573. *Hysteresis in Transitions in Solids.*

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It is pointed out that in transitions in solids hysteresis seems to be confined to those cases in which part, at least, of the change occurs almost isothermally, *i.e.*, to those in which there is a stage in the transition when a new phase has to develop in one physically distinct from it. The theory of nucleation proposed by Turnbull has been applied to such transitions. The essential idea is that the initial development of the new phase is hindered both by the interphase-surface free energy and by the strain to which the growing nucleus is subjected, so that the temperature at which the two phases have the same molar free energies in bulk must be passed before the difference in bulk free energy outweighs the surface and strain effects and makes possible the appearance, at an observable rate, of self-propagating nuclei.

The difficulties in the quantitative application of the theory are considered, but estimates are made of the range in which surface free-energy values would have to fall to account for observed hysteresis effects.

The theory has been qualitatively used in a consideration of the factors which affect the width of hysteresis loops and the sharpness with which transitions set in, and also of observed phenomena within the loops.

A considerable number of transitions in solids exhibit hysteresis in the sense that part or all of the change sets in on warming at a temperature T_W, which is higher than that, T_c, at which this change begins on cooling. A schematic plot of volume against temperature for such a transition is shown in Fig. 1. For some transitions the difference $T_W - T_c$ may be as little as $\sim$0·05°, but for others it may be a hundred or even a thousand times greater. The most detailed studies of this hysteresis have been carried out with molecular and ionic solids, in which equilibrium in the transition region is much more rapidly established than in alloy systems.

We shall classify transitions in solids into three types. Type I are those which occur continuously throughout. Type II are those in which part of the transition is gradual and part isothermal. (Transitions of types I and II are what have been loosely termed second-order or " lambda-point " transitions.) Type III are those normally regarded as first-order phase changes which apparently occur completely isothermally. We must emphasise that we have introduced this classification primarily for convenience; experimentally it may be very difficult to classify a particular transition on this basis, and moreover it is possible that distinction between types II and III is artificial, in that very careful studies of apparently first-order transitions may reveal phenomena analogous to premelting, in which event type III merges into type II (Mayer and Streeter, *J. Chem. Physics*, 1939, **7**, 1019). (It may be mentioned that fusion is normally regarded as a type III phase change, although there is now a considerable amount of experimental evidence that it is preceded by genuine monophase premelting.) Previous studies of hysteresis have been largely confined to transitions of types I and II, so that the impression has been gained that hysteresis is associated only with transitions which are at least partly gradual. We shall endeavour to show, however, that for hysteresis to appear at all it is essential that part at least of the transition should be isothermal, and that the hysteresis is confined to this isothermal part of the change. In contrast, the completely gradual transitions of type I are hysteresis-free.

We must briefly consider whether or not the curves of Fig. 1 can be regarded as equilibrium curves. In the systems which we shall treat, all attempts to eliminate the hysteresis have failed; these include waiting for long periods, inoculation, agitation with supersonic waves, and carrying out the transition in presence of a solvent (Staveley, *Quart. Reviews*, 1949, **3**, 65). Nevertheless we must accept that, if a transition involves a change from one distinct phase into another, then these two phases can only be *in equilibrium when present in bulk in a normal unstrained state* at one temperature at a given pressure : we shall call this temperature T_e. We must therefore conclude that one or both of the temperatures T_w and T_c do not coincide with T_e, and the reason for this constitutes the problem discussed below.

So far as we are aware, two theories have been proposed dealing explicitly with hysteresis in transitions in molecular and ionic solids, one by Schäfer (*Z. physikal. Chem.*, 1939, **44**, *B*, 127) and the other independently by Dinichert (*Helv. Physica Acta*, 1944, **17**, 389), and by Frank and Wirtz (*Naturwiss.*, 1938, **42**, 687).

The essential idea of the first is that the unit in terms of which the transition must be considered is not the whole crystal, but a domain (" Bezirk ") consisting of relatively very few molecules; the properties of the system as a whole then depend on the characteristics of the average domain, which in turn depend on domain size. When the system is cooled, the transition occurs in a small temperature range, producing initially very small domains of the low-temperature form which are assumed to amalgamate below the transition to larger domains, which, in consequence of the dependence of energy parameters on domain size, undergo the reverse change on warming at a higher temperature.

