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CURRENT TRENDS IN PRECISE CALORIMETRY

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ABSTRACT

Views are expressed on the recent decline in the number of scientists engaged in precise calorimetry, some prejudices relating to precise calorimetry are aired, the place of calorimetry in thermochemistry is explained, and the kinds of calorimeter currently in use for precise measurements are reviewed.

INTRODUCTION

Calorimetry of the highest precision seems nowadays to be practised in fewer and fewer laboratories by fewer and fewer experimentalists. Some of the greatest standardizing laboratories, like the United States Bureau of Standards and the National Physical Laboratory in the U.K., have all but lost the art of precise calorimetry, and few young scientists are moving up to replace those who have been moved to administrative or other work, those who have recently retired or are about to retire from university or governmental posts, or those who, like Stig Sunner from Lund and George Armstrong from Washington, most sadly, have died. Metrological calorimetry, and even careful calorimetry leading to measurements of "state-of-the-art" quality, seem to be dying, and that is happening paradoxically at a time when the number of *calorimeters* being used has multiplied enormously, though by nowhere nearly as much as the number of *papers* containing calorimetric results, often produced automatically, very quickly, and rather carelessly, and often on substances, and especially on mixtures or solutions, having little if any academic or practical interest. (I shall return to that point in connexion with measurements of the excess enthalpies of binary mixtures.) The decline of precise calorimetry is potentially disastrous, not only because we shall continue to need precise values of thermochemical quantities for new substances, and improved values for old substances, but also because many modern commercially available instruments, and especially those used for "differential scanning calorimetry" and related techniques, are still notoriously unreliable and desperately need the discipline of results obtained, albeit more long-windedly, by methods of measurement that are at once more rigorous, more precise, and much more reliable.

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SOME PREJUDICES ABOUT PRECISE CALORIMETRY

As a first example I quote an otherwise distinguished thermochemist who claimed in my hearing that for a calorimetric experiment, say in a bomb calorimeter having a temperature rise of 4.6800 K, the experimentalist should arrange the initial temperature to be (298.15 - 4.68/2) K = 295.81 K so as to ensure that "ΔU would be measured at 298.15 K". Simple analysis of the parts of a calorimetric experiment shows that argument to be fallacious. If the calorimeter is adiabatically enclosed and if, when the reaction is allowed to proceed from an initial extent ξ_i to a final extent ξ_f, no work being done, the temperature changes from an initial value T_i to a final value T_f, then

$$U(T_f,V,\xi_f) - U(T_i,V,\xi_i) = 0. \tag{1}$$

If the temperature of the (calorimeter + contents) is now returned to T_i, and is then changed to T_f as the result solely of a measured quantity of work W being done on the calorimeter, then

$$U(T_f,V,\xi_f) - U(T_i,V,\xi_f) = W. \tag{2}$$

When we subtract equation (2) from equation (1) we obtain

$$\Delta U \overset{\text{def}}{=} U(T_i,V,\xi_f) - U(T_i,V,\xi_i) = -W, \tag{3}$$

and we see that ΔU is measured at the initial temperature T_i, and not at some mean of T_i and T_f. Of course, in the second part of the experiment the final temperature need not be exactly the same as T_f; we may do a simple proportion sum to calculate what W would have been to have caused a temperature change exactly equal to $(T_f - T_i)$, though we must then check the validity of the assumption that the dependence of the heat capacity of the (calorimeter + contents) on temperature is negligible over the (usually short) temperature range. If the work W were done *before* the reaction then the temperature at which ΔU was measured would have been T_f. Even that kind of elementary first-law analysis is still too seldom practised.

As a second example I shall discuss the common practice in "isoperibol" calorimetry, that is to say in non-adiabatic calorimetry conducted with the calorimeter in thermal contact with a constant-temperature surroundings or thermostat, of making the rate of heat leakage as small as possible. It is not usually possible to make the rate of heat leakage negligible, if only because of the inevitable connexions, as of metallic leads to the electric "worker" and from the thermometer, between the calorimeter and its surroundings, without introducing the full panoply of precisely and rapidly temperature-controlled heat shields; then we should have moved into the realm of adiabatic calorimetry and that is not what we are proposing to discuss. Let us accept, then, that *some* non-negligible heat leakage is unavoidable, and defend the proposition that it would be better to design any calorimeter so that it has a *large* rate of heat leakage than to follow the traditional pattern by keeping it as small as possible. We begin by emphasizing that *all* methods of allowing for heat leaks, whether in "low rate of heat leakage" calorimetry of the traditional kind, for example by Dickinson's method, or in the "high rate of heat leakage" calorimetry that I shall describe in the following paragraph, depend on three assumptions. These are that the temperature T of the outer surface of the calorimeter is accurately uniform (so that there are no "hot spots" or "cold spots"), that the temperature T_e of the surroundings is constant and uniform, and that the heat flow Q in a time t from the outer surface of the calorimeter to the surroundings is governed by Newton's law:

$$Q = -k\int(T - T_e)dt, \tag{4}$$

where k is the Newtonian cooling coefficient.

The thermogram of a "high-k" calorimetric experiment (for the sake of simplicity, at constant volume) is shown in Fig. 1. In the first part of the experiment we allow a chemical reaction to proceed, allow the temperature to return completely to that of the surroundings, and integrate under the thermogram so as to obtain the area A_1. Then

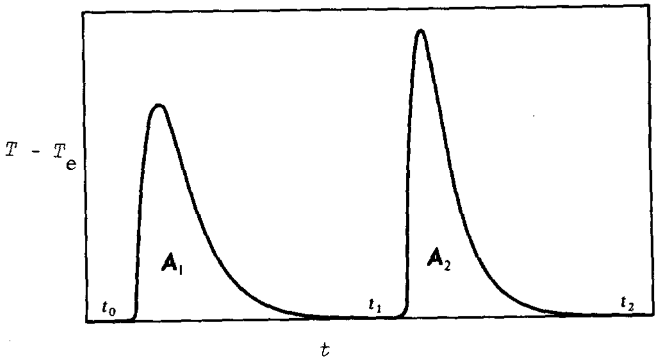

Fig.1. Plot of the temperature difference $(T - T_e)$ against time t (a thermogram) for two parts of a calorimetric experiment.

