



LIONEL STAVELEY'S CONTRIBUTION TO THE THERMODYNAMIC STUDY OF SOLIDS: SELECTED TOPICS

This paper is an edited version of the one delivered at the Symposium held in Oxford on 25th June, 1982 to mark the retirement of Dr. Lionel Staveley.

In the previous paper Dr. WEIR [1] has surveyed the complete range of systems which Lionel Staveley has studied by low-temperature calorimetry. In this article I wish to describe in rather greater detail several of these which I think are of particular interest. Because of the number of systems studied it is a difficult task to select just a few, and the choice is therefore largely a personal one.

THE SALT HYDRATES

The question at issue is the existence or otherwise of disorder of the protons. In ice, having placed the oxygen atoms unambiguously there are then two possible positions on each O ... O line at which the proton can be situated. There is, however, a restriction on the placing of the protons, as formulated in the BERNAL-FOWLER rules [2], according to which on the four H-bonds in which each oxygen is involved there must be two protons in "near" positions and two in "far" positions. In ordinary ice (I h) the protons are distributed according to the Bernal-Fowler rules but otherwise randomly. Of the high-pressure forms of ice most are also disordered, but three are ordered (II, VIII and IX) [3]. What happens in the salt hydrates?

The hydrates were studied by determining the residual entropy (S_{res}) at 0 K from the entropy at a temperature (T_a) near ambient together with the heat capacities from T_a down to near 0 K.

$$S(T_a) = S_{\text{res}}(0 \text{ K}) + \int_0^{T_a} (C_p/T) dT + \sum_{\text{trans}} \Delta H_i/T_i \quad (1)$$

where the integral term includes all the entropy gained in regions where C_p is a continuous function of temperature and the final term gives the entropy gained discontinuously at transitions. The value of $S(T_a)$, which must be obtained independently in this procedure, could be formed from values of $\Delta S(T_a)$ for a reaction involving the salt hydrate of interest, *e.g.*



provided that values of the entropies of the other participating species were obtainable. For such a reaction ΔS was obtained from values of ΔH (from reaction calorimetry) and ΔG (either from measurements of the decomposition water-vapour pressure or electrochemically).

Three out of the four discoveries of proton disorder at 0 K in simple salt hydrates have been made by Lionel Staveley: $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ [4], $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ [5] and $\text{ZnF}_2 \cdot 4\text{H}_2\text{O}$ [6]. The lower hydrates of Na_2CO_3 and Na_2HPO_4 ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ and $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$) did not show this property, neither did $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ [7], $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ [8] and $\text{LiBr} \cdot \text{H}_2\text{O}$ [9]. The details of the proton disordering may be expected to be rather similar to that for $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ [10-12], which has been shown to contain rings of four hydrogen-bonded water molecules in which there are two possible arrangements for the set of four hydrogen bonds:

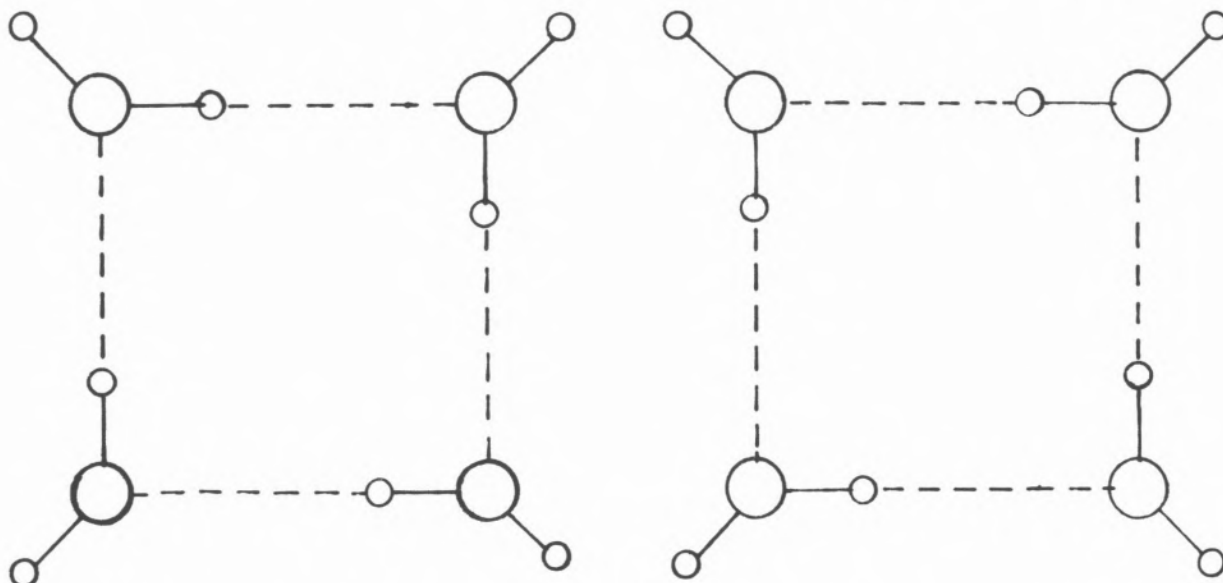
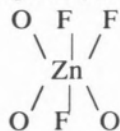


