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A REVIEW OF THE SOLIDS RESEARCH OF DR. L.A.K. STAVELEY

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.

1 — INTRODUCTION

Dr. Staveley's career involving solids alone is remarkable. He has pursued 'disorder' in the solid phase in an 'orderly' way with steady vigour trying to unravel the fascinating duel between those forces within the crystal favoring an ordered structure and those of thermal agitation producing disorder.

This review is intended as an overview of his productive and valuable contributions and is categorized by compound type rather than by the time order in which they were studied. Some license has had to be exercised in assigning the compounds to the categories since some exhibit more than one type of disorder. It should place into perspective the experimental aspects, the ongoing problem of ammonium rotation-libration (to be discussed in detail by Dr. E. Westrum), the hydrates, clathrates, organic systems (to be discussed by Dr. N. Parsonage) and the layered compounds currently being studied.

For this overview, it is convenient to divide disorder into three main types:

- a) positional, which occurs when more sites are available than particles to fill them thereby leaving some randomness in how the particles are distributed.
- b) orientational, which occurs when two or more distinguishable orientations are available for diatomic or polyatomic molecules.
- c) magnetic, which occurs when magnetic spins are involved.

2 — EXPERIMENTAL

Dr. Staveley's forte has been in adiabatic calorimetry covering the temperature range from 1K to 600 K. Among the quantities measured have been C_p , ΔS , ΔH , ΔG , transition temperatures and their heats. These have been supplemented by dilatometric studies of volume changes through transitions, densities in connexion with crystal defects, adiabatic and isothermal compressibility, thermal expansion as well as electrical conductivity. He has constructed at least seven adiabatic calorimeters, devices that must be built in house for the particular application. The dilatometers along with several other pieces of apparatus were also built by him.

The number of solid compounds studied is at least 124. This total is indeed impressive, but more important are the reasons for selecting these particular substances. To my knowledge, Dr. Staveley has never fallen victim to the 'chewing gum and shoe laces' syndrome — that ailment of measuring the properties of any substance just for the sake of publishing. He has judiciously selected his substances to supplement and augment experimental data in order to help answer specific questions about the substance and its family. Sometimes the theorists led and needed the data. Other times, his foresight indicated that data would be useful to the theorists albeit. They may not have realized it at the time, but he was subsequently proven correct. He has provided them with some celebrated and difficult statistical mechanical problems, one of which is ammonium libration-rotation. The positive influence of his philosophy in this regard on his students has been significant and cannot be overemphasized. Concomitant with all of this is his insistence on doing careful experimental work. His published results of 30+ years ago have not been improved upon in spite of the availability of today's more sophisticated measuring techniques and devices.

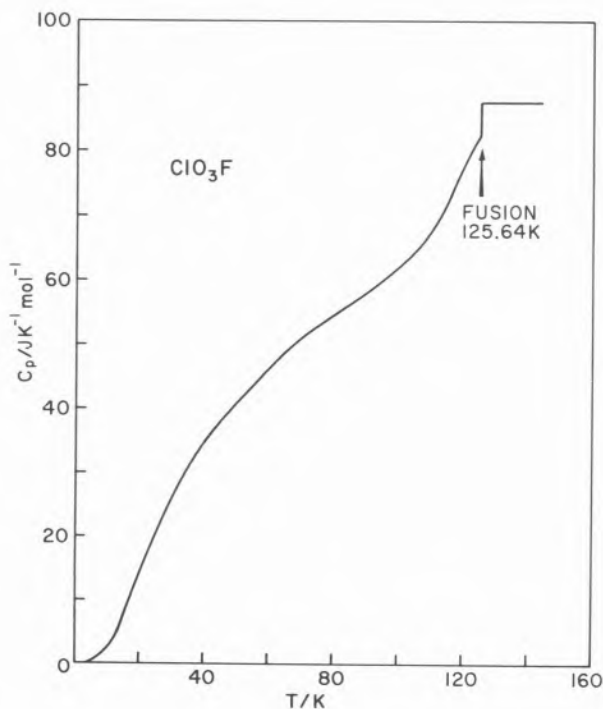


Fig. 1

Heat capacity vs. temperature for perchloryl fluoride

Let us consider briefly what happens when a disordered crystal is cooled. The disorder may remain at absolute zero to become frozen-in. When this occurs, the resulting heat capacity vs. temperature curve is normally smooth as shown in fig. 1 for perchloryl fluoride [1,2], whose residual entropy is $0.83 R \ln 4$.