$$\Delta U \overset{\text{def}}{=} U(T_e,V,\xi_f) - U(T_e,V,\xi_i) = W_1 + Q_1 = 0 - kA_1. \tag{5}$$

We then supply (usually electrically) a measured quantity of work W_2, again allow the temperature to return completely to that (T_e) of the surroundings, and integrate under the thermogram so as to obtain the area A_2. Then

$$0 = U(T_e,V,\xi_f) - U(T_e,V,\xi_f) = W_2 + Q_2 = W_2 - kA_2, \tag{6}$$

so that $k = W_2/A_2$, and equation (5) becomes

$$\Delta U \overset{\text{def}}{=} U(T_e,V,\xi_f) - U(T_e,V,\xi_i) = -W_2A_1/A_2. \tag{7}$$

No problem arises when the reaction is endothermic, instead of exothermic as implied here, or when the calorimeter is a constant-pressure one, rather than a constant-volume one as here. A possible objection to our method, that it requires accurate integration of thermograms and that that is difficult, has faded with the advent of electronic integrators (and in any case is not removed in Dickinson's method in "small-k" calorimetry). Another possible objection, that the method demands a very precise base-line $(T - T_e) = 0$, needs only to be stated to reveal that this is *always* necessary; in "small-k" calorimetry its absence can be more conveniently hidden, even from the experimentalist! The value of k can usually be made large enough to ensure that $(t_1 - t_0)$ and $(t_2 - t_1)$ are about 30 to 60 min by filling the space between the calorimeter and its surroundings with helium at a presure of a few kPa. The method described is not new. It has been extensively used to study slow (and especially biological) processes and is used in "heat flow" or "conduction" calorimeters (refs. 1-3). What does appear to be new is the recommendation of its use with more conventional isoperibol calorimeters.

By contrast there is an enormous literature (see *e.g.* refs. 4-6) giving advice and counter-advice about methods of correcting for heat leaks in "small-k" calorimetry. Dickinson's method (ref. 7), which is by far the most popular, is illustrated in Fig. 2. The temperature rise ΔT that would have been observed had k been zero can be expressed in terms of the observed temperature rise $(T_2 - T_1)$ between times t_1 in the "fore" period and t_2 in the "after" period by use of the slopes $\mathrm{d}T/\mathrm{d}t$ measured at the times t_1 and t_2 and a "Dickinson time" t_D chosen so that the horizontally and vertically shaded areas in Fig. 2 are equal:

$$\int_{t_1}^{t_D}(T - T_1)\mathrm{d}t + \int_{t_D}^{t_2}(T - T_2)\mathrm{d}t = 0, \tag{8}$$

by means of the equation:

$$\Delta T = (T_2 - T_1) - \{(\mathrm{d}T/\mathrm{d}t)_{t_1}(t_D - t_1) + (\mathrm{d}T/\mathrm{d}t)_{t_2}(t_2 - t_D)\}. \tag{9}$$

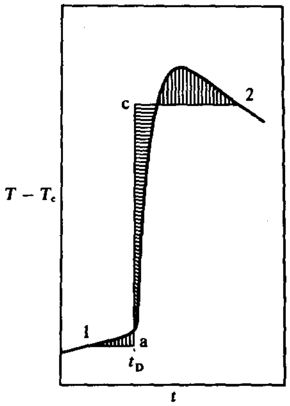

Fig. 2. Dickinson's method of correcting for heat leaks in an isoperibol calorimeter.

Dickinson's method is more tedious to calculate and no more precise than the "large-k" method.

As a final example I invite the reader to formulate precisely the difference of energy $\{U(T_f) - U(T_i)\}$ caused by raising the temperature of a glass ampoule partly filled by a solid substance of non-negligible volatility, the vapour space being filled with a mixture of helium and the vapour of the substance, initially at the pressure p_{i}. Even if the effect of pressure on the glass is neglected and even if the volume enclosed by the ampoule is regarded as being unchanged, neither of which is a good approximation, the contents of the ampoule will have changed in several ways: the amount of solid substance will have changed, some of it will have evaporated into the gaseous mixture, the composition of the gaseous mixture will have changed, and the pressure will have changed.

That is, indeed, an example of the commonest calorimetric problem: even though one has struggled to measure a ΔU or a ΔH as precisely as possible, with the passage of exactly which chemical reaction from which initial extent to which final extent should it be associated? How pure are the initial substances, how are they distributed among different phases, and what is the initial pressure; and exactly what are the final substances, how are they distributed among phases, and what is the final pressure? The calorimetrist must excel as a chemical analyst, too.

THERMOCHEMISTRY

The objective of the thermochemist is the completion of a table giving a precise value for the standard equilibrium constant $K_{\mathrm{f}}^{\ominus}(T)$ for the formation of every substance at temperatures T close enough to allow interpolation and ranging at least over all chemically relevant values.[*] There are two or three main routes to $K_{\mathrm{f}}^{\ominus}(T)$.

If $K_{\mathrm{f}}^{\ominus}(T^{\dagger})$ is known at the particular temperature $T^{\dagger}$, then

$$\ln\{K_{\mathrm{f}}^{\ominus}(T)/K_{\mathrm{f}}^{\ominus}(T^{\dagger})\} = \int_{T^{\dagger}}^{T}(\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\ominus}/RT^{2})\mathrm{d}T, \qquad (10)$$

and the integral can be evaluated if enough is known about the dependence of $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\ominus}$ on temperature either from measured values at several temperatures or, more often, from a measured value at one temperature (usually 298.15 K) together with values of standard molar heat capacities at constant pressure $C_{p,\mathrm{m}}^{\ominus}$ measured at temperatures over the range.

That is one of the reasons for the measurement and tabulation of standard molar enthalpies of formation, though often only at the single temperature 298.15 K, and for the tabulation of the standard molar heat capacities of substances as functions of temperature.

