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Thermophysical Property Measurements: The Journey from Accuracy to Fitness for Purpose[1]

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Until the 1960s much of the experimental work on the thermophysical properties of fluids was devoted to the development of methods for the measurement of the properties of simple fluids under moderate temperatures and pressures. By the end of the 1960s a few methods had emerged that had both a rigorous mathematical description of the experimental method and technical innovation to render measurements precise enough to rigorously test theories of fluids for both gas and liquid phases. These studies demonstrated that, for the gas phase at least, the theories were exceedingly reliable and led to physical insight into simple molecular interactions. The thesis of this paper is, after those early successes, there has been a divergence of experimental effort from the earlier thrust and, in the future, there needs to be focus on *in situ* measurement of properties for process fluids. These arguments are based

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upon the balance between the uncertainty of the results and their utility and economic value as well as upon technical developments, which have provided reliable and robust sensors of properties. The benefits accrued from accurate measurements on a few materials to validate predictions of the physical properties, for a much wider set of mixtures over a wide range of conditions, are much less relevant for most engineering purposes. However, there remain some special areas of science where high accuracy measurements are an important goal.

KEY WORDS: density; electrically conducting; intermolecular pair potentials; MEMS; optical; sound speed; thermal conductivity; vibrating wire; viscosity.

1. INTRODUCTION

The opportunity for one of us (WAW) to deliver this keynote lecture to THERMOInternational 2006 and subsequently to record this written version of it in the International Journal of Thermophysics with our co-authors is much appreciated. We are all grateful to the organizers for their invitation. The paper gives a personal view of the situation with regard to research and its dissemination and application in the general areas of thermophysics and chemical thermodynamics. Necessarily, because of our own background, We draw upon the fields of fluid thermophysics and, in particular, the field of transport properties of fluids for our background examples, but the points made are representative in general of other related topics.

The overall theme of the lecture is a journey from the middle of the twentieth century to the present day, recognizing phases of development in the field of thermophysical properties with an emphasis upon measurement. The journey begins around 1950 with what we call “Base Camp” at which accurate measurement techniques are developed for the first time. This development period extended to about 1970 and provided measurements on simple fluids that demonstrated the predictive power of theories and was a success; this we will describe in detail. In the next phase, which we call “Frontier Expansion,” the same experimental techniques, with perhaps slight modification, were applied to a greater range of fluids containing chemically more complex molecules over a larger range of temperatures and pressures. This extension involved a modest compromise on the precision of the measurement in some cases, but not all, and the results were in general scientifically successful.

From 1986 to 1998 we define the “Plateau of Thermophysics.” That is, the successes of the previous decade were enjoyed with the same measurement techniques but the applications were limited in terms of the fluids studied and the thermodynamic conditions covered. Essentially the field had stagnated and there was little new development in the mainstream. On the other hand, within that same period, many sidetracks were developed. Here the term ‘sidetracks’ is not used in a pejorative sense because we include areas that are important, particularly perhaps from the point of view of physics or engineering, but are essentially diversions from the main thrust of the field. That main thrust is taken to be towards the development of thermophysical properties to serve the purpose of the design and operation of engineering processes and structures. Examples of sidetracks might be the interest generated in the properties of novel refrigerants that were less ozone depleting that began around the time of the Montreal Protocol [1]. A second example is the study of properties of fluids near the critical point for which there was only a developing theory [2–4]. Somewhere in this period it seems that the field begins to be directionless and there is much repetition of what has been done before in terms of fluid conditions with marginal improvements in experimental techniques but with no real fundamental progress in our ability to solve the problems of physics or indeed satisfy engineering demands; for example, that might arise in the oil industry where the chemical composition of the mixture is not well known, indeed, probably undeterminable.

The final period extends from about 2000 into the future, where the basic thesis of our paper is that thermophysics will become increasingly dominated by applications where the specification of particular problems, whether they be physics or engineering, all dominate the work, rather than the thermophysics dominating for its own sake [5]. That can mean, and we think will mean, in some cases, a high demand for *in situ* measurements of thermophysical properties, possibly for fluids for which the chemical composition is ill-characterized in aggressive environments or indeed, it might be the fluid itself that is chemically aggressive. As a consequence, the accuracy of the property measurement will be of secondary importance, but it will always need to be known. Thus, measurements may be of poor accuracy but the accuracy achieved must be known and selected to be consistent with the intended use of the results. Consequently, the instruments used will require working equations, founded on the principles of physics that provide the link between what is measured and the required thermophysical property. This leads to the concept of an accuracy of a measurement that is ‘fit for purpose’ that will be developed later in the paper.

2. BASE CAMP

We begin the journey in around 1950 with the search, led by physicists, for the force potentials between monatomic gases and simple diatomic systems. The motivations for this work originated with the kinetic theory of Chapman and Enskog [6,7], which relates the transport properties of the dilute gases to the pair potential, and to the same potential the relationship between equilibrium statistical mechanics and the second virial coefficient. Armed with this information, it was possible to demonstrate that the measurements were mutually inconsistent and was also inconsistent with the results obtained from molecular beam-scattering experiments [8]. This realization prompted the development of new techniques for the measurement of the viscosity of gases as well as their density and, indeed, other thermodynamic properties.

Between 1950 and 1970 considerable effort was expended to design instruments for the precise and accurate measurement of the viscosity of dilute gases. This work was led by Joseph Kestin of Brown University and involved the development of instruments in which the decay of the torsional oscillations of bodies of revolution suspended within or containing viscous fluids was observed. An instrument of this type is illustrated in Fig. 1 which shows an oscillating disk viscometer of the 1960s for which an exact theory had been worked out in the previous decade [9]. This particular instrument operated with dilute gases at temperatures up to 973 K. The theory of the instrument was rather complicated, because it dealt with the 3-dimensional nature of the fluid flow around the disk that was confined between two fixed plates. To evaluate the measurements in terms of viscosity, a computer was essential. The instrument was complex because the important elements were machined precisely from quartz and these were fragile and had to be assembled with great care. The instrument contained a relatively large volume of gas (about $5\,\mathrm{dm}^3$) within a metal cylinder. The oscillations of the quartz disk in that era were determined by visual observation, because of this, the operator required considerable training to obtain a precise and repeatable result; suitable electronic instrumentation to determine the oscillations were not available at that time. The instrument was used from room temperature up to 1073 K, and it enabled the study of the viscosity of all of the five noble gases and all of their binary and some ternary mixtures over the years 1965–1972. This instrument was restricted to measurement with simple molecules, because the metal casing catalyzed degradation of more complicated molecules.

Armed with accurate values of the viscosity, it was possible, by combining them with data from other measurements, such as infrared spectroscopy of the dimers of monatomic gases, their second virial coefficients, and the results of low energy molecular beam scattering, to deduce intermolecular pair potentials for those noble gases, both for like interactions and eventually the unlike interactions [8]. For that purpose, the kinetic theory of Chapman and Enskog [6,7] was employed. One of the successes of this approach was the determination of the intermolecular

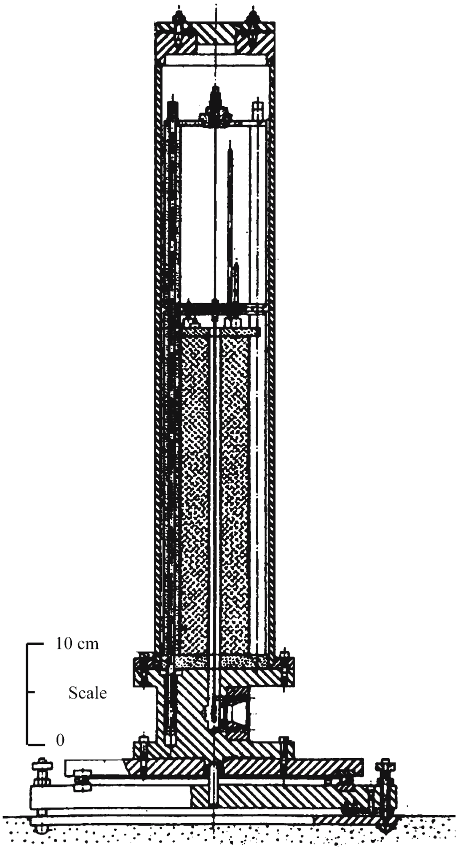

Fig. 1. Oscillating disk viscometer for gases at high temperature and low pressure [9].

pair potential for the noble gas argon, shown in Fig. 2, deduced from measurements of its viscosity and second virial coefficient [14,15]. Figure 2 compares the results with the Barker-Fisher-Watts function [10], that was considered in 1973 to be the best known pair potential for argon; more recently, Boyes [16] has reported a pair potential that also included the second acoustic virial coefficient. The pair potential derived by inversion of viscosity data conforms very well to that deduced in other ways [11–13]. The inversion technique was developed at about the same time but is beyond the scope of this article and the reader should consult, for example, Ref. [8] for further information on this technique. The Chapman and Enskog [6,7] theory also allowed the evaluation of the properties of

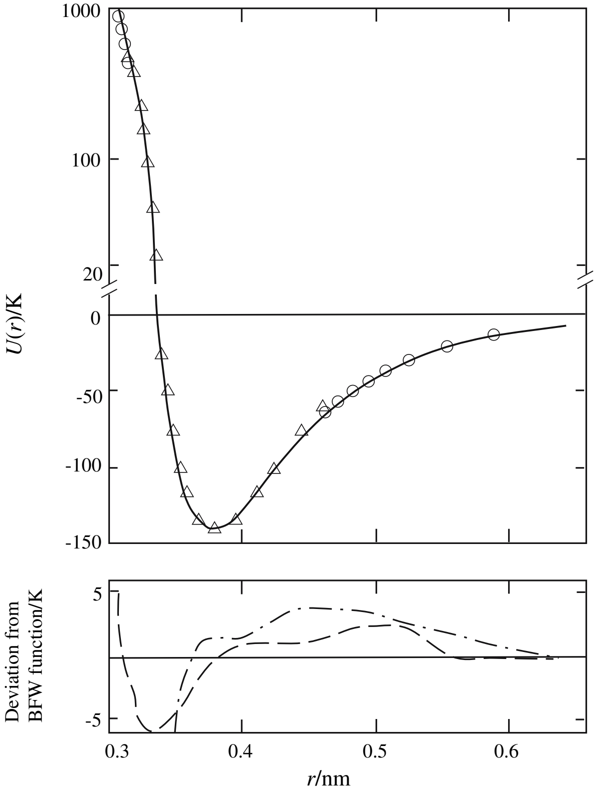

Fig. 2. Top: intermolecular pair potential energy function for argon. —, accurate functions [10–13]; Δ, inversion of gas viscosities [14]; ○, inversion of second virial coefficients [14]. Bottom: deviations from the Barker-Fisher-Watts function [10]; – – – – –, BBMS [11]; [*FX*], Lee et al. [12,13]. Redrawn from Ref. [15].

systems that had not otherwise been measured directly. For example, the thermal conductivity of the pure monatomic gases as well as binary and multicomponent mixtures have been predicted from the viscosity of the pure components and binary mixtures over the relevant temperature range [17,18].

Another result of these studies of viscosity was the capability to predict other transport properties with the inclusion of one empirical observation. We can understand this by superimposing, as shown in Fig. 3, the pair potentials of five noble gases on a reduced scale. Figure 3 shows that

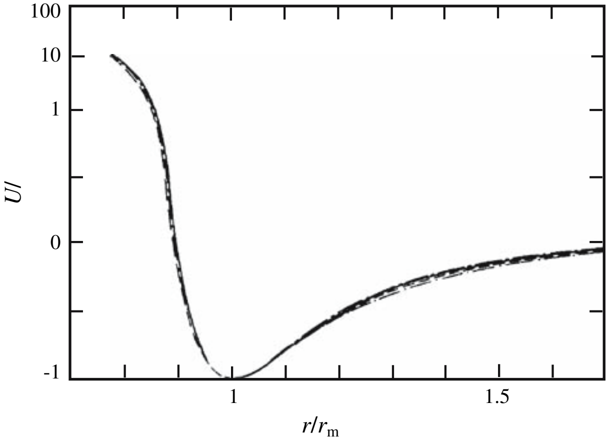

Fig. 3. Reduced intermolecular pair potential U/ε as a function of reduced intermolecular separation r/r_{m} for monatomic gases. Reproduced with notation changes from Ref. [19]. – – – – – – –, He; [*FX*], Ne; [*FX*], Ar; – – – – – – – –, Kr; ——, Xe.

the intermolecular pair potentials conform very closely to the same functional form in reduced units [19]. This observation provides the basis for a predictive method for the properties of these gases based upon a law of corresponding states [20,21]. Indeed, it is possible to predict properties that have not been measured for a particular gas or over a wider temperature range than has been measured. These arguments are readily extended to an arbitrary mixture of five components. So much of this success, of course, was the result of the available theory, but it remained to be tested.

We shall shortly illustrate the results of those tests as they were reported by Kestin, Wakeham, and their collaborators [21–25], but more work was necessary in order to enable rigorous tests, particularly for the measurement of thermal conductivity. This was because there were rather few, if any, means of measuring the thermal conductivity of fluids with high accuracy, because of the failure to properly understand or allow for heat convection in a fluid within the earth's gravitational field. Thus, the early 1970's brought the development of new techniques for the measurement of the thermal conductivity of gases. The most effective new method was based upon the pioneering work of Haarman [26] and took advantage of available high-speed digital electronics in the form of the transient hot-wire technique. Transient hot-wire instruments are illustrated in Fig. 4 and were initially developed at Brown University and subsequently at Imperial College, London. Figure 4 also contains the instruments subsequently

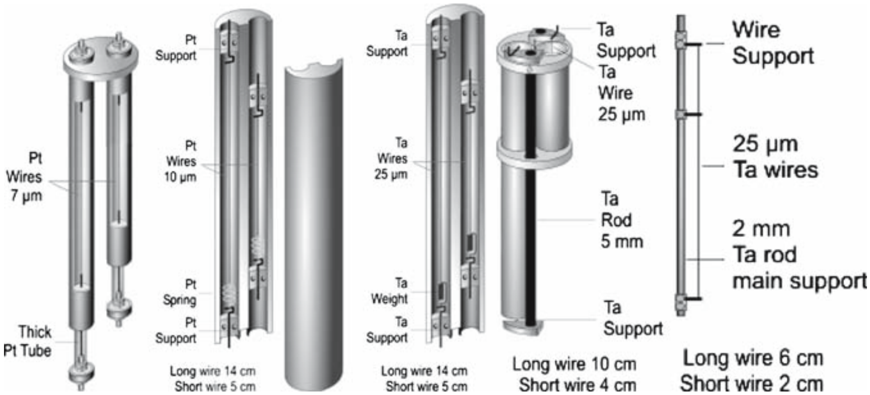

Fig. 4. Instruments to measure thermal conductivity [27–30].

used for liquids [31], about which we shall say more later. The entire cycle of the transient heat conduction experiment was performed before convection made a significant contribution to heat transfer and thus overcame the fundamental flaw of the earlier approaches. In the gas phase, measurements of the thermal conductivity of the five noble gases and their mixtures with an accuracy of a few parts in a thousand were conducted over a large pressure range but in a more limited range of temperatures than for the viscosity [32,33]. Nevertheless, the data provided a perfectly adequate basis for the confirmation of the predictive methods based upon kinetic theory [34,35].

