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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.