	0·126	0·164
Hg .	6 + 6	2·57	0·037	29·0	28·3	0·171	0·182
Al .	12	2·70	0·060	8·4	8·7	0·099	0·122
Ga .	1 + 6	4·42	−0·032*	21·1	22·5	0·054	0·126
In .	4 + 8	1·82	0·027	15·4	16·4	0·125	—
Tl .	12	1·79	0·032	12·4	11·7	0·126	0·150
Sn .	4 + 2	3·35	0·028	14·2	13·1	0·095	0·115
Pb .	12	1·98	0·035	11·6	12·5	0·12	0·13
Sb .	3 + 3	5·25	−0·0095*	(7·1)	7·9	(0·033)	0·10
Bi .	3 + 3	4·78	−0·0335*	(12·6)	14·0	(0·040)	0·12
Fe .	8	2·01	0·007/0·044	5·8	5·2	—	—
Ni .	12	2·45	—	(4·6)	—	0·057	—

It may be noted that as the co-ordination number increases or the crystal structure becomes more complex the entropy of fusion also increases.

* Cf. Section 2.5, below.

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[1] Data quoted by A. Eucken, *Z. angew. Chem.*, 1942, **55**, 163.

[1a] J. E. Lennard-Jones and A. F. Devonshire, *Proc. Roy. Soc.*, 1939, *A*, **169**, 317; **170**, 464.

[1b] O. Kubackewski, *Trans. Faraday Soc.*, 1949, **45**, 931.

TABLE III

Examples of polyatomic molecules with small entropies of fusion

Substance.	Ref.	ΔS_f.	T_f(° K.).	$\Delta V_f/V_s$.	Transitions in the solid between m.p. and the lowest temperature of measurement.	
					No. of transitions.	Total ΔS_{trans}.
Diatomic						
O_2	1, 1*a*, 2	2·0	54·3	—	two	4·9
N_2	1, 2	2·7	63·1	0·075	one	1·5
CO	1, 2	2·9	68·1	—	one	2·5
HCl	1, 2	3·0	158·9	—	one	2·9
HBr	1, 2	3·1	186·2	—	three	2·1
HI	1, 2	3·1	222·3	—	two	1·8
H_2	1	2·06	13·95	0·12	—	—
Polyatomic						
H_2S	1, 2	3·0	187·6	—	two	4·4
D_2S	1, 2	3·0	187·1	—	two	4·6
H_2Se	1	2·9	207·4	—	two	6·12
D_2Se	1	2·9	206·2	—	two	7·05
PH_3	1	1·97	139·4	0·055	two	5·09
CH_4	1, 2	2·5	90·6	0·087	one	0·8
CH_3D	2	2·4	90·6	—	one	2·6
CD_4	1, 2	2·4	89·2	0·087	two	3·1
SiH_4	1, 2	1·8	88·5	—	one	2·3
CF_4	1, 2	2·0	84·5	—	one	4·6
CCl_4	1, 2	2·3	250·3	0·052	one	4·8
$C(CH_3)_4$	1	3·03	256·5	—	one	4·4

TABLE IV

Entropies of fusion of large compact organic molecules

Substance.	ΔS_f.	T_f(° K.).	Substance.	ΔS_f.	T_f(° K.).
Camphane	3·9	427	Bornylamine	3·3	437
*iso*Camphane	2·0	338	*cyclo*Hexane	2·2	279
Camphene	2·8	324	*cyclo*Hexanol	1·3	298
Pinene hydrochloride	3·0	397	*cyclo*Hexanone	1·0	241
Camphor	3·6	451	*cyclo*Hexyl chloride	3·2	230
Camphorquinone	3·4	472			

entropies of fusion. Table V gives values for some of the simpler polyatomic molecules which show this contrast with the values of ΔS_f in the previous Tables.

A clue to this contrast in behaviour in the melting of crystals of the molecules recorded in Tables III and IV and of the molecules recorded in Table V is found to lie in the differences in mode of heat intake of the solids below the melting point. Solids recorded in Table V generally show "normal" vibrational specific heat–temperature curves with unbroken trend, in contrast with solids recorded in Tables III and IV which generally

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[2] A. R. Ubbelohde, refs. detailed in *Ann. Reports*, 1939, **36**, 159.

TABLE V

Examples of simple polyatomic molecules with entropies of fusion greater than 4 e.u. *per g.-mol. in order of increasing number of atoms* (cf. refs. 1, 2, 2*a*)

Substance.	ΔS_f.	T_f(° K.).	$\Delta V_f/V_s$.	Substance.	ΔS_f.	T_f(° K.).	$\Delta V_f/V_s$.
CO_2 .	9·25	216·5	0·285	C_6H_6	8·44	278·5	0·134
N_2O .	8·58	182·3	—	C_6H_5Br	8·25	242·4	0·10
COS .	8·41	134·3	0·116	$C_6H_5{\cdot}NH_2$	9·44	266·9	0·10
CS_2 .	6·51	161·1	0·067	$C_6H_5{\cdot}CH_3$	8·67	177·9	—
				SF_6	5·32	218	—
Br_2 .	9·66	267	—	(—)-Fenchone . . .	12	279	—
Cl_2 .	8·89	172·1	—	α-Aminocamphoric acid	11·2	171·2	—
$(CN)_2$.	7·90	245·3	—				
HCN .	7·73	259·8	—	*Associated in the liquid phase*			
				H_2O	5·25	273·15	—
C_2H_4 .	7·70	103·97	0·116	$CH_3{\cdot}OH$	4·38	172·2	—
C_2H_6 .	7·60	89·9	0·12	*tert.*-Butyl alcohol .	5·5	295	—
SO_2 .	8·95	197·6	—	N_2H_4	3·73	274·5	—
$CHCl_3$.	10·8	210	—	NH_3	6·91	195·4	—
$SiCl_4$.	9·06	203·4	0·14	NO	5·03	109·4	—

show one or more specific-heat maxima below the melting point. These maxima are associated with transitions in the solid, which are processes whereby the molecules in the solid increase their average symmetry of orientation. For example, oscillation of the molecule between two orientations in the crystal separated by a potential barrier would increase the average symmetry of orientation. In certain cases, the molecules probably rotate at temperatures higher than the transition point. Various types of transition have been discussed.[3] Solids containing polyatomic molecules, which fail to acquire sufficient freedom in the crystal to attain such increased average symmetry, do so on melting. On this basis, the sum of the entropies of transition and fusion for molecules which have specific-heat maxima in the solid should be of the same order as the entropy of fusion when the whole process occurs at the melting point. That this is so may be seen by summing columns 3 and 7 of Table III and comparing the sum with ΔS_f in Table V.

Intermediate energy intakes below the freezing point may lead to rotation only about certain axes in the crystal. In such cases complete spherical symmetry is not attained by the molecules in the solid, and the entropy of fusion has an intermediate value.[4, 5] A detailed discussion of the cryoscopic behaviour of carbon tetrachloride has been given on this basis.[6]

[2a] L. O. Fischer, *Bull. Soc. chim. Belg.*, 1940, **49**, 129.

[3] K. Schäfer, *Z. angew. Chem.*, 1943, **56**, 99 ; L. A. K. Staveley, *Quart. Reviews*, 1949, **3**, 65 ; J. Jaffray, *Ann. Physique*, 1948, **3**, 5. For *cyclo*hexane, see O. Hassel and A. M. Sommerfeldt, *Z. physikal. Chem.*, 1938, **40**, *B*, 391, and ref. 4.

[4] F. W. Thompson and A. R. Ubbelohde, *Trans. Faraday Soc.*, 1950, **46**, 349.

[5] For partial rotation in benzene crystals, see A. Rousset, *Compt. rend.*, 1944, **219**, 485, 546, and A. Kastler and A. Rousset, *Physical Rev.*, 1944, **71**, 455.

[6] A. W. Davidson, W. J. Argersinger, and C. I. Michaelis, *J. Phys. Coll. Chem.*, 1948, **52**, 332.

In view of the theoretical considerations below, it is interesting to determine whether the entropy of fusion per g.-mol. shows any continuing trend with increasing molecular weight. This is most conveniently studied by examining homologous series, in cases where the crystal structure shows the same general features as the molecular weight is increased. One such series is presented by the polymethylene compounds $CH_3\cdot[CH_2]_n\cdot X$. The crystal structure consists essentially of an alignment of molecules with the long chains parallel to one another, and normal to or making a small angle with the crystal planes passing through the ends of the chains.[7]

For this series with X = H, I, etc., there is a trend towards higher entropies as n increases. Entropies and heats of fusion increase uniformly according to the empirical equations :

$$\Delta S_f = S_0 + nS_1 \qquad (1.3)$$

$$\Delta H_f = H_0 + nH_1 \qquad (1.4)$$

This observation implies that the freezing point

$$T_f = \Delta H_f/\Delta S_f \qquad (1.5)$$

must converge to a limiting value or "convergence temperature", $T_{\text{lim.}} = H_1/S_1$, above which the substance is liquid however great the molecular weight. For normal paraffins empirical equations proposed are :[8, 9]

$$T_f = (0{\cdot}6085n - 1{\cdot}75)/(0{\cdot}001491n + 0{\cdot}00404)$$

or

$$1/T_f = 0{\cdot}002395 + 0{\cdot}0171/n$$

Calculated convergence temperatures are illustrated in Table VI.

