Thermochimica Acta, 10 (1974) 129–142

NOISE MEASUREMENT AND THE TEMPERATURE RESOLUTION OF NEGATIVE TEMPERATURE COEFFICIENT THERMISTORS

LARRY D. BOWERS AND PETER W. CARR*
Department of Chemistry, University of Georgia, Athens, Ga. 30602 (U.S.A.)
(Received 10 May 1974)

ABSTRACT

The physical parameters inherent in titration calorimetry which limit the temperature resolution of thermistors have been investigated. The individual noise sources were theoretically and experimentally related to the rms temperature noise by an equation of the form:

$$\Delta T_{\mathrm{rms}} = \sqrt{\frac{A}{E_B^2} + B + CE_B^4}$$

The dependence of A, B, and C on the thermistor resistance, mode and rate of stirring, and the physical boundary between the thermistor and the solution have been investigated. The effects of sampling rate and interval on the measurement of the temperature resolution of thermistors in a d.c. Wheatstone bridge circuit have been evaluated.

INTRODUCTION

The analytical limit of detection of solution phase calorimetric techniques such as thermometric enthalpy titrations[1] and direct injection enthalpimetry[2] is established primarily by the resolution of the temperature sensors employed. Ever since the introduction of thermistors in this area by Linde et al.[3], these devices have been almost universally employed. The reported limit of detectable temperature change has improved steadily from about 0.5 m°C[4] to values of 3–15 μ°C[5–7] and most recently Lampugnani and Meites[8] have reported an internal consistency of ±0.6 μ°C. Very few researchers have disclosed the statistical procedure employed in evaluating the resolution; no studies have been concerned with the physical processes which must ultimately limit the resolution nor has any work been presented which states how a given system should be optimized.

The principal objectives of the present work were to determine what processes are most significant in establishing the short term noise and hence the temperature

*To whom requests for reprints should be addressed.

resolution of thermistors in equal arm d.c. Wheatstone bridges which are the most commonly employed measurement configuration for such transducers. Long term or secular drift of thermistors has been studied and an extensive discussion is available[9]. We are not concerned here with drift which may be considered as very low frequency noise.

THEORY

Noise will be defined here as any apparently random fluctuation which appears at the output of the Wheatstone bridge. For a d.c. signal, this variation can be represented as the root-mean square (rms) value of the signal

$$N_{rms} = \sqrt{\frac{\sum_{i=1}^{n} S_i^2}{n-1}} \tag{1}$$

where S_i is the deviation of the signal from a calculated least squares line and n is the number of points sampled. This method has an inherent advantage in that it is statistically identical to a standard deviation. If the variations in the signal are Gaussianly distributed, on the average 99% of the instantaneous fluctuations will be within a band whose width is five times the standard deviation. As a result, the rms noise could be estimated by calculating one-fifth of the peak-to-peak noise. A third method of representing the noise is given by eqn (2):

$$N_{ave} = \frac{\sum_{i=1}^{n} |S_i|}{n} \tag{2}$$

Since the voltage (E_B) applied to a bridge may be easily manipulated, is commonly used to adjust sensitivity, and at exact null, in the absence of self-heating, has no effect on the bridge output, we decided to classify the sources of noise in relation to this parameter. The numerous factors which affect the short term fluctuations can be operationally grouped into three major classes according to their dependence on the applied voltage.

Voltage independent noise sources

Some principle sources of noise inherent in all electrical measurements are: pick-up noise, Johnson noise, and flicker or $1/f$ noise. The pick-up noise originates mainly from 60 Hz lines, stray capacitance, and inadequate shielding. In general, the larger the source impedance is, the greater the pick-up noise is and the more difficult it is to eliminate.

The Johnson noise is defined by the well-known equation[10] given below, and some typical values for source impedances (R) and bandwidths (ΔF) encountered in titration calorimetry are summarized in Table 1.

TABLE I

EFFECT OF BAND-WIDTH AND IMPEDANCE ON THE JOHNSON NOISE

Impedance (Ω)	*Bandwidth* (*Hz*)	*Johnson noise*[a] (μV, *rms*)	*Equivalent temperature noise*[b] (μ°*C*, *rms*)
10^4	1	0.0129	1.29
10^4	10	0.0407	4.07
10^5	1	0.0407	4.07
10^5	10	0.129	12.9
10^6	1	0.129	12.9
10^6	10	0.407	40.7

[a] Computed from eqn (3) assuming $T = 300$ °K, $k = 1.38 \times 10^{-23}$ J/K. [b] Computed from eqn. (7) assuming $\alpha = 4\%$/°C, $E_B = 1$ V.

$$e_{JN} = \sqrt{4kTR\Delta F} \tag{3}$$

This is the minimum noise voltage which can be attained; it cannot be reduced by improved shielding.