Fig. 1

Possible H-bond configurations for a ring of four water molecules, as found in $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. Large circles, O atoms; small circles, H atoms

In the case of $\text{ZnF}_2 \cdot 4\text{H}_2\text{O}$ [6], for which S_{res} ($4.3 \text{ JK}^{-1} \text{ mol}^{-1}$) was found to be close to $R \ln 2$ ($= 5.76 \text{ JK}^{-1} \text{ mol}^{-1}$), it is thought that the disorder arises from there being two possible positions for the



octahedron (by analogy with $\text{FeF}_2 \cdot 4\text{H}_2\text{O}$), which has been examined by X-ray diffraction [13]. Hydrates of the type $\text{MSiF}_6 \cdot 6\text{H}_2\text{O}$ undergo transitions on cooling if $M = \text{Co}$, Fe , Mg or Mn (though not if $M = \text{Zn}$, Ni) and these are thought to be due to modification of the hydrogen-bond system rather

than to order-disorder changes of the anion arrangement [14].

Although $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ [8] had no residual entropy, it was interesting and unusual in having a transition (at $\sim 247 \text{ K}$) which was approximately of the classical (Ehrenfest) second-order type:

Transitions of this kind are very limited in number. $\text{LiBr} \cdot \text{H}_2\text{O}$ [9] exists as two stable forms (an orthorhombic α -form below 307 K ; a perovskite β -form above 307 K). From an X-ray diffraction study the β -form was believed to have extensive disorder of two kinds: with respect to the orientations of water molecules and to the positions of the lithium ions. Since the entropy change at the

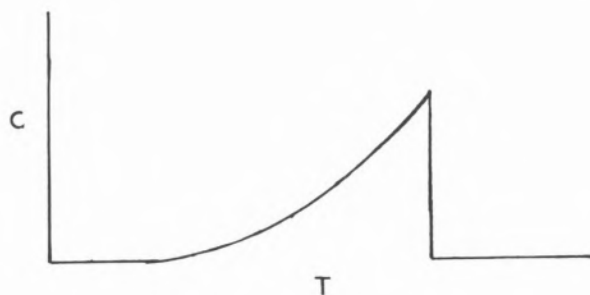


Fig. 2

Heat capacity versus temperature curve for a classical (Ehrenfest) second-order transition. Only the contribution from the order-disorder process is shown

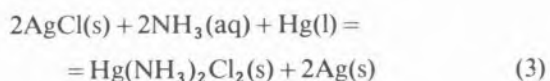
$\alpha \rightarrow \beta$ transition is only $\approx R \ln 2.3$ it would appear that the α -phase should also be disordered. However, S_{res} was found to be zero, so that *either* the α -form becomes ordered in a continuous manner on cooling from 307 K to 0 K *or* the β -form is less disordered than was thought. The latter situation could arise if there were strong correlation between the positions of the lithium ions and the orientations of the water molecules.

"MATHEMATICAL TOYS"

Theoretical physicists have expended much effort on the study of some problems which do not appear to correspond directly to real physical systems. In this way they have improved their methods and also obtained general indications of types of behaviour.

One such problem concerns the number of ways in which "dimers", units which occupy two adjacent sites of a lattice, may be placed on the lattice so that all of the sites are occupied exactly once. This problem was solved analytically for the two-dimensional square lattice (giving $S_{\text{res}} = 4.85 \text{ J K}^{-1} \text{ mol}^{-1}$) [15,16], but no such solution for a three-dimensional array has been found. Lionel Staveley [17] noted that the substances $\text{Hg}(\text{NH}_3)_2 \text{X}_2$ (where $\text{X} = \text{Cl}$ or Br) are good realizations of a three-dimensional problem, that on a simple cubic lattice.