Another route to $K_{\mathrm{f}}^{\ominus}(T)$ lies in the use of the relation:

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[*] Or, of course, of $\ln\{K_{\mathrm{f}}^{\ominus}(T)\}$ or even of $-RT\ \ln\{K_{\mathrm{f}}^{\ominus}(T)\}$. Whether the latter be denoted by $\Delta_{\mathrm{f}}G_{\mathrm{m}}^{\ominus}$ and be called the "standard molar change of Gibbs function for formation" is a matter of choice.

$$\begin{aligned}\ln\{K_{\mathrm{f}}^{\ominus}(T)\} &= -\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\ominus}(T)/RT + \Delta_{\mathrm{f}}\{S_{\mathrm{m}}^{\ominus}(T) - S_{\mathrm{m}}(\mathrm{cr},T\to 0)\}/R + \Delta_{\mathrm{f}}S_{\mathrm{m}}(\mathrm{cr},T\to 0)/R \\ &= -\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\ominus}(T^{\dagger})/RT - (RT)^{-1}\Delta_{\mathrm{f}}\int_{T^{\dagger}}^{T} C_{p,\mathrm{m}}^{\ominus}(T)\,\mathrm{d}T + \Delta_{\mathrm{f}}\int_{0}^{T}\{C_{p,\mathrm{m}}^{\ominus}(T)/RT\}\,\mathrm{d}T \\ &\qquad + \Delta_{\mathrm{f}}S_{\mathrm{m}}(\mathrm{cr},T\to 0)/R, \qquad (11)\end{aligned}$$

in which $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\ominus}(T^{\dagger})$ is often known for $T^{\dagger} = 298.15$ K and each of the standard molar heat capacities $C_{p,\mathrm{m}}^{\ominus}$ is often known from $T\to 0$ to the higher of $T^{\dagger}$ and T.* The only remaining problem is the last term $\Delta_{\mathrm{f}}S_{\mathrm{m}}(\mathrm{cr},T\to 0)/R$. According to Nernst's Heat Theorem that term is often, even usually, zero, but we have no way of being certain that it is zero except that of using a different route!

Another route, restricted to electron-transfer reactions, depends on measurements of the e.m.f.'s of galvanic cells; that route would take us too far afield. So would the most direct route of all to $K_{\mathrm{f}}^{\ominus}(T)$, namely by calculating it from measured values of the extent of reaction at equilibrium.

Yet another route makes use, for reasonably simple gaseous molecules, of statistical-mechanical formulae and spectroscopically derived molecular quantities to calculate $K_{\mathrm{f}}^{\ominus}(T)$ sometimes without any calorimetric help but more often (because of our usual ignorance of the change of zero-temperature energy, though obtainable in principle from spectroscopy) with the help of a single calorimetrically determined $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\ominus}(T^{\dagger})$ at any one convenient temperature, usually 298.15 K.

Thus, thermochemistry implies the measurement of standard molar enthalpies of formation often only at 298.15 K but ideally at all temperatures, the measurement of standard molar heat capacities at constant pressure from temperatures so low that extrapolation to $T\to 0$ can confidently be made, up to the highest temperatures, and the measurement of standard molar enthalpies of transition, of melting, and of evaporation. In the determination of $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\ominus}$ by "Hessing" over a series of calorimetrically feasible steps, measured enthalpies of mixing, of dissolution, of dilution, and of compression, are also needed. The correction of measured ΔH_{m}'s to $\Delta H_{\mathrm{m}}^{\ominus}$'s, and of S_{m}'s to $S_{\mathrm{m}}^{\ominus}$'s, also implies a knowledge of other thermodynamic quantities some of which can be obtained calorimetrically. For example, for a pure gaseous substance:

$$H_{\mathrm{m}}(\mathrm{g},T,p) = H_{\mathrm{m}}^{\ominus}(\mathrm{g},T) + \int_{0}^{p}(\partial H_{\mathrm{m}}/\partial p)_{T}\,\mathrm{d}p, \qquad (12)$$

and the integrand can be determined flow-calorimetrically.

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*If the substance is a liquid at the temperature T then $\Delta_{\mathrm{fus}}H_{\mathrm{m}}^{\ominus}/RT_{\mathrm{fus}}$, and if a gas then $\Delta_{\mathrm{vap}}H_{\mathrm{m}}^{\ominus}/RT_{\mathrm{vap}}$, must be added, and even if the substance is crystalline one or more terms $\Delta_{\mathrm{trs}}H_{\mathrm{m}}^{\ominus}/RT_{\mathrm{trs}}$ might still be needed.

REACTION CALORIMETRY

Much chemical ingenuity has been put into finding reactions that will, or can be made to, go cleanly to completion in a calorimeter, and to the devising of conditions that will ensure that the enthalpies of phase transition, of dissolution, of mixing, of dilution, and of compression, needed for the Washburn corrections from a measured ΔU or ΔH to $\Delta H^\ominus$, are sufficiently accessible.

For all substances containing only C, H, and O, and for many other substances, combustion in oxygen at a pressure usually of about 3 MPa or more in a static bomb calorimeter like that shown in Fig. 3 leads to complete reaction to unambiguous products; static bomb calorimetry is still centrally important. For substances containing other elements a moving or rotating bomb is needed so that liquid added to the bomb before combustion leads to thoroughly equilibrated thermochemically identifiable dilute solutions after the combustion; moving bombs, such as that shown in Fig. 4, have revolutionized precise measurements of energies of combustion, especially for organic substances containing Cl, Br, I, N, P, and S. A new rotating-bomb calorimeter, recently described by Hajiev *et al.* (ref. 8), combines the advantages of a stirred-liquid and an aneroid calorimeter. Many important substances are available only in masses of at most a few mg, too small to allow conventional combustion calorimetry. The development of "mini-bombs" (refs. 9-11) and "mini-rotating-bombs" (refs. 12, 13), capable of the highest precision, is