Many types of materials such as transistors show a noise constituent whose magnitude increases inversely with frequency[10]. The source of this noise is not well understood but is believed to be related to the presence of discontinuities in the conduction band and are therefore not seen in, for example, wire wound resistors.

Noise source dependent on the first power of the applied voltage

A thermistor placed in a thermally inhomogeneous fluid will show irregular temperature changes as the fluid moves by the transducer. In titration calorimetry there are a number of heat sources and sinks including stirring, chemical reaction, and poor adiabaticity. In the absence of instantaneous mixing, these heat fluxes will create thermal inhomogeneities which act as noise sources. The actual temperature fluctuations in the solution are filtered by the thermal time constant of the thermistor so that only an effective temperature noise (ΔT_{IN}) appears at the transducer output. The equivalent voltage noise, e_{IN}, is given by the relation:

$$e_{IN} = \tfrac{1}{4}\alpha E_B \Delta T_{IN} \tag{4}$$

where α is the temperature coefficient of the thermistor (4%/°C) and the numerical factor applies to an equal arm bridge[11]. The magnitude of ΔT_{IN} should be related to the magnitude of the heat fluxes, the mode of stirring, and the heat capacity of the Dewar as well as the time constants of the thermistor and electronic filters.

Noise sources dependent on the third power of the applied voltage

The thermistor itself can contribute to the total possible bridge fluctuations in two distinct ways. First, the power supplied to the thermistor is almost completely transferred to the calorimetric fluid, i.e., the transducer acts as a continuous heat source and could contribute to local thermal inhomogeneities of the type described in the preceding section. The voltage noise equivalent to the thermal inhomogeniety in this case, however, must be proportional to the third power of the applied voltage rather than the first power.

A second noise source related to the thermistor is the inevitable fluctuation in the rate of heat dissipation from the device (vide infra). In the steady-state, the temperature of the thermistor bead must lie above that of the surrounding fluid since heat is generated within the semi-conductor by Ohmic processes[12]. The relationship between the extent of self-heating (ΔT_{sh}) and power applied (P) is:

$$\Delta T_{sh} = \frac{P}{\delta} = \frac{E_B^2}{4R\delta} \tag{5}$$

where δ represents the thermistor's dissipation constant (typically 5 mw/°C in stirred water), E_B is the bridge voltage and R is the thermistor's resistance. The factor of 4 applies in the case of an equal arm bridge. It is well known that a thermistor's dissipation constant depends upon the flow-rate around the device[13,14]. Consequently any irregular motion will cause fluctuations in ΔT_{sh} which will be detected as noise.

Since the self-heating of the thermistor is proportional to the applied power, the voltage equivalent noise (e_δ) will be proportional to the third power of the bridge potential. The net effect of the above two noise sources can be represented by eqn (6)

$$e_\delta = \frac{KE_B^3}{f(\delta)R} \tag{6}$$

where K is a proportionality constant, and $f(\delta)$ is some function of the dissipation constant and its attendant random fluctuations.

There are certainly other conceivable noise sources, e.g., fluctuating thermal e.m.f.'s, changes in the bridge components and vibration. The above discussion was presented primarily to justify the form of the function which is used to describe the dependence of the temperature noise on the applied potential. The total temperature noise (ΔT_N) equivalent to the total voltage noise (e_N) may be calculated from the bridge equation as:

$$\Delta T_N = \frac{4e_N}{\alpha E_B} \tag{7}$$

The assumption that all of the noise sources are independent predicates that they must add as statistical variances[10] leading to the relation

$$\Delta T_N = \sqrt{\frac{A}{E_B^2} + B + CE_B^4} \tag{8}$$

where A is a coefficient related to the voltage independent noise sources (E_B^0), B represents the noise sources dependent on the first power of applied potential (E_B^1)

and C represents the third order sources (E_B^3). It is apparent from eqn (8) that the temperature resolution has unique minima and that a single optimum voltage exists. Differentiation of eqn (8) yields

$$E_B^{opt.} = \left(\frac{A}{2C}\right)^{1/6} \tag{9}$$

$$\Delta T_N^{min.} = \sqrt{B + 3\frac{A^{2/3}}{2}C^{1/3}} \tag{10}$$

EXPERIMENTAL

The apparatus used for the noise studies was an electronically shielded[15] and thermally insulated, non-differential, d.c. Wheatstone bridge. In order to provide reproducible measurements of the noise emanating from the bridge and the thermistor, the signal was amplified by at least 10^3 by a very clean amplifier. The peak-to-peak noise was at least 2 cm and was in all cases much greater than that due to electronics attached to the bridge. We found that at the high electronic gain required to precisely measure the noise, the temperature changes engendered by stirring and heat dissipation in the thermistor drove the recorder off scale so rapidly that useful measurements could not be carried out. The circuit shown in Fig. 1 was devised to amplify the

