TRANSITIONS IN SOLIDS AND LIQUIDS

By L. A. K. Staveley, M.A.

(Fellow of New College, Oxford, and University Demonstrator in Chemistry)

It has long been known that many substances exist in more than one solid form, such that at constant pressure one form changes into another at a constant temperature, just as a pure substance passes isothermally from the solid to the liquid state at the melting point. The thermodynamic description of such transitions is simple. At the transition point, the Gibbs free energies G of equal masses of each of the two solid forms are equal, the free-energy curves (at constant pressure) intersecting as shown in Fig. 1 (*a*). The change from the low-temperature to the high-temperature form takes place with the absorption of latent heat, and so is accompanied by a sudden entropy increase, and there is also an abrupt volume change. The effect of pressure on the transition temperature is governed by the Clapeyron–Clausius equation.

$$dp/dT = \Delta S/(V_{\mathrm{I}} - V_{\mathrm{II}}) \quad . \quad (1)$$

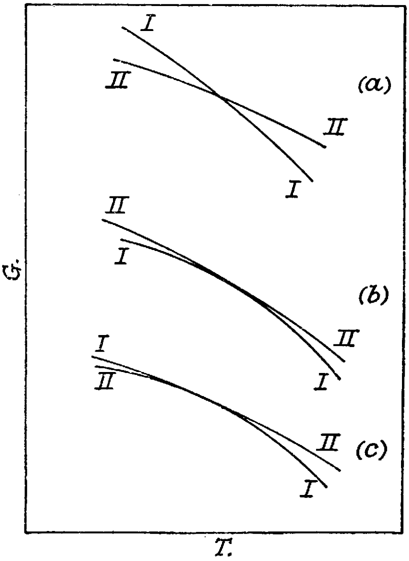

Fig. 1

The relationship between free energy (G) *and temperature in transitions of* (a) *first,* (b) *second, and* (c) *third order.*

There also exist transitions in pure solid substances which do *not* take place sharply but over a range of temperature, even though the major part of the change, whatever it may be, is often concentrated into a small temperature region. Such transitions are now known to occur in substances of widely different chemical types. They are found, for example, in ammonium salts, in condensed gases such as methane and hydrogen bromide, and in alloys. They also include Curie-point phenomena in ferromagnetic materials and the analogous effects which take place in "Seignette-electric" subsubstances. In addition, the one known transition in a purely liquid system, that between the two forms of liquid helium, is of this kind. Few generalisations can be made about these transitions, but they are alike in one respect, of great practical and theoretical importance, namely, that they are all accompanied by an anomaly in the specific heat. As the low-temperature form of the substance is heated, the heat capacity c_p starts to become greater than would be expected from its previous trend with temperature. The rise becomes more and more rapid until a maximum value is reached

(Fig. 2). Sometimes the subsequent fall is continuous, sometimes apparently discontinuous, though even if the drop is discontinuous the "normal" curve is usually not resumed at once. Just above the temperature at which it reaches its maximum the heat capacity lies slightly above the extrapolated normal curve. This behaviour is described as anomalous since it is not possible for the normal heat capacity due to the progressive excitation of the lattice vibrations and of the internal vibrations in molecules or ions to decrease with rising temperature.[1] The coefficient of expansion in a gradual transition likewise shows an anomaly similar to that in the specific heat, except that it sometimes takes the form of abnormally small (*i.e.*, negative) values in the transition region.

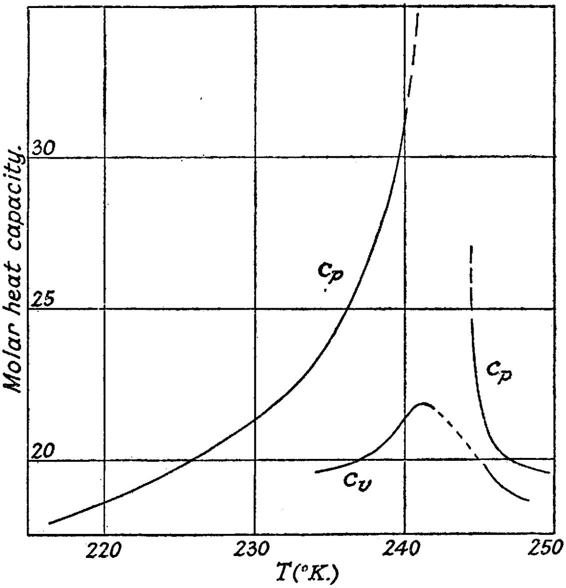

FIG. 2

The variation with temperature of c_p (ref. 36) and c_v (ref. 25) in the gradual transition in ammonium chloride.

There is, however, considerable variability in these anomalies from one substance to another. Sometimes the heat capacity at its maximum is only a few calories above the normal (extrapolated) curve, sometimes it reaches ~ 100 cals./mole or even immeasurably high values. The observable range of the anomaly may be restricted to a few degrees, and its main part to a fraction of a degree only ; or it may spread over more than 100°, particularly in transitions in alloys. In calorimetric and dilatometric studies the transition temperature is taken to be that at which c_p reaches its maximum value, and the coefficient of expansion its maximum or minimum value, as the case may be.

---

[1] R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics" (C.U.P., 1939), p. 147.

The thermodynamic description of these gradual transitions was first attempted by P. Ehrenfest.[2] At a sharp transition we have two physically distinct phases in equilibrium with equal free energies G, and it follows from the relations

$$(\partial G/\partial T)_p = -S, \quad (\partial G/\partial p)_T = V \quad . \quad . \quad . \quad (2)$$

that there is a sudden alteration in entropy and volume. Ehrenfest considered what the thermodynamic consequences would be if at a transition there is equality of the free energies of the two forms and of their first differential coefficients as well, but now a discontinuity in their *second* differential coefficients. (The choice of the rather ambiguous word " form " in the last sentence is deliberate. We shall see that there are cogent reasons for avoiding the word " phase " in dealing with gradual transitions.) At constant pressure, the relationship between the free energies of the two forms will then be as shown in Fig. 1 (*b*). At a certain temperature the curves will touch with the same slope but with different curvatures. At this temperature, from the relations

$$\partial^2 G/\partial T^2 = -C_p/T, \quad \partial^2 G/\partial T\partial p = \partial V/\partial T \quad . \quad . \quad . \quad (3)$$

there will be a discontinuity in specific heat and coefficient of expansion. If now $\partial(\Delta G)/\partial T$ and $\partial(\Delta G)/\partial p$ (where $\Delta G = G_{\mathrm{II}} - G_{\mathrm{I}}$) are to remain zero for changes in T and p, we have the equations

$$\frac{\partial^2(\Delta G)}{\partial T^2}\mathrm{d}T + \frac{\partial^2(\Delta G)}{\partial T\partial p}\mathrm{d}p = 0$$

and

$$\frac{\partial^2(\Delta G)}{\partial T\partial p}\mathrm{d}T + \frac{\partial^2(\Delta G)}{\partial p^2}\mathrm{d}p = 0$$

whence, from (3), and the additional relation $\partial^2 G/\partial p^2 = \partial V/\partial p$, we have

