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NOISE IN THERMISTORS FOR ISOPERIBOL CALORIMETRY: MODEL AND MEASUREMENTS

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ABSTRACT

Equations predicting the noise characteristics of thermistors used in isoperibol calorimetry are derived and tested as a function of frequency. Experimental noise levels are compared with theoretical predictions for NTC thermistors. A circuit with an NTC–PTC thermistor hybrid is characterized by a greater S/N than an NTC–NTC combination.

INTRODUCTION

A new thermometric circuit constructed with operational amplifiers was described by Van Til and Johnson[1]. The sensitivity of the circuit was shown to be nearly equal to the theoretical value. The circuit schematically shown in Fig. 1 of ref. 1 was characterized as to steady-state and transient signal strengths[2]. Noise consideration in thermometric circuits has only recently received detailed attention as a result of the work of Bowers and Carr[3]. Previously, description of noise measurements was sporadic and the basis for such measurements was rather poorly defined[4–6]. Advances in solution calorimetry are presently restricted by the lack of theoretical understanding of the primary sources of noise in temperature measurement. The signal-to-noise ratio (S/N) is derived here for the circuit shown in Fig. 1 of ref. 1.

THEORY

For small changes of temperature, the zero power response of a thermistor is given approximately by eqn (1)

$$R_b = R_t \exp\left\{\beta_t \left[\frac{T_t - T_b}{T_t^2}\right]\right\} \tag{1}$$

where T_b is the bulk solution temperature (K) and R_b is the value of R_t when $T_t = T_b$.

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Noise is a distortion or disruption of the desired signal in either a random or systematic manner. Removal of systematic noise is generally straight forward involving careful experiment design and execution. Reduction of random noise is much more difficult. Ultimate noise levels are determined by the number of physical variables studied and quantization errors caused by the particle-like behavior of energy transmission at the microscopic level. Energy transmission on a macroscopic scale is a continuous function but at the microscopic level it is discontinuous and described by distribution laws governing random events. In thermistors, this is readily seen in consideration of the term β_t in eqn (1). β_t is defined by eqn (2)

$$\beta_t = -E_g/2k_B \tag{2}$$

where E_g is the gap energy of the semiconductor (eV) and k_B is the Boltzmann constant. The parameter β_t describes the energy which discrete charge carriers must possess if they are to move from the valence band into the conduction band of the semiconductor. To summarize: the distribution of electrons in n-type semiconductors such as NTC thermistors is described using a band theory with a multiplicity of energy levels in each band and varying probability that each is populated primarily as a function of temperature.

Noises can be divided into two categories correlated and uncorrelated. Correlated noises are those having the same frequency and phase even though they may differ in amplitude. For example the, circuit was designed so that e_- tracks e_+ and, hence, noise in e_- is correlated with noise in e_+. The result is a reduction of systematic fluctuations of bridge output with change of the bridge supply voltage. Conversely, the two Dewar cells are independent and the fluctuations in bulk solution temperatures are uncorrelated noises.

The output of operational amplifier OA-3 in Fig. 1 of ref. 1 is related to the resistance of thermistors t_1 and t_2 (R_1 and R_2) by eqn (3).

$$e_{0,3} = -\left(\frac{R_f}{R_1}\right)e_- - \left(\frac{R_f}{R_2}\right)e_+ \tag{3}$$

For the NTC thermistor,

$$\frac{1}{R_t}\frac{\mathrm{d}R_t}{\mathrm{d}T_t} \simeq -\frac{\beta_t}{T_t^2} \tag{4}$$

and we defined in ref. 1

$$\Delta R_{b-t} = -\frac{\mathrm{d}R_t}{\mathrm{d}T_t}(T_t - T_b) \tag{5}$$

The first term of eqn (3) will be used in the initial development of an equation for noise strength. From eqns (4) and (5)

$$e_{0,3} = -\frac{R_f\beta_t e_-}{T_t^2}\left[\frac{(T_t - T_b)}{\Delta R_{b-t}}\right] \tag{6}$$

To simplify nomenclature, eqn (6) is rewritten as

$$e_0 = -\frac{R_f\beta_1 e_-}{T_1^2}\left[\frac{\Delta T_1}{\Delta R_1}\right]$$

which can be rearranged to the form

$$\frac{e_0}{R_f} = i_t = -\frac{\beta_1 e_-}{T_1^2}\left[\frac{\Delta T_1}{\Delta R_1}\right] \tag{7}$$

Equation (7) is useful for consideration of the noises produced by the voltage supply and the thermistor apart from amplifier noise.

The random noise in i, ($\sigma_{i_1}^2$) can now be written.

$$\sigma_{i_1}^2 = \left[\frac{e - \Delta T_1}{T_1^2 \Delta R_1}\right]^2 \sigma_{\beta_1}^2 + \left[\frac{\beta_1 \Delta T_1}{T_1^2 \Delta R_1}\right]^2 \sigma_{e-}^2$$

$$+ \left[\frac{\beta_1 e_-}{T_1^2 \Delta R_1}\right]^2 \sigma_{\Delta T_1}^2 + \left[\frac{\beta_1 e_- \Delta T_1}{T_1^2 \Delta R_1^2}\right]^2 \sigma_{\Delta R_1}^2$$

$$+ \left[\frac{-2\beta_1 e_- \Delta T_1}{T_1^3 \Delta R_1}\right]^2 \sigma_{T_1}^2 \tag{8}$$

The term σ_{e-} in eqn (8) can be measured directly. The term $\sigma_{\Delta T_1}$ can be readily calculated from eqn (9) (see eqn (23) of ref. 1).

$$\Delta T_1 = T_t - T_b = \left(\frac{3P_t - 4\pi r_t^3 c_t \gamma_b}{12\pi r_t \lambda_t}\right)\left(\frac{\lambda_i}{h_t r_t}\right) \tag{9}$$

The term σ_{β_1} is derived from eqn (10).

$$\frac{1}{R_t}\frac{dR_t}{dT_t} = -\frac{\beta_t}{T_t^2} + \frac{1}{T_t}\frac{d\beta_t}{dT_t} + \frac{1}{Z_t}\frac{dZ_t}{dT_t} \tag{10}$$