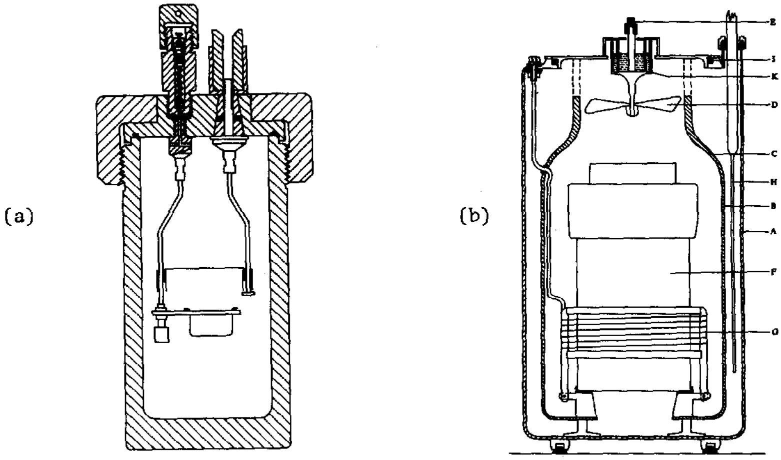

Fig. 3. (a), A typical combustion bomb. [Reproduced with permission from A. Gallenkamp & Co. Ltd.] (b), A complete bomb calorimeter. A, Rhodium-plated copper can; B, cylindrical stainless-steel shield (a poor thermal conductor), constructed in two parts; C, water-tight seal between the two parts of B; D, stirrer; E, bush; F, bomb; G, electric "worker"; H, platinum resistance thermometer; J, neoprene O-ring seal; K, oil seal. [Reproduced with permission from H.A. Gundry, D. Harrop, A.J. Head, and J.B. Lewis, *J. Chem. Thermodynamics*, 1 (1969) 321.]

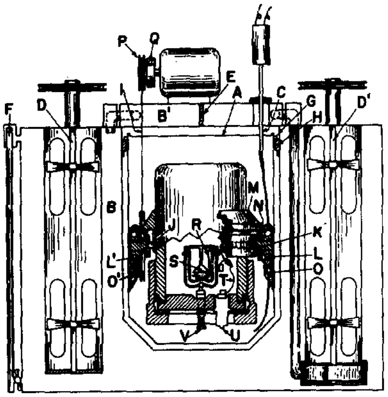

Fig. 4. A moving-bomb calorimeter. A, Calorimeter; B, B', constant-temperature jacket; C, thermometer; D, D', stirrers; E, partition to direct the circulation of water in the jacket lid B'; F, escape for excess water; G, three pegs resting in grooves in plastic blocks H; I, rotatory-mechanism drive wire; J, ball bearing mounted in yoke K which can rotate in ball bearings L, L', resting in grooves in copper blocks O, O'; M, N, gears causing the bomb to rotate about its cylindrical axis; P, pulley; Q, clutch plate. [Reproduced with permission from G. Waddington, S. Sunner, and W.N. Hubbard, in F.D. Rossini (Ed.), *Experimental Thermochemistry*, Interscience, New York, 1977, Chapter 7, p.156.]

therefore greatly to be welcomed; that of ref. 13 is shown in Fig. 5.

Combustion in fluorine (ref. 14), though confined to specialized laboratories, has proved a very fertile alternative. More recently other oxidants have been used, such as crystalline xenon difluoride, for example in the measurement of the energy of the reaction:

$$\mathrm{Ge(cr)} + 2\mathrm{XeF_2(cr)} = \mathrm{GeF_4(g)} + 2\mathrm{Xe(g)},$$

or oxygen difluoride, or caesium fluoroxysulphate.

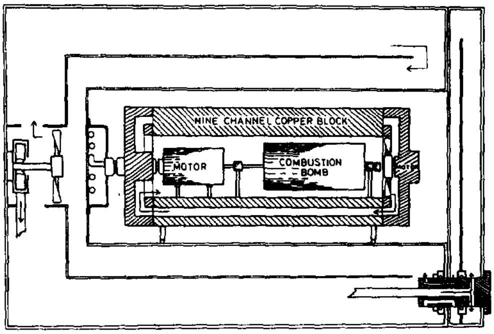

Fig. 5. A miniature rotating-bomb calorimeter. It is of "aneroid" type with helium circulating past the bomb and through channels in the copper block, facilitating heat transfer from the bomb to the block and within the block thereby reducing the equilibration time to about 20 min. The internal volume of the bomb is 18 cm^3 and the rotation motor, directly coupled to the bomb, is an integral part of the calorimeter. [Reproduced with permission from ref. 16.]

For sufficiently volatile substances, including gases, flame calorimetry can be used instead of bomb calorimetry. In a flame calorimeter streams of the gaseous sample (mixed if necessary with argon and pre-mixed with oxygen) and oxygen (or fluorine) are burnt at a jet in a combustion vessel like that shown in Fig. 6. The combustion vessel is immersed in a can of stirred water, the whole constituting the calorimeter, much as for a static bomb calorimeter. The pressure is usually close to atmospheric, which makes the Washburn correction easier, and constant, so that the quantity measured is $\Delta_c H$ rather than $\Delta_c U$. The gaseous products are passed through a spiral so as to bring them to thermal equilibrium with the calorimeter, and are then removed for analysis and determination of the extent of reaction.

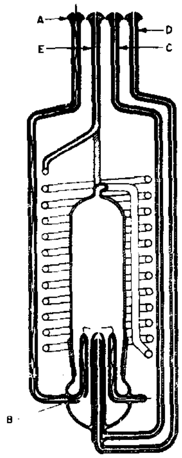

Fig. 6. Combustion vessel for flame calorimetry. The main supply of oxygen enters at A and is directed through orifice B to the bottom of the combustion chamber. Premixing oxygen enters at C, and the substance, carried if necessary in a stream of argon, enters at D. The mixture is ignited by a spark across the 4 mm gap between two platinum wires placed about 1 mm above the jet. The exit gases leave the chamber at its top and pass through a heat-exchange spiral before leaving the vessel at E. [Reproduced with permission from G. Pilcher, H.A. Skinner, A.S. Pell, and A.E. Pope, *Trans. Faraday Soc.* 59 (1963) 316.]

