



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 is presented, to illustrate 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 scientific 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 thermodynamic 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 determine 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

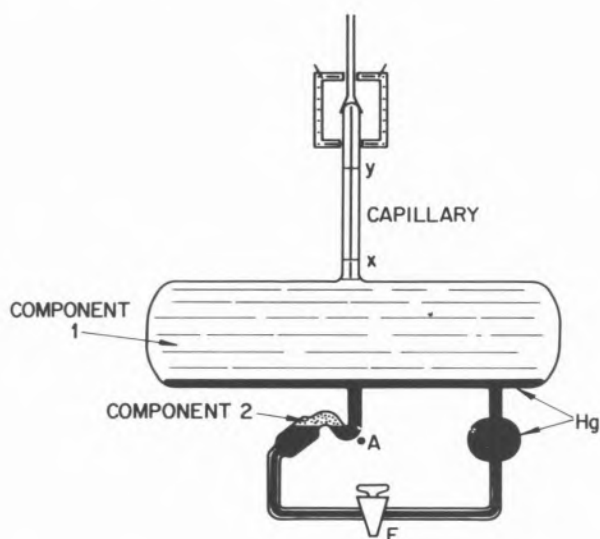


Fig. 1

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 tempera-

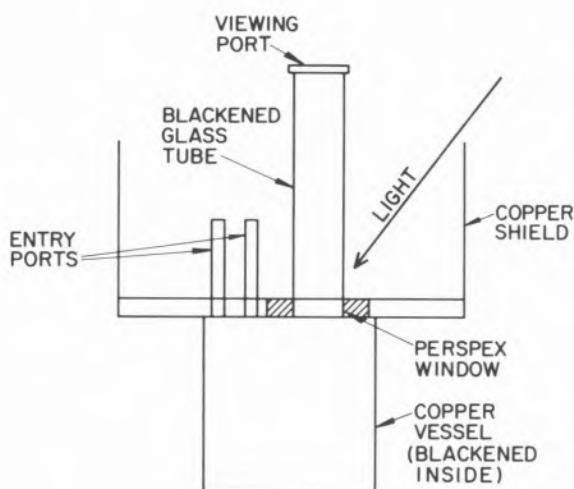


Fig. 2

Apparatus for studying supercooling of drops molecular liquids [3]

ture 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.

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 pycnometer 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 pycnometer and observing temperatures, pressures, and meniscus heights, it is possible to measure the following mixture properties (see reference 4 for details):

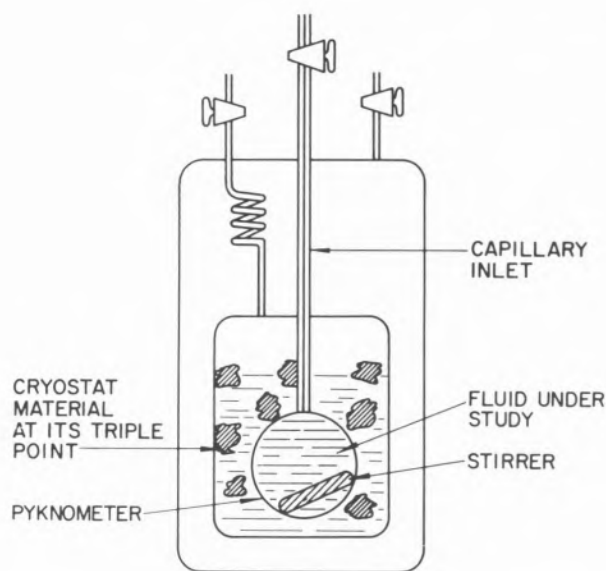


Fig. 3

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 (≤ 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

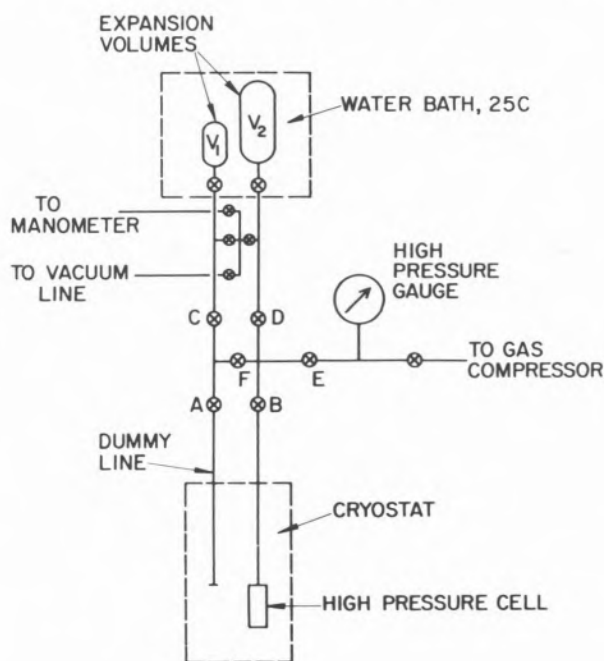


Fig. 4

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

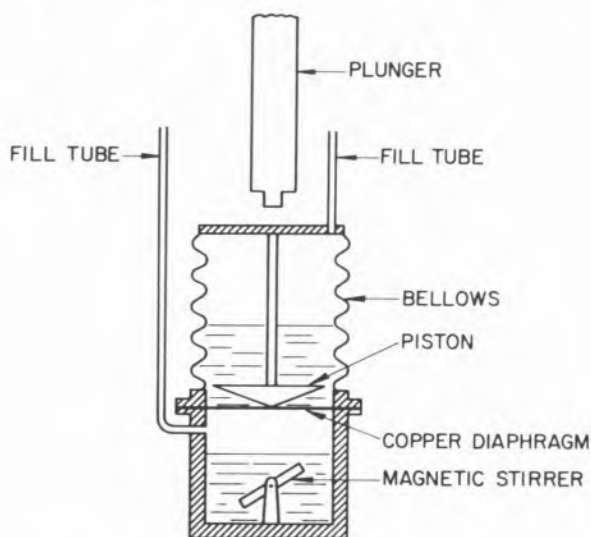


Fig. 5
Calorimeter for measuring the heat of mixing of liquefied gases [15]

(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 .

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 temperature changes of ± 0.001 K through a platinum resistance thermometer, and supplies pre-

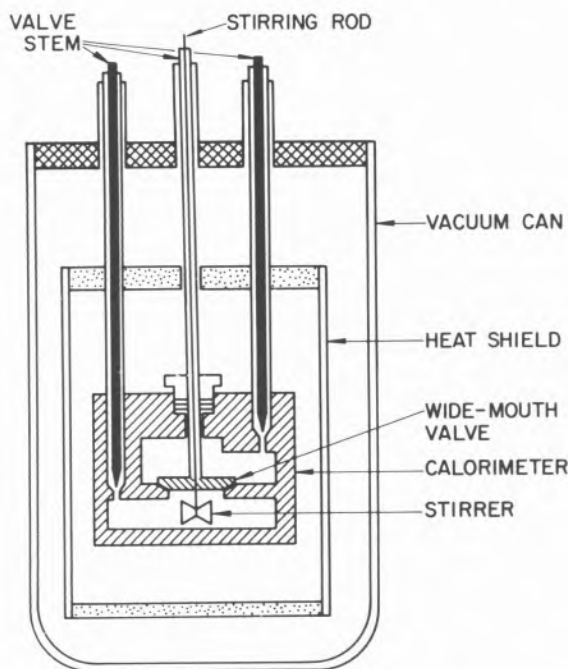


Fig. 6

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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