Knowing that $1/Z_t(dZ_t/dT_t) \ll -\beta_t/T_t + 1/T_t(d\beta_t/dT_t)$ we can write

$$d\beta_1 = \frac{T_1}{R_1}dR_1 + \frac{\beta_1}{T_1}dT_1 \tag{11}$$

Equation (11) is in the standard form for error analysis given by eqn (12). The squaring of eqn (12) will produce a very large equation

$$d\beta_1 = \left(\frac{\partial\beta_1}{\partial R_1}\right)_{T_1} dR_1 + \left(\frac{\partial\beta_1}{\partial T_1}\right)_{R_1} dT_1 \tag{12}$$

containing several cross-product terms, i.e., those resulting from an assumption of correlation. Because fluctuations of the bulk solution temperature are not caused by changes of R_1 and because changes of R_1 as a function of time are not necessarily caused by fluctuations of T_1, we can assume that noises in R_1 and T_1 are not correlated. Hence, the corresponding cross-products are assumed to equal zero and

$$(\mathrm{d}\beta_1)^2 = \left(\frac{T_1}{R_1}\right)^2 (\mathrm{d}R_1)^2 + \left(\frac{\beta_1}{T_1}\right)^2 (\mathrm{d}T_1) \tag{13}$$

Equation (13) may be stated in terms of variances as given by eqn (14).

$$\sigma^2_{\beta_1} = \left(\frac{T_1}{R_1}\right)^2 \sigma_{R_1} + \left(\frac{\beta_1}{T_1}\right)^2 \sigma^2_{T_1} \tag{14}$$

The approximation in eqn (4) is useful and $\sigma^2_{R_1}$ can be written as in eqn (15).

$$\sigma^2_{R_1} = \left(-\frac{R_1\beta_1}{T_1^2}\right) \sigma^2_{T_1} \tag{15}$$

The term $\sigma_{\Delta R_1}$ is derived beginning with eqn (16).

$$\Delta R_{b-t} = \frac{R_t\beta_t}{T_t^2}(T_t - T_b) \tag{16}$$

$$\begin{aligned} \sigma^2_{\Delta R_1} &= \left(\frac{\partial \Delta R_1}{\partial R_1}\right)^2_{\beta_1,T_1,\Delta T_1} \sigma^2_{R_1} \\ &+ \left(\frac{\partial \Delta R_1}{\partial \beta_1}\right)^2_{R_1,T_1,\Delta T_1} \sigma^2_{\beta_1} \\ &+ \left(\frac{\partial \Delta R_1}{\partial T_1}\right)^2_{R_1,\beta_1,\Delta T_1} \sigma^2_{T_1} \\ &+ \left(\frac{\partial \Delta R_1}{\partial \Delta T_1}\right)^2_{R_1,\beta_1,T_1} \sigma^2_{\Delta T_1} \end{aligned} \tag{17}$$

Combining eqns (14), (15), and (17), $\sigma^2_{\Delta R_1}$ can be written as given in eqn (18).

$$\begin{aligned} \sigma^2_{\Delta R_1} &= \left(\frac{\Delta R_1}{R_1}\right)^2 \sigma^2_{R_1} + \left(\frac{\Delta R_1}{\beta_1}\right)^2 \sigma^2_{\beta_1} \\ &+ \left(\frac{2\Delta R_1}{T_1}\right)^2 \sigma^2_{T_1} + \left(\frac{\Delta R_1}{\Delta T_1}\right)^2 \sigma^2_{\Delta T_1} \end{aligned} \tag{18}$$

Substitution of eqn (15) into (14) and (14) plus (15) into (18) yields eqn (19) for σ_{β_1} and eqn (20) for $\sigma^2_{\Delta R_1}$.

$$\sigma_{\beta_1} = 2\left(\frac{\beta_1}{T_1}\right)^2 \sigma^2_{T_1} \tag{19}$$

$$\sigma^2_{\Delta R_1} = \left(\frac{\Delta R_1}{\Delta T_1}\right)^2 \sigma^2_{\Delta T_1} + \left[\left(\frac{\beta_1 \Delta R_1}{T_1^2}\right)^2 + 6\left(\frac{\Delta R_1}{T_1}\right)^2\right] \sigma^2_{T_1} \tag{20}$$

Use of eqns (19) and (20) in (8) yields eqn (21) for σ^2_I.

$$\sigma_i^2 = \left(\frac{\beta_1 \Delta T_1}{T_1^2 \Delta R_1}\right)^2 \sigma_{e_-}^2 + 2\left(\frac{\beta_1 e_-}{T_1^2 \Delta R_1}\right)^2 \sigma_{\Delta T_1}^2 +$$

$$\left[12\left(\frac{\beta_1 e_- \Delta T_1}{T_1^3 R_1}\right)^2 + \left(\frac{\beta_1^2 e_- \Delta T_1}{T_1^4 \Delta R_1}\right)^2\right] \sigma_{T_1}^2 \tag{21}$$

Evaluation of eqn (21) is seen to be very dependent on a knowledge of ΔT_1. Through this entire treatment, ΔT_1 is used as a dynamic variable and ΔR_1 as a steady-state variable. The logic of this assumption is clear since R_1 is controlled by T_1. Accordingly, the transient portion of ΔT_1 is considered to operate on the ratio $\Delta T_1/\Delta R_1$, even though no separate transient term is discussed for R_1.