Here, we simply use a few examples to illustrate the outcome. Figure 5 compares the predictions of the viscosity of ternary mixtures of monatomic gases with that measured directly; relative deviations are typically 5×10^{-3}, roughly equivalent to the combined accuracy of theory and experiment [22,37,36]. Figure 6 shows the results of later comparisons between the predictions of the thermal conductivity of binary mixtures and a direct measurement with the transient hot-wire technique using predictions based upon the principle of corresponding states and viscosity [38,39].

In the liquid phase, the circumstances are slightly different because, for a considerable time, liquid viscosity measurements near ambient conditions had been performed with very high precision. Such measurements were performed in a variety of capillary viscometers, some of which are illustrated in Fig. 7. All of these methods primarily require the observation of the time taken for a defined volume of liquid to flow through a capillary to determine the viscosity. The time taken for the meniscus of

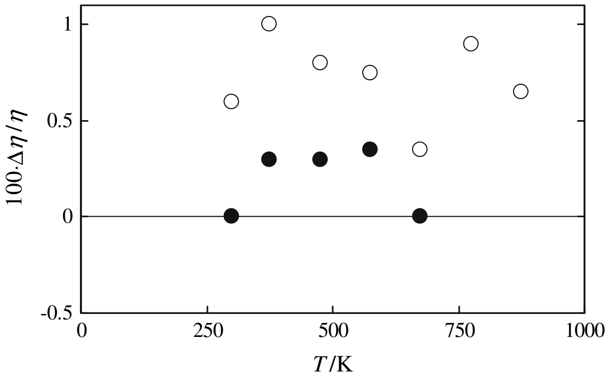

Fig. 5. Fractional deviation $\Delta\eta/\eta = \{\eta(\text{expt.}) - \eta(\text{calc.})\}/\eta(\text{calc.})$ of the measured viscosity η(expt.) of monatomic gas mixtures from a correlation of the viscosity obtained from the extended law of corresponding states η(calc.) as a function of temperature T. ○, (He + Ar + Kr); •, (He + Ne + Kr). Reproduced from data in Refs. [19,36].

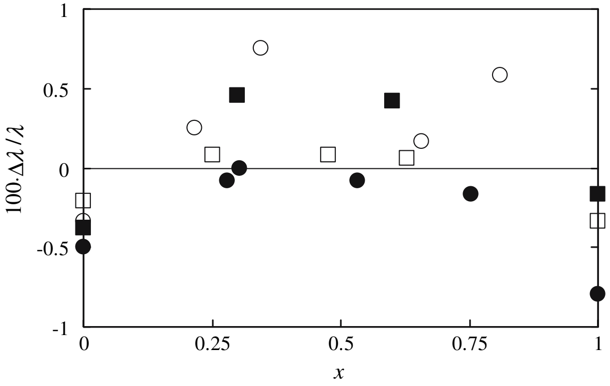

Fig. 6. Fractional deviation $\Delta\lambda/\lambda = \{\lambda(\text{expt.}) - \lambda(\text{calc.})\}/\lambda(\text{calc.})$ of the measured thermal conductivity λ(expt.) from a correlation of the viscosity obtained from the extended law of corresponding states λ(calc.) as a function of temperature T[19]. •, $(1-x)$He + xNe [17]; ■, $(1-x)$Ar + xKr [17]; ○, $(1-x)$He + xAr [18]; □, $(1-x)$Ne + Ar [18].

the liquid to fall from one fiducial mark to another in one limb of the viscometer can be directly related to the viscosity of the liquid in a first-order theory. This measurement was easily conducted with a manual stop-watch with high precision near ambient temperature and pressure. It is noteworthy that whereas the measurements were often highly precise, there were very few, if any, absolute measurements of high accuracy. This was because exact theories of the capillary viscometer require knowledge of the flow regime through a tube of circular cross section and also at the entry and exit where the flow is certainly not one dimensional but more likely either two or three dimensional. Furthermore, probably because much of this early work was done using glass capillaries of non-uniform bore by scientists from disciplines most closely connected to chemistry, the treatment of the fluid mechanics necessary for an exact absolute description of the instrument was often missing. An exception to this statement is the work of Swindells and his colleagues at what was then the National Bureau of Standards [40]. This work was connected with the absolute determination of the viscosity of water at a temperature of 293.15 K. This project took about 20 years to complete, but resulted in an accurate value of the viscosity of water with an uncertainty now estimated to be about 0.17% [41]. This value of the viscosity of water remains at the heart of the standard reference value for the viscosity of water. Measurements over a range of conditions, particularly temperature and pressure, were not really conducted in this period, at least not with high precision, because of the difficulty associated with realizing the capillary technique at high pressures and/or temperatures.

3. FRONTIER EXPANSION

As a result of all this activity, the intermolecular pair potentials among the noble gases were known by the mid-1970s and the prediction of the properties of any dilute gas mixture was possible over a wide range of temperature. Attention therefore turned to expand the frontiers using the same sorts of instruments, but examining new fluids and new conditions. First, there were numerous measurements on polyatomic gases, and of liquids under conditions of pressure and temperature close to ambient. However, there are two essential differences between the study of monatomic and polyatomic gases that had to be realized and solved before progress could be made: one is an experimental and the other a theoretical issue. The experimental issue relates to the materials used to construct the instruments, because the degradation of polyatomic fluids is stimulated by contact with metals and their oxides so that it often occurs at lower temperatures than those associated with the pyrolysis of the material. The other difficulty with polyatomic systems is that the kinetic theory available, while rigorous, is not susceptible to the same type of calculation, or certainly was not in the 1970s because the internal degrees of freedom of the molecules and indeed the non-spherically-symmetric nature

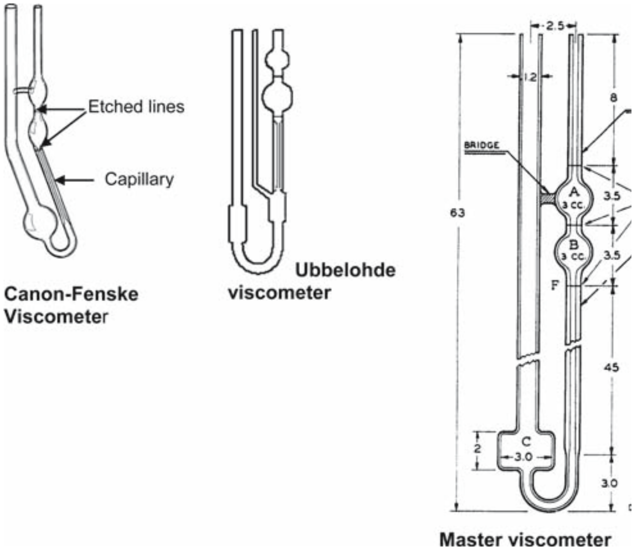

Fig. 7. Capillary viscometers: Left: Canon-Fenske viscometer; Middle: Ubbelohde viscometer; Right: master viscometer. The right hand figure reproduced with permission from ref 164

of the pair potential complicate the molecular dynamics. Even today, the exact calculations of the transport properties of a polyatomic gas are time-consuming and difficult even for a known intermolecular potential [42,43]. The pair potentials for only a few polyatomic systems are known and in the 1970s there were none. However, it was discovered empirically that the functionals of the intermolecular potentials for polyatomic gases upon which the transport properties depend conformed rather well to the same behavior as that of the monatomic systems. Therefore, it was possible to predict the viscosity of dilute polyatomic systems over a wide range of temperature on the basis of a few measurements for pure gases and binary mixtures over a modest range of temperature invoking the law of corresponding states. These predictions could then be extended to the viscosity of multicomponent mixtures of the same molecules. This application is illustrated in Fig. 8 where we plot the measured viscosity of a number of pure polyatomic gases as a function of temperature as deviations from predictions based upon the extended law of corresponding states and the available kinetic theory [46,47]. The relative agreement is typically within $\pm 5 \times 10^{-3}$. Figure 9 shows a similar comparison for multicomponent mixtures, and again the agreement between the experimental and predicted values are within ±0.5% [48]. The extension of this approach to diffusion

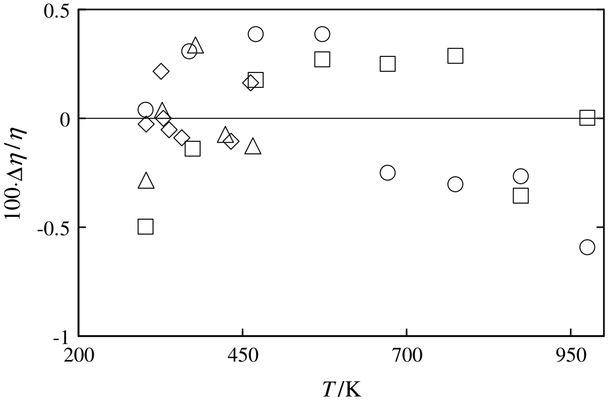

Fig. 8. Fractional deviation $\Delta\eta/\eta = \{\eta(\text{expt.}) - \eta(\text{calc.})\}/\eta(\text{calc.})$ of the measured viscosity η(expt.) of polyatomic gases from the viscosity obtained from the correlation of the extended law of corresponding states η(calc.) as a function of temperature T. ○, N_2 [24]; □, CO_2 [21]; △, CH_4 [44]; ◇, C_4H_{10} [45].

coefficients is straightforward; however, the development of similar predictive schemes for thermal conductivity had to wait another decade owing to the complications introduced by the transport and relaxation of internal energy [49–51].

Another expansion made possible by new technical developments for instrumentation is illustrated in Fig. 10, which shows a primary acoustic thermometer [52] capable of operating at temperatures up to 800 K. In this experiment, the ratio of the speed of sound to the velocity of light is measured. To do so, the spherical resonator was fitted with microwave and acoustic transducers and gas inlet tubes as shown in Fig. 10. One of the motives for the apparatus design was to minimize sources of gas contamination by continuous purging of the resonator during the acoustic measurements. The gas inlets and outlets were designed to neither generate acoustic noise from turbulence (that increases as the eighth power of the Reynolds number) nor so large to couple acoustically to the volume within the gas line; a low-pass acoustic filter was formed. The thermal expansion and dimensional stability of the resonator cavity was determined by *in situ* measurements of transverse magnetic microwave resonance triplets at three locations about the sphere. The triplet is split into a singlet and an unresolved doublet and this leads to a higher uncertainty in the measurements. More recently, Benedetto et al [53] have used a similar acoustic thermometer to measure thermodynamic temperatures between the triple point of mercury and $T = 380$ K. Pitre et al. [54] have

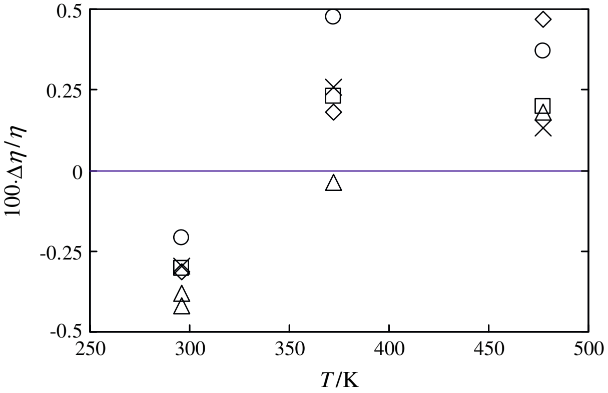

Fig. 9. Fractional deviation $\Delta\eta/\eta = \{\eta(\text{expt.}) - \eta(\text{calc.})\}/\eta(\text{calc.})$ of the measured viscosity of polyatomic gas mixtures η(expt.) from the viscosity obtained from the correlation of the extended law of corresponding states η(calc.) as a function of temperature T. ○, $CH_4 + CO_2 + CF_4$; □, $CO_2 + CF_4 + SF_6$; △, $CH_4 + CF_4 + SF_6$; ◇, $CH_4 + CO_2 + SF_6$; ×, $CH_4 + CO_2 + CF_4 + SF_6$. Reproduced with data from Ref. [48].

also performed acoustic thermometry using a quasi-spherical cavity as an acoustic and microwave resonator to measure the thermodynamic temperatures of the triple points of equilibrium hydrogen, neon, argon, and mercury. The departure of the quasispherical cavities from sphericity was large enough to be measured and to separate the degeneracy of the electromagnetic modes into three non-overlapping components that has decreased the uncertainty in the measured quantity.

Fortunately, to obtain the speed of sound from the measured acoustic frequency requires only the mean resonator radius (the additional complication of microwave thermal expansion measurements are only necessary for acoustic thermometry). This means measurements of the speed of sound can routinely be used to determine thermophysical properties. In particular, the speed of sound is a thermodynamic property which can be integrated readily in association with known theory to yield other thermodynamic quantities and ultimately an equation of state [55].