Dinichert, and Frank and Wirtz, suggested that, as a consequence of the different densities of the two phases, regions of one phase growing within the other are subject to strain, and that this strain changes the transition temperature in accordance with the Clapeyron–Clausius equation.

While we do not consider either of these theories to be wholly satisfactory, we think it true that, on the one hand, in phase transitions the change developing from any one nucleus may well be limited to a very small region, and on the other, strains arising from density differences contribute to the free-energy relations in the transition region.

In their treatment of order–disorder in alloys, Bragg and Williams (*Proc. Roy. Soc.*, 1934, *A*, **145**, 699) pointed out that it appeared to follow that, if the change was partly isothermal, the temperature of this abrupt part would be different on heating and cooling. [Later, Frank (*ibid.*, 1939, *A*, **170**, 182) attempted to explain the supercooling of liquids on this basis.] Bragg and Williams, however, themselves doubted whether their conclusion was physically significant.

It seems to us that hysteresis arises from the well-known difficulty attendant upon the initial appearance of one phase within another. Recently this process of nucleation in solids has been quantitatively treated by Fisher, Holloman, and Turnbull (*J. Appl. Physics*, 1948, **19**, 775), and while it seems they had in mind primarily metallic systems, and although they did not explicitly consider hysteresis, we think that their treatment may be applied to hysteresis phenomena in solids. Ideas similar to those inherent in their treatment have been put forward, but not developed, by Baker and Smyth (*J. Amer. Chem. Soc.*, 1939, **61**, 2798) (see also Ubbelohde, *Trans. Faraday Soc.*, 1937, **33**, 1203).

We regard the gradual part of a transition as representing a growth of disorder throughout the crystal as a whole, which in a type I transition proceeds continuously to completion. In a type II transition the isothermal part must be considered on a different basis, namely, as involving the formation and development of nuclei of one phase within another physically distinct from it.

Following Fisher, Holloman, and Turnbull (*loc. cit.*) we may write the free-energy increase, consequent on the formation of a nucleus of i particles of one phase within another, as :

$$\Delta F_i = Ai^{2/3} + Bi + Ci \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The term $Ai^{2/3}$ represents the contribution of the interfacial free energy of the two phases, on the assumption that the nucleus has such a shape that its surface is proportional to $i^{2/3}$. (In general we suppose A to be positive; we briefly consider below the possible consequences of this not being so.) In Bi, B is the free-energy difference of one mole of the two phases at a particular temperature, divided by the Avogadro number; in future we shall refer to this as the bulk free-energy term. The term Ci represents the increase of free energy consequent on the fact that the two phases have different densities and are to some extent rigid, so that the nuclei will be in a state of strain. The free-energy term due to strain will depend in addition on the shape of the nucleus, and its dependence on the size will be more complicated than simple proportionality, especially when i becomes large.

Below T_e, the true equilibrium temperature at which B is zero, all terms in (1) are positive; when $T = T_e$ the formation of nuclei will still be associated with an increase of free energy due to the A and the C term. When T is greater than T_e, B is negative and increases numerically with rising temperature. If equation (1) is taken literally, at first, just above T_e, $B + C$ will be positive, so that at a particular temperature ΔF_i increases indefinitely with i; however, C probably declines when i becomes large, and, as assumed by Fisher *et al.*, ΔF_i will pass through a maximum as i increases. The value of i, which corresponds to a nucleus of critical size which can grow with a decrease of free energy, will occur at smaller i values as T increases and B becomes greater.

Not until a nucleus of such critical size has appeared within a crystal unit does the bulk transformation of that unit become possible. Similar considerations will apply when the high-temperature form is cooled below T_e. We consider that herein lies the origin of hysteresis; it arises because, for a range of temperature near T_e, the chance of formation of such a nucleus is negligible.

FIG. 1.

Schematic representation of the change in volume for ascending and descending temperature in a type II transition.