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{c_{p_{\mathrm{II}}} - c_{p_{\mathrm{I}}}}{T(\partial V_{\mathrm{II}}/\partial T - \partial V_{\mathrm{I}}/\partial T)} = -\frac{\partial V_{\mathrm{II}}/\partial T - \partial V_{\mathrm{I}}/\partial T}{\partial V_{\mathrm{II}}/\partial p - \partial V_{\mathrm{I}}/\partial p} \quad . \quad (4)$$

Such transitions, in which there is a discontinuity in the *second* differential coefficients of G, can be called second-order transitions, in contrast to sharp transitions which are of the first order. E. Justi and M. von Laue [3] raised doubts about the possibility of the existence of second-order transitions, pointing out that one form would always have the lower free energy [I in Fig. 1 (*b*)] and hence that the transition I ⟶ II could never be observed. As the simplest way out of this apparent difficulty they suggested that there is a sudden change not in the second but in the *third* differential coefficients of G, so that at constant pressure the free energy relationship would be as shown in Fig. 1 (*c*). There would then be no *discontinuity* in c_p or in α (the coefficient of expansion), but the curves of these quantities plotted against temperature would show a sudden alteration in slope at the transition temperature. Justi and von Laue's argument has, however, been criticised on the grounds that it is not permissible to regard the two forms of the substance separated by the anomaly as two phases with a conceivable existence on both sides of the transition point ; in other words,

---

[2] *Proc. Acad. Sci. Amsterdam,* 1933, **36,** 153.

[3] *Sitzungsber. Akad. Berlin,* 1934, 237.

that the two forms are such that one passes continuously into the other so that extrapolation of either beyond the transition temperature is meaningless.[4]

The equations (4) can in principle be subjected to experimental test, the first of them being the more convenient. Unfortunately, the necessary data are only available for a few substances, and moreover, it is difficult in any case to obtain accurate figures for the sudden changes in heat capacity and coefficient of expansion at the transition temperature. The test has, however, been applied to the transition in liquid helium. Here, within the limits imposed by existing experimental technique, there does appear to be a discontinuous drop in c_p (of 1·9 cals./mole) at the temperature (2·19° K.) at which the low-temperature form of liquid helium (II) finally passes into the high-temperature form I. According to W. H. Keesom and A. P. Keesom,[5] this fall in c_p certainly occurs within 0·002°, and probably within 0·0002°. By using experimental figures for the rate of change of the transition point with pressure ($= \mathrm{d}p/\mathrm{d}T$) and for the coefficient of expansion of liquid helium I, W. H. Keesom [6] calculated from equation (4) a value for the coefficient of expansion of helium II at the transition temperature which was in very fair agreement with the experimental figure. The Ehrenfest equation has also been applied to the gradual transitions in methane [7] and ammonium chloride,[8] but there are doubts about its applicability to either of these. For methane there is considerable uncertainty about the value of Δc_p at the transition,* and in fact A. Eucken and E. Bartholomé [9] considered that the possibility of the drop in c_p being continuous could not be excluded. For ammonium chloride, as we shall see, there is evidence that the transition from the low- to the high-temperature form finally reaches completion isothermally, or at least in such a small temperature range as to make an accurate evaluation of Δc_p and $\Delta\alpha$ impossible.

In some gradual transitions there definitely does not appear to be an abrupt fall in the heat capacity, as for example in ferromagnetic elements in the neighbourhood of the Curie point. At this temperature the heat capacity reaches a somewhat pointed maximum and then declines continuously to normal values. This behaviour is consistent with that required of a third-order transition, and specific heat and coefficient of expansion anomalies in ferromagnetic elements have, in fact, been treated thermodynamically as belonging to this class.[10]

The first applications of statistical mechanics to gradual transitions dealt with the so-called order-disorder phenomena in certain alloys,† of

---

[4] J. E. Mayer and S. F. Streeter, *J. Chem. Physics*, 1939, **7**, 1019 ; W. H. Keesom, " Helium " (Elsevier, 1942), Chap. 5.

[5] *Physica*, 1935, **2**, 557.

[6] *Proc. Acad. Sci. Amsterdam*, 1933, **36**, 147.

[7] K. Clusius and A. Perlick, *Z. physikal. Chem.*, 1933, *B*, **24**, 313.

[8] E. O. Hall, *Physical Rev.*, 1947, **71**, 916.

[9] *Göttingen Nachr.*, Math.-Phys. Kl. II, 1936, **2**, 51.

[10] E. F. Lype, *Physical Rev.*, 1946, **69**, 652.

* See ref. (9), p. 55.