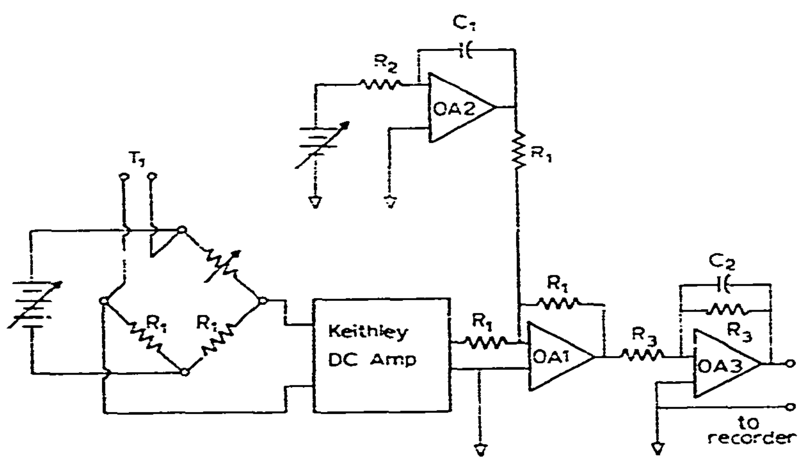

Fig. 1. Schematic diagram of the noice measurement system. $R_1 = 10$ (or 100) kΩ; $T_1 = 10$ (or 100) kΩ; $R_2 = 3.3$ mΩ; $R_3 = 1$ mΩ; $C_1 = 10$ μf; $C_2 = 1$ μf.

bridge output and substract from it a very clean "ramp" thereby flattening the recorder trace and permitting much larger measurements without rebalancing the bridge or adjusting the recorder offset. A Keithley (Model 140) d.c. nanovolt amplifier and operational amplifiers housed in a McKee–Pedersen manifold (Model MP-1001) were used. The signals were recorded on a Leeds and Northrup Speedomax recorder (Model XL). A Hewlett-Packard digital voltmeter (Model 3440 A) was used to measure the applied bridge potential and to ensure that changes in E_B did not constitute a serious noise source (see eqns (4) and (6)).

It is evident from eqn (1) and the above discussion that the band-width of the electronic system will have a considerable effect on the noise. We have adopted a standard band-width of 1 Hz for most of this work, consequently the last stage of the measuring system immediately preceding the recorder was a 1 Hz ($RC = 1$ sec) single pole, low pass filter.

The equal arm bridge circuitry itself was examined to evaluate the thermal e.m.f.'s by a method similar to that of Prosen and Kilday[16]. Although the total thermals were of the order of 6 μV, there was no appreciable change in this value for a period of 15 min and hence it does not appear to contribute to the short term noise.

The thermistors used were of the bead in glass probe design, Types 41A1 and 51A1, (Victory Engineering Corporation, Springfield, N.J.). They were rigidly mounted in a glass tube and connected to the bridge via miniature coaxial cable. Several thermistors were mounted in sealed glass tubes using air and mercury as a buffer between the thermistor and the glass-solution interface.

The isoperibol Dewars used in these studies were similar to those described by Christensen et al.[17] and had volumes of 30, 80 and 250 ml. A constant, high torque motor (Inframo Model RZR1-64, Ft. Wayne, N.Y.) was used in conjunction with a glass stirrer having four 1 cm elliptical blades to homogenize the calorimetric fluid. The experiments were conducted in a large water-bath which was controlled to 0.001 °C by a proportional controller (Yellow Springs Instrument Co., Model 72).

RESULTS AND DISCUSSION

Before beginning a detailed study of the effect of bridge voltage, it was essential to determine whether the data acquisition and treatment procedures might bias the real system noise. In order to establish how to best report the noise, the data of Table 2 were obtained. This table compares the rms noise (eqn (1)), the average

TABLE 2

COMPARISON OF VARIOUS NOISE REPORTING TECHNIQUES[a]

Voltage	*rms (μV)*	*Mean peak-to-peak (μV)*	*Peak-to-peak (μV)*
3.0	0.40	—	1.9
4.5	0.90	0.72	3.4[b]
6.0	2.6	2.0	9.3[b]
7.5	3.6	2.9	9.1[b]
9.0	4.9	3.8	25

[a] For a 10 kΩ thermistor in sealed glass tube, mercury buffer. [b] The peak-to-peak noise was measured over a 75 sec interval which may explain the lower P–P/rms ratio (see ref. 19).

peak-to-peak (eqn (2)) noise, and the peak-to-peak variations defined by drawing an envelope enclosing approximately 99% of the data over an interval of about 75 sec. The data shown indicate that the rms and average peak-to-peak variations are very similar. The peak-to-peak fluctuations, however, are considerably larger as expected. Although it is computationally simpler to measure the peak-to-peak noise, it is much less reproducible than either the rms or average peak-to-peak values. This fact in addition to the statistical advantages inherent in the rms method predicate that reasonable detection limit estimates, and therefore noise estimates, be obtained via eqn (1).