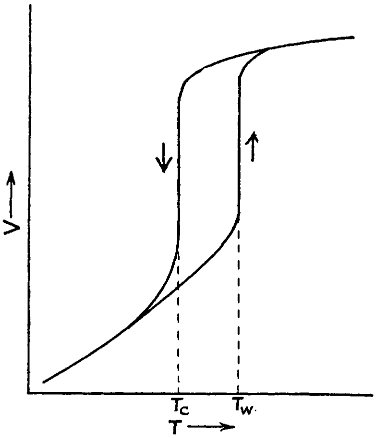
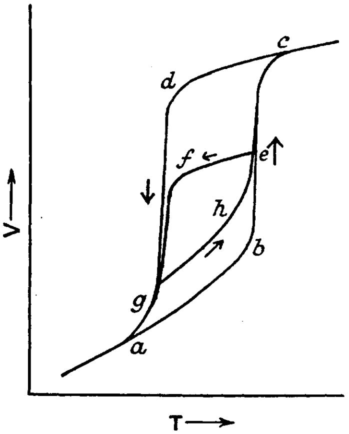


FIG. 2.

The change in volume with temperature starting from points lying on the boundaries of a hysteresis loop.



By applying the theory of absolute reaction rates, Turnbull and Fisher (*J. Chem. Physics*, **1949**, **17**, 71) have derived the following approximate expression for the rate of nucleation in supercooled liquid metals:

$$r^* \approx \frac{NkT}{h} \cdot \exp\left(-\frac{\Delta F_A}{kT}\right) \cdot \exp\left(-\frac{\Delta F_i^*}{kT}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where r^* is the number of nuclei capable of self-propagation formed per mole per sec., ΔF_A is the free energy of activation for the transport of one atom across the interface of the two phases, and ΔF_i^* is the free energy of formation of a nucleus of critical size. For nucleation in liquid metals they have assumed that ΔF_A is about the same as the free energy of activation for viscous flow. The value of ΔF_A is such that the rate of change of the first exponential term with temperature could not possibly account for the extraordinarily large temperature dependence of r^* which is actually observed. (Thus, for mercury, no detectable nucleation occurs for about 60° below the melting point, but when the rate eventually becomes measurable it alters by a factor of about ten for a change of temperature of 1·5°.) As Turnbull has pointed out, this extreme sensitivity to changes of temperature arises essentially from the variation of ΔF_i^* with temperature. We consider that the same is true for our systems also; ΔF_i^*, and *not* an activation energy ΔF_A controlling nuclear growth, is responsible for hysteresis.

By differentiating (1) with respect to i and equating $d\Delta F_i/di$ to zero, we find that the maximum value of ΔF_i is:

$$\Delta F_i^* = 4A^3/[27(B + C)^2] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Turnbull and Fisher, considering nucleation in liquids, for which the C term vanishes, assumed the nuclei to be spherical and the entropy of fusion to be independent of temperature. $\Delta F_i{}^*$ at ΔT° below T_0, the melting point, then becomes :

$$\Delta F_i{}^* = 16\pi\sigma^3 T_0{}^2/3\lambda^2(\Delta T)^2 \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where σ is the interfacial-surface free energy per unit area, and λ is the latent heat of fusion per unit volume. Turnbull and Fisher used the value of $\Delta F_i{}^*$ given by (2) in equation (4); $\dfrac{NkT}{h} \cdot \exp\left(\dfrac{-\Delta F_A}{kT}\right)$ was estimated to be about 10^{-33}. The observed rate of nucleation in small liquid drops was such that $\exp(-\Delta F_i{}^*/kT)$ was then required to have a value of about 10^{-27}.

In attempts to apply these calculations to our systems a number of difficulties arise; we cannot be sure of the applicability of the theory of absolute reaction rates to such systems; even if its application is valid, we are ignorant of ΔF_A. Moreover we do not know the average size of the crystal unit in which we have to consider the formation of a single nucleus. Furthermore, the strain term does not vanish and is difficult to estimate. In view of these uncertainties, we will provisionally neglect the strain term and estimate the values of σ for a range of values of $\exp(-\Delta F_i{}^*/kT)$, choosing values of ΔT representative of hysteresis loops in transitions in molecular and ionic solids, and then we will form an estimate of the sensitivity of rate of nucleation to temperature variation.

We may consider, as roughly typical of average behaviour, an imaginary transition for which T_e is about 300° K., at which temperature the heat absorbed is 300 cals./mole, and we will suppose the molar volume, V, to be 30 c.c., so that λ is 10 cals./c.c.

In Table I are recorded the values of σ which satisfy equation (4), for three arbitrary values of ΔT and for the three values of $\Delta F_i{}^*$ corresponding to $\exp(-\Delta F_i{}^*/kT) = 10^{-10}$, 10^{-30}, and 10^{-50}.

TABLE I.