TABLE VI

Convergence freezing points of polymethylene compounds

X.	T_f(° K.).
H (paraffins) . .	408—417·5 (according to formula)
CO_2H (n even). .	389
CO_2H (n odd) . .	385

When X is CO_2H,[10] acids with odd and even members for n fall on separate curves, owing to a transition below the freezing point in the odd-membered series.

Similar empirical equations have not yet been obtained for other homologous series, which are less easily obtained synthetically and for which the crystal structure depends in a more complex way on n. For polyenes [11] it is interesting to note [11a] that, whereas ΔH_f probably increases

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[7] A. Müller, *Prcc. Roy. Soc.*, 1928, *A*, **120**, 437 ; 1930, *A*, **127**, 417.

[8] W. E. Garner, K. Van Bibber, and A. M. King, *J.*, 1931, 1533.

[9] K. H. Meyer and A. A. van der Wyk, *Helv. Chim. Acta,* 1937, **20**, 1313.

[10] W. E. Garner and F. C. Randall, *J.*, 1924, **125**, 881.

[11] R. Kuhn and C. Grundmann, *Ber.*, 1936, **69**, 224.

[11a] A. R. Ubbelohde, *Ann. Reports*, 1940, **37**, 172.

uniformly with increasing n, ΔS_f remains small, so that much higher melting points can be attained. On a semi-empirical basis the origin of this difference has been attributed to the increased freedom of the flexible chains of paraffin derivatives on melting. Conjugation stiffens chains in the polyenes and lessens the gain of freedom on melting.

A limiting case for the melting of homologous series is presented by certain polymers. On the basis of X-ray data [12] and from determinations of densities [13] and heat capacities [14] as a function of temperature it seems likely that, when the molecules of a polymer are flexible and cross linking can be neglected, freezing can be described in terms of the mutual alignment of *portions* of adjacent molecules. Melting takes place over quite a wide range of temperatures, and within this range any particular chain molecule may traverse several successive " crystalline " and " amorphous " or liquid regions. The notion that such molecules melt in more or less independent segments has been put forward to explain the entropies and heats of fusion of homologues (for refs. see ref. 11*a*). Theories of the range of melting have been proposed by various authors.[2, 15, 16, 17]

Attempts have been made to discuss the general relationship between heat of fusion and melting point for different molecular structures, but definite conclusions appear to be hampered by values of doubtful accuracy.[18, 18a]

1.2 Volume Changes on Fusion.—As has been stated above, the magnitude of the volume change on fusion is less easy to systematise than the entropy change. Volume changes are, however, significant in the molecular theory of melting which deals with the entropy changes resulting from lattice flaws (section 6). Values of $\Delta V_f/V_s$ are illustrated in some of the Tables above.

2. Thermodynamic Properties of the Solid and Liquid Phases in the Immediate Neighbourhood of the Melting Point

A study of such properties as the specific heat and thermal expansion of the two phases in the immediate neighbourhood of the transition point can be informative in two different ways. In so far as these properties are much the same for the liquid a few degrees above the melting point as for the solid a few degrees below the melting point, they lend support to the molecular picture (see below) according to which a liquid near its freezing point is to be regarded as quasi-crystalline ; but very near to the actual melting point, the values for the solid of

$$C_p = (\partial H/\partial T)_p \qquad (2.1)$$

and

$$\alpha_p = (1/V)(\partial V/\partial T)_p \qquad (2.2)$$

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[12] C. W. Bunn and T. C. Alcock, *Trans. Faraday Soc.*, 1945, **41**, 317.

[13] E. Hunter and W. G. Oaks, *ibid.*, p. 49.

[14] H. C. Raine, R. B. Richards, and H. Ryder, *ibid.*, p. 56.

[15] E. M. Frith and R. F. Tuckett, *ibid.*, 1944, **40**, 251.

[16] P. Flory, *J. Chem. Physics*, 1949, **17**, 223 (where earlier references are given).

[17] R. B. Richards, *Trans. Faraday Soc.*, 1945, **41**, 127.

[18] J. Pirsch, *Ber.*, 1937, **70**, 12. [18a] *Idem, ibid.*, 1936, **69**, 1328.

rise steeply for certain solids, as if part of the volume change and heat change on melting took place in a "premelting" region.

2.1 Interrelation of the Solid and Liquid Phases on Melting.—According to the classical theory of phase transitions, equilibrium between two phases is reached at temperatures and pressures where the phases S and L attain the same free energy per unit mass, $G_S = G_L$ say. Diagrammatically, a plot of the free energy G against temperature at constant pressure should give quite distinct curves for the two phases, with intersection at a sharp angle at the transition point. Classical theory does not explain any singularity of behaviour on either curve around the melting point (cf. Fig. 1)..

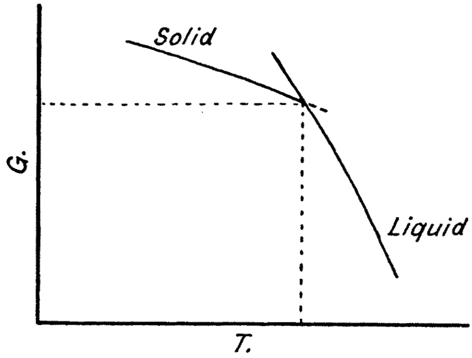

FIG. 1

This classical theory is not wholly adequate in describing melting for two reasons :

(a) Experimentally, it has proved possible to prolong the G–T curve for the liquid, below the freezing point (supercooling). However, no unequivocal proof has been obtained of any prolongation of the G–T curve of the solid by superheating above the freezing point. The experimental G_S–T curve stops in this region (cf. Fig. 2).

(b) Monophase premelting (see below) implies that the G_S–T curve begins to bend round as it approaches the melting point. As long as a distinction can be made between solid and liquid at the freezing point, the G_S curve must meet the G_L curve at a finite angle, but as premelting becomes more important the angle of intersection approaches zero. Diagrammatically the relationship is as shown in Fig. 2.

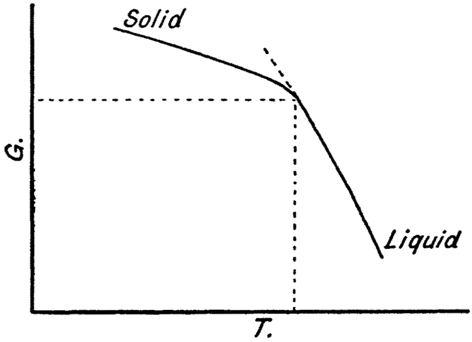

FIG. 2

Formally, in the classical theory of phase transitions the heat of transition is related to the G–T curves by the Gibbs–Helmholtz equation :

$$G_1 - H_1 = T\,\mathrm{d}G_1/\mathrm{d}T$$
$$G_2 - H_2 = T\,\mathrm{d}G_2/\mathrm{d}T$$

At the freezing point $G_1 = G_2$ and by subtraction

$$\Delta H_f = T(\mathrm{d}G_1/\mathrm{d}T - \mathrm{d}G_2/\mathrm{d}T)$$

The difference between the tangents at the point of intersection gives $\Delta H_f/T$.

However, if there is monophase premelting in the solid, this implies an abnormally high specific heat C_p immediately below the freezing point. Since $C_{P_S} = - T\, \partial^2 G_S/\partial T^2$, abnormally high values of C_{P_S} must mean a curling round of the G_S curve as the solid phase approaches the melting point, as illustrated in Fig. 2.

This behaviour is very similar to the C_p–T curves in other thermodynamic transitions taking place wholly in the solid [3] and emphasises the similarity between the solid and the liquid phase.

2.2 Thermodynamic Evidence for the Quasi-crystalline Structure of Liquids within a Few Degrees of the Melting Point.—As an empirical fact, it is interesting to note that the values of C_p a few degrees below the melting point, for the solid, agree in many cases approximately with values a few degrees above the melting point for the liquid (ref. 11 and cf. Table II for metals). This indicates that the thermal molecular processes responsible for heat intake are much the same for the two phases, a fact which has to be explained in any molecular theory of melting. Unfortunately, data are limited owing to the comparatively small number of calorimetric and dilatometric observations in the immediate neighbourhood of the melting point.

The properties of supercooled liquids are of considerable interest in this connection. If the solid and liquid phases have entirely independent p, V, T curves, the supercooled liquids should not show any break in properties at the freezing point.

