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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 The book is something of a curiosity nowadays, having become somewhat out-of-date with regard to the symbolism and terminology, and indeed the approach to the subject.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 \longrightarrow Eucken \longrightarrow Clusius \longrightarrow 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. Giaque, 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.