As discussed in ref. 2, the thermal gradient across the thermal boundary layer, which is in the order of 10^{-4} cm, is much larger than the thermal gradient within the thermistor. The time constant τ_0 in eqn (22) is also

$$\tau_t = \tau_0 + \tau_b = \frac{r_t^2}{6D_t}\left(\frac{h_t r_t + 2\lambda_i}{h_t r_t}\right) \tag{22}$$

$$T_t' - T_b' = \frac{P_t}{8\pi r_t \lambda_t}\left\{1 + \frac{2\lambda_t}{h_t r_t} - \frac{12h_t}{\lambda_t}\sum_{n=1}^{\infty}\frac{\exp(-\alpha_n^2 D_t t)}{\alpha_n[r_t^2\alpha_n^2 + r_t h(r_t h - 1)]\sin r_t\alpha_n}\right\} \tag{23}$$

$$T_t'' - T_b'' = \frac{-\gamma_b r_t^2}{6D_t}\left\{1 + \frac{2\lambda_t}{h_t r_t} - \frac{12h_t}{\lambda_t}\sum_{n=1}^{\infty}\frac{\exp(-\alpha_n^2 D_t t)}{\alpha_n[r_t^2\alpha_n^2 + r_t h(r_t h - 1)]\sin r_t\alpha_n}\right\} \tag{24}$$

approximately 30 times smaller than τ_b. Before turning to the case where noises in e_- and ΔT_1 are completely random, let us consider the case where e_- or T_1 change instantaneously to a new value.

The temperature difference between the thermistor geometric center, T_t, and the bulk solution, T_b, is determined by the electrical power applied to the thermistor, as described by eqn (23), and the heating rate of the bulk solution, as described by eqn (24). The superposition principle commonly used for linear systems and in many problems of heat conduction is applied here. Accordingly, the difference $T_t - T_b$ is assumed given by a linear combination of eqns (23) and (24). Knowing the relative size of terms in eqns (23) and (24) and, using the series approximations for the trigonometric functions represented in the transient portions of each equation, it can be shown that when $r_t \ll 1$

$$\Delta T_1 = \left[\frac{e_-^2}{4\pi r_1 \lambda_t R_1} - \frac{r_1^2 c_t \gamma_b}{3\lambda_t}\right]\cdot\left[\frac{\lambda_{i,1}}{h_1 r_1} - \frac{2\lambda_{eq,1}^2}{h_1^2 r_1}\exp\left(\frac{-3h_1 D_t t}{\lambda_{eq} r_1}\right)\right] \tag{25}$$

The structure of eqn (25) is characteristic of equations defining systems such as RC or RL circuits. Noise models for such circuits have already been derived and tested[8], placing the present analysis on a firmer theoretical foundation.

Since ΔT_1 is essentially controlled by the properties of the thermal boundary layer, variations of h_t must be calculated. Random errors in ΔT_1 are considered ultimately with respect to time, assuming that the mean value of T_1 is constant. The assumption of constant temperature leads to the assumption of constant properties for the bulk solution parameters such as c_b, λ_b, v_b and thermistor properties c_t, λ_i, λ_{eq} and r_t.

Setting $\rho_t = h_t r_t$ as defined by eqn (26), σ_{ρ_t} is

$$\frac{h_t r_t}{\lambda_b} = 0.50 + 0.0875\left(\frac{r_s^2\omega_s 2r_t}{r v_b}\right)^{0.58}\left(\frac{v_b c_b}{\lambda_b}\right)^{0.36} \tag{26}$$

then governed by σ_{ω_s} using the assumption stated above.

$$\sigma_{\rho_t}^2 = \left[\left(\frac{0.0508}{\omega_s}\right)\left(\frac{U(r)r_s\omega_s 2r_1}{U_{max}\, r_b}\right)\left(\frac{v_b c_b}{\lambda_b}\right)^{0.36}\lambda_b\right]^2\cdot\sigma_{\omega_s}^2 \tag{27}$$

With eqns (25) and (27) in hand, eqn (28) can be derived by writing an error equation for ΔT_1 based on eqn (25) followed by the substitution of eqn (27) where appropriate. Hence,

$$\begin{aligned}\sigma_{\Delta T_1}^2 = {} & \left\{\frac{e_-}{2\pi r_1\lambda_t R_1}\left[\frac{\lambda_{i,1}}{\rho_1} - \frac{2\lambda_{eq,1}^2}{\rho_1^2}\exp\left(\frac{-3\rho_1 D_t t}{\lambda_{eq,1}r_1^2}\right)\right]\right\}^2\sigma_{e-}^2 \\
& + \left\{\frac{r_1^2 c_1}{3\lambda_t}\left[\frac{\lambda_{i,1}}{\rho_1} - \frac{2\lambda_{eq,1}^2}{\rho_1^2}\exp\left(\frac{-3\rho_1 D_t t}{\lambda_{eq,1}r_1^2}\right)\right]\right\}^2\sigma_{\gamma_{b,1}}^2 \\
& + \left\{\left[\frac{e_-^2}{4\pi r_1\lambda_t R_1} - \frac{r_1^2 c_1\gamma_{b,1}}{3\lambda_t}\right]\left[\frac{-\lambda_{i,1}}{\rho_1^2} + \frac{4\lambda_{eq,1}^2}{\rho_1^3}\cdot\right.\right. \\
& \left.\left.\exp\left(\frac{-3\rho_1 D_t t}{\lambda_{eq,1}r_1^2}\right) + \frac{6\lambda_{eq,1}D_t t}{r_1^2}\exp\left(\frac{-3\rho_1 D_t t}{\lambda_{eq,1}r_1^2}\right)\right]\right\}^2\cdot\sigma_{\rho_1}^2\end{aligned} \tag{28}$$

Damping of fluctuations in e_-, ΔT_1, and T_1 sensed by the thermistor is evident from Equations 25 and 28. Noises in e_- and γ_b are not correlated making cross-products in eqn (25) zero. Ignoring the damping effect, the steady-state current noise at the input of OA-3 from the sources considered to this point is determined by substitution of eqn (28) into eqn (21) and collecting terms. The form of the result is given by eqn (29).

$$\sigma_{i_1}^2 = a_1 + b_1 e_-^2 + c_1 e_-^4 + d_1 e_-^6 \tag{29}$$

Equation (29) is similar to the thermistor noise equation derived semi-empirically by Bowers and Carr[3] and of identical form if σ_{e-} is assumed to equal zero.