The Cl (or Br) ions occupy the corner positions of the cell with the NH_3 molecules filling the cube-centres. Disorder is related to the positions of the Hg ions, which occupy only one out of the six face-centres of each cube. The $\text{NH}_3\text{—Hg—NH}_3$ units may be regarded as "dimers", each filling two of the cube-centres. For the study of this problem, $S(T_a)$ was formed from the E.M.F. and its temperature derivative of a cell with reaction:



and the corresponding Br equivalent.

S_{res} was found to be 12.0 ± 3 and $20.0 \pm 7.5 \text{ J K}^{-1} \text{ mol}^{-1}$ for the Cl and the Br compound, respectively. Since a rough theoretical estimate gives $6.35 \text{ J K}^{-1} \text{ mol}^{-1}$ [18] it was deduced that the substances possess some disorder with respect to the NH_3 molecules in addition to the "dimer" disorder.

Another problem of this type is that of a chain which visits all the sites of a cubic array exactly once and has a 90° change of direction at each site. No exact solution for the number of ways of achieving this has been found, but a Monte Carlo simulation has yielded the value $6.75 \text{ J K}^{-1} \text{ mol}^{-1}$ for the corresponding entropy [19]. A real system corresponding to this problem is the metastable form of $\text{Hg}(\text{NH}_2)\text{Br}$. Again, there is a cubic structure with the halide ions filling all the corners; the body-centres are occupied by the NH_2 groups. Two of the six face-centres of each cube are occupied by Hg atoms, and every Hg—N—Hg is 90° . Using the electrochemical cell method in conjunction with a calorimetric value of ΔH for the determination of $\Delta S(T_a)$, Lionel Staveley found that the residual entropy was zero, even though there was no transition below T_a [19]. Thus it appears that the disorder noted in the room-temperature crystallographic study is all lost in a continuous fashion in cooling to 0 K.

CHARGE-TRANSFER COMPLEXES

Interest in the 1:1 complex of 1,2,4,5-tetracyanobenzene and pyrene was stimulated by the observation that the crystals shattered on cooling through $\sim 171 \text{ K}$ and that there was no crystallographic change between room temperature and a temperature slightly above 171 K [20]. Closer study by heat capacity calorimetry revealed a transition at $\sim 230 \text{ K}$ for which the entropy change was $\sim R \ln 3$, but no transition near 171 K [21]. The phenomenon at $\sim 171 \text{ K}$ was traced to the delayed ordering of the solid following supercooling through the transition at $\sim 230 \text{ K}$. The entropy value suggests a 3-fold disordering of one of the components, and differs from PROUT'S suggestion [20] of large amplitude oscillations of the pyrene molecules.

Another compound of this type (1:1 pyromellitic anhydride + pyrene) involves components both of which are disordered in the pure form at room temperature. No anomalies were found in the heat capacity of this compound, but an analysis of the data suggested that disordering occurred as the temperature was raised [22]. The analysis suggested that 2-fold disordering of both constituents took place in temperature regions which overlapped. Earlier NMR evidence was that, on raising the temperature, the pyrene sub-lattice became disordered first [23].