In a number of cases measurements of density in the *supercooled liquid* show no major break at the freezing point when the liquid is associated—for instance, liquid resorcinol.[19] For liquids which solidify to glasses,[20] a rapid change in the properties of the supercooled liquid occurs in the temperature region where the viscosity η reaches about 10^{13} poises. Such a break is generally far removed from the melting point. However, in the case of supercooled liquid diphenyl ether it has recently been claimed [21] that a plot of $\log \eta$ against $1/T$ shows a break at the melting point. Similar effects are claimed for *m*-chloronitrobenzene, and for sodium and potassium.[21a]

If the break in the η–T curve of the liquid can be correlated with any marked change in the slope of the p, V, T curves, this would provide further evidence for the interrelation of the solid and the liquid phase near the melting point. However, the interpretation of the observations is not yet clear. When a liquid is capable of being supercooled below the freezing point, this must imply a considerable molecular rearrangement on formation of the crystals. The break in the η–T curve can hardly be attributed to this kind of rearrangement in the liquid since if it occurs spontaneously it is difficult to see how supercooling can persist. An empirical correlation has been proposed between the molar entropy of fusion and the molar

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[19] J. M. Robertson and A. R. Ubbelohde, *Proc. Roy. Soc.*, 1938, *A*, **167**, 138.

[20] G. O. Jones, *Reports Progr. Physics*, 1949, **12**, 133.

[21] C. Dodd and Hu Pak Mi, *Proc. Physical Soc.*, 1949, **62**, 454.

[21a] Y. S. Chiong, *Proc. Roy. Soc.*, 1936, *A*, **157**, 264.

difference ΔC in specific heats between solids and liquids[22] for simple solids such as A, H_2, N_2, O_2, Cl_2, Cd, and Sn, namely:

$$\Delta S_f = \Delta C$$

For more complicated solids a second parameter must be introduced in the formula for ΔS_f.

2.3 Thermodynamic Evidence for Premelting.—When a calorimetrically determined specific-heat curve is carried through the freezing point, so as to include the properties of the liquid, a sharp increase in heat content is generally observed just below the freezing point. This is conveniently termed " premelting ". A corresponding volume anomaly may be observed by dilatometry. One rather trivial cause for the steep rise appears to have been first discussed by H. C. Dickinson and N. S. Osborne,[23] who pointed out that, if the liquid contains a small amount of an impurity *not soluble* in the solid phase, then, on freezing, the concentration of the impurity in the liquid becomes progressively enhanced as more solid separates. As a result, the temperature of equilibrium $(T_f - \Delta T)$ between solid and liquid becomes progressively lower as more solid freezes. On the assumption that normal freezing-point depression laws hold, the solid freezes over a range of temperatures such that the fraction x melted at $(T_f - \Delta T)$ is given by the equation

$$\Delta T/\Delta T_{\text{lim.}} = 1/x \quad . \quad . \quad . \quad . \quad (2.3)$$

This means that part of the latent heat of fusion is taken up below the limiting freezing point $(T_f - \Delta T_{\text{lim.}})$ when the whole mass is just liquid. The additional specific heat ΔC due to this cause at the temperature $(T_f - \Delta T)$ is $\Delta C = \Delta H_f(\mathrm{d}x/\mathrm{d}T)$, *i.e.*,

$$\Delta C/\Delta H_f = \Delta T_{\text{lim.}}/\Delta T^2 \quad . \quad . \quad . \quad . \quad (2.4)$$

There can be no anomaly in specific heat *above* T_f due to this effect. Similarly, the anomalous coefficient of expansion due to this effect would be

$$\mathrm{d}V/\mathrm{d}T = \Delta V_f(\mathrm{d}x/\mathrm{d}T)$$

or

$$(\mathrm{d}V/\mathrm{d}T)/\Delta V_f = \Delta T_{\text{lim.}}/\Delta T^2 \quad . \quad . \quad . \quad (2.5)$$

A recent application of the assumption that premelting phenomena are due to impurities soluble in the liquid but not in the solid phase has been worked out for the hydrocarbons *cyclo*pentane, methyl*cyclo*pentane, and methyl*cyclo*hexane. On the assumption that the observed increase in specific heat just below the melting point is caused solely by the formation of solution, premelting curves have been calculated[24] (cf. Table VII).

Actually the limiting freezing point observed does not agree with the value extrapolated on the above hypothesis, indicating that factors other than heterophase impurities contribute to the high specific heat below the freezing point, or that Raoult's law does not apply rigorously.

As equations (2.4) and (2.5) illustrate, such heterophase segregation of

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[22] S. Procopiu, *Compt. rend.*, 1948, **226**, 1001.

[23] *Bull. U.S. Bur. Stand.*, 1915, **12**, 69.

[24] D. R. Douslin and H. M. Huffman, *J. Amer. Chem. Soc.*, 1946, **68**, 173.

TABLE VII

Computed premelting curves

*cyclo*Pentane.		Methyl*cyclo*pentane.		Methyl*cyclo*hexane.	
% melted.	$(T_f - \Delta T)$, ° K.	% melted.	$(T_f - \Delta T)$, ° K.	% melted.	$(T_f - \Delta T)$, ° K.
37·2	179·666°	21·5	130·660°	9·5	146·552°
59·5	179·678	51·1	130·689	28·0	146·565
90·6	179·690	70·5	130·699	75·7	146·570
100	179·713 (extrap.)	89·9	130·705	94·2	146·573
		100	130·726 (extrap.)		

impurities in the first part of the solid to melt or the last part of a liquid to freeze can make a large numerical contribution to the specific heat and coefficient of expansion immediately below the limiting freezing point, and can also affect other properties of the solid (see section 3). However, in certain systems premelting phenomena are observed, both in the solid below the freezing point and in the liquid immediately above the freezing point, which cannot be attributed to the segregation of impurities *in the liquid phase*. One example of " monophase " premelting is presented by the paraffins $CH_3{\cdot}[CH_2]_n{\cdot}CH_3$ of medium and high chain length, where any likely impurities would remain in solid solution, and for which deliberate addition of likely impurities does not substantially affect the specific-heat curves. Fig. 3 gives the type of curve obtained.[25] Calorimetric evidence for premelting with carefully purified materials also includes experiments on trichloroethane [26] and dimethylacetylene.[27]

Similar premelting anomalies have been observed for zinc and cadmium by dilatometry.[28] The most likely interpretation is that, for certain types of crystal lattice, flaws, which ultimately lead to greater stability of the liquid phase (cf. section 6), make an important contribution to the heat content and volume of the solid below the melting point. Residual order in the liquid in the immediate neighbourhood of the melting point may likewise make a contribution to the heat content and volume of the liquid. For such solids, freezing may be compared with the aggregation of micelles into a gel, with the boundaries between the micelles gradually " squeezing out " lattice defects as the temperature falls (cf. also J. W. Oldham and A. R. Ubbelohde [29]).

Measurements of the thermal conductivity of various organic materials likewise indicate anomalous behaviour near the melting point, which is most

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[25] A. R. Ubbelohde, *Trans. Faraday Soc.*, 1938, **34,** 289. Dilatometric observations have been made by A. Van Hook and L. Silver, *J. Chem. Physics*, 1942, **10,** 686.

[26] T. R. Rubin, B. H. Levedahl, and D. M. Yost, *J. Amer. Chem. Soc.*, 1944, **66,** 279.

[27] D. M. Yost, D. W. Osborne, and C. S. Garner, *ibid.*, 1941, **63,** 3492.

[28] W. F. Hachkovsky and P. G. Strelkov, *Nature*, 1937, **139,** 715.

[29] J. W. Oldham and A. R. Ubbelohde, *Proc. Roy. Soc.*, 1940, *A*, **176,** 50.

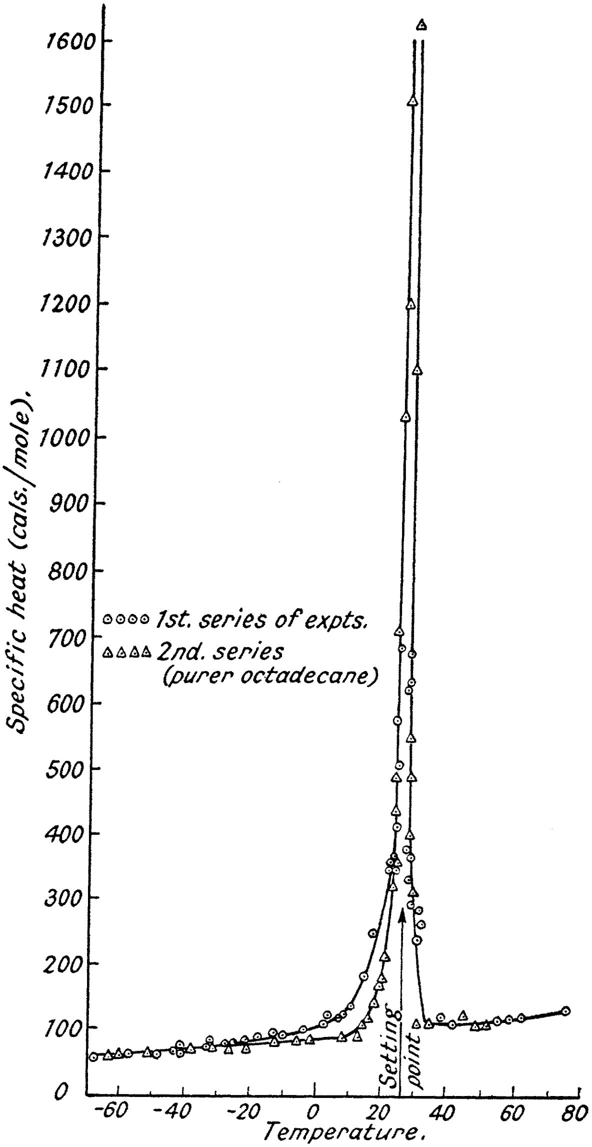

FIG. 3

Molar specific heat of octadecane at various temperatures. The first series of points refers to standard octadecane, the second series to standard octadecane purified by molecular distillation, and also to a sample prepared by a modified Grignard reaction. The setting point is marked with the arrow.