In fully expanded form, $\sigma_{i_1}^2$ is given by

$$\begin{aligned}\sigma_{i_1}^2 = {} & \left\{\left(\frac{\beta_1\tau_1\gamma_{b,1}}{T_1^2\Delta R_1}\right)^2\sigma_{e-}^2\right\} + \left\{2\left(\frac{\beta_1\tau_1}{T_1^2\Delta R_1}\right)^2\sigma_{\gamma_{b,1}}^2\right. \\
& + 2\left(\frac{\beta_1\tau_1\gamma_{b,1}}{\rho_1 T_1^2\Delta R_1}\right)^2\sigma_{\rho_1}^2 + \left[12\left(\frac{\beta_1\tau_1\gamma_{b,1}}{T_1^3\Delta R_1}\right)^2\right.\end{aligned}$$

$$+\left(\frac{\beta_1^2\tau_1\gamma_{b,1}}{T_1^4\Delta R_1}\right)^2\Bigg]\sigma_{T_1}^2\Bigg\}e_-^2+\Bigg\{0.513\left(\frac{\beta_1\tau_1}{r_1^3c_tT_1^2R_1\Delta R_1J}\right)^2\sigma_{e_-}^2\Bigg\}e_-^4$$

$$+\Bigg\{0.114\left(\frac{\beta_1\tau_1}{r_1^3c_t\rho_1T_1^2R_1\Delta R_1J}\right)^2\sigma_{\rho_1}^2$$

$$+\Bigg[0.685\left(\frac{\beta_1\tau_1}{r_1^3c_tT_1^3R_1\Delta R_1J}\right)^2+0.0571\left(\frac{\beta_1^2\tau_1}{r_1^3c_tT_1^4R_1\Delta R_1J}\right)^2\Bigg]\sigma_{T_1}^2\Bigg\}e_-^6 \tag{30}$$

The dependence of σ_{i_1} on σ_{e_-} and noises in the thermal boundary layer is neatly divided in eqn (30) indicating that the coefficients a_1 and c_1 are constants and coefficients b_1 and d_1 are variables in eqn (29).

Actual noise sources are completely random rather than approximating the power surge in a RC system seen when a switch to a battery is turned on.

The frequency dependence of noise must also be accounted for in revision of eqn (30). A finite number of sampling points in noise analysis predicate the use of standard deviation rather than variance in eqn (30). The root-mean-squared (rms) value of the noise wave is equal to the standard deviation of the noise wave. Motchenbacher and Fitchen [7] showed that for a RC or RL circuit, the noise voltage, e_n, at a particular frequency, f, is determined from the rms noise voltage, e_{rms}, by the relationship

$$e_n^2(f)=\left(\frac{1}{1+\omega^2\tau^2}\right)e_{rms}^2 \tag{31}$$

where ω is the angular frequency of the noise in radians sec^{-1}. Noise in e_- is affected by the thermistor body, thermal boundary layer and correlation between the thermistor thermal boundary layer and the bulk solution. Effects of random noises in the heat transfer coefficient, h_t, on the standard deviation of i, S_i, as given by the standard deviation of ρ_1, S_{ρ_1}, are considered to be controlled by the time constants of the thermal boundary layer and the thermistor body. Random fluctuations of the bulk solution temperature involve the preceding time constants and the time constant of solution mixing, τ_m. Hence, the following standard deviations can be written:

$$S_{e_-}^2(f)=\left(\frac{1}{1+\omega^2\tau_0^2}\right)\left(\frac{1}{1+\omega^2\tau_b^2}\right)\left(\frac{1}{1+\tau_t^2/\tau_m^2}\right)e_{-,rms} \tag{32}$$

$$S_{\rho_1}^2(f)=\left(\frac{1}{1+\omega^2\tau_0^2}\right)\left(\frac{1}{1+\omega^2\tau_b^2}\right)\rho_{1,rms}^2 \tag{33}$$

$$S_{\gamma_{b,1}}^2(f)=\left(\frac{1}{1+\omega^2\tau_0^2}\right)\left(\frac{1}{1+\omega^2\tau_b^2}\right)\left(\frac{1}{1+\tau_t^2/\tau_m^2}\right)\cdot\gamma_{b,1,rms}^2 \tag{34}$$

$$S_{T_1}^2(f)=\left(\frac{1}{1+\omega^2\tau_t^2}\right)\left(\frac{1}{1+\omega^2\tau_m^2}\right)T_{1,rms}^2 \tag{35}$$

Substitution of eqns (32)–(35) into eqn (30) followed by multiplication throughout by df and addition of the Johnson noise yields eqn (36).

$$
\begin{aligned}
i^2_{1,s}df = & \left\{ \left(\frac{\beta_1 \tau_1 \gamma_{b,1}}{T_1^2 \Delta R_1} \right)^2 \left(\frac{1}{1 + \omega^2 \tau_{0,1}^2} \right) \left(\frac{1}{1 + \omega^2 \tau_{b,1}^2} \right) \left(\frac{1}{1 + \tau_1^2/\tau_m^2} \right) \cdot \right. \\
& \left. e^2_{-,rms} df + \left(\frac{4k_B T_1}{R_1} \right) \left(\frac{1}{1 + \omega^2 \tau_{0,1}} \right) df \right\} + \left\{ 2 \left(\frac{\beta_1 \tau_1}{T_1^2 \Delta R_1} \right)^2 \cdot \right. \\
& \left(\frac{1}{1 + \omega^2 \tau_{0,1}^2} \right) \left(\frac{1}{1 + \omega^2 \tau_{b,1}^2} \right) \left(\frac{1}{1 + \tau_1^2/\tau_m^2} \right) \cdot \\
& \gamma^2_{b,1,rms} df + 2 \left(\frac{\beta_1 \tau_1 \gamma_{b,1}}{\rho_1 T_1^2 \Delta R_1} \right)^2 \left(\frac{1}{1 + \omega^2 \tau_{0,1}^2} \right) \cdot \\
& \left(\frac{1}{1 + \omega^2 \tau_{b,1}} \right) \rho^2_{1,rms} df + \left[12 \left(\frac{\beta_1 \tau_1 \gamma_{b,1}}{T_1^3 \Delta R_1} \right)^2 + \left(\frac{\beta_1^2 \tau_1 \gamma_{b,1}}{T_1^4 \Delta R_1} \right)^2 \right] \cdot \\
& \left. \left(\frac{1}{1 + \omega^2 \tau_1^2} \right) \left(\frac{1}{1 + \omega^2 \tau_m^2} \right) T^2_{1,rms} df \right\} e^2_- \\
& + \left\{ 0.513 \left(\frac{\beta_1 \tau_1}{r_1^3 c_t T_1^2 R_1 \Delta R_1 J} \right)^2 \left(\frac{1}{1 + \omega^2 \tau_{0,1}^2} \right) \left(\frac{1}{1 + \omega^2 \tau_{b,1}^2} \right) \cdot \right. \\
& \left. \left(\frac{1}{1 + \tau_1^2/\tau_m^2} \right) e_{-,rms} df \right\} e^4_- + \left\{ 0.114 \left(\frac{\beta_1 \tau_1}{r_1^3 c_t \rho_1 T_1^2 R_1 \Delta R_1 J} \right)^2 \cdot \right. \\
& \left(\frac{1}{1 + \omega^2 \tau_{0,1}^2} \right) \left(\frac{1}{1 + \omega^2 \tau_{b,1}^2} \right) \rho^2_{1,rms} \\
& + \left[0.685 \left(\frac{\beta_1 \tau_1}{r_1^3 c_t T_1^3 R_1 \Delta R_1 J} \right)^2 + 0.0571 \left(\frac{\beta_1^2 \tau_1}{r_1^3 c_t T_1^4 R_1 \Delta R_1 J} \right)^2 \right] \cdot \\
& \left. \left(\frac{1}{1 + \omega^2 \tau_1^2} \right) \left(\frac{1}{1 + \omega^2 \tau_m^2} \right) T^2_{1,rms} df \right\} e^6_- \qquad (36)
\end{aligned}
$$

