

PROGRESS IN THE CALORIMETRY AND THERMODYNAMICS OF PHASE AND ORDERING TRANSITIONS

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INTRODUCTION

Though the responsibilities of a plenary lecturer are many and in view of the high level of performance hitherto attained by previous lecturers, certain words of apology may be in order. In some respects our subject does not permit as sophisticated and systematized presentation as we have been treated to in the older and more highly developed areas of calorimetric endeavour. In a real way, we are still in the kindergarten of thermodynamic transition studies. Moreover, the present pair of sessions concerns both the theoretical and the experimental aspects of recent progress in the understanding of the thermodynamics and mechanism of transitions. Wherein lie our immediate and ultimate goals?

Consider that we are approaching the ability to estimate reliably at least some thermal properties of simple substances from spectral and X-ray diffraction data. The recent achievement of Becka and Cruickshank¹ in estimating the entropy of hexamethylenetetramine and of others in the generation of empirical schemes for the estimation of entropies arising from lattice vibrational modes and magnetic moments^{2, 3} provide examples.

Supplementing such endeavours by the ability to predict the occurrence and the magnitude of the associated thermal properties of transitions would enable a much closer approach to the ultimate chemical thermodynamicists' "Utopia". As an intermediate stage we might content ourselves with the elucidation of the *raison d'être*, the nature, and the mechanism of important transitions. I propose to approach the discussion today by noting first some general aspects of the nature and types of transitions, their classification, their mechanism, and some of the current experimental problems in their study as well as the prognostication of trends and avenues for progress in the near future. Much—but not all—of the content will be associated with papers submitted to Sessions VI and VII. That the author may be guilty of having drawn heavily upon his own experiences and studies in illustrating his points should be construed not so much as a token of pride of achievement but rather as an attempt to heed the Biblical injunction⁴ to cast the "timber" out of his own eye before criticizing his scientific brother for the "splinter" obstructing his vision.

TYPES OF TRANSITIONS

Unlike the situation in combustion calorimetry, for example, few scientists

and research groups are concerned exclusively with the study of transitions *per se*. Rather the discovery of an enantiotropic transition in substances tends generally to be a somewhat accidental matter. Not that it is to be imagined, however, that transitions are rare—far from it! Fusion is a characteristic property of most solid substances. In more than one-third of the molecular compounds subjected to detailed thermodynamic investigation in the solid state, some type of thermal anomaly⁵ has been found. In 1942 Deffet⁶ listed nearly twelve hundred organic substances in which polymorphism had been detected by both thermal and adjuvant methods.

Besides fusion and enantiomorphic transitions, a proper phenomenological catalogue would encompass those occasioned by many causes other than a simple change in crystal structure. Important among these mechanisms are the onset of a change in the magnetic ordering of the material. Transitions between para-, ferri-, ferro-, and antiferro-magnetic states complicate the thermodynamic properties of many compounds especially those of the transition group, lanthanide, and actinide elements. The occurrence of transitions in the uranium–oxygen system³ shown in *Figure 1* is mute evidence

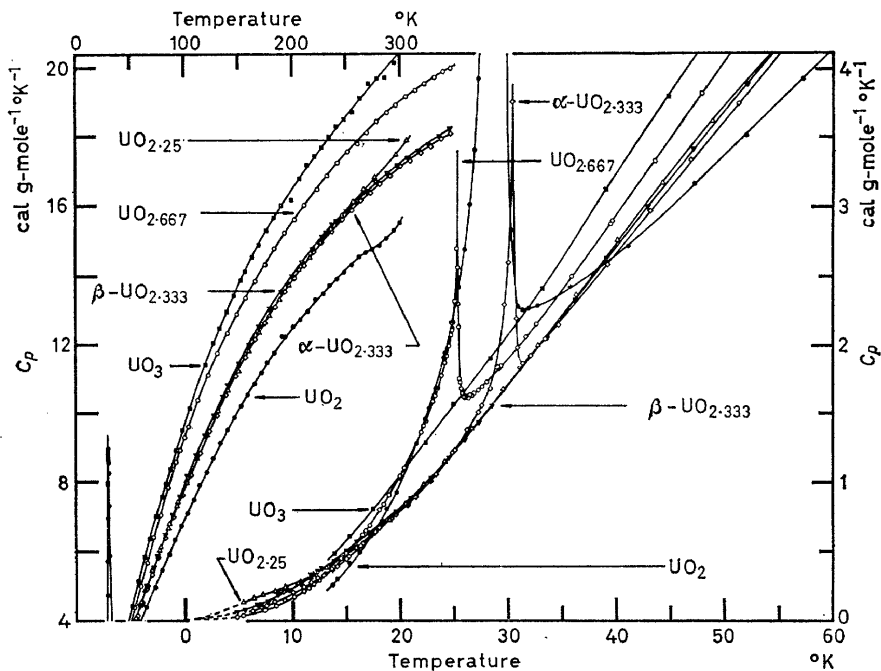


Figure 1. Heat capacities of uranium oxides³

of our present inability to predict the occurrence of magnetic transitions in these materials or indeed to provide a correlation with the new magnetic data of Leask, Roberts, Walter, and Wolf⁷ despite the recent analysis of the interrelationship between thermal capacity and magnetic susceptibility behaviour by Fisher⁸. A related question of considerable interest is the subtle

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one of whether or not an associated phase transition is invariably a consequence of magnetic transformations. Within the last decade the occurrence of analogous important ferroelectrically-related transformations in the dielectric behaviour of many garden varieties of chemical substances has become appreciated though not examined in detail. Unlike most other transitions, those in ferroelectric materials range from the order-disorder type characteristic of ammonium sulphate⁹ with associated entropy increments of the order of $R \ln x$ (where x is an integer) to the pronounced but relatively non-energetic ferroelectric transitions in thiourea¹⁰ depicted in *Figure 2*

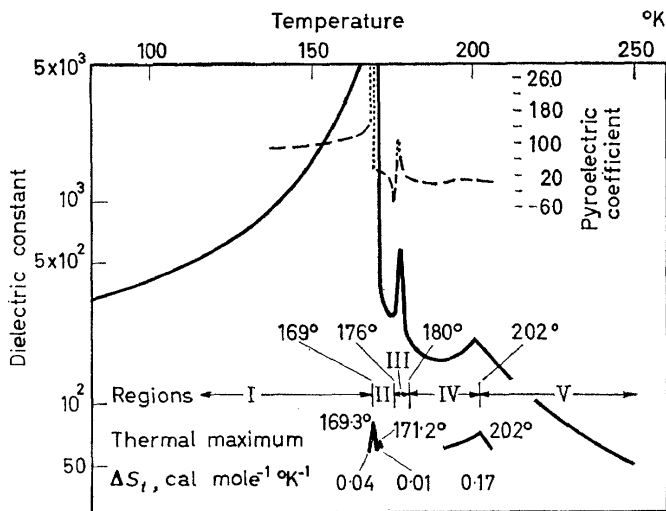


Figure 2. Thiourea¹⁰; dielectric constants, pyroelectric coefficients, heat capacity maxima and associated entropies of transition. The molecular configuration changes in the regions identified are: I, disordering ferroelectric; II, discontinuity in disorder; III, disordering compensated ferroelectric; IV, disordered ferroelectric, statistically antiferroelectric; and V, excitation of molecular oscillation

in which the magnitudes of the entropies of transition tend to be of the order of a few hundredths of an entropy unit. Schottky effects⁵ associated with the promotion of electrons into higher levels are observed with increasing frequency at lower temperatures as a consequence of crystalline field splittings in both magnetically dilute and concentrated materials. This may be seen in *Figure 3* which reveals the complex Schottky transformations in neodymium(III) oxide and their interpretation in terms of the crystalline field levels¹¹. The resolution from the observed heat capacity was achieved by equating the lattice contribution to that of lanthanum(III) oxide. To these types may be added "glass" transitions, the order-disorder transitions (which may indeed be ferroelectrically related as in ammonium sulphate), and the transition to the plastically crystalline state involving molecular reorientational-rotation. Moreover the transformations—be they eutectic, peritectic, enantiotropic or otherwise occurring on binary and ternary phase diagrams—are relevant to our consideration although time will not permit a detailed exploration of them.