[*Reproduced by permission from* Trans. Faraday Soc., 1938, **34**, 292.]

readily accounted for on the hypothesis of a partial breakdown of the lattice structure by premelting just below the freezing point and by residual structure in the liquid just above the freezing point.[30] Elasticity moduli of single crystals, *e.g.*, of sodium chloride, show a steep decrease as the freezing point is approached.[31] Indirect evidence of monophase premelting includes observations such as the absence of a break in a solubility curve on melting of the solid.[32]

Monophase premelting effects are probably of widespread occurrence and are particularly evident in crystals where the molar entropy of fusion is large. As might be expected on account of the very high molecular weights, monophase premelting is of dominant importance for polymers such as " Polythene ".[15, 17, 33]

2.4 Cryoscopic Evaluation of Entropies of Fusion.—It is important to recognise that the cryoscopic evaluation of entropies of fusion from measured freezing-point depressions gives a series of values of ΔS_f which need not correspond exactly with calorimetric entropies of fusion evaluated for the pure substances. Two major factors which may lead to a significant difference in certain cases are :

(i) If the specific heats of the solid and the liquid are abnormally high around the freezing point of the pure solid $(T_f)_{n_2=0}$, the difference in the heat content $\Delta H_f = H_{\text{liq.}} - H_{\text{solid}}$ may change to an appreciable extent as the freezing point is lowered by the addition of a second component at a concentration n_2 (cf. ref. 29).

(ii) If the second component enters into solid solution this may alter ΔH_f, particularly if the orientational entropy is affected (cf. ref. 4 which includes references to methods of cryoscopic evaluation of ΔS_f). Empirical observations on the change in freezing-point depression with concentration of solute have been discussed for solids such as camphor and benzene.[34]

When the molecular configuration of the solute molecule lies sufficiently close to that of the solvent, formation of solid solutions can be so extensive that no *depression* of freezing point of the lower-melting by the higher-melting substance is observed. The solidus curve can approximate fairly closely to a straight line joining the freezing points of the two pure substances. Examples include *n*-hexadecane and *n*-hexadec-1-ene (cf. refs. in ref. 29) and a wide range of pairs of organic molecules with high symmetry.[35, 18a] Other molecules have been described which form extensive solid solutions.[36] Where ordered solid solutions are formed, the phase-rule diagram indicates the formation of a crystal compound, as for bromocamphor (cf. refs. in ref. 36).

2.5 Effect of Pressure on the Freezing Point.—Within recent years a

[30] J. H. Read and D. M. G. Lloyd, *Trans. Faraday Soc.*, 1948, **44**, 721.

[31] Ll. Hunter and S. Siegel, *Physical Rev.*, 1942, **61**, 84.

[32] Solubility curve of octanoic acid in water, F. H. Constable and S. Tegul, *Nature*, 1946, **157**, 735.

[33] P. J. Flory, *J. Chem. Physics*, 1947, **15**, 684 ; 1949, **17**, 223.

[34] A. V. Brancker, S. J. Leach, and V. A. Daniels, *Nature*, 1944, **153**, 407.

[35] L. O. Fischer, *Bull. Soc. chim. Belg.*, 1940, **49**, 129.

[36] A. Kofler *Z. Elektrochem.*, 1944, **50**, 104.

considerable number of freezing parameters have been determined [37] up to 50,000 kg./cm.^{2} The results are of interest in connection with a number of fundamental problems of melting and crystal structure.

(i) The values of some typical freezing parameters are listed in Table VIII.

TABLE VIII

P, kg./cm.^{2}.	dT_f/dP.	ΔH_f, kg.cm./g.	ΔS_f, kg.cm./g./deg.	Substance.
15,000 . . .	0·0064	1850	6·93	Ethyl alcohol
30,000 . . .	0·0055	2700	7·60	
15,000 . . .	0·0068	2050	6·35	n-Butyl alcohol
30,000 . . .	0·0047	3040	7·49	
15,000 . . .	0·0062	845	3·03	Ethyl bromide
30,000 . . .	0·0039	996	2·81	
15,000 . . .	0·0079	890	2·90	n-Propyl bromide
30,000 . . .	0·0062	1040	2·52	
15,000 . . .	0·0088	900	2·80	Carbon disulphide
30,000 . . .	0·0078	1100	2·50	

Whereas ΔH_f increases with increasing compression in all the examples given, ΔS_f decreases for non-hydrogen-bonded molecules but increases for the alcohols. This suggests that the energy required to produce flaws in the solid always increases with increasing compression (cf. section 6). But apparently compression decreases the difference in order between solid and liquid, for " normal " molecules, and increases it when there are directed bonds, such as hydrogen bonds, in the solid and the liquid. In view of the importance of these parameters for correlation of the configurational entropy of melting with molecular structure (section 6), extension of these observations should eventually give valuable theoretical information on melting.

(ii) As the compression is increased, the temperature below which a substance is solid normally rises. By analogy with the critical boiling point for the transition liquid ⟶ gas, it might be expected that the transition solid ⟶ liquid would become continuous above a certain temperature, *i.e.*, that no solid could exist above a " critical melting point ". But no definitive evidence has so far been obtained for such a limitation to the phase region for the solid state, which would have important geophysical implications.[38, 39, 48b, 49b] Observations on the melting of helium may

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[37] P. W. Bridgman, *Amer. Acad. Sci.*, 1942, **74**, 399 ; *Amer. Scientist*, 1943, **31**, 23 ; *Rev. Mod. Physics*, 1946, **18**, 27.

[38] Cf. P. W. Bridgman, *Amer. Scientist*, 1943, **31**, 1.

[39] J. E. Lennard-Jones and A. F. Devonshire, *Proc. Roy. Soc.*, (*a*) 1939, *A*, **169**, 317 ; (*b*) **170**, 464.

permit investigation of the possibility of a critical melting point over a wider effective temperature range.[40] Only four common substances have been found which contract on melting, *viz.*, bismuth, antimony, gallium, and water [41] (cf. Table II). It seems likely that this kind of change is associated with directed bonds in the crystal which form a framework that undergoes partial collapse on melting (cf. ref. 19).

2.6 Kinetics of Melting.—As has been indicated in section 2.1, the forward and the reverse reaction in the rate processes Crystal $\rightleftarrows$ Melt are only balanced when both phases are present. Under these conditions the change from melt to crystal takes place at the crystal face by a " two-dimensional " process.[42, 43, 44] The fact that a crystal cannot be readily superheated implies that this rate process proceeds rapidly and without difficulty at the surface of a solid. But in the absence of a crystal nucleus the reverse process of spontaneous crystallisation may be delayed for many days. This has been attributed [43] to the requirement for a " co-operative fluctuation " in the melt for production of a crystal nucleus. Such co-operative fluctuations have a very low probability of occurrence because of the decrease of entropy involved. A further consequence is that when crystallisation occurs from the melt spontaneously in the absence of nuclei, the *least* stable of a number of possible polymorphs tends to be produced most readily. This " law of successive states " is explained [43] on the basis that formation of a less stable solid involves smaller entropy fluctuations relative to the melt.

2.6.1 *Persistence of Crystal Nuclei in the Melt.* Various discussions of the kinetics of melting and crystallisation indicate that growth of a crystal by deposition of layers of atoms or molecules on preformed crystals is quite distinct from the production of fresh crystallisation nuclei.

Although it has not proved possible to superheat a crystal appreciably without melting occurring, claims that a small but definite concentration of " crystallisation nuclei " persist in the melt are based on a large if somewhat vague body of evidence. Such crystallisation nuclei dissolved in the melt cannot, apparently, pass continuously into the solid but must be separated from it by a region of metastable states. Though such nuclei are important for theories of crystal growth the experimental evidence is as yet too indeterminate to provide much information about melting.[42, 45, 46 ; also refs. in ref. 11a]

2.7 Melting in Adsorbed Layers.—2.7.1 *Melting of Liquids Adsorbed in Capillaries.* Various experiments indicate that the absorption of a liquid in a sorbent with capillaries leads to a lowering of the melting point which

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[40] F. A. Holland, J. A. W. Huggill, G. O. Jones, and F. E. Simon, *Nature*, 1950, **165**, 147.