The definition used here for Johnson noise is that given by Motchbacher and Fitcher[7] for situations where shunt capacitance exists in parallel with a resistance. Indeed, this electrical model is frequently applied to thermistors with negative temperature coefficient.

$$
i^2_{n,\text{Johnson}}(f) = \frac{4k_B T_1}{R_1} \frac{1}{1 + \omega \tau_{0,1}} df \qquad (37)
$$

The parameter ω is equal to $2\pi f$. Integration of equations exemplified by eqns (32)–(35)

is difficult for the usual range in f of zero to infinity. When $\tau_b \gg \tau_0$ and the Reynolds number is greater than 2×10^3, it can be shown that $\tau_t \gg \tau_m$. These relations then lead to the approximation

$$(1 + \omega^2\tau_0^2)(1 + \omega^2\tau_b^2) \simeq \omega^2\tau_b^2 \left[\omega^2\tau_0^2 + \frac{(\tau_b^2 + \tau_0^2)}{\tau_b^2}\right] \tag{38}$$

which in turn can be shown to be in a form readily integrated using standard tables.

$$\int_{f_1}^{f_2} \frac{df}{(1 + \omega^2\tau_0^2)(1 + \omega^2\tau_b^2)} \simeq \frac{1}{16\pi^4\tau_b^2\tau_0^2} \int_{f_1}^{f_2} \frac{df}{f^2\left(f^2 + \frac{1}{4\pi^2\tau_0^2}\right)} \tag{38}$$

The utility of the approximation is apparent when one realizes that analysis of low frequency noise is the goal. Hence, the operation of small values of ω on τ_0, τ_b and τ_s is the key to the analysis. Yet, one should recognize that the approximation is only correct when $\omega^2 \tau_T \gg 1$. This condition, in the case of most thermistors, is reached after 3 Hz. Thus, the frequency needed to obtain a valid approximation is sufficiently low to be applicable. Equation (38) when integrated is given by eqn (39).

$$\frac{1}{16\pi^4\tau_b^2\tau_0^2} \int_{f_1}^{f_2} \frac{df}{f^2\left(f^2 + \frac{1}{4\pi^2\tau_0^2}\right)} = \frac{1}{4\pi^2\tau_b^2}\left(\frac{1}{f_1} - \frac{1}{f_2}\right) +$$

$$\frac{\tau_0}{2\pi\tau_b^2}\left[\arctan(2\pi\tau_0 f_1) - \arctan(2\pi\tau_0 f_2)\right] \tag{39}$$

Making use of extrapolation beyond the range where the initial approximation $\omega^2\tau^2 \gg 1$ is valid, that is, making $f_1 \to 0$, eqn (39) reduces to

$$\frac{1}{16\pi^4\tau_b^2\tau_0^2} \int_{f_1}^{f_2} \frac{df}{f^2\left(f^2 + \frac{1}{4\pi^2\tau_0^2}\right)} \simeq \frac{1}{4\pi^2\tau_b^2}\frac{1}{f_1} - \frac{\tau_0}{2\pi\tau_b^2}\arctan(2\pi\tau_0 f_2) \tag{40}$$

Equation (40) then shows the usual $1/f$ dependence of noise for all electronic devices. Equation (40) suggests that the use of a bandpass filter with $f_1 > 1$ Hz and $f_2 < 10$ Hz would greatly reduce noises due to thermal boundary layer fluctuations and bulk solution temperature fluctuations. The use of a simple single pole RC filter in the feedback path of OA-3 is seen to do little in reducing contributions of coefficients b_1 and d_1 of eqn (29). Increase of the time constant, $R_f C_f$, for OA-3 will reduce the bandwidth, Δf, and consequentially the contributions of coefficients a_1 and c_1 of eqn (29). The arc tan term of eqn (40) for the usual f_2 of 0.5 to 20 Hz is only about 2% of the first term when $f_1 = 0.01$ Hz. The choice of $f_1 = 0.01$ Hz is obviously an arbitrary one, but is a standard used in operational amplifier noise specifications.

