320. *Hysteresis in the Transitions in Ammonium Chloride, Hexamminonickel Nitrate, Silver Mercuri-iodide, Hexachloroethane, and Carbon Tetrabromide.*

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Dilatometric investigations are described on transitions in the substances named in the title. The primary object of these studies was to obtain further evidence bearing on a recently proposed theory of hysteresis. The basis of this theory, that the hysteresis is confined to the almost isothermal part of a transition, was confirmed.

It was found that the presence of solvents, so far from eliminating the hysteresis displayed by ammonium chloride, in fact may widen the hysteresis loop. Unusual behaviour was observed with hexamminonickel nitrate in that the transition region moved several degrees as the sample aged; also for this substance and for silver mercuri-iodide the hysteresis effects depended somewhat on the thermal history of the sample. For the first-order transitions in carbon tetrabromide and hexachloroethane the true equilibrium transition temperatures T_e were established, and here hysteresis was confined to cooling. Also for these transitions, once the change set in, it proceeded to completion, except at T_e.

Some measurements were made on the rates of volume change in the transition regions. Different types of behaviour were observed and it seems that for some transitions, *e.g.*, that in ammonium chloride, the overall rate of change is controlled by the rate of formation of self-propagating nuclei, whereas for others, *e.g.*, that in hexachloroethane, both this and also the rate of subsequent growth from these nuclei determine the overall rate.

In a previous paper (Thomas and Staveley, *J.*, 1951, 2572, which we shall refer to as Part I), it was suggested that hysteresis in solid–solid phase transitions arises simply from the difficulty of the initial formation of a new phase within an old. It was pointed out that hysteresis should only arise when part at least of the transition occurs isothermally and that the hysteresis should be associated with this part; also that the transition should proceed at all temperatures except at an equilibrium temperature, T_e, providing (i) that both forms are present in bulk and in an unstrained condition, and (ii) that there is a genuine dynamic equilibrium between the two forms. In addition it was thought that, though the established instances of hysteresis were confined to co-operative changes, the phenomenon should appear in normal first-order changes as well. This paper describes some experiments on the transitions in ammonium chloride, hexamminonickel nitrate, silver mercuri-iodide, hexachloroethane, and carbon tetrabromide, which were designed to test these predictions.

The λ-point in ammonium chloride was studied in the presence of solvents in an attempt to bring about a dynamic equilibrium between the two forms. We have also investigated whether the transition characteristics are altered if the substance is in contact with liquids of different kinds in which it is insoluble. The transitions in hexamminonickel nitrate and silver mercuri-iodide begin gradually but end almost abruptly, and so should provide further examples of the association of hysteresis only with the nearly isothermal part of the change. Hexachloroethane and carbon tetrabromide have transitions which occur apparently entirely isothermally, and according to our views these should therefore show hysteresis.

Experimental

Preparation of Materials.—Ammonium chloride. "AnalaR" ammonium chloride was purified by a single sublimation in a vacuum.

Hexamminonickel nitrate. A solution of nickel nitrate was obtained by adding an excess of nickel oxide to nitric acid; the oxide was prepared by decomposing the oxalate, which had been precipitated from hot solutions of "AnalaR" nickel chloride and oxalic acid, at 400—500°. Ammonia solution (*d* 0·88) was added dropwise to the cooled nitrate solution, precipitating the complex (King, *J.*, 1932, 2928). The crystals were washed with ammoniacal alcohol and ether and kept in a desiccator over soda-lime in an atmosphere of ammonia, at first at 0°. After about 4½ months a sample was removed from the desiccator and analysed for ammonia volumetrically, and for nickel by means of dimethylglyoxime [Found: NH_3, 35·6; Ni, 20·66. Calc. for $Ni(NH_3)_6(NO_3)_2$: NH_3, 35·87; Ni, 20·60%].

Hexachloroethane. 1 Kg. of technical hexachloroethane was crystallised from alcohol, and 720 g. of the product were then subjected to three fractional sublimations at 70° at a pressure of 1 mm. or less. 243 g. were finally collected. There was no appreciable improvement in the purity after the second and third sublimations.

The constancy of the triple point was used as a criterion of purity. The sample was sealed under vacuum in a glass tube with a re-entrant thermocouple well. No stirring was possible. Heating and cooling curves were taken, and in this simple apparatus the final specimen melted over a range of 0·1°.

