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índice

THE LIONEL STAVELEY RETIREMENT MEETING

Lionel Alfred Kirby Staveley, one of the foremost thermodynamicists of our time, retired from academic life on September 30, 1982. He had been a fellow of New College, Oxford, since 1939 and his research career was even longer, for he published his first paper, while still an undergraduate, in 1933. To mark and celebrate the occasion of his retirement, former students and collaborators organized a scientific meeting in his honour and this was held on June 25, 1982 at the Inorganic Chemistry Laboratory of Oxford University, where most of Dr. Staveley's research was carried out. Principal organizers in England were Drs. Roger Linford (Leicester Polytechnic), Keith Stead (Exeter University) and Neville Parsonage (Imperial College, London) whereas Professor R.D. Weir (Royal Military College, Kingston, Ontario) acted as coordinator for the American Continent. The meeting was attended by about 100 people coming from all over the world. Chemical Thermodynamics in Portugal owes a great deal to Dr. L.A.K. Staveley. He has been a frequent visitor to our country to give lectures and courses, participate in seminars and conferences, and discuss many fruitful research programs. Former students and collaborators of his now teach in five Portuguese universities. For this reason the **Revista Portuguesa de Química** feels very honoured and proud to devote the present issue to the proceedings of the **Lionel Stavely Retirement Meeting**. They are an excellent state-of-the art review on several fields of thermodynamic research and a useful contribution to the history of Thermodynamics in this century.

These proceeding follow closely the organization of the Meeting which was divided in three Sessions, with three invited contributions each.

FIRST SESSION:

This reviews the wide-ranging contributions that Lionel Staveley has made to the study of fluids. He has helped theorists by selecting systems for study that, despite the experimental difficulties involved, have been well suited to testing competing theoretical approaches. His pioneer work on noble liquid mixtures has led to notable studies at Oxford and elsewhere of increasingly diverse cryogenic systems. His precise measurements of liquid molar volumes, cross virial coefficients of gas mixtures and the earlier work on alcohol mixtures have been an example to experimentalists and theoreticians alike.

Speakers: K.E. Gubbins, W.B. Streett and G. Saville

SECOND SESSION:

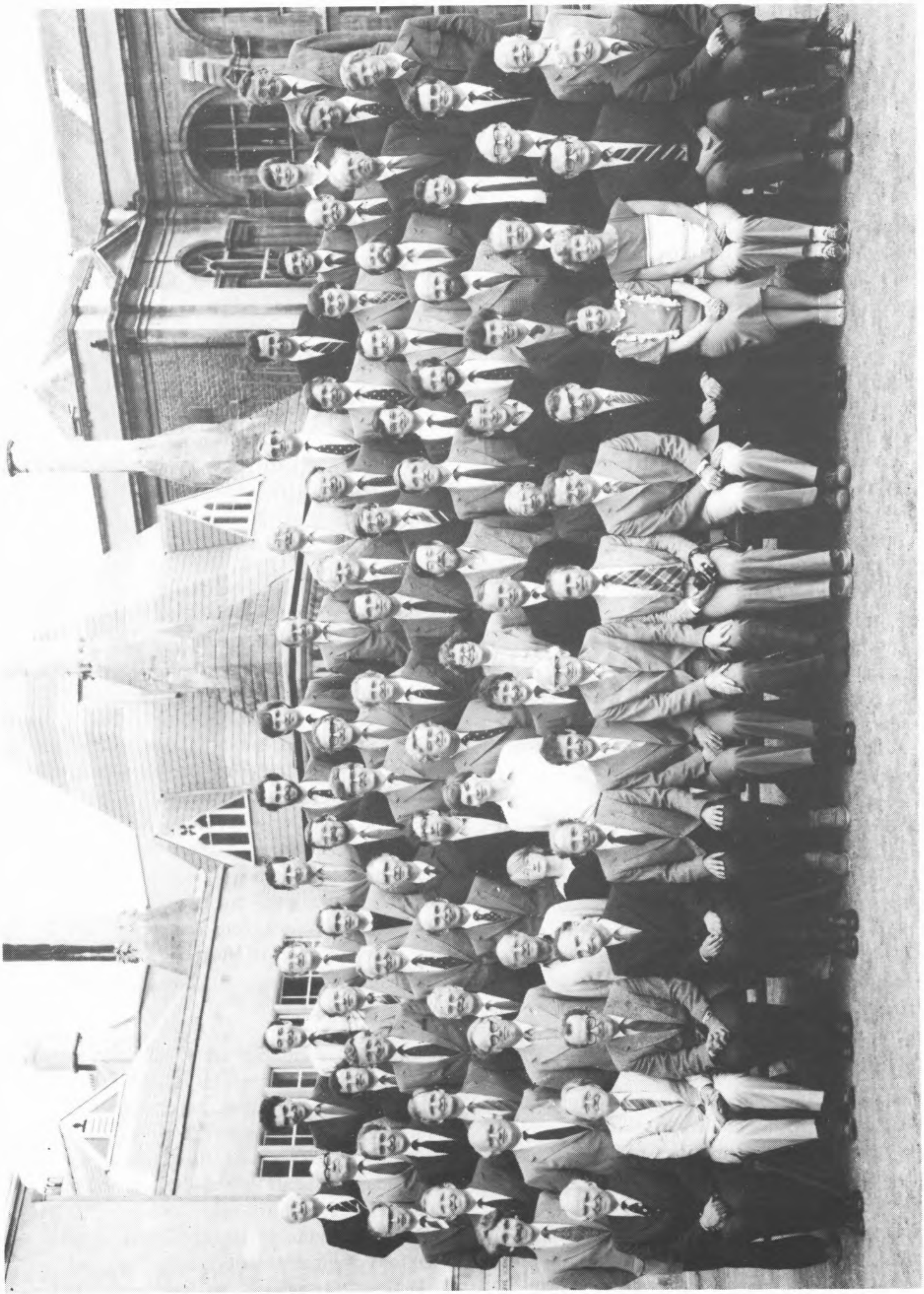
Lionel Staveley's investigation of the properties of solids have been diverse. He has developed refined calorimetric techniques for the measurement of heat capacities and solution enthalpies as well as electrochemical and other methods for Gibbs energy measurements. These have been used to elucidate phenomena ranging from ligand field effects in lanthanide salts to disorder in hydrates and ammoniates from 2K to 500K, from the behaviour of plastic crystals to adsorption on wartime charcoals. He has again helped theorists by studying substances whose structural properties resemble those used in theoretical models. He investigated clathrates to probe aspects of the lattice theories of liquids, worked on systems that model biological membranes, and studied low-dimensional magnetic systems.

Speakers: N.G. Parsonage, R.D. Weir and E.F. Westrum

THIRD SESSION:

Not only has Lionel Staveley influenced science, he has also inspired scientists. To an unusual degree he has encouraged the progress of science in the developed and developing world. He has influenced the course of science and the lives of scientists in Canada, Portugal, Poland, Nigeria and many other countries. For thirty years and more he has been a leading figure in British Thermodynamics and Oxford chemistry circles.

Speakers: J.C.G. Calado, D.H. Everett and L.A.K. Staveley



SOME IMPRESSIONS OF LIONEL STAVELEY

Lionel Staveley retires at the end of Trinity term 1982. The meeting today is proof of the unusual degree of respect and affection that he has won, both from several generations of Oxford chemists and also from the international scientific community. In some ways, a man of Edwardian dignity, yet, like MacMillan, he can display a good-humoured sparkle that causes people to warm to him. No undergraduate can forget the contrast between the first meeting, as part of a nervous group sitting on the edge of that sofa in his college room, listening to the tall, dry, authoritative figure formally explaining the ways of the Oxford Chemistry School; and the sight, a few days later, of the same man donning that amazing fur coat, preparatory to bicycling along the foggy autumnal dusk of Mansfield Road.

It is this frequent combination of the expected and the faintly bizarre that makes him such an effective teacher and leader. He has quietly and modestly shaped or redirected the careers of many men and women of science, not only providing the soundness of knowledge and judgment that they expected when they came to him but also the courage to tackle experimentally difficult problems of great theoretical interest. It has been said that he seems always to put the interests of others before his own. Not only his wide circle of scientific friends notice him. That well-known sceptic, Berni Alder, the father of computer simulation, said in the late '60s that Staveley is, for him, the ideal type of scientist; whenever Berni looked for experimental data on really interesting systems, he found that is was Staveley who provided it and the quality was always good.

His manner puts him with the best of the old Oxford tradition but his mind projects him into the contemporary international scene. He was brought up in the classic mould of successful Oxford scientists. He was born in the small and attractive Lincolnshire town of Stamford (within ten miles of the village of Braunston, home of the forebears of his contemporary and close scientific colleague, the present Warden(*)). His earliest scientific paper predates his degree and presents the results of work he carried out with Moelwyn-Hughes. He studied for his B.A. under C.N. Hinshelwood, then tutor at Trinity College, Oxford when that figure was at the height of his redoubtable intellectual powers. He was awarded a first class honours degree in 1936 but was always remained sensitive to the strain that finals put on students. He would retail the account of an annually recurring dream of being at a viva, not as an examiner but as a student, being awarded a lowly degree by grimly triumphant examiners.

He left England for Munich, to study under Clusius for a doctorat but returned because of the imminence of war. (Eating a dismal British Rail sandwich on a train journey to London in 1965, he recounted how as a student, he would by choice take is evening meal at the station restaurant in Munich because of the combination of quality and cheapness that it offered).

Returning to Oxford as a lecturer in 1938, he was elected a Fellow of New College in 1939, and embarked on research reflecting British war needs. Those of us who would browse among the many theses on his office shelves during the long nocturnal hours of a low temperature calorimetric run, became used to the injunction, found midway in the early volumes, not to read the ensuing sections unless possessing appropriate security clearance from the Ministry of Supply.

From these early studies of kinetics and adsorption, which did not give him the fullest intellectual enjoyment ("I've served my apprenticeship on kinetics; now young Dickens(**) can take his turn, so to say"), he began the series of low-temperature studies of solids and liquids discussed at this meeting. From the '50s to the '80s, he has sought to illuminate theory by experimental study of relevant models, using such analogies as solid clathrates for the early lattice theory of liquids, fusible white precipitate to represent the three-dimensional dimer problem and so on.

This work started in Oxford and might well have stayed there, had it not been for the happy accident of a sabbatical term as Cherwell Visiting Fellow at Pennsylvania State in the summer of 1962. He returned with a new respect for Americans, particu-

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(*) A.H. Cooke

(**) P.G. Dickens

larly students ("I gave them two hour lectures starting at 8 a.m. and, do you know, not only were they keen, but they were always all on time"). The wealth of international collaboration that resulted, is reflected in the awards of:

1957-59	Member of Council of Chemistry Society
1962	Cherwell Visiting Fellow to U.S.A.
1962	Visiting Professor at Pennsylvania State University
1963-67	Chairman of Comission on Data and Standards, I.U.P.A.C.
1968	(Jointly with W.B. Streett) Russel B. Scott Memorial Award of American Chemical Engineering Society for outstanding papers of 1967 in Cryogenic Engineering Research
1970	Visiting Scientist at N.B.S. Boulder and
1970	Visiting Professor, University of Michigan
1973-79	Invited Lecturer at Gordon Conference
1974	Chairman of Sixth Experimental Thermodynamics Conference
1975	Visiting Professor at the New University of Lisbon (first graduate course on Physical Inorganic Chemistry given in any Portuguese University).
1975	Chemical Society Award Thermodynamics and Electrochemistry
1979	Elected Corresponding Member of the Academy of Sciences, Lisbon
1983	Lennard-Jones Lecturer of the Royal Society of Chemistry (Conference on Liquids and Liquid Mixtures, Hull).
1983	Special award by Portuguese Chemical Society

Much of his work is described in that impressive volume with Neville Parsonage "Disorder in Solids" which doubled the publisher's expectation, both with regard to time of writing and to length. A similar version of his liquid studies is eagerly awaited.

Each of us who studied with Lionel probably think we have a reasonable feel for the whole man, yet during discussions about this meeting over the last two years, we have consistently been surprised at the strength of the perception by others of facets of his work that are almost new to us. This is why so many people can each highlight such a variety of scientific achievement at today's meeting.

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Photo: Jorge Calado

L.A.K. STAVELEY

Born	11 November 1914
Attended Stamford School	1921-32
Matriculated at Trinity College, Oxford	1932
B.A. (Hons) Chemistry	1935
B.A. (First Class Hons) Chemistry	1936
M.A. (Oxon)	1939
D. Sc. (Oxon)	1960

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THE IMPACT OF LIONEL STAVELEY'S RESEARCH ON THE THEORY OF LIQUID MIXTURES

A brief survey is presented of the impact of Lionel Staveley's work on the theory of liquid mixtures. Staring in the 1950's with experiments on mixtures of carbon monoxide and methane, his work on liquids has been closely tied to the needs of theory. His studies of simple liquids of spherical molecules played a crucial role in the development of theories of such simple liquids in the period from the mid-1950's to the 1970's. His more recent work on mixtures of molecular liquids is now proving of great value in evaluating theories for liquids of nonspherical molecules. Several examples are presented of this interplay between theory and experiment.

I first met Lionel Staveley in 1974 on a visit to Oxford. At that time our interests had turned to the development of perturbation theory for nonspherical molecules. There was a wealth of experimental data on liquid mixtures at room temperature and pressure, but for the most part these involved rather large and often flexible molecules that were not well suited to testing the theories that we were working on. We needed accurate data on mixtures of relatively small, rigid molecules, such as N_2, CH_4, HCl, CF_4, C_2H_4, N_2O, etc., and it was soon clear to us that Lionel would be the best man to help us. Our initial meeting nearly ten years ago led to a rewarding and most pleasant collaboration. Our discussions were made much easier for me by Lionel's ability to concentrate on the main scientific goals — to "leave out the sordid details of the experiment" as he would put it; these "details" were far from trivial, and involved dealing with a variety of problems of corrosion, toxicity, high pressures, etc.

Since the mid-1950's Lionel Staveley's work on liquid mixtures has been remarkable in that it has focussed on those mixtures of greatest interest to theorists working in this area. In a review of mixture data suitable for testing theories published in 1972 by Mc Donald [1], almost 40% of the papers were from Staveley's laboratory. Of more importance, in cases where there were discrepancies between Staveley's and earlier work, Staveley's measurements were usually judged to be the more accurate [2,3]. His recent work on molecular liquids has provided a wealth of data that will provide a challenge to theorists for some years to come.

1 — EARLY WORK ON LIQUIDS; BEFORE 1955

Lionel's initial work was in the area of kinetics. His first papers [4] were published 50 years ago when he was only 18, with Hinshelwood and Moelwyn-Hughes. His first work in thermodynamics was in 1938, when he spent a year (on a Goldsmith's scholarship) in the laboratory of Professor K. Clusius * in Munich. There he carried out experiments on the effect of isotopic composition on the triple point of various cryogenic liquids, including argon and xenon. This work was published [5,6] in 1941,

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* Clusius was a student of Eucken, who was in turn a student of Nernst. Thus the "genealogy" is Nernst → Eucken → Clusius → Staveley.

during World War II. During the next 14 years there were a series of studies on hydration and hydrogen bonding — particularly the solubility of water in various solvent mixtures (benzene + alcohols and benzene + various organic liquids); these studies continued up to 1949 [7-12]. There were also studies of entropy of vaporization [13] and of heat capacities [14,15], but no further work on cryogenic liquids.

During this early period the theory of Scatchard and Hildebrand (later called regular solution theory by Hildebrand) was influential, and qualitative discussions of experimental results often referred to this theory. The regular solution theory [16] assumes a zero excess entropy, i.e. a mixture in which the molecules surrounding a central A molecule, say, are randomly distributed among other A's, B's, etc. The excess volume is also taken to be zero, and the excess Gibbs energy is given by

$$G^E = v\phi_A\phi_B(\delta_A - \delta_B)^2 \qquad (1)$$

where v is the molal volume of the mixture, ϕ_α is the volume fraction of α, and δ_α is the solubility parameter. The regular solution theory is an extension of the theory of van Laar, and is restricted to mixtures in which G^E is positive (and hence H^E also), while V^E and S^E are small.

2 — THEORY FOR MIXTURES OF SPHERICAL MOLECULES: 1950 — THE 1970's

Starting in the early 1950's a number of theories were developed for mixtures in which the molecules are spherical. These theories used statistical mechanics as a starting point and solved the equations by introducing well-defined approximations (lattice models, random mixing, etc.), in contrast to the older work of Hildebrand. Much of the work in the 1950's and 1960's stemmed from the idea of a random mixture. Although the early work was carried out in the framework of cell models, the theories do not require this and the central ideas are more transparent if the cell model is avoided [1-3]. If we consider the configurational energy U_C, it is given for a mixture of spherical molecules by

$$U_C = 2\pi N\varrho \sum_{\alpha\beta} x_\alpha x_\beta \int_0^\infty dr\, r^2\, u_{\alpha\beta}(\varrho)\, g_{\alpha\beta}(r) \qquad (2)$$

where $\varrho = N/V$ is the number density, x_α is mole fraction of α, $u_{\alpha\beta}(r)$ is the intermolecular pair potential energy, and $g_{\alpha\beta}(r)$ is the radial distribution function for an $\alpha\beta$ pair ($g_{\alpha\beta}$ is proportional to the probability of finding an α molecule at distance r from a β molecule). For a random binary mixture these probabilities are the same for all pairs, i.e.

$$g_{AA}(r) = g_{AB}(r) = g_{BB}(r) = g_x(r) \qquad (3)$$

and (2) becomes the energy of a pure fluid,

$$U_C = 2\pi N\varrho \int_0^\infty dr\, r^2\, u_x(r)\, g_x(r) \qquad (4)$$

where

$$u_x(r) = \sum_{\alpha\beta} x_\alpha x_\beta u_{\alpha\beta}(r) \qquad (5)$$

is the (composition-dependent) intermolecular potential energy for a hypothetical pure fluid, so that the mixture properties are equal to those of an *equivalent pure substance*.

The random mixture theory was actively pursued by PRIGOGINE and his coworkers in Brussels [17-19]. Clearly, the approximation (3) will only be suitable if the molecules are equal or almost equal in size — otherwise the peaks in g(r) will occur at different r values for the various pairs. When the molecules are the same size, and the energy parameter ϵ_{AB} obeys the Berthelot rule,

$$\epsilon_{AB} = (\epsilon_{AA}\epsilon_{BB})^{1/2} \qquad (6)$$

the theory predicts that G^E is positive while V^E is negative. This prediction was in contrast to that of the regular solution theory and its modifications, and also to the conformal solution theory of Longuet-Higgins; these theories predicted that G^E and V^E should have the same sign. At the time this prediction was made there were no suitable experimental data available to test these ideas, however — such data as existed were for relatively large and complex molecules (neopentane, cyclohexane, etc.). It was at this point, in 1951, that Prigogine sent one of his co-workers, Victor Mathot, to Oxford. The original plan called for Mathot to work with Fritz Simon on low temperature physics, but after some initial discussions it was decided that he would work in Staveley's laboratory instead, making careful measurements to test the predictions of the current theories. Molecules of equal size were needed; Kr/CH_4 was considered but rejected because of the expense of krypton, and CO/CH_4 was chosen as a suitable alternative. At that time the Glastonbury Abbey kitchen served as the laboratory in the Inorganic Chemistry Laboratory. Victor Mathot recounts that his apparatus grew higher and higher on top of the bench (the vapour pressure of CO/CH_4 at 90K is of the order 2 atm.) and he eventually had to use a ladder. One day, before leaving, he placed a small Belgian flag at the top of the apparatus. The next day he arrived in the lab to find a Union Jack placed above the Belgian flag. The originator of the Union Jack was never discovered, although Mathot had his own suspicions about this! The experimental work on CO/CH_4 was completed in 1954, and an initial account of the work was published [22] in 1955; this was followed by a more extensive account [23] of the work in 1956. The experiments showed that for this mixture G^E was positive while V^E was negative, as required by the random mixture theory; moreover quantitative agreement between theory and experiment was fairly good (fig. 1). This was a considerable step forward at the time.