Values of σ *in ergs/cm.*^{2} *calculated from equation* (4) *with* $T_0 = 300°$ K., $\lambda = 10$ *cals./c.c., for* $\Delta T = 0{\cdot}1°, 1{\cdot}0°, 10°$, *and for the values of* $\Delta F_i{}^*$ *corresponding to* $\exp(-\Delta F_i{}^*/kT) = 10^{-10}$, 10^{-30}, *and* 10^{-50}.

$\exp(-F_i{}^*/kT)$.	$\Delta T = 0{\cdot}1°$.	$\Delta T = 1{\cdot}0°$.	$\Delta T = 10°$.
10^{-10}	0·10	0·48	2·2
10^{-30}	0·15	0·69	3·2
10^{-50}	0·18	0·82	3·8

In order to compare directly the magnitudes of the surface and bulk-energy terms, following Turnbull we may approximately transform the σ values into cals./mole by multiplying by $N^{\frac{1}{3}}V^{\frac{2}{3}}/4{\cdot}2 \times 10^7 \approx 19{\cdot}5$. The extreme values of σ recorded in Table I then correspond to ~2 and 74 cals./mole, or ~0·7 and 13% of the heat of transition. So far as we know, there are no independent estimates of σ; the range of percentages quoted is well below the values calculated by Turnbull and his co-workers for nucleation in liquid metals, which are mostly between 30% and 50% of the molar heat of fusion. There is no reason to suppose, however, that interface relations in wholly solid systems must closely parallel those in solid–liquid systems; for example, there is the possibility with the former that the boundary between the two phases is not sharp but takes the form of a gradual change over a number of molecular diameters, in order to make the interfacial free energy as small as possible (cf. Bloch walls in ferromagnetics).

Table II shows how, for the σ values of Table I which correspond to $\Delta T = 1°$, the quantity $\exp(-\Delta F_i{}^*/kT)$, *i.e.*, the rate of nucleation, alters with slight temperature changes.

TABLE II.

Values of $-\log[\exp(-\Delta F_i{}^*/kT)]$ *calculated for values of* σ *corresponding to* $\Delta T = 1°$, *for values of* ΔT *between* 0·9° *and* 1·1°.

σ.	$\Delta T = 0{\cdot}90°$.	$\Delta T = 0{\cdot}99°$.	$\Delta T = 1{\cdot}00°$.	$\Delta T = 1{\cdot}01°$.	$\Delta T = 1{\cdot}10°$.
0·48	12·3	10·2	10	9·8	8·25
0·69	37	30·6	30	29·4	24·8
0·82	61·6	50·8	50	49·1	41·2

It is clear from Table II that the theory can account for extremely rapid changes in the rate of nucleation with temperature. Thus if we take $\exp(-\Delta F_i{}^*/kT)$ to be 10^{-30} when $\Delta T = 1°$, a change of only 0·02° (from $\Delta T = 0{\cdot}99°$ to $\Delta T = 1{\cdot}01°$) changes the rate of nucleation by a factor of $10^{1{\cdot}2}$, *i.e.*, about 16, and a change of 0·2° by $\sim 10^{12}$. Thus, though the new phase cannot literally appear suddenly at a particular temperature, this clearly is very much the impression one would get in an experimental investigation.

If in the above example ΔT had been taken to be 0·1° instead of 1·0°, the change of rate of nucleation by a factor of 16 (in the first case produced by a change in ΔT of 0·02°) would now be produced by an alteration in ΔT of only 0·002°, and similarly for $\Delta T = 10°$ the corresponding figure is 0·2°.

We may conclude therefore that, if we disregard any other factors (*e.g.*, impurities, particle size, etc.) which may influence the sharpness of a transition, then, for a group of transitions in different solids for which $\exp(-\Delta F_i^*/kT)$ has about the same value, T_w and T_c would be more precisely defined the narrower the hysteresis loop. There are not sufficient data on rates of attainment of equilibrium to enable this conclusion to be tested. But it may be worth noting that a consideration of transitions in similar substances does give the impression that the maximum rate of volume change (relative to the total volume change) with temperature is greater the narrower the hysteresis loop. [In particular, it is rather striking that for tetradeuterammonium bromide this rate for the upper of the two transitions, which has a very narrow hysteresis loop, is some 10—20 times greater than that for the lower one where the loop is unusually wide (Smits, Tollenaar, and Kröger, *Z. physikal. Chem.*, 1938, **41**, *B*, 215).]