Silver mercuri-iodide. This was prepared by adding silver nitrate (in the dark, with mechanical stirring) to a solution of mercuric iodide in the minimum amount of potassium iodide. Three samples, A, B, and C, were made and studied dilatometrically. In the preparation of A and B, only about three-quarters of the stoicheiometric amount of silver nitrate was added, to avoid the formation of a product containing free silver iodide (cf. Ketelaar, *Z. Krist.*, 1931, **80**, 190). The results obtained with A and B suggested that each of these samples consisted of two solid phases; this was supported by a microscopic examination, which showed both to be a mixture of orange and yellow crystals. Accordingly, in preparing C, exactly stoicheiometric quantities were used, and this, under a microscope, appeared to consist solely of yellow crystals.

In the preparation of sample A, the silver nitrate was added very slowly to a hot solution of mercuric iodide in potassium iodide, in the hope of producing relatively large crystals, but B was made by rapid mixing of the cold reagents with the object of producing small particles. These were probably smaller than those composing A, since they settled more slowly. There were no obvious differences between *X*-ray powder photographs of A, B, and C.

Dilatometers.—The dilatometers were filled with the substance under investigation and then evacuated, if necessary with cooling in solid carbon dioxide, and sealed off. The liquid was usually introduced by breaking open the tip at the top of the capillary of the dilatometer under the surface of the liquid, previously degassed, and any excess of liquid then removed by evaporation. Sometimes the filling was accomplished by distillation. About 20 g. of ammonium chloride were used in each dilatometer with 1 mm. diameter capillaries; similarly about 10 g. of hexamminonickel nitrate and about 40 g. of hexachloroethane were used with capillaries of about 1·3 and 1·4 mm. diameter, respectively.

For carbon tetrabromide considerable difficulty was experienced in finding a suitable confining fluid necessary for a dilatometric investigation. Water was known slowly to hydrolyse the substance. With mercury, dilatometric readings were not reproducible, perhaps partly because mercury does not wet this solid and so cannot penetrate crevices, and partly because of its inability to dissolve occluded gas which is released when crystals break up. Finally, perfluoromethyl*cyclo*hexane was chosen as it was believed that carbon tetrabromide should have a relatively low solubility in this liquid (cf. Hildebrand, Fisher, and Benesi, *J. Amer. Chem. Soc.*, 1950, **72**, 4348), an expectation substantiated by our observations.

Thermostats.—All volume measurements were made at constant temperature. For the examination of ammonium chloride and hexamminonickel nitrate the thermostat, constant to within ±0·002°, previously described (Thomas and Staveley, *J.*, 1951, 1420) was used. For hexachloroethane, where temperatures were required near 40°, the same thermostat was used, but now the vapour-pressure regulator was filled with carbon disulphide in place of methyl chloride; this meant that the external tubes had to be electrically heated, and that thermostated water at about 50° had to be circulated around the mercury column. In addition the temperature was now measured with a platinum-resistance thermometer.

For carbon tetrabromide and silver mercuri-iodide again a Dewar vessel was used as a thermostat, temperature control to within ±0·01° being effected by a toluene regulator with a Sunvic proportionating head. The temperature was measured with a platinum resistance thermometer, or with mercury thermometers calibrated against this.

Results.—*Ammonium chloride.* Seven similar dilatometers were filled from the same batch of ammonium chloride; each was then filled with a different liquid and all were studied in the same thermostat simultaneously. A second batch of crystals was made and this was used to fill three dilatometers. The results were plotted as dilatometer readings against temperature and are not reproduced. The absolute volume changes were not calculated. For each dilatometer 44 readings were obtained with two runs for ascending, and three for descending temperatures. The results were quite reproducible except that on the first descending run, before which the samples had only been through the transition once, T_c occurred 0·06—0·07° below the temperature which was finally adopted after the transition had been traversed several times (T_c and T_w are the temperatures at which $\mathrm{d}V/\mathrm{d}T$ is maximum for cooling and warming runs respectively). This contraction of the loop to a constant width as the sample is repeatedly subjected to the change has been reported previously for other substances (Smits, Tollenaar, and Kröger, *Z. physikal. Chem.*, 1938, *B*, **41**, 215) but not so far for ammonium chloride : it may be connected with the break up of the crystals due to the volume change.