† See F. C. Nix and W. Schockley, *Rev. Mod. Physics*, 1938, **10**, 1, for an excellent review of this subject.

which β-brass (CuZn) is a simple example. The nature of the transition has been established by X-ray studies. In β-brass, both above and below the transition, the atoms are situated at the points of a body-centred cubic lattice. At low temperatures the structure can be regarded as consisting of two interpenetrating simple cubic lattices, one of copper atoms, the other of zinc, so that each copper atom is surrounded by eight zinc atoms, and *vice versa*. Above the transition, however, there is no discrimination on the part of the atoms as to which lattice points they occupy, so that on the average either kind of atom has four coppers and four zincs as nearest neighbours. Certain planes in the high-temperature disordered structure resolve themselves in the low-temperature ordered form into planes alternately consisting of each kind of atom only, with different scattering powers, so that X-rays are diffracted from adjacent layers of this kind with equal intensities at high temperatures and with unequal intensities at low temperatures. Diffraction from these planes at low temperatures produces lines in the diffraction pattern (" superlattice " lines) due to the incomplete cancellation of out-of-phase beams which are absent from the diffraction pattern of the high-temperature form. This evidence shows that it is the ordered form in which the potential energy is least, but thermal agitation tends increasingly to produce the disordered state, and the degree of order at any given temperature depends on a balance between these opposing factors. The definition of the degree of order s in the treatment of the problem given by W. L. Bragg and E. J. Williams [11] may be illustrated as follows. To produce β-brass, we could take a body-centred cubic lattice with each of its n lattice points occupied by a copper atom, and then replace half of them by zinc atoms. To obtain the completely ordered alloy, the replacements would have to be made at certain definite lattice points only (" correct " positions), $n/2$ in number. If, now, when the substitutions are made the average chance that a zinc atom is placed at a " correct " position is p, then s is defined as

$$\frac{(\text{the actual value of } p) - (\text{value of } p \text{ for complete disorder})}{(\text{value of } p \text{ for complete order}) - (\text{value of } p \text{ for complete disorder})}$$
$$= (p - \tfrac{1}{2})/(1 - \tfrac{1}{2}) = 2(p - \tfrac{1}{2})$$

Hence, $s = 1$ or 0 for complete order or disorder, respectively.

We now come to a most important point. Changing the places of a copper and a zinc atom in the completely ordered alloy will involve an increase of potential energy W_0, but for the completely disordered alloy no alteration in potential energy will accompany the interchange. In any intermediate state the increase in potential energy W will lie between 0 and W_0, *and will be a function of* s. In Bragg and Williams's treatment, W was taken to be a linear function of s. But there will clearly be another relation involving s, W, and T, since in a sense the transition is analogous to a chemical reaction with s playing the part of an equilibrium constant and W that of a heat of reaction (with the peculiarity that the " heat of reaction " varies with the extent to which the reaction has taken place). This second

---

[11] *Proc. Roy. Soc.*, 1934, *A*, **145**, 699 ; 1935, *A*, **151**, 540.

equation can be derived by the methods of statistical mechanics, and from the two equations involving W and s the equilibrium value of the degree of order at any temperature T can be determined. It is found that s falls more and more rapidly with increasing temperature until it becomes zero at a temperature T_c. (For alloys of the type AB, such as CuZn, the fall to zero is continuous. For some systems of the type AB_3, such as Cu_3Au, s, after a continuous fall, drops *abruptly* to 0 at T_c, so that here the final disappearance of order is accompanied by the absorption of latent heat.) The calculated values of the anomalous specific heat below T_c are of the right order of magnitude. The theory accounts successfully for the essential features of the transition, except that it predicts that the system would have a normal specific heat immediately T_c is passed, whereas in fact for a short range above T_c the c_p values are still slightly greater than normal. The reason for this is that the degree of order as defined above is an average quantity which relates to the crystal as a whole. At all temperatures, however, there is a tendency for the immediate environment of a given atom to be such that the potential energy of this atom and its neighbours is a minimum, and the local order to which this tendency gives rise will, in virtue of its contributory potential-energy term, manifest itself in an addition to the specific heat, decreasing in value as T increases. H. Bethe [12] and R. Peierls [13] have presented treatments of order-disorder transitions in alloys in which the degree of order σ is defined with reference to an atom and its nearest neighbours only ; σ is thus a measure of the short-range order which, unlike s, does not become zero at T_c. From this starting point the slightly anomalous specific heat above T_c can be accounted for quantitatively.

There is some similarity between Curie-point phenomena in ferromagnetic substances and transitions in alloys. The atoms in a ferromagnetic substance are elementary magnets with a preference for a common orientation, which at sufficiently low temperatures results in a state of permanent magnetisation. As the temperature rises, thermal agitation tends increasingly to overcome this common orientation. The disappearance of permanent magnetisation at the Curie point is accompanied by a maximum in the specific heat.

Of all gradual transitions, those occurring in molecular and ionic solids have probably the greatest interest for the chemist. The majority take place below room temperature, and the discovery of many of them has been a consequence of systematic low-temperature calorimetry. Usually the compound contains hydrogen in its molecule or one of its ions, and it may possess two or even three such transitions. In finer points of detail, these gradual transitions show great sensitivity to the chemical nature of the compound in which they occur. Even isotopic replacement can cause qualitative changes. The first to be definitely discovered was that in ammonium chloride by F. Simon,[14] R. Ewald [15] having previously observed that the heat capacity of this substance below room temperature was

---

[12] *Proc. Roy. Soc.*, 1935, *A*, **150**, 552.

[13] *Ibid.*, 1936, *A*, **154**, 207.

[14] *Ann. Physik*, 1922, **68**, 241.

[15] *Ibid.*, 1914, **44**, 1213.

anomalous. They have since been found to exist in numerous ammonium and other salts, and in many condensed gases and organic compounds. A considerable stimulus to their experimental and theoretical investigation resulted from L. Pauling's suggestion [16] that they might mark the onset of molecular or ionic rotation in the crystal lattice. The possibility of such rotation seems to have been first considered by F. Simon and C. von Simson [17] to account for the cubical symmetry of the high-temperature form of hydrogen chloride. Pauling applied the Schrödinger equation to a molecule, the potential energy of which was assumed to be a periodic function of its orientation. At low temperatures the molecule executes torsional oscillations. At high temperatures it rotates, non-uniformly at first but more and more smoothly as the temperature rises. The change from the first type of motion to the second is favoured by a small moment of inertia of the molecule or ion, and by a low barrier separating two minima in the potential energy. Pauling concluded that molecules like the hydrogen halides and methane should be capable of rotation in the crystal lattice at temperatures below the melting point, whereas this would not be true of a molecule like iodine with its much larger moment of inertia. He suggested that in solid hydrogen halides the change from torsional oscillation to rotation takes place at a transition, and predicted that at these transitions the dielectric constant would show a marked increase. This prediction has since been verified,[18] and similar effects observed at transitions in many other polar substances.[19]

This association of transitions in molecular and ionic solids with the change from librational to rotational movement undoubtedly provides a simple explanation of many of the facts.[20] In the first place, we can easily understand why so many of these transitions are gradual. At low temperatures, the molecules are constrained to undergo torsional oscillations by the directed, nonspherical field of force acting on them. If a molecule commences to rotate, however, the resulting increase in symmetry in its own field of force weakens its orientating influence on its neighbours and makes their rotation an easier process. In other words, we have here, as in order–disorder transitions in alloys, a change which becomes progressively less exacting in its energy requirements as it proceeds. Like the atomic rearrangements in alloys, it will be a co-operative phenomenon giving rise to abnormal physical properties over a range of temperature. In *sharp* transitions, where there is evidence that molecular rotation sets in at the transition point, it may be that this does not occur at all at lower temperatures, and that the conditions which make it possible are created by the change in crystal structure at the transition. But it is also possible that just below the transition point a few molecules or ions begin to rotate, with

---

[16] *Physical Rev.*, 1930, **36**, 430.

