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The art of calorimetry

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Abstract

An introduction to the various types of calorimeters is given. The requirements for precise temperature measurements with thermistors are derived. Methods and equations for accurate heat exchange corrections for isoperibol temperature-change calorimetry under various conditions are derived. The characteristics and design principles for constant temperature baths are discussed. The construction of devices for addition of reagents, of stirrers, and of calibration heaters is described.

Keywords: Calorimetry; Temperature; Thermistor; Heat exchange corrections; Constant temperature baths; Stirrers; Heaters; Calibration

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1. Introduction

The science of calorimetry consists of only two laws; the law of conservation of energy and the law of heat transfer. The art of calorimetry is the large, and still growing, body of knowledge on the craft required to make accurate measurements of heat and rate of heat exchange.

There are only three methods for measuring heat: (1) measurement of a temperature change which is then multiplied by a thermal equivalent (the apparent heat capacity) determined in a calibration experiment; (2) measurement of the power required to maintain isothermal conditions, with the power being supplied either through an electronic temperature controller or by an isothermal phase change in a substance in contact with the calorimeter; and (3) measurement of a temperature difference across a path of fixed thermal conductivity, the thermal conductivity being determined in a separate calibration experiment. All of the methods are based on measurement of relative temperatures except the method which uses a phase change, in which case the measurement consists of determining the amount of phase change that has occurred and multiplying by the enthalpy change for the phase change. All calorimetric measurements thus require at least two separate experiments, one for the measurement and one for calibration, and may require a third for a baseline (zero) determination.

A reaction calorimeter always has three identifiable components that directly affect the quality of the data: (1) the calorimeter vessel, including the means for heat measurement; (2) the immediate surroundings of the reaction vessel which may range from a high precision liquid bath or temperature-controlled metal block to simply the laboratory atmosphere; and (3) a means for initiating the reaction which may again be complex or may be simply some means for insertion of a sample. The design of the calorimetric vessel and reaction initiation method are largely determined by the nature of the reaction and the physical properties of the reactants and products. The choice of a method for heat measurement is largely dictated by the time resolution desired in the measurement. In general, the temperature rise method has a shorter time constant than power compensation, which in turn has a shorter time constant than the heat conduction method. The calorimeter may contain duplicate reaction vessels (twins) with one vessel acting as a blank reference for the measurements. The blank or reference vessel serves to subtract extraneous effects from the measurements. The surroundings may be either isoperibol (i.e. constant T and p) or adiabatic (i.e. controlled to be at the same T as the reaction vessel). Reaction initiation may be done by changing the temperature, pressure, or volume (for example, by scanning the temperature), or by changing the concentration of a reactant or catalyst. Concentration changes may be accomplished by mixing the reactants all at once (batch reac-

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tor), by incremental or continuous titration, by mixing in a continuous flow reactor, or by changing the partial pressure of a gas in the calorimeter vessel. Reactants may be completely contained within the calorimetric vessel at the beginning of an experiment or may be added from outside the vessel.

2. Nomenclature

Calorimeter designs have traditionally been named for either the developer or some unique characteristic, e.g. the Bunsen ice calorimeter, the Parr oxygen bomb calorimeter, the Tian-Calvet calorimeter, a titration calorimeter, and a differential scanning calorimeter. Such names were appropriate before the advent of commercially available calorimeters which are often acquired and operated by people with little historical knowledge of the field of calorimetry, but continued use of such nomenclature other than for historical purposes is detrimental to further development of calorimetry. A simple and widely acceptable systematic nomenclature for calorimeters such as suggested in [1] would help both novices and long-time devotees of calorimetry to better organize their knowledge of and access to the subject. The scientific name of a calorimeter should consist of four parts, with the first three describing one of the necessary components of the calorimeter. These are, in order, (a) the surroundings (either isoperibol or adiabatic), (b) the principle of heat measurement (either temperature-change, power-compensation, or heat-conduction), (c) the method of reaction initiation (e.g. batch, incremental titration, continuous titration, flow, temperature scanning, pressure scanning), and (d) other descriptors. The fact that many calorimeters can be operated in more than one way has given rise to glaring misnomers like "isothermal DSC" (which literally means "*isothermal* differential *temperature-scanning* calorimeter"). In such a case the calorimeter should be named according to the way it is operated in a given application.

3. Temperature measurements with thermisters

Accurate measurement of heat invariably involves control and/or measurement of temperature, but the absolute temperature is only required for establishing the temperature of the measurement. Only relative temperature need be measured for a heat determination, but the sensitivity of the heat measurement can be no better than the sensitivity of the temperature measurement. The thermometer must be very stable, but only for a time period exceeding the period of the experiment. Long-term stability is a convenience rather than a requirement. Although other sensors can be used, thermistors are particularly useful for this application for two reasons; high sensitivity thermometers are easily constructed from very simple and inexpensive components, and because of the very small mass of the sensor, the time constant can also be very small. In practice, most other sensors have a lower sensitivity and/or a longer time constant than a thermistor.

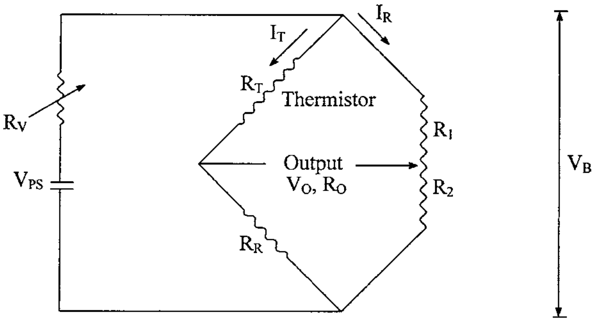

Fig. 1. Wheatstone-type thermistor bridge for high-sensitivity measurements of changes in relative temperature.

The major disadvantage of thermistors is that they are self-heated. This is important in some applications because the temperature measured by a self-heated sensor depends on the power generated in the sensor and the thermal conductivity between the sensor and surroundings. The power generated in the sensor is fixed by the electrical power, but thermal conductivity to the surroundings may be altered by changes in the surroundings. For example, a change in the wetting properties or a change in stirring pattern or velocity of the liquid the sensor is immersed in or formation of a precipitate or bubble around the sensor can cause large changes in the sensor temperature that are not reflective of temperature changes in the medium.

Although there are several thermistor circuits that can be used for temperature measurement [2], a simple Wheatstone-type bridge as shown in Fig. 1 is suitable for most applications. Properly designed, such a bridge with a sensitivity of tens of $\mathrm{mV\,K^{-1}}$, a noise level less than $1\,\mu\mathrm{K}$, a time constant of less than 0.1 s, an output very close to linear in temperature over more than 1 K, and stable over more than a day can be constructed in a few minutes and at a very nominal cost. The problem of designing such a bridge consists of choosing components and constructing the bridge to minimize noise sources and optimize sensitivity. Any other resistance type sensor may replace the thermistor in the following discussion, only the details will differ.

The bridge should be designed to obtain the required temperature resolution without an amplifier if possible and with an impedance 1000 times less than the output detector. Most digital devices currently available have input impedances in the GΩ range, but strip chart recorders and some older amplifiers and digital devices still in use have input impedances in the MΩ range. To avoid loading a bridge connected to a lower impedance device, the sum of $R_1 + R_T$ or of $R_R + R_2$ must be less than about 10 kΩ. In addition, as a practical matter, each of the resistive components of the bridge should be below 50 kΩ to avoid problems associated with leakage currents. Also, thermistors with room temperature resistance above 50 kΩ are generally made from materials that are not as stable over a long time period. Most detectors have a natural detection limit, i.e. without additional amplification, of about ±1 μV. Therefore, the bridge sensitivity should be such that 1 μV is equal to the desired detection limit in ΔT.

The output voltage of a bridge as shown in Fig. 1 operated in a near balance condition is given by Eq. (1).

$$V_o = V_B \left[\frac{R_2}{R_1 + R_2} - \frac{R_R}{R_R + R_T} \right] \tag{1}$$

The sensitivity S of the bridge is obtained by taking the temperature derivative of Eq. (1) as given in Eq. (2)

$$S = \alpha r(1 - r)V_B \tag{2}$$

where α is the relative temperature dependence of the sensor (equal to $(dR_T/dT)/R_T$ with units of reciprocal temperature), r is the ratio $R_R/(R_R + R_T)$ and V_B is the voltage across the bridge. Because the voltage drop across the thermistor V_T is equal to $(1 - r)V_B$, S is also given by Eq. (3)

$$S = \alpha r V_T \tag{3}$$

Note that S is independent of the value of $R_1 + R_2$ and that the bridge does not have to have equal arms, i.e. R_R does not have to equal R_T. What can be said so far about the choice of components is that the sums $R_1 + R_2$ and $R_R + R_T$ must be high enough not to overload the current capability of the power supply V_{ps} and that S will increase linearly with V_B.

The optimum values for R_R, R_T and V_B depend on the relative magnitudes and sources of noise in the measurement and on the time constant selected. Three sources of noise must be considered; the thermistor and its immediate surroundings, the power supply and the remainder of the bridge elements. Because the noise actually seen in the detector will be a function of the overall time constant τ of the thermometer circuit, τ should be chosen to be the maximum value consistent with the measurements to be done with the bridge. The best means for establishing τ is with a low-pass RC filter placed across the input to the detector. To minimize the effects of noise, this RC filter should have a time constant longer than any other component in the circuit.

Three types of noise in the thermistor itself must be considered, i.e. noise that is independent of V_B, noise that increases linearly with V_B, and noise that increases as some higher power of V_B. Johnson (or white) noise, $1/f$ (or pink) noise and shot noise are independent of V_B. Shot noise is of such high frequency that it will be filtered out if $\tau > 0.5$ s and thus will not be considered further here. The $1/f$ noise depends on the surface properties of the semiconductor material in the thermistor. Because generation and recombination rates of carriers in surface energy states and the density of surface carriers are important in determining the level of this noise, thermistors from different manufacturers and in different resistance ranges, i.e. made of different materials, may have significantly different $1/f$ noise. At the low frequencies considered here $1/f$ noise will have approximately the same dependence on circuit properties as Johnson noise. Johnson noise can be calculated by Eq. (4)

$$V_{Jrms} = (4kTR_T\,\Delta f)^{0.5} \tag{4}$$

where V_{Jrms} is the root mean square of the Johnson noise voltage, k is Boltzmann's constant, T is the kelvin temperature, and Δf is the noise frequency bandwidth. Assuming the circuit is equivalent to a simple, one RC circuit, Δf can be replaced by $1/4\tau$ as shown in Eq. (5)

$$\Delta f = (2\pi RC)^{-1}\left(\frac{\pi}{2}\right) = (4RC)^{-1} = \frac{1}{4\tau} \tag{5}$$

Substituting (5) into (4) and combining constants gives Eq. (6)

$$V_a = \left(\frac{aR_T}{\tau}\right)^{0.5} \tag{6}$$

which represents the sum of the $1/f$ and Johnson noise if a is an empirical constant.