Each limb of the hysteresis loops covered 0·1°; this diffuseness is almost certainly derived from the lack of careful purification, for previous experiments have shown that the transition can be much sharper (Thomas and Staveley, *loc. cit.*, p. 1420). Nevertheless, it was easy to detect differences in the behaviour of different samples. The table summarizes the results of these experiments, and those of previous investigations are included for comparison. For batch no. 2 the saturated solutions of the ammonium chloride in the alcohol–water mixtures at the temperature of the transition were very roughly 1·2N and 0·6N for the 50% water and 25% water mixtures respectively.

Transition characteristics for ammonium chloride as obtained by different authors using different dilatometric fluids.

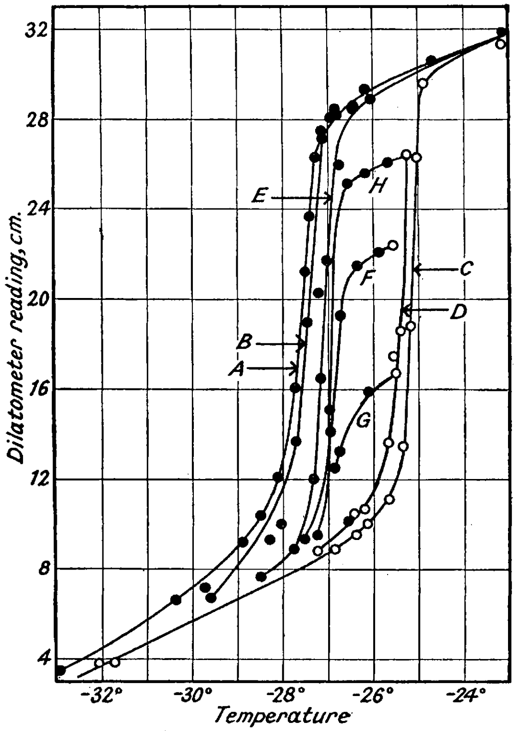
Batch no. or ref.*	Composition of surrounding fluid	T_w	T_c	Width of loop, ΔT
1	CS_2	−30·59°	−30·88°	0·29°
	$CHCl_3$			
	$COMe_2$			
	n-C_7H_{16}			
	MeOH			
	90% MeOH + 10% H_2O (by wt.)			
	39% MeOH + 61% H_2O	−30·55	−30·93	0·38
2	CS_2	−30·60	−30·86	0·26
	~75% MeOH + 25% H_2O	−30·615	−30·91	0·295
	~50% MeOH + 50% H_2O	−30·555	−30·955	0·40
a	Cymene	−30·52	−30·79	0·27
b	CS_2 (large crystals)	−30·55	−30·90	0·35
	CS_2 (small crystals)	−30·61	−30·86	0·25

* (*a*) Smits and MacGillavry, *Z. physikal. Chem.*, 1933, *A*, **166**, 97.
(*b*) Thomas and Staveley, *loc. cit.*, p. 1420.

It can be seen that from one batch of crystals to another there are significant differences in the widths of the hysteresis loops, and also in the values of T_w and T_c. These differences can probably be ascribed to differences in crystal size, the nature of the surfaces, and so forth. However, for one batch of crystals there is no detectable difference in the hysteresis characteristics in the presence of any of the liquids tried, except for the water-rich methyl alcohol–water mixtures when the loop is definitely broadened, *e.g.*, from 0·29° to 0·38°. Despite the considerable solubility of the salt in these mixtures the volume still reached a steady value both on the limbs of the loop and within it, in the usual time of 2—3 hours. Thus, if, as we have supposed, at intermediate points on the limbs two phases exist side by side, in this instance the solvent does not set up rapid equilibrium between them. On the contrary, in broadening the loop it would appear to hinder nucleation. How it does this is not clear. The effect may be due to the influence of the dynamic equilibrium on the surface irregularities, or since water–alcohol mixtures are capable of strong interaction with ions, it may be connected with the forces between the surface and the liquid which will, in principle, affect free-energy relationships in the system as whole.