Alternatively and the more common occurrence, the disorder is removed as temperature falls to produce an ordered crystal at 0 K. The solids may undergo transitions during this cooling process and there may occur a change in crystal structure or in the orientation of the molecules within the lattice. A well known example to undergo changes in crystal structure is NH_4Cl . Its discontinuous C_p vs T curves is shown in fig. 2 [3]. Not always is the C_p vs T curve discontinuous as NH_4BF_4 shows in fig. 3 [4].

The hump or gradual transition in this plot reflects a change in the orientational order of the ammonium ion. The plot for the KBF_4 salt is also shown for comparison.

3 — THE COMPOUNDS

3.1 — POSITIONAL DISORDER

It is well known that the disordered phase in this group shows ionic conductivity. Dr. Staveley measured electrical conductivity of KCl , KBr and KI [5]. From his heat capacity work on HgNH_2Br [6], it was found that the unstable cubic form becomes ordered at 0 K, but that $\text{Hg}(\text{NH}_3)_2\text{Cl}_2$ and $\text{Hg}(\text{NH}_3)_2\text{Br}_2$ [7] showed no transitions yet both remain disordered at 0 K. It has been suggested that this may be due to orientational disorder of the NH_3 . The last family within this group is the β -modification phthalocyanines. Their C_p results are complex and show unexpected behaviour at very low temperature, particularly the Ni compound [8]. The Cu compound undergoes two phase transitions, one of which is an order-disorder type.

3.2 — ORIENTATIONAL DISORDER

3.2.1 - SALTS

(i) Diatomic, triatomic (non-linear), tetraatomic (planar) ions — This group of compounds is listed in Table 1 with the main results as indicated. It is in