The Nyquist criteria[10] states that in order to completely define a signal it should be sampled at twice its highest frequency component. As a result, we felt that sampling over increased intervals and at low acquisition rates might produce some averaging of the lower frequency components of the signal; therefore, the effect of both the sampling rate and sampling interval was studied. In addition we introduced the 1 Hz low pass filter to give a well-defined band-width. The data are summarized in Table 3.

TABLE 3

EFFECT OF SAMPLING INTERVAL AND RATE ON MEASURED NOISE

ΔT_{rms} (μ°C)[a]	*Sample rate (Hz)*[b]	ΔT_{rms} (μ°C)[c]	*Sample interval (sec)*
15	2.1	11	4.7
15	1.1	14	9.4
14	0.54	16	18.8
13	0.27	17	28.2
		16	37.5
		15	46.9

[a] Total sampling interval of 50 sec. [b] Defined as the inverse of the time between consecutive data points. [c] Sampling rate 2.13 Hz.

Although it might appear that the noise varies with both sampling rate and interval, *F* tests at the 90% confidence level indicate that the sampling rate has no effect and only one pair of the sampling interval data was different. In view of these statistical considerations, we adopted a standard interval of 60 sec and a sampling rate of slightly greater than 1 Hz. This seemed a reasonable choice in light of our band-width and our inability to obtain and process large volumes of data.

In order to verify that the ramp generator and related circuits were not contributing to the noise or biasing it in some unsuspected fashion, the single thermistor bridge was modified to accept a second thermistor which was connected to the circuit and immersed directly in the test fluid. This differential arrangement circumvents the need for continuous baseline adjustment. No significant change in the noise was observed.

Inspection of the residuals of the least squares analysis through construction of a correlation diagram[18] indicated a strong correlation of the noise when a voltage was applied to the thermistor. An investigation was initiated to determine the frequency dependence of the noise. By varying the time constant of the single pole filter, the data of Fig. 2 were collected. As would be expected for white noise, a decrease in the band pass of the system yields a monotonic decrease in the observed magnitude of the noise.

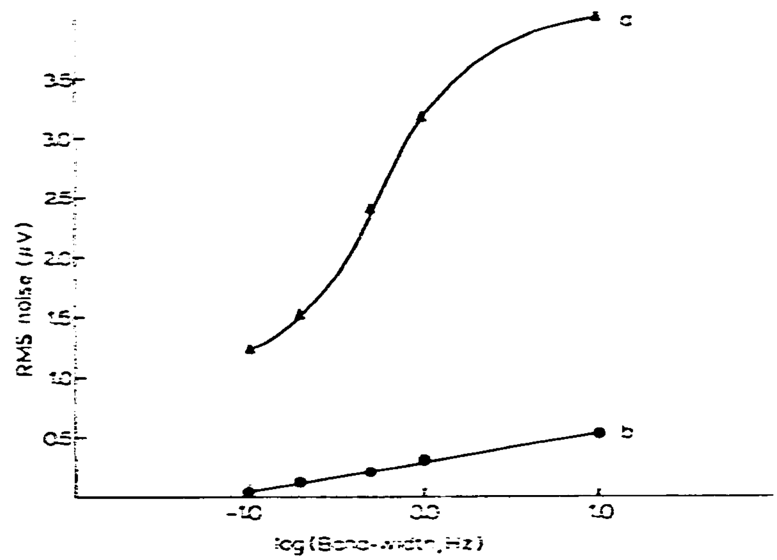

Fig. 2. Plot of rms voltage noise vs. system band-width. Curve a, noise measured at 9 V; curve b, noise measured at 3 V.

There is no apparent discrete noise source which could be eliminated by the use of more elaborate filtering techniques such as a notch filter. Although successive addition of poles to the low pass filter ($RC = 1$ sec) produced a slightly cleaner noise wave form, no significant decrease in the noise envelope was observed.

The results of our measurement of the temperature resolution of both 10 kΩ and 100 kΩ thermistors as calculated from eqn (7) are shown in Fig. 3. The continuous curve is an empirical one based only on the measurement of the noise without an applied bridge voltage, i.e., at $E_B = 0$, and a measurement of the noise at a very high applied potential (9 and 27 V for the 10 kΩ and 100 kΩ thermistors, respectively.) We assumed the value of B in eqn (8) to be zero. It is clear that a function of the form of eqn (8) does indeed fit the data in the region of the minima and, at least in our system with no heat flux due to a chemical reaction, thermal inhomogeneity is not a significant noise source. It is apparent from Fig. 3 that, as expected, a 100 kΩ thermistor has a much smaller C term, i.e., noise dependent upon the third power of the applied voltage, than a 10 kΩ thermistor. This is also noted in Table 4. It is vital to note that the temperature resolution at the minima of both curves is very similar. This is a consequence of the interaction of the increased Johnson and pick-up noise in the 100 kΩ thermistor and the relatively small effect of a large change in the C term.