A number of observations were made on the rate of attainment of equilibrium. These showed that there was always a continuous decrease of the velocity of the transition as the change proceeded. By the time temperature equilibrium had been reached a considerable proportion of the change was over, but the following two examples show that the maximum velocity occurred, if not at zero time, at least well before a half or even a third of the volume change had been recorded. In going from −30·885° to −30·915° the meniscus in the dilatometer containing ammonium chloride and acetone fell by 3·04 cm. in 3 hours and was still falling after this time. No measurements were made in the first half hour, during which the meniscus fell by 1·08 cm., but from the end of this period onwards the velocity fell continuously. Similarly in going from $-30{\cdot}915°$ to $-30{\cdot}953°$ the fall in the dilatometer containing ammonium chloride and 39% methyl alcohol and 61% water, over 140 minutes was 3·48 cm., of which only 0·98 cm. occurred in the first 20 minutes, yet after this period the rate was already diminishing.

Hexamminonickel nitrate. A calorimetric study of this salt (Long and Toettcher, *J. Amer. Chem. Soc.*, 1942, **64**, 629) has revealed a gradual transition from 173° to 247° K, with a maximum value of dC_p/dT at 243·3° K (−29·9° C). The change is associated with the disordering of the orientation of the nitrate ions. It also seemed likely from rough cooling curves that the transition exhibited hysteresis. Since a thermostat for this temperature region was available it was decided to investigate the change dilatometrically. It was found that hysteresis was associated with the final part of the change which occurred almost isothermally, and the general behaviour was similar to that of ammonium chloride. But a number of unusual observations were made on the dependence of the transition characteristics on the age of the sample and on its thermal history.



Plot of dilatometer readings against temperature in the region of transition in hexammino-nickel nitrate (fourth sample). Open circles warming, full circles cooling.

Four samples of the substance were investigated, all taken from the same material; this had been kept in a desiccator at 0° over soda-lime in an atmosphere of ammonia for a week, after which the first sample was removed. Subsequently it was kept in the same desiccator with ammonia but at room temperature. The salt has a considerable vapour pressure of ammonia at room temperature and will decompose if left in the open, but under the conditions employed this decomposition appeared to be avoided, as was indicated by the analysis made 4 months after the preparation.

The first runs on the first sample confirmed the presence of a transition with hysteresis, but no part of the change was at all sharp, the limbs of the loop stretching over 4°. However, as the change was repeated it became sharper, and the loop rather narrower. Also it was found that for descending temperatures T_c depended somewhat upon the temperature from which the sample had been cooled. Very roughly for this sample T_w was $-30{\cdot}6°$, and T_c was $-33{\cdot}1°$.

The second sample was taken from the desiccator 23 days after its preparation. It had a fairly sharp transition, and again the descending limit of the loop depended on the temperature from which cooling occurred, though a limiting value was reached when it was cooled from well above the transition. However, T_w was $-27{\cdot}1°$ and T_c was $-29{\cdot}7°$, a rise of no less than 3·5° and 3·4° respectively over the values for the first sample.

The third sample, removed after 34 days in the desiccator, behaved similarly except that there was a further rise in T_w and T_c, which were now $-26{\cdot}0°$ and $-28{\cdot}3°$, respectively.

The fourth sample, removed after 120 days, was more carefully examined than any of the others. Capillary readings are plotted against temperature in the figure. The limbs of the hysteresis loop are seen to be not far from vertical, covering 0·1—0·5°. The contraction in the loop as the transition is repeated is illustrated by curves *A* and *B*, and *C* and *D*, *B* and *D* occurring after *A* and *C* : here the contraction is 0·1—0·3°. *A* and *B* were obtained by cooling the specimen from room temperature. Curves *H*, *F*, and *G* show what happens if the system is cooled from the limb for ascending temperatures : it appears that a limiting downward limb is followed at about $-26{\cdot}9°$, whereas curve *B* from room temperature lies at about $-27{\cdot}4°$ (T_c). If the system is cooled from just above the transition, *e.g.*, from $-23{\cdot}15°$ (after being warmed from $-78°$), the intermediary curve *E* is followed. It would seem that there is a family of curves that can be followed falling between *H*, etc., and *B* depending upon the starting point. No such effect occurs for warming : curve *D* has on it points representing the system when it had been warmed from $-78°$, and from $-27{\cdot}5°$ (reached by following a curve such as *F*) just below the transition. This is further confirmed by the fact that on warming from one of the downward curves the ascending limiting curve is regained, as previous experiments on the other samples had shown. T_w for this transition is about $-25{\cdot}3°$. These effects may be connected with the growth of the crystallites and the gradual elimination of their imperfections which would affect the transition characteristics : it is conceivable that the effect is more marked for cooling than for warming because the disordered regions above the transition may more readily fuse together than the ordered regions, existing below the transition, which will have their symmetry axes randomly directed. Possibly the preservation in crevices of nuclei may also play a part (Turnbull, *J. Chem. Phys.*, 1950, **18**, 198).