The noise linear in V_B results from thermal noise in the material in which the thermistor is immersed. The noise voltage at the detector from this source is described by Eq. (7)

$$V_b = \left(\frac{b}{\tau}\right)^{0.5} V_T \tag{7}$$

where b is an empirical constant. The magnitude of this noise source depends on the nature of the material in contact with the thermistor. For example, a vigorously stirred liquid will have a higher thermal inhomogeneity than a block of high thermal conductivity metal.

The third type of noise results from self-heating in the thermistor and thus depends on the rate of heat dissipation from the thermistor to the surroundings as shown in Eq. (8)

$$V_c = \left(\frac{c}{\tau}\right)^{0.5} \frac{P_T}{\kappa} \tag{8}$$

where c is an empirical constant, P_T is the power generated in the thermistor, and κ is the thermal conductivity from the thermistor bead to the surroundings.

Combining Eqs. (6)–(8) as required by the statistics of independent noise sources and substituting ${V_T}^2/P_T$ for R_T in Eq. (6) results in Eq. (9)

$$V_{\text{rms noise}} = \left\{ \left[\frac{{V_T}^2}{\tau}\right] \left[\frac{a}{P_T} + b + \frac{cP_T}{R_T\kappa^2}\right] \right\}^{0.5} \tag{9}$$

for the root mean square noise expressed as a voltage. To express the noise as the peak-to-peak temperature noise T_n, Eq. (9) is multiplied by 6 and divided by the bridge sensitivity from Eq. (3). The result is Eq. (10)

$$T_n = \frac{6V_{\text{rms noise}}}{\alpha r V_T} = \left[\frac{6}{\alpha r \tau^{0.5}}\right] \left[\frac{a}{P_T} + b + \frac{cP_T}{R_T\kappa^2}\right]^{0.5} \tag{10}$$

Similar, but not identical, equations have previously been published by others [3,4]. What is clear from both Eq. (10) and the literature equations is that there is a well defined minimum in T_n as a function of P_T and thus an optimum P_T at which a given bridge should be operated.

T_n can be determined as a function of P_T with an experimental system such as that described in Fig. 2. The important

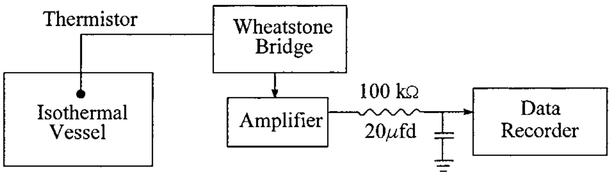

Fig. 2. Experimental setup for thermistor-bridge noise measurements with a fixed time constant of 2 s.

features of the equipment shown in Fig. 2 are (a) the time constant of the isothermal vessel must be long compared to that of the RC filter, 2 s in the case shown, (b) the environment of the thermistor in the isothermal vessel must closely resemble the actual environment the thermistor will be used in, (c) the RC filter must determine the time constant of the system or τ must be a constant determined by some other component of the system, and (d) the data collection rate must be several times faster than τ. Under these conditions, measurement of the width of the band of ink on a plot of voltage versus time is a good measure of the peak-to-peak noise if the time scale is compressed so that a solid band of ink is produced. The isothermal vessel need not be truly isothermal so long as the time constant of the drift rate is much smaller than τ, and the actual calorimeter reaction vessel will usually serve this purpose. The value of τ should be reported with any description of the bridge. The literature on temperature measuring circuits contains many examples of reportedly better, i.e. lower noise, circuits which are in fact poorer designs, but which have longer time constants than the circuits used for comparison. Passive noise in the circuit and detector with $V_B = 0$ should also be measured and reported.

Fig. 3 shows a typical set of T_n noise data obtained as a function of P_T with $\alpha = 4\%/K$. Several different bridge configurations tested at the same τ value of 2 s with the thermistor in stirred water gave very similarly shaped curves with the minimum at about the same P_T value. The minimum in T_n establishes the optimum P_T value and the detection limit for a particular bridge. The branch of the curve at low P_T values is largely determined by the values of a and b in Eq. (10) and is curved as predicted. The curve at high P_T values is essentially linear as predicted by Eq. (10) if the third term is much larger than the first term. The slope of the curve at high P_T values is thus a measure of $c/R_T\kappa^2$. A value for κ can be obtained as the slope of a plot of the apparent temperature measured against P_T as in the example shown in Fig. 4. The data shown in Fig. 5 verify the functional dependence of T_n on P_T given in Eq. (10) and show that the thermal inhomogeneities present in the medium surrounding the thermistor are very important in determining the value of the minimum in curves such as shown in Fig. 3.

Since P_T at the minimum T_n value is largely dependent on the surroundings and not on bridge configuration, P_T for a given condition may be treated as a constant. Substitution of the square root of P_TR_T for V_T in Eq. (3) gives Eq. (11)

$$S = \alpha r (P_T R_T)^{0.5} \tag{11}$$

showing that bridge sensitivity is linear with the square root of R_T. Assuming $\alpha = 0.04\,K^{-1}$ and $P_T = 0.25\,mW$ then allows construction of Fig. 6. The large triangle outlined in bold in Fig. 6 defines all of the bridges with $S > 50\,mV\,K^{-1}$ (i.e. 20 μK gives ≥1 μV), $r \le 0.9$, and $R_T \le 62.5\,k\Omega$. The small triangle defines all the low impedance bridges with $R_T \le 10\,k\Omega$.

As an example of how a figure like 6 can be used to design a bridge, assume a thermistor bridge with an output sensitivity of $100\,mV\,K^{-1}$ is desired for use in a stirred

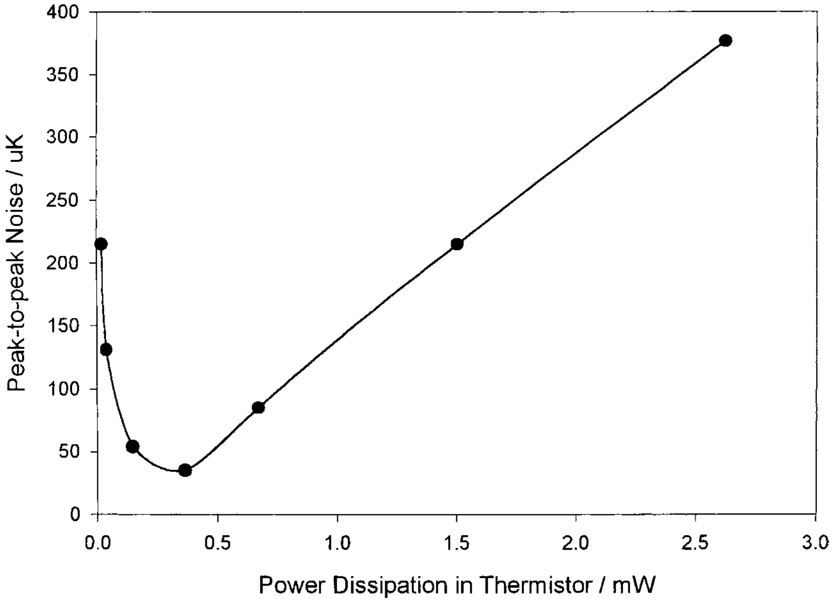

Fig. 3. Temperature noise data collected in a 25 ml Tronac isoperibol power-compensation calorimeter vessel stirred at 600 rpm.

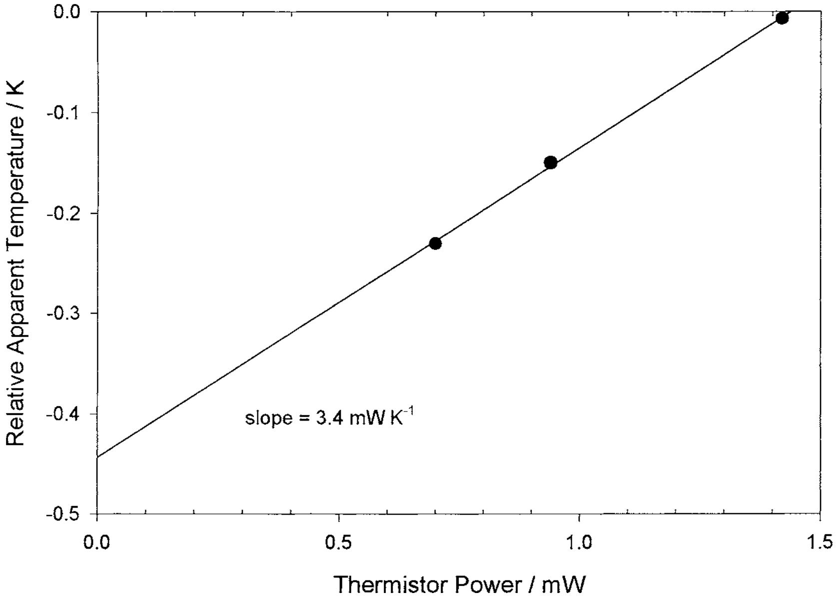

Fig. 4. Sample of data showing how κ, the thermal conductivity between the thermistor and surroundings, may be determined.

liquid similar to water. Assuming the same values for α and P_T used to generate Fig. 6, any thermistor resistance between 30 and 60 kΩ would be suitable. Selecting 50 kΩ for the thermistor resistance then determines the values of $r = 0.7$ and $V_T = 3.6$ V. V_B therefore equals 12 V for this sensitivity (see the derivation of Eq. (3)).