[17] *Z. Physik*, 1924, **21**, 168.

[18] (*a*) R. M. Cone, G. H. Dennison, and J. D. Kemp, *J. Amer. Chem. Soc.*, 1931, **53**, 1278; (*b*) C. P. Smyth and C. S. Hitchcock, *ibid.*, 1933, **55**, 1830.

[19] C. P. Smyth, *Chem. Reviews*, 1936, **19**, 329; Faraday Society Discussion on Dielectrics, 1946, 175.

[20] A. Eucken, *Z. Elektrochem.*, 1939, **45**, 126.

such an effect that the lattice is compelled to alter radically before the incipient rotation has given rise to a detectable anomaly in such properties as specific heat and coefficient of expansion. Later we shall see that it is unwise to regard sharp and gradual transitions as being fundamentally different, since some appear to have the character of both in that they commence gradually but probably reach completion isothermally.

Evidence in support of Pauling's theory comes from a consideration of the temperatures at which transitions occur in substances of different chemical types. The temperatures at which c_p reaches its maximum in the gradual transitions in methane, hydrogen bromide, ammonium chloride, and sodium nitrate are 20·42°, 89·75°, 242·7°, and 548° K., respectively. (Hydrogen bromide has two more transitions some 25° higher.) In methane the intermolecular action is due almost entirely to weak London dispersion forces, but in hydrogen bromide there are stronger orientating forces between the permanent dipoles. In ammonium chloride and sodium nitrate there are still more powerful interionic effects. The nitrate ion has a much larger moment of inertia than the ammonium ion. It is therefore readily understandable that on passing along these four substances there should be an increase in the temperatures of the transitions if these are due to the commencement of rotation of the molecules of the first two and the cations and anions of the third and fourth. Two other interesting series are provided by water, hydrogen sulphide, and hydrogen selenide, and ammonia, phosphine, and arsine. In each of these groups the first substance (with the most strongly polar molecule) only exists in one solid form at ordinary pressures. In the other two compounds of each series the lowest transition occurs in that which has the smallest dipole moment.

For gradual transitions, which are seldom accompanied by more than a slight change in crystal structure, the entropy change rarely exceeds 2 e.u. (cals./mole/°), whereas for a sharp transition it is often greater. A substance possessing either kind of transition, however, invariably has a lower entropy of *fusion* than a substance which is chemically similar but non-polymorphic. Thus, the entropy change at the sharp transition (at 225·35° K.) in carbon tetrachloride [21] is 4·86 e.u., and that on melting (at 250·3° K.) is 2·4 e.u., while the entropy of fusion of silicon tetrachloride [22] (which has no transition) is 9·1 e.u. Sometimes the entropy of transition is so much larger than that of fusion that the high-temperature form of the solid must already, in a sense, be very " liquid-like ". For *cyclo*hexanol,[23] for example, the entropy increases by 7·44 e.u. at the transition at 263·5° K., and by only 1·37 e.u. at the melting point (297·0° K.). This state of affairs is quite comprehensible if at the transition the molecules acquire the orientational freedom which otherwise is only gained when the solid melts. Likewise if the dielectric constant increases considerably at a transition in a polar substance, its further change on melting is usually only small.

Nevertheless, it is wrong to conclude that *all* gradual transitions in

---

[21] J. F. G. Hicks, J. G. Hooley, and C. C. Stephenson, *J. Amer. Chem. Soc.*, 1944, **66**, 1064.

[22] W. M. Latimer, *ibid.*, 1922, **44**, 90.

[23] K. K. Kelley, *ibid.*, 1929, **51**, 1400.

molecular and ionic solids are associated with the change from torsional oscillation to comparatively free rotation of molecules or ions, even about one axis only. We shall see that experimental evidence, while indicating that in some lattices these particles may have almost the same rotational freedom that they enjoy in the gaseous state, can for other solids only be reconciled with the persistence of librational movement both above and below the transition, so that here the increase in disorder is to be attributed not to the change from libration to rotation but from libration about ordered axes to libration about disordered axes. Consequently, the indiscriminate application of the term " rotational transition " to these gradual changes in the kind of solid we are discussing is not justifiable, just as the expression " second-order transition " likewise takes too much for granted. Less objectionable terms are " lambda-point " and " ammonium chloride-type transition ". The first of these was coined by P. Ehrenfest and was suggested by the shape of the c_p anomaly in liquid helium.

The first attempt to account quantitatively for specific heat and coefficient of expansion anomalies assumed to be due to incipient molecular rotation in crystal lattices was made by R. H. Fowler.[24] His treatment was similar to that which Bragg and Williams had applied to order-disorder transitions in alloys. A molecule was assumed to be in a potential field of $- W \cos \theta$. An order parameter s was introduced which was regarded as representing the average degree of non-rotation of the molecules, and for the all-important dependence of W on s Fowler assumed that they were related by the equation $W = W_0 s$. The calculated values of the heat capacity refer, of course, to constant volume, and cannot strictly be compared with directly determined c_p values. For ammonium chloride, however, experimental values of c_v are now available [25] which show that the anomalous rise in c_v is much less pronounced than that in c_p (see Fig. 2), and indeed is much what would be expected from Fowler's theory. Actual specific-heat anomalies are usually concentrated into a smaller temperature range than the theory predicts, for which the neglect of the effect which any volume change accompanying the transition may have on the potential energy is probably partly responsible.[26, 27] Further theoretical work in this field has been carried out by J. G. Kirkwood [27] and K. Schäfer,[28] both of whom have treated the transition as involving a change from a preferred to a random molecular orientation, rather than from non-rotation to rotation. An essential point in Schäfer's theory is that the unit to which statistical considerations are applied is not the whole crystal but a domain consisting of comparatively few molecules (perhaps ~ 1000), so that the interaction energy of the molecules in it is a function of the size of the domain.