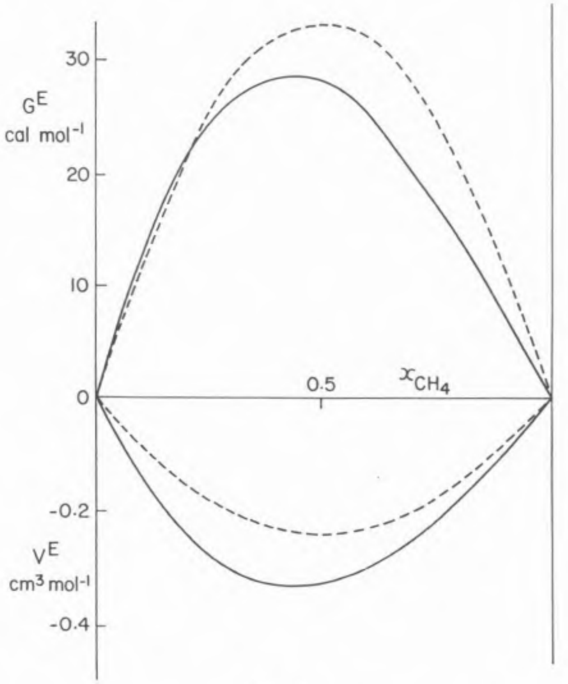

Fig. 1

Comparison of experiment (solid lines) and random mixture theory with ϵ_{AB} given by (6) (dashed lines) for G^E and V^E of CO/CH_4 mixtures at 90.67K (from MATHOT *et al. [22])*

The work with Mathot marked the beginning of Lionel's work on cryogenic liquid mixtures, and the development of his very precise cryogenic techniques. Over subsequent years the emphasis of his liquid phase research shifted more and more to the study of simple cryogenic liquids (see fig. 2).

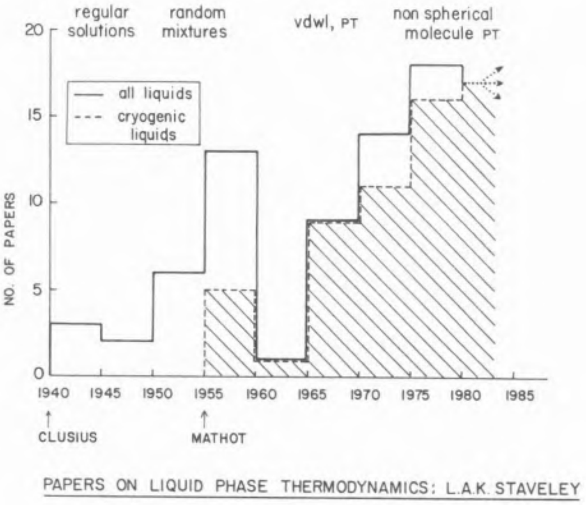

Fig. 2

Research papers on liquid phase thermodynamics authored by Lionel Staveley and collaborators, averaged over 5 year intervals

Although the random mixture theory works fairly well for G^E and V^E of CO/CH_4 (fig. 1), later measurements of H^E for this system by POOL and STAVELEY [24] were not even in qualitative agreement with the theory. In particular, the experimental S^E is negative in CO-rich mixtures but positive in CH_4-rich mixtures. This cubic behaviour was not predicted by any of the existing theories in 1957. The initial work on CO/CH_4 was followed by studies of the excess properties of a variety of cryogenic mixtures of spherical or nearly spherical molecules [25-40], including Ar/N_2, Ar/O_2, O_2/N_2, CO/N_2, Ar/CO, Ar/Kr, Kr/CH_4, Kr/Xe and Ar/CH_4. In many of the earlier papers (see e.g. refs. 25-32) comparisons of the experimental data are made with the random mixture theory, and also with related theories of the time such as the average potential model (a 2-fluid theory) [19,41] and with Scott's three-fluid theory [41]. In the average potential model eq. (3) is replaced by

$$g_{AB}(r) = \tfrac{1}{2}[g_{AA}(r) + g_{BB}(r)] \tag{7}$$

Physically, this leads to an approximation in which the properties of the real mixture are equated to those of an ideal solution composed of two pseudo-components A′ and B′, whose potentials are given by

$$u_{x\alpha}=\sum_{\beta} x_{\beta} u_{\alpha\beta}(r) \qquad \alpha=A',B' \tag{8}$$

Comparisons with experiment showed that none of these theories gave good agreement. Later comparisons with computer simulation results [1,2] showed that the theories themselves were at fault (and not just the potential models used). These theories are particularly poor when the molecules differ in size; the peaks in $g_{\alpha\beta}(r)$ for the various pairs then occur at different locations, so that eq. (3) will be a very poor approximation. Much of the early work was reviewed by PARSONAGE and STAVELEY [42] (see also refs. 1-3).

In the 60's there were two significant developments in liquid theory which moved away from the older concept of a random mixture; these were the van der Waals 1-fluid conformal solution theory, and the hard sphere perturbation theory. The van der Waals 1-fluid (vdW1) theory [43-46] attempts to account for nonrandomness due to molecular size differences. In this theory (3) is replaced by

$$g_{AA}(r/\sigma_{AA})=g_{AB}(r/\sigma_{AB})=g_{BB}(r/\sigma_{BB})= \\ =g_{x}(r/\sigma_{x}) \tag{9}$$

Eq. (4) again holds for the internal energy, with the potential parameters of the pure reference fluid given by the vdW1 mixing rules:

$$\epsilon_{x}\sigma_{x}^{3}=\sum_{\alpha\beta} x_{\alpha} x_{\beta}\epsilon_{\alpha\beta}\sigma_{\alpha\beta}^{3} \tag{10}$$

$$\sigma_{x}^{3}=\sum_{\alpha\beta} x_{\alpha} x_{\beta}\sigma_{\alpha\beta}^{3} \tag{11}$$

In the hard sphere perturbation theory the reference molecules have repulsive forces only, and the configurational energy is written as a reference plus a first order term:

$$U_{c}=U_{0}+U_{1} \tag{12}$$

The reference fluid properties are equated to those of a fluid of hard spheres through a second expansion. Three versions of the theory exist [47-49], which differ only in detail. The form due to WEEKS, CHANDLER and ANDERSEN [49], and extended to mixtures by LEE and LEVESQUE [49], is usually the most accurate. Around 1970 the first extensive computer simulations of Lennard-Jones mixtures were carried out, and were used to test these and the earlier theories [1,2]. These tests showed that the vdW1 and hard sphere perturbation theories were much more accurate than the earlier random mixture theories. The vdW1 theory breaks down for molecules that are much different in size, but the hard sphere perturbation theory does not suffer from this defect because size difference effects are included in the reference fluid [50].

The experimental work of Staveley and his collaborators provided much of the data needed to test these theories, and many of their papers from about 1971 onwards have included comparisons with the more recent theories (see, for example, references 32,33,37,38 and 40). Mixtures of spherical molecules are most suitable for such tests, and typical comparisons with the experimental data of Staveley *et al.* are shown in Table 1 and fig. 3. Agreement with experiments is quite good. In these comparisons ϵ_{AB} and σ_{AB} are given by

$$\epsilon_{AB}=\zeta_{AB}(\epsilon_{AA}\epsilon_{BB})^{1/2} \tag{13}$$

$$\sigma_{AB}=\tfrac{1}{2}\,\eta_{AB}(\sigma_{AA}+\sigma_{BB}) \tag{14}$$

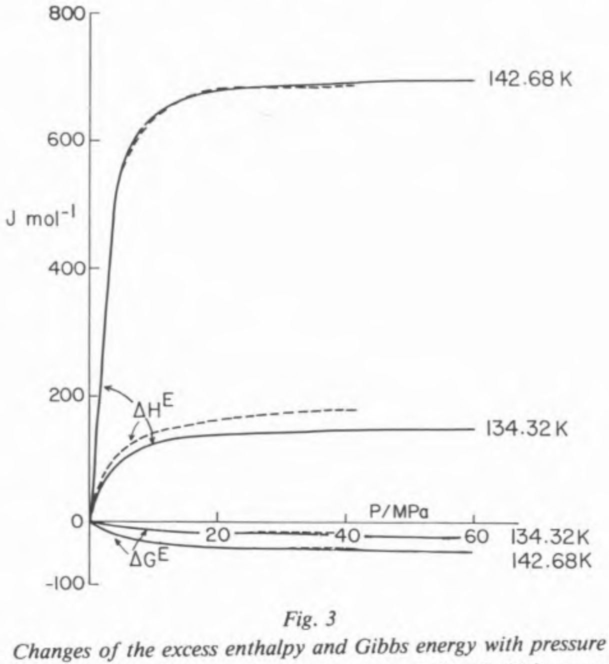

Fig. 3

Changes of the excess enthalpy and Gibbs energy with pressure for mixtures of argon and krypton at $x_{Ar}=0.485$. Solid lines are from experimental data, dashed lines are calculated from vdW1--fluid theory. In the theoretical calculations eqn. (13) and (14) were used for ϵ_{AK} and σ_{AK}, with ζ_{AK} taken from Monte Carlo data and η_{AK} fitted to excess volume data (from BARREIROS el al. *[40])*

when $\zeta_{AB} = \eta_{AB} = 1$ these equations reduce to the usual Lorentz-Berthelot rules.

Table 1
Results for Ar/Kr mixtures, T = 116K, P = 0
*(From McDONALD [1] and HENDERSON and LEONARD [2] **

	$G^E_{½}/J\ mol^{-1}$		$H^E_{½}/J\ mol^{-1}$		$V^E_{½}/cm^3\ mol^{-1}$	
	$\zeta_{AB}=1$	$\zeta_{AB}\neq 1$	$\zeta_{AB}=1$	$\zeta_{AB}\neq 1$	$\zeta_{AB}=1$	$\zeta_{AB}\neq 1$
Monte Carlo	+ 46	+84	− 29	+29	−0.69	−0.60
RM	+203	—	+254	—	+0.42	—
VDW1	+ 46	+84	− 30	+24	−0.68	−0.66
PERT (LHB)	+ 39	+84	− 28	+32	−0.62	−0.57
EXPT.[29,39]	+84		+42.7		−0.52	

* In these calculations $\eta_{AB} = 1$ in eqn. (14]. $G^E_{½}$, $H^E_{½}$, and $V^E_{½}$ are the excess properties for the equimolar solution; RM = random mixture theory, VDW1 = van der Waals 1-fluid theory, PERT (LHB) = the hard sphere perturbation theory of Leonard, Henderson and Barker; ζ_{AB} is defined by eqn. (13). For the cases where $\zeta_{AB} \neq 1$ the ζ_{AB} value is adjusted to make theory and experiment match for $G^E_{½}$.

3 — THEORY FOR MIXTURES OF NONSPHERICAL MOLECULES: 1974 — THE 1980'S

Lionel and his collaborators realised at an early stage that the assumption of central isotropic intermolecular forces was likely to lead to error even for such relatively simple molecules as CO, CO_2, etc. In 1957 POOL and STAVELEY [24] wrote:

"For CO...there is evidence that the rotational movement in the pure liquid is restricted... The chief need on the theoretical side is for further consideration to be given to the effect of directional forces. On the experimental side, almost all the systems suitable for study should be investigated, since their number is very limited".

The same concern was expressed in the 1959 review by PARSONAGE and STAVELEY [42]:

"Even a (symmetric) diatomic molecule will have a quadrupole moment...It is now realized that quadrupole forces can have a more important influence on the physical properties...than was at one time supposed (as shown by Buckingham)".

However, it was not until the early 1970's that serious attempts were made to include the noncentral nature of the intermolecular forces in theoretical calculations of thermodynamic properties [51]. In the most widely used perturbation theory approach, the reference fluid is one of spherical molecules with intermolecular potential $u_0(r)$ defined by

$$u_0(r) = \langle u(r\omega_1\omega_2) \rangle_{\omega_1\omega_2} \tag{15}$$

where $\langle \ldots \rangle_{\omega_1\omega_2}$ means an unweighted average over the orientations ($\omega_i = \theta_i\phi_i$ or $\phi_i\theta_i\chi_i$ for linear or nonlinear molecules, respectively), $u(r\omega_1\omega_2)$ is the pair potential in the fluid of interest, and r is the vector from the centre of molecule 1 to the centre of molecule 2. In practice the Lennard-Jones (n,6) model is often used as the reference potential, and the potential for the full system is written as a sum of multipole, induction, overlap (shape) and dispersion terms:

$$u(12) = u_0(r) + u_{mult}(12) + u_{ind}(12) + \\ + u_{ov}(12) + u_{dis}(12) \tag{16}$$

where $(12) \equiv (r\omega_1\omega_2)$. The Helmholtz energy A is then given by (the A_1 term vanishes in this series)

$$A = A_0 + A_2 + A_3 + \ldots \simeq A_0 + A_2\left(\frac{1}{1 - A_3/A_2}\right) \tag{17}$$

where A_0 is the free energy of the reference system and A_2 and A_3 are the second- and third-order perturbation terms. General expressions have been worked out [52-53] for A_2 and A_3, and involve two- and three-body correlation functions for the reference fluid. The second form of eqn. (17) is a Padé approximant to the series porposed by STELL *et al.* [54], and is found to agree remarkably well with computer simulation results even when strong electrostatic forces are present, provided that the molecules are not too nonspherical in shape. Calculations based on (17) show that the electrostatic forces have a very large effect on the thermodynamics properties [55], whereas the effect of nonspherical shape is smaller [53].

The more recent studies of molecular liquid mixtures by Staveley and coworkers have been designed to elucidate the role of electrostatic and other anisotropic forces. This can be achieved by comparing the data with eq. (17) and similar theories. This work has now resulted in a substantial body of data on G^E, V^E and H^E for mixtures involving the inert gas liquids and such small rigid molecules as CO, NO, N_2O, C_2H_6, C_2H_4, NF_3, HCl, HBr, CH_4, CF_4, etc. Much of this data has been compared [56-60] with the predictions of eq. (17), and these tests throw considerable light on the relative importance of the various kinds of intermolecular forces. In these comparisons it is usual to fit the three (n,6) potential parameters (n,ϵ,σ) to the pure fluid data, and to fit the unlike pair parameters ζ_{AB} and η_{AB} in eqns. (13) and (14) to $G^E_{½}$ and $V^E_{½}$ at a single temperature. The ability of the theory to fit G^E and V^E at that temperature is then only a weak test; a much stronger test is that provided by H^E and by G^E and V^E at temperatures other than the temperature of fit. The excess enthalpy is particularly sensitive to details of the intermolecular forces.

For Xe/N_2O [58] and Xe/CF_4 [59] mixtures the theory and experiment are found to be in essentially quantitative agreemnt for all three excess properties, using the lowest order spherical harmonic terms to represent the multipolar, dispersion and overlap potential terms in eq. (16). The multipolar forces have a much larger influence on the thermodynamics than the anisotropic dispersion or overlap forces in these systems; for CF_4 the leading multipole term is the octopole-octopole, and for N_2O the main contribution is from quadrupole-quadrupole forces, the dipolar terms being negligible in this case.

For the mixtures Xe/HCl, Xe/HBr and HCl/HBr the situation is more complex. Using intermolecular potentials that include the leading multipole (dipole and quadrupole), induction, dispersion and overlap terms it is possible to describe G^E and V^E for these systems quite well, and also the vapor-liquid equilibria and azeotropic compositions (for Xe/HCl) [56]. This is shown in fig. 4 and 5. It is interesting that the theory correctly predicts the "cubic" behaviour of V^E for Xe/HBr, such behaviour is quite common in polar/nonpolar mixtures [3]. However, the same intermolecular potential models give H^E values that are too large by 60-100%, depending on the precise details of the model used [57] (see fig. 6). the reason for this discrepancy is not yet understood. It may be due to an improper treatment of the electrostatic or induction forces. The latter are now known [61] to be very poorly represented by the isotropic pair term used in these calculations; both anisotropy of the polarisability and multibody effects are known to be important.

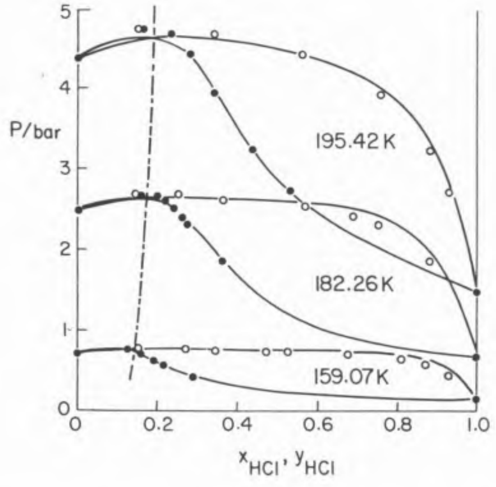

Fig. 4
Vapour-liquid equilibria for HCl + Xe from experiment (points) and theory of eqn. (17) (lines). The dash-dot line is the azeotropic locus (from CALADO *et al. [56])*

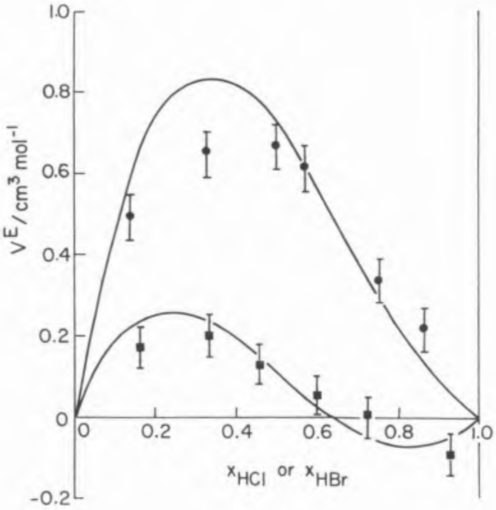

Fig. 5
Excess molar volumes for HCl + Xe (●) and HBr + Xe (■) at 195.42K compared with theory of eqn. (17) (lines) (from CALADO *et al. [56])*

Mixtures containing ethylene are interesting in that ethylene is the simplest example of a molecule with a nonaxial quadrupole [62] — i.e. in contrast to such highly symmetrical molecules as HCl, CO_2 and NH_3, ethylene has two independent quadrupole moments Q_{xx} and Q_{zz} (where z is along the C = C axis); similarly the dispersion and overlap forces are nonaxial for this fluid. Early calculations neglected the nonaxial nature of the molecule and used an "effective axial" approximation — i.e. a single

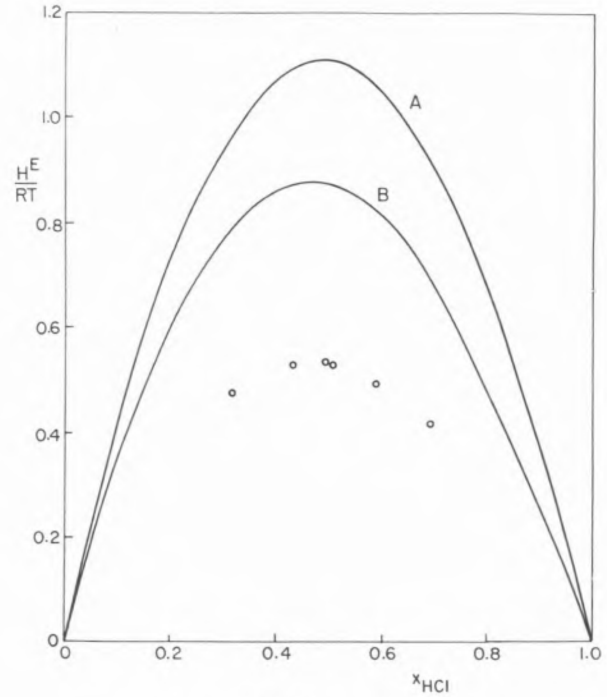

Fig. 6

Comparison of the theory of eqn. (17) for HCl-HCl potential models A and B (lines) with experiment (points) for H^E of HCl + Xe at 182.32K. In model A the potential consists of an (n,6) term plus multibody terms (dipole and quadrupole). In model B anisotropic overlap and dispersion terms are also included. In both calculations the two-body induction potential between Xe and HCl is included (from L*OBO* et al. *[57])*

"effective" quadrupole moment. However, the values of Q_{xx}, Q_{yy} and Q_{zz}, and also of the polarisabilities, are accurately known for ethylene, so that it should be possible to determine the magnitude of the nonaxial effects from eqn. (17]. It is found that for ethylene the effects are small for the pure fluid [62,63], but are large in mixtures. Careful studies for mixtures of nitrous oxide + ethylene, carried out by Lélio Lobo and Lionel Staveley at Oxford, show clearly the importance of such effects. The nonaxial nature of the molecule affects all three excess properties, but the excess enthalpy is especially sensitive, as seen from fig. 7. Although the fit between theory and experiment is rather poor in this case, the calculation shows clearly the importance of correctly accounting for the nonaxial nature of the intermolecular forces. The fit to experiment can be improved in this case by modifying the N_2O-N_2O potential.