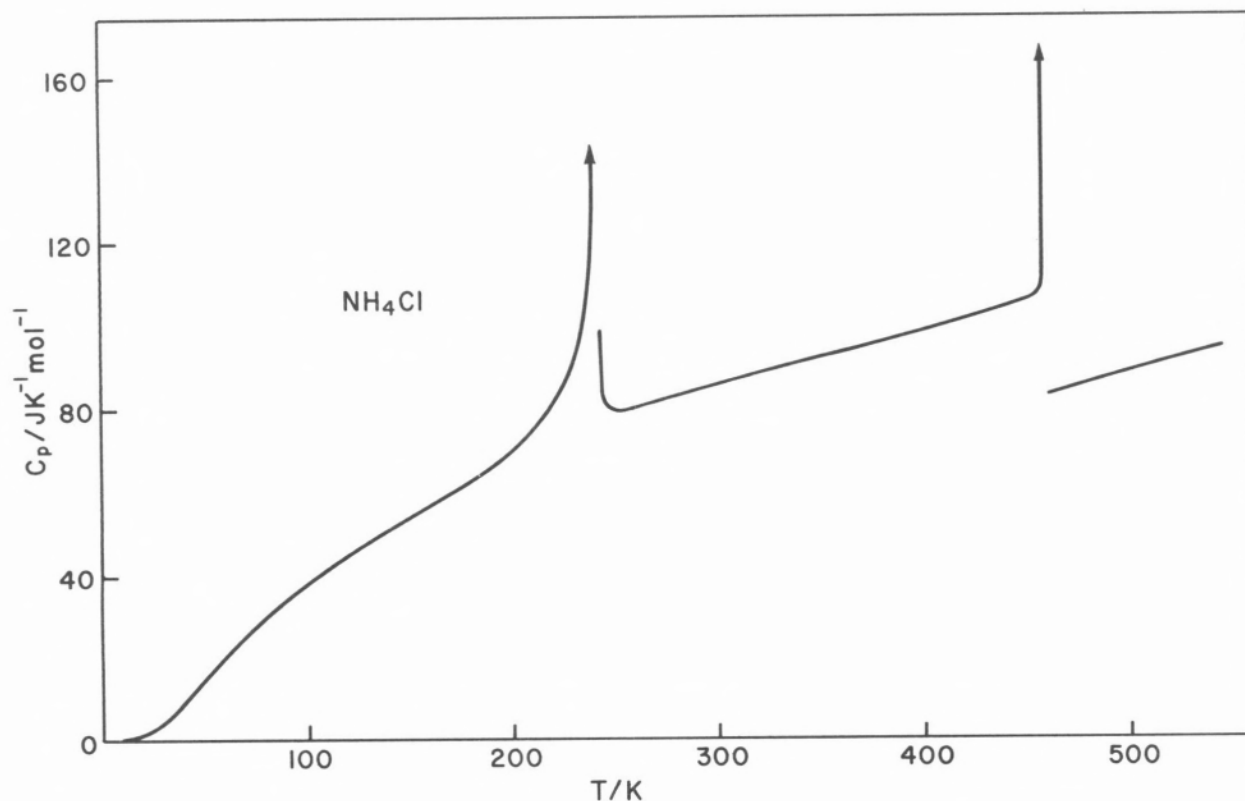


Fig. 2
Heat capacity curve for ammonium chloride

the paper on monovalent nitrates [16] that the ΔS for transition to the disordered phase is shown to be $R \ln n$, where n is some simple integer.

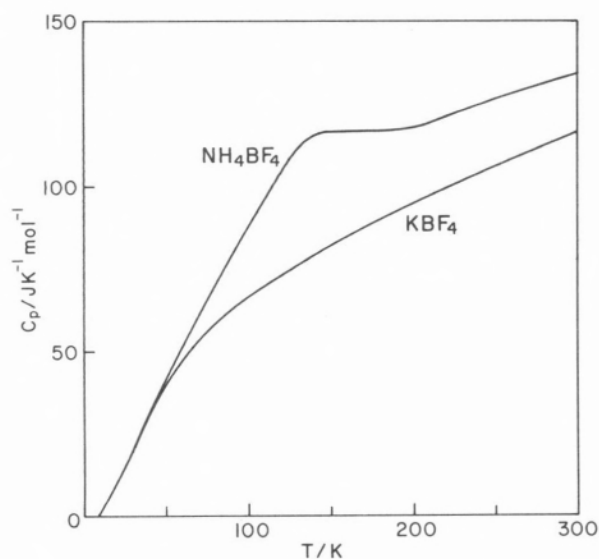


Fig. 3
Heat capacity curves for NH_4BF_4 and KBF_4

Table 1
Salts with di-, tri- and tetraatomic ions

Benzoic acid	[9]	reference standard, C_p
NOBF_4	[10]	order-disorder transition 'NO'
CsNO_2	[11]	order-disorder transition 'NO ₂ '
KNO_2	[12]	order-disorder transition 'NO ₂ '
Silver mercuri-iodide	[13]	hysteresis & transition
CaCO_3 — calcite	[14]	lattice vibrational frequency spectrum
— aragonite	[14]	
$\text{CuNO}_3 \cdot \text{NC}(\text{CH}_2)_2\text{CN}$	[15]	order-disorder transition
Monovalent nitrates	[16]	review

(ii) Tetrahedral cations — These include the ammonium halides from which significant information can be obtained by comparison with the alkali halide salts that have been so well studied. Shown in

fig. 4 are the two orientations available to an NH_4^+ ion at the centre of a cube of eight Cl^- ions and the two phase transitions for NH_4Cl are shown in fig. 2. Dr. Staveley's contributions to knowledge about this family include molar volumes, heat capacity, thermal expansion, isothermal compressibility and ionic conductivity. His pioneering work in the mixed halide crystals have provided heat capacity data over a wide temperature range. Table 2 contains the list of compounds.

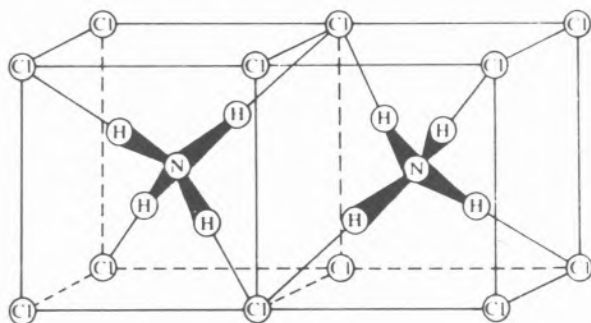


Fig. 4

The two orientations available to an NH_4^+ ion at the centre of a cube of eight Cl^- ions

(iii) Tetrahedral anions — Experimental data on this group containing the monovalent cation (Table 2) permit a direct comparison with the compound containing the tetrahedral cation thereby allowing an assessment of the latter's contribution to the motion within the crystal.