One feature of these transitions has yet to be mentioned, namely, the hysteresis which often (though by no means invariably) accompanies them.

---

[24] *Proc. Roy. Soc.*, 1935, *A*, **149**, 1.

[25] A. W. Lawson, *Physical Rev.*, 1940, **57**, 417.

[26] O. K. Rice, *J. Chem. Physics*, 1937, **5**, 492 ; cf. R. Eisenschitz, *Proc. Roy. Soc.*, 1938, *A*, **168**, 645 ; H. Bethe and J. G. Kirkwood, *J. Chem. Physics*, 1939, **7**, 578.

[27] *Ibid.*, 1940, **8**, 205.

[28] *Z. physikal. Chem.*, 1939, *B*, **44**, 127.

The temperature of a transition showing hysteresis is higher when approached from the low-temperature side than that at which the reverse change occurs on cooling (Fig. 3). Some very careful investigations of this phenomenon have been made, from which it appears that when it exists it shows no sign of vanishing in a reasonable period of time and that it is unaffected by the measures which normally assist the establishment of equilibrium. (Thus, the hysteresis in the transition in sulphur hexafluoride is not altered by the presence of liquid carbon tetrafluoride, in which it is somewhat soluble.)[29] Although it is by no means fully understood, it is not unlikely that it is connected with the mosaic structure of the crystal. Schäfer[28] has applied his theory to the problem, and suggests that the ordered domains first formed on cooling the solid through the transition will be smaller than the larger ones produced later on and hence have different properties and a different transition temperature. Another view is that the volume changes occurring in small regions of the crystal cause strains to be set up and that the hysteresis arises from the effect of the resulting pressure on the transition temperature.[30]

We shall now consider some typical transitions in detail. Different forms of a solid are designated as I, II, III, etc., I being the form stable between the melting point and the highest transition temperature, II that existing between this and the next lower transition temperature, and so on. Reference will be made to the recently developed nuclear magnetic resonance method of deciding whether or no molecules or ions rotate in crystal lattices, which has been applied to compounds containing hydrogen atoms.[31] This depends on the fact that the effect of an applied magnetic field on the spins of the protons is to cause them to adopt parallel or anti-parallel orientations with respect to the field. The energy difference between the two orientations varies with the field strength, and for the strengths employed corresponds to a quantum of radiation of frequency of the order of ten metres. In the presence of the magnetic field the substance absorbs radiation of the correct frequency, but if the protons are present in a lattice in molecules or ions which are not rotating, there will exist in the crystal an inhomogeneous magnetic field, which, superimposed on the applied field, will result in the absorption of radiation over a frequency range. If the molecules or ions rotate with a frequency greater than that of the radiation, the internal field will be effectively homogeneous, and the range of frequencies absorbed much smaller. The change from libration to rotation will therefore be manifested by a decrease in the width of the absorption line.

Ammonium Halides.—In Table I are given the absolute temperatures, entropy changes ΔS (in cals./mole/°), and volume changes ΔV (in c.c./mole) for the transitions in light and heavy ammonium halides. The entry in the column headed " H " gives the width of the hysteresis loop in degrees.

---

[29] A. Eucken and E. Schröder, *Göttingen Nachr.*, Math.-Phys. Kl. II, 1938, **3**, 65.

[30] F. C. Frank and K. Wirtz, *Naturwiss.*, 1938, **42**, 687 ; P. Dinichert, *Helv. Physica Acta*, 1944, **17**, 389.

[31] F. Bitter, N. L. Alpert, H. L. Poss, C. G. Lehr, and S. T. Lin, *Physical Rev.*, 1947, **71**, 738.

" No " means that the transition does not show hysteresis. The reference numbers indicate the source of the information in the column above them.

TABLE I

	II → I.			III → II.				IV → III.
	T, °K.	ΔS	ΔV	*T*, °K.	ΔS	ΔV	*H*	*T*, °K.
NH_4Cl .	457	~ 2·2	+ 5·26	242·7	0·82	~ + 0·16	~ 0·27	—
ND_4Cl .	448	—	—	249·3	—	~ + 0·13	No	—
NH_4Br .	414	—	+ 6·34	234·4	0·34	~ − 0·06	~ 0·06	—
ND_4Br .	405	—	—	215	—	~ − 0·17	~ 0·15	168
NH_4I .	258	—	+ 8·14	233	0·30	~ − 0·1	No	—
ND_4I .	—	—	—	229	—	~ − 0·1	No	—
Ref. .	32	33	34	32, 35	36	35	35	32, 35

All of the transitions III $\rightleftharpoons$ II and IV $\rightleftharpoons$ III are gradual. Sometimes the anomalies in specific heat and coefficient of expansion extend for as much as 30° or 40°. The I and II forms of these salts have face-centred and body-centred cubic lattices respectively. II-NH_4Cl passes into III-NH_4Cl with no fundamental lattice change,[37, 38] but III is piezoelectric [39] and therefore of lower symmetry than II. The very careful dilatometric study by A. Smits and C. H. MacGillavry [35] revealed that a considerable part of the volume change in the III $\rightleftharpoons$ II transition occurs within a few hundredths of a degree (see Fig. 3). This important observation suggests that this transition begins gradually in one and the same phase, but that eventually it is perhaps completed isothermally. By contrast, the III $\rightleftharpoons$ II transition in ND_4Cl takes place continuously, with no sudden volume change, and without hysteresis (Fig. 3).

III-NH_4Br, on the other hand, is doubly refracting and has a tetragonal structure, though only slight displacements of the ions from their positions in the body-centred cubic II-form are involved.[35, 37, 40] Here also much of the anomalous volume change takes place in an extremely small temperature interval—within 0·01°, according to A. Smits, J. A. A. Ketelaar, and G. J. Muller.[35] ND_4Br provides one of the few examples of a qualitative

[32] K. Clusius, A. Kruis, and W. Schanzer, *Z. anorg. Chem.*, 1938, **236,** 24.