[41] P. W. Bridgman, *Amer. J. Sci.*, 1945, **243**, *A*, 90.

[42] Faraday Soc. Discussion, " Crystal Growth ", 1949, **5**.

[43] A. R. Ubbelohde, *Trans. Faraday Soc.*, 1937, **33**, 1198.

[44] S. S. Penner, *J. Phys. Coll. Chem.*, 1948, **52**, 949.

[45] " Supersaturation limits of solutions ", R. Gopal, *J. Indian Chem. Soc.*, 1948, **25**, 87, 443.

[46] L. G. Carpenter, L. J. C. Connell, and A. B. Osborn, *Nature*, 1949, **163**, 23.

may extend over several degrees.[47, 48] The effect might in principle be correlated with the change of internal pressure in a capillary, but in addition adsorption may stabilise the liquid relative to the solid phase by imposing a preferred orientation on the molecules in the liquid phase. For example, studies of the dielectric constant of ethyl chloride adsorbed on silica gel show that the molecules have their rotation hindered in the adsorbed layer.[49]

2.7.2 *Melting of Surface Films on Liquids.* Application of the Langmuir–Harkins–Adam film-pressure technique has revealed that in a limited number of cases films which are " rigid " below a certain temperature become " liquid " above a " melting point ". Such " melting points " are not far from, but have not been quantitatively related with, the melting points of the bulk phases.

Since molecules in the films are less constrained than in a three-dimensional crystal, melting might be expected at a lower temperature (but see ref. 50). Actually the lessened constraint may decrease both ΔH_f and ΔS_f and no unique difference of sign between T_f for the crystal and for the film can be predicted. Structural observations (cf. ref. 11*a*) suggest that in the crystals of long-chain compounds " lateral " melting with a large increase of lateral freedom appears to precede " long-spacing " melting. Lateral packing in unimolecular films of long-chain compounds is closely similar to the packing in bulk crystals, so that much the same melting phenomena might be expected.

2.7.3 *Grain Boundary Melting.* It is not yet clear whether the earlier melting at the boundaries of crystal grains, *e.g.*, in very pure aluminium,[51] is caused by segregation of impurities at these boundaries, or whether the more disordered solid in this region passes into a liquid at a lower temperature than the more highly ordered atoms at the centres of the grains.

3. Other Properties of the Solid and Liquid near the Melting Point in Relation to Molecular Structure

As with other transitions in the solid state, the origin of the energy intake on melting has been investigated in special cases by making use of a whole range of molecular properties, in addition to the thermodynamic parameters described in sections 1 and 2.

3.1 *X*-Ray Investigations on the Structure of Solid and Liquid near the Melting Point.—3.1.1 For crystals composed of arrays of single atoms, *X*-ray studies show that in the liquid the molecules have approximately the same close packing as in the solid (short-range order) but that there is

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[47] H. Reiss and I. B. Wilson, *J. Colloid Sci.*, 1948, **3**, 551.

[48] (*a*) W. T. Richards, *J. Amer. Chem. Soc.*, 1932, **54**, 479; (*b*) P. W. Bridgman, *Physical Rev.*, 1914, **3**, 126, 153; 1915, **6**, 1, 94; 1934, **46**, 930.

[49] (*a*) R. McIntosh, H. S. Johnson, N. Hollies, and L. McLeod, *Canadian J. Res.*, 1947, **25**, *B*, 566; (*b*) F. Simon, M. Ruhemann, and W. A. Edwards, *Z. physikal. Chem.*, 1929, **2**, *B*, 340; 1930, **6**, *B*, 62, 331; Simon, *Trans. Faraday Soc.*, 1937, **33**, 65.

[50] N. K. Adam, " Physics and Chemistry of Surfaces ", Oxford, 1941, p. 55.

[51] G. Chaudron, P. Lacombe, and N. Yannaquis, *Compt. rend.*, 1948, **226**, 1372.

no evidence of long-range order in a liquid (for recent studies of liquid metals see refs. 52 and 53).

Other evidence on premelting suggests that if X-ray measurements on atomic liquids were made sufficiently near to the freezing point, rudimentary order of longer range might be observed even in the liquid. Careful temperature control and monochromatic radiation would be required, and such experiments do not appear to have been reported.

3.1.2 For crystals made up of more complex molecules, X-ray evidence frequently indicates an approximation of the structure of the solid to that of the liquid, as the melting point is approached (cf. ref. 11*a*, and refs. for *cyclo*hexane in ref. 4). In the case of sodium palmitate the solid "melts" so far as lateral packing is concerned whilst it preserves the long spacing to higher temperatures.[54] Studies of the melt really near the freezing point would also be of interest, but do not appear to have been carried out.

3.2 Mechanical Properties of the Solid and the Liquid near the Melting Point.—A description of the transition from the solid to the liquid state in terms of the change in mechanical properties is complementary to the description in terms of the change in thermodynamic properties. In this connection the most significant mechanical property is the rigidity. Whereas solids can assume finite shear strains, in liquids the shear stresses F are relaxed at a rate determined by their viscosity, according to the Maxwell relationship, where E is the modulus of elasticity and S is the strain (cf. ref. 20), τ is the relaxation time :

$$\frac{dF}{dt} = E\frac{ds}{dt} - \frac{F}{\tau}$$

Empirical formulæ have been proposed for the temperature coefficient of shear strain of solids, according to which the rigidity modulus μ vanishes at the melting point, for example,

$$\mu = \mu_0[1 - (T/T_f)^2]$$

(refs. in ref. 11*a*, p. 174).

Studies on the viscosity of melts which suggest some survival of crystalline structure very near the melting point have been referred to in section 2.2. The temperature coefficient of viscosity of mesomorphic liquids is also of interest in giving information about the structure near the melting point.[54a]

No discontinuity is apparent in the compressibility of a substance on melting.[37]

3.2.1 *Acoustic Vibrations in Solid and Liquid Phases.* Closely related to the postulated change in mechanical rigidity, there should be a difference in the type of acoustic vibrations which can be present in the liquid, com-

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[52] H. Hendus, *Naturforsch.*, 1947, **2a**, 505.

[53] O. Kubackewski, *Trans. Faraday Soc.*, 1949, **45**, 931.

[54] H. Nordsieck, F. B. Rosevear, and R. H. Ferguson, *J. Chem. Physics*, 1948, **16**, 175.

[54a] R. Schenck, *Z. physikal. Chem.*, 1898, **27**, 167 ; cf. the second report on Viscosity and Plasticity prepared by the Committee for the Study of Viscosity of the Academy of Sciences at Amsterdam.

pared with those which are present in the solid. However, the fact that C_p for the liquid a few degrees above the melting point lies close to the value of C_p for the solid a few degrees below the melting point (see above) suggests that no very clear theoretical distinction can be made between solid and liquid on the basis of different acoustic vibrations (cf. refs. 1 and 11*a*).

3.3 Scattering of Light by Solid and Liquid Phases.—For an increasing number of crystals, studies on infra-red absorption or Raman scattering give evidence about the structural changes which occur on melting. These are of two kinds.

(*a*) The orientations assumed by individual molecules show increased freedom on melting, and frequently in the premelting region.

An illustration of this change is presented by observations on single crystals of benzene, in which a limited number of Raman lines of long wave-length (35—100 cm.$^{-1}$) attributed to a vibration of the molecules in the crystal *disappear* on melting.[55]

(*b*) For molecules capable of changing their shape by intramolecular rotation, configurational isomers may be formed in the liquid, on melting, whereas the crystal structure may incorporate only one isomer. Evidence in favour of such a process has been obtained by comparing the Raman spectra of solid and liquid polymethylene hydrocarbons (*n*-paraffins). When the solid melts, *additional* Raman lines appear in the liquid phase. These have been attributed to " rotational " isomerism. In the solid only the stretched zigzag form of the molecule is present, but on melting a fraction of the molecules isomerise by rotation about C–C bonds to give more-or-less coiled molecules.[56]

An analogous possibility has been tentatively suggested for *cyclo*hexane.[57]

(*c*) The Brillouin scattering of monochromatic light by stationary waves in the medium gives a broadened central line for gases, a doublet for solids, and both a doublet and a central line for liquids.[58] Light scattering attributed to rotation of molecules in crystals has been discussed,[59] but the correlation with melting is not yet very complete.

