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## THE EXPERIMENTAL CRYOGENIC CALORIMETRIC CRAFT OF LIONEL STAVELEY

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### 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 propagated 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

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 assignment.

## 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

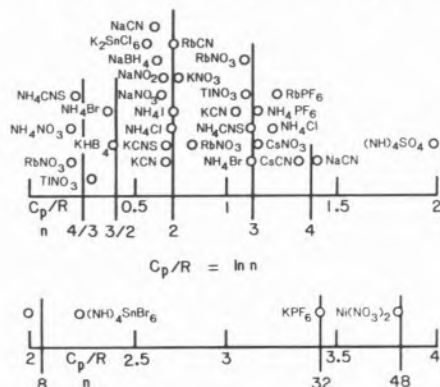


Fig. 1

Entropies of transition on a scale  $R \ln N$  ( $N$  = number of equivalent positions of a globular ion)

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 am 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

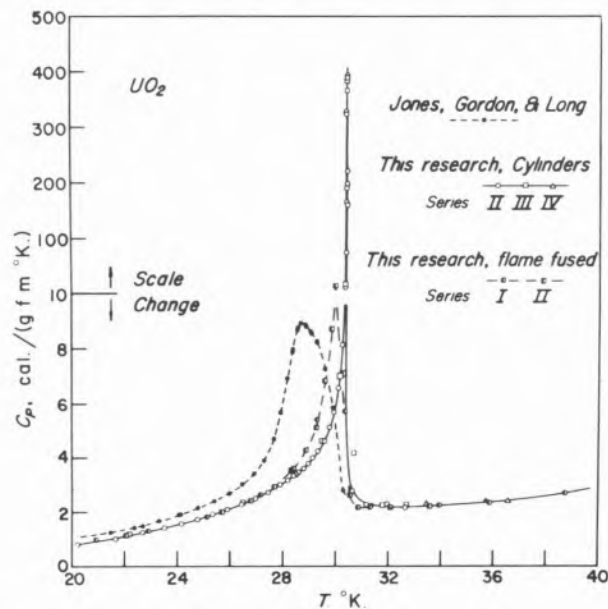


Fig. 2

The heat capacity of  $\text{UO}_2$  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 rami-

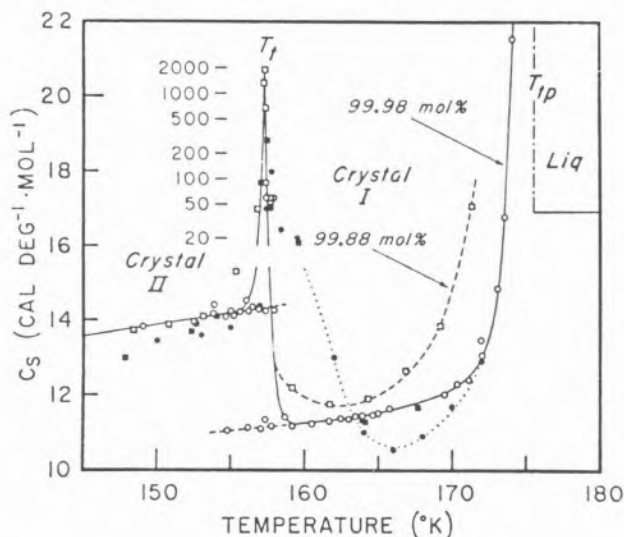


Fig. 3

The heat capacity of methanol over the transition and melting regions. Data for Sample I and II from [4] are represented by  $\circ$  and  $\square$ , those of KELLEY by  $\blacksquare$ , and those of STAVELEY and GUPTA from [7] by  $\bullet$

fications 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. 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

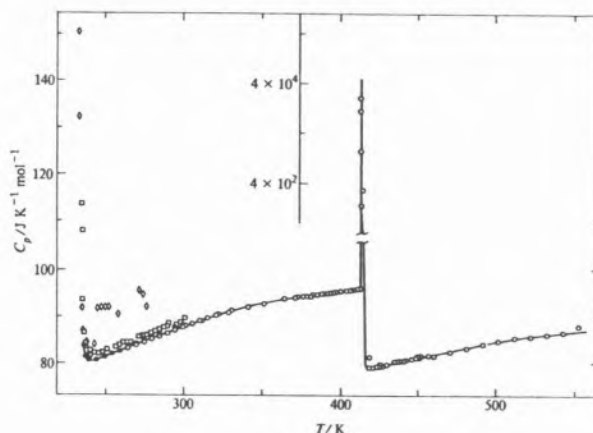


Fig. 4

Molar heat capacity of  $\text{NH}_4\text{Br}$ .  $\diamond$ , Simon, von Simson, and Ruhemann;  $\blacksquare$ , Cole, Sorai, Suga, and Seki; and  $\circ$ , that of reference [4]

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.