A similar kind of development in instrumentation has taken place concerning the measurement of density. The uncertainty in the measurements of density has decreased by several orders of magnitude and applied to a wide range of phases, substances, temperatures, and pressures. For example, the density of a solid can be determined from the mass obtained by comparison with a prototype standard kilogram and the volume from

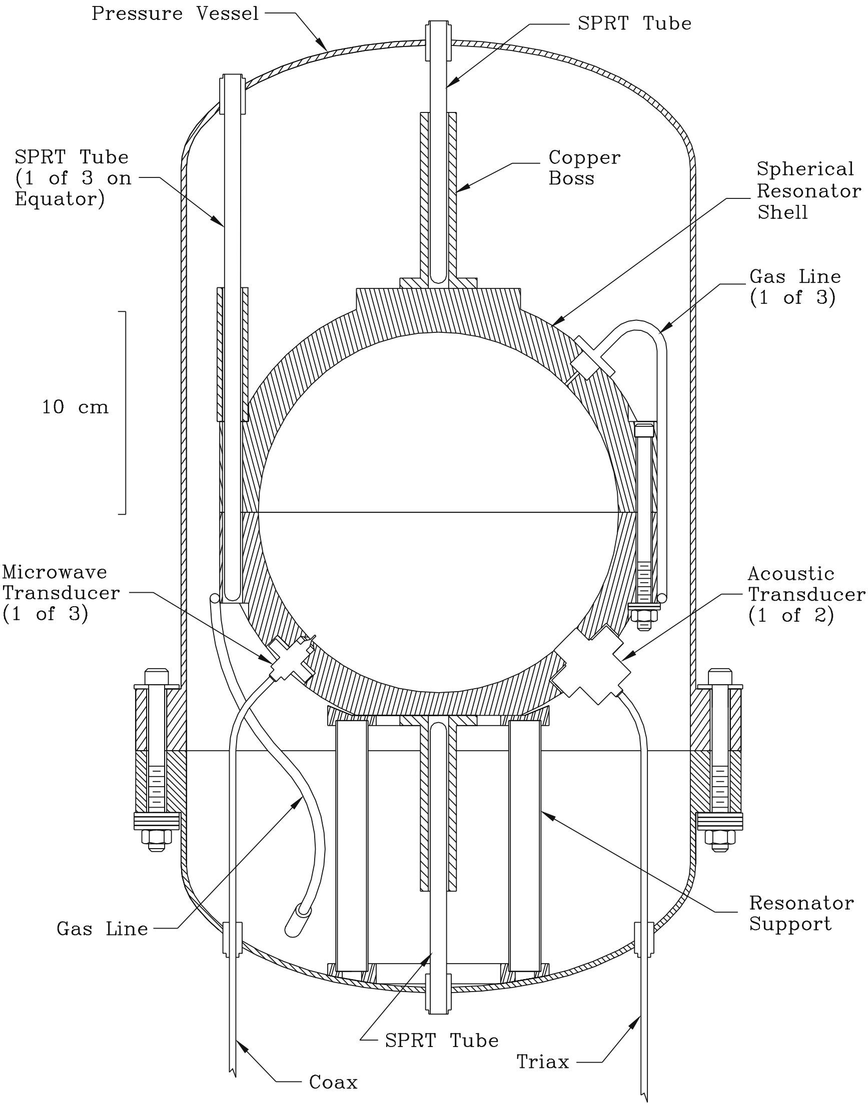

Fig. 10. Simplified cross section of the acoustic thermometer of Ripple et al. [52] for operation at temperatures up to 800 K. This apparatus includes a 3 L resonator with the capability to continually purge the gas within the cavity and directly measure contaminates in the exiting gas. It is fitted with three microwave probes and two acoustic transducers. The three microwave transducers are used to determine the thermal expansion and, with the acoustic measurements, the creep of the resonator. The resonator and thermometer wells are mounted within a pressure vessel. The furnace surrounding the pressure vessel is not shown.

an optical interferometer. The relative combined standard uncertainty for a density measurement obtained with this approach has been reduced to 10^{-7} and has been discussed recently by Fujii [56,57]. Precise knowledge of the density of a solid is important, because the solid can be used for differential density measurements between solids and liquids by hydrostatic weighing, pressure of flotation, and magnetic suspension methods based on Archimedes' buoyancy principle but applied in a novel compensation method. Kuramoto et al. [58] have published precise density measurements of liquids obtained with a magnetic suspension balance with a silicon sinker, the volume of which was determined with a combined standard uncertainty of 1.4×10^{-6} from the pressure-of-floatation method. The relative combined standard uncertainty in the density measurement of bromobenzene has been estimated to be 6.7×10^{-6} at $T = 293\,\mathrm{K}$ and $p = 0.1\,\mathrm{MPa}$. Wagner et al. [59] and Wagner and Kleinrahm [60] have described methods of determining liquid densities with magnetic suspension densimeters. As an example of this technique, we take the two-sinker method illustrated in Fig. 11. The densimeter consists of a copper measuring cell, three copper radiation shields and a copper intermediate plate, a stainless-steel vacuum vessel, a magnetic suspension coupling, and a commercial analytical balance; further details are provided in Refs. [61] and [62]. Two specially matched sinkers are required: typically, one is a gold-coated quartz sphere, the other a disk of solid gold. Both sinkers have the same mass, the same surface area, and the same surface material but a considerable difference in volume. The sinker is connected to a commercial analytical balance by a thin wire via a magnetic suspension coupling so that the "apparent mass difference" of the sinkers, surrounded by the sample fluid, can be measured precisely and the density, ρ, of the fluid determined with uncertainties as low as 0.001%. The key component of the weighing system is the magnetic suspension coupling. The principle of contactless weighing was developed by Clark [63], the first type of magnetic suspension coupling presented by Gast [64,65], and the technique developed further by Lösch [66] and Lösch et al. [67,68].

This dual-sinker densimeter shown in Fig. 11, covers a density range from (1 to 2000) $\mathrm{kg \cdot m^{-3}}$ at temperatures from (60 to 340) K and pressures up to 12 MPa. The total uncertainty in the density measurement of pure fluids is (0.02–0.01)% in most regions of the (p, ρ, T) surface. As a typical example of such measurements, Fig. 12 shows the (p, ρ, T) surface of nitrogen which has been investigated by Nowak et al. [69]. The two-sinker densimeter covers the homogeneous gas and liquid regions, including the critical region, and also the entire phase boundary from the triple-point temperature to the critical temperature. The uncertainties of the measurements in the various regions are also given in Fig. 12.

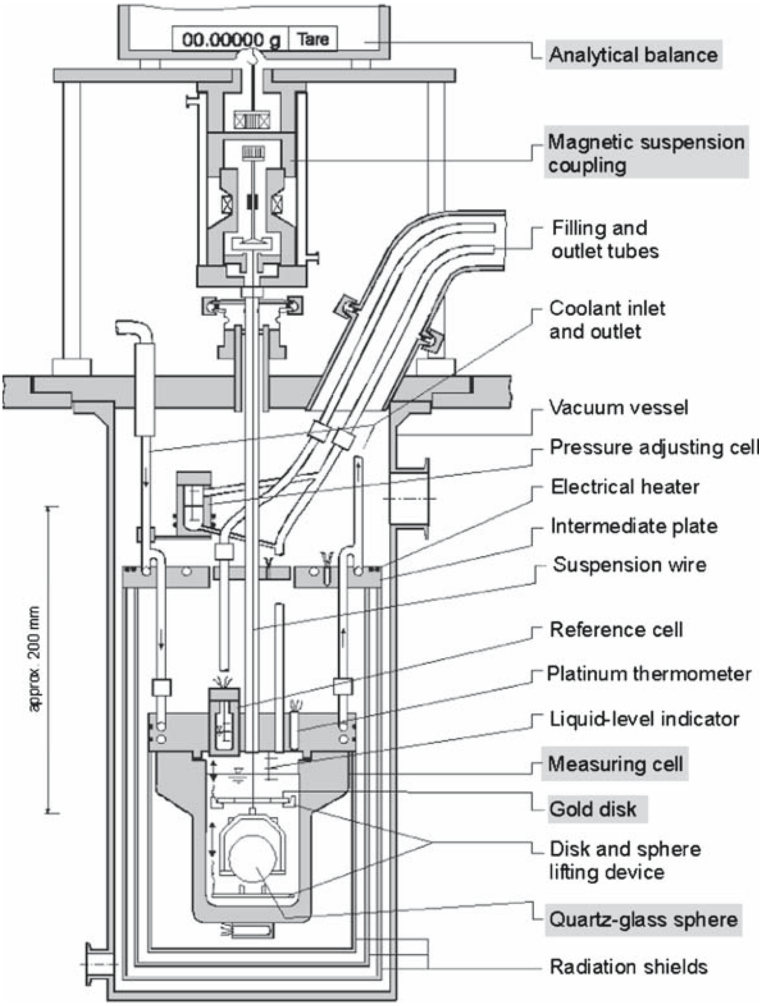

Fig. 11. Basic design of a two-sinker magnetic suspension densimeter. Reproduced with permission from IUPAC [59].

Other instruments were developed to extend the thermodynamic states and fluids covered by the instruments of proven accuracy discussed above. An example of the latter is the oscillating-disk viscometer developed by Vogel and collaborators [70–74] that was entirely made of quartz and therefore avoided the difficulties of the interaction between metal and the polyatomic gases. Vogel and his collaborators have been able to

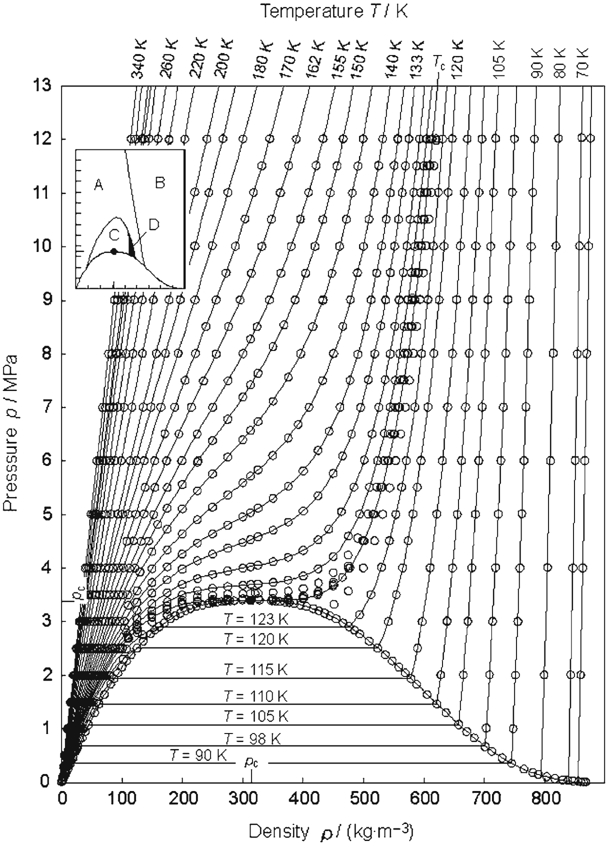

Fig. 12. Survey of the (p, ρ, T) surface of nitrogen measured with the two-sinker densimeter (taken from Nowak et al. [69]); each circle corresponds to a measuring point. The small diagram in the upper left-hand corner gives a survey of the total uncertainties in the various regions: A, (0.009 to 0.015) % in density; B, 0.01% in density; C, 0.015% in pressure; D, 0.03% in pressure.

measure the viscosity of polyatomic gases over a wide range of temperature without suffering sample degradation. Another example, is the hot-wire thermal conductivity instrument developed by Assael and Wakeham [27–29], shown in Fig. 4 that was used to measure the thermal conductivity of electrically-conducting liquids. In this instrument, the platinum wire traditionally used in the transient hot-wire method [30] was replaced with tantalum wire that was anodized electrolytically to produce an

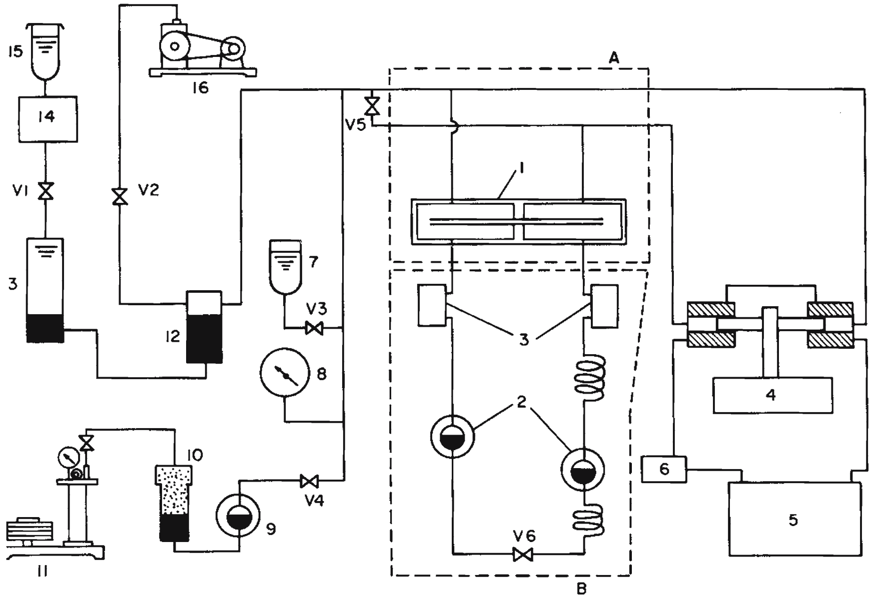

Fig. 13. Capillary viscometer employed by Nagashima and his collaborators for measurements at high temperature and high pressure [75].

insulating oxide. This allowed measurements of the transient temperature rise of the metallic element without complicating electrical effects arising from a finite electrical conductivity. A final example is the capillary viscometer designed by Nagashima and his colleagues [75], and shown in Fig. 13, to measure the viscosity of steam over wide ranges of temperatures and pressures. This instrument consists of a metal capillary mounted in a hot zone so that the test fluid is heated just before it passes into the capillary. This approach allows the fluid movement and pressure measurement to be conducted at temperatures near ambient in a second thermostat. The fluid is circulated through the capillary by a pumping system and the pressure drop between the chambers that house the ends of the capillary measured; from this measurement the viscosity can be evaluated.