3.4 Dielectric Constant and Dielectric Losses in the Losses in the Solid and Liquid.—When the molecules in a crystal are carriers of permanent dipoles, the onset of rotation or of increased freedom of orientation in the solid is normally accompanied by a large increase in the dielectric constant. For dipole carriers where there is no rotational anomaly in the solid, the increase in dielectric constant would be expected at the melting point. Comparatively few investigations have been reported of measurements taken through the melting point. However, studies on the dielectric constant and dielectric relaxation of long-chain molecules in crystals, either

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[55] A. Frühling, *J. Physique et Radium*, 1948, **9**, 88.

[56] J. G. Aston, D. H. Rank, N. Sheppard, and G. J. Szasz, *J. Amer. Chem. Soc.*, 1948, **70**, 3525 ; D. H. Rank, N. Sheppard, and G. J. Szasz, *J. Chem. Physics*, 1949, **17**, 83 ; N. Sheppard and G. J. Szasz, *ibid.*, pp. 86, 93 ; San-ichiro Mizushima and Hiroatsu Okazaki, *J. Amer. Chem. Soc.*, 1949, **71**, 3411.

[57] F. W. Thompson and A. R. Ubbelohde, see ref. 4.

[58] P. Debye, *Z. Elektrochem.*, 1939, **45**, 174.

[59] E. Gross and A. Raskin, *Acta Physicochim. U.R.S.S.*, 1942, **17**, 127.

pure[60] or in solid solution,[61] give evidence for the increased torsional or rotational mobility about the long axis of the chain which accompanies other premelting phenomena.

3.5 Diamagnetic Susceptibility.—The diamagnetic susceptibility of many organic substances increases by 5% or more on melting, usually with evidence of premelting phenomena[62] (cf. Fig. 4). No definitive explanation of this effect has been given in terms of the change of structure, though it appears to indicate some mutual interference of the bound electron orbits of the molecules in the crystal. This interference is lessened in the liquid. In metals the conduction electrons make an additional contribution to the atomic magnetism which may be positive or negative. A decrease in diamagnetism is observed on melting of metals such as zinc, tin (grey), lead, gallium, or bismuth, and an increase for gold and germanium.[63] This must be correlated with changes of co-ordination number of the metal atoms on passing from solid to liquid,[52] but no detailed explanation has been proposed.

When the molecules pass through a "liquid-crystal" phase on melting, intermediate between the solid and the isotropic liquid, applied magnetic fields can orient the anisotropic molecular clusters in the nematic phase. For example, in *p*-azoxyanisole the diamagnetism falls through a minimum and then rises again, to the temperature where the liquid becomes isotropic. This is because in the liquid the long dimension of the molecule which is least diamagnetic orients along the lines of force.[64]

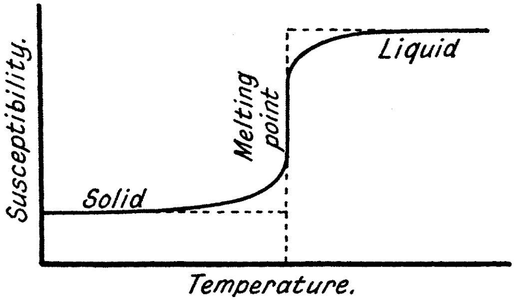

FIG. 4

General relationship between susceptibility and temperature for a diamagnetic substance in the neighbourhood of the melting point. The change in susceptibility may amount to 5% or more.

3.6 Ionic Conductivity.—For ionic crystals, the big jump in ionic conductivity which is generally observed on melting is illustrated in Table IX. σ_L is the conductivity of the liquid and σ_S that of the solid.

This jump in conductivity is directly associated with the large increase in the number of lattice flaws on melting, and with the fact that the expansion

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[60] A. Müller, *Proc. Roy. Soc.*, 1937, *A*, **158**, 403 ; 1938, *A*, **166**, 316 ; 1940, *A*, **174**, 137.

[61] V. Daniel, *Nature*, 1949, **163**, 725.

[62] A. E. Oxley, *Phil. Trans.*, 1914, **214**, 109 ; 1915, **215**, 79 ; 1920, **220**, 247 ; *Science Progr.*, 1920, **14**, 588 ; B. Cabrera and H. Fahlenbrach, *Z. Physik*, 1933, **85**, 568 ; 1934, **89**, 682 ; B. Cabrera, *J. Chim. physique*, 1940, **37**, 86.

[63] K. Honda, *Ann. Physique*, 1910, **32**, 1027 ; M. Owen, *ibid.*, 1912, **37**, 657 ; K. Honda and T. Ishiwara, *Sci. Rep. Tohoku Imp. Univ.*, 1915, **4**, 215.

[64] C. Mauguin, *Compt. rend.*, 1911, **152**, 1680 ; G. Föex, *J. Physique et Radium*, 1929, **10**, 421 ; *Trans. Faraday Soc.*, 1933, **29**, 958.

TABLE IX

Conductivity change on melting of ionic crystals [$\sigma = A \exp.(-E/\boldsymbol{k}T)$]

Substance.	σ_L/σ_S.	A_{solid}.	E_{solid}, $\times 10^{13}$ ergs/g.-mol.	A_{melt}.	E_{melt}, $\times 10^{13}$ ergs/g.-mol.
KCl	10,000	2×10^7	36·9	6·5	1·6
NaCl	3000	$9{\cdot}5 \times 10^4$	27·5	7·4	1·1
KBr	7000	1×10^6	31·3	6·3	1·9
AgCl	30	$2{\cdot}8 \times 10^3$	11·2	6·8	0·5
AgBr	20	$8{\cdot}5 \times 10^3$	10·6	4·9	0·4
$PbCl_2$	900	1·4	7·4	28·6	3·3

References are given in ref. 65 and 65*a*.

in volume on fusion reduces the activation energy for migration of the ions (cf. columns 3 and 6).

3.7 Electrical Conductivity.—In contrast with ionic conductors, for

TABLE X

Effect of melting on the specific conductivity of metals

Section of ref. 66.	Metal.	Crystal structure.				$\frac{\sigma \text{ above m.p.}}{\sigma \text{ below m.p.}}$
		Type.*	*a*, A.	*c*, A.	*d*, A.	
a	Li	b.c.c.	3·46	—	3·00	0·51
a	Na	b.c.c.	4·24	—	3·67	0·75
a	K	b.c.c.	5·25	—	4·54	0·72
b	Cs	b.c.c.	6·05	—	5·24	0·61
c	Cu	f.c.c.	3·609	—	2·55	0·48
c	Ag	f.c.c.	4·078	—	2·88	0·51
c	Au	f.c.c.	4·070	—	2·87	0·44
d	Zn	h.c.p.	2·65	4·930	2·65	0·48
e	Cd	h.c.p.	2·97	5·61	2·97	0·51
f	Hg	—	—	—	—	0·24
d	Al	f.c.c.	4·04	—	2·86	0·61
g	Ga†	—	—	—	—	1·72
d	Sn	—	—	—	—	0·495
d	Pb	f.c.c.	4·93	—	3·48	0·49
g	Sb†	—	—	—	—	1·43
d	Bi†	—	—	—	—	2·33

* b.c.c. = body-centred cubic ; f.c.c. = face-centred cubic ; h.c.p. = hexagonal close-packed.

† Cf. Table II.

a = edge length of fundamental cube in cubic lattices ; *d* = nearest interatomic distance ; *c* = other parameter in hexagonal close-packed lattices.

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[65] S. E. Rogers and A. R. Ubbelohde, *Trans. Faraday Soc.*, 1950, **46**, 1051.

[65a] AgCl + AgBr : W. Lehfeldt, *Z. Physik*, 1933, **85**, 717.

[66] (*a*) A. Bernini, *Cim.*, 1903, [v], **6**, 21, 289 ; *Physikal. Z.*, 1904, **5**, 241, 406 ; *Nuovo Cim.*, 1904, [5], **8**, 262 ; *Physikal. Z.*, 1905, **6**, 74 ; (*b*) L. Hackspill, *Compt. rend.*, 1910, **151**, 305 ; (*c*) E. F. Northrup, *J. Franklin Inst.*, 1914, **177**, 1, 287 ; **178**, 85 ; (*d*) H. Tsutsumi, *Sci. Rep. Tohoku Univ.*, 1918, **7**, 93 ; (*e*) G. Vassura, *Cim.*, 1892, [3], **31**, 25 ; (*f*) C. L. Weber, *Wied. Ann.*, 1885, **25**, 245 ; (*g*) P. W. Bridgman, *Proc. Amer. Acad.*, 1922, **57**, 41.

metals, there is normally a decrease in electrical conductivity on melting. This is generally attributed to the increased scattering of electrons in the molten metal owing to the greater disorder of the atoms, and is thus analogous to the effect of cold working or straining of the metal. The order of magnitude of the change is illustrated in Table X and should be compared with the temperature coefficient of electrical conductivity of the solid.

For the few abnormal metals (bismuth, antimony, gallium) the electrical conductivity increases on melting. This is related to the presence of a proportion of unusual " non-metallic " bonds in the crystal which are broken on melting and may be correlated with the anomalous sign of $\Delta V_f/V_s$ (referred to in Table II) for these crystals.