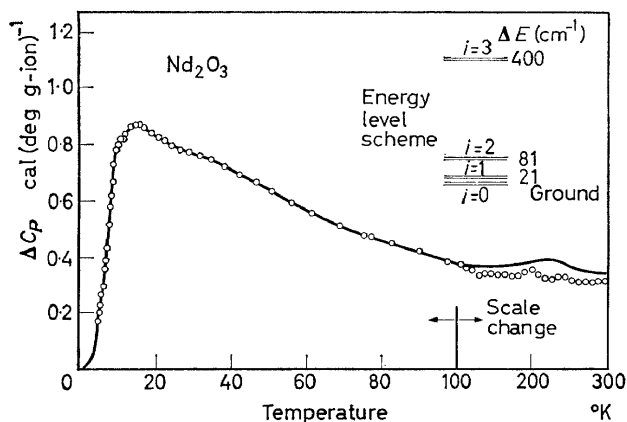


Figure 3. The Schottky anomaly in neodymium(III) oxide with indication of the derived energy level scheme¹¹

ON THE THEORETICAL SIDE

Although in principle the methods of statistical mechanics can be used to interpret transitions of the solid state, in practice the application has been mainly limited thus far to hypothetical two-dimensional systems. Even so, the application proves to be quite complex and not entirely in accord with experiment. It may be fair to say in summary that the theoretical treatments yield a qualitative, or at best a semi-quantitative, agreement with experimental data. The notion of order-disorder concepts may also be useful in the partial interpretation of transitions but the general lack of adequate structural data often tends to make such discussions only tentative. A detailed review of progress in this area has however been provided by Domb¹².

Thermodynamic analyses of phase behaviour akin to those proposed by Ehrenfest in 1933¹³ in terms of the behaviour of the Gibbs energy curve provide a basis for the classification of an n th order transition as one in which the derivative $(\partial^n F / \partial T^n)_p$ is discontinuous. On this basis a *first-order* transition would have a continuous Gibbs energy and a discontinuous entropy and enthalpy through the transition region, whereas one classified as *second-order* would be continuous in these functions and discontinuous in the heat capacity, *etc.* It is not always realized, however, that the behaviour of a given transition does depend on the choice of constraints, for example, the evaporation of a solid or liquid is a first-order transition at constant pressure whereas it becomes second order under constraint of constant volume. Unfortunately, the bulk of experimental data cannot be readily classified with reference to a scheme such as this. Individual attempts to devise a generally acceptable scheme by Jaffray¹⁴, by McLaughlin¹⁵, and by Fischer¹⁶ have in general met with less than fair acceptance. That of McCullough¹⁷ is a good example of one of the most recent of these schemes, but like other empirical classifications on a phenomenological basis considerable arbitrariness resides in its application by others. Ubbelohde¹⁸ has urged recognition of the notion of continuous transitions and suggests that we abandon

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the classical picture of two phases in equilibrium. The theoretical treatment of Allen and Eagles¹⁹ involves the same point of view and suggests a continuous transition to be of "infinite order". The concept of a second-order transition as a critical point²⁰⁻²³ might be tested by studying transitions as a function of pressure as well as of temperature. Further progress in this direction would seem to be stimulated by more detailed studies of crystal structural data through the transition region to ascertain if the concept of two distinct phases must sometimes be abandoned, and with it the type of classification proposed by Ehrenfest.

EXPERIMENTAL ASPECTS

At the present time the bulk of thermal data on transitions has been obtained by adiabatic calorimetric studies in the cryogenic region. This situation is probably a simple consequence of the fact that adiabatic calorimetry has not been extensively developed in higher temperature regions and

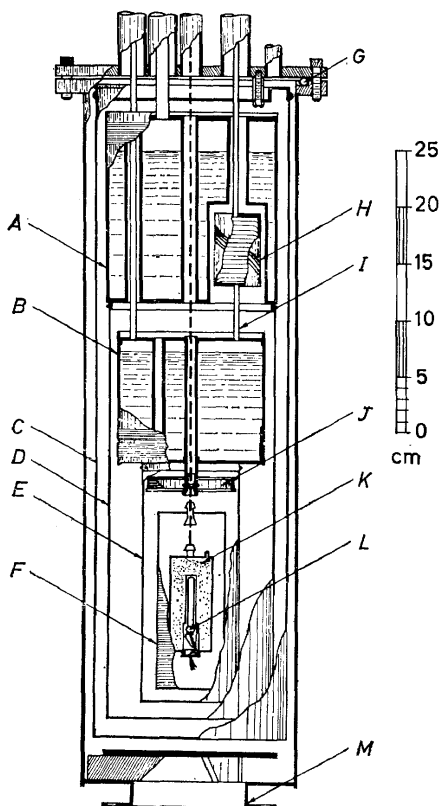


Figure 4. Schematic cross-section of modern cryostat for low temperature adiabatic calorimetry: *A*, liquid nitrogen tank; *B*, liquid helium tank; *C*, *D*, and *E*, radiation shields; *F*, adiabatic shield; *G*, O-ring gasket sealing brass vacuum jacket; *H*, effluent helium vapour exchanger ("economizer"); *I*, helium exit tube; *J*, ring for adjusting temperature of leads; *K*, calorimeter assembly; *L*, platinum-resistance thermometer; and *M*, connection to vacuum diffusion pump

that in contrast to *isothermal* calorimetry it permits a more deliberate study under equilibrium conditions of the behaviour of these transitions. Modern adiabatic calorimetric cryostats²⁴ such as that depicted in *Figure 4*, when supplemented by automatic adiabatic shield control²⁵, permit the convenient exploration of thermal properties associated with transitions from temperatures below 1°K to somewhat above the ambient (room) temperature. Extension of the range of an instrument of this type to at least 600°K is provided by an intermediate temperature calorimeter²⁶ depicted in *Figure 5*, or by the more elaborate instrument of West and Ginnings²⁷.

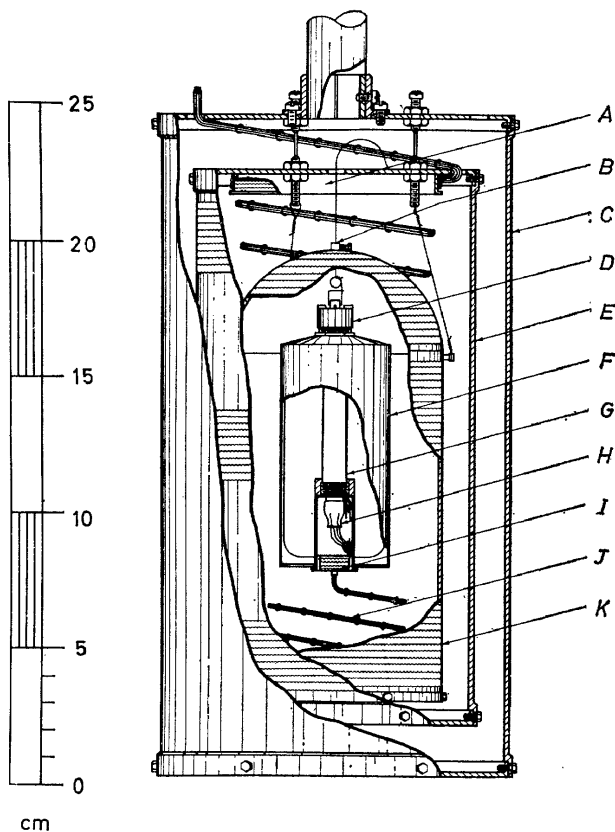


Figure 5. Cross-sectional diagram of intermediate temperature thermostat. *A*, guard shield ring; *B*, calorimeter suspension collar; *C*, primary radiation shield; *D*, calorimeter closure assembly; *E*, guard shield; *F*, calorimeter assembly; *G*, thermometer-heater well; *H*, thermometer; *I*, thermal equilibration spool; *J*, lead bundle; *K*, adiabatic shield

The calorimetric examination of phase transitions is beset with difficulties of various types. To mention a few of those most frequently encountered, one might note first those aspects of the apparent thermal behaviour in transitions which are occasioned by the nature of the calorimetric method employed. For example, in the transition in ammonium sulphate the results of Hoshino *et al.*²⁸ deviate considerably in showing a bifurcated peak at the

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transition as examined by their conduction-calorimeter in comparison with the single-peaked anomaly originally observed by Shomate *et al.*²⁹ and that observed more recently by others⁹. The introductions of these artefacts may lead to interpretations which are not justified by measurements made under equilibrium conditions irrespective of their possible significance as involving processes with different relaxation times^{28, 30}. The second difficulty is our inability to determine or to resolve the true, detailed temperature-dependent behaviour of the transition. This may seem surprising to those not acquainted with the 8- to 14-hour wait required for thermal equilibrium in some solid-state transformations in molecular lattices and the consequent uncertainty in the determination of the temperature increment involved in the apparent heat capacity determination. An unusually finely delineated study of the transformation of the lambda transition of helium-4 by Fairbank *et al.*³¹ deserves mention. These authors used temperature increments as small as a micro-degree in the delineation of the temperature dependence of the thermal properties of this important substance. Few other substances, however, would lend themselves to a similar exploitation. As a consequence of these two limitations in the experimental study, the apparent lack of strict isothermal behaviour in a transition is reliably interpreted with difficulty as being a consequence of imperfect calorimetry, the presence of impurities, the formation of solid solutions, or the effect of vacancies. As an example, let us consider methyl alcohol which has been repeatedly examined. *Figure 6* reveals the results of measurements by Kelley³², by Staveley and Gupta³³,