Fig. 6 was derived on the assumption that $P_T = 0.25$ mW gives the minimum noise possible in the system. This value of P_T was based in turn on $T_n = 20$ μK peak-to-peak, which is probably the minimum achievable noise in stirred water. Fig. 5, however shows that lower noise levels can be achieved in other media, namely a metal block in the example shown, as a result of a lower value of b in Eq. (10). Eq. (10) shows that the value of P_T moves to a smaller value as b and c are reduced. According to Fig. 6, achieving higher sensitivity requires going to higher values of V_B, r and R_T. There are practical limits to increasing these parameters, however, and sensitivities above about 150 mV K^{-1} are better achieved by increasing the detection limit of the detector or adding an amplifier to the system. With an amplifier or detector capable of resolving 0.1 μV, a simple DC thermistor bridge can detect temperature changes of about 1 μK.

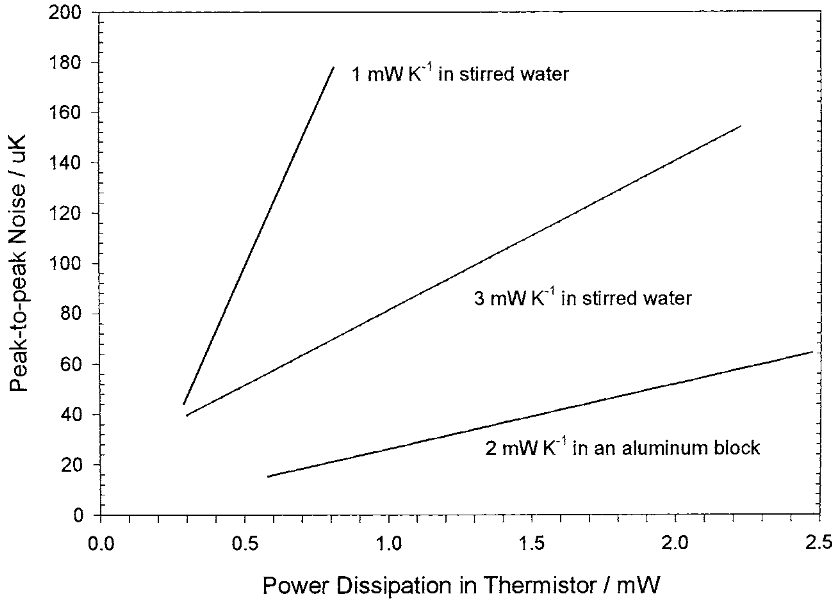

Fig. 5. Data showing examples of the dependence of T_n on κ and surroundings of a thermistor in a wheatstone-type bridge.

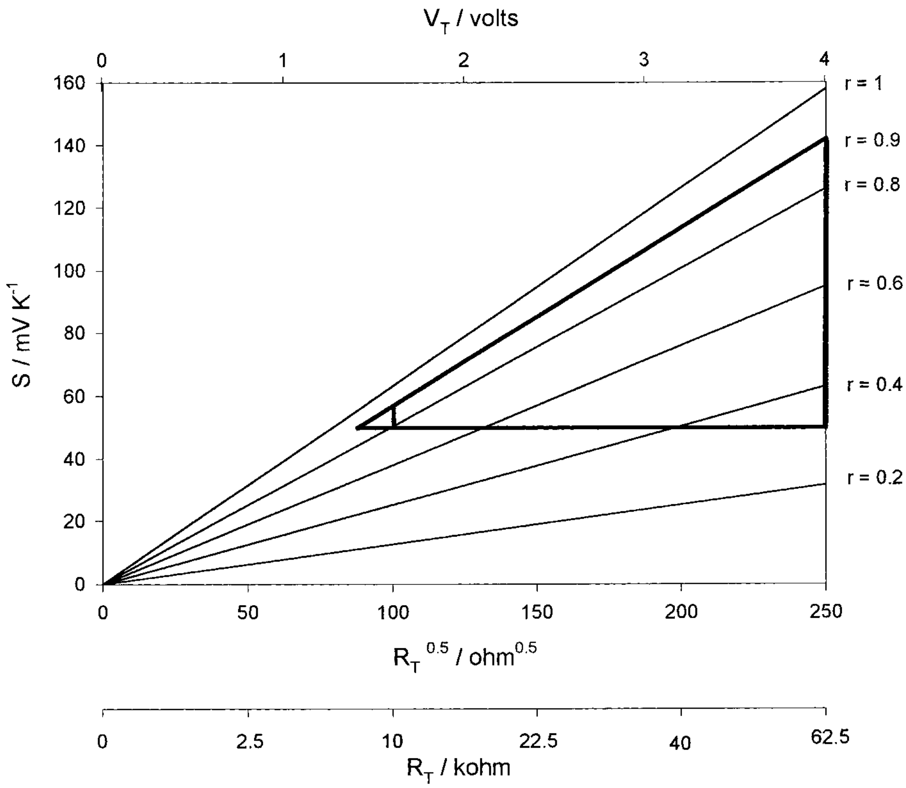

Fig. 6. Plot of bridge sensitivity (S) as a function of V_T, R_T, and r assuming $P_T = 0.25\,\mathrm{mW}$ and $\alpha = 0.04\,\mathrm{K}^{-1}$.

The use of an amplifier with a thermistor bridge has other advantages. Because the power and hence self-heating in the thermistor can be greatly reduced, thermistors can be used to measure the temperature of systems where the flow rate or stirring is variable [5]. Amplifiers with very low noise or noise rejection must be used however. On the other end of the scale, using a high self-heating rate makes thermistors useful as sensors to measure flow and thermal conductivity. A familiar application is the use of thermistors in thermal conductivity detectors in gas chromatography.

Besides the choice of the operating parameters such as resistances and voltages, the choice of materials and how they are used also has a significant effect on performance of thermistor bridges. Resistors should all be metal film or wire wound and of low temperature coefficient materials. Carbon resistors tend to be noisy and have a sizeable temperature coefficient. Any change of resistance of the resistors in the circuit will be indistinguishable from a change in resistance of the thermistor and will be interpreted as a temperature change. Metal film resistors typically have a temperature coefficient of $100\,\mathrm{ppm\,K}^{-1}$, or about 0.25% of the sensitivity of the thermistor. The resistors are also self-heated elements and subject to the same noise as the thermistor if the surroundings are variable. R_1 and R_2 should be thermally coupled to minimize any differential effects of the environment on these two resistances. The simplest way to do this is to use a single, multi-turn potentiometer for both of the resistors as shown in Fig. 1, and heat sink the potentiometer to the chassis or a metal block. Resistors R_R and R_V cannot be paired, so they should be thermostatted or at least thermally attached to a large metal block. The sensitivity of the bridge is a linear function of V_B and therefore the stability of the bridge will be no better than the stability of the power supply. Power supplies with output voltage regulation to 0.02% are readily available, but it is sometimes necessary to add some capacitance to the output of the bridge to eliminate any residual ripple in the voltage. An inexpensive alternative is to use batteries. Either primary batteries with a nearly constant voltage such as mercury or lithium batteries, or a rechargeable battery connected to a trickle charger can be used. Electrical connections of unlike materials should be avoided in construction of bridges to be operated with dc voltage because such connections will act like thermocouples in response to environmental temperature changes. For example, use of common Pb/Sn solders on tinned copper wires results in a thermocouple with a Seebeck coefficient of about $5\,\mu\mathrm{V\,K}^{-1}$. Since the thermocouple effect is not a function of either bridge voltage or resistance, its significance can be reduced by maximizing V_B, R_T and r, or eliminated completely by using ac voltage and a phase-locked detector. Other than elimination of thermocouple effects, there are no advantages to using an ac voltage instead of a dc voltage on thermistor bridges. Thermocouple effects can be measured by setting V_B to zero and measuring the change in bridge output when the temperature of the bridge or a component is changed.

4. Heat exchange corrections for isoperibol temperature-change calorimeters

Measurement of heat by measuring the temperature change in a well-insulated (sometimes called pseudo-adiabatic) reaction vessel is perhaps the most direct and simplest method of calorimetry, in its simplest form requiring only a thermometer and a dewar flask. However, doing accurate work with such a calorimeter requires correcting for heat exchange with the surroundings, a procedure that becomes more and more complex as the physical size of the reaction vessel decreases, as the rate of heat exchange with the surroundings increases, as the reaction time increases, and as the difference in the physical properties of the reactants and products increases. The purpose of this section is to discuss the fundamentals of corrections that must be made to obtain an accurate heat of reaction from the temperature change measurement and assess the accuracy of these corrections under various conditions.

The raw data collected with an isoperibol temperature-change calorimeter may include heat effects from stirring, electrical sensors and heaters, and evaporation and condensation of liquids, as well as the effects of heat exchange with the surroundings. All of these extraneous effects must be properly accounted for to obtain an accurate heat for the process of interest. In the following discussion, the surroundings are assumed to be perfectly constant. In reality, some noise will arise from fluctuations in the surroundings, and transfer of that noise to the measuring system will depend on the noise frequency, time constant, and thermal conductivity for heat exchange between the reaction vessel and surroundings.

The following discussion is limited to measurements made in batch or titration calorimeters. Heat measurements in isoperibol temperature-change flow calorimeters in which the temperature change is measured between reactants and products also require correction for heat loss to the environment. However, accurate calculation of heat loss in this case requires knowing the temperature profile along the length of the reaction vessel. Because of the difficulty of obtaining and interpreting such data, this type of flow calorimeter has not yet been proven to be generally useful for accurate heat measurements, and is not further considered here.

In a typical batch or titration experiment, the data collected are separated into three time periods; an initial baseline collected before the reaction is initiated, the period during which reaction occurs, and a final baseline taken after the process of interest is finished. The rate of change of temperature during these three periods is described respectively by Eqs. (12)–(14),

$$\frac{\mathrm{d}\theta_\mathrm{i}}{\mathrm{d}t} = -k_\mathrm{i}\theta_\mathrm{i} + \omega_\mathrm{i} \tag{12}$$

$$\frac{\mathrm{d}\theta_\mathrm{r}}{\mathrm{d}t} = -k_\mathrm{r}\theta_\mathrm{r} + \omega_\mathrm{r} + \nu \tag{13}$$

$$\frac{\mathrm{d}\theta_\mathrm{f}}{\mathrm{d}t} = -k_\mathrm{f}\theta_\mathrm{f} + \omega_\mathrm{f} \tag{14}$$

where θ is the relative temperature, t is time, k is the heat exchange constant in Newton's law of heat transfer, ω is the rate of temperature change resulting from heat lost or gained from all effects other than exchange with the surroundings and the process of interest, and ν is the rate of temperature change resulting from heat from the process being measured. Subscript i indicates the initial period, r the reaction period, and f the final period. The purpose of the experiment is to extract either ν or its integral from the data by use of Eqs. (12)–(14). How this must be done depends on the properties of the calorimeter and contents during each period of the experiment, on the nature and initiation of the process generating ν, and on how the data are to be interpreted.