It must be emphasized that it is necessary to achieve the highest precision in combustion calorimetry because the desired enthalpy of formation is often a small difference between large quantities.

For reactions other than combustions "reaction calorimeters" like those shown in Fig. 7 are used and may according to need be either (a) static or (b) rocking or rotating.

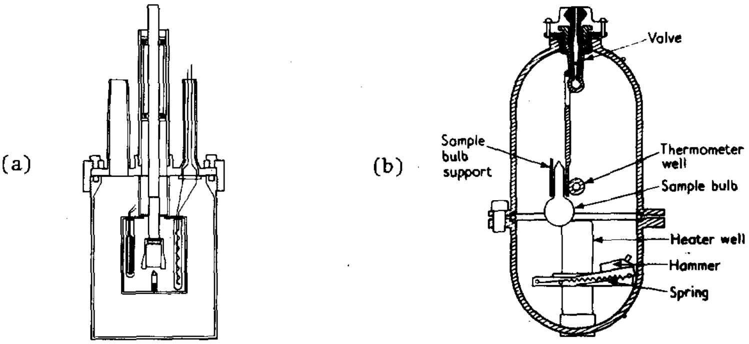

Fig. 7. (a), A carefully designed "reaction calorimeter". [Reproduced with permission from S. Sunner and I. Wadsö, *Acta Chem. Scand.* 13 (1959) 97.]
(b), A rocking closed calorimeter suitable for measurements of enthalpies of dissolution, and of other enthalpies of reaction. [Reproduced with permission from S.R. Gunn, *Rev. Sci. Instr.* 29 (1958) 397.]

The subject of reaction calorimetry has recently been reviewed (Refs. 15,16).

HEAT-CAPACITY CALORIMETRY

The measurement of $\{H(T_2,p) - H(T_1,p)\}$, or of $C_p \overset{\text{def}}{=} (\partial H/\partial T)_p$, for a substance differs from measurements of the enthalpy changes for chemical reactions or mixings or dissolutions or dilutions, all at constant temperature, because advantage can no longer be taken of the possibility of making the heat leaks identical, or otherwise correcting for them, in the two parts of a calorimetric experiment exemplified by equations (1) and (2). It is now mandatory for precise measurements, therefore, to resort to the full panoply of precisely and rapidly temperature-controlled shields so as to achieve as nearly as possible adiabatic working.

An adiabatic heat-capacity calorimeter, suitable for the study of solids or liquids, is shown in Fig. 8(a), and a recently developed laser-flash heat-capacity calorimeter is shown in Fig. 8(b). An alternative method for solids at high temperatures is that of dropping a sample of accurately known temperature into a calorimeter consisting of a vessel of liquid at a known initial and

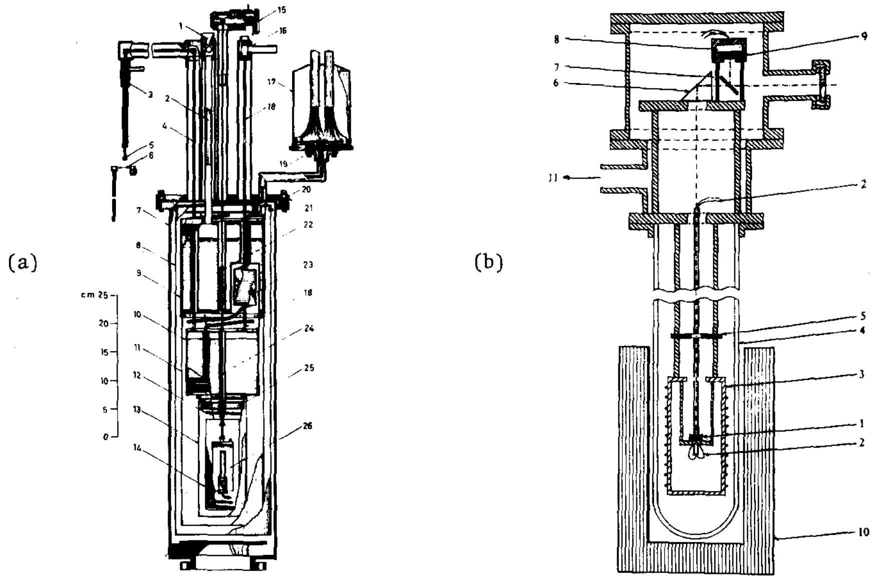

Fig. 8. (a), Cryostat for low-temperature heat-capacity calorimetry. 1, Liquid-nitrogen inlet and outlet connector; 2, liquid-nitrogen filling tube; 3, sleeve fitting to liquid-helium transport Dewar; 4, liquid-helium transfer tube; 5, screw fitting at the inlet of the liquid-helium transfer tube; 6, liquid-helium transfer-tube extender and cap; 7, brass vacuum jacket; 8, outer "floating" radiation shield; 9, liquid-nitrogen tank; 10, liquid-helium tank; 11, nitrogen radiation shield; 12, bundle of lead wire; 13, helium radiation shield; 14, adiabatic shield; 15, windlass; 16, helium-exit connector; 17, copper shield for terminal block; 18, helium-exit tube; 19, vacuum seal and terminal plate for leads; 20, O-ring gasket; 21, cover plate; 22, coil spring; 23, helium economizer; 24, supporting braided-silk line; 25, "floating" ring; 26, calorimeter. [Reproduced with permission from E.F. Westrum Jr., F.T. Furukawa, and J.P. McCullough, Chapter 5 in J.P. McCullough and D.W. Scott (Eds.), *Experimental Thermodynamics, Vol. I: Calorimetry of Non-reacting Systems*, Butterworths, London, 1968.]