The preceding discussion of the random noise characteristics of eqn (37) integrated with respect to frequency simplifies the expression of the total input noise, $I_{1,n}$ of OA-3 contributed by thermistor t_1.

$$I_{1,n}\Big|_{f_1}^{f_2} = \sqrt{\int_{f_1}^{f_2} i_{1,n}^2 df} = \Bigg[\Bigg\{\left(\frac{\beta_1\ _1\gamma_{b,1}e_{-,rms}}{T_1^2 \Delta R_1}\right)^2\left(\frac{1}{1+\tau_1^2/\tau_m^2}\right)\cdot$$

$$\left[\frac{1}{4\pi^2\tau_{b,1}^2 f_1} - \frac{\tau_{0,1}}{2\pi\tau_{b,1}^2}\arctan(2\pi\tau_{0,1}f_2)\right]$$

$$+\left[0.636\left(\frac{k_B T_1}{R_1}\right)\right]\left[\,[\arctan(2\pi\tau_{0,1}f_2)]\right.$$

$$+\left\{\left(\frac{\beta_1\tau_1\gamma_{b,1,rms}}{T_1^2\Delta R_1}\right)^2\left(\frac{1}{1+\tau_1^2/\tau_m^2}\right)\left[\frac{1}{2\pi^2\tau_{b,1}f_1}\right.\right.$$

$$-\left.\frac{\tau_{0,1}}{\pi\tau_{b,1}^2}\arctan(2\pi\tau_{0,1}f_2)\right] + \left(\frac{\beta_1\tau_1\gamma_{b,1}\rho_{1,rms}}{\rho_1 T_1^2\Delta R_1}\right)^2\cdot$$

$$\left[\frac{1}{2\pi^2\tau_{b,1}^2 f_1} - \frac{\tau_{0,1}}{\pi\tau_{b,1}^2}\arctan(2\pi\tau_{0,1}f_2)\right]$$

$$+\left[12\left(\frac{\beta_1\tau_1\gamma_{b,1}}{T_1^3\Delta R_1}\right)^2 + \left(\frac{\beta_1^2\tau_1\gamma_{b,1}}{T_1^4\Delta R_1}\right)^2\right]\left[\frac{1}{4\pi^2\tau_1^2 f_1}\right.$$

$$-\left.\frac{\tau_m}{2\pi\tau_1^2}\arctan(2\pi\tau_m f_2)\right] T_{1,rms}^2\Bigg\} e_-^2$$

$$+\left\{0.513\left(\frac{\beta_1\tau_1 e_{-,rms}}{r_1^3 c_1 T_1^2 R_1 \Delta R_1 J}\right)^2\left(\frac{1}{1+\tau_1^2/\tau_m^2}\right)\cdot\right.$$

$$\left.\left[\frac{1}{4\pi^2\tau_{b,1}^2 f_1} - \frac{\tau_{0,1}}{2\pi\tau_{b,1}^2}\arctan(2\pi\tau_{0,1}f_2)\right]\right\} e_-^4$$

$$+\left\{0.0182\left(\frac{\beta_1\tau_1\rho_{1,rms}}{r_1^3 c_1\rho_1 T_1^3 R_1\Delta R_1 J}\right)^2\left[\frac{1}{2\pi^2\tau_{b,1}^2 f_1}\right.\right.$$

$$-\left.\frac{\tau_{0,1}}{\tau_{b,1}^2}\arctan(2\pi\tau_{0,1}f_2)\right] + \left[0.109\left(\frac{\beta_1\tau_1}{r_1^3 c_1 T_1^3 R_1\Delta R_1 J}\right)^2\right.$$

$$+ 0.0909 \left(\frac{\beta_1^2 \tau_1}{r_1^3 c_1 T_1^4 R_1 \Delta R_1 J} \right)^2 \Bigg] \Bigg[\frac{1}{2\pi\tau_1^2 f_1}$$

$$- \frac{\tau_m}{\tau_1^2} \arctan (2\pi\tau_m f_2) \Bigg] \left[T_{1,rms}^2 \right\} e_-^6 \Bigg]^{1/2} \quad (41)$$

The value of $e_{-,rms}$ in eqn (41) must also be calculated separately from manufacturers data for the frequency range under consideration.

The total circuit noise is measured at the output of OA-3 and is given by eqn (42), which is derived by the method of Motchenbacher and Fitcher[7], with C being the correlation coefficient between $I_{1,n}$ and $I_{2,n}$, noises of thermistors t_1 and t_2.

$$I_{0,n}^2 = I_{1,n}^2 + 2\,C\,I_{1,n} + I_{2,n}^2 + I_{a,n}^2 \quad (42)$$

The total noise contribution of OA-3 itself is given in the form of a noise current, $I_{a,n}^2$. The cross-product term, $2\,C\,I_{1,n}\,I_{2,n}$, is only non-zero for noises that are correlated, those of e_- and e_+. Hence, coefficients b_1 and d_1 are assumed to equal zero in calculation of $I_{1,n}$ as used in the cross-product term of eqn (42). As noted earlier, noises in e_+ only are completely discriminated against when circuit gains are equal for changes in R_1 and R_2. The value of the correlation coefficient, C, is -0.5 rather than -1 which would be true if noises in e_- also were discriminated against.

Calculation of a theoretical S/N ratio is now possible and comparisons with experimental results can be made for variations in circuit parameters and sampling time employed in noise measurements. Shot noise in the thermistors was not incorporated into the present model of thermistor noise since thermistors $\leq$ 10 K only were considered with currents $\leq$ 100 μA flowing in them. Noise contributions from the Zener reference diode can be straight-forwardly added to the present model since the Zener mechanism exhibits primarily shot noise[7].