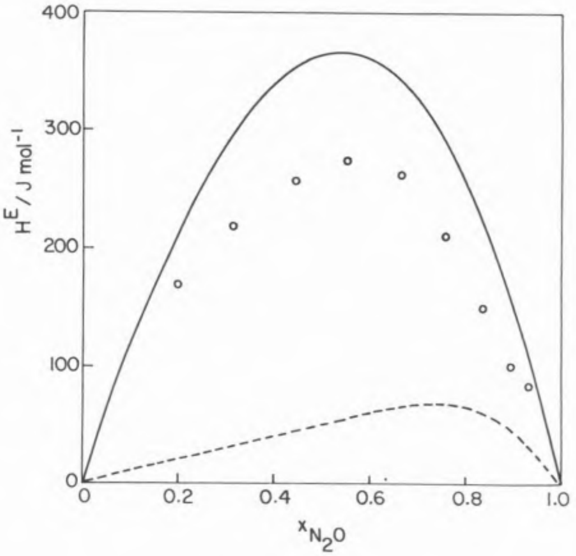

Fig. 7

The excess enthapy of $N_2O + C_2H_4$ at 184.01K from experiment (points) and theory (lines); ——— correct nonaxial treatment; - - - - approximate effective axial treatment (from L*OBO* el al. *[60])*

Much of the most interesting experimental data is yet to be compared with theory, including the mixtures $HCl + N_2O$ and $HCl + CF_4$ studied by Lobo and Staveley, while Lobo was at Oxford; the latter mixture exhibits liquid-liquid separation, and should provide a challenge to the theorists. In addition, new and more powerful forms of perturbation theory are now being developed, based on nonspherical reference molecules. These have yet to be compared to experiment, but such comparisons will probably be made in the next few years.

4 — CONCLUSION

Starting in the 1950's with his work with Victor Mathot on CO/CH_4 mixtures, Lionel's experiments on liquids have been closely tied to the needs of current theoretical studies. Because of the perception he has shown in choosing the most suitable systems for study, the interplay between experiment and theory has been especially strong and effective. His measurements on simple liquids of spherical molecules played a crucial role in the development of the simple liquid theories during the period from the 1950's to the 1970's. His more recent studies of nonspherical molecules are now playing a similar role in developing theories for more complex liquids. These data are likely to serve as a standard for testing theoretical ideas for many years to come.

His work will also continue to have great impact through the work of his many students and collaborators, several of whom have set up flourishing laboratories of their own.

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THE EXPERIMENTAL RESEARCH OF L.A.K. STAVELEY ON THERMODYNAMICS OF LIQUIDS

In a career spanning more than forty years, Lionel Staveley established himself as one of the premier thermodynamicists of the twentieth century. A brief survey of his experimental work on the thermodynamics of liquids in presented, to illustrated some of the simple but elegant techniques he devised for precise measurements of the excess properties of liquid mixtures.

1 — INTRODUCTION

In the early nineteen sixties I was a Captain in the U.S. Army, teaching at the Military Academy at West Point, and continuing the experimental studies of fluid phase equilibria in low temperature systems that I had begun several years earlier during my graduate studies at the University of Michigan. The receipt, in 1964, of a NATO Postdoctoral Fellowship gave me the opportunity to go abroad for a year of advanced research; my first choice was Britain, and I set about finding a laboratory that would accept both me and my experimental apparatus, which the Army generously allowed me to take along. A book about research in British universities, provided by the British Information Services in New York City, gave the names of several scientists, including Lionel Staveley, whose research interests included experimental studies of liquids, and I promptly wrote to several of these, asking if they could accommodate me. For the most part the replies were politely negative; the exception was the reply from Lionel, who, in characteristic generosity, immediately replied that he would be glad to have me and would provide the necessary space in his laboratory. I shipped several large crates of scientific equipment to Oxford in the summer of 1965, and flew to England with my family in late December that year. It was only after my arrival in Oxford that I learned that when my equipment reached England, Lionel was summoned to the docks in London to verify that it was indeed scientifc equipment, and should be allowed in the country.

I lived in Oxford and worked in Lionel's laboratory during all of 1966. It was a marvelously successful year, leading to the publication of seven or eight scientific papers. Several of these were coauthored by Lionel, and were based on experiments that combined my interests in high pressure measurements with the elegantly simple thernodynamic experiments he had developed for liquids at low pressure. It was the beginning of a treasured friendship, and scientific collaboration that has continued to this day.

My association with Oxford in 1966, and especially the thermodynamics and experimental techniques I learned from Lionel, laid the foundations for whatever success I have since achieved as an experimentalist. They were instrumental in my appointment to a permanent faculty post at West Point from

1967-78, to the award of a Guggenheim Fellowship for a second year of research in Oxford in 1974-75 (I hasten to point out that the fellowship carries the name of J.S. Guggenheim, an American, not that of the eminent British scientist, E.A. Guggenheim), and to my present appointment as a member of the faculty of chemical engineering at Cornell University. I have visited Lionel's laboratory many times since, and he has visited my laboratories at West Point and Cornell. During the past two years he has been a consultant for a Cornell project in which we have built a heat-of-mixing calorimeter similar to the one used in his laboratory in recent years.

During each of the two years I lived in Oxford, 1966 and 1974-75, national elections were held. To a foreign visitor these were fascinating and enlightening, for they provided insights into important political and social issues of the day. They left me with an abiding interest in British politics. When Roger Linford asked me to speak at this retirement celebration, I gave considerable thought to how one might describe the full range of Lionel's contributions, in science and in other fields, over more than four decades, and it occurred to me then that his influence in Britain extends beyond science and into politics, for he was not only one of the teachers of Prime Minister Margaret Thatcher (during her Oxford undergraduate days), but he was also the Moral Tutor of Anthony Wedgewood Benn! Indeed, when I considered a title for my address to you today, my first thoughts were along the lines, "The Influence of L.A.K. Staveley on British Political Philosophy in the Twentieth Century"; However, I soon realized how ill-equipped I am to undertake the analysis of an influence as subtle and complex as this, so I settled on the more conventional title, "The Experimental Research of L.A.K. Staveley on Thermodynamics of Liquids", leaving the more intriguing political questions to the historians of the next century.

2 — EXPERIMENTAL METHODS FOR THE STUDY OF PURE LIQUIDS AND LIQUID MIXTURES

EARLY WORK

In his studies of liquids, Lionel set for himself the difficult task of devising simple but accurate thermodynamic experiments, carried out on bulk liquids, that yield information about interactions and structure at the molecular level. This led him to concentrate on the so-called excess properties of mixtures — that is, the difference between the real properties of a mixture and those of a corresponding ideal mixture. Keith Gubbins has already given you an idea of how useful these properties are in developing and refining improved molecular theories of liquids.

Lionel's early work in this field, extending from 1939 to about 1955 was concerned mainly with experimental studies of the excess thermodynamic properties of mixtures of alcohols in nonpolar solvents. An early paper on this work, by STAVELEY, JOHNS, and MOORE [1], describes a number of simple but effective experimental methods that were to be used over and over again in his later work. These include:

(1) simple methods for introducing precisely measured quantities of liquids or gases into a previously evacuated system,

(2) the use of liquid air to freeze and isolate components of a liquid mixture,

(3) the use of ideal gas relations (corrected where necessary) to detemine gas quantities,

(4) the weighing of displaced volumes for accurate mass determinations, and

(5) control and measurement of temperatures to within ± 0.01 K.

Among his collaborators in the early work on liquids were B. Spice, J.H.E. Jeffes, J.A.E. Moy, K.R. Hart, W.I. Tupman, W.P. McKinney, and G.F. Skinner. For a study of volume relations in dilute alcohol solutions in 1952, he examined the methods used by others for similar studies and found them wanting. He then devised the simple apparatus illustrated in fig. 1, for measuring volume changes on mixing liquids when the volume of one is much smaller than that of the other [2]. The apparatus is pivoted at point **A**. A small amount of component 2 is confined in mercury in the elbow just above and to the left of **A**, and the large chamber is filled with component 1, until the meniscus is visible in the precision-bore capillary between x and y. After reading the position of the meniscus with a travelling microscope, the tap **F** is opened

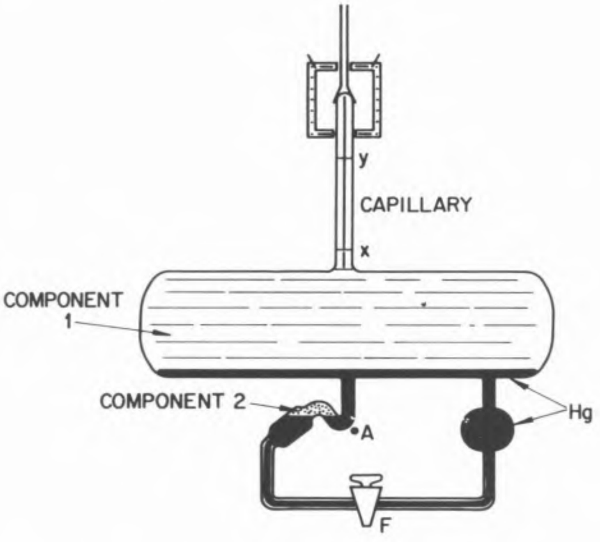

Fig. 1
Apparatus for measuring volume changes on mixing liquids, when the volume of one is much smaller than the volume of the other [2]

and the apparatus rotated clockwise 45°, displacing component 2 into the large chamber. After mixing the change in height of the meniscus gives the volume change on mixing. Through careful control of the temperature (to ± 0.001 K), volume changes as small as 0.006 cm^3 were accurately measured.

SUPERCOOLING OF SMALL LIQUID DROPS

An example of Lionel's remarkable ability to find simple solutions to seemingly complex experimental problems is illustrated by his 1952 study, with D.G. THOMAS, of supercooling of small drops of molecular liquids [3]. These experiments grew out of an interest in theories of homogeneous nucleation of supercooled liquids. At that time, experiments had been performed only on water and liquid metals, and few details of experimental methods suitable for ordinary liquids had been published. After surveying the available data, Lionel quickly settled on a cloud method, using the apparatus illustrated in fig. 2. The device is immersed to within 1 cm of the tops of the shield in an alcohol solution cooled by solid CO_2, and a puff of vapor is blown into the copper vessel. The cloud is observed through the viewing port from light admitted through the perspex window. If it consists of liquid droplets it appears as a dull mist; if it consists of crystals a bright sparkling is observed. The temperature is measured by thermocouples inside the copper vessel. (See reference 3 for more complete details). The experiments of Thomas and Staveley were the first of their kind to be undertaken; they produced, in a short period of time, new data on supercooling and homogeneous nucleation in sixteen different liquids, and set the stage for many subsequent experiments of this kind.

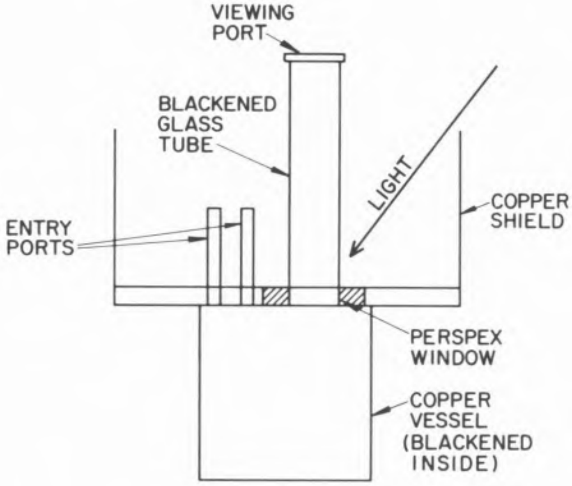

Fig. 2
Apparatus for studying supercooling of drops molecular liquids [3]

THERMODYNAMICS OF SIMPLE LIQUID MIXTURES

Lionel's collaboration in 1956 with the Belgian chemist Victor Mathot marked the beginning of his extensive work on mixtures of simple liquids — that is, mixtures composed of liquids having simple molecular structures. This resulted in renewed interest in cryogenic experiments, since most of the fluids of interest (Ar, N_2, O_2, CH_4, Kr, etc.) exist as liquids only at low temperatures. This work has continued up to the present time. The key to much of his remarkable experimental success in this area is the simple but versatile apparatus shown in fig. 3 [4]. The precisely calibrated pyknometer is connected to an external system of gas reservoirs through a capillary inlet, and held at constant temperature by means of a cryostat material at its triple point. By condensing carefully measured quantities of fluids into the pyknometer and observing temperatures, pressures, and meniscus heights, it is possible to measure the following mixture properties (see reference 4 for details):

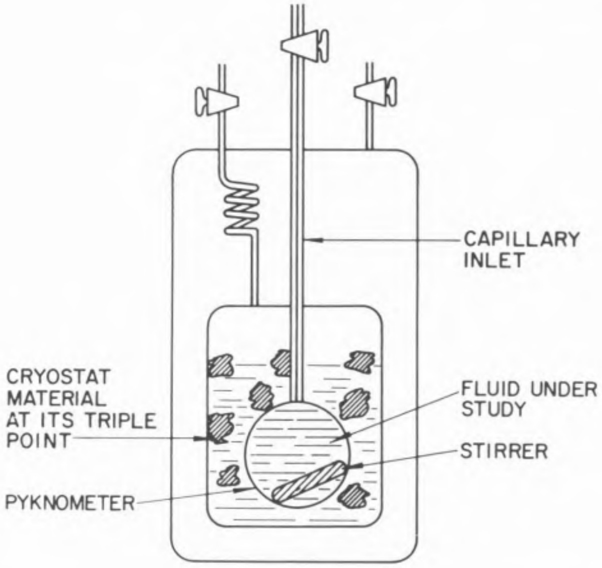

Fig. 3
Apparatus for measuring properties of mixtures of condensed gases at low pressures [4]

(1) total vapor pressure,
(2) condensation pressure,
(3) volume change on mixing,
(4) virial coefficients of gases,
(5) isothermal compressibility, and
(6) thermal expansion coefficient.

A slight modification allows measurement of pure liquid densities. Subsequent versions of the mixture apparatus were built by R.G. Davies, A.G. Duncan and J.C.G. Calado (including a duplicate apparatus in Lisbon) although the basic design has remained unchanged. Measurements on pure fluids were carried out by M.J. Terry, J.T. Lynch, M. Bunclark, K.R. Mansell, and others (see complete list of publications of L.A.K. Staveley elsewhere in this volume).

In addition to precise measurement of temperature, pressure and volume, successful experiments on mixtures of simple liquids required samples having a purity of at least 0.9999 mole fraction. To achieve these high purities Lionel designed and built a low-temperature distillation apparatus [5] that has subsequently been duplicated in the laboratories of J.C.G. Calado in Lisbon and W.B. Streett at Cornell.

EQUATION OF STATE MEASUREMENTS AT HIGH PRESSURES

In 1966, Staveley and Streett [6] collaborated in the design of a high-pressure apparatus for measuring the densities of cryogenic liquids at pressures up to 4000 atmospheres, employing methods similar to those previously used for liquids at low pressures. A schematic diagram of the high pressure apparatus is shown in fig. 4. The fluid under study is compressed into a high-pressure cell of known volume, held in a cryostat at constant temperature. After the pressure is recorded, valves **B**, **E** and **F** are closed, and the connecting lines and calibrated expansion volumes V_1 and V_2 are evacuated. The contents of the cell are then expanded into V_2 where the low pressure ($\leq$ 1 atm) is measured by a precision manometer, and the amount of fluid calculated from the known low-pressure equation of state for the gas phase. The amount of fluid expanded from the connecting capillary line between valve B and the cell is estimated from a similar expansion from the dummy line into V_1, and subtracted from the mass of fluid expanded into V_2. The difference gives the mass (and hence the density) of the fluid in the cell at high pressure, before the expansion. Each

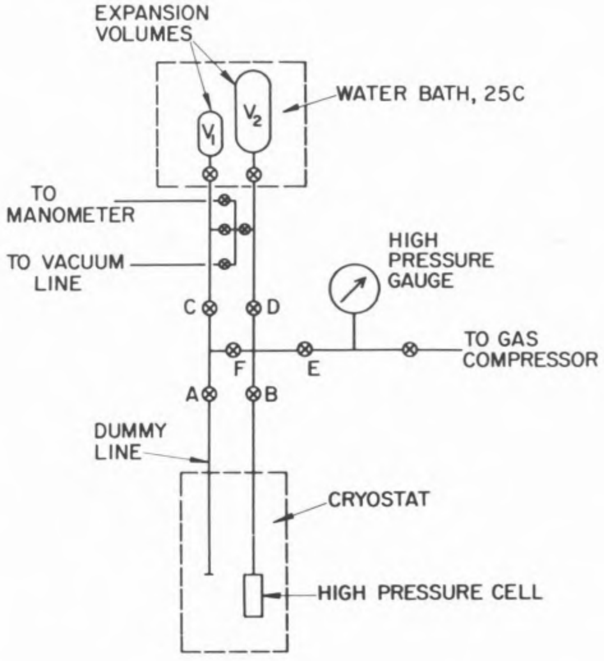

Fig. 4
Apparatus for measuring densities of liquefied gases at pressures to 4000 atmospheres [6,8]

expansion yields one P-V-T point. This apparatus has been used for studies of the equations of state of liquid nitrogen [6], argon [7], krypton [8] and xenon [9], at pressures as high as 4000 atmospheres. Subsequent versions in Lisbon and at Cornell have been used for high-pressure equation of state experiments on pure fluids such as tetrafluoromethane [10] and ethylene [11], and mixtures such as nitrogen/methane [12], argon/krypton [13] and argon/methane [14].