It can be seen that from the first to the last specimen the mean temperature of the transition rose by about 5·5°; in the last specimen the loop was about 2·1° wide. Since the fourth sample had a higher transition temperature than the third, there is no reason to suppose that the fourth represents the limit : T_w for the fourth sample is 4·6° higher than that reported by Long and Toettcher (*loc. cit.*). Once the specimens are in the dilatometers and surrounded by carbon disulphide, the transition characteristics remain approximately the same. This would indicate that whatever change was occurring to alter the transition temperature, took place in the desiccator. Thus this process might have been drying or possibly a gradual perfection of the crystals by the dynamic equilibrium of ammonia set up between the solid and the gas phase, though neither suggestion seems convincing. Indeed, it is hard to see that impurities, etc., should be the cause of the effect, for the sharpness ultimately obtained of the final part of the transitions did not alter markedly from one sample to the next. The analysis, carried out 15 days after the fourth sample had been removed, was satisfactory (see above).

The kinetic behaviour resembles that of ammonium chloride. Away from the immediate vicinity of the hysteresis loop, equilibrium is attained at once, but on the limbs of the loop several hours elapse before the meniscus becomes constant, yet the velocity of the change is always observed to decrease as the change proceeds, and has certainly reached a maximum before 50% of the change has occurred. Thus, on cooling of the fourth sample from $-26{\cdot}734°$ to $-26{\cdot}995°$ an alteration in dilatometer reading of 6·5 cm. during 2 hours took place and the volume was still changing very slowly at the end of this time, but 3 cm. of this change occurred in less than the first 20 minutes.

As discussed in Part I we believe that there is only one temperature T_e at which the high- and low-temperature forms can coexist in true equilibrium. An unsuccessful attempt was made to determine T_e for this system as follows. By alternately heating and cooling the sample five times over part of the transition region, and then plunging the dilatometer into the thermostat at $-25{\cdot}53°$, the point falling at the highest temperature on curve *F* was obtained. Curve *F* was traced out on cooling from this temperature and was similar to curves *H* and *G*, where no attempt had been made to secure intimate mixing of the two forms.

Hexachloroethane. Hexachloroethane has two first-order transitions, one near 44°, and one near 71°; only the first of these was studied and the sample was never taken through the high-temperature change. Previous work had shown that hysteresis of a kind occurred at both transitions, though it was thought that it was different from that typified by ammonium chloride because T_e could be definitely established, and only at this temperature did the two forms coexist in equilibrium (Wiebenga. *Z. anorg. Chem.*, 1935, **225**, 38). Nevertheless, supercooling occurred at both transitions, but the evidence left the question of superheating open, though if superheating occurred at all it was less than the supercooling.

The system behaved very differently from those previously investigated; once the transition had begun either on cooling or warming it always proceeded to completion, the rate beginning slowly, rising to a maximum usually at about 50% conversion, and then declining. Rate measurements were made at different temperatures for ascending and descending runs, and these rates, measured both by the maximum value achieved and the time taken to reach this maximum value, varied very rapidly with temperature (cf. Hartshorne, *Discuss. Faraday Soc.*, " Crystal Growth," 1949, **5**, 149). The rates also depend on the temperature from which heating or cooling had taken place.

Wiebenga found the true equilibrium temperature for the transition to be 43·6°, by arranging that both forms should be simultaneously present by previously heating and cooling the sample partially through the transition, and then observing the temperature at which the meniscus was steady. We similarly found T_e to be 44° ± 0·1°. The highest temperature at which the transition was observed to commence on cooling was 41·00°; at 42·44° the specimen remained in the high-temperature form for 5 days without sign of change (though if both forms were present at this temperature the transition proceeded comparatively rapidly). This showed that the change could be supercooled by several degrees. Measurements at 44·08° and 44·26°, lasting 4 or 5 days each, showed that at both these temperatures the change started spontaneously, although very slowly, without the introduction of the high-temperature form. Hence superheating of the transition is either non-existent or very small.