4.1. Electrical calibration

In this case $k_\mathrm{i} = k_\mathrm{r} = k_\mathrm{f}$, $\omega_\mathrm{i} = \omega_\mathrm{r} = \omega_\mathrm{f}$, ν is constant, and the problem reduces to solving three equations for three unknowns once values for θ_i, θ_r, and θ_f, and matching values for $\mathrm{d}\theta_\mathrm{i}/\mathrm{d}t$, $\mathrm{d}\theta_\mathrm{r}/\mathrm{d}t$ and $\mathrm{d}\theta_\mathrm{f}/\mathrm{d}t$ have been obtained from the data. Since the value of ν in units of $\mathrm{J\,s^{-1}}$ is already known from data on the voltage and current in the heater, one purpose for doing this calculation is to obtain ν in units of (temperature change $\mathrm{s^{-1}}$), and thus determine the thermal equivalent to convert measured temperature changes in whatever units θ is measured to Joules. A second reason for doing electrical heating at constant power is to characterize the time constant and heat exchange properties of the calorimeter, see Fig. 7.

If k and the time constant of the calorimeter are both negligibly small, the temperature–time data in each period will be linear, the value of θ in each period is simply the midpoint, and the slopes are easily obtained. Defining what is meant by a negligibly small time constant is simple, i.e. if the time constant is less than one-sixth of the data interval, the system can be assumed to be at steady state and each data point represents the true temperature at that point in time. The time constant of the calorimeter will be determined by the time constant of the temperature sensor, the time constant for equilibration of unstirred mass in the reaction vessel, or by the time constant for heat exchange with the surroundings, whichever is longest. The last is determined by the sharpness of the boundary between the system and surroundings [6,7]. Defining what is meant by a negligibly small k value is more complex.

The k values of carefully designed and constructed dewar flasks have been measured and reported [8]. The minimum k value achievable is about $0.002\,\mathrm{min^{-1}}$, a value that produces a 1% deviation from linearity over a 5 min period, so the effects of k on $\mathrm{d}\theta/\mathrm{d}t$ must probably be considered in all practical systems. Thus, the temperature–time data must be fit to a mathematical function and $\mathrm{d}\theta/\mathrm{d}t$ obtained as the derivative of the function. There are three possible functions that can reasonably be fit to the temperature–time data. The data

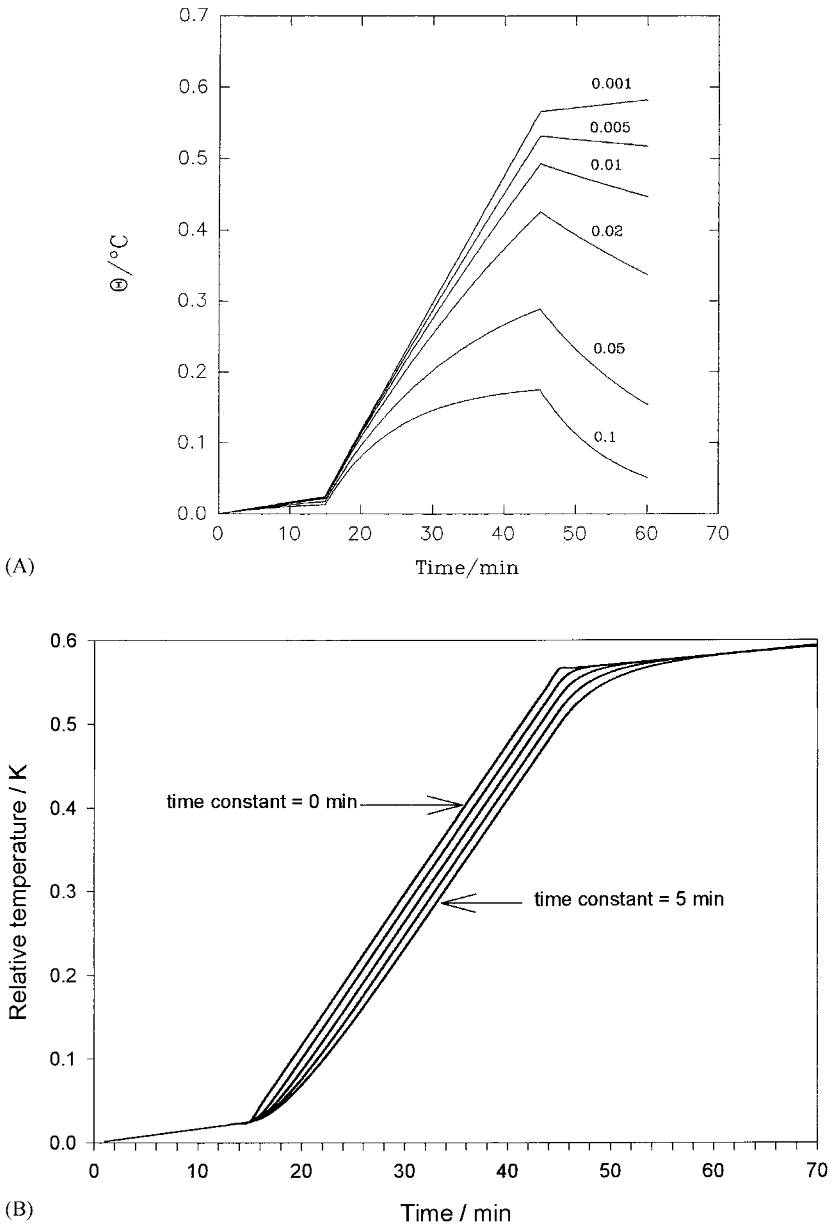

Fig. 7. Temperature–time curves calculated with various values of the heat leak coefficient k (A with k values given in min^{-1}) and the time constant τ (B with τ values incremented by 1 min and k fixed at $0.001\,\text{min}^{-1}$). In all cases $\omega = 0.1\,°\text{C}\,\text{h}^{-1}$ and $\nu = 1\,°\text{C}\,\text{h}^{-1}$.

can be fit to the integral of Eqs. (12) and (14), i.e. Eq. (15),

$$\theta = \left(\theta_0 - \frac{\omega}{k}\right) \mathrm{e}^{-kt} + \frac{\omega}{k} \qquad (15)$$

the data can be fit to a linear, or the data can be fit to a polynomial expansion of Eq. (15), i.e. a quadratic. If k is small, fitting Eq. (15) to real data will give an uncertain k value unless data are taken over a sufficiently long time period. Also, the magnification of the error in k that results from calculation of the derivative $\mathrm{d}\theta/\mathrm{d}t$ must be taken into account. Surprisingly, a quadratic fit gives a larger error in $\mathrm{d}\theta/\mathrm{d}t$ at the midpoint in time than a linear fit. Fig. 8 gives the error in $\mathrm{d}\theta/\mathrm{d}t$ at the midpoint as a function of kt. For the case of a negligible time constant and kt values up to about 0.2, accurate results can be obtained by fitting data in the initial and final periods to linear equations and solving Eqs. (12)–(14) for ν, but more accurate results can probably be obtained by fitting the data to Eq. (15).

If k is negligibly small, but the time constant is not, the temperature–time data in the initial and final periods will be linear, but a nonlinear curve will be obtained in the middle period. This is the condition found for some temperature-change calorimeters. Examples are solution calorimeters constructed with common laboratory dewars [6] and combustion-bomb calorimeters [9]. The approach used in this case is to use Eqs. (12) and (14) to obtain values

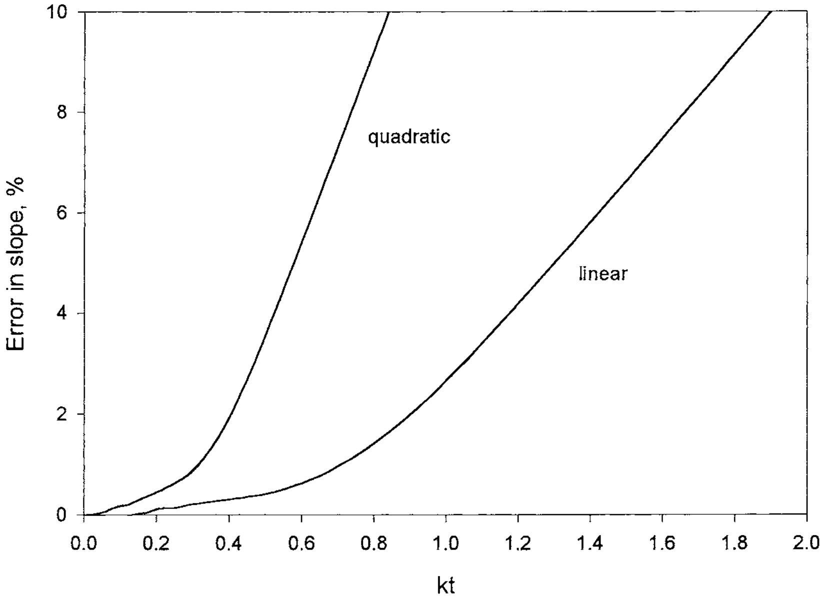

Fig. 8. Error in rate of temperature change at the mid-point obtained by fitting temperature–time data to quadratic and linear functions.

for k and ω, and then in effect use the integral form of Eq. (13) to obtain the integral of ν as a temperature change, $\Delta\theta_{\mathrm{corr}}$. The usual procedure for doing this is to obtain $\mathrm{d}\theta/\mathrm{d}t$ and θ values at the midpoint in time of the initial and final periods by fitting a linear equation to the temperature–time data in these periods as described above, calculating a mean temperature θ_{m} for the middle period, and using these values to calculate $\Delta\theta_{\mathrm{corr}}$ [9]. This procedure is simple to implement with a computer program using data collected at equal time intervals Δt and Eqs. (16)–(19)

$$k = \frac{[(\mathrm{d}\theta_{\mathrm{i}}/\mathrm{d}t) - (\mathrm{d}\theta_{\mathrm{f}}/\mathrm{d}t)]}{\theta_{\mathrm{f}} - \theta_{\mathrm{i}}} \tag{16}$$

$$\theta_{\mathrm{m}} = \left[\Sigma\theta + \frac{\theta_{\mathrm{b}} + \theta_{\mathrm{e}}}{2}\right] \Delta t[t_{\mathrm{e}} - t_{\mathrm{b}}]^{-1} \tag{17}$$

$$\delta\theta = -\left[\left(\frac{\mathrm{d}\theta_{\mathrm{f}}}{\mathrm{d}t}\right) + k(\theta_{\mathrm{f}} - \theta_{\mathrm{m}})\right][t_{\mathrm{e}} - t_{\mathrm{b}}] \tag{18}$$

$$\Delta\theta_{\mathrm{corr}} = \theta_{\mathrm{e}} - \theta_{\mathrm{b}} + \delta\theta \tag{19}$$

where the $\Sigma\theta$ is taken from $\theta_{\mathrm{b}+1}$ to $\theta_{\mathrm{e}-1}$ and b and e are the indices on the data points chosen as the beginning and end of the middle period. The thermal equivalent is given by Eq. (20)

$$\epsilon = \frac{Q}{\Delta\theta_{\mathrm{corr}}} \tag{20}$$

where Q is the total heat input by the heater, i.e. the product of heater voltage, heater current, and heater-on time.