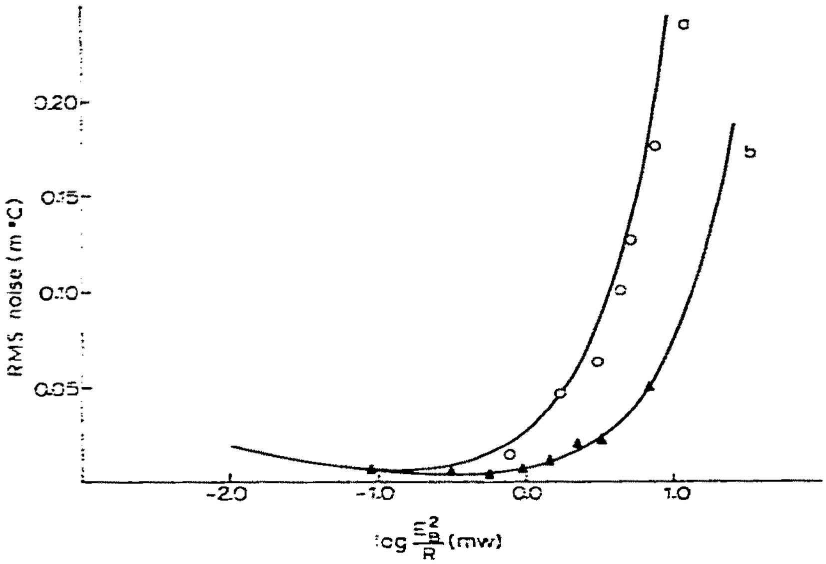

Fig. 3. Plot of rms noise vs. the logarithm of the applied voltage. Curve a, theoretical curve for a 10 kΩ thermistor; curve b, theoretical curve for a 100 kΩ thermistor; open circles, experimental 10 kΩ data; closed triangles, experimental 100 kΩ data.

TABLE 4

TYPICAL NOISE PARAMETERS AND THEIR DEPENDENCE ON RESISTANCE AND CONFIGURATION[a]

Device	*Impedance* (*k*Ω)	$e_{n,o}$ (*μV, rms*)[b]	*A*[c]	*C*[d]	*δ* (*mW/°C*)
Wire wound resistor	10	0.047	22	0.008	—
Wire wound resistor	100	0.18		—	—
Thermistor	10[e]	0.059	35	7.7	2.35
Thermistor	10[f]	0.058	34	0.084	2.31
Thermistor	10[g]	0.054	35	0.12	4.54
Thermistor	100[e]	0.19	380	0.0057	—

[a] All data obtained at a sampling rate of 1.04 Hz over an interval of 75 sec. [b] The measured noise with a dead short in place of the bridge driving voltage (E_B). [c] See eqn (8). Calculated from $e_{n,o}$. Units are μ°C^2 V^{-2}. [d] See eqn (8). Calculated for the noise at an applied power greater than 8 mW. Units are μ C^2 V^{-4}. [e] Thermistor in direct contact with the solution. [f] Thermistor encased in air. [g] Thermistor encased in Hg.

An attempt was made to quantitatively evaluate the dependence of the *B* term on heat fluxes. It was very easy to induce the thermal inhomogeneity effect simply by replacing the Dewar by a beaker of warm water. The observed equivalent temperature noise increased by a factor of approximately ten in such experiments. Although this was sufficient to illustrate the existence of a *B* term, we were concerned with the effect under conditions commonly encountered in thermometric titrimetry. The thermal inhomogeneity was induced in essentially two ways. First, a non-equilibrated volume of water was added to the calorimeter; this produced an effect similar to that observed in the beaker although the magnitude of the noise enhancement was much smaller. Allowing the Dewar and its contents to equilibrate overnight reduced the observed noise. Second, a calibration heater was used to simulate the effects of localized addition of titrant. At heating rates of 0.1 °C/100 sec, the temperature–time curve at the sensitivity required to observe the noise was non-linear; we attribute this to heat leakage from the Dewar. At lower heating rates, e.g., 0.05 °C/100 sec, the noise enhancement was found to be less than a factor of two. Due to the difficulty encountered in quantitating the B term, no absolute values for it were obtained. Apparently the B term is not a significant noise source provided that heat fluxes are kept below the equivalent of 500 μ°C/sec, the solution is adequately stirred and the system band width is less than 1 Hz.

The dependence of the C term on the thermistor configuration is shown in Figs. 4 and 5. The data of Fig. 4 were collected using thermistors encased in air and in mercury. This damps out the effect of variations in the solution velocity which change the dissipation constant of the device. The data of Fig. 4 again indicate that even large changes in the C term only slightly improve the temperature resolution as predicted by eqn (10).