HEATS-OF-MIXING FOR LIQUEFIED GASES

For fluid mixtures the equation of state experiments described above yield the excess volume V^E and excess free energy G^E. A third excess property that is sensitive to the form of the intermolecular potential function and to the interactions between unlike molecules, and therefore useful in testing molecular theories, is the excess enthalpy H^E. In 1957 POOL and STAVELEY [15] built a calorimeter for measuring heats-of-mixing of liquefied gases, from which H^E can readily be determined. The first calorimeter is illustrated in fig. 5. To begin an experiment carefully measured amounts (typically several cm^3) of the two pure liquids are condensed into the upper and lower chambers, separated by a thin copper diaphragm. After the temperature has been stabilized the diaphragm is ruptured, allowing the liquids to mix. The mixing causes either absorption (usually) or release of heat, resulting in a temperature change that is detected by a copper resistance thermometer. The observed temperature change is duplicated by the addition of precisely measured amounts of heat energy, introduced through an electrical resistance heater wound on the calorimeter. The calorimeter is surrounded by a heat shield maintained at a constant temperature close to that of the calorimeter before mixing, so that the heat gain (or loss) from the calorimeter to the surroundings remains small and measureable. After corrections for vaporization, volume change on mixing, and other minor effects, the observed heat of mixing yields the excess enthalpy H^E.

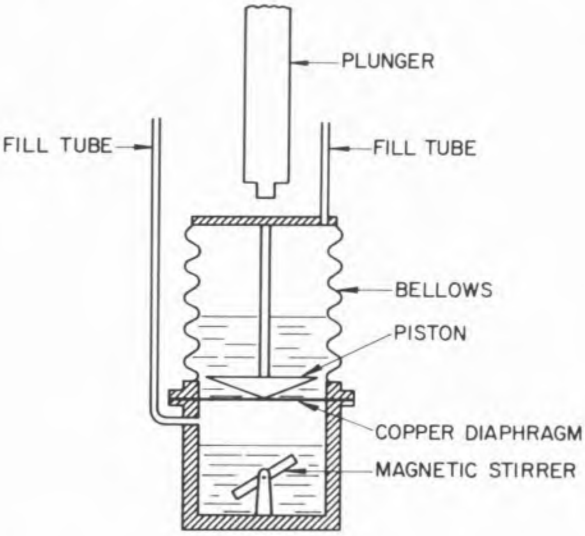

Fig. 5
Calorimeter for measuring the heat of mixing of liquefied gases [15]

A later version of the calorimeter [16] consisted of a mixing vessel machined from a single block of copper, with the two chambers separated by a wide-mouth valve, eliminating the need for disassembly after each experiment. This calorimeter has been used extensively for heat of mixing measurements from about 1975 up to the present time. Lionel's collaborators in this work include K.L. Lewis, G. Saville, A.J. Kidnay, R.C. Miller, L.Q. Lobo, D.W. McLure, E.G. de Azevedo, and others. Measurements with an accuracy of a few percent in H^E were consistently achieved, and of the 40 or so liquefied gas mixtures for which H^E measurements are presently known, about 35 were studied by Lionel and his students and colleagues, using the Oxford calorimeter.

With advice and encouragement from Lionel, a new version of this calorimeter has recently been built and tested in my own laboratory at Cornell [17]. The design, which is similar to the most recent Oxford calorimeter, is shown in fig. 6. Improvements include a mechanical stirrer, operated by a stirring rod inside the hollow stem of the wide-mouth valve that separates the mixing chambers, and a stainless steel vacuum can that is immersed in a cryostat fluid maintained at a temperature within a few K of the calorimeter temperature. This calorimeter is connected to a Hewlett-Packard HP-85 computer through a precision digital voltmeter. The computer is programmed to control the experiment from the time that wide-mouth valve is opened (by hand) until the mixing is complete and the required amount of heat has been added. The computer senses temperatures changes of ± 0.001 K through a platinum resistance thermometer, and supplies pre-

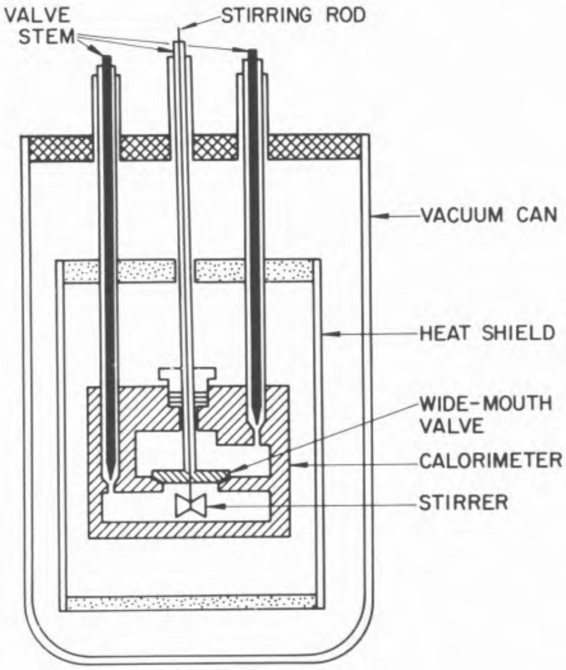

Fig. 6
Improved version of calorimeter shown in fig. 5 [16,17]

cisely measured quantities of heat through an electronic power supply. As the experiment progresses the computer fits a curve to the temperature-time data, and extrapolates forward to ensure that heat input is terminated at the instant the calorimeter temperature reaches the desired value.

Although the Oxford calorimeter has been disassembled, many of its component parts have shipped to the laboratory of L.Q. Lobo in Coimbra, Portugal, where an improved version will be built.

3 — CONCLUDING REMARKS

In surveying Lionel's work on the thermodynamics of liquid mixtures, one cannot fail to be impressed with the simplicity and elegance of the equipment and techniques that he devised, and how effectively he used them to carry out his research and to instruct his students. He used simple but effective methods, based on elementary principles of physics and thermodynamics, that served to deepen the students' understanding of fundamental laws and the behavior of matter. He insisted on high accuracy, developing techniques for measuring temperatures to ± 0.001 K and pressures to ± 0.01 mm, for purifying gases to 99.99 per cent, and for measuring mixture compositions to ± 0.01 mole per cent. He insisted that his students get early "hands-on" experience, and he provided the guidance to keep them on the right track.

His kindness and generosity towards visitors, and that of his wife Joyce, became widely known, and his willingness to accept and train foreign visitors served to extend his influence on experimental thermodynamics to many other countries, including Belgium, Portugal, the United States, Canada and Poland.

His work on liquids is an important building block in the edifice of science. The quality of his experiments is such that few, if any, will ever be repeated, and they will serve as a standard against which future work can be measured.

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THERMODYNAMICS AND STATISTICAL MECHANICS OF THE FLUID STATE

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

The behaviour of a substance in its gaseous or liquid state tends to be dominated by the fact that the molecules within it exert forces upon one another. We do, of course, have the concept of a perfect gas, for which $PV = RT$, an equation which results when all intermolecular forces are set to zero, but real substances only approximate to this in the gaseous state at low pressures. At higher pressures, generally above a few bars, the influence of the intermolecular forces becomes increasingly important until at about 100 bars pressure they may even dominate. In the case of liquids, there is no such thing as a perfect liquid, and intermolecular forces are important at all times. Indeed, were it not for the existence of intermolecular forces, liquids would not exist. The task facing anyone conducting research into the fluid state is therefore twofold: (1) to quantify the forces which molecules exert on one another and (2) to supply the link between these intermolecular forces and the observable, macroscopic, properties of the fluid phase.

This is an enormous task made particularly difficult by the fact that the two questions are closely coupled. Normally we have to make experimental measurements on some macroscopic systems and infer from these measurements what the intermolecular forces might be, by assuming a particular link between the microscopic and the macroscopic quantities involved. In a few cases, this link is well known, but usually it is not.

For example, if we make measurements of the P-V-T properties of a monatomic gas at low pressures, we find that we can represent the behaviour as

$$PV/RT = 1 + B/V$$

and statistical mechanics allows us to write, rigorously,

$$B(T) = -2\pi N \int_0^\infty [\exp(-U(r)/kT) - 1] r^2 dr$$

where B is the second virial coefficient and U(r) is the potential energy of a pair of atoms a distance r apart. It has the general functional form shown in fig. 1 for argon-argon and krypton-krypton interactions.

LIONEL STAVELEY has contributed substantially to the body of knowledge on this subject by a series of precision measurements of B, particularly for the rare gases argon, krypton and xenon [7, 15]. These

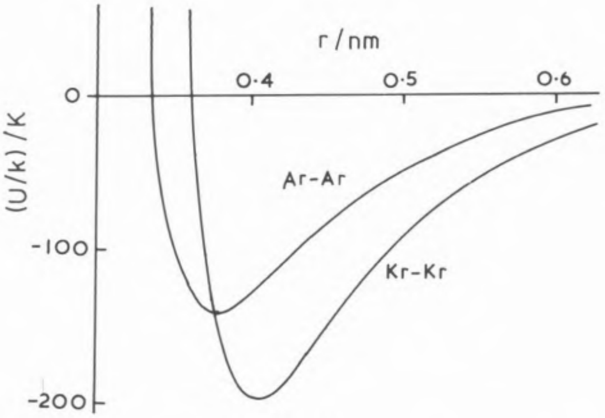

Fig. 1
Intermolecular potential energy curves for argon-argon and krypton-krypton interactions

have then formed the basis of various inversion procedures to obtain U(r).

For other fluid states one does not have this simplification and the problem is more intractable. However, in recent years, computer simulation has improved things considerably, and more about this will be found in the later papers at this meeting.

LIQUID MIXTURES

Much of LIONEL STAVELEY's work has been concerned with liquid mixtures and I would like to illustrate the importance of these measurements by describing a common chemical engineering situation.

A chemical process plant rarely handles pure substances. Thus, for example, a petroleum refinery will have as its feed, a complex multicomponent mixture of hydrocarbons which it will endeavour to split into a number of smaller streams each containing a rather more restricted range of the same hydrocarbons. This separation process is usually based on distillation and in the distillation column shown in fig. 2, each tray is a plate with holes through which vapour from the lower stage can pass, bubbling through the liquid trapped on each tray, excess liquid flowing down to the tray beneath.

Clearly, the composition of the liquid on each tray is different, being richer in the more volatile components as one goes higher up the column.

Faced with the design of such a column, one clearly needs the relevant thermodynamic information, both for the liquid and vapour phases, from which the liquid-vapour equilibrium can be calculated.

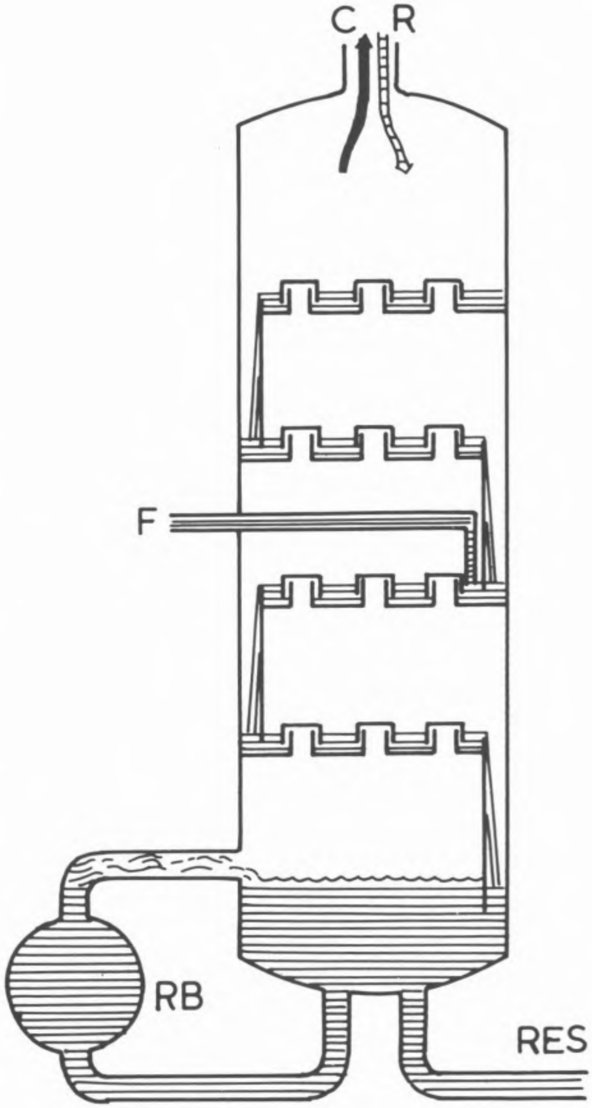

Fig. 2
*Distillation column showing: the feed F, the reboiler **RB**, the residue **RES**, the vapour stream to the condenser C and the liquid reflux stream from the condenser **R***

Usually it is information about the liquid phase which is lacking, since one often has adequate approximations for the vapour phase.

One can see why this information is likely to be lacking; there is hope of our being able to measure the thermodynamic properties of each pure substance present in the mixture; there is no hope of our ever being able to measure the same properties for every possible mixture which can be formed from them.

We therefore need a means of predicting liquid mixture properties, perhaps from a knowledge of the properties of the pure components. But however we do it, it is more likely to be reliable if the method is soundly based on theory rather than being a purely empirical averaging procedure.

Liquid mixture properties are usually expressed in terms of the so-called excess functions. If we mix two liquids together at a given pressure and temperature, the volume of the resulting mixture is very often close to the sum of the two original volumes. We therefore write

$$V^E = V_{mix} - V_1 - V_2$$

where V_{mix} is the volume of the mixture and V_1 and V_2 are the volumes of the two unmixed liquids, with the expectation that V^E will be small. A similar situation holds for the excess enthalpy of a mixture

$$H^E = H_{mix} - H_1 - H_2$$

The excess Gibbs free energy is particularly important when studying liquid-vapour equilibrium. In this case the definition is, per mole of mixture of composition (x_1, x_2),

$$G^E = G_{mix} - x_1G_1 - x_2G_2 - x_1RT \ln x_1 - x_2RT \ln x_2$$

Once we have a complete set of the values (V^E, H^E and G^E) as a function of pressure, temperature and composition, then we have completely determined the thermodynamics of the system. We note also that for an ideal mixture, all excess functions are zero.

Dr. STAVELEY began his experimental work on liquid mixtures around 1950. Initially he investigated mixtures in which the components are liquids at normal temperatures — alcohols, benzene, cyclohexane, etc. He found that the excess functions varied enormously in magnitude, the alcohols with their hydrogen bonds tending to form very non-ideal solutions whereas the less polar molecules formed mixtures which were much closer to ideal [1-4].

This early work led him to conclude that the non-ideality of a liquid mixture was very sensitive to the molecular species involved. Molecular shape and specific interactions were having a very large influence on the excess functions, thus making it very difficult to make any sensible test of the molecular theories of liquids then available. The whole situation was just too complicated.

It was at about this time that substantial progress was being made in the theory of liquid mixtures and in particular, relating the excess properties directly to the intermolecular forces. These theories drew heavily on the assumed structure of the liquid phase, whether pure or mixed. An early example was the cell theory in which each molecule is presumed to move in a cell or cage formed by the others. In the case of a mixture, the cell wall could be made up of molecules chosen randomly and so in the case of a binary mixture, would contain molecules of both species. This theory is not particularly accurate, but it does illustrate the problems encountered in developing a theory of liquid mixtures.

Fig. 3 shows a "wanderer" molecule in a cell formed by other molecules. The motion of this wanderer molecule depends on the forces exerted on it by all of the molecules in the wall of the cell. If these molecules are not spherical, or if the wanderer molecule is not spherical, one has great difficulty in describing the force quantitatively. Even if all of the molecules are spherical, problems still remain; the cell is a dynamic entity, not a static one, so one needs some sort of time average; the cell is complicated in shape but can one approximate it as a spherical cavity?

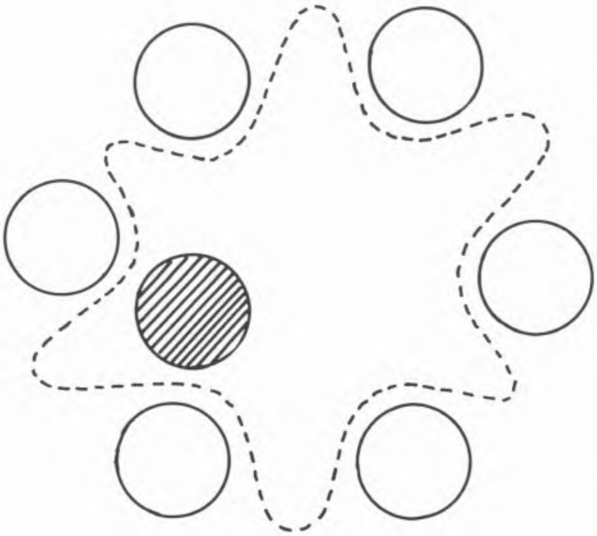

Fig. 3

Caging of the "wanderer" particle (shaded) in a cell formed by its nearest neighbours (open circles). The dashed line shows the approximate shape of the cell

Clearly, many approximations must go into a theory of liquid mixtures and it is desirable to chose to examine systems which require as few approximations as possible. From an experimental point of view we can begin by avoiding molecules of complex shape and examine only spherical molecules such as the rare gases argon, krypton and xenon. To this rather short list we can add the almost spherical oxygen, nitrogen, carbon monoxide, methane and carbon tetrafluoride.

All of these substances exist in the liquid phase only at low temperatures, generally around 100 K. LIONEL STAVELEY was the first person to grasp this nettle and measure experimentally V^E, H^E and G^E at these cryogenic temperatures. Experimentally, this is an order of magnitude more difficult than making the same measurements at room temperature. It is greatly to his credit that he showed that not only was it possible, but also obtained values of the quantities concerned which were of a precision that would have been considered remarkably good had they been determined at room temperature.

The first system investigated in this way was carbon monoxide-methane [5,6]. This choice might seem a little surprising, but was made for a number of reasons. First, as a purely practical one, the overlap of the two liquid ranges is such that measurements are possible at 90 K with pressures which do not exceed 2.5 bar. Secondly, it provides an excellent system with which to test the cell theory since this theory suggests that where two molecular species in a mixture are of essentially the same size, as are carbon monoxide and methane, V^E will be negative and G^E positive. This was to be compared with all other theories then current which predicted that both V^E and G^E would be positive. Fig. 4 shows what a triumph the cell theory appeared to have.

From this early success, Dr. STAVELEY moved on to increase the precision of his measurements and the range of substances covered, investigating most of the binary systems which can be formed from argon, nitrogen, oxygen, carbon monoxide, methane, krypton and xenon [7-15]. In many respects, argon-krypton and krypton-xenon should be ideal for testing theories of mixing since all three molecules involved are truly spherical and there is no possibilty of molecular shape entering the argument. All three molecules obey the principle of corresponding states, i.e. they all have the same shape for the intermolecular potential energy curve, only the scales are different (fig. 1). However, there are severe experimental problems. The minimum temperature at which argon and krypton co-exist as liquids involves working with pressures of up to 10 bar. Development of experimental methods to deal with these conditions took some time and it was only five years ago that H^E for this system was finally measured [15].