RESULTS AND DISCUSSION

Power supply stability

The power supply described in Figure 1[1] has required little adjustment over a one-year period of successful operation. Typical stability was determined by measurement of e_+, e_- and $|e_+ - e_-|$ at irregular intervals over a two-week period with at least one measurement per working day. The results fitted by linear least squares are:

$e_+ = 1{,}000.0 \pm 0.02$ mV $- 0.0025 \pm 0.0021$ mV day^{-1}
$e_- = 1{,}000.2 \pm 0.02$ mV $- 0.0010 \pm 0.0021$ mV day^{-1}
$|e_+ - e_-| = 0.175 \pm 0.007$ mV $+ 0.003 \pm 0.001$ mV day^{-1}

With the bridge connected and 10-kΩ metal film resistors replacing the thermistors, the peak-to-peak noise and drift over a 24-h period was 10 ppm for a room temperature constant to $\pm$ 1 °C. Recovery time from a transient voltage applied to the output of OA-1 was 0.3 sec for $C_f = 0.047$ μF. Circuit B had a peak-to-peak noise of 7 ppm for $C_f = 2$ μF. Measurements made of circuit noise over 24 h would yield noise down

TABLE 1

THERMISTOR CIRCUIT NOISE (CIRCUIT A)

Reference	Literature values		ΔT_n
	Bridge voltage	Amplifier damping	
10	2.037 V	3 sec	50 μ°C
11	12.000 V	not given	30 μ°C
	This work: r_s = 1.27 cm N_s = 540 rev/min C_t = 0.047 μF		

Thermistor	R_t	R_tC_t	e	ΔT_n
$t_{STC,3}$	100.04 kΩ	0.005 sec	0.50000 V	125 μ°C
			1.00000 V	125 μ°C
t_{PTC}	100.04 kΩ	0.005 sec	0.50000 V	94 μ°C
			1.00000 V	94 μ°C
$t_{STC,3} - t_{PTC}$	100.04 kΩ	0.005 sec	0.50000 V	50 μ°C
			1.00000 V	60 μ°C
$(t_{STC,1} + t_{STC,3}) - t_{PTC}$	100.04 kΩ	0.005 sec	0.50000 V	43 μ°C
$t_{STC,1}$	1.0016 mΩ	0.05 sec	1.00000 V	25 μ°C
$t_{STC,1} - t_{STC,2}$	1.0016 mΩ	0.05 sec	1.00000 V	75 μ°C

to at least 0.0001 Hz. To obtain a value for use in comparison to the case where thermistors are used, at an f_1 equal to 0.01 Hz, the peak-to-peak noise is divided by 10. This yields a short term p–p noise for the bridge circuits of ± 1 ppm which corresponds to a p–p temperature noise of 25 μ°C.

Circuit noise

Uncertainty (noise) in the temperature measurement for various thermistors and thermistor combinations is given in Table 1. The value of ΔT_n was calculated from experimental data by the PARD convention[8] and represents the uncertainty in T_b for an isothermal solution as determined from the mean of $e_{0,3}$ over a 5-min recording period. It is interesting to note the successive decrease in ΔT_n as the number of thermistors in the circuit is increased. Thermistors are generally accused of being noisy. The predominant sources of noise determined in this research are stray electrostatic and electromagnetic pickup by the lead wires; the precaution of double-shielding had a noticeable benefit to decrease ΔT_n. Maximum noise levels determined by recording $e_{0,3}$ for a 1-h period are about 3× the values in Table 1 which is in agreement with the observation of LaForce et al.[9].

Calculations using parameters listed were used in the numerical evaluation of eqn (41) for Circuit A:

$T_1 = 298$ K, $\Delta R_1 = 3.2\ \Omega$, $N_s = 600$ rev min^{-1},

$\rho_1 = h_1 r_1 = 2.13 \times 10^{-2}$ cal cm^{-1} sec^{-1} °C^{-1},

$\sigma_{\rho_1} = 5.72 \times 10^{-7}$ cal cm^{-1} sec^{-1} °C^{-1} assuming $\sigma_{\omega_s} = 5$ ppt,

$\tau_1 = 5.0$ sec, $\tau_{b,1} = 4.8$ sec, $\tau_{0,1} = 0.199$ sec.
$\tau_m = 1.08$ sec, $f_1 = 0.01$ Hz, $f_2 = 20$ Hz,
arc tan $(2\pi\tau_{m-2}) = 1.57$, arc tan $(2\pi\tau_{0e2}) = 1.53$.

The value of $e_{-,rms}$ was calculated from the noise spectrum plot given by Motchenbacher and Fitchen[7] for the 741C operational amplifier. For frequencies < 1000 Hz, the noise spectrum plot shows that e_n of the amplifier is predominantly $1/f$ in character. By extrapolation for frequencies < 10 Hz, $e_{-,rms}$ was calculated to equal 6.4×10^{-7} volt Hz^{-1} for 0.01 to 20 Hz. Values must be assumed for $\gamma_{b,1,rms}$ and $T_{1,rms}$ since quantitative theory is still lacking. Hence, the assumptions of $\gamma_{b,1,rms} = 1.3 \times 10^{-9}$ °C sec^{-1} and $T_{1,rms} = 1 \times 10^{-6}$ °C although reasonable are only best estimates of these parameters at this time.

The numerical evaluation of eqn (35) yields:

$$
\begin{aligned}
I_{1,n} = [&\{(2.50 \times 10^{-25})(0.0482)(0.110 - 0.002) \\
&+ (2.62 \times 10^{-25})(1.53)\} + \{(6.63 \times 10^{-21}) \cdot \\
&(0.0482)(0.220 - 0.004) + (4.78 \times 10^{-22}) \cdot \\
&(0.220 - 0.004) + (8.96 \times 10^{-17} + 1.06 \times 10^{-15}) \cdot \\
&(0.101 - 0.006)(1 \times 10^{-12})\} e_-^2 \\
&+ \{(2.50 \times 10^{-19})(0.0482)(0.110 - 0.002)\} e_-^4 \\
&+ \{(1.76 \times 10^{-22})(0.691 - 0.013) + (1.46 \times 10^{-12} \\
&+ 1.74 \times 10^{-10})(0.637 - 0.068)(1 \times 10^{-12})\} e_-^6]^{1/2}
\end{aligned}
$$

$$
\begin{aligned}
I_{1,n} = [&4.02 \times 10^{-25} + 1.74 \times 10^{-22} e_-^2 + 1.36 \times 10^{-21} \cdot \\
&e_-^4 + 2.19 \times 10^{-22} e_-^6]^{1/2}
\end{aligned}
$$