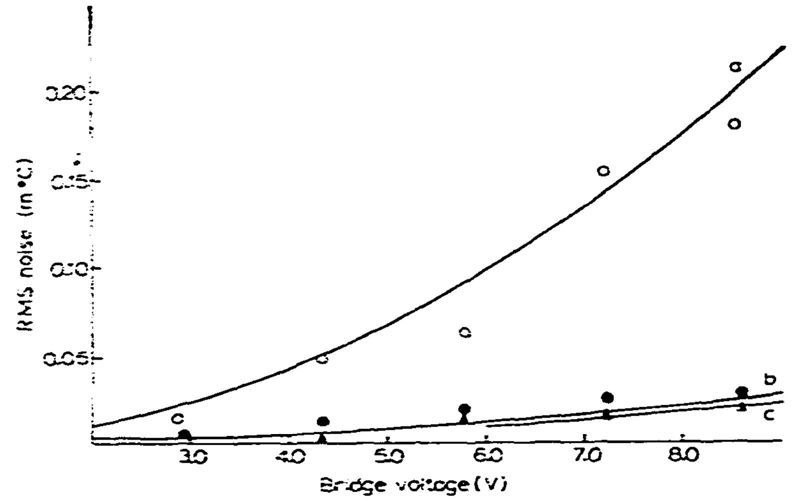

Fig. 4. Plot of rms noise vs. applied bridge voltage for various thermistor-solution boundaries. Curve a, theoretical curve for a 10 kΩ thermistor directly immersed in water; curve b, theoretical curve for a 10 kΩ thermistor with Hg buffer; curve c, theoretical curve for a 10 kΩ thermistor with air buffer; open circles, 10 kΩ directly in water data; closed circles, 10 kΩ Hg buffer data; closed triangles, 10 kΩ air buffer data.

If the flow of the fluid does indeed have an important role in the determination of the C term, then variations in the stirring rate should substantially affect the noise. Fig. 5 shows the results of this phenomeon in the area of $\Delta T_{N}^{min.}$. With no stirring in the Dewar, the thermistor self-heats to a steady state which is relatively noise free, i.e., is affected only by the electrical noise. This is borne out by the value of the C term in unstirred solution, which is essentially zero. Unfortunately, a thermistor in an unstirred solution is of little use in any calorimetric application. Stirring at a high rate of speed also "smooths out" the variations in the flow around the transducer thereby decreasing the C term. This can be seen in Fig. 5, the actual value of C being 1.56 $\mu^{\circ}C^2/V^4$. Rapid stirring of the solution is undesirable due to excessive heat

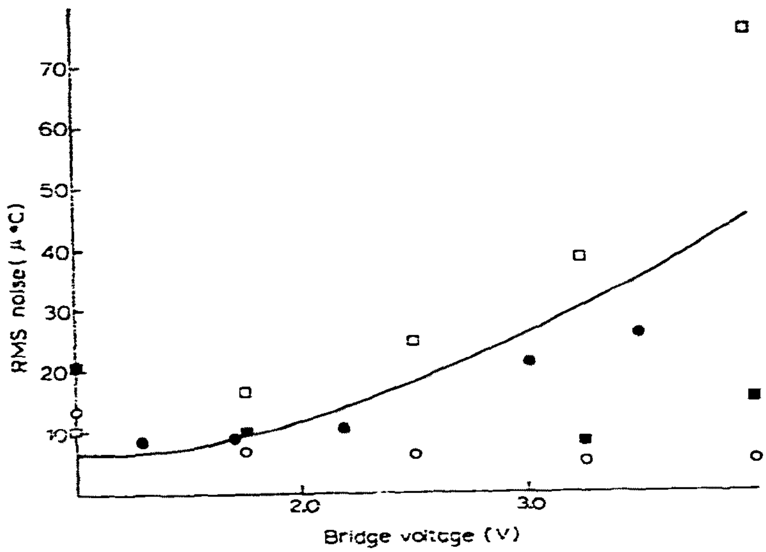

Fig. 5. Plot of rms noise vs. applied bridge voltage for various stirring rates. Open circles, steady-state self-heated 10 kΩ thermistor data; closed squares, stirring rate of about 2500 rpm for 10 kΩ thermistor; closed circles. standard 1000 rpm stirring rate; open squares. stirring rate of less than 500 rpm; continuous curve is theoretical curve given for reference.

production and swamping of chemical heat generation. In contradistinction slow stirring results in larger flow fluctuations, a larger temperature noise, and a C term of 38.8 $\mu^{\circ}C^2/V^4$. Thus it appears that the C term is more strongly controlled by fluctuations in the dissipation constant than by its actual value which increases monotonically with stirring velocity[11]. This is further evidenced by the measured dissipation constant for the air and mercury encased thermistors (last column Table 4). Although enclosing the thermistor did alter the actual dissipation constant there was a much more pronounced effect upon the C term. Obviously the actual C term must be considered as a function of the dissipation constant (see eqn (6)) but it is primarily related to irregular fluctuations in δ.