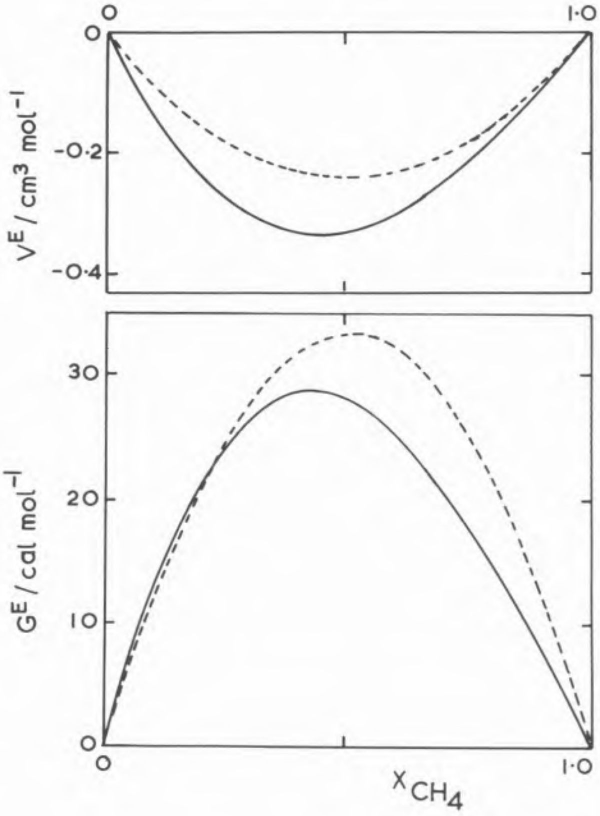

Fig. 4

Excess volume and Gibbs free energy for binary mixtures of carbon monoxide and methane at 90 K. The full lines are from experimental measurements, the dashed lines are calculated from cell theory

Unfortunately, all of this work showed that the early success of the cell theory could not be maintained. Measurements on the argon-oxygen system resulted in values for V^E, H^E and G^E which were an order of magnitude greater than those predicted by the theory. The same was true for carbon monoxide-nitrogen. For argon-krypton the theory leads to a value for G^E which is only one half of that observed experimentally (fig. 5); for V^E the calculation fails completely.

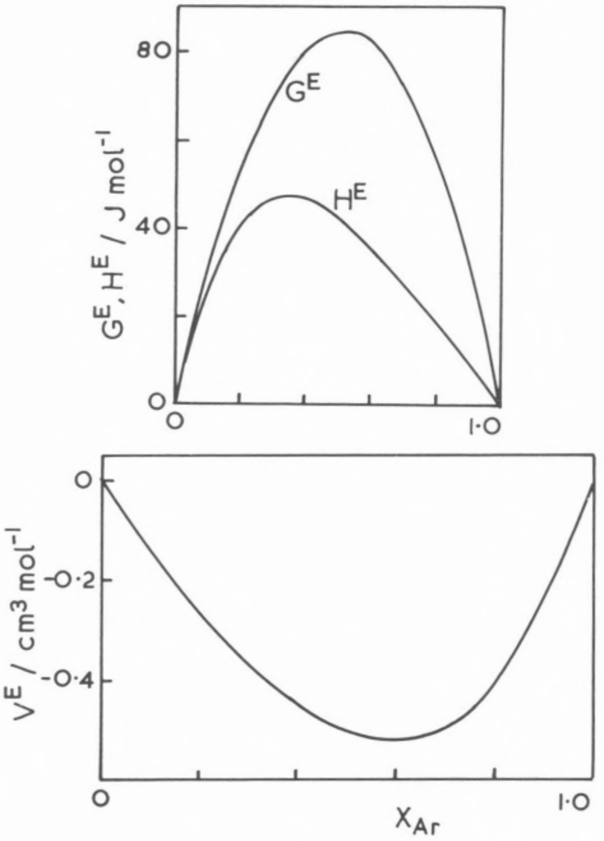

Fig. 5

Experimental measurements of the excess Gibbs free energy, enthalpy and volume for binary mixtures of argon and krypton at 116 K

As a result of Dr. STAVELEY'S efforts over the years, the scientific world now has in its possession an extensive body of experimental information on cryogenic liquid mixtures. It has shown the old cell theory to be inadequate for describing liquid mixtures but it has also paved the way for the more modern theories which will be described in the following paper.

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

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.

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

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.*

$$X\,nH_2O = X + n\,H_2O \qquad (2)$$

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).

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.

Three out of the four discoveries of proton disorder at 0 K in simple salt hydrates have been made by Lionel Staveley: $Na_2CO_3.10H_2O$ [4], $Na_2HPO_4.12H_2O$ [5] and $ZnF_2.4H_2O$ [6]. The lower hydrates of Na_2CO_3 and Na_2HPO_4 ($Na_2CO_3.H_2O$ and $Na_2HPO_4.7H_2O$) dit not show this property, neither did $Na_4P_2O_7.10H_2O$ [7], $K_4\ Fe(CN_6).3H_2O$ [8] and $LiBr.H_2O$ [9]. The details of the proton disordering may be expected to be rather similar to that for $Na_2SO_4.10H_2O$ [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:

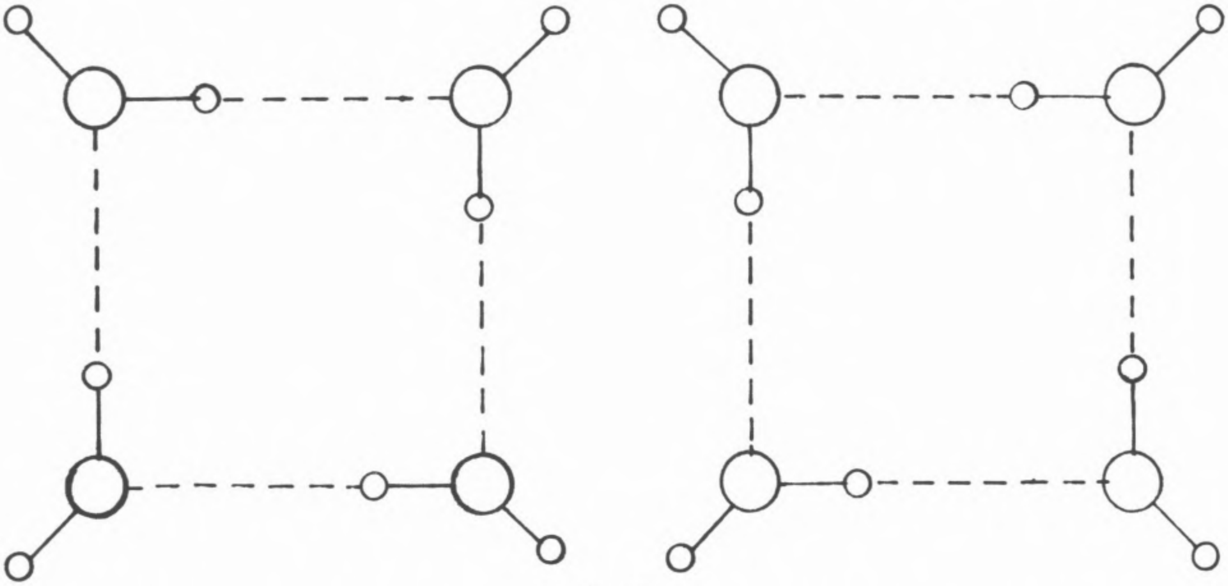
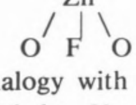


Fig. 1

Possible H-bond configurations for a ring of four water molecules, as found in $Na_2SO_4.10H_2O$. Large circles, O atoms; small circles, H atoms

In the case of $ZnF_2.4H_2O$ [6], for which S_{res} ($4.3\ JK^{-1}\ mol^{-1}$) was found to be close to $R \ln 2$ ($= 5.76\ JK^{-1}\ mol^{-1}$), it is thought that the disorder arises from there being two possible positions for the



octahedron (by analogy with $FeF_2.4H_2O$), which has been examined by X-ray diffraction [13]. Hydrates of the type $MSiF_6.6H_2O$ undergo transitions on cooling if M = Co, Fe, Mg or Mn (though not if M = 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 arragement [14].

Although $K_4Fe(CN)_6.3H_2O$ [8] had no residual entropy, it was interesting and unusual in having a transition (at ∼ 247 K) which was approximately of the classical (Ehrenfest) second-order type:

Transitions of this kind are very limited in number. $LiBr.H_2O$ [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

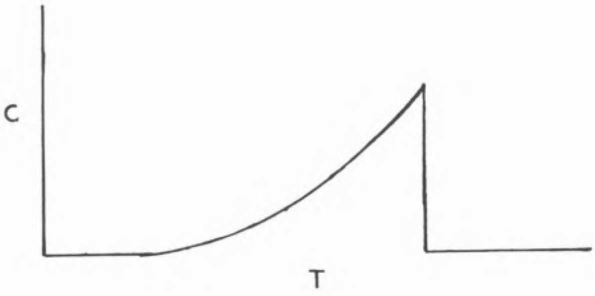


Fig. 2

Heat capacity versus *temperature curve for a classical (Ehrenfest) second-order transition. Only the contribution from the order-disorder process in 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 $S_{res} = 4.85$ J K^{-1} mol^{-1}) [15,16], but no such solution for a three-dimensional array has been found. Lionel Staveley [17] noted that the substances $Hg(NH_3)_2X_2$ (where X = 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 $NH_3-Hg-NH_3$ 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:

$$2AgCl(s) + 2NH_3(aq) + Hg(l) = \\ = Hg(NH_3)_2Cl_2(s) + 2Ag(s) \qquad (3)$$

and the corresponding Br equivalent.

S_{res} was found to be 12.0 ± 3 and 20.0 ± 7.5 J K^{-1} mol^{-1} for the Cl and the Br compound, respectively. Since a rough theoretical estimate gives 6.35 J K^{-1} 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 J K^{-1} mol^{-1} for the corresponding entropy [19]. A real system corresponding to this problem is the metastable form of $Hg(NH_2)Br$. 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 $Hg-\widehat{N}-Hg$ 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 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 K for which the entropy change was $\sim$ R ln 3, but no transition near 171 K [21]. The phenomenon at $\sim$ 171 K was traced to the delayed ordering of the solid following supercooling through the transition at $\sim$ 230 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].

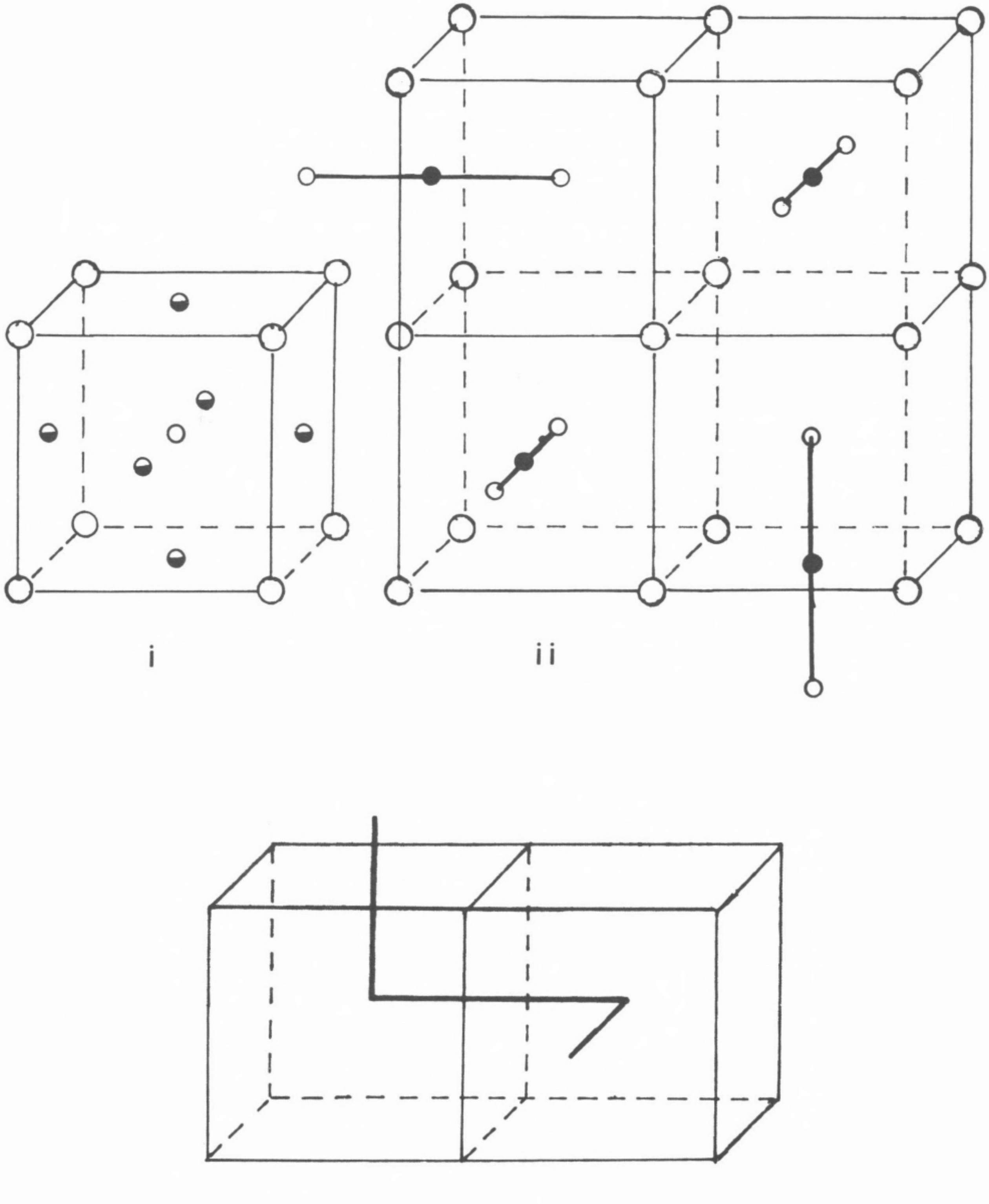


Fig. 3

a) *The structure of* $Hg(NH_3)_2X_2$, *where* $X = Cl$ *or* Br. *(i) A unit cell; (ii) a group of unit cells showing* $H_3N-Hg-NH_3$ *"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* $H_2N-Hg-NH_2-Hg-$ *chain (bold line) in* $Hg(NH_2)Br$

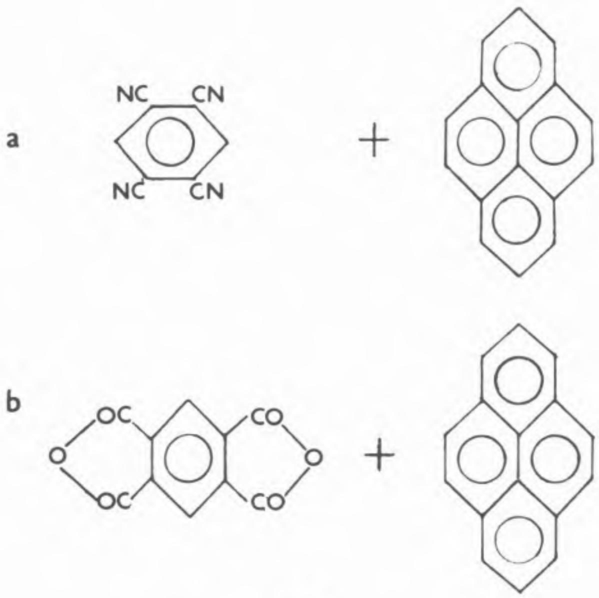


Fig. 4
Charge-transfer complexes

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, futher study on these compounds employing other tecniques 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.

* * *

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.

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

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.

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 inspite of the availability of today's more sophisticated measuring techniques and devices.

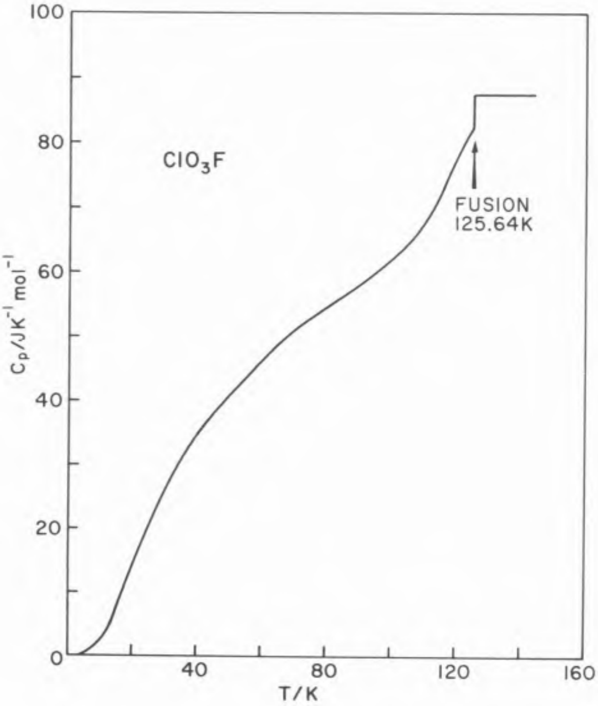

Fig. 1
Heat capacity vs. *temperature for perchloryl fluoride*

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 Rln4.

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 $Hg(NH_3)_2Cl_2$ and $Hg(NH_3)_2Br_2$ [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

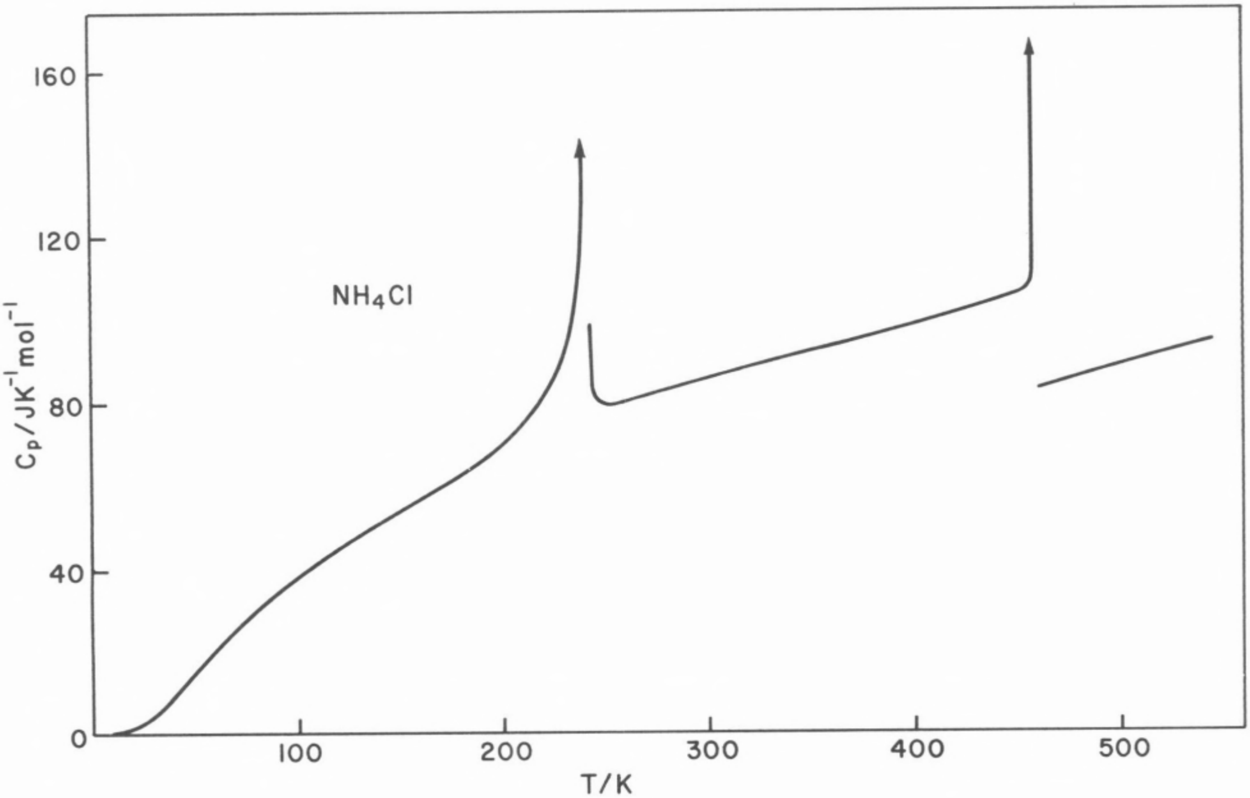

Fig. 2
Heat capacity curve for ammonium chloride

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

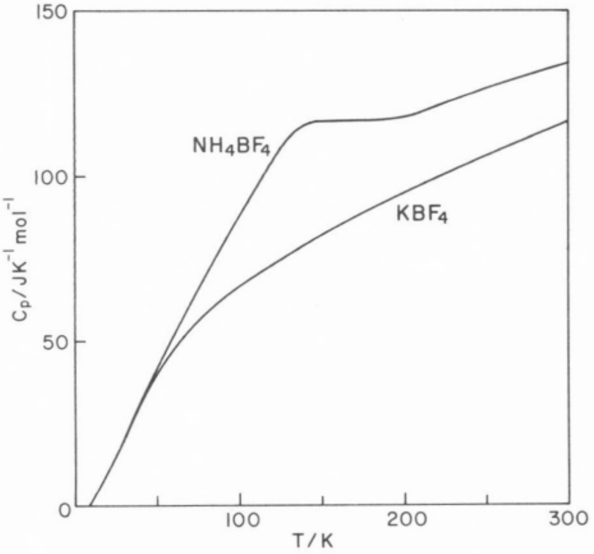

Fig. 3
Heat capacity curves for NH_4BF_4 and KBF_4

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]	
$CuNO_3.NC(CH_2)_2CN$	[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.