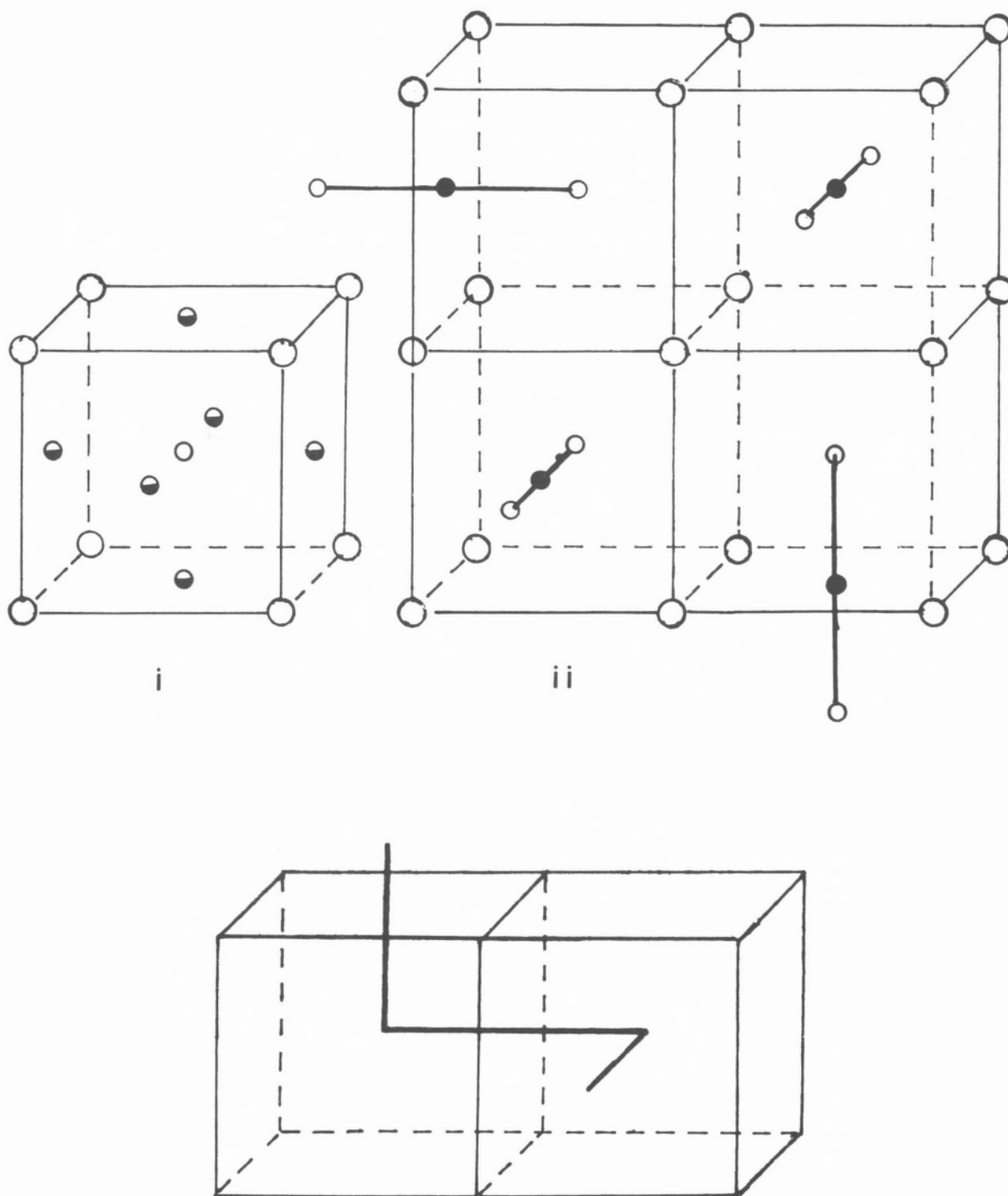


Fig. 3

a) The structure of $\text{Hg}(\text{NH}_3)_2\text{X}_2$, where $\text{X} = \text{Cl}$ or Br . (i) A unit cell; (ii) a group of unit cells showing $\text{H}_3\text{N}-\text{Hg}-\text{NH}_3$ "dimers" (bold lines). Large open circles, Cl^- or Br^- ; small open circles, NH_3 ; small filled circles, Hg ; small half-filled circles, sites with probable occupancy by Hg atoms of $1/6$. b) The $\text{H}_2\text{N}-\text{Hg}-\text{NH}_2-\text{Hg}-\text{NH}_2-\text{Hg}$ chain (bold line) in $\text{Hg}(\text{NH}_3)_2\text{Br}$

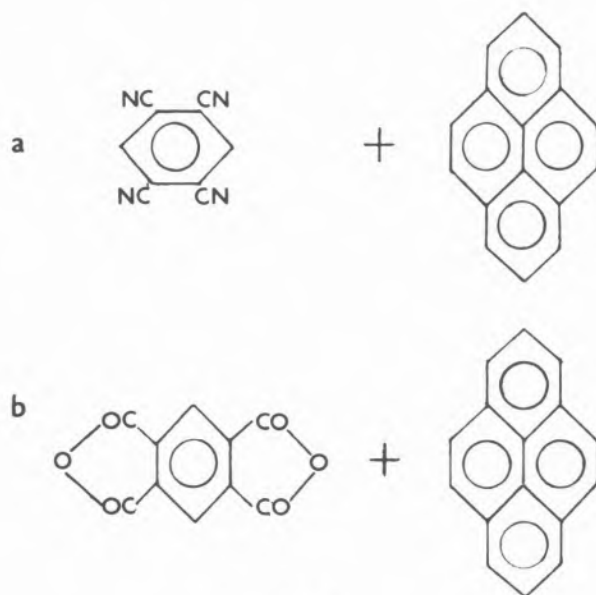


Fig. 4
Charge-transfer complexes

METAL TETRA-ALKYLS

This was one Lionel Staveley's earliest pieces of research into the thermodynamics of transitions, and it produced some very surprising results [24-25].