In view of the effects of stirring variations, the position of the thermistor is conceivably a critical parameter in that changes in flow about the thermistor could influence the dissipation. A 10 kΩ thermistor driven by a 9 V battery was moved within a 2 cm band above the stirrer at a distance of 0.6 cm from the stirrer axis. No sigificant change in the noise was observed. This would indicate that at least for our system, the flow about the thermistor is rather constant in the region studied.

In principle, the volume of the Dewar might well have some influence on the noise since the Dewar's adiabaticity and heat capacity will moderate the heat fluxes as well as the time of mixing and therefore interact with the thermal inhomogeneity noise (eqn (4)). Secondly, the distribution of flow patters might vary with volume in such a way as to alter the dissipative noise (eqn (6)). Thus the Dewar size could affect either B or C but certainly not A.

Figure 6 illustrates the temperature noise as a function of Dewar size. From these data, it appears that for our system the B term is negligible. Figure 6 indicates that a 250 ml Dewar has a slightly larger C term than either the 30 or 80 ml Dewar This may be due to a wall effect on the flow pattern around the thermistor.

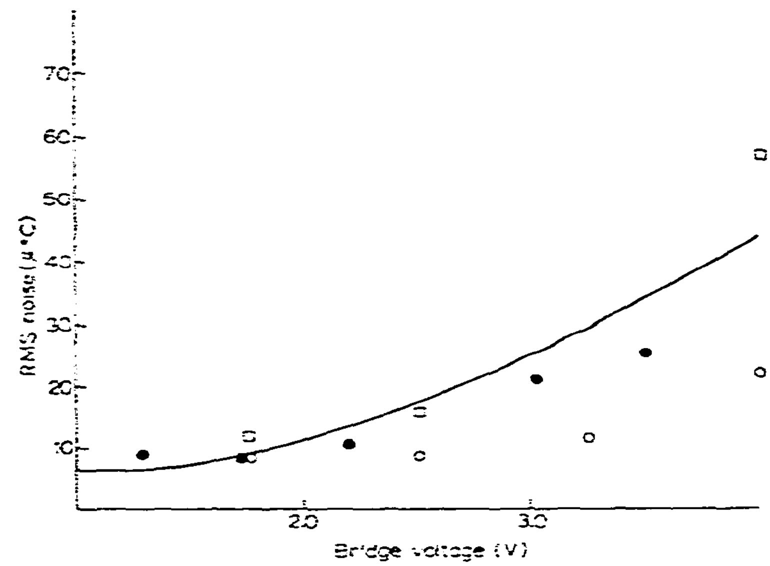

Fig. 6. Plot of rms noise vs. applied bridge voltage as a function of Dewar size. Open circles, 30 ml Dewar ($C = 7.3\ \mu°C^2/V^4$); closed circles, standard 80 ml Dewar ($C = 7.7\ \mu°C^2/V^4$); open squares, 250 ml Dewar ($C = 18\ \mu°C^2/V^4$); continuous curve is theoretical curve shown for reference.

CONCLUSION

A major inference of the above work is that a function of the form of eqn (8) adequately describes the dependence of the temperature equivalent noise upon the applied bridge potential. In fact, under most experimental conditions thermal inhomogeneity is of minor importance. This permits simplification of eqn (8) as well as the predicted optimal temperature resolution.

$$\Delta T_N^{min.} = 2.2 A^{1/3} C^{1/6} \qquad (11)$$

Since in all cases the theoretical curve (solid line in Figs. 3–6) was derived by measurement at two points ($E_B = 0$ and $E_B \gg E_B^{opt.}$) one can readily adjust E_B to the optimum value for a given system by making such measurements and substituting the results in eqn (9).

The very weak dependence of $\Delta T_N^{min.}$ on dissipative noise leads us to believe that an rms temperature resolution below a few μ°C is virtually impossible with a band width of 1 Hz. Even if all sources of noise other than Johnson noise are eliminated the results shown in Table 1 indicate that the rms temperature resolution of a 100 kΩ thermistor operated at ~3 V would be slightly greater than 1 μ°C. In fact we see no way to eliminate dissipative noise under useful experimental conditions, i.e., the thermistor in reasonable thermal contact with the stirred test solution. Equation 11 indicates that to improve the temperature resolution by a factor of 10 one must improve C by a factor of 10^6.

In order to estimate a practical resolution limit we have assumed that the pick-up noise can be reduced to the Johnson limit, i.e.,

$$A_{JN} = \frac{64kTR\Delta F}{\alpha^2} \qquad (12)$$

This value of A was combined with our experimental values of C for a 10 and 100 kΩ thermistor to calculate both $\Delta T_N^{min.}$ and $E_B^{opt.}$. The results are presented in Table 5. There are evidently some variations in the inherent dissipative features of thermistors (Table 4) but the trend is clear that rather new technology will be needed to increase the temperature resolution below a few μ°C. The recently introduced positive temperature coefficient thermistors offer some hope in this direction[20].