4. Phenomenological Description of Melting

From the volume increase which is observed in all simple cases of melting, it seems plausible that the packing in the liquid must involve lattice defects or holes. The various lines of evidence indicate that the proportion of defects increases to such an extent on passing from solid to liquid that long-range order breaks down. Simple types of lattice defects may be accompanied by co-operative defects in some crystals.[29] Both types of change may be described as a decrease in positional order.

When the molecules are not spherically symmetrical, orientational order can also decrease on melting.

Finally, in crystals where the linkages between the atoms are strong, as, for example, in quartz, melting may leave strings and networks of molecules linked together in the liquid. In such cases the viscosity of the liquid may show an anomalous increase on cooling, and in the absence of crystal nuclei the liquid may " polymerise " to a glass as an alternative to freezing to a crystal.[20]

5. Special Types of Transition from Crystal to Disordered State

5.1 Mesomorphic States intervening between Three-dimensional Crystals and Non-crystalline Liquids.—Various crystals " melt " to " liquids ", in which optical and thermal evidence indicates residual crystallinity, which may be attributed to bundles or clusters of molecules in the liquid, with an arrangement within the cluster more orderly than that which prevails in the usual liquids. In such cases a second temperature or " clearing point " can usually be observed above the normal melting point, at which the liquid becomes optically isotropic.[67] Both the melting point and the

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[67] (*a*) D. Vorländer *et al.*, *Ber.*, 1938, **71**, *B*, 501; (*b*) *Z. Krist.*, 1937, **97**, 485; (*c*) P. Chatelain, *Compt. rend.*, 1936, **203**, 1169; (*d*) B. Jones, *J.*, 1935, 1874; (*e*) C. Weygand and R. Gabler, *Ber.*, 1938, **71**, *B*, 2399; (*f*) G. A. Knight and B. D. Shaw, *J.*, 1938, 682; (*g*) H. Stolzenberg and M. E. Huth, *Z. physikal. Chem.*, 1910, **71**, 641. For other examples cf. D. Vorländer, *Trans. Faraday Soc.*, 1933, **29**, 907; C. Weygand, *Z. physikal. Chem.*, 1943, **53**, *B*, 75; C. Weygand, R. Gabler, and J. Hoffmann, *ibid.*, 1941, **50**, *B*, 124; C. Weygand, R. Gabler, and N. Bircan, *J. pr. Chem.*, 1941, **158**, 266; C. Weygand and R. Gabler, *Z. physikal. Chem.*, 1940, **46**, *B*, 270; C. Weygand and W. Lanzendorf, *J. pr. Chem.*, 1938, **155**, 221; D. Vorländer *et al.*, *Ber.*, 1938, **71**, *B*, 501;

clearing point are associated with increases in heat,[68] entropy, and volume. Typical values are illustrated in Table XI. Though the change from crystal to isotropic liquid by stages is unusual, it does not seem to present major difficulties of interpretation in terms of structural changes on the basis of the previous sections.

TABLE XI

Melting and clearing temperatures of some liquid crystals

Section of ref. 67.	Compound.	M.p.	Clearing point.
a	4-(*p*-Benzylideneamino)diphenyl	243—245°	254°
b	Et 4-(*p*-methoxybenzylideneamino) cinnamate, form (i)	83—85	139
	,, (ii)	106	139
c, e	*p*-Azoxyanisole	115—116	134
d	*p*-Amyloxybenzoic acid	122	148
f	1-Tetradecylpyridinium chloride	77	205
g	Silver bromide	259	398

5.2 Crystallisation on Stretching or Freezing of Rubber-like Solids.—In certain polymers with rubber-like properties, the molecules are normally present in coiled form and give *X*-ray reflection patterns similar to those obtained from gases or liquids. When they are strongly cooled, a crystal structure develops. This change from disorder to order on cooling is analogous to those described in the previous sections, except that it occurs over a rather wider range of temperatures.

Rubber-like solids present a new phenomenon, however, in that they also crystallise when stretched at constant temperature. As with cooling, crystallisation by stretching involves an increase in order. The statistical interpretation of this phenomenon has been discussed in numerous papers in view of its technological importance.[69]

6. Theories of Melting

Any theory of melting must in principle account quantitatively for the coexistence of two condensed phases at the same temperature and pressure. A major aim is to relate the temperature of melting, the volume change on melting, and the latent heat directly to the intermolecular forces. Calculations on melting in terms of a critical temperature of vibrational instability

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1937, **70,** *B,* 2096. For reviews see: *Ann. Reports,* 1931, **28,** 280; " General Discussion on Liquid Crystals ", *Trans. Faraday Soc.*, 1933, **29,** 881; L. S. Ornstein, *Nederl. Tijds. Natuurk.*, 1940, **7,** 373; *Proc. Acad. Sci. Amsterdam,* 1938, **41,** 1046; A. S. Lawrence, *J. Roy. Microscop. Soc.*, 1938, **58,** 30; W. Kast, *Physikal. Z.*, 1937, **38,** 627; W. Bragg, *Nature,* 1934, **133,** 445; *Proc. Roy. Inst.*, 1934, **28,** 57.

[68] C. Kreutzer, *Ann. Physik,* 1938, **33,** 192; K. Kreutzer and. W. Kast, *Naturwiss,* 1937, **25,** 233.

[69] Cf. the review by K. H. Meyer, *Chem. Reviews,* 1939, **25,** 137.

of the crystal lattice,[70] or a critical temperature of mechanical instability of the crystal under vanishingly small external shear,[71] cannot account directly for the thermodynamic parameters which govern the coexistence of two phases. Even when such non-thermodynamic theories contain interesting and valid concepts about the effect of temperature on the properties of the crystalline state, the account they give of melting must be basically incomplete.

Examination of the experimental evidence (sections 1—5) indicates that many factors may contribute to a thermodynamic parameter such as the entropy of fusion. Typical examples are presented by molecules of complex shape. Calculations on melting also become more complicated when several kinds of interatomic forces affect the stability of condensed phases, as in the solids containing hydrogen bonds, or in metals. No general thermodynamic theory of melting has yet been proposed which covers all types of entropy increase in the Boltzmann expression (equation 1.2).

An interesting and suggestive model has been proposed [39a, b] for the limited problem of the melting of a crystalline face-centred cubic solid composed of particles with spherically symmetrical force fields. Such a model solid can account for the quantitative aspects of melting of simple crystals like solid argon. It also gives semi-quantitative information about changes of positional entropy on melting of more complex crystals.

All the evidence suggests that in a *simple* crystalline solid even near its melting point, the number of lattice flaws is only a small fraction of the total number of atoms, and is insufficient to affect the long-range order appreciably. In the liquid the number of defects is comparable with the number of atoms, so that no long-range order can be recognised. In their theory of melting, Lennard-Jones and Devonshire [39a, b] simplify the formal treatment by considering only the " interstitial " type of lattice defect. For convenience, interstitial " defect " positions are considered to lie on a face-centred cubic lattice which interpenetrates the " normal " lattice like the Na^+ and Cl^- lattices in sodium chloride. In this model, each " normal " or α-site is surrounded by Z defect or β-sites and *vice versa.*

A fundamental parameter for melting is the interaction energy W of each pair of atoms occupying adjacent α- and β-sites ; W is assumed to be a function only of the specific volume. The degree of order at equilibrium is calculated by processes similar to those for order–disorder in alloys. The degree of order Q being defined as $Q = N_\alpha/N$, where N_α is the number of atoms on α-sites and N the total number of atoms, the partition function F_Q of the disordered assembly is shown to be

$$\mathrm{F}_Q = \mathrm{f}^N \times Y(Q) \exp[-ZNWQ(1-Q)/kT] \quad . \quad . \quad (6.1)$$

where f^N refers to the partition function of atoms in a state of perfect order, and the second factor takes account of the disorder. $Y(Q)$ is the number of ways of distributing $N_\alpha = NQ$ atoms on α sites and $N_\beta = N(1-Q)$

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[70] *E.g.*, F. A. Lindemann, *Physikal. Z.*, 1910, **11**, 609 ; W. Braunbek, *Z. Physik*, 1926, **38**, 549.

[71] R. Lucas, *Compt. rend.*, 1938, **207**, 1408. For other aspects of mechanical theories of melting cf. M. Born, *Nature*, 1940, **145**, 741, and ref. 11*a*, p. 174.

atoms on β sites. $Y(Q) = \{N!/[NQ!(1 - Q)!]\}^2$. For a given volume, temperature, and energy of interaction F_Q has a maxmium given by:

$$(2Q - 1) = \tanh ZW(2Q - 1)/4\boldsymbol{k}T \quad . \quad . \quad . \quad (6.2)$$

This equation is always satisfied by $Q = \frac{1}{2}$. When $ZW/4\boldsymbol{k}T > 1$, there is another root greater than $\frac{1}{2}$. If it exists it corresponds to the maximum of the partition function, but when it does not exist the maximum is given by $Q = \frac{1}{2}$. Large values of $W/\boldsymbol{k}T$ give $Q \approx 1$, *i.e.*, order nearly perfect, and values $W/\boldsymbol{k}T \leqslant 4/Z$ give $Q = \frac{1}{2}$, *i.e.*, complete disorder. This property of equation (6.2) gives the essential possibility of equilibrium between a highly ordered and a disordered condensed phase.