[33] H. Klindhardt, *Ann. Physik,* 1927, **84,** 167.

[34] P. W. Bridgman, *Proc. Amer. Acad.*, 1916, **52,** 55.

[35] A. Smits and C. H. MacGillavry, *Z. physikal. Chem.*, 1933, *A*, **166,** 97 (NH_4Cl) ; A. Smits, G. H. Muller, and F. A. Kröger, *ibid.*, 1937, *B*, **38,** 177 (ND_4Cl) ; A. Smits, J. A. A. Ketelaar, and G. J. Muller, *ibid.*, 1936, *A*, **175,** 359 (NH_4Br) ; A. Smits, D. Tollenaar, and F. A. Kröger, *ibid.*, 1938, *B*, **41,** 215 (ND_4Br) ; A. Smits and G. J. Muller, *ibid.*, 1937, *B*, **36,** 140 (NH_4I) ; A. Smits and D. Tollenaar, *ibid.*, 1942, *B*, **52,** 222 (ND_4I).

[36] F. Simon, C. von Simson, and M. Ruhemann, *ibid.*, 1927, *A*, **129,** 339.

[37] J. A. A. Ketelaar, *Nature,* 1934, **134,** 250.

[38] P. Dinichert, *Helv. Physica Acta,* 1942, **15,** 462.

[39] A. Hettich, *Z. physikal. Chem.*, 1934, *A*, **168,** 353 ; S. Bahrs and J. Engl, *Z. Physik,* 1937, **105,** 470.

[40] J. Weigle and H. Saini, *Helv. Physica Acta,* 1936, **9,** 515.

difference between hydrogen and deuterium compounds, in that it possesses another transition at a still lower temperature at which it reverts to a body-centred cubic lattice.[35] None of the forms of ND_4Br is piezoelectric,[41] and as there is nothing to distinguish forms II and IV Smits has called the change III ⟶ IV a retrograde transition and has discussed it in terms of his theory of allotropy. This transition is accompanied by an unusually wide hysteresis loop ($\sim 9°$). K. Clusius [42] has referred to some unpublished experiments on mixed crystals of light and heavy ammonium bromide which showed that the supercooling which precedes the formation of IV from III increases with the hydrogen content until finally the transition can no longer be observed.

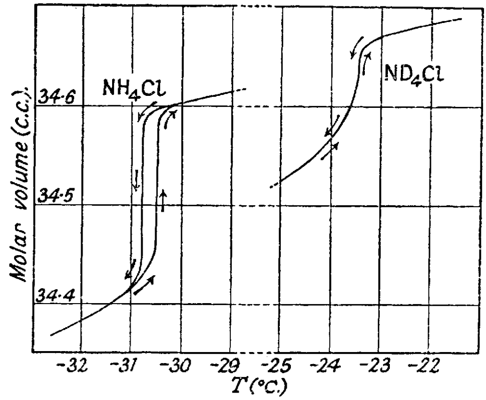

FIG. 3

The variation with temperature of the molar volumes of NH_4Cl *and* ND_4Cl (*ref.* 35) *in the final stages of the gradual transitions in these substances.*

The III ⇌ II transitions in NH_4I and ND_4I involve the same structural change as for NH_4Br,[35, 37] but they are more extended, free from hysteresis, and continuous throughout.

By measuring Young's modulus and the rigidity modulus of compressed rods of ammonium chloride, A. W. Lawson [25] obtained values for the isothermal compressibility β above and through the transition region. He also determined the coefficient of expansion α, and, using the relation $c_p - c_v = T\alpha^2 V/\beta$, calculated c_v (see Fig. 2). The anomaly in c_v is very much less marked than that in c_p (never exceeding $\sim$ 4 cals./mole), and just above the transition c_v is 18 cals./mole. The 6 cals./mole left after deduction of 12 for the lattice vibrations of the NH_4^+ and Cl' ions (which at this temperature make a classical contribution of $\boldsymbol{R}$ per degree of freedom) is exactly the amount to be expected if each of the ammonium ions executes torsional oscillations in three degrees of freedom, whereas their free rotation would contribute 3 cals./mole to c_v, making a total of 15. This strong evidence against free rotation of the NH_4^+ ions in form II is supported by the nuclear

---

[41] A. Smits and P. G. Meermann, *Z. physikal. Chem.*, 1941, *B*, **49**, 13.
[42] *Z. Naturforsch.*, 1946, **1**, 142.

magnetic resonance method : [31] the width of the broad absorption line shows no change in passing through the transition. It would therefore seem that, in NH_4Cl at least, both above and below the III $\rightleftharpoons$ II transition the cations undergo torsional oscillations, presumably about ordered axes in III and disordered axes in II. Whether the motion more nearly approaches free rotation in the high-temperature form I remains an open question.

In studying the Raman effect in ammonium chloride, bromide, and iodide at temperatures down to – 150°, A. C. Menzies and H. R. Mills [43] discovered that with the transformation into III there appears in the spectrum of the chloride (but not of the other two salts) a line of low frequency (183 cm.$^{-1}$). This they attributed to asymmetric lattice vibrations of the cations with respect to the anions. They suggested that the equilibrium position of an ammonium ion is such that each face of the tetrahedron is perpendicular to a cube diagonal, and that the low-temperature form of ammonium chloride is built up by simple translation of an elementary cube. The halogens are then not symmetrically placed with respect to the ammonium ions, so that the low-frequency Raman line is accounted for, but the asymmetry would vanish if the cations were to undergo torsional oscillations of " moderate amplitude ". On the other hand, by constructing the lattice from elementary cubes so that the tetrahedra are arranged antisymmetrically, a group of eight would possess complete cubic symmetry. Such an arrangement in the structure of III-NH_4Br and III-NH_4I is consistent with the absence of a low lattice vibration frequency from their Raman spectra. (A similar hypothesis had been advanced by A. Hettich [39] from a consideration of piezoelectric properties.) Menzies and Mills showed that on this basis a plausible explanation could be given of the opposite sign of the volume changes at the III $\rightleftharpoons$ II transition in ammonium chloride and bromide.