Carbon tetrabromide. The investigation of carbon tetrabromide was not as thorough as that of hexachloroethane, but the essential characteristics were revealed. Hysteresis of the order of 1° was definitely present: for ascending temperatures the system remained in the low-temperature form for at least 9 hours at 46·80°, but at 46·96° after 24 hours the change was about 85% finished, and was still occurring. For descending temperatures the system remained in the high-temperature form for 4 hours at 46·11° and showed no sign of changing, but at 45·98° the transition had taken place completely in about 12 hours. To find T_e, the same technique of " activation " was used as had been adopted for hexachloroethane, and showed that T_e lay above 46·78°, but below 46·88°. Thus, as before, superheating is absent or too small to be detected. As with hexachloroethane, it was not possible for the two forms to co-exist side by side in the dilatometer except at T_e; once the change had started it proceeded to completion.

The remarkable fact about this transition is that for *ascending* temperatures the rate of change is maximum at least as soon as measurements become possible and certainly well before half the change has taken place, just as for ammonium chloride, but for *descending* temperatures the change begins slowly, rises to a maximum when half the mass is transformed, and then declines again just as for hexachloroethane.

Silver mercuri-iodide. The existence of a transition in this substance, accompanied by a colour change, has long been known. Ketelaar (*loc. cit.*; *Z. physikal. Chem.*, 1934, *B*, **26**, 327; 1935, **30**, 53) has shown that it is partly gradual and partly sharp, and has elucidated the ionic redistribution which it involves. The accompanying volume change is relatively small, and in the transition region equilibrium is attained very slowly. These factors make a precise dilatometric study rather difficult. Nevertheless, our investigations revealed some interesting features.

All three samples of this substance appeared to undergo two transitions, the first reaching completion between 46° and 47°, the second at 51°. Both transitions displayed hysteresis. We consider, however, that pure silver mercuri-iodide has only one transition, namely, that culminating at ~51°, not only because this agrees with the temperature recorded by Ketelaar, but also because with the third sample C, the lower transition was much less pronounced. In the light of these facts, together with the results of the microscopic examination and the phase-rule study of the silver iodide–mercuric iodide system carried out by Steger (*Z. physikal. Chem.*, 1903, **43**, 595), it is probable that our samples were mixtures of two phases, one being the pure substance, and the other a solid solution of mercuric iodide in silver mercuri-iodide.

We shall deal first with the transition in pure silver mercuri-iodide. We agree with Ketelaar that, while this begins gradually, the greater part of the change involved occurs almost isothermally. For samples A and B about half of the total volume change occurred between 50·7° and 50·8°, and for C, between 51·3° and 51·4°. The coefficient of expansion of the solid, however, did not revert to its normal low value until the temperature of 50·8° (for A and B), or 51·4° (for C), had been exceeded by several tenths of a degree. As was expected, the hysteresis, which amounted to ~4°, was confined to the discontinuous part of the change. For samples

A and B, for example, the volume–temperature curve for the gradual part of the transition (*i.e.*, up to ~50·7°) was exactly retraced on cooling from a maximum temperature not exceeding 50·7°. It was observed, however, that the cooling and warming curves did not differ very much even when the maximum temperature attained on warming was as high as 51·4°, and that the hysteresis was only fully developed when this maximum temperature was about 2° above that of the almost isothermal part of the transition. Similar results were obtained with sample C. With sample B (believed to consist of smaller crystals than the others), the cooling curves were more uniformly distributed across the hysteresis loop : some of the cooling curves for sample B were near the middle of the loop, whereas those for samples A and C were near one of the two boundary curves.

No attempt was made to assess T_e for this transition, but the results suggest that it is very close to T_w (*i.e.*, 50·7° for samples A and B). We have already noted that, on warming, the transition is not completed until the temperature is definitely above 50·7°, and it is therefore likely that if 51·0°, for example, is the maximum temperature reached, the majority of crystals still retain at this temperature nuclei or small regions wholly or partially in the low-temperature form. On cooling, these nuclei will induce reversion to the low-temperature form on reaching T_e, so that if this is very near 50·7°, the volume–temperature curve should revert to the warming curve. That such a cooling curve falls slightly above that for warming would then mean that at 51·0° all traces of the low-temperature form have disappeared from a few crystals, and that for these, nucleation will not set in on cooling until the temperature is 3—4° below T_e. Since the proportion of such crystals at a given maximum temperature should, *ceteris paribus*, be greater for smaller than for larger crystals, we can understand why the cooling curve for the former is found to lie further away from the warming curve. But for small or large crystals the full hysteresis effect will only appear when the substance has been heated to a sufficiently high temperature for all vestiges of the low-temperature form to have vanished. For samples A and B, this temperature is about 52·5°. Our observations on this transition indicate that, unlike that in ammonium chloride, it is not a change which proceeds rapidly throughout a crystal unit once nucleation has set in. It would, in fact, be expected that the ionic migration involved would have a considerable activation energy.