(b), Laser-flash heat-capacity calorimeter. 1, Sample; 2, thermocouple wires; 3, internal heater; 4, quartz container; 5, adjusting slit; 6, prism; 7, reflecting glass; 8, silicon photoelectric cell; 9, attenuating glass; 10, outer heater or liquid-nitrogen bath; 11, vacuum line. [Reproduced with permission from Y. Takahashi, H. Yokokawa, H. Kadokura, Y. Sekine, and T. Mukaibo, *J. Chem. Thermodynamics* 11 (1979) 379.]

a measured final temperature (ref. 17).

For the heat capacities of gases it was until recently true that the problem as of weighing the captain of a ship by weighing the ship before and after he goes ashore made flow-calorimetric measurements necessary. Flow calorimetry will be dealt with below. Recently, however, static measurements of the heat capacity C_V have been made in a constant-volume calorimeter (see *e.g.* ref. 18); the method is one of great potential.

In spite of our use of the heading "heat-capacity calorimetry", no direct measurement of a heat capacity is actually possible; what is measured is the enthalpy increment $\{H(T_2,p) - H(T_1,p)\}$ (or an energy increment in constant-volume calorimetry). The heat capacity C_p is then derived from the relation:

$$C_p \overset{\mathrm{def}}{=} \lim_{T_2 \to T_1} [\{H(T_2,p) - H(T_1,p)\}/(T_2 - T_1)], \qquad (13)$$

but there seems little point in deriving it if all that is to be done with it is to integrate it again to find the enthalpy increment or the entropy increment, the latter being given by

$$S(T_2,p) - S(T_1,p) = \int_{T_1}^{T_2} T^{-1}\mathrm{d}\{H(T,p) - H(T_1,p)\}. \qquad (14)$$

However carefully it is carried out, a differentiation followed by an integration must be less accurate than an equally careful summation or integration.

FLOW CALORIMETRY

The flow calorimeter shown diagrammatically in Fig. 9 can be used to measure the molar enthalpy difference of a fluid flowing at an amount-of-substance rate $\dot{n}$ from left to right through a throttle and over an electric "worker" dissipating a power P:

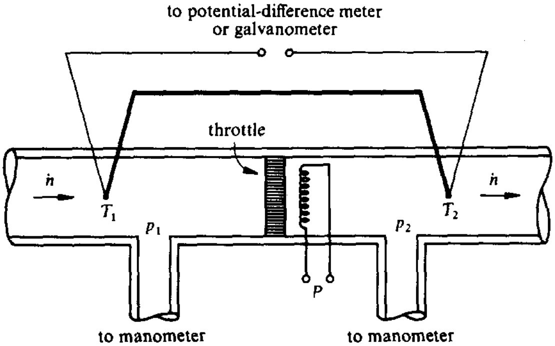

Fig. 9. A flow calorimeter fitted with a throttle, a difference (and an absolute) thermometer, a difference (and an absolute) manometer, an electric "worker", and a device for measurement of the amount-of-substance flow rate $\dot{n}$.

$$H_\mathrm{m}(T_2,p_2) - H_\mathrm{m}(T_1,p_1) = P/\dot{n}. \qquad (15)$$

If the throttle is fully open so that the pressure p_2 is very nearly equal to p_1 (though not quite equal, else $\dot{n} = 0$) then the measured quantity is the enthalpy increment discussed in the previous section. If the throttle is partly closed and the power P supplied to the fluid on the downstream side of the throttle is adjusted so that $T_2 = T_1$ then the measured quantity: $\{H_{\rm m}(T_1,p_2) - H_{\rm m}(T_1,p_1)\}$ is the isothermal Joule-Thomson enthalpy increment:

$$H_{\rm m}(T,p_2) - H_{\rm m}(T,p_1) = \int_{p_1}^{p_2}\{V_{\rm m} - T(\partial V_{\rm m}/\partial T)_p\}{\rm d}p. \tag{16}$$

If the throttle is partly closed but the electric "worker" is not used ($P = 0$) then $H_{\rm m}(T_2,p_2) = H_{\rm m}(T_1,p_1)$ and

$$\lim_{p_2 \to p_1}\{(T_2 - T_1)/(p_2 - p_1)\}, \tag{17}$$

is the (isenthalpic) Joule-Thomson coefficient. Only two of the three special cases are independent.

Modern flow calorimetry has recently been reviewed (ref. 19) and examples of even more recent work can be found (refs. 20, 21).

PHASE-CHANGE CALORIMETRY

For solid-to-solid transitions or for melting little need be added; it is true that calorimeters have been specially designed for such purposes, but any calorimeter that can be used to measure an enthalpy increment can be used through, or at, a transition temperature. For evaporation, however, the great disparity between the molar volumes of liquid and gas usually demands a calorimeter specially designed for the purpose. A typical design, combined with a heat-capacity flow calorimeter, is shown in Fig. 10.

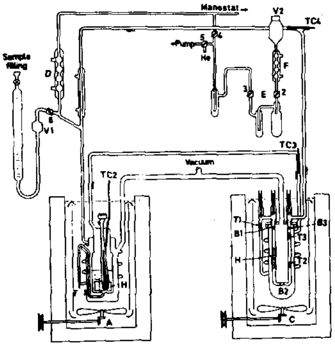

Fig. 10. A calorimeter for the measurement of an enthalpy of evaporation $\Delta_{\rm l}^{\rm g}H$ (left-hand part) and of the heat capacity at constant pressure $C_p({\rm g})$ of the gas (right-hand part). A, Thermostat for calorimeter to measure $\Delta_{\rm l}^{\rm g}H$; C, thermostat for calorimeter to measure $C_p({\rm g})$; D,F, condensers; E, sample receiver; 2,3, sample-receiver valves; 4,5,6, valves; V1,V2, solenoid-operated valves; T1,T2,T3, platinum resistance thermometers; H, heaters; TC1, TC2, TC3, TC4, thermocouples; B1,B2,B3, indentations to baffle the flow of vapour. [Reproduced with permission from J.P. McCullough and G. Waddington, Chapter 10 in J.P. McCullough and D.W. Scott (Eds.), *Experimental Thermodynamics, Vol. I: Calorimetry of Non-reacting Systems*, Butterworths, London, 1968.]