Tetrahydrides of Carbon, Silicon, and Germanium. Table II gives the absolute temperatures and heats of transition and fusion for the compounds so far investigated. The values of ΔH for the transitions (except that in

TABLE II

	III → II.		II → I.		Fusion.	
	T, °K.	ΔH	T, °K.	ΔH	T, °K.	ΔH
CH_4[44] . .	—	—	20·42	15·7	90·64	224
CH_3D[44] . .	15·88	13·6	23·19	44·4	90·42	217·5
CD_4[44] . .	22·25	19·8	27·10	58·7	89·78	215·7
SiH_4[45] . .	—	—	63·45	166	88·48	159·5
GeH_4[46] . .	73·20	130·7	76·55	129·6	107·26	199·7

---

[43] *Proc. Roy. Soc.*, 1935, *A*, **148,** 407.
[44] K. Clusius and L. Popp, *Z. physikal. Chem.*, 1940, *B*, **46,** 63.
[45] K. Clusius, *ibid.*, 1933, *B*, **23,** 213.
[46] K. Clusius and G. Faber, *ibid.*, 1942, *B*, **51,** 352.

silicane) are the amounts of energy in calories required to heat one mole of the substance through a short temperature range enclosing the transition; *i.e.*, they include the " normal " contribution from c_p for which it is difficult to make an exact allowance. For silicane the figure represents the true heat of transition.

All of these transitions are gradual, and all show hysteresis, except perhaps that in silicane. The hysteresis in the methane transition has been particularly carefully investigated by A. Eucken and E. Bartholomé.[9] In addition to the transitions recorded in Table II, III-GeH_4 shows an anomaly in the heat capacity: c_p rises gradually to a maximum value of 21 cals./mole at 62·9° K. and then falls abruptly, according to K. Clusius and G. Faber,[46] to 13 cals./mole. No simultaneous change can be detected optically (by means of a polarisation microscope) and the anomaly may perhaps be an example of a genuine second-order transition.

An *X*-ray investigation of methane by H. H. Mooy [47] gave no evidence of any alteration in the face-centred cubic structure at the transition. K. Clusius and his colleagues have studied all forms of the above substances with a polarisation microscope.* For the methanes, forms I and II are all isotropic, but III-CH_3D and III-CD_4 are doubly-refracting. I-SiH_4 and I-GeH_4 both show weak double refraction, which is much more pronounced in the low-temperature forms. The III $\rightleftharpoons$ II transition in germane is detectable in this way, but only a slight change in optical behaviour accompanies it. It seems therefore that the II $\rightarrow$ I change in germane and silicane produces a high-temperature form of greater internal symmetry, in contrast to this transition in the methanes. Although the transition in silicane begins with an anomalous rise in c_p, 88% of the heat of transition is absorbed within 1°, and it may well be that the change begins gradually but reaches completion in a first-order phase change. It will be seen from Table II that the entropy change at the transition is greater than the entropy of fusion.

The presence of two transitions in mono- and tetra-deuteromethane suggests that it is methane which is abnormal in only having one. In the lattices of these compounds almost identical intermolecular forces prevail, and torsional oscillations will have the largest frequencies and hence the greatest zero-point energies for the lightest molecules. A potential barrier restricting rotation will have almost exactly the same absolute height in all three lattices, and will therefore first be overcome by methane molecules, which retain the most energy at the absolute zero. (It is significant that the temperature of the II $\rightarrow$ I transition increases with replacement of H by D, and that $\Delta H_{\mathrm{II} \rightarrow \mathrm{I}}$ for CH_4 is very much less than for CD_4.) Probably, therefore, the form III is one in which methane is incapable of existing (at least at ordinary pressures) on account of its high zero-point energy. Interesting experiments were carried out by E. Bartholomé, G. Drikos, and A. Eucken [48] on mixed crystals of CD_4 and CH_4. They

---

[47] *Proc. Acad. Sci. Amsterdam*, 1931, **34**, 550.

[48] *Z. physikal. Chem.*, 1938, *B*, **39**, 371.

* See ref. (46) for a summary of this work.

found that the temperature of the upper transition varies linearly with the deuterium content (a striking demonstration that a co-operative change is involved) and that the transition never becomes more diffuse than in the pure compounds. The temperature of the lower transition in tetradeuteromethane, on the other hand, falls more and more rapidly with increasing hydrogen content, and the specific heat anomaly becomes less and less marked and finally vanishes at about 20% CD_4. In mixed crystals of methane and krypton [49] the II $\rightleftharpoons$ I transition becomes less pronounced, and its temperature lower, with increasing krypton content, and when this has reached about 30% the transition disappears. This result is readily comprehensible if the transition involves a co-operative librational–rotational change, for replacement of tetrahedral methane molecules by the spherically symmetrical rare-gas atoms will clearly weaken the forces tending to orientate any one methane molecule and therefore reduce the height of the potential barrier, and also make less acute the dependence of this height on the fraction of molecules already rotating.

A. Eucken and H. Veith [49] carried out an analysis of the heat capacity of solid methane and solid solutions of methane and krypton and by skilful use of rather fragmentary data for the required compressibilities and coefficients of expansion arrived at values for the rotational heat capacity of the methane molecules in the lattice. Both for the pure substance and for the solid solutions from about 50° K. upwards these are remarkably near the $\frac{3}{2}R$ of a classical three-dimensional rotator. Indeed, in the mixture richest in krypton, its values even at lower temperatures (where quantisation becomes important) are still very close to those calculated for gaseous methane. This evidence for attributing rotational freedom to the methane molecules in form I is supported by the nuclear magnetic resonance method.[31] The absorption band narrows considerably in the neighbourhood of the transition as the temperature is raised.

Hydrogen and Deuterium Halides. Some facts about these substances are recorded in Table III. The values of ΔH for the transitions in the bromides and iodides have the same significance as in Table II.

The only sharp transition is that in hydrogen chloride, from a form of very low symmetry (II) to a cubic structure (I).[17] With the change II $\rightarrow$ I the dielectric constant rises abruptly,[18] but from a quantitative consideration of the polarisation–temperature relationship for phase I, G. Hettner [50] concluded that the molecules are not rotating freely in this phase. According to a provisional report,[51] this conclusion is confirmed by the nuclear magnetic resonance method, the absorption line being equally broad above and below the transition point. Presumably, therefore, the molecules in the high-temperature form undergo torsional oscillations about disordered axes, but are capable of changing their orientation sufficiently frequently to account for the high dielectric constant. The infra-red and Raman spectra [52]

---

[49] *Ibid.*, 1936, *B*, **34**, 275; 1937, *B*, **38**, 393.