Hitherto we have neglected the strain term; an upper limit of the magnitude of this may be very roughly estimated by assuming that a nucleus of one phase in another is either compressed or extended, so that it occupies the same volume as the same mass of the second phase. On this basis

$$\Delta F_i^* = \frac{16\pi\sigma^3}{3\left\{-\frac{\lambda\Delta T}{T_0} + \frac{1}{2\beta}(\delta V)^2\right\}^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

If we take β, the isothermal compressibility, to be 5×10^{-6} atm. and δV, the volume change per unit volume at the transition, to be 0·003 (these figures are roughly those for the transition in ammonium chloride), $\frac{1}{2\beta}(\delta V)^2$ equals 0·02, while $\lambda\Delta T/T_0 = 0{\cdot}03\ \Delta T$. Although this is probably an overestimate of the effect of strain, it is clear that this effect could be important. It will operate to reduce the calculated values of σ, and it will also enhance the sensitivity of the dependence of nucleation rate on temperature.

Since strain effects broaden the hysteresis loop, one might enquire whether there is any correlation between ΔV, the value of the comparatively abrupt part of the volume change, and $T_w - T_c$ for transitions in a series of solids which have roughly the same values of β and of λ. The available data for ammonium salts are summarised in Table III. The values of ΔV can only be assessed very roughly. It will be seen that it is broadly true that the greater ΔV the greater $T_w - T_c$.

TABLE III.

ΔV *Values in c.c./mole for various transitions in ammonium salts occurring at* T_w,°K., *compared with the width of the hysteresis loop,* $T_w - T_c$.

Salt.	ΔV.	$T_w - T_c$.	T_w,°K.	Ref.
NH_4Br	0·03	0·06°	234·4	*A*
NHD_3Cl	0·07	0·07	247·95	*B*
ND_4Br	0·08	0·11	214·89	*C*
NH_3DCl	0·11	0·12	244·61	*B*
NH_4Cl	0·15	0·35	242·61	*B*
$(NH_4)_2SO_4$	0·35	1·2	223·40	*D*
ND_4Br	0·6	9·0	168·1	*C*
8·5% NH_4Br +91·5% NH_4Cl	0·65	14·6	232·5	*E*
11·6% NH_4Br +88·4% NH_4Cl	1·09	20·0	212·2	*E*

References: *A*, Smits, Ketelaar, and Müller, *Z. physikal. Chem.*, 1936, **175**, *A*, 359. *B*, Thomas and Staveley, *loc. cit.* *C*, Smits, Tollenaar, and Kröger, *Z. physikal. Chem.*, 1938, **41**, *B*, 215. *D*, Hogg and Staveley (unpublished). *E*, Mandelberg and Staveley, *J.*, 1950, 2736.

We shall now examine in greater detail the available experimental data, beginning with those which bear on the correlation of the sharpness of transition with the presence of hysteresis. Strictly speaking, no part of a transition is observed to occur completely isothermally, just as the melting point of a substance always shows some drift as melting proceeds. No doubt, just as in melting, impurities will tend to make a transition less abrupt, and in addition for solid–solid transitions other factors will produce the same result. Thus T_w and T_c can vary with particle size (Thomas and Staveley, *J.*, 1951, 1420), so that non-uniformity of crystal size will be such a factor; different crystals being in different states of strain may lead to transformation at different temperatures. In calorimetric work, electrical heating can result in local overheating and cause a part of a sample to undergo a transition before the main body, and in the region of a hysteresis loop this is an irreversible process. Nevertheless it is difficult to resist the impression given by careful studies of transitions showing hysteresis (Staveley, *loc. cit.*) that part at least of these would occur isothermally in ideal circumstances, and moreover that hysteresis is associated primarily with the almost sharp, and not with the gradual, part of the transitions. Examples of transitions to which this statement applies occur in ammonium chloride, monodeuterammonium chloride, trideuterammonium chloride, ammonium sulphate, tetradeuterammonium sulphate, hydrogen sulphide, deuterium sulphide, ammonium bromide, and tetradeuterammonium bromide; further examples can be found in organic solids where the transitions have been studied by dielectric-constant measurements (see, *e.g.*, Crowe and Smyth, *J. Amer. Chem. Soc.*, 1950, **72**, 4009).