TABLE 5

MINIMUM TEMPERATURE RESOLUTION[a] FOR VARIOUS THERMISTORS

Device	$\Delta T_N^{min.}$ (μ°C)	$E_B^{opt.}$ (V)
10 kΩ thermistor[b]	10	1.28
100 kΩ thermistor[b]	6.6	6.30
10 kΩ thermistor[c]	4.6	2.72
10 kΩ thermistor[d]	4.9	2.57
10 kΩ thermistor[e]	3.6	0.77
100 kΩ thermistor[e]	2.3	3.8

[a] Calculated from the data of Table 4 and eqns (9) and (11). [b] Immersed directly in water. [c] Air encapsulated. [d] Hg encapsulated. [e] Calculated using the Johnson noise of Table 1 assuming a 1 Hz bandwidth.

The dependence of the achievable resolution upon thermistor resistance is of considerable interest. There appears to be a clear cut trend toward the use of higher resistance[8]. The C term can be related to thermistor resistance via eqn (6).

$$C = \frac{16K^2}{(f(\delta))^2 R^2 \alpha^2} \qquad (13)$$

Presuming that A can be reduced to its Johnson limit (see eqn (12)) it follows that:

$$\Delta T_{\text{min.}} = \frac{K'}{\alpha}\left(\frac{kT\Delta F}{f(\delta)}\right)^{1/3} \tag{14}$$

and

$$E_B^{\text{opt.}} = (2kT\Delta F)^{1/6}\left(\frac{f(\delta)}{K}\right)^{1/3}\sqrt{R} \tag{15}$$

where K' is a numerical constant approximated by:

$$K' \cong 14K^{1/3} \tag{16}$$

The result of this analysis is that if the Johnson limit can be achieved the rms temperature resolution is independent of the transducer resistance. Equation (15) indicates that an increase in transducer resistance leads to greater bridge sensitivity (V/°C) at the optimum voltage since $E_B^{\text{opt.}}$ increases with thermistor impedance. Thus it is very advisable to use as high an impedance source as the amplifier can tolerate in order to swamp out all voltage-independent noises. One must recognize that, all other factors being held constant, pick-up noise increases with impedance. In general we have been able to get closer to the Johnson limit with 100 kΩ thermistors than with 10 kΩ devices.

ACKNOWLEDGMENTS

The authors would like to thank Professor Louis Meites of Clarkson College of Technology for several interesting discussions and the National Institutes of Health for a grant (GM 17913) in support of this work.

REFERENCES

1 H. J. V. Tyrrell and A. E. Beezer, *Thermometric Titrimetry*, Chapman and Hall, London, 1968.
2 J. C. Wasilewski, P. T. S. Pei and J. Jordan, *Anal. Chem.*, 36 (1964) 2131.
3 H. W. Linde, L. B. Rogers and D. N. Hume, *Anal. Chem.* 25 (1953) 404.
4 J. Jordan in I. M. Kolthoff and P. J. Elving (Eds.), *Treatise on Analytical Chemistry*, Part I, Volume VIII, Interscience, New York, 1968.
5 T. Meites, L. Meites and J. Jaitly, *J. Phys. Chem.*, 73 (1969) 3801.
6 E. B. Smith, C. S. Barnes and P. W. Carr, *Anal. Chem.*, 44 (1972) 1663.
7 R. E. Dohner, A. H. Wachter and N. Simon, *Helv. Chim. Acta*, 50 (1967) 2193.
8 L. Lampugnani and L. Meites, *Thermochim. Acta*, 5 (1973) 351.
9 E. C. Robertson, R. Raspet, J. H. Swhartz and M. E. Lillard, *Geological Survey Bulletin 1203-B*, U.S. Government Printing Office, Washington, D.C.
10 E. J. Bair, *Introduction to Chemical Instrumentation*, McGraw-Hill, New York, 1962.
11 P. W. Carr, *Crit. Rev. Anal. Chem.*, 5 (1972) 519.
12 F. J. Hyde, *Thermistors*, Illiffe Books, London, 1971.
13 R. A. Rasmusson, *Rev. Sci. Instrum.*, 32 (1962) 38.
14 W. D. Bostick and P. W. Carr, *Anal. Chem.*, 46 (1974) 1095.
15 D. Nalle, *ISA Journal*, 59 (1965).
16 E. J. Prosen and M. V. Kilday, *J. Res. N.B.S.*, 77A (1973) 179.
17 J. J. Christensen, I. M. Izatt and L. D. Hansen, *Rev. Sci. Instrum.*, 36 (1965) 779.
18 R. Bracewell, *The Fourier Transform and Its Applications*, McGraw-Hill, New York, 1965.
19 V. D. Landon, *Proc. IRE*, 50 (1941).
20 R. J. Reilly and L. G. Hepler, *J. Chem. Educ.*, 49 (1972) 514.