[50] *Ann. Physik*, 1938, **32**, 141.

[51] F. Bitter *et al.*, M.I.T. Quarterly Progress Report, Oct. 1947.

[52] E. Lee, G. B. B. M. Sutherland, and C. K. Wu, *Proc. Roy. Soc.*, 1940, *A*, **176**, 493.

likewise provide no evidence of molecular rotation in the solid, but instead show that the condensation of gas to liquid involves a considerable change in the intramolecular vibration frequency, comparable with that which the frequency associated with a hydroxyl group experiences when the group enters into hydrogen-bond formation. Thus in the condensed states of hydrogen chloride there would appear to be marked intermolecular association.

TABLE III *

	III → II.		II → I.		Fusion.	
	T, °K.	Δ*H*	*T*, °K.	Δ*H*	*T*, °K.	Δ*H*
HCl . . .	—	—	98·36	284·3	158·91	476·0
DCl . . .	—	—	105·03	320·1	158·44	473·2
HBr . . .	89·75	160·1	113·62II → E 116·86E → I	264·5	186·28	575·1
DBr . . .	93·5	169·7	120·26	303·0	185·62	574·2
HI . . .	70·1	146·8	125·68	359·9	222·31	686·3
DI . . .	77·3	175·6	128·28	386·4	221·23	684·3

* The information in this table has been taken from the report by K. Clusius, FIAT Review of German Science, 1939—1946, The Physics of Solids, Part I, p. 193. Full details of the investigations by Clusius and his co-workers of the deuterium halides are not yet available. The hydrogen halides were studied by W. F. Giauque and R. Wiebe, *J. Amer. Chem. Soc.*, 1928, **50,** 101 (HCl); *ibid.*, p. 2193 (HBr); *ibid.*, 1929, **51,** 1441 (HI).

Hydrogen bromide, unlike any other of the halides, including deuterium bromide, has three transitions. In mixed crystals of these two bromides, the region of existence of the extra form, designated E in Table III, diminishes with increasing deuterium content and vanishes at 47% of DBr.[42] From the similarity between DBr and HI it would appear to be HBr and not DBr which is abnormal. From *X*-ray investigations it appears that hydrogen iodide has a face-centred tetragonal lattice in all its forms, but unambiguous conclusions about the structure of hydrogen bromide have not been reached in this way. Polarisation microscope studies on HBr, DBr, and HI, have revealed that I is always isotropic, and II and III anisotropic.[42, 53] The dielectric constant of hydrogen bromide rises very rapidly as it approaches the III → II transition, and thereafter drops almost as rapidly to a fairly steady value.[18b, 54] It is not certain whether the molecules of hydrogen bromide and iodide can rotate freely in their lattices. They are more likely to do so than those of hydrogen chloride, in view of their smaller dipole moments.

The III $\rightleftharpoons$ II transition in hydrogen bromide exhibits hysteresis which has been carefully examined both thermally [55] and by dielectric constant measurements.[54] The width of the hysteresis loop as determined by heating

---

[53] A. Kruis and R. Kaischew, *Z. physikal. Chem.*, 1938, *B*, **41,** 427.

[54] G. Damköhler, *Ann. Physik*, 1938, **31,** 76.

[55] A. Eucken and W. Güttner, *Göttingen Nachr.*, Math.-Phys. Kl. II, 1936, **2,** 167.

and cooling curves was found to remain the same even if a sample previously warmed to a point about half-way up the hysteresis loop was inoculated with the high-temperature form, or alternatively subjected to supersonic waves for six hours. The dielectric-constant study did in fact show a slight shrinking of the hysteresis loop with time, but limiting conditions were reached, the hysteresis still persisting, beyond which no further change was observable.

Many other substances besides those discussed above have transitions of considerable interest. They include nitrates,[56] perchlorates,[57a] and other salts [57b] in which there is evidence of anion rotation ; resorcinol ; [58] " Seignette-electric " substances like potassium dihydrogen phosphate ; [59] and numerous organic compounds with long hydrocarbon chains where the transitions are probably connected with the onset of the rotation of the chain about its axis.[60] In addition, many new transitions have been observed in a variety of compounds at high pressures.[61] The nature of the transition in liquid helium, which of course has nothing to do with molecular rotation, is fully discussed in W. H. Keesom's book [4] on this element.

The Reviewer wishes to thank Dr. A. H. Cooke for helpful discussions, and Mr. C. J. Mandleberg for assistance in surveying recent literature.

---

[56] F. C. Kracek, *J. Amer. Chem. Soc.*, 1931, **53,** 2609 ; F. C. Kracek, E. Posnjak, and S. B. Hendricks, *ibid.*, p. 3339 ; J. B. Austin and R. H. H. Pierce, *ibid.*, 1933, **55,** 661 ; C. Finbak and O. Hassel, *Z. physikal. Chem.*, 1937, *B*, **35,** 25.

[57] *Idem*, (*a*) *ibid.*, 1936, *B*, **32,** 130 ; (*b*) *ibid.*, p. 433.

[58] J. M. Robertson and A. R. Ubbelohde, *Proc. Roy. Soc.*, 1938, *A*, **167,** 136.

[59] W. G. Cady, " Piezoelectricity " (McGraw-Hill Book Co., 1946) ; C. C. Stephenson *et al.*, *J. Amer. Chem. Soc.*, 1944, **66,** 1397, and following papers ; J. C. Slater, *J. Chem. Physics*, 1941, **9,** 16.

[60] A. Müller, *Proc. Roy. Soc.*, 1932, *A*, **138,** 514 ; W. O. Baker and C. P. Smyth. *J. Amer. Chem. Soc.*, 1938, **60,** 1229 ; J. C. Southard, R. T. Milner, and S. B. Hendricks, *J. Chem. Physics*, 1933, **1,** 95.

[61] P. W. Bridgman, " The Physics of High Pressures " (G. Bell and Sons, 1931), Chap. 8.