The lower transition, which we believe to be associated with a mixed-crystal phase, was not investigated so thoroughly. This transition was, however; found to present a rather striking example of a phenomenon to which we have called attention elsewhere (p. **1731**), namely, the dependence of T_c (the temperature at which the cooling curve rejoins the warming curve) on $T_{\text{max.}}$, the highest temperature reached, *i.e.*, the dependence of the width of the hysteresis loop on the thermal history of the substance. This is shown by the following figures :

$T_{\text{max.}}$	48·0°	49·3°	52·2°	70·6°
T	42·8	41·8	40·7	27·0

DISCUSSION

A complete treatment of the results we have presented would require consideration both of the factors affecting the rate of nucleation and of those determining the subsequent growth rate of a phase from a nucleus. It is not easy, and perhaps not justifiable, to attempt to separate these two processes from each other. It will, however, be convenient to consider first these results in the light of the theory relating hysteresis with nucleation (Part I).

The fundamental idea on which the theory was based is upheld, namely, that hysteresis is confined to the almost isothermal part of a transition, and conversely that any change which is partly or wholly isothermal displays hysteresis. The question arises, however, whether it is correct to identify the hysteresis exemplified by that at the λ-point in ammonium chloride (where it is possible to stop at any point on the limbs of, or within, the loop), with that associated with a completely first-order transition such as that in hexachloroethane (where the two forms can only coexist at one temperature). Smits and his school (*e.g.*, Wiebenga, *loc. cit.*) considered that the two kinds of hysteresis are fundamentally different. We believe, however, that the basic reason for hysteresis existing at all is universal, namely, the difficulty of the appearance of a new phase within an old. We suggest that what determines whether hysteresis at a transition resembles that in ammonium chloride on the one hand, or that in hexachlorethane on the other, is whether or not a crystal unit in one form can affect neighbouring units in the other form in which nuclei have not yet appeared. As discussed in Part I, the phenomena within the hysteresis loop for ammonium chloride and hexamminonickel nitrate are comprehensible if we suppose that the crystal units are quite independent of one another. (Here we may recall that for ammonium chloride even solvent does not establish equilibrium.) By contrast, for hexachloroethane, since once the change has started it proceeds throughout the whole crystal mass, and since in our experiments the two forms can only coexist at one temperature, we must conclude that contact between adjacent units in the two forms in these circumstances can bring about transformation of the less stable. With silver mercuri-iodide it seems that growth from nuclei is slow so that it can proceed part of the way in any one crystal unit and then be reversed; but that again there is no interaction between different crystal units. The apparent lack of mutual interaction for ionic solids may perhaps be connected with their hardness and involatility. Furthermore, when a form of one density grows within another, it may happen that the strains set up result, with a comparatively incompressible ionic crystal, in its fracture into very small units which may be further subdivided when subjected to the transition again. (This may be connected with the observations to which we have already drawn attention—that hysteresis loops can contract on repeated passage through the transition until a limiting state is reached.) In molecular crystals it is possible that their greater compressibility renders them less prone to disruption through internal strain, so that the crystal unit which can be changed by one nucleus may be much larger, and further that the greater volatility of such substances may make possible molecular movement across narrow gaps between crystals of the two forms.

We have already observed that with carbon tetrabromide and hexachloroethane the hysteresis is confined to the supercooling. It is impossible to say whether the same is true for ammonium chloride and hexamminonickel nitrate since we have been unable to establish T_e for these transitions. That superheating, however, is sometimes possible in first-order phase change has been demonstrated, *e.g.*, by Meerman for 1 : 2-dibromoethane (*Rec. Trav. chim.*, 1942, **61**, 860). In the nucleation theory of hysteresis under discussion, nucleation was assumed to start in crystals from within; if this is so both for heating and for cooling, the theory would require hysteresis in both directions. It was, however, pointed out that if energetic relationships are such that in one direction, for example on heating, nuclei start on the surface, then it could happen that there would be no, or at least much reduced, hysteresis on warming, though it would then seem inevitable that on cooling, nucleation would begin within the crystals and that there would be supercooling. We may mention that although it is normally impossible to superheat a solid above its melting point, Haykin and Bénet (*Compt. rend. Acad. Sci. U.R.S.S.*, 1939, **23**, 31) have shown that for tin, provided superficial melting is prevented, the solid can be superheated by at least 2°.