MIXING CALORIMETRY

The problem of measuring the enthalpy of mixing of two liquids depends on keeping the two liquids apart before they are mixed, usually with the help of mercury, and on mixing with absolutely no vapour space above either liquid and with the volume change absorbed with little or no change of pressure. The problem has been solved (perhaps too well!) as in the batch calorimeter shown in Fig. 11 or more recently in the continuous-dilution calorimeter shown in Fig. 12.

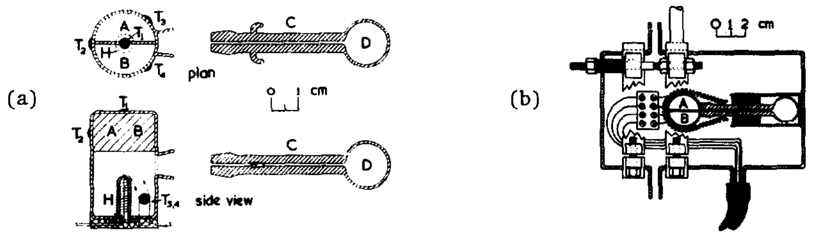

Fig. 11. A calorimeter for measurements of enthalpies of mixing. The liquids are separately confined by mercury and mixed by rotation of the calorimeter. The side-arm C, partly filled with mercury, allows expansion or contraction against an air space D, never in contact with the liquids, so that mixing is at virtually constant pressure. (a), Plan and side view of the calorimeter: T, thermistors; H, electrical heater. (b), The calorimeter in its evacuable jacket arranged so that it can be rotated backwards and forwards through an angle of π clockwise (so as to keep the liquids away from the side arm) about a vertical axis in the plane of the diagram. [Reproduced with permission from J.A. Larkin and M.L. McGlashan, *J. Chem. Soc.* (1961) 3425.]

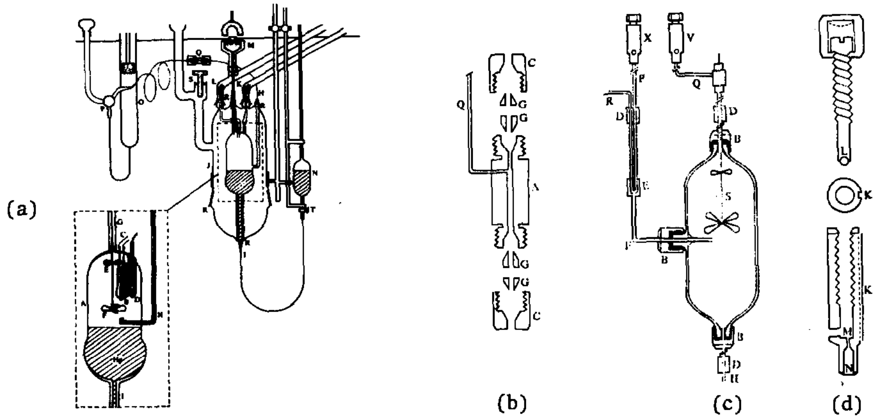

Fig. 12. Isothermal displacement calorimeter. (a), Original version. A, Mixing vessel silvered except for viewing strip, heat capacity (empty) about 20 J/K, capacity 38 cm^3; B, nichrome-wire heater ($R \approx 100\ \Omega$) 0.008 cm diameter on 2 cm × 2 cm flat mica former; C, heater-lead seals (tungsten-to-pyrex); D, thermistor well; E, two-bladed stirrer, 12 mm in diameter; F, four-bladed stirrer, 15 mm in diameter; G, stirrer-shaft tube, with sufficient clearance to allow bubbles to be ejected up the tube during filling; H, stainless-steel inlet tube of 0.66 mm i.d. cemented into glass capillary tube; I, stainless-steel outlet tube; J, vacuum jacket; K, thermistor leads; L, heater leads; M, drive chamber; N, mercury pipette; O, piston-burette; P, 3-way tap, teflon-to-glass, with stainless-steel tubes attached; Q, inlet coupling; R, soldered seals; S, high-vacuum teflon tap; T, tap on mercury pipette. (b-d), Later version. (b), Stirrer-shaft union. (c), Modified calorimeter vessel. (d), Detail of miniature ball valve at X and V of (c). [Reproduced with permission from R.H. Stokes, K.N. Marsh, and R.P. Tomlins, *J. Chem. Thermodynamics* 1 (1979) 211; and M.B. Ewing, K.N. Marsh, R.H. Stokes, and C.W. Tuxford, *J. Chem. Thermodynamics* 2 (1970) 751.]

Unfortunately, the literature has been deluged during the past fifteen years or so with measurements of the excess molar enthalpy H_m^E of mixtures of two liquids, often chosen only because they are cheap and happen (usually for perfectly good reasons) not to have been measured before, often measured at only one temperature or, little better, at only two or three very closely spaced temperatures, and all too often having a precision well below that of the "state of the art". It is hard to justify publication of such measurements; they are not scientifically interesting, whether metrologically or otherwise. It is even harder to justify publication of the "interpretation" or "rationalization" of such measurements; in the absence of an algebraic theory, only the wildest and most undisciplined speculation is possible. The measurement of excess enthalpies has become too easy; far too many workers are using the ritual performance of such measurements as a substitute for thought. (Only the corresponding measurements of excess volumes, which are even easier to make nowadays, lead to a greater flood of second-rate work.)