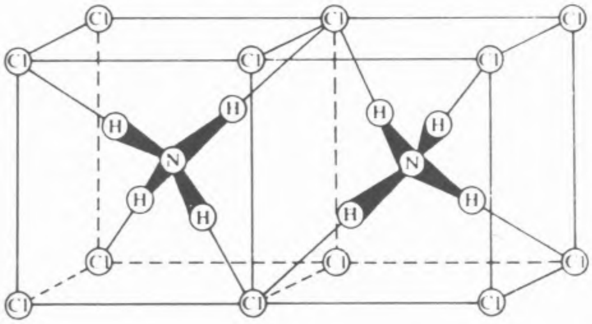

Fig. 4
The two orientations available to an NH_4^+ ion at the centre of a cube of eight Cl^- ions

(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 Cp *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 $(RNH_3)_2MCl_4$, 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 $(RNH_3)_2$ 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 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 2
Compounds containing tetrahedral ions

NH_4Cl	[5,13,17]	transitions
NH_3DCl, NHD_3Cl	[18]	transitions
NH_4Br	[5]	
NH_4Cl-NH_4Br	[19]	
$NH_4Cl_{0.26}Br_{0.74}$	[20]	transition temperatures
$NH_4Cl_{0.45}Br_{0.55}$	[75]	vary with mole
$NH_4Cl_{0.80}Br_{0.20}$	[20]	fraction
NH_4I	[5]	
KBF_4	[10]	
KIO_4	[37]	
$KBPh_4$	[21]	
$RbBPh_4$	[21,22]	
NH_4BPh_4	[21,22]	
$(NH_4)_2SnCl_6$	[5,23,24]	hindered NH_4^+ rotation
$(NH_4)_2SnBr_6$	[24]	
NH_4PF_6	[25]	
NH_4ReO_4	[26,27]	models for NH_4^+ libration
NH_4BF_4	[4]	inadequate

Table 3
Current status of the layered compounds

$N(CH_3)_4I$	[5]	
$(CH_3NH_3)_2CdCl_4$	[28]	
$(\quad)_2MnCl_4$	[29]	also magnetic
$(\quad)_2CuCl_4$	[30]	
$(\quad)_2CrCl_4$	[35]	also magnetic
$(CH_3CH_2CH_2NH_3)_2MnCl_4$	[31]	also magnetic
$(\quad)_2CdCl_4$	[31]	
$(n-C_7H_{15}NH_3)_2MnCl_4$	[32]	also magnetic
$(\quad)_2CdCl_4$	[33]	
$(n-C_{18}H_{37}NH_3)_2CdCl_4$	[33]	
$(CH_2=CHCH_2NH_3)_2CdCl_4$	[34]	
$(CH_3)_4NMnCl_3$	[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	
$K_4Fe(CN)_6$	[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 is it found in those with low proportions of water. The list is in Table 5.

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]	

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 adamantane ($C_{10}H_{16}$). (ii) As considerable orientational freedom is gained, molucules 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
CEt_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
ter-butyl chloride	[55]	
ter-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 componds 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.* $K_4Fe(CN)_6$, $K_4Fe(CN)_6.3H_2O$ 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.* $CuCl_2.2H_2O$ to $Ni(NH_3)_6I_2$ 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.* NiI_2 to $(n-C_7H_{15}NH_3)_2MnCl_4$ of Table 8.

Table 8
Magnetic compounds

$K_4Fe(CN)_6$	[39]	
$K_4Fe(CN)_6.3H_2O$	[39]	
$CuCl_2.2H_2O$	[9,65]	
$CuF_2.2H_2O$	[65]	
$Ni(NH_3)_2I_2$	[66]	
$Ni(NH_3)_6I_2$	[66]	
NiI_2	[66]	
$NiBr_2$	[67]	
$\{ZnBr_2\}$	[68]	diamagnetic for comparison
$(CH_3NH_3)_2MnCl_4$	[29]	
$(\quad)_2CrCl_4$	[35]	
$(CH_3CH_2CH_2NH_3)_2MnCl_4$	[31]	
$(n-C_7H_{15}NH_3)_2MnCl_4$	[32]	
$LiCuCl_3.2H_2O$	[65]	

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" 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 forseen 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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THE EXPERIMENTAL CRYOGENIC CALORIMETRIC CRAFT OF LIONEL STAVELEY

1 — INTRODUCTION

The eyes of the world have been on England much these days — the yeoman endeavors in the Falklands to provide self-determinism — the birth of a Royal baby — and indeed these are propitious events; but in a related sense, we are gathered here to recognize publicly an impressive scientific genealogy which has already borne fruit, which will continue to do so, and which will make its mark on the scientific world.

But, interestingly enough, in the few hours that I have been on this hallowed campus of academia, the one question which I've been asked time and time again has been simply, "Where do you fit into the 'family" tree?" the answer is, simply, that I don't! But a man of Staveley's stature can certainly be expected to have an influence beyond the "family" circle and so it should be no great surprise that when I first came abroad in 1951 (indeed, to participate in a cryogenic conference here at Oxford University) I made my first visit to the towering oracle already famous for thermophysical and adjuvant studies. In my perspective from that visit, I should judge that the statement in the "official" biography of Lionel that refers to him as "a man of Edwardian dignity" was at best a horrendous understatement. Nonetheless, when I had opportunities to bring his students to work in my laboratory, this was done, and when the rich flow of ideas suggested still other ideas, these were often sifted, tested, checked, and pursued. Consequently, I am truly honored to have this privilege. Lionel has been one of my heroes for many years. Today, we are gathered here representing hundreds of others of our calling to recognize and to thank Lionel Staveley for his wisdom, his leadership, and his unlimited capacity for friendship.

His contributions to chemical thermodynamics, to thermochemistry, and to thermophysics — especially cryogenic thermophysics — are dramatic. He applied many varieties of calorimeters to the problems which he tackled for the good of the discipline, and if I understand correctly, these same calorimeters are indeed being propogated this very week into the bloodstream of thermodynamic research. Unfortunately, in many areas of the world, thermodynamics is today in troublesome times, funding is hard to come by, and all too often the contribution is minimized or undersold. That

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[Presentation made on the occasion of The Lionel A. K. Staveley Retirement Meeting in the Inorganic Chemistry Laboratory, Oxford University, Oxford, U. K., Friday, 25 June 1982].

Oxford seems not to have suffered this blight over the past three decades or so is unquestionably due to the boundless energy and enthusiasm of Lionel. No cursory summary of his research achievement would be complete without recognition of that fact. True, I do not know what local and national administrative endeavors were concurrently shouldered by Lionel, but I do know that by precept and example he made an international tidal wave. I do know that he impressed the Staveley hallmark on more than a generation of students.

Perhaps by not being a family member I can look in on developments more dispassionately? Certainly this would be an advantage — but I am reminded again of my first trip abroad and being ushered into the Washington Atomic Energy Commission Office and told what I could and what I could not discuss with the European and Soviet scientists. In one sense the Committee's assignment seemed especially perverse in that the topics I was allowed to discuss were topics hard for an "outsider" to appreciate fully — or even to completely integrate — but bear with me — I'll do my best in this parallel assigment.

2 — PROLEGOMENA

I want to show four viewgraphs of rather significant historical interest. I've used them innumerable times because together they tell a profound story and represent points of overlap and/or of initiation and innovation.

The first of these (see fig. 1) came to Ann Arbor with John T. S. Andrews who began his doctoral studies with me. I have long since forgotten which document this preliminary version might have migrated across the Atlantic in, but it does represent a profound discovery in analysis of transition, and hence, of what the community has come to call "ODIC". The community of which I an speaking is now half a thousand strong, holds biennial Gordon Conferences, Symposia, etc., has a periodically appearing Newsletter, and brings a variety of techniques to focus on the area. As many of you are certainly aware, the acronym refers to "Orientational Disorder in Crystals". Lionel is the great grandfather of this ODIC community and continues to engineer relevant research in this area. In particular, when a considerable interest in the "plastic crystals" seems to have been overlooked during the war years, interest in this area was effectively revised by Lionel's chairmanship of a conference in Oxford University in 1951. The proceedings of this conference [1] continue to be a terse summary of the state of this active and very productive field. A further shot in the arm was provided by the monograph co-authored with Dr. Parsonage [2] which puts the field in perspective two decades later and far more recently.

The second figure (see fig. 2) has no Staveley data on it, but it reminds me to comment that Staveley

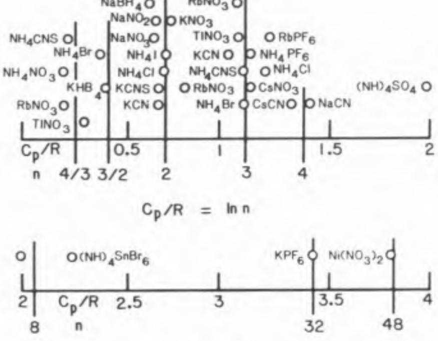

Fig. 1

Entropies of transition on a scale R 1n N (N = number of equivalent positions of a globular ion)

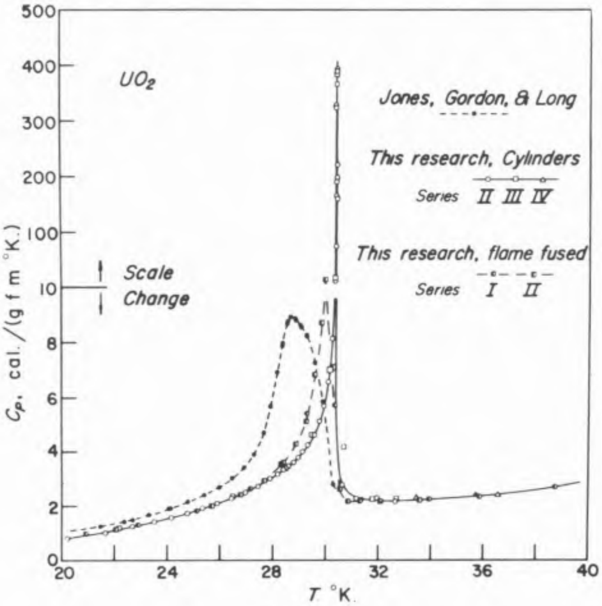

Fig. 2

The heat capacity of UO_2 as a function of purity. The curve ---•--- is that of Ref. 3; the curve ---●--- is earlier work on a sample in which the estimation of purity took no account of the phase diagram. The remaining curve and points are those on a flame-fused non-stoichiometric sample was a chemist first and foremost and consequently appreciated the importance of a well- characterized sample. In particular, he would not have fallen into the trap of failing to recognize on a basis both of chemical analysis and phase diagram interpretations that a serious lack of chemical and phase purity characterized one of the samples.

The third figure (fig. 3) may be recognized as the methanol system and in contrast does have a good bit of Staveley and Company data on it — but only a small part of the total study by them on the ramifications of this system including even isotopic substitutions. This figure is also a poignant reminder that there are still things we don't totally understand about transitions. Here is another instance where water acts in a catalytic fashion to promote the phase transition whether it is approached from above or below. No water; no transition — would seem to be a safe interpretation of the extrapolation from impure to pure and on to even purer samples.

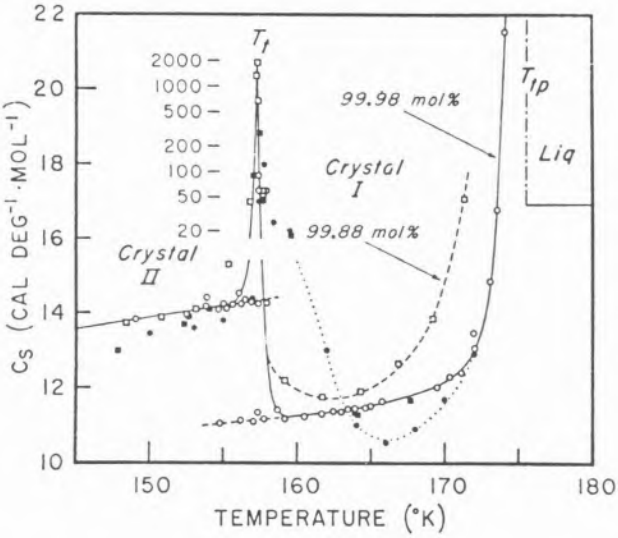

Fig. 3

The heat capacity of methanol over the transition and melting regions. Data for Sample I and II from [4] are represented by ● and □, those of Kelley by ■, and those of Staveley and Gupta from [7] by ●

The fourth figure (fig. 4) shows another system dear to Staveley and his fellow researchers, although a great deal more recent than the previous one. It pertains to heat capacity of the ammonium bromide system and a solid-solid transition which is probably as close to being a classical first-order transition as any that we have ever studied. But it is a very sluggish transition, and challenged us mightily in devising a way to study it adiabatically. But the pure compound was not sufficiently challenging for Staveley and his friends, so a composition variable was introduced. We'll come back later to such complexities.

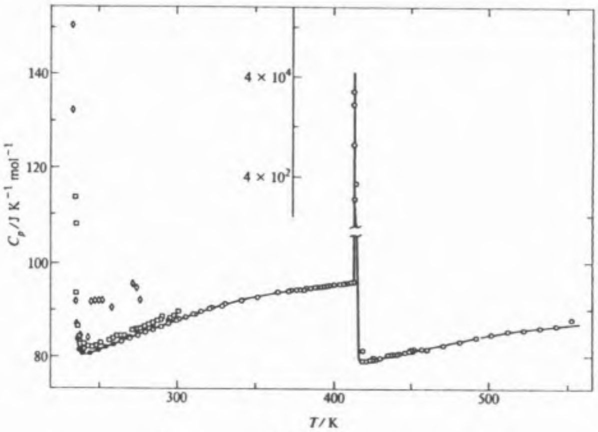

Fig. 4

Molar heat capacity of NH_4Br. ◇, Simon, von Simson, and Ruhemann; ■, Cole, Sorai, Suga, and Seki; and ○, that of reference [4]

3 — THE CRAFT ITSELF

I don't think this audience needs to be reminded that "thermodynamics is an experimental science, and not a branch of metaphysics." [6]. Moreover, it is a science in which most investigators must fabricate their own equipment — rather than buy it across the counter. This tests the engineering design ingenuity of the researcher who must usually not only design, but construct, wire, calibrate, and then utilize the apparatus. It was not alone by "sticks, string, and sealing wax" that *thermo*-physics was kept alive, but certainly the component of "blood, sweat and tears" was also involved. Dr. Staveley has left the field before it became so computer saturated and complex that one could be both personally angry and frustrated at a very deep level since no one of us can have hands-on control or understanding of all of the complicated gadgets that are now being assembled as part of the calorimetric package. To bolster my understanding of Dr. Staveley's "craft" I yesterday visited the Inorganic Chemistry instrument shop and discovered the man who has for decades been doing fabrication, coil-winding, and engineering on calorimeters. I was not surprised to find that he had only the highest of praise for the very meticulous design drawings provided by Dr. Staveley for the instruments to be built. I would have expected this! The experimental thermophysicist is clearly a Jack-of-all-Trades, i.e., a versatile but amateur craftsman. He must do metal work, wire electric circuits, master gadgets of all kinds and finds some engineering design to be a valuable asset, but he can always profit utilizing his gifts as a mathematician. In such activities he will be engaged for three quarters of his working day. During the rest he must be a thermophysicist and cultivate an intimacy with the behaviour of the temperature-dependent world. Fortunately he need not be preeminent in many of them, but the experimental thermophysicist must be enough of a theorist to know what experiments are worth doing and enough of a craftsman to be able to do them. He is preeminent probably only in being able to do both. So, the good experimenter must possess the power of designing an apparatus that can work and actually making it do so. He must be able to spot faults quickly and must be able to judge between the various possible causes of failure. Actually handling the apparatus is an essential mode of acquiring this facility, but a knowledge of thermodynamics to keep him from gross error and a knowledge of physical chemistry to provide guidance and insight and with such varied manual and mental skills which have been described, he can go about the work in the laboratory — an amateur in each one but unique in commanding them all. It has been my experience that it is the exigencies of the moment which determine which of the manifold aspects are important for the day at hand.

4 — SOME CRYOGENIC CALORIMETERS

Although there is certainly much insight to be obtained by looking at all of the successive cryogenic calorimeters representing the timely development of the measurements, time constraints do require that we be reasonably selective. I should like here to begin with one developed about 35 years ago to make heat-capacity determinations over the region from 100 to 300 K [7]. It was of the "dunking" variety in which a submarine is used to provide a working vacuum space submerged in a bath of appropriate refrigerant. It proved to be useful in the studies done by Staveley an his co-workers [4] on the isotopic CH_3OH system. The cryostat itselft, shown in fig. 5, was provided with a massive block which proved very convenient in the ensuing enthalpy of vaporization studies. Calorimetrists often have the reputation of being very greedy folks and wanting samples which are impossibly large. However, in sharp contrast, are measurements of Giauque on gold in which he used more than two kg. Staveley — as usual, years ahead of the competition — pioneered in the miniaturization of the calorimeter so that a few grams of isotopic methanol samples were sufficient to make reasonably precise measurements, as has already been shown in fig. 3.