A relatively new viscometer, shown in Fig. 14, is the vibrating wire [76]. Although the idea of the instrument was theoretically formulated by Stokes [77] in 1901, early versions of its implementation were inhibited by various elements of the measurement technology available and a failure to develop a theory applicable to a real instrument. The vibrating-wire viscometer simply consists of a metallic wire, usually tungsten or stainless steel, which is tensioned by either a mass, suspended from the lower end,

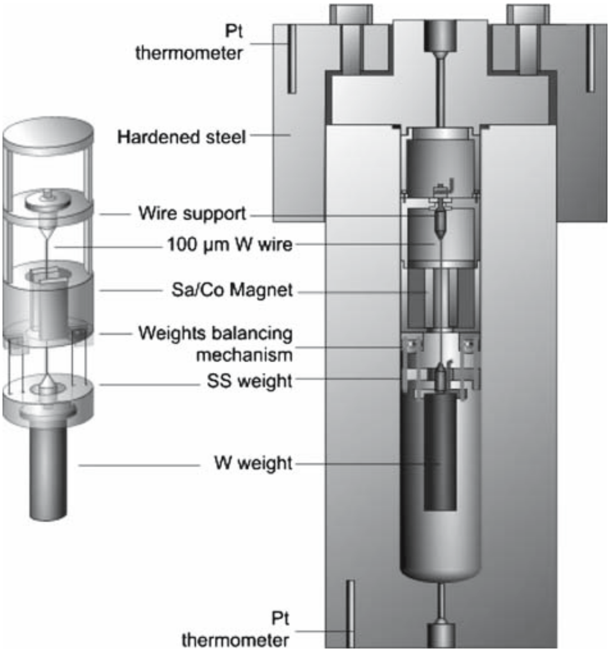

Fig. 14. Vibrating wire optimized with a pulley system to maintain tension for measurement of viscosity [76].

or clamped between two rigid supports. A current is then passed through the tensioned wire, which in a permanent magnetic field perpendicular to its length, forces it to move. A continuous alternating current can be used (forced vibrations) or a current applied to displace the wire from its rest position, and after release, observing the decay of its amplitude or velocity when immersed in a viscous medium. In the late 1980s, the development of high magnetic flux intensity samarium–cobalt permanent magnets, which provide a high intensity magnetic field per unit area, completely revolutionized the design of such instruments and their applications. Measurements of the current induced in the wire by its motion in the magnetic field provide the resonance in the forced oscillation mode or the logarithmic decrement and frequency in the transient decay mode. From either measurement method, it is possible to determine both the viscosity and density of the fluid and the instrument can be made more sensitive to one or other by mechanical design. In the version illustrated in Fig. 14, which has a compensation mechanism for the buoyancy effect acting on the suspended weight, the design was arranged to concentrate on the measure-

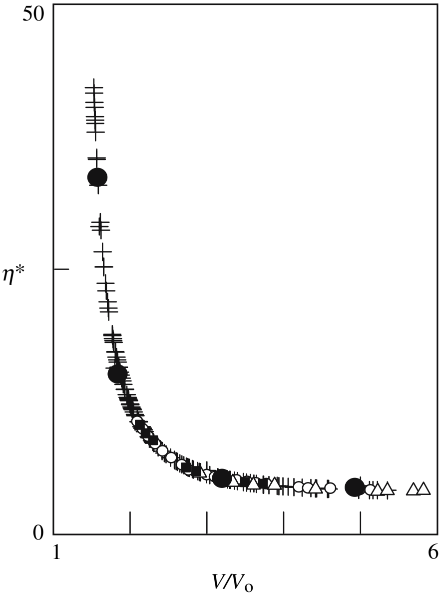

Fig. 15. Reduced viscosity η^*, for monatomic fluids, as a function of volume ratio (V/V_0). •, computed values for hard spheres; △, Kr; ○, Xe; ■, Ne; +; Ar. Reproduced from the information within [82], [83].

ment of viscosity. When the buoyancy compensation mechanism is omitted, far greater sensitivity to density can be achieved and simultaneous determination of both density and viscosity are possible from measurements of the variation in resonance frequency and line-width, respectively [78,79]. This type of viscometer can be made compact and has no moving parts, so it is particularly suited to measurements at elevated pressures [80].

It is from measurements of the viscosity of liquids as a function of pressure (or density) that there has been a development of a predictive method for the transport properties of liquids based upon a simple, but physically realistic model [81]. Figure 15 shows a dimensionless viscosity as a function of reduced volume for a series of liquefied monatomic gases [82,83]. Also in Fig. 15 are values obtained from simulation for a hard-sphere fluid that show a significant degree of agreement with experiment [84]. Similar studies for polyatomic liquids over a large temperature and pressure range are shown in Fig. 16 [82] along with values obtained from a hard-sphere approximation. The values shown in Fig. 16 have been sup-

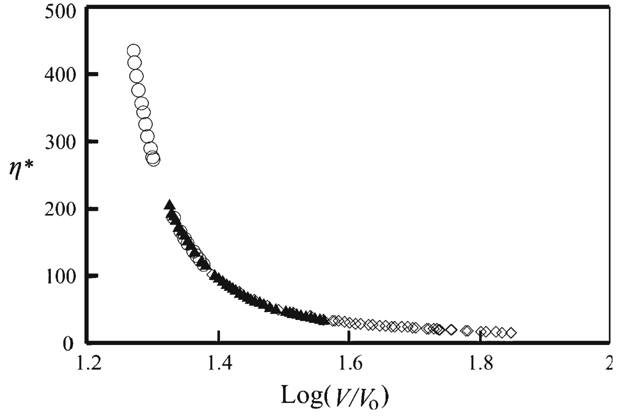

Fig. 16. Reduced viscosity η^*, for polyatomic fluids including both alkanes and aromatic compounds, as a function of volume ratio (V/V_0). ○, hexane; ◇, methylbenzene; ▲, decane. Reproduced from the information within [82].

plemented with the results of measurements made using the vibrating-wire instruments described earlier on alkanes and other pure hydrocarbons and mixtures at pressures up to 500 MPa and thus over a significant range of density. It has been found that the reduced viscosity of many systems conforms to a universal curve relating reduced viscosity to the reduced volume. Once more, this semi-empirical correlation enables a simple representation of the viscosity of the fluids measured but also allows prediction of the viscosity of fluids that have not been measured or at densities where they have not been measured. An analogous representation has also been developed for the thermal conductivity of liquids of polyatomic species [82]. Of course, the further the system departs from the molecular simplicity of the liquefied monatomic gases and ambient conditions, the accuracy of representation and the reliability of the predication decreases but, nevertheless, the approach remains useable for a large number of practical applications [85].

4. PLATEAU OF THERMOPHYSICS

The work described in Sections 2 and 3 demonstrated that combining accurate measurements on a few well-characterized systems with statistical mechanical and kinetic theory, in either a rigorous or at least semi-empirical fashion, allowed the prediction of properties not studied experimentally. Clearly, this approach has many applications. Such predictions can be carried out over ranges of thermodynamic states and for mixtures where experiments have never been carried out. The methodology is now available to design engineers and is incorporated into the software of many process engineering design packages. The bulk of this work was complete by the mid-1980s and what remained was to further extend the methodology of prediction by the incorporation of more fluids of increasing complexity using a similar approach. For that reason, the period between the mid-1980s and the present should have been occupied with sets of measurements designed to complement and extend what had gone before concentrating on more 'difficult' but also relevant materials. Such work would have been reasonable, respectable, and useful even if not entirely novel. However, the reality of what has happened in the same period is quite different.

A literature search using SciFinder$^{\mathrm{TM}}$ reveals that since 1980 there have been about 900 references reporting measurements on argon, 387 for the thermal conductivity, 296 for viscosity, and 217 for the second virial coefficient. Removing the restriction to measurements increases the number of articles in each category by a factor of about four. The scientific effort expended on a fluid, for which we know the properties with sufficient accuracy, for all foreseen purposes is quite remarkable. If you add to this comment the facts that argon itself is not of enormous technical significance and that the molecular theory that describes it is well understood, one might ask "why are all these measurements being conducted"? The cynic might say because they can be conducted and that there is little risk in a measurement that yields values that are well established. Indeed, there is a tendency to validate an instrument by first proving its operation using well-known properties and that is entirely legitimate. However, it is unfortunately true that seldom have the workers moved on to more difficult, perhaps more valuable, new measurements, and new fluids.

A similar example can be found in studies of thermodynamic properties and has perhaps been exacerbated by the creation of a new type of instrument, the vibrating-tube densimeter. Majer and Pádua [86] and Stansfeld [87] have discussed vibrating body densimeters and they show that technological improvements in fields far removed from thermophysics have made something possible that was not possible hitherto. A vibrating-tube densimeter allows the density of a fluid to be determined from observations of the resonant frequency of a 'U'-tube in a direction normal to its plane when it is evacuated or filled with fluid. The instrument is now the basis of several commercial devices that permit measurements to be carried out with a precision superior to that obtained by the majority of earlier workers over a modest range of temperature and pressure in a short time and certainly no more than a few minutes. The instrument is sufficiently robust that it frequently is featured in undergraduate laboratory experiments in university courses on physical chemistry. As a clear consequence, it has become possible to make routine measurements of the volumes, densities, and volumes of mixing of a very large number of binary and ternary mixtures. This conjecture is supported by taking just one issue of any journal focusing on thermodynamic properties. The reader will often find that 50% of the articles in an issue are devoted to reports of volumes of mixing of binary mixtures near ambient temperature and at atmospheric pressure. Scientifically, little has been learned from these measurements, although the authors often explain the observed trends in their results with arguments based on molecular interactions rather surprisingly without recourse to both spectroscopic data and a statistical mechanical model. For volumes of mixing, the work reported in one paper could easily be performed by a pair of undergraduate students in a few afternoons. One has to therefore question what this work adds to the literature with respect to thermophysical properties and why such measurements should be published? Some answers are fairly obvious; there is enormous peer and professional pressure to publish in the open literature, and this undoubtedly drives the observations made about volumes of mixing and the measurements of the transport properties of argon. In many cases, the sheer volume of results and perhaps in all of these cases their accuracy provides its own rationale for an individual's career advancement. Those reasons may be perfectly legitimate, but they do lead to the proliferation of results in the literature that are seldom, if ever, referenced and certainly of very little use for engineering design and of almost no value for scientific purposes. The topic has indeed been the subject of editorials in journals [88]. It is this type of behavior, which causes us to identify the period of development as directionless.

However, in this sea of directionless activity over the last 15 years, some specific things have arisen that have generated a special interest either from the point of view of physics or engineering; we just give two examples here, but there are obviously more. The most obvious general physical investigation has been connected with the study of the critical point. Here we focus our attention on the experimental methods and the instrumentation required for the optical techniques frequently employed in this region. For example, measurements of the thermal diffusivity of fluids near the critical temperature were performed by Becker and Grigull [89] with a method that uses holographic interferometry. This instrument itself proved quite effective and was employed by van den Berg and colleagues at the Van der Waals Laboratory together with Trusler and Wakeham at Imperial College in microgravity experimentation on ESA's experimental package on board NASA's Shuttle [90,91]. This instrument is an example of one that is designed to exploit particular characteristics of the fluid and its thermodynamic state, in this case the increasing gradient of refractive index with respect to temperature and pressure as the critical point is approached. Further examples are the use of photon-correlation spectroscopy for the study of light scattering in the neighborhood of the critical point [92], forced Rayleigh scattering which has been used by Nagasaka and colleagues [93] to study the thermal conductivity of materials [94] and the work by Leipertz and Frϕba on light scattering from liquid surface waves [95]. These very special techniques have taken us forward either in the study of the physics of the critical point, where an enormous amount of progress has been made and recorded by Sengers and colleagues [96–99], or under extreme conditions.

Another example of a sidetrack was brought about by the realization of the deleterious effects upon the ozone layer of the then current types of refrigerants such as dichlorodifluoromethane (R12) and the desire to replace them with less damaging materials such as 1,1,1,2-tetrafluoroethane (R134a). That realization, expressed in the Montreal Protocol of 1987 [1], spawned, initially, an engineering need for the bulk production of the new refrigerants. That generated a need for thermophysical properties of these materials for two reasons. The first reason was associated with the design of plants to make these materials and second to enable the design of heat-transfer equipment for refrigeration. Those two requirements drove an enormous ‘industry’ in the measurement of the properties of materials that had never been studied before. It is very interesting to note that, unlike the continuous study of argon, which yielded results always in quite good agreement with what had been measured earlier, the study of new materials produced very disparate results from laboratories with, hitherto, a record of considerable consensus [100–102]. At the time, and still today, those findings call into question the understanding of several of the experimental techniques employed. Indeed, discrepancies of up to 25% between the results of several laboratories for the viscosity of R134a [103] prompted a study by the Subcommittee on Transport Properties of the International Union of Pure and Applied Chemistry (IUPAC) through a ‘Round Robin’ project to identify their causes. The principle outcome of the project was a greater consensus between laboratories on values for the various properties [104, 105]. The causes for some of the original discrepancies remained unresolved however.

5. THE PRESENT AND FUTURE

There are now a number of reasons why the philosophy that has underpinned work in thermophysics to date needs to change or at least the balance between that philosophy and a new philosophy needs to be adjusted. First there is no time. The process set out before that led to understanding through theory and then to the prediction of many systems on the basis of careful experiments on a few systems combined with theory took at least two decades. Many industrial problems of today need solutions long before that. The second problem is the fluids for which properties are now required are really quite different from those of the earlier era. For example, the chemical composition of the fluid is unknown, a situation that is frequently encountered in the oil industry, yet the physical properties are still required for design and evaluation. Furthermore, the properties are often required under extreme conditions, that is, under extremely high pressures and temperatures, for which the theory developed is inappropriate and, finally, there are sometimes fluids that have quite different properties than those that have been studied before such as those of molten metals for which there is little or no theoretical guidance. For these systems, it will be necessary to provide values for the thermophysical properties rapidly with accuracy adequate for the purpose for which they are intended; there is no need to achieve the highest accuracy in all measurements but the accuracy achieved must be known. This means that all of the previous experimental methodology for the development of accurate measurements must still be used but the measurements need not be performed to realize the highest possible accuracy. That is, it is sufficient to secure an accuracy fit for the purpose for which the data are required. Here we only have time to provide a few examples of this approach, but we hope that they will suffice to make the point. Once again they are drawn from the area of fluids but are equally applicable to many areas related to the solid state.

In the initial discussion of this paradigm, we look at the development of a viscosity standard for industrial purposes that are appropriate for the fluids of moderate viscosity perhaps most often encountered there. The current, agreed viscosity standard mentioned earlier is the viscosity of water of about $1\,\mathrm{mPa\cdot s}$ at $T = 293.15\,\mathrm{K}$. In an industrial context, most fluids have a significantly greater viscosity than this, so that standard oils have been developed to have significantly higher viscosity. The viscosity of these oils is certified by a calibration traced, through several different master capillary viscometers shown in Fig. 7, back to the viscosity of water. The step-up process required means a loss of accuracy in each step of the process and is certainly quite time-consuming and onerous.

Therefore there is a need for a standard reference fluid and a reference value for viscosity, perhaps at around room temperature, which is not necessarily a standard of metrological quality but does provide a viscosity standard with a viscosity of around $100\,\mathrm{mPa\cdot s}$ that is readily available, does not require immense amounts of effort for the calibration of a practical viscometer, and which itself is traceable to the viscosity of water at a temperature of 293.15 K. On that basis, an instrument has been developed by Fareleira and colleagues in Instituto Superior Tecnico in Portugal [106] which enables measurements of the viscosity of diisodecylphthalate (DIDP) with an uncertainty of about 1% and is traceable to the viscosity of water. The instrument illustrated in Fig. 17 is really a vibrating-rod viscometer rather than a vibrating-wire viscometer because the diameter of the wire is now of the order of 200 μm instead of 50 μm as it was in early versions, and the design is necessarily more robust in order to be able to set this kind of rod in transverse oscillation. Nevertheless, the principles have remained the same and so there is no need to give any further description. This is an example of a measurement made with an accuracy fit for purpose. Although we do not seek the highest possible accuracy, in this case it is still necessary to make sure that the accuracy of the result is known and therefore that the behavior of the instrument conforms to what is expected. A presentation of the recommendation with respect to the standard reference viscosity was presented at THERMO International 2006 [107].