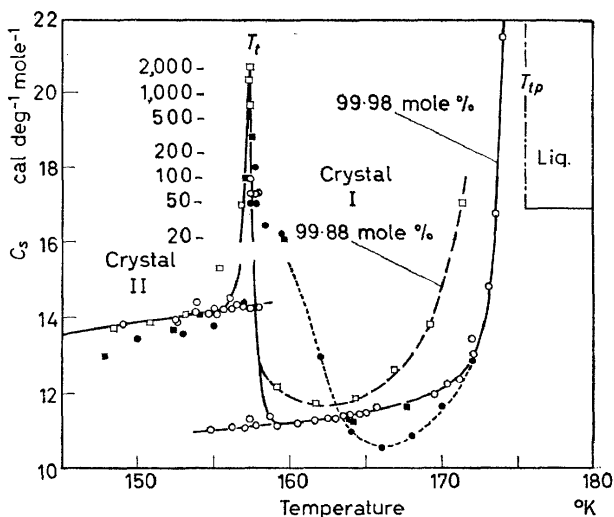


Figure 6. The heat capacity of methanol³⁴ in the fusion region; data for a high-purity sample are represented by ○ and those for a less pure sample by □³⁴; values of Staveley and Gupta³³ and of Kelley³² are indicated by ■ and ●, respectively

and by Carlson *et al.*³⁴ The behaviour observed on transition in the last-named research was that not only does the transition undercool by as much as 25°K but that it tended to superheat and to begin to transit only when the sample attained a temperature more than 2°K above the peak in the heat

capacity curve. In particular, a sample of 99.98 mole per cent purity (as determined from fractional fusion) did not permit measurement of the heat capacity rise into the transition. However, a sample rendered impure by the addition of a small amount of water (99.88 per cent methyl alcohol) was found to readily undergo this transition from either direction. Extrapolation to even higher purity levels results in concern as to whether or not the transition would have been observable at all calorimetrically.

Another subtle aspect of the presence of impurities is hinted at by the studies at the University of Strasburg³⁵⁻³⁹. These investigators studied the effect of inert gases upon transition temperatures, and the results of their non-equilibrium studies suggest a striking effect from the presence of inert gases on transition temperatures of finely divided solid substances. Further examination of these phenomena by equilibrium methods are obvious desiderata. Although the importance of having single domain, single crystal specimens for studies on ferroelectrics seems to be generally recognized, the possible effect of particle size on magnetic transformations appears to be less well appreciated. However, recent measurements on hot-pressed, flame-fused, and sintered uranium dioxide samples⁴⁰ revealed a heat capacity maximum extending to $400 \text{ cal g-mole}^{-1} \text{ }^\circ\text{K}^{-1}$ in marked contrast with the literature value of $8 \text{ cal g-mole}^{-1} \text{ }^\circ\text{K}^{-1}$ reported by Jones, Gordon and Long⁴¹! Admittedly we are here dealing with a complex oxide system where questions of exact stoichiometry, homogeneity, *etc.* are also contributing factors. However, a further suggestion of the reality of this effect is occasioned by measurements on hauerite⁹ (mineralogically occurring manganese disulphide with pyrite structure) which has a transition to the antiferromagnetic state of the heat capacity maximum of $100 \text{ cal g-mole}^{-1} \text{ }^\circ\text{K}^{-1}$ at the Néel point of 49.7°K as shown in *Figure 7*. Certainly hauerite and the nearly isostructural manganese dichalcogenides present an interesting basis for further studies of this effect. Moreover, the transition in essentially isostructural manganese ditelluride is of a more diffuse type at 83°K , whereas that in manganese

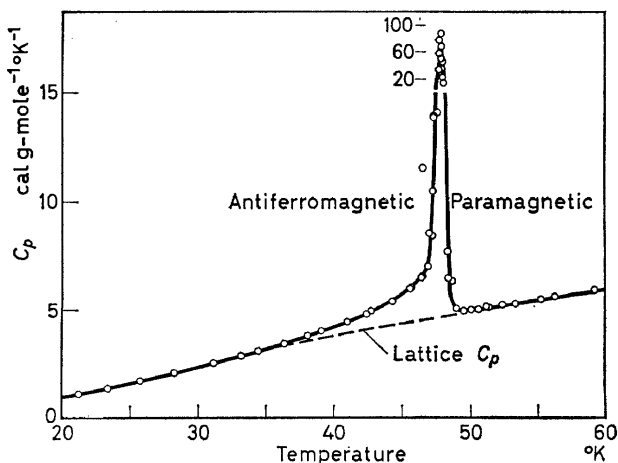


Figure 7. The lambda-type anomaly in hauerite (MnS_2) occasioned by the transformation from the antiferromagnetic state to the higher temperature ferrimagnetic state²⁴

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diselenide is of special interest because, as has been pointed out by Dimmock⁴², the diselenide structure cannot exist in the immediate vicinity of the transition point between the paramagnetic and antiferromagnetic phases provided there is a single, second-order transition.

Interpretation of transitional thermodynamic properties invariably involves their resolution into lattice contributions and those associated with the transformation. To achieve this either (i) a more or less empirical method ("spline and eyeball" method), (ii) use of single or combined Debye and/or Einstein functions, (iii) comparison with an isostructural solid, or (iv) some combination of these methods has been employed. The difficulty increases for those transitions which occur over a fairly large range of temperature. Although several initiatory attempts have been made to delineate a basis for a corresponding states theory of isostructural solids⁴³⁻⁴⁵, no real solution has yet resulted. Interpretation of the mechanism of the transition is all too frequently hindered by the absence of data on the crystal structure, the dielectric constant behaviour, the volumetric behaviour, or such useful ancillary information as may be provided by nuclear magnetic resonance or those determinations of energy levels by techniques which may be collectively branded as spectroscopic. Stephenson⁴⁶ has discovered that the very important matter of pre-transitional heat capacity rise can be expressed satisfactorily in terms of the exponential functions used to describe the generation of vacancies.

SOME EXPERIMENTAL DESIDERATA

Extension of the adiabatic technique of measurement to higher temperatures is perhaps the most urgently needed. The use of the adiabatic intermediate range calorimeter²⁶ has already made possible measurements through fusion and into the liquid range for several molecular lattices. A combined calorimeter for operating over the cryogenic and intermediate temperature range would greatly facilitate operations on many substances. Extension to even higher temperatures such as that provided in the work of West and Ginnings²⁷, of Grønvold *et al.* (to 1100°K)⁴⁷, of Dench and Kubaschewski (which extends at least as high as 1700°K)⁴⁸, and that of Backhurst (to 1870°K)⁴⁹ is especially useful for metallurgical systems and systems of nuclear technological import. Nor should the extension to lower temperatures be overlooked. Utilization of germanium-resistance thermometry and helium-3 refrigerant will make possible a better delineation of the energetic effects in the lanthanide(III) oxides, for example, and will undoubtedly be important in many transition-element and actinide compounds. An important impending development is that of a semimicro-thermal calorimeter which will permit operation on samples of approximately one gram mass without significant sacrifice of precision and accuracy compared to that which is currently obtained in the best work using samples two orders of magnitude larger. This should facilitate the study of fascinating materials difficult to synthesize, inherently rare or costly, or dangerous.

MOLECULAR DISORDER — GLOBULAR MOLECULES

One area of recent intensive activity in the study of transitions has been that of the behaviour of globular molecules in the crystalline state occurring

immediately below their melting temperatures. The term "plastic crystal" was first used by Timmermans⁵⁰ to characterize this phase as distinguished by the following characteristics: an unusually small entropy of fusion $< 5 \text{ cal mole}^{-1} \text{ }^\circ\text{K}^{-1}$ compensated for by one or more energetic transitions prior to fusion; high triple-point pressure and temperature; high—usually cubic or hexagonal—symmetry and transparency, tackiness, and relatively facile plasticity. Microscopic evidence for the high disorder of globular molecules at lattice sites is provided by the interpretation of the small entropy of fusion in terms of about 10 distinguishable orientations. These represent the minimum degree of disorder to be found in substances normally considered to be plastic crystals or to be in "rotator phase". In this light "rotation" in plastic crystals can be more adequately described in terms of orientational disorder with the molecules "flipping" into discrete, distinguishable positions in the crystalline lattice with such high frequency that X-ray and nuclear magnetic resonance measurements cannot be expected to distinguish between this movement and free rotation. A stochastic treatment of the transition entropies has been achieved by Guthrie and McCullough⁵¹ for simple tetrahedral molecules. As is well known, other tetrahedral molecules such as pentaerythritol $[\text{C}(\text{CH}_2\text{OH})_4]$ and pentaerythrityl fluoride $[\text{C}(\text{CH}_2\text{F})_4]$ do manifest characteristic plastically crystalline behaviour. A somewhat more complex molecule of tetrahedral symmetry, adamantane $[\text{C}_{10}\text{H}_{16}]$ depicted in *Figure 8*