The cryostat itself was of the adiabatic vacuum type resembling most closely that constructed by Eucken

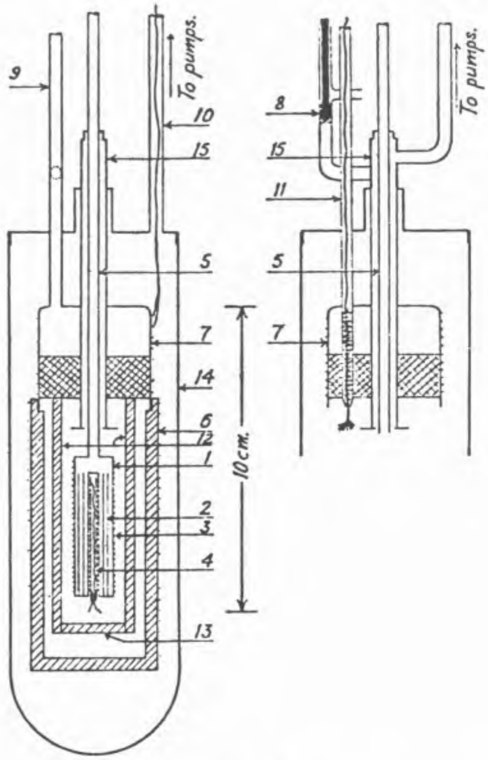

Fig. 5

The cryostat. The diagram on the right shows the upper part of the apparatus as seen from the right-hand side of the complete diagram. (1) Cylindrical copper calorimeter; (2) concentric, perforated copper cylinders to hasten the attainment of thermal equilibrium; (3) platinum resistance thermometer; (4) constantan heating-coil; (5) German silver inlet tube to calorimeter; (6) cylindrical copper mantle; (7) copper vessel half filled with lead; (8) valve; (9), (10), (11) German silver tubes; (12) copper rods; (13) copper crosspiece joining copper rods; (14) chromium-plated brass can; (15) German silver tube. From [7] and Schroeder a decade earlier but with a filling tube provided with a copper heater. Thermal inertia was provided by a copper block half filled with lead. Refrigerants were liquid oxygen or an alcohol-carbon dioxide slush. Provision was made for controlling the depth of immersion. Frequent calibration of the thermometer was mandated by the non-strain-free mounting. These were achieved from vapor pressure determinations on methyl chloride, methyl bromide, phosphine, methane, and ethylene. Tests of the accuracy of the calorimeter were made on methyl alcohol and on carbon tetrachloride. The calorimeter was characterized as semi-micro in scale. A subsequent calorimeter extended the range from 2 to 100 K [8]. This — as was true of Staveley's work in general — was characterized by very careful thermometry and seems to have been the introduction of multiple vacuum systems into cryogenic calorimeters to facilitate rapid quenching or cooling. A further difference of this unit from traditional adiabatic designs is that the adiabatic shield is not freely suspended but is rigidly mounted inside the inner vacuum can. A thermal switch provides cooling, thus preserving the inner vacuum. The indium-clad jaws of the thermal switch shown in fig. 6 eliminate the need for helium exchange gas. The small germanium resistance thermometer was calibrated in a separate gas thermometer.

The initial calorimeter was replaced two decades later by an updated version of Waterfield and Staveley [9]. Its range was 79-310 K.

Another more recent cryostat [10] for the region 2 to 100 K is an improved version of the Clay and Staveley instrument [8] with three independent vacuum chambers as depicted in fig. 7. The platinum/iridium sample vessel **(A)** was brazed with gold, and cooled by means of the thermal switch **(E)**. A small cylindrical vessel **(H)** atop the adiabatic shield permits cooling by subsequent evaporation of ^{3}He condensed in it. The intermediate vacuum vessel **(I)** contains the vessel **(K)** for evaporative cooling with either liquid helium or liquid nitrogen pumped through a fine diameter capillary. The data resulting from this ingenious instrument have already been discussed by other lecturers today.

As much as he was committed to calorimetric measurements, he appreciated fully the importance of appropriate adjuvant measurements to supplement the calorimetric data and to aid in the interpretation of his results. The supplementary measurements included not only chemical equilibrium measurements of various varieties, but as well PVT measurements, dilatometry, and whatever was appropriate in a particular case.

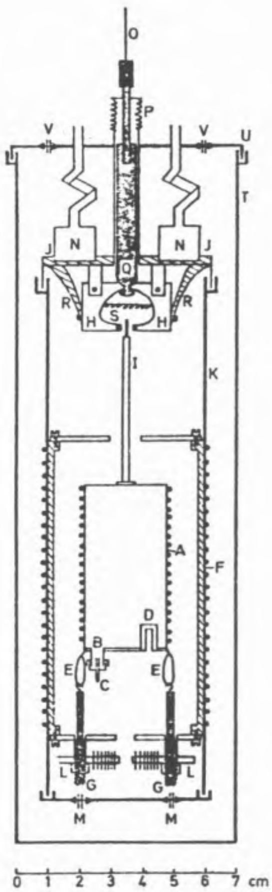

Fig. 6

(A) the sample container (calorimeter), (D) the germanium thermometer, (E) nylon loops, (F) adiabatic shield, (H) thermal switch, (I) copper tube, (K) thin-walled inconel tube, (T) outer vacuum can. From [8]

His thermophysical calorimetric measurements were by no means limited to the cryogenic regions, but included also measurements extending into the superambient temperature region [11]. The desirability of extending the measurements into the superambient temperature regions led to the construction of calorimeter for adiabatic measurement in the region above 300 K [11]. This was similar to one already described [12].

Excellent work was also done in the region usually reserved for physicists below the helium-boiling point [8,10]. A particularly interesting example is

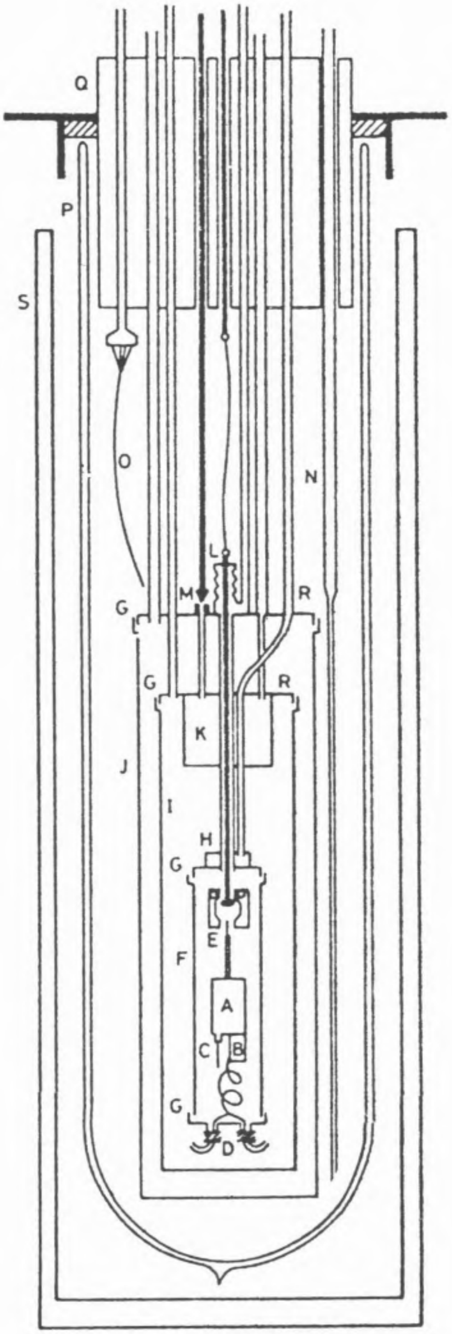

Fig. 7

Low-temperature calorimeter A for heat capacity measurements from 2 to 100 K. (A) sample vessel, (B) compartment for germanium thermometers, (C) filling port and silver tube, (D) epoxy lead-seals, (E) thermal switch, (F) adiabatic shield and inner vacuum chamber, (G) demountable indium-solder seals, (H) ^3He vessel, (I) intermediate vacuum chamber, (J) outer vacuum chamber, (K) liquid helium/nitrogen vessel, (L) metal bellows, (M) needle valve, (N) liquid helium syphon — normally removed after filling P, (P) inner glass Dewar, (Q) "economizer" vessel (filled with liquid nitrogen), and (S) outer metal Dewar vessel. From [10]

that of the magnetic transition in $CuCl_2.2H_2O$ with the magnetic transformation occurring almost exactly at the helium boiling point [8].

Although other speakers have addressed the topic of his choice of materials to be investigated, I am not so chemically unoriented but that I wish to call attention to his splendid work on the stannihalides [13]. This work, like the other papers, is characterized by a thorough, meticulous, experimental study of carefully selected "key" compounds. Despiste the tedium of measurement of pre-automation days, he not only managed to do it, promptly and expeditiously, but demonstrated originality of mind in the selection of the right compounds to study, and the theoretical relevance of the experimental endeavors which he pursued. Another system of particular interest is that of NH_4BF_3 [14]. Portions of the calorimetric results of this system are shown in fig. 8 and represent the kind of results which Staveley has become famous.

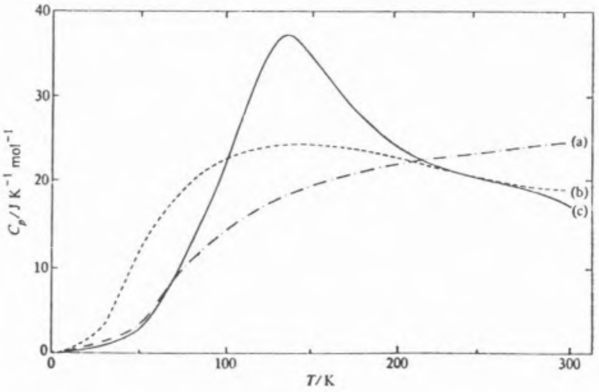

Fig. 8

Excess heat capacity of NH_4BF_3. Curve (a), —·—, C_p of a three-dimensional Einstein oscillator of wavenumber 190 cm^{-1}; curve (b), ———, C_p for a three-dimensional restricted rotator with a potential-barrier height of 4.2 kJ mol^{-1}; curve (c) ——, experimental values of the quantity $\{C_p(NH_4BF_4) - C_p(KBF_4) - C(NH_4^+, int)\}$. From [14]

5 — MEASUREMENTS ON IMPORTANT SYSTEMS

The mixed ammonium halide systems are some of the systems which have proven popular in other laboratories and to which Staveley and his colleagues have made very significant contribution and pioneering measurements by their calorimetric measurements [2,11,15,16]. Having ventured into some of the safer realms of this interesting region, I can appreciate better the problems which are involved in coping with the hysteresis, and the long thermal equilibration times. The subject has been well summarized by PARSONAGE and STAVELEY [2] and is of such complexity and replete with so many adjuvant measurements that time does not permit further discussions of its thermophysics here. The so-called charge-transfer complexes — or the π-π molecular compounds — represent complex systems of utter fascination, of weird and strange behavior, and occasionally of hysteresis in achieving thermal equilibration. We undertook the study of some members of the system so that we can speak from first-hand acquaintance with the problem. In the meantime, Staveley also chose to unravel some of the behavior of these exciting systems. To make a long story short, all of them that have been studied to date in either laboratory have shown behavior significantly different from that of any other. One system in particular, the 1,2,4,5-tetracyanobenzene-pyrene-system [18] was investigated by Staveley *et al.* We found it hard to believe that his finding were indeed the limit of resolution, of reproducibility, and wondered if something had not been missed. In the hope of improving them we prepared our own sample and remeasured the system. We found that the system was substantially as reported and this fact, more than any other, has served to convince us of the utter reliability of his endeavors. Many other examples could be selected since these points of interest are highly ramified, but it is clear that we have reached a point where it is up to his students to carry the torch and to further the endeavor which has been so creatively initiated here at Oxford.

Finally it should be noted that I have chosen to emphasize almost exclusively the thermophysical cryogenic calorimetric aspects of his experimental science at the expense of the great diversity of his thermochemistry, kinetics, rectification of gases, volumetric and dilatometric aspects of fluids, solutions and mixing, undercooling, compressibility, enthalpies of mixing, etc. etc.

It is my sincere hope that along the way someone will take time off from science to produce a family tree so that pre-Staveley and post-Staveley relationships will become more evident. That such an endeavor would not be without meritorious interest is, I think, clearly shown by the large number of people who have gathered here today in tribute to Lionel Staveley.

ACKOWLEDGMENT

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LIONEL STAVELEY AND THE DEVELOPMENT OF THERMODYNAMICS ABROAD

1 — PREAMBLE

The quality and importance of Lionel's research in Chemical Thermodynamics have been assessed by previous speakers. My contribution will be different, and will focus on the impact of his work on others, in particular on those, like myself, who came from abroad to work with him in Oxford. This flow of knowledge, this passing on of experience and skills, this chain of papers and ideas are features of scientific life to which Lionel himself is particularly sensitive. I know how much he values the strength of tradition, the organic vitality of scientific schools, the historic links with the past; how much he prides himself on having been a disciple of Hinshelwood — his tutor at Trinity College — and of Clusius, who was himself a direct scientific descendant of Nernst, through Eucken. Lionel's stay in Munich, just before the war, may have been brief and, in many ways, dramatic (his name could not appear as that of an equal author in the papers with Clusius because, in the meantime, the war had broken out) but it was to mark profoundly the course of his later work, leading him to low-temperature thermodynamics. I treasure the stories that he has told me about Hinshelwood, as others will treasure the stories that I shall be telling about Lionel, and there is a kind of continuity in this, too.

His research has influenced many people in many countries. Scientists came from Europe (both East and West), Africa, Asia, Australia, the Americas to work with him, and we have heard many success stories in the course of this meeting. What I have to tell is a kind of fairy tale, and since fairy tales are supposed to have happy ending, it is fitting that this third session should begin with one. It concerns the establishment of thermodynamics as a promising field of research in my own country, Portugal.

2 — THE PORTUGUESE CONNECTION

First, some raw data. Portugal is a country where, still in our days, only 0.2% of the GNP is spent in Research and Development, where the number of research workers with a university degree is still less than 3 per 10 000 inhabitants, where the total number of PhDs obtained in the physical sciences and engineering for the 1955-64 decade was a mere 62, most of these abroad. Graduate studies had not

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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. L.A.K. Staveley.

been implemented (no masters' degrees and no courses at the graduate level). There was, in those days, no research in chemical thermodynamics.

I came to Oxford to work with Lionel, having had no experience in low-temperature thermodynamics. My background was in Physical Inorganic Chemistry, mainly studies of chemical equilibria in solution. I had never done any glass blowing, nor had I seen, let alone used, liquid nitrogen. And yet I remember, with affection, Lionel sitting at the laboratory bench to teach me the essentials of glass blowing. Nowadays I wish I had the time and generosity to do the same with my own students in Lisbon.

I first came to Oxford in 1966 and Lionel went to Portugal for the first time in 1971. Ten years later the situation is quite different from that pictured above, and here I would like to stress what I call the *Portuguese connection* in Lionel's output and scientific genealogy:

Two of us (I and Lélio Lobo) got our D. Phils with Lionel in Oxford, another (Manuel Nunes da Ponte) did his post-doc here and many others spent their Summer holidays working in this laboratory under Lionel's guidance, or profited from his lectures in Lisbon. Now my research group in Lisbon is a large umbrella embracing eighteen people, all involved in thermodynamics research. Six doctorates have been obtained there, a national record, and soon another generation will rise. I got my D. Phil. with Lionel, Manuel got his with me, and already he has a student completing her Ph. D. with him. This, which may be trivial in a scientifically developed country, is also a unique achievement in Portugal. Directly or indirectly the Staveley school of thermodynamics is alive in four Portuguese universities — the three universities of Lisbon (Classical, Technical and New) and Coimbra university — where six of us who teach there can claim direct scientific descendance from him. An impressive success story in a country where, out of fourteen universities, only seven have chemistry departments.

In a fortnight Lionel will make his eighth trip to Portugal, to lecture in a Summer School organized by yet another university, the university of Oporto. No mere coincidence here for Lionel Staveley was instrumental in the setting-up of graduate courses in Portuguese universities back in 1975, when he went as a Visiting Professor to teach at the *first* graduate school of Physical Inorganic Chemistry, organized by the recently created New University of Lisbon. For all these reasons it was highly appropriate that the organizing committee of the International Conferences on Thermodynamics of Solutions of Non--Electrolytes (a joint venture of the Chemical Societies of France, Spain and Portugal) should honour him by creating the Lionel Staveley Lecture, and that he should have been invited to deliver the first one at the II Conference, in Lisbon, in March, 1982.

I should like to emphasize that the success of thermodynamics in Portugal has nothing or very little to do with me and my Portuguese colleagues and a lot to do with Lionel. Other young Portuguese scientists, like me in 1966, also went abroad and dutifully got their PhDs, and yet, in many cases, very little or nothing came out of it. The exception seems to be what has already been called in my country, the *Oxford School of Chemistry in Lisbon*.

3 — LIONEL'S APPROACH

The success of thermodynamical research in Portugal and, to a lesser extent, in other countries is entirely due to Lionel. To his wonderful qualities as a man, to the humanity of his approach to science, to his original way of picking up problems and of solving them, to the beauty of his scientific thinking which is, at once, simply elegant and elegantly simple.

I had all this confirmed by another foreign collaborator of Lionel's, Dr. Andrzej F. Kozdon, from the Polish Committee for Standardization and Measures in Warsaw, who in a recent letter to me spoke with nostalgic gratitude of the "help, encouragement, attention to detail" that he always got from Lionel during his year at Oxford in 1972-3. Dr. Kozdon had wanted to work in Lionel's laboratory ever since he came across Lionel's classical paper (with Betty Spice) on the excess volumes of diluted alcohol solutions. He was also puzzled by the ingenuity of Lionel's ideas when it came to designing a suitable apparatus for measuring an important property. And he wrote: "In an age of the most sophisticated electronic equipment I formerly thought that his [Lionel's] thermostatting devices, for instance, were rather primitive, but after having used them I must admit that they gave more reliable reference conditions than anything else I have used". Dr. Kozdon was referring, for instance, to the triple-point cryostat described by Bill Streett in his paper at this meeting.

Dr. Kozdon also reminded me in his letter of Lionel's *daily* interest in the work of his collaborators, and the way we were individually greeted, usually around coffee time, after he had done the morning's teaching in New College, with an almost reticent, but genuine concern, ''How are things?''. And he never left in the evening without checking with each one of us on the day's progress. Dr. Kozdon's words also sum it up — ''a classical but open-minded gentleman''.

Keith Gubbins spoke about the impact of Lionel's work on the development of theories. I should like to stress his use of thermodynamics as a ludic instrument, a source of intellectual pleasure as witnessed, for instance, in the selection of suitable molecules and mixtures as models, windows into the harsh complexities of the real world, of which Graham Saville spoke this morning. Then there is the didactic, pedagogical nature of the problems he tackled, never caring whether they were fashionable, simply that they were important bridges to the islands of knowledge. Much of his work was done on a shoe-string budget, just by the sheer inventiveness of brainpower. All this made Lionel's approach to science particularlly suited to a country, like mine, with really no scientific tradition. Students are attracted by the joys of designing and building an apparatus from scratch, still a way of life in experimental thermodynamics; and they are kept interested by the pride one feels in obtaining accurate results. One of the first things I learnt from Lionel is that if something is worth doing, it should be done as well as possible. I hope that I have also profited from his modesty and the economy of his thinking, that somehow these admirable qualities have rubbed off on me — like not publishing two papers when one will do.

Whatever I have achieved scientifically I owe it to him. Through him I met Bill Streett, Keith Gubbins, Mike Hiza and many others, and thus successful collaborations and invaluable friendships began. Lionel Staveley has taught me how to think and, I hope, I am a better person because of him.

I should like to end with a thankyou, for myself, on behalf of the Portuguese Chemical Society whose President asked me to publicly express the debt of gratitude of Thermodynamics and Chemistry in general, in Portugal, to the action and example of Lionel Staveley:

''We, that are young, shall never see so much nor live so long''.

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LIONEL STAVELEY: his wider influences

The meeting today has been hearing mainly about Lionel Staveley's contributions to science through his work on the thermodynamics of fluids and fluid mixtures, and his studies of the solid state. Professor Calado has also told us something about his influence on the development of thermodynamic research in Portugal during the last decade or so. But Lionel's influence on science and the scientific community goes much further than this. Some hundreds of the undergraduates he has tutored across the whole spectrum of inorganic and physical chemistry are now part of the scientific, educational and technical community of many countries. In addition the dozens of research workers he has trained have played an important role in the development of experimental thermodynamics.