By contrast those transitions which are continuous throughout are quite free from hysteresis. Examples are not numerous but the transitions in sodium nitrate (Kracek, *J. Amer. Chem. Soc.*, 1931, **53**, 2609), ammonium iodide, and tetradeuterammonium chloride are certainly of this type; and the same is probably true of those in basic beryllium acetate between 30° and 40° (Jaffray, *Ann. Physique*, 1948, **3**, 5) and in copper sulphate pentahydrate (Brun and Jaffray, *Cah. Phys.*, 1944, **21**, 25).

An apparent exception to our generalisation that sharpness and hysteresis go together is provided by the transition in hydrogen bromide at about 90° K. Hysteresis is present here and is certainly associated with that part of the transition where the physical properties are changing most rapidly, but at no temperature does the heat content or dielectric constant change abruptly (Damkohler, *Ann. Physik*, 1938, **31**, 76; Eucken and Güttner, *Gottingen Nachr., Math.-Phys. Kl.* II, 1936, **2**, 167). Perhaps the same is true of the transition in methane where only heat capacity has been measured (Eucken and Bartholomé, *ibid.*, 1936, **2**, 51).

As we shall discuss below, there is evidence that the hysteresis characteristics in certain systems do not become reproducible until they have been subjected to the transition many times. In the light of this and of what has already been said about the factors that tend to make a sharp transition apparently diffuse, we consider that in spite of these apparently anomalous phenomena the generalisation is still of value.

The transitions exhibiting hysteresis which have been most carefully studied are of type II. With regard to type III (first-order) transitions, it is usually supposed that the steady temperature attained when one form is produced from the other, either in heating or in cooling, is the true equilibrium temperature; the supercooling of the high-temperature form below this temperature is a common phenomenon. Superheating of the low-temperature form above T_e has been more rarely observed, *e.g.*, with α–β-sulphur. Perhaps the most complete investigation of these effects is that carried out by Wiebenga (*Z. anorg. Chem.*, 1935, **225**, 38) on hexachloroethane which has two type III transitions. For each of these he established T_e by finding the temperature at which, with two phases present, the interconversion rate was zero. For each transition, T_e is certainly above the temperature at which the change sets in on cooling and, for the lower transition at least, T_e may be lower than the temperature at which the change takes place on warming. Although more experimental evidence is needed it seems clear that many type III transitions display hysteresis, at least in one direction (*i.e.*, either $T_w > T_c = T_e$ or $T_c < T_w = T_e$), if not in both (*i.e.*, $T_c > T_e > T_w$) (see, for instance, Smyth, *loc. cit.*, and Connell and Gammel, *Acta Cryst.*, 1950, **3**, 75).

It is possible that in some systems factors which we have not yet considered come into play and modify the conclusion reached from the theory outlined above, namely, that all type III and type II transitions should show hysteresis in both directions. It may be possible for nuclei of the high-temperature modification, at least, to form most easily on the crystal surface (cf. fusion); this could prevent T_w from rising above T_e, but, on cooling, nucleation would then presumably have to start within the crystals leading to hysteresis on cooling (cf. the solidification of liquids).

Another factor is that, whereas we have supposed hitherto that the formation of an interface between two phases is accompanied by a free-energy increase, it is possible that the reverse may sometimes be true and so hysteresis could vanish on the basis of the theory given above. (The mathematical formulation would now be different since the nuclei would no longer be spherical.) Further, a negative surface free energy will tend to make the interfacial surface area as large as possible; this will lead in the limit to the growth of order or disorder homogeneously throughout the crystal. The transition could then be completely gradual (type I) (cf. Mayer and Streeter, *loc. cit.*) and, as we have seen, such transitions appear to be hysteresis-free.