Whereas the mere collection of more and more excess enthalpies is a waste of time, effort, and money, there are of course some classes of mixtures which lead to scientifically most interesting results. A good example is mixtures of simple condensed gases like $\{(1 - x)\mathrm{Ar} + x\mathrm{CH_4}\}(\mathrm{l})$, or even $\{(1 - x)\mathrm{Xe} + x\mathrm{CO_2}\}(\mathrm{l})$ in which one of the molecules is strongly quadrupolar, for which a family of theoretical treatments exists (ref. 21) and cries out to be tested. Another example is an attempt (ref. 22) to discover whether chiral discrimination is revealed, for example, by measurements of H_m^E on (+) and (-) enantiomers; it *is* revealed, though only to the extent, for $\{0.5\mathrm{A}_+ + 0.5\mathrm{A}_-\}$, of -(4.51±0.07) J/mol when A = $\mathrm{C_{10}H_{16}O}$ (fenchone) and of +(7.34±0.06) J/mol at 303.11 K and +(5.28±0.04) J/mol at 313.11 K when A = $\mathrm{C_6H_5CH(CH_3)NH_2}$ (α-methylbenzylamine). A final example is an attempt (ref. 23) to discover as much as possible about the nature of the singularity at a critical point by measurements of H_m^E made on an apparatus like that of Fig. 12 at temperatures extremely close to the upper critical solution temperature ($T^\mathrm{c} \approx 318.4$ K) of $\{(1 - x)c\text{-}\mathrm{C_6H_{12}} + x\mathrm{CH_3OH}\}$. For an experiment at $(T - T^\mathrm{c})/T^\mathrm{c} = 2.07 \times 10^{-5}$, that is to say at a temperature only 0.0066 K above the critical temperature, the deviations $\delta_{|}\ln H_\mathrm{m}^\mathrm{E}$ plotted in Fig. 13 are deviations from a complex theoretical formula (with a so-called Wegner correction included) containing only three disposable parameters (apart from two which are found from the shape of the coexistence curve of temperature against composition). The deviations are nowhere greater than 5×10^{-4} and the standard deviation is 2×10^{-4}, or 0.15 J/mol in a measured H_m^E of about 770 J/mol. That is the kind of precision necessary in such work, and must of course be combined with exquisite control of the temperature. The experiment shown in Fig. 13 is one of five made at temperatures from 1.288 to 0.007 K above T^c and four from 0.032 to 0.322 K in the two-phase region below T^c.

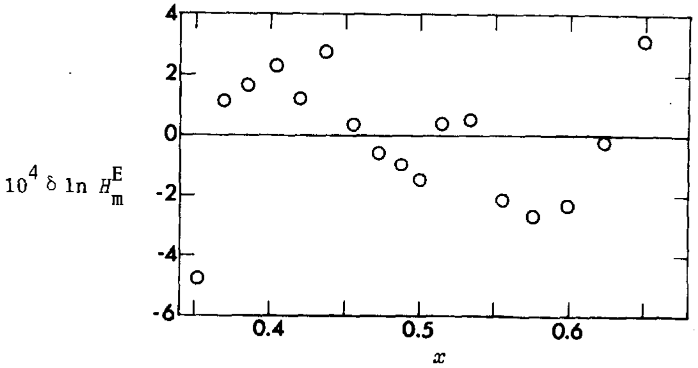

Fig. 13. Plot of the deviations $\delta \ln H^E_m$ of measured excess molar enthalpies from a theoretical formula against mole fraction x for $\{(1 - x)c\text{-}C_6H_{12} + x CH_3OH\}$ at $(T - T^c)/T^c = 2.07 \times 10^{-5}$ or $T = T^c + 0.0066$ K.

We have still to deal with the measurement of the enthalpy of mixing of two gases, and so conclude this lecture by returning to flow calorimetry and showing in Fig. 14 an example of a suitable apparatus.

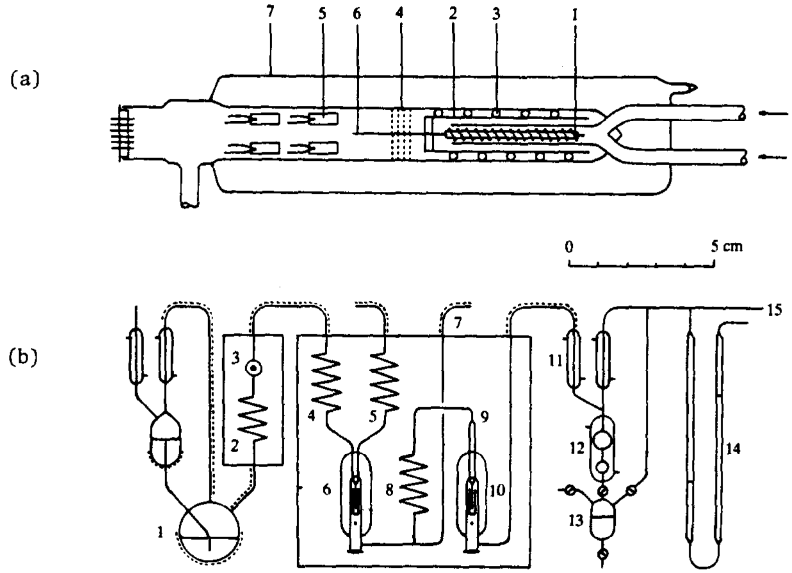

Fig. 14. Flow calorimeter for measurements of the enthalpy of mixing of gases. (a), The calorimeter: 1, heater; 2, cylindrical tufnol baffle to reverse flow; 3, helical woven-glass sleeve to direct flow in a spiral path over the outside of the baffle; 4, copper-gauze disks to ensure that the gas flows over thermometer 5 at uniform speed and that any heat conducted up the electrical lead 6 is returned to the gas stream; 7, silvered vacuum jacket. (b), Arrangement of flows and of the second (non-mixing) calorimeter: 1, boiler; 2,4, 5,8, heat-exchanger coils; 3, needle valve; 6, mixing calorimeter; 7, to manometer; 9, stream splitter; 10, second (non-mixing) calorimeter as nearly as

possible identical to 6; 11, condenser; 12, calibrated bulbs for measurement of volumetric flow rate; 13, vessel from which a sample of liquid can be withdrawn for determination of its composition; 14, manometer used to measure the outlet pressure; 15, to vacuum pumps and controller. [Reproduced with permission from J.A. Doyle, D.J. Hutchings, J.C. Mayr, and C.J. Wormald, *J. Chem. Thermodynamics* 13 (1981) 261.]

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