5.1. Molten Metals

The thermophysical properties of molten metals, in particular, the density, heat capacity, thermal conductivity, and viscosity are required for the design of molds used for casting. This is particularly important when particular properties of the casting are required in particular locations within it; for example, additional material strength is required in one region and that might be accomplished by more rapid cooling than generally possible. To design a process, the fluid properties of the molten metal are required to model the behavior of the particular casting process employed. Second, and related to the environment, there is an increasing demand for the use of solders for electronic component work that are free of lead. Historically, lead has been the base of many of the alloys employed as solders in the electronics industry, particularly for automatic soldering in large-scale mass production. Increasingly, there is a move towards solders without lead for which the physical properties, in particular, the thermal conductivity and viscosity need to be known; this information has a role in the design and control of automatic soldering equipment. For these reasons, some ten years ago, a program was devised to try to improve on the existing knowledge of the thermal conductivity of molten metals. The existing knowledge has been summarized and evaluated in the work at Purdue University of Touloukian and others

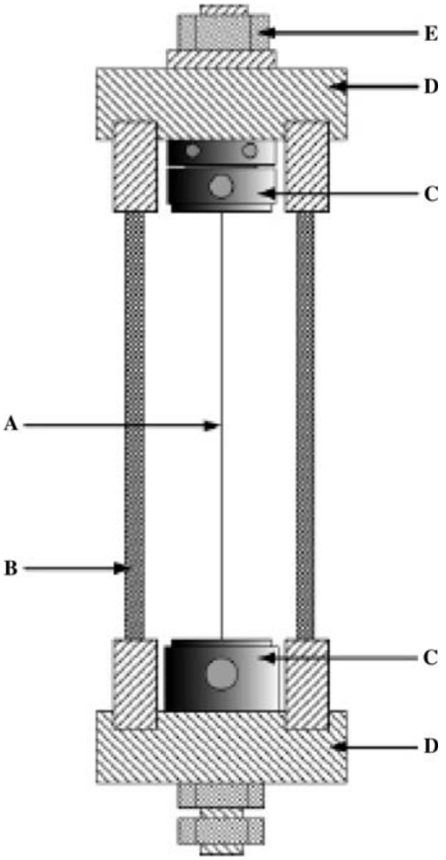

Fig. 17. Schematic drawing of the vibrating-wire sensor; A, Tungsten vibrating wire; B, Tungsten rod spacers; C, Inconel clampers for the vibrating wire; D, Inconel plates; E, Fine threaded nut, for tensioning without torsion of the wire. Reproduced with permission of American Chemical Society [106].

[108] that is part of CINDAS and the Thermophysical Properties of Matter Database (TPMD). These sources set out the thermophysical properties of molten metals and indeed solid metals and rocks. A review of that publication shows there is a wide range of values for the thermal conductivity of molten metals. For example, Fig. 18 shows the thermal conductivity of the most familiar molten metal, mercury, as a function of temperature that

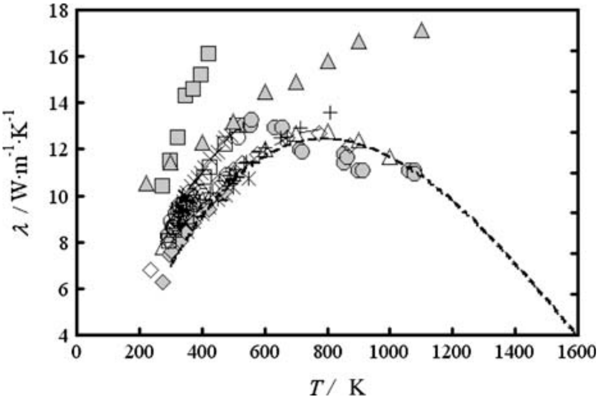

Fig. 18. Thermal conductivity of mercury as a function of temperature. □, Gehlhoff and Neumeier [109]; □, Peralta-Martinez [110,111]; -, Vel'tishcheva et al. [112]; × Hall [113,114]; •, Meneaxidis [115]; ○, Powell and Tye [116]; ▲, Vukalovich et al. [117]; △, Prabduram [118]; +, Ewing et al. [119]; ∗, Duggin [120]; ◇, Grosse [121]; ◆, Bush et al. [122]; ——, Ho et al. [123].

illustrates the wide spread of values that have been reported in the literature in the past [109–123].

Faced with this enormous range of data, the European Union was persuaded to fund a program to study a new technique for the measurement of thermal conductivity of molten metals based on the transient hot-wire method, which has proved so successful for simpler fluids such as organic liquids and dilute gases discussed earlier. Of course, the technique cannot be identical but the same methodology was used in the construction of the apparatus: one looks for an accurate description of the experimental method, and then seeks to define or construct an instrument that replicates the theoretical model as nearly as possible [124]. Figure 19 shows the basis of the idea [125]. A circular section platinum wire is contained on the central plane of a sandwich made from two alumina ceramic elements, and this planar substrate structure is immersed in the molten metal for which the thermal conductivity is desired. As in the transient hot-wire method, a current is passed through the platinum wire and the temperature rises at a rate that is initially determined by the thermal conductivity and heat capacity of the metal itself, then that of the surrounding substrate, and eventually of the molten metal [126,127]. The difference, of course, is that there is no direct contact, either electrical or thermal, between the hot wire and the molten metal. Instead, the thermal pulse must first heat the wire, then pass through the substrate, and finally reach

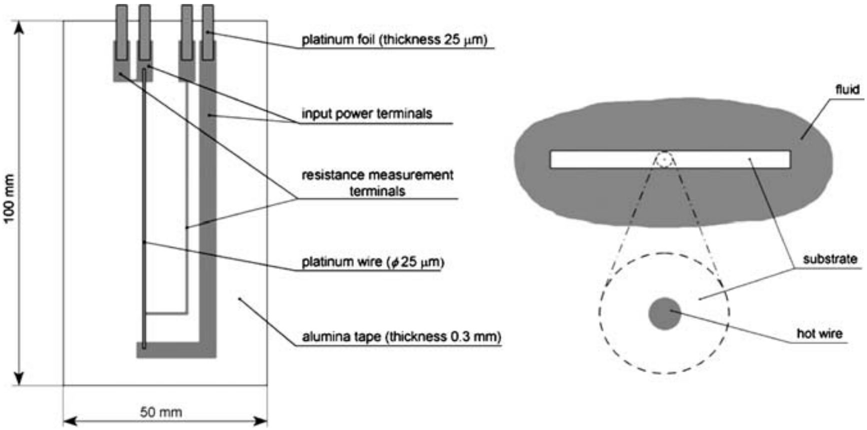

Fig. 19. Left: Schematic of the hot wire thermal conductivity device for molten metals. Right: Cross-section of the sensor illustrating how the wire is isolated from the fluid by a rigid substrate [125].

the molten metal. The duration of the transient heating is maintained on the order of 1 s to avoid convective heat transfer in the melt. In practice, as shown in Fig. 19, short and long platinum wires are formed from one wire with an off-center tap which allows measurement of the resistance of a finite length of the platinum wire essentially eliminating end effects. The wire is part of a conventional Wheatstone bridge, and measurements of the out-of-balance signal determine the resistance change of the hot wire as it heats. This information allows an evaluation of the temperature rise of the wire encased in the substrate as a function of time. Figure 20 shows the complete sensor mounted for assembly in a high-temperature furnace which houses the crucible containing the molten metal.

The heat conduction in the system, shown in Fig. 19, is, of course, not radial as it was for the transient hot wire immersed in fluids. Thus, the description of this heat transfer process is rather more complicated. For each of the three zones, the wire, the substrate, and the molten metal, a different set of coupled partial differential equations for the energy transfer is derived from Fourier's law and describes the process subject to appropriate initial and boundary conditions at each interface [128,125]. It must also be recognized that at each interface there may exist a heat transfer resistance caused by the imperfect contact between one solid and another and between one solid and a molten metal. It is quite clear that the solution of this complicated heat transfer problem is not amenable to an exact analytic treatment. However, it is amenable to a sufficiently exact numerical solution, because it is possible using modern finite element

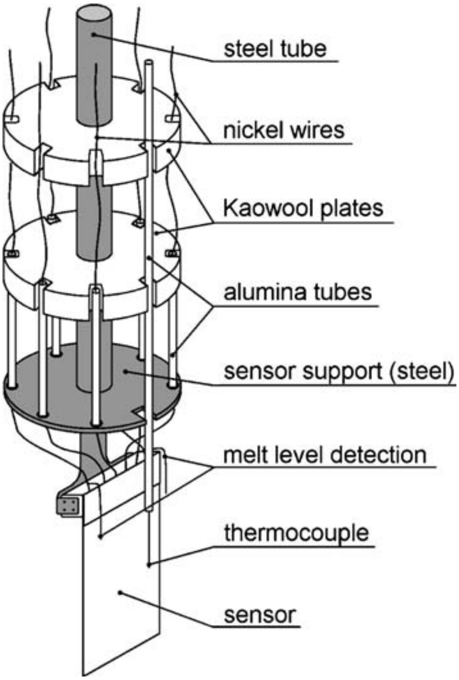

Fig. 20. Hot wire thermal conductivity sensor encapsulated within alumina mounted on a steel support for insertion within a high-temperature furnace [125].

modeling to describe this heat transfer process. For that purpose, the complete system is divided into a series of meshes that accounts for the fact that there is a mixture of geometry between the circular wire and the rectangular elements, and a finite element model based upon conventional Fourier equations can be built and solved as described elsewhere [124, 126, 127]. It is then possible to predict from assumed values of the thermal conductivity, heat capacity, and density of the wire, the substrate, the molten metal and, if necessary, any interface elements, the temperature history of the wire subject to a transient heat input. That prediction can then be compared with the experimental observations for the same heat input and the properties adjusted to achieve a match between the two. In fact, it is usual to concentrate only upon a match between the two in the region in which the heat pulse is passing through the substrate and that when it is passing through the molten metal. In this way, it becomes possible to determine the thermal conductivity and heat capacity of the

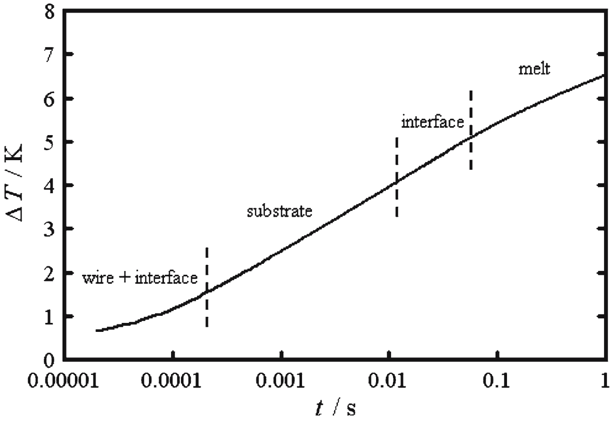

Fig. 21. Typical temperature rise ΔT of the hot wire as a function of time t with the main time regions [125].

substrate and of the surrounding metal directly. This is illustrated schematically in Fig. 21 where we show the superposition of the temperature rise of the metal wire as a function of time over five orders of magnitude of time from 10μ s up to about 1 s [125].

This process is adequate, as Fig. 22 shows, to determine the thermal conductivity of the molten metal. In Fig. 22, we compare the experimentally determined temperature rise of the wire when the sensor is immersed in molten tin at $T = 682\,\mathrm{K}$ with that predicted by the finite element model for three estimated values of the thermal conductivity. The differences between the model and experiment are within ±0.1%. At longer times, shown in Fig. 22, the sensitivity to the assumed thermal conductivity of the molten metal is clear and variations of as little as 1% in estimated thermal conductivity can be discerned readily; this is a measure of the precision of the measurement.

In order to make this experiment a reality, the sensors have been constructed from alumina tape which is obtained in its green state. One piece of tape is printed with all of the electrical connections in platinum. The hot wire itself, which is made from a 25 μm platinum wire, is laid on the substrate and the sandwich is completed by adding a second layer of tape. A structure, shown in Fig. 19, is then produced by co-firing. It is estimated that the uncertainty of this measurement technique is something like ±3%, and Fig. 23 shows the results obtained for the thermal conductivity of molten tin [125, 129] compared with those obtained by other authors [130–135]. Again, the large discrepancies between the various sets of results are evident. The results of Bilek [125] obtained with this

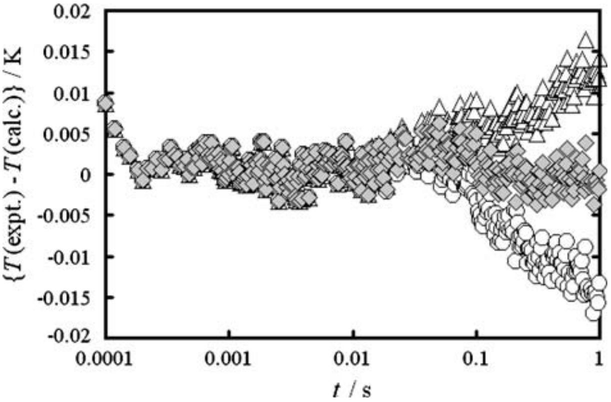

Fig. 22. Difference between the measured temperature T(expt.) and the value estimated with a finite element model T(calc.) as a function of time t and the estimated thermal conductivity of the molten metals at a temperature of 628 K [125]. The sensitivity to the thermal conductivity shown is ±1%. ◆, $\lambda_{\mathrm{Pb}} = 17.12\,\mathrm{W \cdot m^{-1} \cdot K^{-1}}$; △, $\lambda_{\mathrm{Pb}} = 17.29\,\mathrm{W \cdot m^{-1} \cdot K^{-1}}$; ○, $\lambda_{\mathrm{Pb}} = 16.95\,\mathrm{W \cdot m^{-1} \cdot K^{-1}}$.

method are in good agreement with those reported by Hemminger and his colleagues in 1985 and with some recent correlations, but there is a considerable difference from another group of results. It is contended that the results of Bilek [125] enjoy greater credibility because of the care taken to verify that the experiment conforms to the theory and the claim of an overall uncertainty of ±3% has significant justification. This level of accuracy is adequate for the design purposes referred to at the start of this section, so that we have a second example of an accuracy fit for purpose.