We shall now consider the relation between the two phases at temperatures between T_w and T_c. From experiments, particularly by Smits and his co-workers, it appears that the curve obtained on warming to some point *b* (Fig. 2), before the really rapid volume alteration sets in, is completely reversible on cooling from *b*; the same applies on cooling to *d* and then warming. On warming to *e* and then cooling, however, a path such as *efga* is followed, and on warming from *g* a path such as *ghc*. Furthermore, it is possible to stop on such curves as *efg* or *ghc*. Moreover, although equilibrium is usually quickly attained along curves *ab* and *cd*, along *bc* and *da* it may be only very slowly reached. One must assume that points on *bc* and *ad* and within the loop represent a mixture of the two forms. If there is some mechanism of transference between the two phases they can co-exist in equilibrium only at one temperature T_e. For systems which give curves as in Fig. 2 we must conclude that such a mechanism is absent. This is comprehensible if a whole crystal can change without influencing its neighbours, and if, after a self-propagating nucleus has appeared in a single crystal unit, the whole unit changes almost at once (it may be that the crystal unit in this sense is very small). Thus at the point midway between *b* and *c* half the crystal units are at *c* and half at *b*; on cooling, those at *c* follow the path *cdga*, the others the curve *ba*, so that the observed curve *efg* is a weighted mean of these two limiting curves. Observations of V–T relationships within hysteresis loops are essentially consistent with this picture, but we cannot rule out the possibility that circumstances may arise in which transference is possible between the two forms and in which the change spreads only slowly from a nucleus, so that the two forms co-exist within the same crystal unit over an appreciable time. Thus, if for such a system in which equilibrium between the two modifications can be easily attained, T_e is very near T_w, then on cooling from *e* the path followed will be near the curve *eba*, and the hysteresis on cooling will only be apparent if the system is first heated so that the transformation to the high-temperature form is complete.

The transition in ammonium chloride must presumably be one in which the transformation takes place in small crystal units between which there is no interaction, for, with both forms present, the transformation velocity is immeasurably small inside the loop. With ammonium chloride it is not hard to understand why the phase change, once initiated, should be very rapid, for over the whole transition the ammonium ions can execute to some extent the motion required to bring about the final sudden change.

Rather similar observations have been made by Bridgman in his studies of transitions under high pressures. (Just as thermal hysteresis occurs at constant pressure, so also hysteresis is possible when the pressure is varied at constant temperature.) For some transitions at constant temperature he found a " region of indifference "—that is, a region of pressure in which the interconversion velocity was apparently zero even though both forms were present (Bridgman, " The Physics of High Pressures," G. Bell and Sons, 1931).

We have already mentioned the possibility that nucleation may commence on the crystal surface; in this event one must expect that, in principle, particle size would influence the hysteresis characteristics. In fact, for extremely small crystals of ammonium chloride the loop is slightly narrower than for larger crystals (Thomas and Staveley, *loc. cit.*). One could also imagine that the nature of the medium in contact with the crystal surface might influence the hysteresis loop; experiments in this laboratory (to be more fully reported later), in which the transition in ammonium chloride has been studied dilatometrically in a variety of fluids, showed that with the most polar liquids used (mixtures of methyl alcohol and water) the loop is appreciably wider: it is interesting that the hysteresis persists in methyl alcohol–water mixtures in which ammonium chloride is appreciably soluble. One must therefore suppose that even under these conditions transference between the two forms is very slow.

It has been observed that as a substance is repeatedly subjected to a transition the hysteresis loop sometimes becomes narrower, until a limiting condition is reached. This may be due to a progressive break-up of the crystals, and in this connection the following point may be noted. If, on the first occasion on which the substance is subjected to the transition, the crystal units are relatively large, it is then possible that in some of these more than one self-propagating nucleus could develop. Wherever this produces a form with some particular orientation between molecules and ions, the ordered regions arising from these nuclei will eventually meet and form interfaces at which the orientation of the particles concerned may change, so that the particles break up. In a repetition of the experiment, the transition is then being studied with smaller crystal units, so that the width of the loop is slightly changed.

Clusius and Weigand (*Z. Elektrochem.*, 1938, **44**, 674) found that increase of pressure broadens the hysteresis loop in the III $\rightleftharpoons$ II transitions in hydrogen and deuterium sulphides; in view of the very sensitive dependence of the intermolecular forces on distance, this may be caused by an increase in the interfacial free energy as the molecules are brought together.

Finally, we may observe that small quantities of impurities have relatively little effect on hysteresis phenomena in solid–solid transitions. This is in contrast to the solidification of supercooled liquids where a nucleus, the formation of which has arisen from some impurity, can result in the crystallisation of the whole mass (cf. Turnbull and Cech, *J. Appl. Physics*, 1950, **21**, 804). If in solid–solid transitions, as we believe, the change takes place in comparatively small unconnected crystal units, then the induction of nucleation in a few of these by chance impurities will not affect the behaviour of the majority.

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