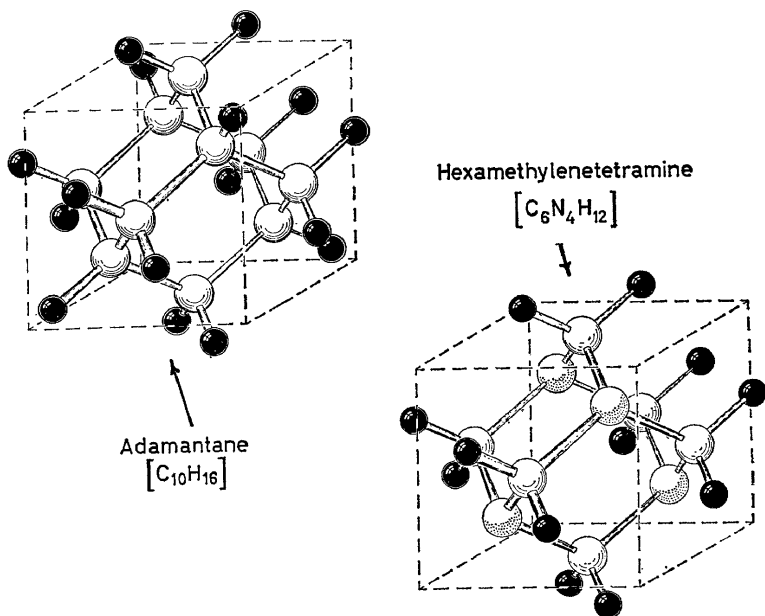


Figure 8. Structures of adamantane and hexamethylenetetramine molecules

is the simplest saturated, polycyclic hydrocarbon that has its carbon atoms arranged in a cage-like skeleton identical with that of the so-called "characteristic cell" of the diamond lattice. A sharp transition to the plastically crystalline state with apparent heat capacities in excess of 4

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kcal mole⁻¹ °K⁻¹ has been observed at 208.6°K, with an associated entropy of transition⁵², ΔS_t , of 3.87 cal mole⁻¹ °K⁻¹. Proton magnetic resonance studies on adamantane by McCall and Douglass⁵³ have confirmed the interpretation of this transition. Although normal decane has a melting point of 242°K, the phase properties of adamantane have been so profoundly affected that the substance does not melt below 548°K. Substitution of four nitrogen atoms at the bridgehead positions in adamantane yields another diamondoid molecule of identical symmetry with that of adamantane (*cf. Figure 8*), but one in which the plastically crystalline phase apparently does not appear⁵².

The study of the plastically crystalline state is by no means an innovation. After discovery of the state by Timmermans in the late 1930's, "universal recognition of such crystals as a new phase of matter has come slowly"⁵⁴. Postwar studies on camphor by Schäfer *et al.*⁵⁵ were among the earliest thermodynamic investigations. A stimulating Symposium on the status of research in this field in 1960 is summarized elsewhere⁵⁶. Even more recent, excellent surveys concerning the transitional aspects of this interesting field are those by Aston⁵⁴ and by Staveley⁵⁷. Popular reviews in Japanese by Seki⁵⁸ have also appeared.

In the endeavour to interpret the mechanisms of fusion and of the plastically crystalline transition, it is desirable to vary the symmetry and the peripheral groups in the molecules under investigation. Although many adamantane derivatives are known, those with the most interesting symmetries are very difficult to prepare and attention has therefore shifted from derivatives of a spherical molecule to those of a symmetrical-top type, represented by the homologues of bicyclo-octane [C₈H₁₄].

Representative thermal data for a typical member of this series, triethylenediamine [C₆N₂H₁₂], are presented in *Figure 9*. The apparent continuity

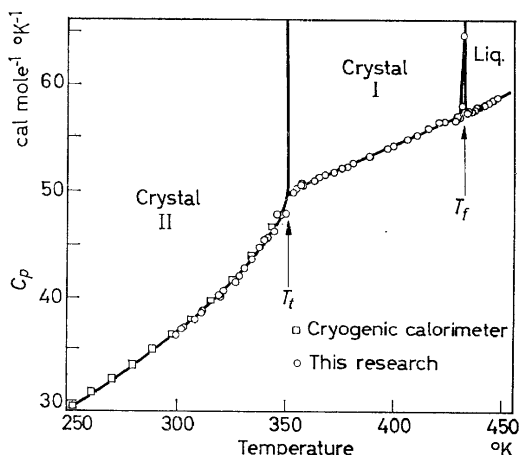


Figure 9. Heat capacity of triethylenediamine²⁶. The \square show data from the adiabatic calorimetric cryostat, the \circ from the intermediate range thermostat

of the heat capacity trend of the plastically-crystalline phase (Crystal I) into the liquid is especially evident here. Data on this and other related molecules are presented in *Table 1*.

However, plastically-crystalline properties are not restricted to organic crystals, as the hexafluorides of the third group transition metals, tungsten, rhenium, iridium, and platinum, furnish an unusually finely-graduated set of closely-packed molecular crystals of orthorhombic symmetry, all of which undergo transition to the cubic plastically-crystalline phase a few degrees

Table 1. Recent transition data on plastic crystals (Units: cal, mole, °K)

Compound		T_i	ΔS_i	T_m	ΔS_m
Name	Structure				
Pentaerythryl fluoride ^{69,60}	Methane derivatives $C(CH_2F)_4$	249.40	12.66	367.43	3.35
1,4-Azabicyclo-[2,2,2]-octane ⁶¹	Bicyclo-octane "derivatives" $N(CH_2CH_2)_3N$	351.08	7.19†	433.1	4.10†
3-Azabicyclo-[3,2,2]-nonane ^{62,63}	$HC \left\{ \begin{array}{l} (CH_2CH_2)_2 \\ (CH_2NHCH_2) \end{array} \right\} CH$	297.78	11.68	467.12	3.55
Bicyclo-[2,2,1]-heptane ⁶¹	$HC \left\{ \begin{array}{l} (CH_2CH_2)_2 \\ -(CH_2)- \end{array} \right\} CH$	$\left. \begin{array}{l} 131.5 \\ 305.8 \end{array} \right\}$	$\left. \begin{array}{l} 7.53 \\ 0.06 \end{array} \right\}$	—	—
Exo-2-cyano-bicyclo-[2,2,1]-heptane ⁶³	$HC \left\{ \begin{array}{l} (CH_2CH_2)_2 \\ -(CH_2)- \\ (CH_2CH)- \end{array} \right\} CH$ CN	237.7	7.97	300.27	2.34

† Other values for these entropy increments (6.62 and 3.3 cal mole⁻¹ °K⁻¹ at 353.0 and 434.3°K) derived from vapour pressure data by Wada *et al.*⁶⁴ are considered less reliable.

below fusion as shown in Figure 10 for three members of the series⁶⁵. The nuclear framework of these interesting molecules in the vapour phase is that of a regular octahedron which undergoes a small tetragonal distortion in the transition to the crystalline phase. Removal of the electronic degeneracy in

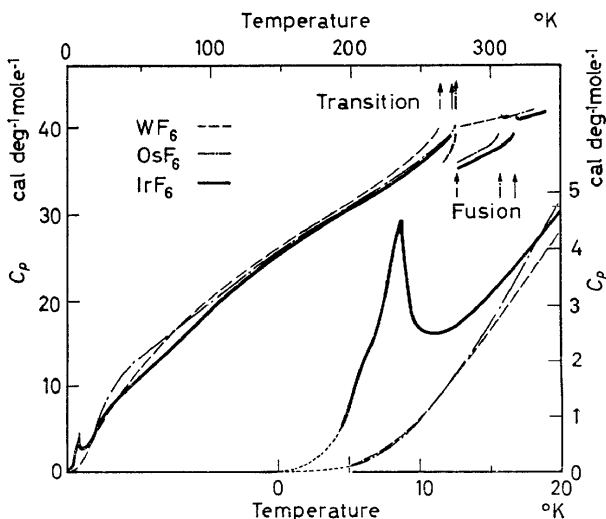


Figure 10. The heat capacities of three platinum-metal hexafluorides⁶⁶ showing the low temperature orthorhombic phases, the cubic plastically crystalline phase and the liquid phase

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rhenium and osmium hexafluorides gives rise to the Schottky anomalies which are evident below 100°K. Optical spectra obtained at low temperature provide quantitative details concerning the splitting of the vibrational electronic degeneracies arising from the molecular distortion in these compounds and permit an unusually thorough discussion of the energy spectrum and the Jahn-Teller effect in these crystals⁶⁶. Regularities and trends in the entropies of fusion and transition are especially marked in the values presented in *Table 2*. This table is expanded to include extant data on the

Table 2. Thermodynamics of some transition-metal hexafluorides (Units: cal, mole, °K)

<i>Com- pound</i>	<i>Atomic weight</i>	T_i	ΔS_i	T_{iD}	ΔS_m	$\Delta S_i + \Delta S_m$
WF ₆	183.9	264.7 ^a (265.0) ^b	7.81 ^a (5.28) ^b	275.2 ^a (275.2) ^b	3.56 ^a (1.45) ^b	11.37
ReF ₆	186.22	269.8 ^a (271.3) ^b	7.49 ^a (7.71) ^b	291.7 ^a (291.9) ^b	3.56 ^a (3.21) ^b	11.05
OsF ₆	190.2	274.5 ^a (273.8) ^b	7.29 ^a (7.20) ^b	306.4 ^a (306.6) ^b	3.63 ^a (5.72) ^b	10.92
IrF ₆	193.1	272.0 ^a (273.6) ^b	7.08 ^a (6.21) ^b	317.1 ^a (317.0) ^b	3.77 ^a (3.74) ^b	10.85
PtF ₆	195.09	276.5 ^a	6.77 ^a	334.8 ^a	~3.80 ^a	10.57
MoF ₆	95.95	263.6 ^c 263.5 ^d (264.5) ^b	7.72 ^c 7.41 ^d (7.40) ^b	290.7 ^c 290.7 ^d (290.6) ^b	3.65 ^c 3.56 ^d (3.15) ^b	10.97
TcF ₆	99	268.31 ^d	7.15 ^d	311.11 ^d	3.55 ^d	10.70
UF ₆	238	—	—	337.21 ^e	13.85 ^e	13.85

(a) Calorimetric data of Westrum and Weinstock⁶⁵.