(iv) Tetrahedral cations and anions — In this group are the other ammonium salts. Both cation and anion may show orientational disorder. The six compounds are also in Table 2. The NH_4ReO_4 and NH_4BF_4 are especially interesting as both show broad bumps in their C_p vs T curves without a phase transition. Mathematical models have so far failed to account for the librational energy and to reproduce the experimental heat capacity.

(v) Substituted ammonium salts — Study of this family $(\text{RNH}_3)_2\text{MCl}_4$, where R = an alkyl group, M = metal, provides a bridge between simple ionic solids and molecular crystals. The divalent metal forms MCl_4 layers separated by $(\text{RNH}_3)_2$ layers. The alkyl ammonium ions do not interpenetrate so that the chains are lined up and spaced at fixed intervals from one another much like the situation in membrane bilayers. Hydrogen bonding causes tilting of the MCl_4 layers and along with changes

Table 2
Compounds containing tetrahedral ions

NH_4Cl	[5,13,17]	transitions
$\text{NH}_3\text{DCl}, \text{NHD}_3\text{Cl}$	[18]	transitions
NH_4Br	[5]	
$\text{NH}_4\text{Cl} - \text{NH}_4\text{Br}$	[19]	
$\text{NH}_4\text{Cl}_{0.26}\text{Br}_{0.74}$	[20]	transition temperatures
$\text{NH}_4\text{Cl}_{0.45}\text{Br}_{0.55}$	[75]	vary with mole
$\text{NH}_4\text{Cl}_{0.80}\text{Br}_{0.20}$	[20]	fraction
NH_4I	[5]	
KBF_4	[10]	
KIO_4	[37]	
KBPh_4	[21]	
RbBPh_4	[21,22]	
NH_4BPh_4	[21,22]	
$(\text{NH}_4)_2\text{SnCl}_6$	[5,23,24]	hindered NH_4^+ rotation
$(\text{NH}_4)_2\text{SnBr}_6$	[24]	
NH_4PF_6	[25]	
NH_4ReO_4	[26,27]	models for NH_4^+ libration
NH_4BF_4	[4]	inadequate

in the motion of alkyl chains gives rise to transitions and melting. When a paramagnetic divalent metal is involved, 2-D magnetic ordering occurs producing a transition. Some of this current heat capacity work is as yet unpublished and its status is shown in Table 3. It has been found that the transitions are sensitive to the choice of metal M , contrary to theoretical predictions, and the heat capacity analysis can be generalized per CH_2 group, which is not possible in other compounds where coiling of alkyl chains around each other occurs.

Table 3
Current status of the layered compounds

$\text{N}(\text{CH}_3)_4\text{I}$	[5]	
$(\text{CH}_3\text{NH}_3)_2\text{CdCl}_4$	[28]	
$(\quad)_2\text{MnCl}_4$	[29]	also magnetic
$(\quad)_2\text{CuCl}_4$	[30]	
$(\quad)_2\text{CrCl}_4$	[35]	also magnetic
$(\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_3)_2\text{MnCl}_4$	[31]	also magnetic
$(\quad)_2\text{CdCl}_4$	[31]	
$(n-\text{C}_7\text{H}_{15}\text{NH}_3)_2\text{MnCl}_4$	[32]	also magnetic
$(\quad)_2\text{CdCl}_4$	[33]	
$(n-\text{C}_{18}\text{H}_{37}\text{NH}_3)_2\text{CdCl}_4$	[33]	
$(\text{CH}_2=\text{CHCH}_2\text{NH}_3)_2\text{CdCl}_4$	[34]	
$(\text{CH}_3)_4\text{NMnCl}_3$	[36]	

(vi) Octahedral ions — These compounds are listed in Table 4. The most likely ones to show disorder are AXF_6 with A in Group I and X in

Group V of the periodic table. The ammonium cation salts for this group are included in (iv) above.

(vii) Salts with ferro or antiferroelectric phase — The ordered phase is either ferro- or antiferroelectric while the disordered phase is paraelectric with random orientations. The two salts studied are shown at the bottom of Table 4. The hydrated $K_4Fe(CN)_6$ is hydrogen bonded into layers with ferro- and antiferroelectric forms.