The only theoretical relationship that exists for the prediction of the thermal conductivity of molten metals is derived from the treatment of the thermal conductivity of solid metals without change. The theory assumes that all the heat is carried by electrons and thus it relates the thermal conductivity of the metals to the electrical conductivity [136]. The prediction of the theory is that

$$\lambda = \frac{T \cdot L_0}{\rho_e}, \tag{1}$$

where, theoretically, $L_0 = 2.445 \times 10^{-8}\,\mathrm{V^{-2} \cdot K^{-2}}$ is the Lorentz number and ρ_e is the electrical resistivity of the molten metal at temperature T. Figure 24 contains a plot of the experimental quantity $L = \rho_e \lambda / T$ as a function

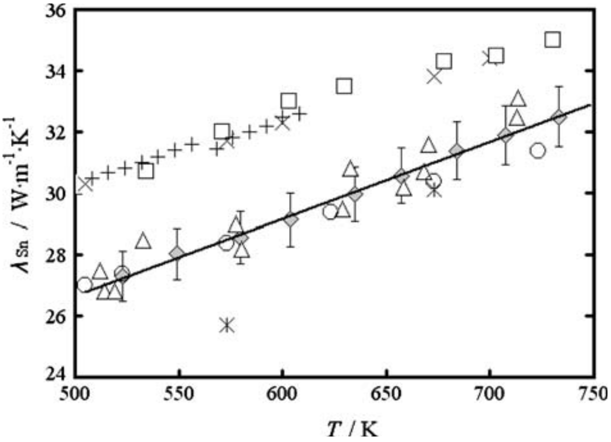

Fig. 23. Thermal conductivity of tin λ_{Sn} (normal melting temperature about 505 K) as a function of temperature T [129]. ♦, Bilek [125]; +, Sklyarchuk and Plevachuk [130]; ∗, Yamasue et al. [131]; □, Peralta-Martinez and Wakeham [132]; △, Hemminger [133]; ×, Ho [134]; ○; Mills et al. [135] ———, best fit to the results reported in Ref. [125]. Uncertainties shown for the measurements of Ref. [125] are ±3%.

of temperature and shows that the theory is remarkably accurate for the three metals studied by this new experimental technique to date.

5.2. *In situ* Applications

It is our opinion that there will be an increasing move towards the use of measurements of the thermophysical properties of the fluids within an actual process. In part this will arise because conditions in some processes are very variable, so that the properties of the fluids that are sought may be different on each occasion. It might also be because the measurement of the property enables control of the process, it might be that the process fluid is ill-characterized in terms of its chemical components or it could be that it is simply too difficult to take a sample of the fluid and analyze chemically as well as determine its properties in a laboratory.

It is the latter case that we consider now in the final section of this article, where our example derives from the oil industry. Let us first state the problem. We are accustomed to the notion of off-shore oil platforms drilling in depths of perhaps 50 m or so of water, and being perhaps 500 km from the refinery and storage facilities to which the platform is

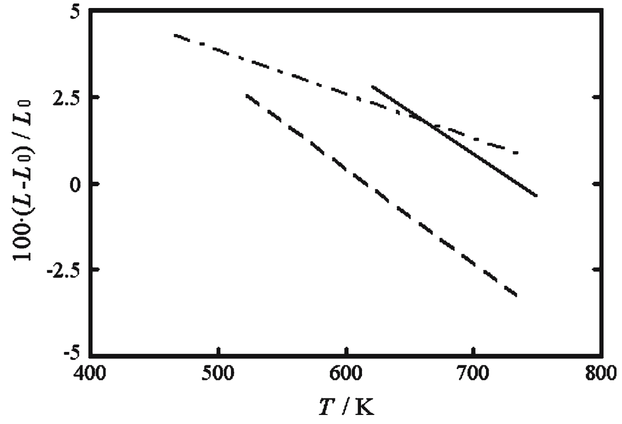

Fig. 24. Relative deviation $(L - L_0)/L_0$ of the experimental quantity $L = \rho_e\lambda/T$ from the value L_0 where ρ_e is the electrical resistivity of the molten metal at temperature T and λ is the thermal conductivity as a function of temperature T [125]. ———, Pb; [FX], Sn; [FX], In.

connected by pipeline. But, increasingly, there will be a move of such systems further off-shore where the oil will be 5 km or so below the sea bed which is itself perhaps more than 1 km below the surface of the sea. Evidently, the issue of drilling becomes much more complicated and it becomes very important to know the potential value of the reservoir before expensive exploitation begins. For an oil company then, there is a financial risk associated with developing any hydrocarbon resource which is related in part at least to the uncertainties in the viscosity, density, and phase behavior of the fluid that makes up the reservoir. Typically the temperature in a petroleum reservoir is somewhat less than 473 K, with pressure somewhat less than 200 MPa. The density of the fluid will cover the large range of (300–1300) kg.m^{-3} with a viscosity somewhere between (0.1 and 1 000) MPa · s; in some reservoirs the viscosity can be orders of magnitude higher than the upper limit given here.

A complete reservoir typically consists of a group of fluid-bearing layers separated by impermeable shale. The physical properties of the fluids can be determined from measurements performed on a sub-sample of an aliquot extracted from each layer. Often the extraction is performed after a borehole has been drilled but before the production system, consisting of metal tubes surrounded by cement, is installed. Figure 25 shows a typical phase diagram for sample retrieval that can lead to phase separation as the sample is transported to the surface. The reduction of sample pres-

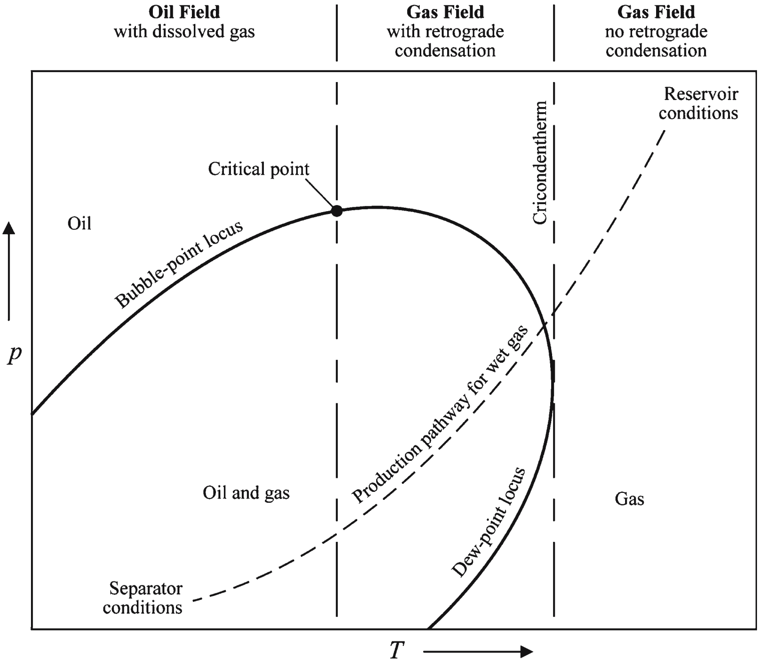

Fig. 25. (p, T) section at constant composition for a reservoir fluid showing bubble curve, dew curve, and temperatures, relative to the critical point, at which oil and gas, with or without retrograde behavior, occur. ——-, production pathway for a wet gas and the same for non-pressure compensated sample retrieval. Figure from Ref. [137] reproduced with permission of Elsevier.

sure within a chamber arises from the decrease in temperature, and this pressure decrease can be overcome when a nitrogen pressure compensation system is used to maintain the sample pressure. The physical properties of the fluid are then determined in a laboratory at the reservoir temperature as well as the variations with temperature and pressure that will be experienced throughout the production system. Clearly, there is a demand for other *in situ* measurements of the properties of these reservoir fluids. At the same time, one has a series of constraints, which will be explained further below.

The measured thermophysical properties are combined with knowledge of the permeability, size, shape, and compartmentalization of the reservoir to perform analyses concerning the development of that petroleum reservoir. From this list, the thermophysical properties and their uncertainty are usually considered to be lower in priority than the other items in the financial analysis, but in the case of retrograde condensates, uncertainties in the location of the phase boundary can be significant. To a first approximation, measurements of density provide an estimate of the commercial value of the produced fluid, while viscosity is an indicator of the ease with which the fluid can be extracted from the formation. Since ease of extraction plays a hugely important role in the overall financial budget of a reservoir, viscosity is arguably, the single most important thermophysical property. In general, measurements of density and viscosity with uncertainties of about ±1% and ±10%, respectively, are considered adequate to guide value and exploitation calculations with sufficient rigor. Thus, methods that can provide *in situ* measurements of fluid density and viscosity with these uncertainties at reservoir temperature are desirable because they reduce the time required for analysis and systematic errors that might arise from variations in chemical composition caused by transferring the fluids from one container to another and subsequent transportation.

Typically, the diameter of the tools used to sample fluids is restricted by the borehole diameter to about 150 mm. To contain the mechanical and electrical systems, these tools need to be tens of meters long, must be capable of sustaining accelerations of the order of 100 times the acceleration of gravity, and must operate 10 km from the well head at temperatures up to 473 K with fluids of a viscosity of about 100 mPa · s that may contain corrosive components. Thus, it is desirable that any measurement device should have dimensions on the order of 10 mm and mass on the order of 1 g. Selecting a particular sensor system for a specific application requires consideration and weighting of each design, implementation, and fabrication method. The selection processes are crucial when no off-the-shelf commercial sensor is available. In this case, a sensor must be developed by carefully matching the requirements to the potential characteristics of the sensor. Except perhaps for the measurement of pressure, transducers that are operated in the bore hole have, historically, placed robustness as a superior priority to accuracy in the design process.

Of the viscometers described in the literature [138–143], vibrating wires have exact working equations, and it is our opinion that they are of simple construction and can be operated over a wide range of temperature and pressure. Recently, they have been used to provide the viscosity of the fluids required to calibrate downhole viscometers [144,145], and in doing so, have demonstrated that a vibrating wire could be used downhole to provide the viscosity to an uncertainty within ±10%. This is an example of how understanding the theory of the viscometer completely and applying it properly to the measurements made, (even though final accuracy may be a factor of 10 less then attainable) is sufficient for the industrial application. It also shows that refining the measurement to lower uncertainties, which would take considerable time, has no benefit and indeed

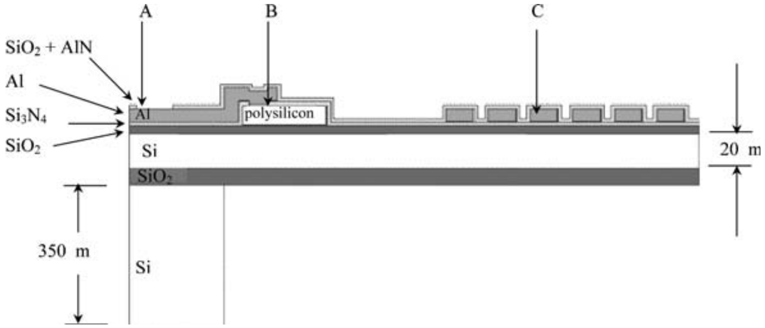

Fig. 26. Schematic cross section through the vibrating plate and supporting 350 μm thick silicon. Wire-bond pads A, Wheatstone bridge boron-doped polycrystalline silicon resistor B, and aluminum wire C that formed the coil. Figure reproduced with permission of the American Chemical Society from Ref. [147].

may even be detrimental because the problem will be solved by another means so that the commercial opportunity can be met. Indeed, the industrial drive has shown that the vibrating wire viscometer can be used to measure viscosities up to 2000 mPa · s [146].

Further steps to address the constraints of size and mass are provided by one further example of an oscillating plate viscometer fabricated by the methods of micro-electro-mechanical systems (MEMS) [147]. The transducer, shown in Fig. 26, is a rectangular plate connected to a support along one edge with a width of about 2 mm, a length of about 1.5 mm and a thickness of about 20 μm. The density and viscosity of the fluid in which the plate is immersed has been determined from measurements of the first, non-zero frequency, eigenmode, which is a symmetrical bending mode with flexural motion. The vibrating object developed for this work was fabricated from mono-crystalline silicon, a mechanically stable material, by addition of layers to produce a means of exciting and detecting the motion of the plate near resonance. This MEMS sensor utilizes silicon-on-insulator (SOI) wafers, photolithography (as used in integrated circuit fabrication), and deep reactive ion etching for the micro-machining [148]. A physical description of the motion of the plate in a fluid, which is used to obtain the density and viscosity, requires a geometrically defined structure of known dimensions. When the sensor is formed by the methods of MEMS, this requirement necessarily precludes the use of curved surfaces.

When the MEMS fabricated device, illustrated in Fig. 26, is placed in a fluid, its resonance frequency decreases with increasing density because of added mass, while the quality factor decreases as the viscosity increases owing to the shearing motion at the tip of the plate. The sensitivity to

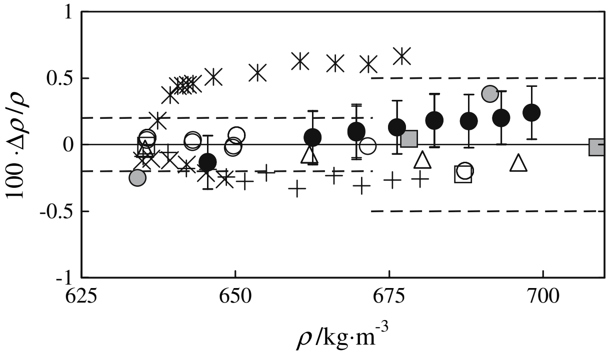

Fig. 27. Fractional deviations $\Delta\rho = \rho(\text{expt.}) - \rho(\text{calc.})$ of the experimental densities $\rho(\text{expt.})$ of octane, at $T = 373.15$ K from values $\rho(\text{calc.})$ estimated from the correlation of Span and Wagner [149] as a function of density ρ. •, This work, with error bars representing the expanded uncertainty, determined with the calibration coefficients obtained at $T = 323.15$ K when immersed in methylbenzene; △, Ref. [150]; □, Ref. [151]; $*$, Ref. [152]; $+$, Ref. [153]; gray filled circle, Ref. [154]; gray filled square, Ref [155]; ◇, Ref. [156]; ○, Ref. [157]; ×, Ref. [158]; and - - - - -, uncertainty of the correlation [149]. Figure reproduced with permission of the American Chemical Society [147].

density arises because the plate has a large surface-to-volume ratio and a mass of about 0.12 mg. A zeroth-order theory has been developed for this MEMS transducer. This theory requires the determination of three calibration parameters that can then be applied to other fluids. As an example, the density and viscosity of octane has been determined at temperatures of (323, 348, 373, and 423) K and pressures below 70 MPa [147]. Figure 27 compares the density so obtained with a literature correlation reported by Span and Wagner [149] (which is identical to that reported by Span [159]) as a function of density at a temperature of 373 K. The results lie between (−0.1 and 0.2)% of Ref. [149], while the literature values lie within (−0.3 and 0.5)% of Ref. [149]. Similar differences were observed at lower temperatures. The densities reported by Caudwell [150], obtained using a vibrating wire with a mass suspended from one end, are also shown in Fig. 27. These differ from the MEMS results by about 1.5 times the estimated expanded uncertainty in the MEMS measurements. The viscosity of octane determined from the MEMS at $T = 348$ K is shown in Fig. 28 as deviations from the correlation of other literature values reported by Huber et al. [160]. As Fig. 28 shows, the results lie within a combined uncertainty of the correlation and values obtained from the MEMS device

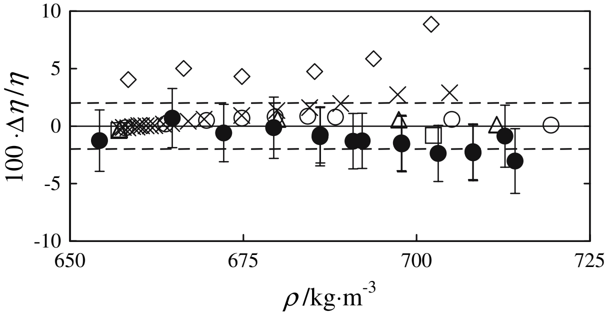

Fig. 28. Fractional deviations $\Delta\eta = \eta(\text{expt.}) - \eta(\text{calc.})$ of the experimental viscosities $\eta(\text{expt.})$ of octane at $T = 348.15\,\text{K}$ from values $\eta(\text{calc.})$ obtained with the correlation of Huber et al. [160] as a function of density ρ. The density required in Ref [160] was taken from Ref. [149]. •, This work, with error bars representing the expanded uncertainty, determined with the calibration coefficients obtained at $T = 323.15\,\text{K}$, when immersed in methylbenzene, and the densities from Table 2; ○, [161]; ◇, [156]; △, [150]; □, [151]; ×, [162]; and - - - - -, uncertainty of the correlation [160]. Figure reproduced with permission of the American Chemical Society [147].

except for those reported by Kiran and Sen [156] that deviate from Huber et al. [160] by 5% at the lowest pressure to about 10% at the highest pressure studied. The viscosity reported by Caudwell [150], and obtained with a vibrating wire viscometer, agree within the estimated expanded uncertainty of the MEMS results, as do the measurements of Agaev and Golubev [162].