(b) From vapour pressure data of Cady and Hargreaves⁶⁷.

(c) Calorimetric data of Brady, Meyers, and Clauss⁶⁸.

(d) Calorimetric data of Osborne and Schreiner⁶⁹.

(e) Calorimetric data of Brickwedde, Hoge, and Scott⁷⁰.

second group of transition metal hexafluorides from data on the calorimetry of phase transitions in molybdenum and technetium hexafluorides in a paper presented by Osborne and Schreiner at this Symposium⁶⁹. In both substances the high-temperature phase is body-centred cubic; but the structures of the low-temperature phases are uncertain. Radioactive decomposition which occurred at a rate of about 0.003 mole per cent per day occasioned a slow shift in equilibrium temperature of the technetium hexafluoride sample. Additional complications as noted by those authors include the presence of a gradual transition or a Schottky anomaly below 5°K, as well as the possibility of a ferromagnetic transition at helium temperatures⁷¹. A more significant improvement over literature data on molybdenum hexafluoride than may be immediately apparent has been achieved by Osborne and Schreiner. Data in *Table 2* which are designated (b) are values derived from vapour pressure measurements. As is previously noted

in the case of triethylenediamine (*cf.* Table 1 footnote), exceeding care must be taken in obtaining precise vapour pressure measurements for this purpose in order to obtain values which are of sufficient accuracy to indicate the real trends taking place in series of the sort presented. The sum of the entropies of transition and fusion in the last column of the table show (as in the case of the tetrahedral molecules⁵¹) close similarity with only small trends through the series.

The theory of fusion of molecular crystals by Pople and Karasz⁷² introduces a physically realistic coupling between orientational and positional disorder and predicts a solid-state reorientational-rotational transition as well as fusion. For certain values of the selected parameters, rotational disorder obtains in the solid. "Rotation" obtains in the solid if the quantity ν defined as the ratio of $(z'w'/zw)$ is less than $0.3w$, otherwise no "rotational" transition occurs (prior to fusion). Here w' and w are relative potential energy barriers for rotation of the molecule and for diffusion to an interstitial site, whereas z' and z are respectively the number of "abnormal" sites (in which rotation can occur) surrounding an "abnormal" site and a "normal" site as in the theory of Lennard-Jones and Devonshire⁷³ for monatomic substances. Comparison of the entropies of sublimation of methane derivatives with those of the "inert gas" solids have provided Chihara and Shinoda⁷⁴ with a basis for estimation of the barriers hindering rotation.

A paper submitted to this symposium by Wulff and Westrum⁷⁵ presents data on a molecule, succinonitrile $[\text{NC}(\text{CH}_2)_2\text{CN}]$, which though not obviously very globular, evidences the plastically-crystalline state. X-ray diffraction analysis⁷⁶ indicates Crystal II to be a completely ordered monoclinic phase (consisting only of *gauche* forms) whereas infrared data⁷⁷ show Crystal I as a highly disordered body-centred cubic phase composed of a temperature-dependent equilibrium mixture of *gauche* and *trans* geometrical isomers. The disorder is ascribed in part to the onset of rotation about the principal axis passing through the length of the molecule. The entropy of transition therefore reflects a disordering process concomitant with the phase transition. Three factors influence this process: (i) change in crystalline symmetry, (ii) onset of hindered internal rotation or of overall (*i.e.*, rigid) rotation about a single axis, and (iii) the volume increment. The magnitudes of these contributions have been estimated and appear in Table 3. They accord well with the observed entropy of transition. The low entropy of fusion, $2.68 \text{ cal mole}^{-1} \text{ }^\circ\text{K}^{-1}$, indicates that the Crystal I phase of succinonitrile is indeed that of a plastic crystal. The sum of the entropies of transition and fusion, $9.03 \text{ cal mole}^{-1} \text{ }^\circ\text{K}^{-1}$, is to be compared to literature values for the entropies of fusion of 7.9 for malonitrile, 9.3 for acetonitrile as well as the values of 9.4 and 12.32 (only the last one calorimetrically determined⁷⁸ for glutaronitrile). Moreover, the agreement obtained between the third-law entropy of the gas, $79.04 \pm 0.10 \text{ cal mole}^{-1} \text{ }^\circ\text{K}^{-1}$ at 298.15°K , and the corresponding value obtained from spectroscopic data, $79.09 \pm 0.10 \text{ cal mole}^{-1} \text{ }^\circ\text{K}^{-1}$, is ample indication of the absence of residual disorder in Crystal II and justifies the assumptions in Table 3.

Studies of phase transitions in some fluoride compounds by Pace⁷⁹ in a contribution to this Symposium involve pairs of structurally related compounds. Both nitrogen trifluoride⁸⁰ and phosphorus trifluoride⁸¹ have

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first-order transitions. The former has one at 65.62°K involving a ΔS_t of 6.39 cal mole⁻¹ °K⁻¹, while melting occurs at 66.37°K with a ΔS_m of 1.43 cal mole⁻¹ °K⁻¹. For the latter, a third discontinuity at 84.02°K is apparently second order with a ΔS_t of 0.71 cal mole⁻¹ °K⁻¹ and transitions similar to those in the nitrogen analogue at 110.78°K and 121.85°K with respective ΔS_t 's of 4.83 and 1.84 cal mole⁻¹ °K⁻¹. Corresponding ($\Sigma \Delta S_t + \Delta S_m$)'s

Table 3. Analysis of entropy of transition of succinonitrile (Units: cal mole⁻¹ °K⁻¹)

Factors	ΔS_t
Alignment of axes [$\Delta S = R \ln 4$]	2.755
Rigid rotation of molecule [$\Delta S' = R \ln 2$]	1.377
Entropy of mixing <i>gauche</i> and <i>trans</i> isomers [$\Delta S'' = -R(X_t \ln X_t + X_g \ln X_g - X_g \ln 2)$]	2.08
Volume change on transition [$\Delta S''' = R \ln (V_2/V_1)$; "free" volume]	0.18
Calculated:	6.39 ± 0.09
Observed:	6.35 ± 0.03

of 7.82 and 7.38 cal mole⁻¹ °K⁻¹ may be compared to the ΔS_m of ammonia⁸², 6.92 cal mole⁻¹ °K⁻¹, which has no transitions in the solid.

Although Kostroykov *et al.*⁸³ have reported a second-order transition for carbon tetrafluoride at 76.09°K involving a ΔS_t of 5.11 cal mole⁻¹ °K⁻¹ and fusion at 88.44°K with a ΔS_m of 1.85 cal mole⁻¹ °K⁻¹, the unpublished work of Pace and Mosser⁸⁴ on silicon tetrafluoride reveals no solid transitions between 15° and the triple point at 186°K. These authors estimate a rotational contribution of 1.8 cal mole⁻¹ °K⁻¹ at 30°K and 5.7 cal mole⁻¹ °K⁻¹ just below the melting temperature. Although no indication is given of the method of resolution of these values, the latter value is very close to the value of 3R for three-dimensional free rotation. Refreshing work recently published by Colwell, Gill and Morrison⁸⁵ on the thermodynamic properties of methane and deuterio-methane is highlighted by discovery of a second transition in methane. An accounting for the apparent zero point entropies of both these substances quantitatively is achieved by recognizing the existence of different nuclear spin species each tending to occupy its lowest available quantum level as 0°K is approached. No conversion between different species has been observed. The thermal transitions in the methanes have also been examined and thermodynamic results correlated with information derived from spectroscopy, neutron scattering, and theory. Yet it is noteworthy that the fundamental causes of the transitions can still not be established.