Table 4

Salts with octahedral ions and ferro — antiferroelectric phase

$Ni(NH_3)_6(NO_3)_2$	[13]	hysteresis
K_2SnCl_6	[5,23,24]	
Rb_2SnCl_6	[23,24]	For comparison
K_2SnBr_6	[23,24]	with corresponding
Rb_2SnBr_6	[24]	NH_4^+ salt
KPF_6	[25]	
$RbPF_6$	[5,25]	
$Co(NH_3)_6Cl_3$	[38]	transition, Schottky
$M.SiF_6.6H_2O$	see hydrates	
<hr/>		
$K_4Fe(CN)_6$	[39]	
$K_4Fe(CN)_6.3H_2O$	[39]	also magnetic

3.2.3 — ICE AND HYDRATES

Since ice retains disorder at 0 K [46], it is natural that other crystals in which hydrogen bonding is involved should be investigated for a similar phenomenon. Dr. Staveley's strategy consisted of determining the heat capacity and the calorimetric entropy at a reference temperature. At the reference temperature, the equilibrium entropy was found from a suitable reaction involving the compound. The findings showed that few hydrates retain order at 0 K and where it does occur, it is in compounds with a high proportion of water. Exceptionally it is found in those with low proportions of water. The list is in Table 5.

3.2.3 — MOLECULAR SOLIDS

These solids are characterized by intermolecular forces that are different from ionic solids so their study can shed considerable light on order-disorder phenomena. Two types of disorder are encountered within this group. (i) The ability of a molecule to switch from one orientation to another as temperature is increased is known as reorientation and it is this orientational freedom that is usually acquired first. Continuous rotation is known but is rare and does include ortho-hydrogen and possibly adaman-

Table 5
Hydrate compounds

H_2O	[40]	
$K_4Fe(CN)_6$	[39]	
$K_4Fe(CN)_6.3H_2O$	[39]	also magnetic
$Na_2HPO_4.H_2O$	[41]	
$Na_2HPO_4.7H_2O$	[41]	
$Na_2HPO_4.12H_2O$	[41]	disordered at 0 K
Na_2CO_3	[47]	
$Na_2CO_3.H_2O$	[47]	
$Na_2CO_3.10H_2O$	[47]	disordered at 0 K
$Na_4P_2O_7$	[42]	
$Na_4P_2O_7.10H_2O$	[42]	
$ZnF_2.4H_2O$	[43]	disordered at 0 K
$LiBr.H_2O$	[44]	
$MgSiF_6.6H_2O$	[45]	no transition
$NiSiF_6.6H_2O$	[45]	» »
$CoSiF_6.6H_2O$	[45]	transition
$FeSiF_6.6H_2O$	[45]	»
$ZnSiF_6.6H_2O$	[45]	»
$MnSiF_6.6H_2O$	[45]	

tane ($C_{10}H_{16}$). (ii) As considerable orientational freedom is gained, molecules can diffuse and migrate between sites.

For either type, either a plastic or non-plastic crystal may result. Plastic crystals are defined as having low entropy of fusion, isothermal order-disorder transition and a diffuse X-ray diffraction pattern in the disordered (plastic) phase. In addition, the disordered phase can be extruded by the application of small pressures. The compounds studied by Dr. Staveley are listed in Table 6.

Table 6
Molecular solids

CBr_4	[13,17,48]	
$SnMe_4, PbMe_4$	[49,50]	polymorphic
$CeEt_4, SiEt_4, GeEt_4, SnEt_4, PbEt_4$	[49,50,61]	polymorphic
CH_3OH, CH_3OD	[52,53]	
$Ni(CO)_4$	[54]	
CCl_4	[55]	
C_6H_6	[40]	
C_6H_{12}	[40,55]	
$C_6H_{11}OH$	[55]	
tetra cyano benzene (T.C.B.)	[56]	
T.C.B. + pyrene complex	[56]	
$AgClO_4.C_6H_6$	[57]	
C_2Cl_6	[13]	
tri methyl sulfonyl methane	[58]	disordered at 0 K
<i>ter</i> -butyl chloride	[55]	
<i>ter</i> -butyl bromide	[55]	
pyrometallic dianhydride (P.D.A.)	[59]	
P.D.A. + pyrene complex	[59]	

3.2.4 — THE CLATHRATES (β -QUINOL COMPOUNDS)

The clathrate compounds form fairly rigid lattice or cage-like structures that can serve as hosts for guest molecules occupying the interstitial positions. A varying number of the holes may be occupied in a given clathrate thereby giving rise to disorder in the distribution of the vacancies. Orientational disorder of the guest molecule may also occur. A summary is given in Table 7 of the guest molecules in the β -quinol clathrates studies by Dr. Staveley.