The beginning point (t_{b}, θ_{b}) should be chosen as the last data point taken before the heater was turned on and the ending point (t_{e}, θ_{e}) must be taken at some time after the calorimeter has reached steady state in the final period. These points are thus at the intersection of the initial and middle and final and middle periods. The θ_{b} and θ_{e} data at these two points may be improved over using a single experimental value by fitting the data in the initial and final periods to Eq. (15) and using the θ values obtained at times t_{b} and t_{e}. Use of a quadratic instead of an exponential function for this purpose has been recommended [9], but the ready availability of commercial software and computers makes such simplification and the introduced error unnecessary. Use of a linear equation to obtain θ_{b} and θ_{e} values results in larger errors than use of a quadratic.

When k is large, the temperature–time data in the initial and final periods should be fitted directly to Eq. (15) to obtain $\mathrm{d}\theta/\mathrm{d}t$ and θ values followed by application of Eqs. (16)–(20) to obtain a value for ϵ. Note that in this case, k is obtained both from fitting Eq. (15) and from Eq. (16). These values should agree. There are no published studies that have dealt with this case, but it may have some interesting uses in situations that dictate a large k or in which data in the final period with $\nu = 0$ are unobtainable.

4.2. Chemical reactions

Experiments involving only electrical heating are always simpler than experiments in which the heat effects result from a chemical reaction because some physical change usually must be made in the system to initiate the reaction, the reaction results in changes in the physical properties of the system, and the reaction may not have a clearly defined endpoint in time. Initiating the reaction is usually done in one of two ways, i.e. by adding material of a known temperature from outside the reaction vessel or by allowing materials already present inside the reaction vessel to come in contact. Either procedure can result in significant changes in k, ω, and ϵ. Changes resulting from reaction initiation are stepwise, i.e. k, ω and ϵ change quickly to a different, but constant value. The chemical reaction can also change k, ω and ϵ, but the time course of the change to the new value depends on the time course of the reaction and on the dependence of k, ω and ϵ on the extent of reaction. Possible changes in these parameters must be evaluated for each situation by running electrical calibrations on both the reactant and product systems, i.e. by determining k, ω and ϵ for both conditions. If these parameters do not change significantly, then the time–temperature data may be analyzed for ν or the integral of ν in the same manner as for an electrical calibration. Multiplication of ν or the integral of ν by ϵ then gives respectively the heat rate or total heat of the reaction.

In all cases of chemical reactions, the effects of the time constant on the time–temperature data must still be considered, and $k_{\mathrm{i}} \neq k_{\mathrm{r}} \neq k_{\mathrm{f}}$, $\omega_{\mathrm{i}} \neq \omega_{\mathrm{r}} \neq \omega_{\mathrm{f}}$, and $\epsilon_{\mathrm{i}} \neq \epsilon_{\mathrm{r}} \neq \epsilon_{\mathrm{f}}$ must be assumed until proven otherwise. If ϵ changes significantly during the reaction, the slopes of the time–temperature curves in the initial and final periods are not directly comparable because the same slope represents different rates of heat exchange. Therefore, Eqs. (12)–(14) must be multiplied by ϵ as shown in Eqs. (21)–(23).

$$\epsilon_{\mathrm{i}}\left(\frac{\mathrm{d}\theta_i}{\mathrm{d}t}\right) = -\epsilon_{\mathrm{i}}k_{\mathrm{i}}\theta_{\mathrm{i}} + \epsilon_{\mathrm{i}}\omega_{\mathrm{i}} \tag{21}$$

$$\epsilon_{\mathrm{r}}\left(\frac{\mathrm{d}\theta_{\mathrm{r}}}{\mathrm{d}t}\right) = -\epsilon_{\mathrm{r}}k_{\mathrm{r}}\theta_{\mathrm{r}} + \epsilon_{\mathrm{r}}\omega_{\mathrm{r}} + \epsilon_{\mathrm{r}}\nu \tag{22}$$

$$\epsilon_{\mathrm{f}}\left(\frac{\mathrm{d}\theta_{\mathrm{f}}}{\mathrm{d}t}\right) = -\epsilon_{\mathrm{f}}k_{\mathrm{f}}\theta_{\mathrm{f}} + \epsilon_{\mathrm{f}}\omega_{\mathrm{f}} \tag{23}$$

ϵ_{i} and ϵ_{f} must be determined with heater calibration runs made respectively before and after the reaction is run. Data taken during the heater calibrations also supply values of k_{i}, ω_{i}, k_{f} and ω_{f}. Integration of Eq. (22) gives Eq. (24)

$$\int \epsilon_{\mathrm{r}}\nu\,\mathrm{d}t = \int \epsilon_{\mathrm{r}}\,\mathrm{d}\theta_{\mathrm{r}} + \int \epsilon_{\mathrm{r}}k_{\mathrm{r}}\theta_{\mathrm{r}}\,\mathrm{d}t - \int \epsilon_{\mathrm{r}}\omega_{\mathrm{r}}\,\mathrm{d}t \tag{24}$$

where the term on the left side of the equation is equal to the heat of the reaction. The integrals are taken from θ_{b} to θ_{e} or t_{b} to t_{e} where the b subscript indicates a data point taken shortly before the reaction is initiated and the e subscript indicates a data point taken some time after the reaction has reached equilibrium. An exact solution of Eq. (24) is only possible if ϵ_{r}, k_{r} and ω_{r} can each be expressed as both a function of θ_{r} and of t. Careful design of the experimental conditions and of the calorimeter make this possible for most reactions. Note that the values of the beginning and endpoints of the functions describing ϵ_{r}, k_{r} and ω_{r} are always known from the heater calibration data.

If the objective of the experiment is to determine the total heat effect of the reaction, the integrals on the right side are evaluated between t_{b} and t_{e} and the corresponding values of θ where the time interval t_{e}–t_{b} includes all heat effects of the chemical reaction(s). If the objective is to determine the total heat liberated to any point in time during the course of the reaction, as in a continuous titration, the integrals are evaluated from t_{b} to t_{r}, where t_{r} is a time between t_{b} and t_{e}. If the objective is to obtain the kinetics of the reaction, the differential form of Eq. (24) is simpler to use since $\epsilon_{\mathrm{r}}r$ is the heat rate at any point during the course of the reaction and $\mathrm{d}\theta_{\mathrm{r}}/\mathrm{d}t$ is readily obtained by numerical methods. The latter procedure, followed by integration of $\epsilon_{\mathrm{r}}r$ over time or summation of $\epsilon_{\mathrm{r}}r\,\Delta t$, can also be used to obtain total heat to any point or the overall total heat of the reaction.

The many reports in the literature on heat exchange corrections for isoperibol, temperature-change calorimeters (e.g. [7–11]) are descriptions of various means to evaluate the integrals in Eq. (24) under various circumstances. Although these reports appear to arrive at quite different solutions, the differences are due to different approximations forced by the conditions of the experiment and not to differences in the fundamental approach. The possible situations that may usefully arise are too numerous to delineate here, but two examples will illustrate some of the more common methods of approximating the integrals required in Eq. (24).

First, consider a simple laboratory dewar partially filled with a solution of one reactant. The solution is stirred with a magnetic stir bar and the relative temperature is recorded with a recording thermometer. The reaction is to be initiated by lifting the stopper and adding the second reactant. Such a simple system can be used to do fairly accurate calorimetry if certain conditions are established. The rate of energy input from stirring must be kept constant, the amount of material added at reaction initiation must be kept small enough that ϵ does not change significantly, and the calorimeter is calibrated with a chemical reaction with a known enthalpy change under very similar conditions. Under these conditions, Eqs. (16)–(20) apply. Any errors resulting from small changes in ϵ or ω will tend to cancel between the calibration reaction and the test reaction if the temperature changes from the two reactions are very close in magnitude and done at the same temperature. Note that under these conditions, the thermometer can be read in any arbitrary units and that the temperature of added reactant need not be known as long as it is close to the temperature of the experiment.

Some of the problems of using magnetic stirrer bars also become apparent from the requirement that the rate of energy input from stirring be kept constant. The energy input from any stirrer depends on the viscosity of the stirred liquid, but in addition a stirring bar creates heat from the friction of rubbing against the vessel or submerged bearing which is dependent on the lubricity of the liquid. Thus, most calorimeters are stirred with synchronous-motor driven propellers with shaft bearings above the liquid.