Aston had previously shown that $C(CH_3)_4$ and $Si(CH_3)_4$ each had an orientationally disordered phase, although this was metastable in the case of the latter compound [26,27]. Lionel Staveley then found that there was no polymorphism in $Sn(CH_3)_4$ or $Pb(CH_3)_4$ [25] and subsequently $Ge(CH_3)_4$ was also shown to have no phase transition [28]. It was when attention was turned to the tetraethyls that really interesting results were found. The lower members (C, Si, Ge) were again "simple", but the compounds of Sn and Pb showed a rich variety of forms: at least 10 could be obtained for $Sn(C_2H_5)_4$ (using different rates of cooling) and at least six for the Pb compound. (These were recognised by their different melting-points. For $Pb(C_2H_5)_4$ the melting-points were up to 11° below the true melting-point). Some similar results were obtained for $Pb(C_2H_5)_4$ at the U.S. Bureau of Mines (G. B. Guthrie, unpublished work). Staveley suggested that the forms arose from the packing of different rotational isomers. Substances having alkyl chains usually exist in several stable forms, but the large

numbers for $Sn(C_2H_5)_4$, and $Pb(C_2H_5)_4$, even though they may be metastable, is, I think without parallel. Certainly, further study on these compounds employing other techniques should be well worthwhile.

CLATHRATES OF β -QUINOL

The presence of "Tiny" Powell, the father-figure of clathrates, in the same laboratory at Oxford obviously stimulated Lionel Staveley's interest in these substances. Evans and Rex Richards, in the Physical Chemistry Laboratory at Oxford, had also made measurements (ΔH_f) on some of these and had found proportionality of that quantity with the polarizability of the encaged molecules [29]. A still more searching test of any theory of these substances would be to explain the C_p values for a wide range of temperature (12-300 K). These experiments were typical of Lionel Staveley's approach to research: the system studied was, molecularly, simple enough for a sound interpretation of the results to be possible. Indeed, just as the experimental work was about to commence J. H. van der Waals published his cell theory of the clathrates — which he compared with values for ΔH_f and the decomposition pressure [30]. By measuring C_p for several degrees of filling of the cavities it was possible to separate out the contribution arising from the encaged molecules from that for the quinol cage. The results thus obtained were in good agreement with van der Waals' theory in the upper part of the temperature range (100-300 K) for both the argon and the krypton clathrates [31,32]. Agreement in this range could be improved with adjustment of a "semi-disposable" parameter. As the theory was classical it could not reproduce the "quantum fall-off" in C_p which was found at lower temperatures. However results in this low-temperature region could be fairly well reproduced by fitting an oscillator model (simple harmonic or anharmonic) to the lower part of the potential well in which the encaged molecule moved.

Rotation of molecules in the cages, one of Lionel Staveley's favourite topics, could now be studied as there was a good treatment of the "rattling" motion, which was essential for analysis of the data. Thus methane was found to undergo almost free rotation at least above ~ 150 K [33]. The diatomic molecules N_2 , CO and O_2 , however, all experienced

potential barriers tending to align the molecules with the c-axis of the cage, the barriers being 4.60, 4.60 and 0.84 kJ mol⁻¹ respectively [34]. Staveley's work has thus put the thermodynamics of clathrates on a very sound footing.

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Lionel Staveley's research work has been marked by an extraordinary ability to pick out the important experiment to do. As a consequence of this almost every project he has turned his hand to has yielded interesting results. As a director of research he may be said to have a very high "batting average" indeed.