In this work, $e_- = 1.00000$ volt except where noted and accordingly, $I_{1,n} = 4.19 \times 10^{-11}$ A. I_f equals I_{in} for OA-3 and $e_{0,n} = 4.19 \times 10^{-5}$ V (rms). The definition that p–p noise is 6.6 times rms noise was used, although a standard definition seems to be lacking[3, 7]. Hence, $e_{0,n}$ (p–p) = 0.28 mV for thermistor t_1 from the theory developed earlier. Calculation of the total thermometric circuit noise proceeds from eqns (41) and (42) assuming that both thermistors t_1 and t_2 contribute equally to the total circuit output. Using the measured value of amplifier noise for OA-3 of 3.03×10^{-11} A (rms) for 0.01 to 20 Hz, Equation (36) yields $I_{0,n} = 5.5 \times 10^{-11}$ A (rms) and $e_{0,n}$ (p–p) = 0.37 mV which corresponds to a temperature noise of 92 μ°C. Comparison to the earlier cited measured value of 75 μ°C is excellent considering the assumptions made in the theoretical treatment and difficulty of experimental measurement of circuit noises. The theoretical S/N equals approximately 110 for a temperature change of 0.01 °C when the temperature change occurs over a time span of 100 sec.

Theoretical noise calculations for Circuit B using the same procedure as above for $N_s = 1000$ rev min^{-1} and $r_s = 1.63$ cm yields:

$$
\begin{aligned}
I_{1,n} = [&4.04 \times 10^{-25} + 9.36 \times 10^{-22} \cdot e_-^2 + 3.22 \times 10^{-22} \cdot \\
&e_-^4 + 2.26 \times 10^{-22} \cdot e_-^6]^{1/2}
\end{aligned}
$$

and $T_{0,n}$ (p–p) = 97 μ°C. The measured value of 90 μ°C was in closer agreement with the theoretically derived value presumably because of a more closely defined value of e_n for OA-1 and OA-2 in Circuit B. The larger size of $T_{0,n}$ for Circuit B was due to the increase in N_s and r_s which increased the turbulence around the thermistor bead. The factor of 3 found by LaForce and confirmed in this work is readily seen in eqn (41), since when the lower frequency f_1 changes by a decade, $I_{1,n}$ changes by 3.16. The present study confirmed the conclusion of Bowers and Carr[3] that the temperature noise of thermistors is in the order of 5–15 μ°C (rms) for DC systems. However, two new conclusions proceeded from this work, namely, the use of several NTC thermistors in a NTC–PTC hybrid thermistor probe reduced the size of $T_{0,n}$ (Table 1), and concurrently, the S/N also increased for such probes, since the temperature sensitivity increased. The S/N for the hybrid combination of two NTC thermistors and one PTC thermistor was approximately 235 (calculated as above) or twice that of a NTC thermistor alone.

The noise for thermistor, $t_{NTC,3}$ is greater than thermistor $t_{NTC,1}$ primarily since the time constant of $t_{NTC,3}$ is approximately half of that for $t_{NTC,1}$. However, their dissipation constants are nearly the same making ΔR the same for each. The ratio $(1/(1 + \tau e/\tau p))$ in eqn (35) is thereby recognized to be very important and accordingly, τ_t^2/τ_m^2, should be maximized to minimize thermistor noise.

LIST OF SYMBOLS

a_1, b_1, c_1, d_1	coefficients
C	Correlation coefficient of circuit noises
c_b	Volume heat capacity of bulk solution (cal cm^{-3} °C^{-1})
C_f	Feedback capacitor for operational amplifier (μF)
c_t	Volume heat capacity of thermistor material (cal cm^{-3} °C^{-1})
D_t	Thermal diffusivity of thermistor material (cm^2 sec^{-1})
E_g	Gap energy of semiconductor (eV)
$e_{0,3}$	Output voltage of Operational Amplifier 3 (V)
e_{rms}	rms noise voltage (V)
e_+, e_-	Positive and negative voltages applied to thermistors t_2 and t_1 respectively (V)
f	Frequency (Hz)
h	h_t/λ_{eq} (cm^{-1})
h_t	Convective heat transfer coefficient of thermistor bead (cal cm^{-2} sec^{-1} °C^{-1})
$I_{0,n}$	Output noise of circuit expressed as current noise at output of summing amplifier (amp)
J	Mechanical equivalent of heat
k_B	Boltzmann constant
P_t	Electrical power applied to thermistor (cal sec^{-1})
r	Distance thermistor bead is from longitudinal axis of calorimeter cell
r_s	Radius of stirrer disk (cm)
r_t	Radius of thermistor bead (cm)
R_f	Feedback resistance of operational amplifier (Ω)

R_t	Resistance of thermistor at its geometric center (Ω)
t	Time (sec)
T_b	Temperature of bulk solution (K)
T_t	Thermistor temperature at the geometric center (K)
U	Fluid velocity (cm sec^{-1})
$U_{max.}$	Radial velocity of bulk fluid at outer edge of stirrer disc (cm sec^{-1})
Z_t	Pre-exponential term in thermistor resistance functions (Ω)
α_n	Roots of the transcendental equation $r_t \alpha_n \cot r_t \alpha_n + r_t h - 1 = 0$
β_t	Material coefficient of thermistor with negative temperature coefficient (K)
γ_b	Bulk solution heating rate (°C sec^{-1})
λ_b	Thermal conductivity of bulk solution (cal cm^{-1} sec^{-1} °C^{-1})
λ_{eq}	Equivalent thermal conductivity of thermistor material plus epoxy and stem (cal cm^{-1} sec^{-1} °C^{-1})
λ_i	Inner thermal conductivity of thermistor material corrected for epoxy and stem effects (cal cm^{-1} sec^{-1} °C^{-1})
λ_t	Thermal conductivity of thermistor material (cal cm^{-1} sec^{-1} °C^{-1})
ν_b	Kinematic viscosity of bulk solution (cm^2 sec^{-1})
ρ	$h_t r_t$ (cal cm^{-1} sec^{-1} °C^{-1})
τ_b	Time constant of epoxy plus stem and boundary layer (sec)
τ_m	Time constant of mixing (sec)
τ_0	Time constant of thermistor bead (sec)
τ_t	Time constant of thermistor assembly (sec)
ω	$2\pi f$, angular frequency (rad sec^{-1})
ω_s	Angular velocity of stirrer (rad sec^{-1})

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