If a large amount of reactant is added, ϵ will change and Eqs. (16)–(19) do not apply. Assuming the response time of the system is short compared to the data interval, $\epsilon_{\mathrm{r}} \neq \epsilon_{\mathrm{i}}$, but $\epsilon_{\mathrm{r}} = \epsilon_{\mathrm{f}}$ and electrical calibration will allow determination of these parameters. Under these conditions, it is also likely that k and ω will change to their final values immediately on addition of the second reactant. Application of Eqs. (14),

(16) and (20) to data from an electrical calibration run on the final system provides values of ϵ_f, k_f and ω_f for use in Eq. (24). The applicable equation then becomes

$$Q = \epsilon_f(\theta_e - \theta_b) + \epsilon_f k_f \int \theta \, dt + \epsilon_f \omega_f (t_e - t_b) \qquad (25)$$

where the integral is readily evaluated by a numerical method such as a summation (e.g. Eq. (17)), the trapezoidal rule, or Simpson's rule. Note that data in the initial period are not used except to determine θ_b so no electrical calibration on the initial system is needed. The specific heat capacity C, mass m, and relative temperature θ_{addition} of the added reactant material must be known for this case. The heat effect for addition of the reactant is given by Eq. (26),

$$Q_{\text{addition}} = C(\theta_{\text{addition}} - \theta_b)m \qquad (26)$$

and must be subtracted from the total measured heat Q. A common error is to use some temperature other than θ_b in Eq. (26), but the thermodynamics of the situation require that the reactants be mixed at the beginning temperature. If the thermal equivalent of the final system is then applied in calculating Q, the ΔH value calculated applies at θ_b [12].

If the kinetics of a moderately slow reaction are to be studied, the problem becomes only slightly different unless the reaction changes the physical properties of the solution significantly. To determine the kinetics, the rate of heat due to the reaction at each data point during the reaction must be determined. The data from an electrical calibration on the final system, i.e. ϵ_f, k_f and ω_f and a rearrangement of Eq. (22) provides the means for this calculation.

$$\phi_r = \epsilon_f \left(\frac{d\theta_r}{dt} \right) + \epsilon_f k_f \theta_r + \epsilon_f \omega_f \qquad (27)$$

In Eq. (27), ϕ is the heat rate at each data point r in the reaction region. The derivative $d\theta_r/dt$ must be evaluated from the θ–t data by a numerical method. Usually $\Delta\theta/\Delta t$ is a sufficiently accurate approximation. Again the results must be corrected for the heat effect caused by addition of material at a different temperature than θ_b.

For a second example, consider the case of a continuous titration which might be done in the same calorimeter as described above if the time constant is very short [7,8]. For such an experiment to be more useful than an experiment done with a single injection, the heat produced to each data point in the titration must be calculated. Eq. (24) can be used to do this calculation if values of ϵ_r, k_r and ω_r can be calculated at each data point in the titration. Values of ϵ_i, k_i and ω_i and ϵ_f, k_f and ω_f can be obtained from electrical calibrations made on the initial and final systems. These values fix the beginning and endpoint values for the functions describing ϵ_r, k_r and ω_r, but the function must be determined in other experiments or assumed from auxiliary data. If the physical properties of the material in the reaction vessel do not change significantly with the extent of titration, then ϵ_r, k_r and ω_r are functions only of the reaction vessel and the amount of contents and linear functions as shown in Eqs. (28)–(30) may be safely assumed.

$$\epsilon_r = \epsilon_i + \xi_r(\epsilon_f - \epsilon_i) \qquad (28)$$

$$k_r = k_i + \xi_r(k_f - k_i) \qquad (29)$$

$$\omega_r = \omega_i + \xi_r(\omega_f - \omega_i) \qquad (30)$$

In Eqs. (28)–(30), ξ is the fraction of titration completed to point r. These functions then provide the values needed to integrate Eq. (24) to any point in the titration.

The time constant of the calorimeter is unimportant if only a total heat is to be measured, but a short time constant is a condition for doing continuous titrations and for readily extracting reaction kinetics from temperature–time data. Construction of a calorimeter system with a short time constant requires that three design constraints be met. The thermometer must have a short time constant, the unstirred mass in the reaction vessel must be very small, and the boundary between the system and surroundings must be well defined [6]. Glass dewars with time constants <1 s can be constructed if careful attention is paid to these constraints [7,8]. Such calorimeters have been available commercially since about 1965.

When the physical properties of the reaction mixture change significantly in a nonlinear fashion with the extent of reaction, or if chemical reactions do not completely cease within a reasonable time, accurate correction for heat exchange with the surroundings may not be possible. For example, in polymerization reactions, the viscosity of the reaction mixture often changes exponentially with the degree of polymerization. In such a case, it is not possible to accurately correct for the heat of stirring. The heat transfer characteristics may also change, affecting the output of self-heated temperature sensors and the heat exchange characteristics of the reaction vessel. Situations are often encountered where the products of a reaction are not stable and continue to react or a side-reaction continues into the final period. In this situation, it may be difficult at best and often impossible to obtain accurate values for ϵ_f, k_f, and ω_f. The best that can be done in such cases is to measure ϵ_i, k_i, and ω_i and attempt to estimate values for these parameters during the reaction period. Errors resulting from such estimates should be determined by assuming worst case estimates and calculating the extreme Q value.

5. Constant temperature baths

Operation of any calorimeter always also involves a temperature bath that surrounds the calorimeter. Whether simply the air in the laboratory or a sophisticated, high-precision bath, effects of fluctuations in the temperature of the surroundings must always be considered in making calorimetric measurements. This section considers constant temperature baths for isoperibol calorimeters, but considerations for operation of an adiabatic calorimeter in which the bath is controlled to be the same temperature as the reaction vessel are the same except that the response time for the bath must also be taken into consideration. The primary purpose of this section is to provide the calorimetrist with the information needed to select a commercially available bath or bath components. Detailed procedures for design of constant temperature baths such as constant temperature rooms, fluid flow loops, and laboratory water baths have been previously published elsewhere [13].

Perhaps the simplest type of constant temperature baths are those in which temperature control is achieved by having two or more phases of the bath material present. The control temperature is thus the melting point, triple point or boiling point of the bath material. No controller or temperature sensor is needed for such a bath. External power need only be supplied to "recharge" the bath for liquid–solid systems, and only roughly controlled continuous power is required to maintain liquid–gas baths at the boiling point. Such baths must be well mixed to achieve temperature uniformity if significant amounts of heat are to be dissipated to the bath.

Liquid baths with temperature control to a few hundredths of a degree are commonly found in routine laboratory use. These baths usually consist of a large container (compared to the calorimeter reaction vessel) filled with water, a stirrer, an electrical heater controlled by an electronic controller, and a coil of tubing with coolant flowing through it. The container is usually insulated if the bath is to operate very far from room temperature. The insulation should be sealed to prevent condensation if the bath is operated below room temperature and must be open to allow for expansion if the bath is operated above room temperature. The water must be replaced with some other fluid if the bath is operated above about 70 °C or below 0 °C. Use of air as the bath fluid avoids the problems associated with submerging the reaction vessel in a liquid, but because of the low heat capacity, heat transfer is slow and control is usually not better than a few tenths of degree. Table 1 gives a list of suitable fluids and their temperature ranges. The coolant may simply be tap water, fluid from a refrigeration system, or may even be from a heated bath if the bath is operated at high temperature. If carefully designed, liquid baths of this type can be controlled to about a millidegree.

Table 1
Fluids for use in constant temperature baths

Fluid	Useful temperature range (°C)
Halocarbon 0.8	−100 to +70
Ethylene glycol/water (1:1)	−30 to +110
Silicone oil type 200.10	−30 to +160
Silicone oil type 200.20	+10 to +230
Silicone oil type 200.50	+30 to +275
Silicone oil type 550	0 to +230
Silicone oil type 710	+80 to +300
Mineral oil	0 to +120
$KNO_3/NaNO_2/NaNO_3$ eutectic (52:40:7 wt.%)	+150 to +550

Thermostatted metallic blocks into which the calorimeter is inserted are usually used to control the temperature of the surroundings at high temperature, and have found wide use in heat-conduction and power-compensation calorimeters at all temperatures. Metallic blocks can be controlled in the microdegree range, but obtaining such control requires a carefully designed system which includes the operating environment. Such baths require at least two layers of temperature control, an outer bath actively controlled in the millidegree range and an inner bath passively controlled by the outer bath through carefully designed thermal connections.

There are several characteristics that must be specified to describe temperature control in a bath. "Gradient" describes the long-term average temperature differences that exist between different parts of the bath. "Noise" is used to refer to short-term, random temperature fluctuations. "Cycling" refers to a regular pattern, usually sinusoidal, that may occur in the bath temperature. "Drift" denotes a long-term shift in the mean bath temperature. The "dead band" is twice the temperature offset from the control temperature required to activate the controller. "Settling time" is the time required for the bath to regain control after a small upset occurs. "Slew rate" is the maximum rate at which the bath temperature can change and is important in applications where large upsets occur and a rapid return to control is needed. The temperature sensor used to characterize any of these parameters must have a time constant shorter than the characteristic being determined. Measurements must be made over a period of days to distinguish between cycling, which may have a frequency of per day, from drift.

A temperature controlled bath is a steady state system, not an equilibrium system. Constant temperature is maintained by balancing the rates of heat input and output. Because fluctuations in the temperature of the surroundings will affect the rate of heat flow to or from the bath, the bath surroundings must also be considered in operation of the bath. The system will undergo a transient response whenever the steady state changes, and since control is not maintained during the transient, precise control depends on precise control of heat flows into and out of the bath and on keeping these heat flows as constant as possible. Heat flows that must be considered are (a) evaporation and condensation of the bath fluid, (b) the heat due to stirring, (c) heat exchange by conduction through the walls of the container, (d) heat loss to the cooler, and (e) heat provided by the heater. Either the heater or the cooler should be operated at constant power while the other is controlled. The control element should be operated near the middle of its power range, and the heater and cooler should be no larger than necessary to provide firm control. Stirring is often a major part of the heat input. Heat exchange with the bath surroundings through the walls of the container should be minimized by insulation since the surroundings are difficult to control.

Because heat can only flow if there is a temperature gradient, elimination of significant gradients requires careful attention to placement of the various heat sources and the temperature control sensor in the bath. The only point in the bath that is actually controlled is the sensor. The fluid flow in the bath will determine which parts of the bath are free from temperature gradients. Optimum control of the temperature surrounding the calorimeter reaction vessel will be obtained with the stirrer, heater, and cooler clustered in one location so that fluid flow is from the stirrer to the constant control element (usually the cooler), to the variable control element (usually the heater), to the sensor, and then to the reaction vessel.