In view of the factorising of the partition function in equation (6.1), the free energy, internal energy, and entropy can be separated into the contribution from the order (single prime) and from the disorder (double prime) $A = A' + A''$, $U = U' + U''$, etc. Since

$$-A/N\boldsymbol{k}T = (1/N)\log(\mathrm{F}_{Q\,\mathrm{max.}})$$

$$-A'/N\boldsymbol{k}T = \log \mathrm{f}$$

$$-A''/N\boldsymbol{k}T = -[ZWQ(1 - Q)/\boldsymbol{k}T] - 2(1 - Q)\log(1 - Q) - 2Q\log Q \quad (6.3)$$

and similarly

$$U'' = ZNWQ(1 - Q) \quad . \quad . \quad . \quad . \quad . \quad . \quad (6.4)$$

$$S''/N\boldsymbol{k} = -2(1 - Q)\log(1 - Q) - 2Q\log Q \quad . \quad . \quad (6.5)$$

The pressure $p = -(\partial A/\partial V)_T$ can similarly be expressed as the sum of the pressure p' of an ordered assembly plus the additional pressure p'' due to a state of disorder.

The important result follows that

$$p'' = -ZN(\mathrm{d}W/\mathrm{d}V)_T Q(1 - Q) \quad . \quad . \quad . \quad (6.6)$$

or since n'', the number of pairs of atoms in adjacent α- and β-sites, is

$$n'' = ZNQ(1 - Q) \quad . \quad . \quad . \quad . \quad (6.7)$$

and $U'' = n''W$ (from 6.4)

$$p'' = -n''(\mathrm{d}W/\mathrm{d}V) \quad . \quad . \quad . \quad . \quad (6.8)$$

If W depends on volume according to an inverse-power law, so that it can be written in the form

$$W = W_0(V_0/V)^x$$

the simple formula for p'' is obtained

$$p'' = +xU''/V$$

($x = 4$ corresponds with an inverse twelfth power of the repulsive potential; this gives reasonable values for argon). At small volumes, U'' vanishes owing to the state of high order. At large volumes, U'' tends to $\frac{1}{4}NZW$, but W diminishes at large volumes, so that U'' vanishes at large volumes also. Thus, p'' passes through a maximum (cf. Fig. 5).

This new term p'' in the equation of state of the disordered condensed assembly has a profound effect on the shape of the isotherm.

The corresponding free energy as a function of volume is shown in Fig. 6. Curve II shows the actual isotherm of the solid (argon) at the temperature at which it melts at zero pressure.

The comparatively ordered phase corresponding with A coexists with the expanded disordered phase C.

The original papers must be consulted for further details and refinements of the theory, but the following numerical results may be noted. The melting temperature at zero pressure is taken as an empirical parameter to determine the value of W_0 in the above equations. Results which are directly calculated from this value of W_0 are :

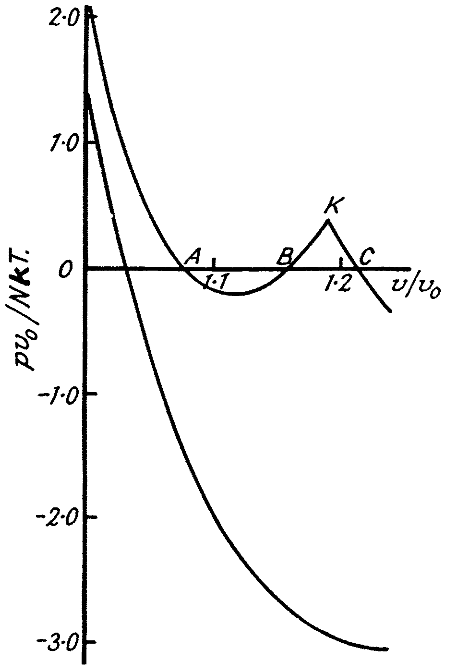

FIG. 5

The pressure as a function of volume for a given temperature ; the lower curve gives p′, *the pressure for a state of order, the upper one* p *the sum of* p′ *and* p″.

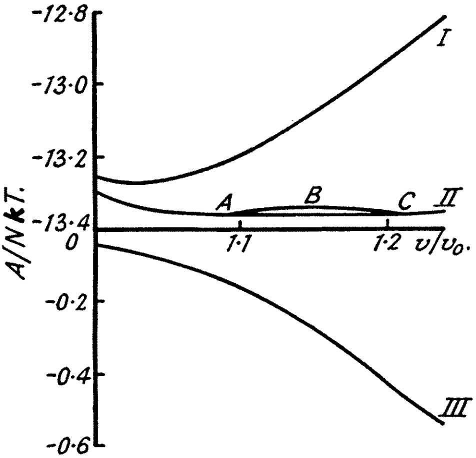

FIG. 6

The free energy as a function of volume. The curves I, II, and III correspond to A'/NkT, A/NkT, *and* A''/NkT *respectively. The points A, B, C correspond to the same points as in Fig.* 2.

Argon

	Calc. (two methods).	Observed.
$\Delta V_f/V_s$ on melting at zero pressure . .	13·5 and 12·8%	12%
ΔS_f at zero pressure (83·8° K.) . . .	1·70k and 1·74k	1·66k
Pressure of melting at 90·3° K. (megadynes/cm.^{2})	286 and 294	291
Coefficient of expansion of liquid in immediate neighbourhood of the m.p.	0·0040 and 0·0049	0·0045

Other semi-empirical relationships follow from a correlation between W_0 and ϕ_0, where ϕ_0 is the potential energy of a pair of particles at the equilibrium distance r_0 which can be calculated from the known force fields. The temperature of melting at zero pressure is given by $T_f = \beta\phi_0/\boldsymbol{k}$, and from argon the empirical parameter β is calculated to be 0·7. Other simple crystals may be compared on this basis (see table).

	$\phi_0/\boldsymbol{k}$.	T_f, calc., ° K.	T_f, obs., ° K.
Neon . . .	35·3	24·7	24·4
N_2 . . .	96	67·2	63·2
CO . . .	96·4	67·5	73
CH_4 . . .	142·4	99·5	89
H_2 . . .	30·7	21·5	14
O_2. . . .	122·5	85·8	46

Except for hydrogen, where quantum effects begin to be important, and for oxygen, where the magnetism probably affects the force fields, the correlation between T_f and ϕ_0 is very promising.

The theory predicts that the coefficient of expansion of the liquid just above the melting point should be $\alpha = 0{\cdot}48\boldsymbol{k}/\phi_0$, which appears to hold fairly well for argon. The Lindemann correlation between the characteristic temperature θ for lattice vibrations, and the melting temperature T_f is shown to follow from the fact that the same force field controls the atomic vibrations and the energy required to form lattice defects.

An attempt has been made to extend the theory to include the melting of crystals of molecules with non-spherically symmetrical force fields,[1] by introducing entropy terms corresponding with hindered rotators in the crystal. This leads to a semi-quantitative treatment of orientation entropy in the solid, and of the changes in orientation entropy on melting.

Summary

Experimental methods of investigating melting include:

(1) a study of entropy and volume changes at the melting point;

(2) studies of the thermodynamic properties of solid and liquid phases in the immediate neighbourhood of the melting point, such as the specific heat and the coefficient of expansion; and

(3) investigation of other properties related to structure, including the modulus of elasticity and the viscosity, the scattering of light by the solid and liquid phases, the electrical resistance (for ionic solids and for metals), the dielectric constant and dielectric losses, and the diamagnetic susceptibility; and X-ray studies on solid and liquid.

The results lead to a convenient experimental classification of factors determining the transition from solid to liquid, including:

(i) the decrease in positional order, which is the dominant effect for the simplest crystals made up from inert-gas atoms or spherically symmetrical molecules;

(ii) the decrease in orientational order which accompanies the melting of crystals of non-spherically symmetrical molecules;

(iii) for crystals in which there are strong linkages between molecules,

as in quartz, various glasses, or graphite, the breaking of these linkages, which is of major significance for liquefaction ; and

(iv) for molecules of very abnormal shape, special melting phenomena. In polymers such as " Polythene " there is very marked premelting. In rubber-like substances, a transition from the amorphous to the crystalline state can be induced by cooling or by stretching. For crystals containing rod-like molecules, *e.g.*, with several aromatic nuclei, mesomorphic states intervene between the crystal and the fully amorphous liquid.

Recent molecular theories of melting are amenable to detailed quantitative treatment only in the case of the simplest and most general change of positional order.