In order to apply *in situ* measurement techniques such as those offered by the MEMS sensor or other viscometers, it will be necessary to carry out calibration with Newtonian fluids of known viscosities within an appropriate range of temperature and pressure [144,145,163]. Thus, whereas the emphasis of the work in thermophysics will be on expeditious solutions of problems, there will still be the need for some very accurate measurements of the type discussed at the start of "Base Camp."

6. SUMMARY

The story presented here suggests that in the future there will be a decreasing demand for measurements of the thermophysical properties of fluids of high accuracy. This will be balanced by an increasing demand for industrially-relevant measurements with an accuracy suited to the application. The trend will be towards smaller instrumentation with a well understood theory as the demand for work on fluids that are chemically aggressive in extreme thermodynamic states accelerates. Speed will also be an important factor, so there will be very much less opportunity to perform many repetitions of measurements by several authors. Furthermore, the demand for *in situ* measurement of the properties of ill-characterized materials will increase.

All of these trends will affect the literature of the subject where one expects to see the practical problem to be solved discussed alongside the property measurement and potentially an enhanced role for molecular simulation in supplementing experimental studies. These trends will make the field of thermophysics of fluids look very different from that of 40 years ago.

REFERENCES

1. *Montreal Protocol on Substances that Deplete the Ozone Layer: Final Act*, United Nations Environmental Programme (UNEP) (Sept. 16, 1987).
2. M. E. Fisher and R. J. Burford, *Phys. Rev.* **156**:583 (1967).
3. J. S. Rowlinson, *J. Stat. Phys.* **87**:957 (1997).
4. J. V. Senger and J. Luettmer-Strathmann, in *Transport Properties of Fluids: Their Correlation, Prediction and Estimation*, J. Millat, J. H. Dymond, and C. A. Nieto de Castro, eds. (Cambridge University Press for International Union of Pure and Applied Chemistry, Cambridge, UK, 1996), Chap. 6, pp. 113–137.
5. W. A. Wakeham, *Fluid Phase Equilib.* **117**:334 (1996).
6. S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases*, 2nd edn. (Cambridge University Press, New York, 1952).
7. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), pp. 478–480.
8. G. Maitland, M. Rigby, E. B. Smith, and W. A. Wakeham, *Intermolecular Forces: Their Origin and Determination* (Clarendon Press, Oxford, 1987).
9. R. DiPippo, J. Kestin, and J. H. Whitelaw, *Physica* **32**:2064 (1966).
10. J. A. Barker, R. A. Fisher, and R. O. Watts, *Mol. Phys.* **21**:657 (1971).
11. G. C. Maitland E. B. Smith, *Mol. Phys.* **22**:861 (1971).
12. P. E. Siska, J. M. Parson, T. P. Schafer, and Y. T. Lee, *J. Chem. Phys.* **55**:5762 (1971).
13. J. M. Parson, P. E. Siska, and Y. T. Lee, *J. Chem. Phys.* **56**:1511 (1972).
14. G. C. Maitland and E. B. Smith, *Proc. 7th Symp. Thermophys. Props.* (Amer. Soc. Mech. Eng., 1977), pp. 412–420.
15. G. C. Maitland and E. B. Smith, *Chem. Soc. Rev.* **2**:181 (1973).
16. S. J. Boyes, *Chem. Phys. Lett.* **5-6**:221 (1994).
17. A. A. Clifford, R. D. Fleeter, J. Kestin, and W. A. Wakeham, *Physica* **98**:467 (1979)
18. M. J. Assael, M. Dix, A. Lucas, and W. A. Wakeham, *J. Chem Soc.: Faraday Trans. I* **77**:439 (1981).
19. B. Najafi, E. A. Mason, and J. Kestin, *Physica A* **119**:387 (1983).
20. J. Kestin, S. T. Ro, and W. A. Wakeham, *Physica* **58**:165 (1972).
21. J. Kestin, S. T. Ro, and W. A. Wakeham, *J. Chem. Phys.* **56**:4119 (1972).

22. J. Kestin, W. A. Wakeham, and K. Watanabe, *J. Chem. Phys*. **53**:3773 (1970).
23. J. Kestin, S. T. Ro, and W. A. Wakeham, *J. Chem. Phys.* **56**:4086 (1972).
24. J. Kestin, S. T. Ro, and W. A. Wakeham, *J. Chem. Phys.* **56**:4036 (1972).
25. J. Kestin, S. T. Ro, and W. A. Wakeham, *Physica* **58**:165 (1972).
26. J. W. Haarman, *Ph. D. Thesis* (Technische Hogeschool Delft, Netherlands, 1969).
27. W. A. Wakeham and M. Zalaf, *Physica* **139**:105 (1986).
28. M. Dix, W. A. Wakeham, and M. Zalaf, *Thermal Conductivity 20*, D. P. H. Hasselman, ed. (Plenum, New York, 1988).
29. M. J. Assael, E. Charitidou, G. P. Georgiadis, and W. A. Wakeham, *Ber. Bunsen-Ges. Phys. Chem.* **92**:627 (1988).
30. E. N. Haran and W. A. Wakeham, *J. Phys. E* **15**:839 (1982).
31. J. Menashe and W. A. Wakeham, *Ber. Bunsenges. Phys. Chem.* **85**:340 (1981).
32. E. N. Haran and W. A. Wakeham, *J. Phys. E* **15**:839 (1982).
33. M. J. Assael, C. A. Nieto de Castro, H. M. Roder, and W. A. Wakeham, in *Experimental Thermodynamics*, Vol. III, *Measurement of the Transport Properties of Fluids*, W. A. Wakeham, A. Nagashima, and J. V. Sengers, eds. (Blackwell Scientific for International Union of Pure and Applied Chemistry, Oxford, UK, 1991), Chap. 7, pp. 163–194.
34. E. A. Mason and L. Monchick, *J. Chem. Phys.* **36**:1622 (1962).
35. L. Monchick, A. N. G. Pereira, and E. A. Mason, *J. Chem. Phys.* **42**:3241 (1965).
36. J. Kestin, H. E. Khalifa, and W. A. Wakeham, *J. Chem. Phys.* **67**:4254 (1977).
37. J. Kestin, S. T. Ro, and W. A. Wakeham, *Trans. Faraday. Soc.* **67**:2308 (1971).
38. J. Kestin, R. Paul, A. A. Clifford, and W. A. Wakeham, *Physica* **100A**:349 (1980).
39. M. J. Assael, M. Dix, A. Lucas, and W. A. Wakeham, *J. Chem. Soc. Faraday Trans.* **77**:439 (1981).
40. J. F. Swindells, J. R. Coe, and T. B. Godfrey, *J. Res. Nat. Bur. Stds.* **48**:1 (1952).
41. *ISO/TR 3666*, Viscosity of Water (1998).
42. V. Vesovic and W. A. Wakeham, *J. Phys. Chem. Ref Data* **15**:1073 (1986).
43. V. Vesovic and W. A. Wakeham, *Chem. Eng. Sci.* **44**:2181 (1989).
44. J. M. Hellemans, J. Kestin, and S. T. Ro, *Physica* **65**:376 (1973).
45. J. Kestin, S. T. Ro, and W. A. Wakeham, *Ber. Bunsen-Ges. Phys. Chem.* **78**:20 (1974).
46. J. Kestin and W. A. Wakeham, *Transport Properties of Fluids: Thermal Conductivity, Viscosity and Diffusion Coefficient* (Hemisphere/CINDAS, New York, 1988)
47. U. A. T. McLaughlin, M. Rigby, V. Vesovic, and W. A. Wakeham, *Mol. Phys.* **59**:579 (1986).
48. J. Kestin, E. H. Khalifa, and W. A. Wakeham, *J. Chem. Phys.* **65**:5186 (1976).
49. V. Vesovic and W. A. Wakeham, *High Temp.-High Press.* **23**:179 (1991).
50. V. Vesovic and W. A. Wakeham, *Physica A* **201**:501 (1993).
51. V. Vesovic and W. A. Wakeham, *High Temp.-High Press.* **26**:187 (1994).
52. D. C. Ripple, D. R. Defibaugh, K. A. Gillis, and M. R. Moldover, in TEMPMEKO '99, *Proc. II 7th Int. Symp. Temp. Therm. Meas. Ind. Sci.*, J. Dubbeldam and M. de Groot, eds. (NMI van Swinden Laboratorium, Delft, Netherlands, 1999), p. 418.
53. G. Benedetto, R. M. Gavioso, R. Spagnolo, P. Marcarino, and A. Merlone, *Metrologia* **41**:74 (2004).
54. L. Pitre, M. R. Moldover, and W. L. Tew, *Metrologia* **43**:142 (2006).
55. A. R. H. Goodwin and J. P. M. Trusler, in *Experimental Thermodynamics, Vol. VI, Measurement of the Thermodynamic Properties of Single Phases*, A. R. H. Goodwin, K. N. Marsh, and W. A. Wakeham, eds. (Elsevier for International Union of Pure and Applied Chemistry, Amsterdam, 2003), Chap. 6, pp. 208–225.
56. K. Fujii, *Metrologia* **41**:S1 (2004).

57. K. Fujii, in *Experimental Thermodynamics*, Vol. VI, *Measurement of the Thermodynamic Properties of Single Phases*, A. R. H. Goodwin, K. N. Marsh, and W. A. Wakeham, eds. (Elsevier for International Union of Pure and Applied Chemistry, Amsterdam, 2003), Chap. 5, pp. 191–208.
58. N. Kuramoto, K. Fujii, and A. Waseda, *Metrologia* **41**:S84 (2004).
59. W. Wagner, R. Kleinrahm, H. W. Lösch, and J. T. R. Watson, in *Experimental Thermodynamics*, Vol. VI, *Measurement of the Thermodynamic Properties of Single Phases*, A. R. H. Goodwin, K. N. Marsh, and W. A. Wakeham, eds. (Elsevier for International Union of Pure and Applied Chemistry, Amsterdam, 2003), Chap. 5, pp. 127–235.
60. W. Wagner and R. Kleinrahm, *Metrologia* **41**:S24 (2004).
61. R. Kleinrahm and W. Wagner, *Entwicklung und Aufbau einer Dichtemeßanlage zur Messung der Siede—und Taudichten reiner fluider Stoffe auf der gesamten Phasengrenzkurve.*, Fortschr.-Ber. VDI, Reihe 3 (VDI-Verlag, Düsseldorf, 1984), Nr. 92.
62. R. Kleinrahm and W. Wagner, *J. Chem. Thermodyn.* **18**:739 (1986).
63. J. W. Clark, *Rev. Sci. Instrum.* **18:**915 (1947).
64. Th. Gast, in *Vacuum Microbalance Techniques*, K. H. Behrndt, ed. (Plenum Press, New York, 1963), Vol. 3, p. 45.
65. Th. Gast, *Acta Imeko* **4:**159 (1967).
66. H. W. Lösch, *Entwicklung und Aufbau von neuen Magnetschwebewaagen zur berührungsfreien Messung vertikaler Kräfte*, Fortschr.-Ber. VDI, Reihe 3 (VDI-Verlag, Düsseldorf, 1987), Nr. 138.
67. H. W. Lösch, R. Kleinrahm, and W. Wagner, *Chem.-Ing.-Tech.* **66:**1055 (1994).
68. H. W. Lösch, R. Kleinrahm, and W. Wagner, *Jahrbuch 1994: Verfahrenstechnik und* Chemieingenieurwesen (VDI-Verlag, Düsseldorf, 1994), p.117.
69. P. Nowak, R. Kleinrahm, and W. Wagner, *J. Chem. Thermodyn.* **29**:1137 (1997).
70. E. Vogel, E. Bastubbe, and S. Rohde, *Wiss. Z. Univ. Rostock-Naturw. Reihe.* **33**:34 (1984).
71. E. Vogel, *Wiss. Z. Univ. Rostock* **21**:169 (1972).
72. E.Vogel, E. Bicj, and R. Nimz, *Physica* **139A**:46 (1986).
73. E. Vogel, B. Holdt, and T. Strehlow, *Physica* **148A**:46 (1988).
74. T. Strehlow and E. Vogel, *Physica* **161A**:101 (1989).
75. K. Kobayashi and A. Nagashima, *High Temp.-High Press.* **17**:131 (1985).
76. M. J. Assael, S. Polimatidou, and W. A. Wakeham, *Int. J. Thermophys.* **14**:795 (1993).
77. G. G. Stokes, *Mathematical and Physical Papers* (Cambridge University Press, 1901).
78. A. A. H. Pádua, J. M. N. A. Fareleira, J. C. G. Calado, and W. A. Wakeham, *J. Chem. Eng. Data* **41**:731 (1996).
79. A. A. H. Pádua, J. M. N. A. Fareleira, J. C. G. Calado, and W. A. Wakeham, *Int. J. Thermophys.* **17**:781 (1996).
80. D. R. Caudwell, J. P. M. Trusler, V. Vesovic, and W. A. Wakeham, *Int. J. Thermophys.* **25**:1339 (2004).
81. D. Enskog, *Kungl. Svenska. Vet.-Ak. Handl.* **63**:4 (1922).
82. J. H. Dymond and M. J. Assael, in *Transport Properties of Fluids: Their Correlation, Prediction and Estimation*, J. Millat, J. H. Dymond, and C. A. Nieto de Castro, eds. (Cambridge University Press for International Union of Pure and Applied Chemistry, Cambridge, UK, 1996), Chap. 10, pp. 226–249.
83. M. J. Assael, J. P. M. Trusler, and T. F. Tsolakis, *Thermophysical Properties of Fluids: An Introduction to their Prediction* (Imperial College Press, London, 1996).
84. J. H. Dymond and T. A. Brawn, *Proc. 7th Symp. Thermophys. Props.* (Amer. Soc. Mech. Eng., 1977), pp. 660–667.
85. W. A. Wakeham, *Thermal Sci. Eng.* **6**:53 (1998).