The size of a bath also has an important impact on the achievable temperature control. The minimum achievable temperature noise at a 10 s time constant in water filled baths has been shown to increase linearly with bath size from about 0.1 to 100 L [13]. This result is counterintuitive because the total heat capacity and thus obviously the thermal inertia increase with bath volume. Also, the thermal inhomogeneity is inversely proportional to the product of the specific heat capacity and volume of the bath. However, the thermal inhomogeneity is also directly proportional to the product of the power dissipation through the bath and the eddy current lifetime in the fluid, and eddy current lifetime increases as a power of bath volume. Because of the effects on mixing, the shape of a bath also influences eddy current lifetime, and hence temperature noise. Baths should not have square corners or other “dead” spots in which fluid is not well mixed. The bath fluid should have a high heat capacity and a low viscosity to minimize noise.

Temperature sensors used to control constant temperature baths are of two types. Mercury thermoregulators and bimetallic switches are examples of “off/on” or “make-and-break” sensors. These sensors provide only too-hot or too-cold information and can only be used with on-off or two-level control. These sensors are typically used in baths with control in the range of ±0.1 to ±0.02 K. The other type of sensors are resistors, thermistors, thermocouples or other electronic devices in which the properties change continuously with temperature. These sensors also provide information about how far the temperature is from the set point and this information can be used with more sophisticated controllers to reduce noise, cycling and drift in the bath temperature. The time constant of the sensor must be adjusted to match the response time of the other components of the bath such as the heater, fluid mixing time, etc.

In order of increasing sophistication, controllers are on/off, two-level, proportional (or type zero), proportional with reset (or type one), and proportional with reset and look ahead. As implied by the name, an on/off controller simply turns the power to the control element on or off depending on the signal from the temperature sensor. A two-level controller turns a portion of the power on or off. A proportional controller changes the power to the control element in proportion to the signal from the sensor. Automatic reset is used to adjust for long-term changes in the steady state power needed to control the bath, and look ahead (also known as derivative or rate control) is used to damp inherent instabilities in type one control. Cycling and drift are inherent with on/off and two-level control. Proportional control eliminates cycling, but not drift which is eliminated with automatic reset. Control may be done by an analog device or may be done with a simple digital computer.

6. Initiating the reaction

All calorimetric measurements on reactions or phase changes must somehow involve a mechanism for initiating the reaction or process of interest. The four distinct mechanisms are (a) mixing of the reactants, (b) addition of a catalyst, (c) passing electrical current through the system, and (d) changing the temperature, pressure or volume. Changing the temperature is the process that gives rise to the temperature scanning methods commonly known as DSC and DTA. Changing the pressure and volume can also be used to initiate reactions. The system pressure may be changed by addition of an inert gas (e.g. see [14]) or by compression of a liquid linked to the reaction vessel (e.g. see [15]). In parallel with the temperature scanning methods, such methods should properly be called pressure scanning calorimetry, but the name has been preempted to describe methods in which the pressure of a gaseous reactant is varied, and thus the method is called pressure-controlled scanning calorimetry or transitiometry [16]. Electrolytic methods have been used almost entirely to study reactions during both discharge and charging of batteries (e.g. see [17]), although a few studies have been done for other purposes [18,19]. Although electrolytic methods appear to be an elegant means for initiating and controlling reactions, only in rare cases of either electrolysis or cell discharge does the reaction go cleanly without side reactions or recycling of products. Catalyst addition is most commonly done with enzymes, but is a method that should be considered in studies of non-biological systems. The major advantages of this method are that only relatively tiny amounts of material need be added to the reaction vessel and that the reaction rate can be controlled since it will be directly proportional to the amount of catalyst added. Direct mixing of reactants is the most common method for initiating the process to be studied and is the subject of the remainder of this section.

For very slow reactions, the reactants may simply be premixed shortly before insertion into the calorimeter. This method is commonly used in studies of degradation and corrosion reactions, e.g. see [20]. Methods may be further subdivided as to whether the reactants are all within the reaction vessel before mixing, or if one is added from outside the reaction vessel. In the latter case, a correction must be made for the temperature difference between the added reactant and the contents of the reaction vessel at the time of reaction initiation. In the former case, correction must be made for the effects of opening the barrier between the reactants. Addition from outside the reaction vessel is often much simpler than maintaining and breaking separation inside the reaction vessel.

Both solids and liquids can be added from outside the reaction vessel. Liquids may be added with a syringe and solids may simply be dropped or pushed out of a tube with a syringe-like device. The latter is often easily constructed by cutting the delivery end from a liquid syringe. Solids must be retained in the syringe with a foil or plug in the end of the syringe. The plug or foil also prevents contact between vapors in the calorimeter and the solid prior to addition. Difficult-to-wet solids may be contained within a weighted, porous bag to prevent them from floating on the surface. Correction for incomplete transfer of a reactant can often be done by measuring the amount remaining in the delivery system at the end of the experiment.

Techniques for mixing of reactants within the reaction vessel usually involve some type of syringe or pipet. Syringes for delivery of liquids can often simply be immersed in the liquid in the reaction vessel. Separation can often be maintained with a gas bubble in a narrow bore needle attached to the syringe. Addition of solids can be done with the same devices used to inject from outside the reaction vessel if the solid is contained between two plugs. Breaking a glass bulb containing the solid is a common method of mixing a solid reactant into a system. The glass must be made very thin to minimize the heat of breaking, and the bulbs must be kept very uniform to obtain a constant blank value. Fig. 9 shows a simple device that replaces the bulb with microscope cover slips [21]. The advantages of the cover slips over bulbs are the ready availability and uniformity. The cover slip device is also much easier to fill with solids than narrow-necked bulbs. Glass bulbs and the device shown in Fig. 9 can also be used for addition of liquids that cannot be handled with a syringe because they are too reactive or too viscous. Many devices used for addition of solids have incorporated a bulb smashing or opening device as an integral part of the stirrer. Combining the stirrer and addition device is usually unnecessary and only results in complicating the mechanical design of both stirrer and the addition device.

Addition of liquids with syringes is convenient, but care must be taken that the liquid is not significantly heated by too rapid passage through a narrow bore tube. Eq. (31) gives the temperature rise in K in a fluid from frictional flow in a tube

$$\Delta T = \frac{21 \times 10^{-10} \mu l(\dot{v})}{\pi \rho C d^4} \qquad (31)$$

where μ is the fluid viscosity in centipoise, l is the length of the tube in cm, $\dot{v}$ is volume flow rate in $\mathrm{cm^3\,min^{-1}}$, ρ is the fluid density in $\mathrm{g\,cm^{-3}}$, C is the fluid heat capacity in $\mathrm{J\,g^{-1}\,K^{-1}}$, and d is the tube diameter in cm. For water flowing through a 0.4 mm diameter tube 30 cm long at $1\,\mathrm{cm^3\,min^{-1}}$, $\Delta T = 0.002\,\mathrm{K}$.

Another means of mixing reactants within the reaction vessel is to invert the reaction vessel and allow the reactants to flow together. Further mixing is done by repeated inversion of the reaction vessel. Inversion of the reaction vessel may be done by inverting the vessel or the entire calorimeter. A similar, two container method can be used with calorimeters and vessels that cannot be inverted. The device is shown in Fig. 10. A slight difference in pressure between the two containers is used to transfer and mix the reactants. If further

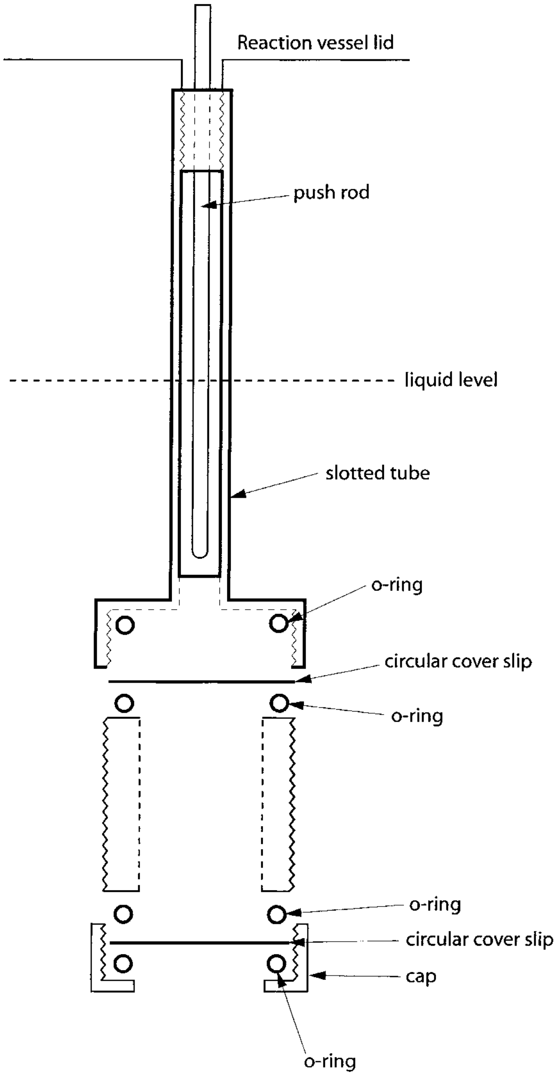

Fig. 9. Device for mixing solids or liquids by breaking glass cover slips.

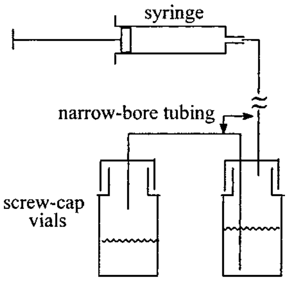

Fig. 10. Device for transfer of a liquid reactant.

mixing is desired, the transfer can be repeated in reverse. To account for incomplete transfer, the two containers can simply be weighed after the experiment. The device is simple to construct and can be made from disposable materials for study of reactions that result in difficult to remove materials such as polymers and glues.

7. Continuous titration

Continuous titration is a very efficient means for collection of data as a function of the total concentration of a reactant. It has been much used to determine the thermodynamics of reactions in solution, especially for metal–ligand and proton ionization where several reactions may occur simultaneously. The primary requirement of a buret for continuous delivery is that the delivery rate be constant. Constancy of delivery rate should not be confused with accuracy of delivery of a total volume. The latter only requires that the distance of movement of the piston be accurate, the former that the piston move at a constant speed. A common fault of many syringe-type burets is a sinusoidal delivery rate because of wobble in the lead screw or rack-and-pinion driving mechanism. A buret that is submersible in a constant temperature bath is convenient, but thermal equilibration of titrant can be done with a coil of tubing placed in a constant temperature environment.