Our observations on the *kinetics* of the transitions may be summarized as follows. For ammonium chloride and hexamminonickel nitrate, on alteration of the temperature in the region of the almost isothermal parts of the transitions, by the time temperature equilibrium has been obtained and quantitative measurements of the rate become possible, this rate is found to decrease continuously as the change proceeds. Admittedly, by the time measurements can be made nearly half the change may be over, but there is no doubt that the rate is maximum at or near the start of the transition.

For hexachloroethane, as mentioned above, the behaviour was quite different. The rate of change always passed through a maximum at approximately 50% conversion, and the change once started always led to *complete* conversion of the whole sample from one form into the other.

With carbon tetrabromide the behaviour was again different. Whereas the rate of formation of the low- from the high-temperature form passed through a maximum at about 50% conversion as for hexachloroethane, yet the rate of the reverse change apparently decreased continuously with time and so must have had its maximum at or near the start of the transition. In this latter respect it therefore resembles ammonium chloride except that once the change has begun it leads eventually to complete conversion.

It seems to us that many more results of the kinetics of transitions are needed before generalizations can safely be made and before all the factors involved can be fully understood. The rate at which a transition takes place without artificial inoculation or " seeding " must in principle be dependent both on the rate of production of nuclei and on that of subsequent growth. It may be that in some systems one of these two factors predominates. Thus the rate of nucleation may be slow relatively to that of subsequent growth, and so rate-determining. If the crystal mass consists of a large number of independent particles then the rate of nucleation will be proportional to the amount of unchanged material so that, if we assume that subsequent growth is very rapid, the overall observed rate, reflecting exactly the nucleation rate, will decline with time, resembling that of radioactive decay. This may be the state of affairs for ammonium chloride and hexamminonickel nitrate. It is not unreasonable for the transitions in these substances that the changes emanating from nuclei should proceed rapidly since they only involve ionic reorientation, in contrast to the transition in, say, hexachloroethane where there is a deep-seated structural change. There is, in addition, a secondary factor which will also operate to give a steadily declining rate as the transition proceeds, namely, the fact that different crystal units are almost certainly not identical. Evidence has already been presented (Thomas and Staveley, *J.*, 1951, 1420) that factors such as particle size, impurities, and so on can affect the transition characteristics and hence must modify nucleation rates. It is this factor which must make it possible for the system to reach apparent equilibrium on the nearly vertical limbs of the hysteresis loop.

On the other hand, subsequent growth may also be slow. If this rate depends upon the area of the interphase boundary, which is probably often true, we should expect a maximum in the rate of about 50% change, as indeed we find for the transition in hexachloroethane where there is a radical crystal change, the development of which may be far from rapid. In general, if neither the rate of nucleation nor subsequent growth predominates, a combination of the two could lead to a maximum in the rate somewhere between zero and 50% conversion, and if it happens to fall near the start of the transition it may be difficult to establish its existence experimentally.

A further complication is that, as already indicated, nuclei may sometimes appear on surfaces, and the interphase area would reach a maximum before half the transformation is complete. Thus even if the observed rate of change is controlled by the rate of growth from nuclei and hence by the interphase area, its maximum would fall before 50% conversion. Although we do not fully understand why on warming of carbon tetrabromide the rate of conversion shows no observable maximum (in contrast to the behaviour on cooling and to that displayed by hexachloroethane), we think that it might be explained in terms of suitable relationship between nucleation rate and rate of subsequent growth, and that in addition surface nucleation may play an important role. We have already pointed out that the temperature at which the transition proceeds on warming is very near T_e so that the relationship between nucleation and growth rates may well be different from that prevailing in the region where the transition sets in on cooling. It must, however, be admitted that T_w is likewise very near T_e for the transition in hexachloroethane although here the rate of production of the high-temperature form shows a maximum.

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