REFERENCES

- [1] R. D. WEIR, *Rev. Port. Quím.*, **25**, ... (1983).
- [2] J. D. BERNAL, R. H. FOWLER, *J. Chem. Phys.*, **1**, 515 (1933).
- [3] N. G. PARSONAGE, L. A. K. STAVELEY, "Disorder in Crystals", Clarendon Press, Oxford, 1978, Section 8.1.
- [4] C. G. WATERFIELD, R. G. LINFORD, B. B. GOALBY, T. R. BATES, C. A. ELYARD, L. A. K. STAVELEY, *Trans. Faraday Soc.*, **64**, 868 (1968).
- [5] C. G. WATERFIELD, L. A. K. STAVELEY, *Trans. Faraday Soc.*, **63**, 2349 (1967).
- [6] R. O. COOK, A. DAVIES, L. A. K. STAVELEY, *J. Chem. Soc., Faraday Trans. I*, **68**, 1384 (1972).
- [7] R. E. D. REYNOLDS, R. D. WORSWICK, L. A. K. STAVELEY, *Trans. Faraday Soc.*, **67**, 618 (1971).
- [8] I. R. MALCOLM, L. A. K. STAVELEY, R. D. WORSWICK, *J. Chem. Soc., Faraday Trans. I*, **69**, 1532 (1973).
- [9] P. R. CLAYTON, A. G. DUNN, S. HOLT, L. A. K. STAVELEY, *J. Chem. Soc., Faraday Trans. I*, **76**, 2362 (1980).
- [10] K. S. PITZER, L. V. COULTER, *J. Am. Chem. Soc.*, **60**, 1310 (1938).
- [11] G. BRODALE, W. F. GIAUQUE, *J. Am. Chem. Soc.*, **80**, 2042 (1958).
- [12] H. W. RUBEN, D. H. TEMPLETON, R. D. ROSENSTEIN, I. OLOVSSON, *J. Am. Chem. Soc.*, **83**, 820 (1961).
- [13] B. R. PENFOLD, M. R. TAYLOR, *Acta Crystallogr.*, **13**, 953 (1960).
- [14] R. D. WEIR, K. E. HALSTEAD, L. A. K. STAVELEY, *Faraday Discuss. Chem. Soc.*, **69**, 202 (1980).
- [15] M. E. FISHER, H. N. V. TEMPERLEY, *Rev. Mod. Phys.*, **32**, 1029 (1960).
- [16] P. W. KASTELEYN, *Physica*, **27**, 1209 (1961).
- [17] M. D. COOKE, R. G. LINFORD, L. A. K. STAVELEY, R. D. WORSWICK, *J. Chem. Soc., Faraday Trans. I*, **74**, 2363 (1978).
- [18] R. G. FOWLER, G. S. RUSHBROOKE, *Trans. Faraday Soc.*, **33**, 1272 (1937).
- [19] R. D. WORSWICK, D. F. MAYERS, L. A. K. STAVELEY, *J. Chem. Soc., Faraday Trans. II*, **68**, 539 (1972).
- [20] C. K. PROUT, T. MORLEY, I. J. TICKLE, J. D. WRIGHT, *J. Chem. Soc., Perkin Trans. II*, **5**, 523 (1973).
- [21] P. R. CLAYTON, R. D. WORSWICK, L. A. K. STAVELEY, *Mol. Cryst. Liq. Cryst.*, **36**, 153 (1976).
- [22] A. G. DUNN, A. RAHMAN, L. A. K. STAVELEY, *J. Chem. Thermodyn.*, **10**, 787 (1978).
- [23] C. A. FYFE, *J. Chem. Soc., Faraday Trans. II*, **70**, 1633 (1974); C. A. FYFE, D. HAROLD-SMITH, J. RIPMEESTER, *ibid.*, **72**, 2269 (1976).
- [24] L. A. K. STAVELEY, H. P. PAGET, B. B. GOALLY, J. B. WARREN, *J. Chem. Soc.*, 2290 (1950).
- [25] L. A. K. STAVELEY, J. B. WARREN, H. P. PAGET, D. J. DOWRICK, *J. Chem. Soc.*, 1992 (1954).
- [26] J. G. ASTON, G. H. MESSERLY, *J. Am. Chem. Soc.*, **58**, 2354 (1936).
- [27] J. G. ASTON, R. M. KENNEDY, G. H. MESSERLY, *J. Am. Chem. Soc.*, **63**, 2343 (1941).
- [28] G. W. SMITH, *J. Chem. Phys.*, **42**, 4229 (1965).
- [29] D. F. EVANS, R. E. RICHARDS, *Proc. R. Soc. London. Ser. A*, **223**, 238 (1954).
- [30] J. H. VANDER WAALS, *Trans. Faraday Soc.*, **52**, 184 (1956).
- [31] N. G. PARSONAGE, L. A. K. STAVELEY, *Mol. Phys.*, **2**, 212 (1959).
- [32] N. R. GREY, N. G. PARSONAGE, L. A. K. STAVELEY, *Mol. Phys.*, **4**, 153 (1961).
- [33] N. G. PARSONAGE, L. A. K. STAVELEY, *Mol. Phys.*, **3**, 59 (1960).
- [34] N. R. GREY, L. A. K. STAVELEY, *Mol. Phys.*, **7**, 83 (1963).