Table 7

Clathrates (β -quinol compounds with guest molecules as shown)

Ar	[60]	5 compounds (20-80% Ar)
Kr	[61]	3 + compounds
CH ₄	[62]	3 compounds (17-76% CH ₄)
CO	[63]	3 compounds
N ₂	[63]	1 compound
O ₂	[63]	2 compounds
Clathrates, gas hydrates	[64]	review

3.3 — MAGNETIC DISORDER

Magnetic compounds are studied because distinguishable orientations of magnetic spins do result from the disordered paramagnetic state and lead to ferroelectric or antiferroelectric alignment. Dr. Staveley has determined heat capacity of magnetic substances whose crystal structures are known.

When the permanent dipoles align in the same direction, a transition from paramagnetic to ferromagnetic phase occurs at the Curie point, *e.g.* K₄Fe(CN)₆·K₄Fe(CN)₆·3H₂O in Table 8. When they align in opposite directions, and this is the more common occurrence for magnetic insulators, the transition to the antiferromagnetic state occurs at the Néel point, *e.g.* CuCl₂·2H₂O to Ni(NH₃)₆I₂ of Table 8. the other group studied by Dr. Staveley is made up of the layered compounds, also known as metamagnetic. These may be either ferromagnetic within layers and antiferromagnetic between layers or vice versa, *e.g.* NiI₂ to (*n*-C₇H₁₅NH₃)₂MnCl₄ of Table 8.

4 — THE REVIEW PAPERS

The review papers about solids outline succinctly his areas of interest and are summarized in Table 9. They culminated in the "Disorder in Crystals"

Table 8
Magnetic compounds

K ₄ Fe(CN) ₆	[39]	
K ₄ Fe(CN) ₆ ·3H ₂ O	[39]	
CuCl ₂ ·2H ₂ O	[9,65]	
CuF ₂ ·2H ₂ O	[65]	
Ni(NH ₃) ₂ I ₂	[66]	
Ni(NH ₃) ₆ I ₂	[66]	
NiI ₂	[66]	
NiBr ₂	[67]	
{ ZnBr ₂ }	[68]	diamagnetic for comparison
(CH ₃ NH ₃) ₂ MnCl ₄	[29]	
() ₂ CrCl ₄	[35]	
(CH ₃ CH ₂ CH ₂ NH ₃) ₂ MnCl ₄	[31]	
(<i>n</i> -C ₇ H ₁₅ NH ₃) ₂ MnCl ₄	[32]	
LiCuCl ₃ ·2H ₂ O	[65]	

published in 1978 which is now regarded as the standard reference text in the field.

Table 9

1. Transition in solids and liquids	[69]
2. Hysteresis in transitions in solids	[70]
3. Thermodynamic studies of molecular rotation in solids	[71]
4. Phase transitions in plastic crystals	[72]
5. Nonstoichiometry in clathrate compounds	[64]
6. Physics and chemistry of inclusion complexes	[73]
7. The significance of entropies of transition in salts with special reference to nitrates	[16]
8. Disorder in Crystals	[74]
9. Disorder in Crystals	[46]
10. The thermodynamics of mixed crystals of ammonium chloride and ammonium bromide	[3]

5 — CONCLUDING REMARKS

Throughout the papers of Dr. Staveley runs an obvious thread that arises from his conviction that a thermodynamicist should wherever possible consider his findings, not in isolation, but in relation to information about the given system that has been derived from different techniques. Usually in the study of disorder in crystals, a variety of experimental methods will have been applied to a solid and experimental thermodynamics is but one of them. As he has often said, experimental thermodynamics is neither superior to, nor inferior to, any of

the other methods. Currently, the demand for thermodynamic data to exceed the rate of supply and the gap will widen with his retirement from the laboratory.

This writer is struck by the wise investment made at the outset of Dr. Staveley's career at Oxford. The royal Society awarded him £ 13 to set up his lab in the Abbott's kitchen. It would be fair to say that even they could not have foreseen the tremendous contributions he was to make to science. The episode serves to remind us that it is the person that matters.

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