My own acquaintance with Lionel goes back to the early years of the war when we were both associated with Hinshelwood's team working on respirator charcoals. I was concerned very much with the dirty end of the work — carbonising coal briquettes, activating the product with steam and studying its adsorptive properties under flow conditions. Lionel was concerned with somewhat more fundamental problems. Several of us, in association with Hinshelwood, had derived equations which represented adequately the behaviour of charcoal columns in adsorption.

Of equal importance however was the study of the redistribution of adsorbed species in the column, and the subsequent desorption when clean air was drawn through the column — the so-called retentivity problem. Lionel had a group working on this latter aspect which contributed both to the experimental study and the theoretical interpretation of the observed phenomena. Later work for the Ministry of Supply with which I was no longer associated was devoted to research into pyrotechnics — specifically the kinetics and thermochemistry of the burning of mixtures of an oxidising and an oxidisable solid. Although the problems were severely practical and not conducive to precise and reproducible experiment, he and John Spice succeeded in placing the work on a rational theoretical basis.

This contact with the problems of solids and their reactivity, and with calorimetry together with his period in Germany just before the war no doubt influenced his decision after the war not to return to his earlier studies of gas kinetics, but to embark on a new area of research concerned with the solid

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state. In particular he chose to study the thermodynamic properties as determined by low temperature calorimetry. To this was added, more or less simultaneously, work on liquids and liquid mixtures. We have heard today accounts of the way in which these two main streams of Lionel's work have evolved and developed in the last thirty-odd years. I would like to add two comments. The first concerns his contributions to our knowledge of the hysteresis in phase transitions in solids. Hysteresis phenomena are not easy to study, since account has to be taken not only of the current values of independent variables, in this case the temperature, but also of the whole history of the system under investigation. The width of the hysteresis loop in solid transitions is also dependent on the particle size of the solid, an aspect which he investigated. He also showed how sensitive the phenomenon is to isotopic substitution of deuterium for hydrogen in the ammonium halides. In collaboration with Thomas he identified the presence of hysteresis with those parts of a solid transition which occur isothermally, and by studying the kinetics of the phase changes showed that in some instances the change once initiated continued isothermally to completion, whereas in others the rate passed through a maximum. Although an exact quantitative theory is difficult to formulate, Staveley and Thomas were able to account for many of their results in terms of a domain model in which the transition points were controlled by internal stress within the domain. Somewhat later Norden and I used very similar ideas in the interpretation of the hysteresis observed in the adsorption of hydrogen by palladium.

The other interesting feature which Lionel and his colleagues found was that the width of the hysteresis loop could be reduced, but not eliminated by successive cycling through the transition. They used a dilatometric method confining the solid with a liquid in which it is insoluble. Some years later we found in Bristol that in the case of the 32°C transition of ammonium nitrate a similar contraction occurred, but that if the confining liquid was a saturated aqueous solution of ammonium nitrate, then after four or five cycles a reversible state could be reached in which the direction of the phase change could be reversed by changing the temperature by a few thousandths of a degree. Lionel's work had shown the importance both of nucleation and growth processes in hysteresis phenomena, and our own data would certainly confirm that view. It is perhaps a pity that Lionel did pursue this work further, although from the thermodynamic point of view hysteresis is a nuisance and to be avoided wherever possible. It is easy to see that it was more satisfying and possibly more valuable scientifically to return to a precise thermodynamic study of simpler phase transitions. But Lionel's work on the hysteresis in solid phase transitions still sets a standard not often achieved in later work.

My second comment is in a somewhat different vein, and relates to the way in which Lionel's work on liquids has evolved. As already pointed out this morning he began with what most of us regarded, thirty years ago, as rather simple liquids — namely of small organic molecules and their mixtures. Such systems were relatively easy to study using more or less conventional techniques. However, when these looked as though they might prove difficult to understand in detail, he moved to quasi-spherical molecules, and then in an endeavour to reach ultimate simplification, to condensed gases and finally to mixtures of rare gas liquids. In this context it is interesting to note as Keith Gubbins showed that, with a few exceptions, his work on liquid mixtures since 1970 has dealt with molecules no more complicated than rare gas liquids, nitrogen, oxygen, the hydrogen halides and simple hydrocarbons up to propane.

In this evolution we see — whether consciously or not I am not sure — efforts by the experimentalist to reach out to make contact with the theoretician who 20-30 years ago was able only to provide well founded theories of mixtures of spherical molecules of equal size. This kind of development, in which attempts are made at the experimental level to match the models developed by theoreticians, seems to be a pattern which is becoming familiar in other areas. In effect, the rate at which theoretical models can be developed for real systems of polyatomic molecules is slower than one might have predicted optimistically a couple of decades ago. Consequently it is of increasing importance that the experimentalist should be called upon to make the major contribution to bridging the gap by working with molecules of increasing simplicity. And this is a challenge which Lionel took up which such conspicuous success as was shown this morning. The extent of this achievement is not always realised. For while, in general, the simpler the molecule the easier it is to treat theoretically, the problems of planning meaningful experiments, and the difficulties in their practical realisation, increase enormously as one moves to simpler molecules. I well remember my feelings of admiration and envy or hearing — it must have been in the early 1950's — that Lionel was investigating the thermodynamics of liquid mixtures of methane and carbon monoxide while most of the rest of us working on liquid mixtures were toiling away with organic mixtures which could be studied in a more easily handled temperature range. One of the most important aspects of Lionel's research was his pioneering work on the development of techniques for achieving high precision in measurements which others at that time hesitated to attempt. This has been said several times today — it bears repeating once again. I wonder whether this point is sufficiently appreciated by theoreticians generally. Those here today, of course, are well aware of the magnitude of Lionel's achievement in this area; but I suspect that too many theoreticians underestimate the difficulties faced by the experimentalist who tries to provide them with data on systems which approach the idealised nature of most theoretical models. Too often they take for granted that the experimentalist will produce data on any model system they conjure up. A particularly fruitful situation is that in which the experimentalist, having succeeded in reproducing in the laboratory systems close to theoretical models, is able to participate activily in the interpretation of his work in partnership with theoreticians — this Lionel has been able to do on many occasions and we have been given examples of his collaboration.

Work of the calibre of that produced in Lionel's laboratory cannot fail to attract international attention. Likewise the man behind such work is bound to be called upon to contribute to international scientific affairs. In Lionel's case this began with his involvement in the work of IUPAC, and in particular his membership of the Commission on Data and Standards of which he was Chairman during the period 1963-67. There is no doubt that this Commission was one which exerted considerable influence on the scientific community, not least through the Report which Lionel edited on the "Characterisation of Chemical Purity".

Although he served on the Council of the Chemical Society in the late 1950's, Lionel did not become deeply involved in the formal organisation of science in this country. Yet he has exerted his influence widely among the practitioners who like himself are more interested in getting a job done than sitting on committees. For many years he was — as it was put to me recently — the Father figure of the Dense Fluids and Mixtures Group: this informal but very active gathering looked to him for support and guidance over many years until it merged with the Statistical Mechanics and Thermodynamics Group of the Faraday Division of the Chemical Society. Likewise the Experimental Thermodynamics Conference of which he has served as Chairman owes a great deal to his wise advice and guidance. It is thus through his unobtrusive leadership that he has been able to exert such a significant influence on the development of thermodynamics. In particular he has provided wise and inspiring leadership for several generations of younger scientists in this field.

With the increasing international recognition of the high standards of thermodynamic work carried out here in Oxford it was inevitable that there should have been both a succession of research scientists from overseas to learn the secrets of work of this calibre, and invitations to visit overseas laboratories. Among those who spent time here as visiting scientists were Blinowska from Poland, Fritz Stoeckli from Switzerland, and as we have heard this afternoon, Calado, Nunes da Ponte, Soares and Lobo from Portugal. In each case Lionel has influenced their scientific careers, and he development of thermodynamics in the countries they represented.

Of equal importance, as will have been amply demonstrated today, have been the periods which Lionel has spent in the U.S.A. as visiting Professor: here not only has he given much, but through the friends and collaborators which have resulted from such visits has flowed some of the most significant collaborative work of his scientific career.

The study of thermodynamics has in the last few decades become increasingly unfashionable compared with the study of, and research in, the newer powerful spectroscopic techniques which tend to be increasingly described (in this country at least) as chemical physics, or even — sometimes quite incongruously — as theoretical chemistry. This movement of pure scientists away from is after all one of the foundation stones of physical chemistry is greatly to be regretted.

Experimental thermodynamics has tended world-wide to become more concentrated in Departments of Chemical Engineering, and the emphasis of theoretical work has swung towards the devising of schemes for the correlation of experimental data and of methods for the prediction of the thermodynamic properties of mixtures from a knowledge of the properties of the pure components making use of a variety of empirical rules. As these predictive schemes have developed in range and in power there has I think been an increasing tendency in many industrial and government circles to overlook the need for primary experimental data of high precision, and to suppose that an accuracy adquate for many practical purposes can be achieved on the basis of the already developed correlation methods. What seems not be appreciated is that if improved correlation and predictive schemes are to be developed — and many of them are really of somewhat doubtful general applicability — then experimental data of unquestionable reliability must continue to be provided. Yet we have seen both the decreased funding of fundamental experimantal work and the closing down of Government laboratories concerned with thermodynamic measurements not only in the U.K. but also in the U.S.A. and elsewhere.

It has therefore been of great importance that during this decline in experimental thermodynamics, Lionel's laboratory has continued its vigorous programme.

From this point of view, therefore, we must greatly regret Lionel's retirement which will be a considerable loss to experimental thermodynamics in the U.K.; and this at a time when already so many centres have declined or been closed down. But one should not take such a narrow view. We must seek a much wider perspective, since what matters for science as a whole is the overall world picture. And here we see that Lionel has been responsible for the training of many overseas scientists, and for the initiation of work in many other countries. In particular we have heard today that much of his equipment has been transferred to Portugal where one is confident much work of the kind for which his laboratory has been rightly famous will be continued and developed. So that although Lionel will, himself, withdraw from active experimental thermodynamic work and devote himself to other pursuits, the enthusiasm which he has inspired in others will ensure the continuation of work of the quality with which his name has always been associated in many countries. One prediction which can be made with absolute confidence is that decades hence Lionel Staveley's experimental data will remain as examples of standards of excellence to be strived for but which I believe will rarely be matched, let alone surpassed.

Today's symposium has amply demonstrated the high regard in which Lionel is held by the Invisible College of Thermodynamicists, of which such a representative group are gathered together today to honour him. In saying farewell to him as a practising scientist we both look on the extraordinary amount of superb work he has contributed to our subject, and looking forward extend to him our warmest good wishes for his retirement which we hope will be both long and happy.

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SOME RANDOM REFLECTIONS OF A RETIRING THERMODYNAMICIST

Let me begin by expressing my admiration for the excellence of the lectures we have had today, and my deep appreciation of the trouble and effort that have gone into their preparation. I have a feeling of guilt, however, in that the speakers have said so many over-generous things about me, and so little — virtually nothing, in fact — about their own valuable contributions.

When I came to Oxford many years ago to read chemistry, I had the great good fortune to have as my tutor a very remarkable man. He was later to become Professor Sir Cyril Hinshelwood, but at that time he was plain Mr. Hinshelwood, known to all his pupils and friends simply as "Hinsh". He it was who introduced me to chemical thermodynamics. I still remember the tutorial in his room in my first term at Oxford at which he said "You might read a little book on thermodynamics, concocted by me, which you will find in the College library, from the sales of which" (he added drily) "I don't seem to profit very much". The book is something of a curiosity nowadays, having become somewhat out-of-date with regard to the symbolism and terminology, and indeed the approach to the subject. But it has in it some very interesting and shrewd observations on the nature and meaning of thermodynamics, and although I was only just eighteen when I read it, it made me aware of the power and elegance of the subject. I still remember Hinsh making the point that the second law of thermodynamics is not, in a literal sense, absolutely true, but that it is stating something which, for macroscopic systems, is so probable that one can forget about the possibility of any breach of the law. I seem to remember that in this connection he remarked that it is conceivable that the Andes were raised by a sudden, enormous violation of the second law of thermodynamics, but that it is exceedingly unlikely that this actually happened.

My first research was not done in thermodynamics, however, but in the field of reaction kinetics with Hinsh. My career as a thermodynamicist began when I went to work with Clusius in Munich in 1937-1938. These were traumatic years, as the war clouds were gathering and the writing on the wall was all too evident. Nevertheless, I got a great deal out of this year with Clusius. A year or so before I went to Munich, a friend of mine, Dr. James Lambert, whose name will be known to many of you, had gone to Germany to work with another famous chemist, Eucken, at Göttingen. James Lambert had also been a pupil of Hinshelwood and he too had started his research in reaction kinetics. He told me that he hadn't been in Göttingen very long before Eucken, who was a great chemist but something of a martinet, I think, said to him "We're not doing any reaction kinetics here, you know. We work precisely. (*Wir arbeiten genau*)!" So having been warned about this, I left for Munich prepared to work as *genau* as I possibly could.

I began by measuring the triple-point pressures of a number of condensed gases. Clusius had formed the view that substances which are isotopic mixtures might melt over a range of temperature, small though this might be, and that accordingly their triple-point pressures might change as melting proceeded. Of the substances I studied, only xenon appeared to show a measurable effect of this kind, and although, with hindsight, this was almost certainly due to impurities, Clusius suggested that I should try and effect some separation of the xenon isotopes by fractionating the liquid. The attempt failed, but elsewhere in the laboratory at this time Clusius was developing with Dickel the famous thermal diffusion column with which spectacular isotopic separations were later achieved.

So I didn't in fact do any low-temperature calorimetry with Clusius, but I saw it going for the first time and I developed an interest in it, and an interest too in the kind of systems that were being studied in his laboratory, which were simple condensed gases. Many of these, as you know, have both ordered and disordered crystalline forms, and this is really, I think, where my interest in the subject of disorder in crystals started.

The word genealogy has been used more than once today in a scientific sense. Well, Clusius had himself been a pupil of Eucken, and Eucken had been a disciple of the great Nernst who was of the founding fathers of low-temperature physics and chemistry, so that I was proud to feel that I fitted into a sort of genealogical sequence, namely

Nernst ⟶ Eucken ⟶ Clusius ⟶ Staveley.

A few years ago I was momentarily perplexed when Professor Alan Leadbetter said to me "I think of you as my cryogenic grandfather", until I realized that what he had in mind was a continuation of this sequence, I having had Dr. John Spice as one of my pupils, who in turn, while at Liverpool University, had Alan Leadbetter as a pupil.

I only met Clusius once after the war, when he came to Oxford to give a lecture. This was when he had recently moved to Zürich. I recall him explaining to me why he had decided to leave Germany for Switzerland (though I hadn't asked him for an explanation), and that one of the reasons he gave was not wanting to be on the losing side in a world war for the third time.

When I have had the privilege and good fortune to get to know distinguished scientists with interests similar to my own, I have sometimes asked them if they had any fundamental beliefs which governed or influenced the course of their research work. I remember, for example, putting this question to Professor Simon (Sir Francis Simon), whose distinguished career began in Germany and ended at the Clarendon Laboratory in Oxford. His answer was, yes, he'd always believed that any experiment had been worthwhile if it had suggested another worthwhile experiment. Just before I left Munich in 1938 I asked Clusius the same thing, and after reflection he replied that he'd always had in mind that if you measured suitable physical properties accurately enough, you might come across some new, important qualitative truth. One can certainly find cases of this in the development of the physical sciences. An example of where precise thermodynamic measurements were undoubtedly linked with a matter of very basic importance can be taken from the work of a great man and chemist, W. F. Giauque, for whom, I may say, my admiration verges on idolatry. He kept hydrogen liquid for nearly two hundred days, and found that the triple-point pressure of the sample then seemed to be 0.4 mmHg less than that of "ordinary" hydrogen, corresponding to a change in the melting-point of only 0.04 K. The last man to make exaggerated claims, he said of this in his paper "We do not feel that we can claim with certainty that a difference exists, but the apparent difference is beyond the limit of any error of which we are aware", (The observed change was, of course, due to the spontaneous transformation of ortho- into para-hydrogen).

I think, however, that those engaged in quantitative experimental work can run the risk of becoming too preoccupied with precision for precision's sake, in that their outlook can then become rather sterile and the real significance of the quantities being measured can be relegated to a subordinate position. I would like to feel that in my own work precision has been a means to an end, and not an end in itself. I must confess that my research interests have often put me in the position where a fairly high degree of precision was essential, because the quantity that mattered, namely that on which we hoped to base some conclusion about the system under study, was really a relatively small difference between two much larger, measurable quantities. Professor Weir, for example, referred to work designed to discover whether a particular crystal retains entropy, and hence has frozen-in disorder, at the absolute zero. Any residual entropy emerges as the difference between the calorimetric entropy and the "true" entropy as determined by a study of a suitable equilibrium, and it may be only of the order of one per cent of these two quantities. The position has been much the same in our experimental work on simple liquid mixtures, where in effect one had to measure the relatively small differences between the actual thermodynamic properties of the liquid mixture and those it would have if the mixture were ideal.

I have already referred to my early association with Professor Hinshelwood. By the time he retired, he had received almost every honour a scientist in Britain can get — a Nobel prize, a knighthood, the Order of Merit (a very high-ranking honour), President of the Chemical Society, President of the Royal Society — the lot, as you might say. I remember that, shortly before he retired, he gave a lecture to the University Chemical Society, which in Oxford is called the Alembic Club. He began without any preamble by saying that science is simply a matter of asking yourself questions about the physical world and trying to think up ways and means of getting some sort of answer to those questions. He went on to say that it had nothing whatever to do with the economic, social, financial or other kinds of advantage that you might hope to gain from your activities. I like to think that my own investigations, for what they may be worth, have been prompted simply by intellectual curiosity. I have thought of myself as using just one approach among many others which might make a helpful contribution to the solution of certain problems. I feel that the experimental thermodynamicist should avoid working in isolation. He should rather consider his findings whenever possible in relation to the information provided by other techniques, and look upon his own approach as being neither superior to — nor, indeed, inferior to — other techniques which can be applied to the problem in hand. As a thermodynamicist, I have never felt that I was dealing with a declining or vanishing subject, knowing that thermodynamics will never be out of date so long as chemists and physicists continue to be concerned with matter in bulk. I have long been aware, however, that young chemists looking for a research project tend to think of experimental thermodynamics as being somewhat old-fashioned, and as lacking the glamour of the latest spectroscopic techniques and so on. This may have contributed to the apparent shortage of research students in some thermodynamics laboratories, as a result of which — and the point has been made by other speakers today — the demand for thermodynamic data now exceeds the available supply. Right up to the time my calorimeters closed down, people would write to me, or colleagues would drop in, to ask "Could you possibly measure the heat capacity of such and such a compound — I think it's a very interesting substance?" And very often I'd have to say "I'm sorry, but I don't have the manpower at the moment".

I have never really had any doubts about the permanence of the subject to which I've devoted a considerable part of my professional career. If at any time I'd needed comfort and reassurance, I could have found it in a comment by the great Einstein in his autobiographical notes. Speaking of classical thermodynamics, he said "It is the only theory of universal content, concerning which I am convinced that, within the framework of the applicability of its basic concepts, it will never be overthrown".

It is quite impossible for me to thank adequately all those who have contributed in so many ways to this Symposium. I can only say that I feel tremendous pride and great humility that so much trouble has been taken to organize it, and that so many people have come, some of them from great distances, to take part in it.