86. V. Majer and A. A. H. Pádua, in *Experimental Thermodynamics*, Vol. VI, *Measurement of the Thermodynamic Properties of Single Phases*, A. R. H. Goodwin, K. N. Marsh, and W. A. Wakeham, eds. (Elsevier for International Union of Pure and Applied Chemistry, Amsterdam, 2003), Chap. 5, pp. 158–168.
87. J. W. Stansfeld, in *Experimental Thermodynamics*, Vol. VI, *Measurement of the Thermodynamic Properties of Single Phases*, A. R. H. Goodwin, K. N. Marsh, and W. A. Wakeham, eds. (Elsevier for International Union of Pure and Applied Chemistry, Amsterdam, 2003), Chap. 5, pp 208–225.
88. "Scope and Editorial Policy," *J. Chem. Eng. Data* **51**:9A (2006).
89. H. Becker and U. Grigull, *Waerme Stoffuebertrag Thermo Fluid Dyn.* **11**:9 (1978).
90. A. C. Michels, R. De Bruijn, T. D. Karapantsios, R. J. J. van Diest, H. R. van den Berg, B. van Deenen, E. P. Sakanidou, W. A. Wakeham, J. P. M. Trusler, A. Louis, M. Papadaki, and J. Straub, presented at *9th Eur. Symp. Gravity-Dependent Phenomena*, Berlin (1995).
91. A. C. Michels, R. de Bruijn, T. D. Karapantsios, R. J. J. van Diest, H. R. van den Berg, B. van Deenen, E. P. Sakonidou, W. A. Wakeham, J. P. M. Trusler, A. Louis, M. Papadaki, and J. Straub, *Proc. Nat. Heat Transfer Conf.*, Portland, Oregon, (ASME, New York, 1995), Vol. 3, p. 137.
92. J. N. Shaumeyer, R. W. Gammon, J. V. Sengers, and Y. Nagasaka, in *Experimental Thermodynamics*, Vol. III, *Measurement of the Transport Properties of Fluids*, W. A. Wakeham, A. Nagashima, and J. V. Sengers, eds. (Blackwell Scientific for International Union of Pure and Applied Chemistry, Oxford, UK, 1991), Chap. 8, pp. 197–213.
93. Y. Nagasaka, in *Experimental Thermodynamics*, Vol. III, *Measurement of the Transport Properties of Fluids*, W. A. Wakeham, A. Nagashima, and J. V. Sengers, eds. (Blackwell Scientific for International Union of Pure and Applied Chemistry, Oxford, UK, 1991), Chap. 8, pp. 213–223
94. Y. Nagasaka and A. Nagashima, *Int. J. Thermophys.* **9**:923 (1988).
95. A. P. Fröba and A. Leipertz, *Int. J. Thermophys.* **24**:895 (2003).
96. A. Michels, J. V. Sengers, and P. S. van der Gulik, Physica **28**:1201 (1962).
97. B. M. Law, R. W. Gammon, and J. V. Sengers, *OSA Proc. Photon Correlation Techniques and Applications*, J. B. Abbiss and A. E. Smart, eds. (Optical Society of America, Washington, DC, 1988), Vol. 1, p. 147.
98. H. C. Burstyn and J. V. Sengers, *Phys. Rev. A* **25**:448 (1982).
99. B. M. Law, R. W. Gammon, and J. V. Sengers, *Phys. Rev. Lett.* **60**:1554 (1988).
100. D. E. Diller, A. S. Aragon, and A. Laesecke, *Fluid Phase Equilib.* **88**:251 (1993).
101. I. R. Shankland, R. S. Basu, and D. P. Wilson, *Proc. MEEET IIR*, COMM. B1, B2, E1, E2, Purdue Univ., West Lafayette, Indiana (1988), p. 305.
102. A. Kumagai and S. Takahashi, *Int. J. Thermophys.* **12**:105 (1991).
103. C. M. B. P. Oliveira and W. A. Wakeham, *High Temp.-High Press.* **27-28**:91 (1995).
104. M. J. Assael, Y. Nagasaka, C. A. Nieto de Castro, R. A. Perkins, K. Ström, E. Vogel, and W. A. Wakeham, *Int. J. Thermophys.* **16**:63 (1995).
105. M. J. Assael and W. A. Wakeham, *Int. J. Refrig.* **18**:355 (1995).
106. F. J. P. Caetano, J. M. N. A. Fareleira, C. M. B. P. Oliveira, and W. A. Wakeham, *J. Chem. Eng. Data* **50**:201 (2005).
107. F. J. P. Caetano, J. M. N. A. Fareleira, A. P. Fröba, K. R. Harris, A. Leipertz, C. M. B. P. Oliveira, and W. A. Wakeham, presented at *16th Symp. Thermophys. Props.*, Boulder, Colorado (July 30 to August 4, 2006).
108. R. F. Roy, A. E. Beck, and Y. S. Touloukian, *Physical Properties of Rocks and Minerals, CINDAS Data Series on Material Properties*, Vol. II(2) (1989), pp. 409–502.
109. G. Gehlhoff and F. Neumeier, *Verhandl. Deut. Physik. Ges.* **21**:201 (1919).

110. V. Peralta-Martinez, *Ph. D. Thesis* (Imperial College, London, UK, 2000).
111. M. V. Peralta-Martinez and W. A. Wakeham, *Int. J. Thermophys.* **22**:395 (2001).
112. V. A. Vel'tishcheva, N. A. Kalakutskaya, and N. A. Nikol'skii, *Teploenergetika* **5**:80 (1958).
113. W. C. Hall, *Physica Rev.* **2**:1004 (1938).
114. W. C. Hall, *Ph. D. Thesis* (Univ. Kansas, Lawrence, Kansas, 1936).
115. G. Meneaxidis, *Ph. D. Thesis* (Univ. Pierre et Marie Curie, Paris, 1979).
116. R. W. Powell and R. P. Tye, *International Developments in Heat Transfer, ASME* **103**:856 (1961).
117. M. P. Vukalovich, A. I. Ivanov, L. R. Fokin, and A. T. Yakovlev, *Thermophysicial Properties of Mercury*, Monograph No. 9 (State Committee for Standards at the Board of Minister of the Soviet Union, Moscow, 1971), p. 203
118. S. M. P. Prabhuram, *Ind. Eng. Chem. Fundam.* **21**:484 (1982).
119. C. T. Ewing, R. E. Seevold, J. A. Grand, and R. R. Miller, *J. Phys. Chem.* **59**:529 (1995).
120. M. J. Duggin, *Phys. Lett. A* **27**:257 (1968).
121. A. V. Grosse, *J. Inorg. Nucl. Chem.* **28**:803 (1966).
122. G. Bush, H. J. Guntherodt, and P. Wyssmann, *Physica Lett. A* **41**:29 (1972).
123. C. Y. Ho, R. W. Powell, and P. E. Liley, *J. Phys. Chem. Ref. Data* **3**:1 (1974).
124. M. V. Peralta-Martinez, M. J. Assael, M. Dix, L. Karagiannidis, and W. A. Wakeham, *Int. J. Thermophys.* **27**:353 (2006).
125. J. Bilek, *Sensors for Thermal Conductivity at High Temperatures* (Ph. D. Thesis, University of Southampton, UK, 2006).
126. J. Bilek, J. K. Atkinson, and W. A. Wakeham, *Int. J. Thermophys.* **27**:92 (2006).
127. J. Bilek, J. K. Atkinson, and W. A. Wakeham, *Proc. EuroSimE*, (Berlin, 2005), pp. 134–138.
128. W. A. Wakeham and V. Peralta-Martinez, *J. Chem. Thermodyn.* **33**:1623 (2001).
129. J. Bilek, J. K. Atkinson, and W. A. Wakeham, *Int. J. Thermophys.* (in press, DOI : 10.1007/s10765-006-0124-4).
130. V. Sklyarchuk and Yu. Plevachuk, *Meas. Sci. Technol.* **12**:467 (2005).
131. E. Yamasue, M. Susa, H. Fukuyama, and K. Nagata, *Int. J. Thermophys.* **24**:713 (2003).
132. M. V. Peralta-Martinez and W. A. Wakeham, *Int. J. Thermophys.* **22**:395 (2001).
133. W. Hemminger, *High Temp.-High Press.* **17**:465 (1985).
134. C. Y. Ho, R. W. Powell, and P. E. Liley, *J. Phys. Chem. Ref. Data* **1**:279 (1972).
135. K. C. Mills, B. J. Monaghan, and B. J. Keene, *Int. Mat. Rev.* **41**:209 (1996).
136. G. Wiedemann and R. Franz, *Ann. Physick* 2 **89**:497 (1853).
137. M. Hiza, J. Nighswander, and A. Kurkjian, in *Experimental Thermodynamics*, Vol. VI, *Measurement of the Thermodynamic Properties of Single Phases*, A. R. H. Goodwin, K. N. Marsh, and W. A. Wakeham, eds. (Elsevier for International Union of Pure and Applied Chemistry, Amsterdam, 2003), Chap. 4.
138. J. F. Johnson, J. R. Martin, and R. S. Porter, *Physical Methods of Chemistry*, Pt. VI, A. L. Weissberger and B. W. Rossiter, eds. (Interscience, New York, 1977), p. 63.
139. W. Künzel, H. F. van Wijk, and K. N. Marsh, in *Recommended Reference Materials for the Realization of Physicochemical Properties*, K. N. Marsh, ed. (Blackwell Scientific for International Union of Pure and Applied Chemistry, Oxford, UK, 1987), pp. 45–72.
140. J. C. Nieuwoudt and I. R. Shankland, in *Experimental Thermodynamics*, Vol. III, *Measurement of the Transport Properties of Fluids*, W. A. Wakeham, A. Nagashima, and J. V. Sengers, eds. (Blackwell Scientific for International Union of Pure and Applied Chemistry, Oxford, UK, 1991), Chap. 2, pp. 9–48.
141. M. Kawata, K. Kurase, A. Nagashima, and K. Yoshida, in *Experimental Thermodynamics*, Vol. III, *Measurement of the Transport Properties of Fluids*, W. A. Wakeham, A. Na-

gashima, and J. V. Sengers eds. (Blackwell Scientific for International Union of Pure and Applied Chemistry, Oxford, UK, 1991), Chap. 3, pp. 51–75.

142. M. Kawata, K. Kurase, A. Nagashima, K. Yoshida, and J. D. Isdale, in *Experimental Thermodynamics*, Vol. III, *Measurement of the Transport Properties of Fluids*, W. A. Wakeham, A. Nagashima, and J. V. Sengers eds. (Blackwell Scientific for International Union of Pure and Applied Chemistry: Oxford, UK, 1991), Chap. 5, pp. 97–110.
143. D. E. Diller and P. S. van der Gulik, in *Experimental Thermodynamics*, Vol. III, *Measurement of the Transport Properties of Fluids*, W. A. Wakeham, A. Nagashima, and J. V. Sengers, eds. (Blackwell Scientific for International Union of Pure and Applied Chemistry, Oxford, UK, 1991), Chap. 4, pp. 79–94.
144. R. Lundstrum, A. R. H. Goodwin, K. Hsu, M. Frels, D. R. Caudwell, J. P. M. Trusler, and K. N. Marsh, *J. Chem. Eng. Data* **50**:1377 (2005).
145. T. Sopkow, A. R. H. Goodwin, and K. Hsu, *J. Chem. Eng. Data* **50**:1732 (2005).
146. C. Harrison, M. Sullivan, S. N. Godefroy, N. Matsumoto, A. R. H. Goodwin, and K. Hsu, *J. Chem. Eng. Data* DOI: 10.1021/je0603980.
147. A. R. H. Goodwin, E. P. Donzier, O. Vancauwenberghe, A. D. Fitt, K. A. Ronaldson, W. A. Wakeham, M. Manrique de Lara, F. Marty, and B. Mercier, *J. Chem. Eng. Data* **51**:190 (2006).
148. E. Donzier, O. Lefort, S. Spirkovitvh, and F. Baillieu, *Sens. Actuators* A **25–27**:357 (1991).
149. R. Span and W. Wagner, *Int. J. Thermophys.* **24**:41 (2003).
150. D. R. Caudwell, *Viscosity of Dense Fluid Mixtures* (Ph. D. Thesis, University of London, 2004).
151. J. H. Dymond, J. Robertson, and J. D. Isdale, *Int. J. Thermophys.* **2**:133 (1981).
152. W. A. Felsing and G. M. Watson, *J. Am. Chem. Soc.* **64**:1822 (1942).
153. M. Dix, J. M. N. A. Fareleira, Y. Takaishi, and W. A. Wakeham, *Int. J. Thermophys.* **12**:357 (1991).
154. J. H. Dymond, J. Robertson, and J. D. Isdale, *J. Chem. Thermodyn.* **14**:51 (1982).
155. D. I. Sagdeev and G. Kh. Mukhamedzyanov, *Teplo-Massoobmen Khim.Tekhnol.* **5**:21 (1977).
156. E. Kiran and Y. L. Sen, *Int. J. Thermophys.* **13**:411 (1992).
157. W. G. S. Scaife and C. G. R. Lyons, *Proc. R. Soc. London, Ser. A* **370**:193 (1980).
158. T. S. Banipal, S. K. Garg, and J. C. Ahluwalia, *J. Chem. Thermodyn.* **23**:923 (1991).
159. R. Span, *Multiparameter Equations of State: An Accurate Source of Thermodynamic Property Data* (Springer, Berlin, 2000), pp. 247, 248, 255.
160. M. L. Huber, A. Laesecke, and H. W. Xiang, *Fluid Phase Equilib.* **224**:263 (2004).
161. C. M. B. P. Oliveira and W. A. Wakeham, *Int. J. Thermophys.* **13**:773 (1992).
162. N. A. Agaev and I. F. Golubev, *Gazovaia Promyshlennost* **8**:50 (1963).
163. C. V. Jakeways and A. R. H. Goodwin, *J. Chem. Thermodyn.* **37**:1093 (2005).
164. M. R. Cannon, *Ind Eng. Chem.* **16**:708 (1944).