DETERMINATION OF BARRIER HEIGHTS

A subject very much akin to that of plastically-crystalline behaviour is the determination of barrier heights hindering rotation of molecules and internal rotation of functional groups on molecules. Thermal data frequently have

been used to determine barrier heights by comparison of experimental and statistically calculated values of the vapour phase heat capacity and/or third-law vapour entropy values. However, experimental determination of the third-law entropy of the gas, for example, requires that the low-temperature, solid-phase heat capacity be augmented by: enthalpy of vaporization or sublimation, vapour pressure measurements, and equation of state data for the vapour. The advantages and feasibility of determining barrier heights exclusively from low-temperature solid-phase heat capacities are demonstrated in a Symposium paper by Wulff⁸⁶. His method involves the evaluation of the degrees of freedom contributing to the heat capacity, C_p , of a crystal: (i) the inter-molecular vibrations (lattice vibrations) correspond to the translation and over-all rotational contributions for the gas, (ii) the intra-molecular vibrations calculated within the harmonic oscillator approximation by combination of Einstein functions based upon the observed spectrum, (iii) ($C_p - C_v$) resulting from the expansion of the lattice as occasioned by the anharmonicities of the vibrations, and (iv) the internal rotations. No *a priori* method exists for determining contributions (iii) and (iv). Terms (i) and (iii) were treated in the manner described by Lord, Ahlberg and Andrews⁸⁷ and amplified by Lord⁸⁸ which involves the treatment of this term reduced to the form:

$$C_p - C_v \simeq [aC_v^I + bC_v^L]^2 T$$

in which C_v^I is the summed contribution of the intra-molecular vibrations and C_v^L is the lattice contribution to the heat capacity. Although a and b have been assigned values by Nernst and Lindemann⁸⁹, agreement with these predictions is sacrificed by evaluating them empirically. The success of this representation has been demonstrated by the agreement of calculated and experimental heat capacities for a number of molecular lattices. The internal rotation term (iv) is then evaluated in terms of the commonly assumed potential function, V , which is equal to $0.5 V_0 (1 - \cos n\phi)$. Actually three different treatments may be needed for the heat capacity contribution from the internal rotation. At low temperatures a torsional oscillator approach may be used; at high temperatures the contribution approaches that of a free rotator and can be treated as such; but at intermediate temperatures the tabulated functions of Pitzer and Gwinn⁹⁰ are used. Some measure of the success of the method may be seen by examination of *Table 4* and although criticisms of the method may be levelled both with respect to the parameters used and to the uniqueness of the derived barrier heights, the accord with values in the table does show considerable success. It should be noted, of course, that the barriers in the crystalline state potentially involve inter-molecular forces absent in the gaseous phase. A situation in which it has proved singularly successful is the evaluation of the torsional frequency of the hydroxyl rotation in anhydrous perchloric acid⁹⁵ as $309 \pm 14 \text{ cm}^{-1}$. This was found to be in good accord with the frequency ν_{12} of 307 cm^{-1} for the gaseous molecule⁹⁶.

The calorimetric determination of rates and activation energy by Mitacek and Aston⁹⁷ illustrates the utility of precise adiabatic calorimetry in establishing the relevant kinetic parameters for the migration of hydrogen in the

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Table 4. Barrier heights derived from thermal data†

Substance	$I_r 10^{40}$	n	θ_E	V_o	V_o	Source of V_o (gas) (Ref.)
	(g cm ²)			(crystal)	(gas)	
			(°K)	(cal/mole)	(cal/mole)	
Toluene	5.008	6	171	200 ± 25	0- 300‡	91
<i>o</i> -Xylene	5.41	6	500	1850 ± 75	2000-2500	92
<i>m</i> -Xylene	5.41	3-6	141	300 ± 75	0-1000	92
<i>p</i> -Xylene	5.32	6	220	350 ± 25	0- 900	92
Mesitylene	5.46	3	160	190 ± 25	0- 900	92
1,1-Dichloroethane	5.20	3	350	3490 ± 200	3100-4000	93
1,1,1-Trifluoroethane	5.125	6	340	3250 ± 200	3040-3950	94

† I_r is the reduced moment of inertia, θ_E , the Einstein characteristic function, and V_o the cosine potential energy barrier hindering rotation.

‡ Estimated from data given by Scott *et al.*⁹¹

system hydrogen-palladium. The real worth of this Symposium paper lies not in the analysis of the particular system selected for investigation but in its potential utility in the study of many other transitions, the subtler aspects of which have been largely neglected. Moreover, it is timely in that it applies calorimetry to an irreversible process within the domain of true thermodynamics (as distinguished from thermostatics).

ROTATION OF ANIONS IN INORGANIC LATTICES

A very logical extension of our discussion on plastic crystals concerns freedom (particularly with regard to re-orientation) of complex, reasonably symmetrical anions in inorganic crystalline lattices. Although transitions in the usual sense may not be involved here, the area is one in which the kind of calorimetry that we have been considering may make very significant contributions. The question of re-orientation-rotation in such inorganic salts is, at least in principle, a simpler situation than in the typically plastic crystal. If one of the sets of ions is monatomic then the re-orientating polyatomic ion is separated from its neighbouring polyatomic ions by more or less of a screen of protecting monatomic ions. Staveley and Andrews⁹⁸ have just communicated some very interesting results which they may wish to amplify in the subsequent discussion. As a consequence of literature search, these authors ingeniously established that the entropy increments associated with the phase transformations in ionic lattices containing polyatomic anions might be attributed to the acquisition of orientational entropy and therefore also be explicable in terms of an $R \ln N$ in which N is the ratio of available orientations in the two states. Admittedly other factors exist whose contributions tend to obscure this relationship, but it was anticipated that these might be negligible in comparison with the orientational entropy. Perhaps the most significant of these effects is the dependence of entropy increment upon volume increment for which no complete solution has yet been presented. The striking result of preliminary investigation is that their transitional entropy increments do indeed tend to cluster about integral or simple fractional values of N . For example, transitions in KBH_4 and $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ all cluster closely about $R \ln (3/2)$, those for NaCN ,

NaBH_4 , K_2ReCl_6 , AgNO_3 , CsNO_3 , NH_4Cl , NH_4I and NH_4NO_3 about $R \ln 2$ while those for NaCN , KCN , RbNO_3 , TlNO_3 , NH_4Cl , NH_4PF_6 , and $\text{NH}_3\text{C}_5\text{H}_{11}\text{Cl}$ about $R \ln 3$ that for $\text{NH}_4\text{Cr}(\text{SO}_4)_2$ at $R \ln 4$, KNO_3 near $R \ln 6$, $(\text{NH}_4)_2\text{SO}_4$ near $R \ln 8$, $(\text{NH}_4)_2\text{SnBr}_6$ at $R \ln 10$, KPF_6 at $R \ln 32$ and $(\text{NiNO}_3)_2 \cdot 6\text{NH}_3$ at $R \ln 48$. Only five substances are shown at intermediate values. Further extension of this concept is highly desirable to broaden the base of the correlation.

Staveley and his co-workers have also devised a method for estimating the freedom of the rotational movement of the ammonium ions in the lattices of some salts containing highly symmetrical anions⁹⁹. The principle of their method is simply one of comparing the molal heat capacities of corresponding isostructural ammonium and rubidium salts which have nearly the same lattice dimensions. For such a pair it is reasonable to suppose that the contributions to the heat capacity of the following terms will not differ significantly: (i) $C_p - C_v$; (ii) the contribution from the internal vibration of the anion; and (iii) the contributions from the torsional oscillations of the anion. Consequently, at temperatures sufficiently high for the lattice vibrations to contribute the classical limit to C_p (a state which should be reached well below 300°K) the quantity

$$\Delta C_p = C_p(\text{NH}_4 \text{ salt}) - C_p(\text{Rb salt}) - 2 \times C_{\text{int.}}(\text{NH}_4)$$

should be the heat capacity contribution from the torsional or rotational movement of the ion. The last term, $C_{\text{int.}}$, is a relatively small contribution from the internal vibrations of the ammonium ion which can be calculated from the frequency assignment. On this basis, these authors concluded that the ammonium ions in the stannic chlorides are restricted rotators prevented from freely rotating by comparatively low-energy barriers. That part of the heat capacity due to the torsional oscillation of the ammonium ion for both the stannic chloride and stannic bromide was found to increase with temperature, reaching at 300°K a value roughly half-way between free rotation and classical torsional oscillation. Application of the same method to ammonium perchlorate (using potassium perchlorate as a stand-in) by Justice *et al.*¹⁰⁰ leads to the conclusion that these ions are restricted rotators also restrained by comparatively low-energy barriers. These conclusions are corroborated by nuclear magnetic resonance studies by Ibers¹⁰¹, by Richards and Schaefer¹⁰², and by the neutron diffraction studies of Smith and Levy¹⁰³. Rush, Taylor, and Havens¹⁰⁴ have gone further in predicting a barrier of only 0.1 to 0.2 kcal/mole by cross-section measurements with slow neutrons. Historically, Osaka University has been one of the centres most concerned with the molecular reorientational-rotation. The extensive studies of Professor Nitta are being extended by Dr Seki. In a paper for presentation at this Symposium the authors, Suga, Matsuo and Seki¹⁰⁵ have studied order-disorder phase transitions of KCN crystals by adiabatic calorimetry. The higher-temperature phase transition at 168.3°K with a ΔS_t of $R \ln 4$ has been reported by Bijvoet and Lely¹⁰⁶. Here the cyanide ions are either rotating freely or assuming randomly the eight [111] directions in the high-temperature phase in contrast to the parallel array in the [010] direction of the orthorhombic lattice of the low-temperature phase. However, Matsubara and