### 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 *thermophysics* 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 calo-

rimeters. 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 and his co-workers [4] on

the isotopic  $\text{CH}_3\text{OH}$  system. The cryostat itself, 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

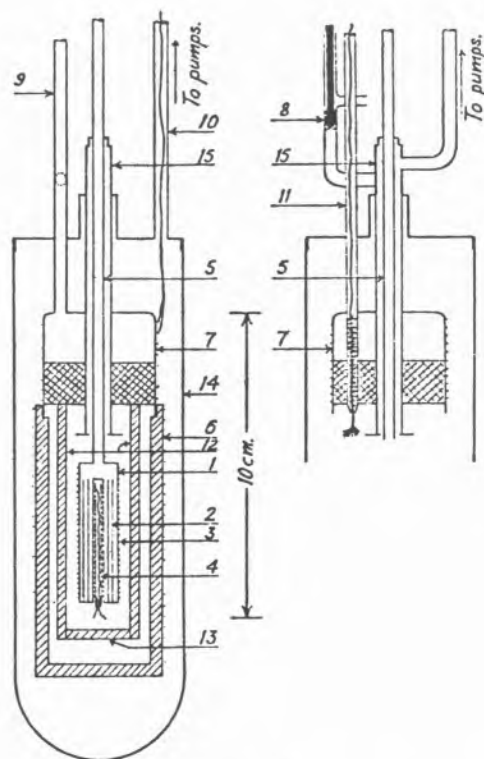


Fig. 5

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  $^3\text{He}$  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

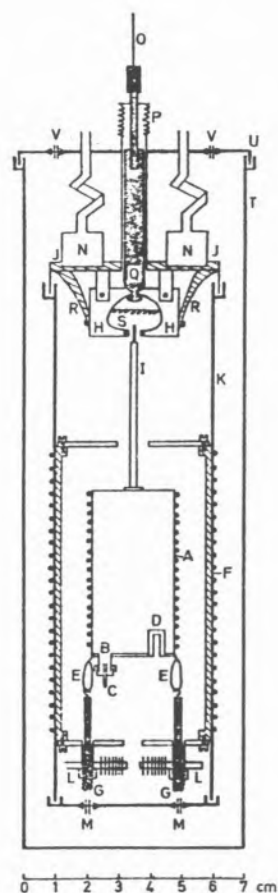


Fig. 6

(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]

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.

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

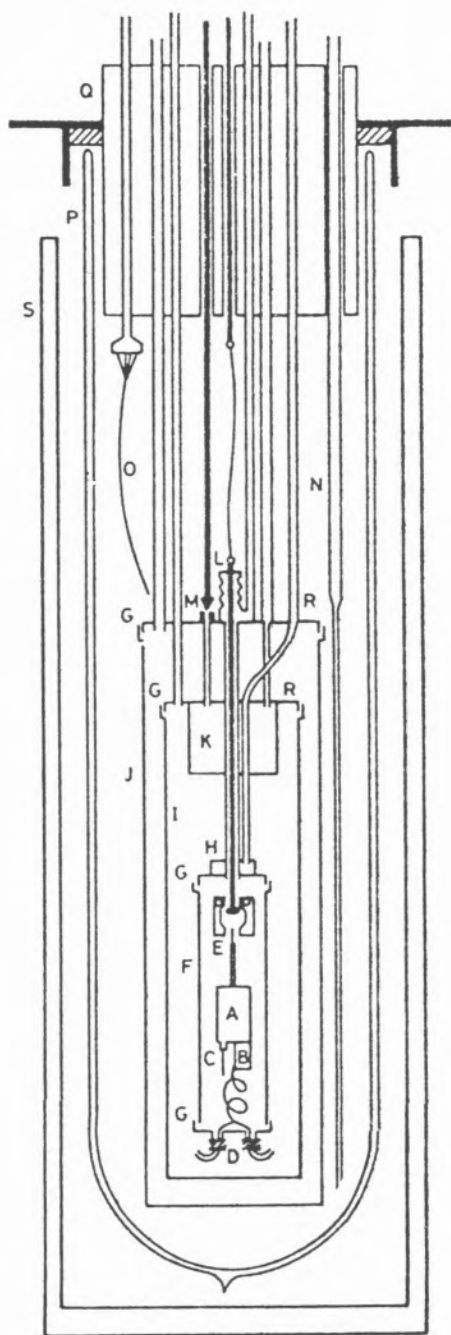


Fig. 7

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)  $^3\text{He}$  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  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  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 stannihallides [13]. This work, like the other papers, is characterized by a thorough, meticulous, experimental study of carefully selected "key" compounds. Despite 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  $\text{NH}_4\text{BF}_3$  [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.

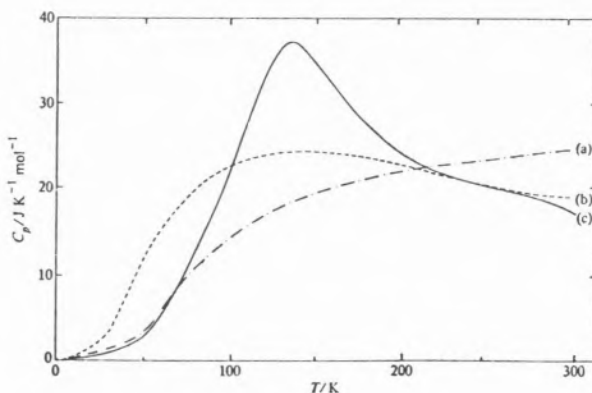


Fig. 8

Excess heat capacity of  $\text{NH}_4\text{BF}_3$ . Curve (a), —,  $C_p$  of a three-dimensional Einstein oscillator of wavenumber  $190\text{ cm}^{-1}$ ; curve (b), ---,  $C_p$  for a three-dimensional restricted rotator with a potential-barrier height of  $4.2\text{ kJ mol}^{-1}$ ; curve (c) —, experimental values of the quantity  $\{C_p(\text{NH}_4\text{BF}_3) - C_p(\text{KBF}_4) - C(\text{NH}_4^+, \text{int})\}$ . 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  $\pi$ - $\pi$  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 findings 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.

## ACKNOWLEDGMENT

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