8. Stirrer design

The stirrer used to mix the reaction vessel contents is an important component of the calorimeter. Stirring controls the rate of mixing of reactants and is often the major heat input to the calorimeter during baseline periods. Stirring of liquids is often done with a simple rotating propeller. The rate of energy input with a rotating propeller depends somewhat on the pitch and aspect ratio of the propeller and on the width, height and shape of the reaction vessel with respect to the propeller, but is a much more sensitive function of the liquid viscosity and paddle length and speed. The equation for power input from a rotating propeller is

$$P = s\mu f^3 d^3 \tag{32}$$

where P is the power, s is a nondimensional shape factor, μ is viscosity, f is the frequency of rotation, and d is the diameter of the propeller. Because of the sensitivity to frequency, the stirrer must be driven with a constant speed motor. Wobble should also be avoided since its effect is to change d. Reactions that produce a significant change in viscosity, such as polymerizations, will cause a change in the baseline power input by the stirrer and this must be taken into account in analyzing the data. To prevent settling of dense material and a vortex, the propeller should be placed near the bottom of the reaction vessel and should rotate in the direction that causes lift along the propeller shaft. The speed of rotation should be the minimum that still gives the necessary mixing. Minimizing power input from the stirrer also minimizes the magnitude of variations in baseline heat rate.

The efficiency of a stirrer may be defined as the ratio of power input to mixing time. A flat paddle is often more efficient than a pitched propeller. Unless baffles are included, a propeller provides only circular motion with very little vertical mixing. Obtaining efficient vertical mixing is a problem in many reaction vessel designs. A tall, narrow, notched, flat paddle is useful in vessels with large height to width ratios. Another approach is to use a rotating tube with holes in the sides. Liquid is thrown out through the holes and drawn in the open end of the tube. Such a design may be the most efficient type of stirrer when the aspect ratio and hole size are correctly adjusted to match viscosity and shape parameters.

Penetration of the stirrer shaft through the reaction vessel lid is a problem when the vessel must be sealed because of volatility of the contents or for work above ambient pressure. In either case the rate of heat loss from evaporation is directly proportional to the product of the heat of vaporization, the vapor pressure, and the effective area through which the vapor must pass.

There are basically three approaches to solving the problem of sealing the stirrer shaft: (a) use of a rotating seal, (b) replacement of the shaft with a magnetic coupling, and (c) use of a non-rotating, mechanical coupling. Three types of rotating seals are commonly available. Although they do not totally seal the system, lubricated rubber ring seals similar to those used on automobile axles are often sufficient to control loss of volatiles. Ferrofluid and mercury seals as shown in Fig. 11 are useful to a differential pressure of several atmospheres. Ferrofluid seals cannot be used with volatile organics because of dissolution of the ferrofluid. Mercury seals are a problem because of the toxicity of Hg vapor. Magnetic stirring avoids the problem of sealing a shaft, but the paddle bearing must be placed within the reaction vessel and the rotating magnetic fields can cause problems with sensors by induction of electric currents. Stirring can also be erratic if the magnetic coupling is not strong enough. The bearing for a magnetic stirrer should be placed above the liquid level if possible. The drive shaft can then support the stirring magnet near the bottom of the reaction vessel. The third approach makes use of a rubber seal glued to both a shaft and the lid of the vessel. The stirrer can then be oscillated vertically or horizontally or rotated through a circle with an eccentric. The eccentric arrangement is probably the most efficient.

9. Design of calibration heaters

The accuracy of a calorimetric measurement can be no better than the calibration accuracy. Electrical calibration can be subject to large systematic error because of poor heater design. The accuracy of electrical calibration should be verified whenever possible with a well-known chemical system.

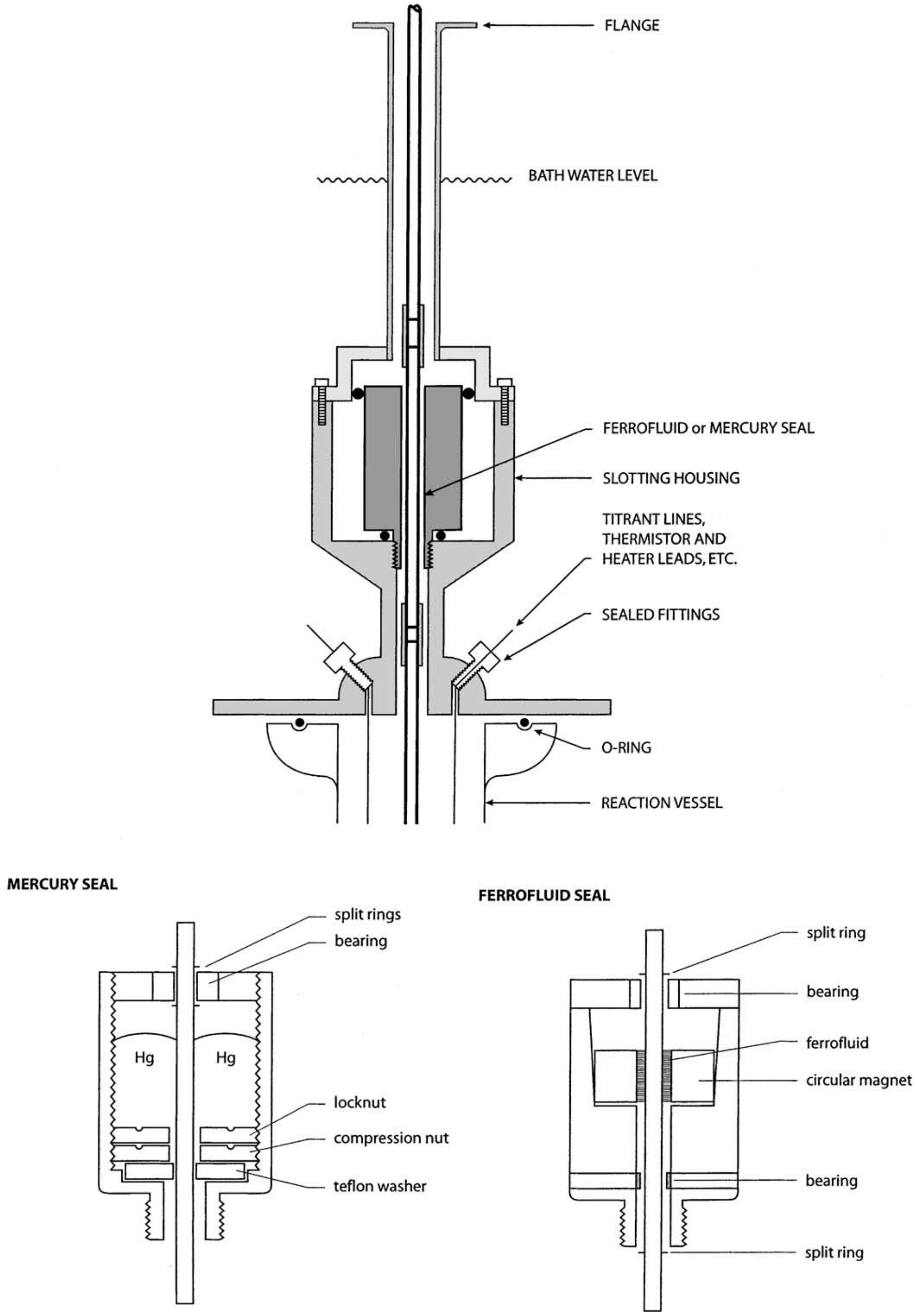

Fig. 11. Designs for ferrofluid and mercury seals on a rotating shaft.

At least two conditions must be met for electrical calibrations to be accurate: (a) all of the heat must be generated in the heater, and (b) all of the heat must be transferred to the calorimeter. Because an electrical heater must be connected to the calorimeter surroundings by wires that have both finite thermal conductivity and electrical resistance, neither condition can be exactly met, only approached. The requirements of reducing both thermal conductivity and electrical resistance are antithetical, and thus any heater design must be a compromise. The first condition requires large diameter, short lead wires with negligible resistance compared to the heater. The second condition requires thin, long lead wires to minimize thermal conductivity between the heater and surroundings. Designing a heater thus requires finding a compromise that makes both errors negligible.

The fraction of the resistance, and thus the fraction of the heat generated in the lead wires, can be reduced by increasing heater resistance, but there is a practical upper limit to heater resistance. As heater resistance increases, voltage must also be increased to achieve a given power. (Note that power $= V^2/R$.) The higher the voltage, the more difficult it becomes to avoid leakage currents bypassing the heater. Increasing electrical insulation on the heater exacerbates the problem of getting all of the heat generated in the heater transferred to the calorimeter. Experience shows that electrical calibration heaters should have a resistance between 100 and 1000 Ω, lead wire resistance should be $<0.1\,\Omega$, and lead wire thermal conductance should be $<0.1\%$ of the thermal conductance between the heater and the calorimeter.

Accurate low power (<1 W) heaters are easier to construct than heaters for higher powers. A low power heater for solution calorimeters can be constructed from a variable, 12 V power supply with output stable to better than 0.1%; a 100 Ω, quarter-watt, wire-wound, low thermal-coefficient resistor; small gauge, varnished Cu wire; and a length of thin wall, shrinkable teflon tubing. Break the case and end caps from the resistor by squeezing with pliers, solder the Cu wires to the resistor (two lengths on each end, one to carry the current, one to measure voltage), thread the assembled heater through the teflon tube, and shrink the tubing by heating. The lead wires and resistor must be carefully supported during the last operation because the solder will melt at the temperature required to shrink the tubing. The teflon tubing can be replaced with a carefully applied coat of epoxy or other varnish in some circumstances. Higher power heaters (up to about 10 W) can be similarly constructed from several resistors connected in series with short lengths of heavy gauge Cu wire so the total resistance is about 100 Ω. The set of resistors replaces the single resistor as described above. Using several resistors increases the surface area of the heater and hence the thermal conductance to the solution. Heaters for flow calorimeters are conveniently made by winding varnished, low thermal-coefficient resistance wire directly on the flow tubing. Ceramic and metal clad wire sold for construction of thermocouples is also very useful for winding heaters on cylindrical tubes and vessels. In all cases heat losses through the lead wires can often be reduced by thermally connecting the leads to the calorimeter.

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