Nagamiya¹⁰⁷ have calculated potential barriers hindering the rotation of the cyanide ions in both phases and concluded that these ions are subject to hindered rotation with a barrier height of approximately 1.4 kcal/mole in the high-temperature phase. Since in this phase the ions have orientational entropy of $R \ln 8$ it might reasonably be expected that on cooling the crystal will undergo another phase transition corresponding to the orientational order-disorder end-for-end rearrangement of the ions. Alternatively, the crystal may be expected to possess residual entropy of $R \ln 2$ at lower temperatures. Seki and his collaborators have found a gradual lambda-type transition at 82.9°K with a ΔS_t of nearly $R \ln 2$ possibly occasioned by the anticipated end-for-end ordering. Confirmation of this point by neutron diffraction or other means would, of course, be highly desirable. Since this type of transition has already been observed in the NaCN crystal, the ordering process may proceed by similar mechanisms in both crystals. Using an Eucken-Morrison type of analysis (rather similar to that already described by Wulff⁸⁶), these authors conclude that in the low-temperature phase the cyanide ions are undergoing torsional oscillation with a frequency of about 150 cm^{-1} and as the temperature rises torsional motion is gradually excited into the hindered-rotational mode with a barrier height of approximately 1.35 kcal/mole and into a state of essentially free rotation at even higher temperatures.

ADSORBED FILMS

Though our understanding of transitions in bulk phases is still rudimentary in many respects, that concerning transformations in adsorbed films is even less secure. Although it may be said that general agreement has been reached on the thermodynamic interpretation of the calorimetric heats of adsorption and other adsorption data¹⁰⁸⁻¹⁰⁹, the utility of derived thermodynamic quantities (either from calorimetry or from adsorption isotherms) has been less generally accepted in the discussion of adsorption. The study of the isosteric heats of adsorption of water and benzene vapour by Madeley and Sing¹¹⁰ for this Symposium features isosteric heats of adsorption calculated from the adsorption isotherms of water and benzene determined at various temperatures on silica gels of selected surface area and porosity. Initial values both of the isosteric heat and the entropy of adsorption increase significantly when the equivalent pore diameter is reduced to about 35Å.

TRANSITIONS IN METALS

The heat capacity of a sodium sample is a very involved function of the thermal history since different amounts of the body-centred cubic phase and the faulted-hexagonal, close-packed phase may be present and because the apparent heat capacity may be reduced by annealing effects or increased by reversion effects. Nevertheless, the calorimetric investigation of the Martensitic transition in sodium—once regarded as the ideal metal because the electronic properties could be understood rather well on the free-electron approximation—has been instrumental in the interpretation of the transformation and in its exploitation in the determination of the thermodynamic properties of the coexistent stable and metastable phases. The

Symposium paper by Martin summarizing this work¹¹¹ permits a re-examination of the meticulous thermal studies for which he has become justly renowned during the past six years. Apart from interest in the transition *per se*, the studies also provide calorimetric observations of annealing at lower temperatures than have been made previously and show that the electronic heat capacities of the two phases of sodium are probably identical despite the fact that the Fermi surface is contained within the first Brillouin zone in the body-centred cubic phase but intersects the zone boundary in the hexagonally close-packed phase. Moreover, Filby and Martin¹¹² have used the same technique to obtain the lattice thermal properties of the two phases. Certainly it is worthy of note that the unambiguous identification of spontaneous heating in the present work must be attributed to the use of an adiabatic calorimeter which eliminates uncertain temperature drifts due to other causes.

TRANSITIONAL STUDIES AT ELEVATED TEMPERATURES

While most of the papers discussed thus far in this session of the Symposium have been concerned with work at or below ambient temperatures, calorimetrists need not be reminded how scanty our knowledge of the thermal properties, especially enthalpy increments of transitions, is in the higher temperature ranges. Consequently, it is with special interest that we review the contribution to this Symposium providing data on substances at temperatures relatively far above the ambient. Since little work has been done by adiabatic calorimetry at temperatures in excess of 800°K, the drop calorimeter employing the method of mixtures is—despite its limitations—still the real provider of most data in the high-temperature area. Olette and Ferrier¹¹³, in a paper submitted to this Symposium, have contributed new data on the enthalpies of fusion of three pure metals (silicon, iron, and nickel) together with the description of a new drop calorimeter featuring a furnace with a molybdenum heating element wound on a Morgan alundum tube and protected against oxidation with a 10 per cent hydrogen–nitrogen atmosphere. The furnace was maintained constant up to $2220 \pm 2^\circ\text{K}$ over a 100 mm zone. The entire furnace and calorimeter space can be evacuated to pressures of 10^{-3} Torr, although in most instances a controlled atmosphere of about 20 Torr of argon was employed. Silica glass capsules sealed in helium were used for relatively low-temperature measurements on the enthalpies of fusion. The sample was contained in a thin alumina tube within a molybdenum container which could be sealed by welding. Temperatures were determined with a 13 per cent rhodium–platinum thermocouple and by optical pyrometry. The calorimeter proper consists of a massive high-conductivity copper block of 16 kg mass in a stainless steel submarine immersed in a 70 l. water thermostat which an electronic regulator¹¹⁴ maintained in adiabatic accord with the calorimeter. A thermistor device was used for measuring the temperature rise. The apparatus was calibrated by means of the Calorimetry Conference sample of pure synthetic sapphire as recommended by Furukawa *et al.*¹¹⁵

They report a value for the enthalpy of fusion, $\Delta H_m = 12.11 \pm 0.10$ kcal/g-atom at the melting point of silicon, $1685 \pm 2^\circ\text{K}$. This datum is

significantly higher than that of Körber and Oelsen¹¹⁶, 11.10 ± 0.40 kcal/g-atom, which was obtained on technical silicon (98 per cent silicon) but is in good agreement with data published by Kantor, Kasil, and Fomichev¹¹⁷, 11.95 ± 0.18 kcal/g-atom. The enthalpy increment for the γ - δ transition is stated as 0.263 ± 0.070 kcal/g-atom at $1645 \pm 1^\circ\text{K}$ and the value of the enthalpy of fusion of δ -iron is 3.29 ± 0.08 kcal/g-atom. This value is about 10 per cent lower than previous ones but is supported by computations based on binary iron phase diagrams made by Ferrier¹¹⁸, 3.30 ± 0.10 kcal/g-atom. The enthalpy of fusion of nickel found by these authors is 4.18 ± 0.05 kcal/g-atom at the 95 per cent confidence level and is in good agreement with the estimated one of Hultgren¹¹⁹.

Even higher temperatures are claimed as within the working range of an electron-bombardment furnace drop calorimeter described by Greenbaum, Weiher, and Farber¹²⁰ in a contribution to this Symposium. This apparatus was designed to provide heat capacity data on beryllium oxide (BeO) through its melting temperature. A tungsten heating coil and a concentric tungsten target cylinder are the electrodes of the electron-bombardment furnace and are surrounded by suitable molybdenum shields suspended within a section of standard commercial glass pipe. The basic design of the calorimeter is that of Ginnings and Corruccini¹²¹. A study of the phase transitions in the tungsten-carbon system by Orton¹²² in a Symposium paper utilizes tests made at constant temperature of the formation and dissolution of the carbide on tungsten metal by X-ray diffraction of the surface film about two microns thick. The strongest diffraction lines indicated for each of the three species were examined after exposure of the sample at constant temperature to a methane-hydrogen atmosphere. As the carbide grows on the surface of the tungsten the intensity of its diffraction lines increase; inversely, the intensity of its lines decreases as it dissolves. The mixture of gases at which a carburizing-decarburizing reaction reverses yields the equilibrium transition point. From the equilibrium constants the Gibbs energies of formation and reaction and a more detailed phase diagram for the tungsten-carbon system were obtained. This phase diagram shows a eutectoid at 1488°K at which W_2C decomposes to W and WC as well as a peritectoid at 1598°K at which W_2C and C react to form WC.

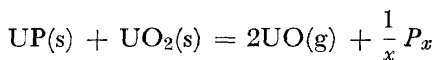
Well-defined, phase diagrams do indeed often provide the thermodynamicist with a wealth of implicit data which can generally be garnered with due attention to the equilibrium relationships involved. In a very interesting note concerning the calculation of enthalpies of fusion from phase diagrams, Ferrier's Symposium report¹²³ demonstrates how by taking into account the temperature-dependence of the activity coefficients of the several phases by means of the relationship

$$[\partial \ln (N_1^s \gamma_1^s / N_1^l \gamma_1^l) / \partial (1/T)]_p = \Delta H_m / R$$

in which N_1 and γ_1 represent the mole fractions and activity coefficients of the solvent substance in the solid and liquid states (as indicated by superscripts). ΔH_m is the enthalpy of melting of the solvent. Using this approach Ferrier utilized recent determinations on the system iron-phosphorus¹²⁴ considered as an ideal solution of tri-iron phosphide in iron to obtain a

value for the enthalpy of melting of δ -iron of 3.22 kcal/g-atom. Likewise, utilizing the recent determinations of the solidus for the system iron-sulphur¹²⁵ and data on the activity of sulphur in liquid solution¹²⁶⁻¹²⁸ they obtain a value for the enthalpy of melting of δ -iron of 3.36 kcal/g-atom. From recent re-investigations on the system iron-carbon¹²⁹⁻¹³⁰ and the relevant activity coefficients¹³¹⁻¹³² they obtain a value for the enthalpy of melting of δ -iron of 3.27 kcal/g-atom. As noted previously the mean value of these three calculations, 3.28 kcal/g-atom, is in excellent accord with the direct calorimetric determination of this quantity. An interesting feature of this method is its utility in the estimation of enthalpies of transition unavailable by direct experimentation. For example, the data on the iron-carbon system already referred to also provided an enthalpy of melting of γ -iron (face-centred cubic) of 4.4 kcal/g-atom at the hypothetical 1790°K melting temperature of pure γ -iron.

Chemical thermodynamicists will appreciate that not only may thermal quantities be evaluated from phase diagrams but that, conversely, phase diagrams may be delineated calorimetrically, thereby providing a knowledge not only of the invariant temperatures but of the magnitudes of the enthalpies and entropies of transition as well. The calorimetric method becomes especially sensitive at temperatures well below the ambient but is by no means limited to this situation. The method, moreover, provides real advantages over thermal analysis in that determinations can be made at or very closely approaching equilibrium and is of such sensitivity as to reveal minute thermal effects that would escape detection by usual thermal analysis and even in instances (*e.g.*, relatively slow transformations), by differential thermal analysis. Where this method has been employed the presence of solid solution ranges has often been detected (by the disappearance of the eutectic transformation), as for instance in the system ammonium fluoride-water¹³³, for the system ammonium fluoride-hydrogen fluoride¹³⁴, and more recently for the system tetramethylmethane-tetrachloromethane¹³⁵. Another technique often being exploited for the procurement of Gibbs energy data on molecular crystals near ambient temperatures and on refractory substances at considerably higher temperatures is the use of Knudsen diffusion techniques. Gingerich, Efimenko and Lee¹³⁶ have submitted to this Session a thermodynamic study of the uranium monophosphide-uranium dioxide system with a mass spectrometer. They find that when the substances are present in approximately equimolar ratio, the principal reaction is



in which x is either 1 or 2. The thermodynamic data for the corresponding process have been evaluated with due regard for instrument factors, relative ionization cross-sections and possible interactions with container materials.

High-temperature enthalpies between 500 and 1200°K and enthalpy increments by conventional drop calorimetry for sodium nitrate and three alkali carbonates were presented to this Symposium by Janz¹³⁷. Although (as shown in *Table 5*) the entropy of melting of sodium nitrate is in good

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accord with previous "best" values, that of the transition is not. The sums of the entropies of transition plus fusion for compounds which show solid-state heat-capacity maxima are often quite similar in magnitude to entropies of fusion of compounds which have no solid-state transitions. This observation is borne out by a summary of recent data for the alkali nitrates,

Table 5. Entropies of transition and fusion for sodium nitrates (Units: cal, mole, °K)

T_t	ΔS_t	T_m	ΔS_m	Source
549.2	0.32	580.0	6.1	Janz ¹³⁷
—	0.0	579.6	6.2	Sokolov and Shmidt ¹³⁸
549.2	1.7	579.2	6.0	Mustajoki ¹³⁹
549.2	1.6	—	—	Miekk-Oja ¹⁴⁰

some of which have as many as three solid-state transitions. The sum of their respective entropies are (in cal mole⁻¹ °K⁻¹): Li (11.7), Na (6.4), K (8.1), Rb (6.0), NH₄ (7.6), and Cs (7.1).

It will be seen that the entropies of fusion of alkali carbonates as determined calorimetrically by Janz show somewhat the same trend (Table 6).

Table 6. Entropies of fusion for alkali metal carbonates† (Units: cal, mole, °K)

Salt	T_m	ΔS_m	Method
LiCO ₃	726	10.7 ± 0.1	Drop calorimetry
		10.2 ± 1	Phase diagram
		11.4 ± 1	Phase diagram
Na ₂ CO ₃	858	5.9 ± 0.2	Drop calorimetry
		10.3 ± 1	Phase diagram
K ₂ CO ₃	899	5.6 ± 0.1	Drop calorimetry
		8.4 ± 1	Phase diagram
		8.7 ± 1	Phase diagram
Ternary	Eutectic	6.0 ± 0.1	Drop calorimetry

† Drop calorimetric data from Janz¹³⁷; phase diagrams reported by Janz and Lorenz¹⁴¹

Although the electronic conductance, viscosity, and X-ray diffractational behaviour indicate a highly ionic nature for these carbonates, their entropy of fusion deviates significantly from the value of 3 cal mole⁻¹ °K⁻¹ noted for NaCl and KCl, for which positional randomization is a predominant factor. Further discussion of this point hinges on more detailed information on the solid-state structures and ambient temperature and cryogenic thermal data for these salts. In contrast to the excellent accord noted between the calorimetric entropy of melting of iron and that obtained from the solidus curve, Table 6 reveals considerable discord between the calorimetric values and those obtained from freezing-point phase diagrams. It is probable that attention to the significant deviation from unity of the activity coefficient

in these ionic melts might considerably improve the accord and status of the latter values.

ORDERING TRANSITIONS IN IONIC COMPOUNDS

In contrast to the situation in alloys, ordering transitions occur relatively rarely in ionic compounds. In lithium ferrite—a sodium chloride-type of mixed oxide—the short-range order is determined by the Coulombic interaction although other forces may determine the long-range ordering of the compounds. According to Fayard's paper submitted to this Symposium¹⁴², three structural varieties of the mixed lithium ferrite $\text{Li}^{\text{I}}\text{Fe}^{\text{III}}\text{O}_2$ are known. In the high temperature, NaCl-type (cubic) phase, designated C, the lithium(I) and the iron(III) ions occupy the cationic sites randomly. The two other forms, Q_{I} and Q_{II} , are ordered and tetragonal with a ratio of c/a near two for Q_{I} and unity for Q_{II} . The stability ranges and modes of transition of the several phases are indicated in *Figure 11*. Fayard's contribution shows the existence of an important short-range order in the C

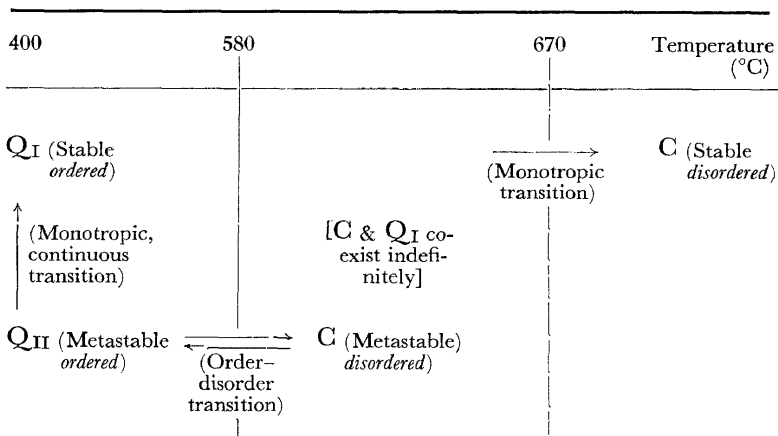


Figure 11. Structural varieties of lithium ferrite

form, which is great enough to explain the possibility of existence of the disordered form (in that its network energy is lowered enough to be comparable with that of the ordered forms). The presence of this short-range order also explains why the metastable, Q_{II} , form is obtained only by annealing the disordered C form. Although the sluggishness of most of the transitions involved would render calorimetric determination of the transition enthalpies difficult in general, that of the $\text{Q}_{\text{I}} \rightarrow \text{C}$ transition would appear to be feasible. This might provide confirmation for some of the estimates suggested in this system and thereby increase the relatively limited thermochemical data on the ordering in non-metallic compounds.

In summary, it is evident that interesting advances in our understanding of the mechanism and chemical thermodynamics of transitions have been made, but that even more exciting prospects may be anticipated during the

next decade and perhaps even before the next Thermodynamics Symposium. Certainly the chemical thermodynamicists' Utopia still lies far ahead.

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