NEW DEVELOPMENTS IN THE FIELD OF ELECTROLYTIC CONDUCTIVITY MEASUREMENTS

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TEMPERATURE COMPENSATION OF ELECTROLYTIC CONDUCTIVITY BY MEANS OF THERMISTORS

Introduction

Principle

The temperature coefficient of metal-resistance thermometers is often not high enough for compensation purposes. The thermistor offers good possibilities. Although the thermistor tolerances are a serious drawback in series production, the characteristics of the thermistor can be changed so easily that applications are available. By using series and parallel resistors a thermistor offers great advantages over other compensation instruments.

The thermistor characteristic is known:

$$\begin{aligned} R_T &= A e B/T; \\ B &= \text{thermistor constant in } {}^\circ\text{K}; \\ R_T &= \text{resistance at temperature } T\ {}^\circ\text{K}; \\ A &= \text{thermistor constant in ohm}; \\ T &= \text{temperature in } {}^\circ\text{K}. \end{aligned} \tag{1}$$

For calculation purposes, it is not easy to operate with (1). When a suitable series resistor is chosen the thermistor curve approximates to the curve

$$R'_t = R_t + R_s = \frac{R_{20} + R_s}{1 + \beta(t - 20)}, \tag{2}$$

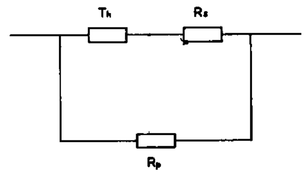
where R'_t = sum of thermistor and series resistor; R_{20} = sum of thermistor and series resistor at 20°C; R_s = series resistor; β = temp. coeff. of combination; t = temperature in °C.
For linearization of thermistors, see also Beakly [1].

With the aid of a parallel resistor, the temperature coefficient β may be decreased.

$$R''_t = \frac{(R_t + R_s) R_p}{R_t + R_s + R_p} = \frac{(R_{20} + R_s) R_p}{R_{20} + R_s + R_p} \Big/ \left[1 + \frac{R_p}{R_{20} + R_p + R_s} \beta(t - 20)\right], \tag{3}$$

where R''_t = resistance of combination at t°C, and R_p = parallel resistor. The circuit is given in Fig. 1.

Fig. 1.—Thermistor circuit.



Conclusions

1. Linearization is obtained with R_s.
2. The temperature coefficient of the combination may be chosen with R_p.
3. The resistance of the combination at 20°C is given by

$$R''_{20} = \frac{(R_{20} + R_s)\,R_p}{R_{20} + R_s + R_p}. \qquad (4)$$

Calculation of R_p and R_s

Series Resistor

Reversing formula (2) on p. 420 we obtain

$$\frac{1}{R'_t} = \frac{1}{R_t + R_s} = \frac{1 + \beta(t - 20)}{R_{20} + R_s}. \qquad (5)$$

It will be clear that we may determine R_s by measuring R_t at three different temperatures, i.e., $t = 20$, 40 and 60°C.

In that case we get the relation

$$\frac{1}{R_{20} + R_s} + \frac{1}{R_{60} + R_s} = \frac{2}{R_{40} + R_s} \qquad (6)$$

from which R_s may be obtained

$$R_s = \frac{R_{20} - J\,R_{60}}{J - 1}, \qquad (7)$$

where

$$J = \frac{R_{20} - R_{40}}{R_{40} - R_{60}}. \qquad (8)$$

The result is that the curve $1/(R_t + R_s)$ has three intersections with the straight line $[1 + \beta(t - 20)]/(R_{20} + R_s)$ at $t = 20$, 40 and 60°C.

The deviations from linearity between these temperatures depend on the *B* value of the thermistor. We have now obtained an almost temperature-linear conductivity. The temperature coefficient between 20 and 60°C may be found by substitution of (7) in (5).

$$\beta = \frac{R_{20} - R_{60}}{40\,(R_{60} + R_s)}. \qquad (9)$$

Parallel resistor

If the required temperature coefficient for compensation purposes is less than β, the value of R_p may easily be found by combining (3) and (9).

$$\frac{R_p}{R_{20}+R_s+R_p}\beta=\alpha,$$

where α = required temperature coefficient. Thus,

$$R_p=\frac{(R_{20}+R_s)\alpha}{\beta-\alpha}=\frac{R_{20}+R_s}{J-2}. \qquad (10)$$

We now made a thermistor combination with optimal linearity and predetermined temperature coefficient.

Tolerances

The resistance of the combination at 20°C is determined by (*1*) tolerances of R_{20} ($\pm$ 10 per cent or $\pm$ 20 per cent) and (*2*) tolerances of B ($\pm$ 5 per cent or $\pm$ 10 per cent). For practical use it is necessary to make some sort of bridge-circuit or voltage divider with a predetermined fixed resistor to cancel the effect of the spread in R_{20}''.

In series production it will be necessary to find out the best B values together with the R_{20} value. With the aid of formula (1) it will be possible to find the best B values if a temperature coefficient of about 2.5 per cent/°C is desired.

$$2100 \leqslant B \leqslant 3200^\circ K. \qquad (11)$$

A very valuable factor is J, for it is found from the three temperature measurement. According to (11) we find

$$1.90 \leqslant J \leqslant 2.45 \qquad (12) \qquad\qquad 0.19 \leqslant \frac{R_s}{R_{20}} \leqslant 0.24 \qquad (13)$$

$$7.2 \leqslant \frac{R_p}{R_{20}} \leqslant 13.0 \qquad (14) \qquad\qquad 0.86 \leqslant \frac{R_{20}''}{R_{20}} \leqslant 1.20 \qquad (15)$$

In case the value of J is $1.90 \leqslant J \leqslant 2.05$, R_s will be found best from

$$R_s = R_{20} - 2\,R_{60}. \qquad (16)$$

In this case R_p is superfluous.

Graphs of the calculated functions

In Fig. 2 J, R_s/R_{20}, R_p/R_{20} and B are given as a function of R_{20}/R_{60}.

It can be seen that the value of R_s is not critical to B when B is greater than 2500°K.

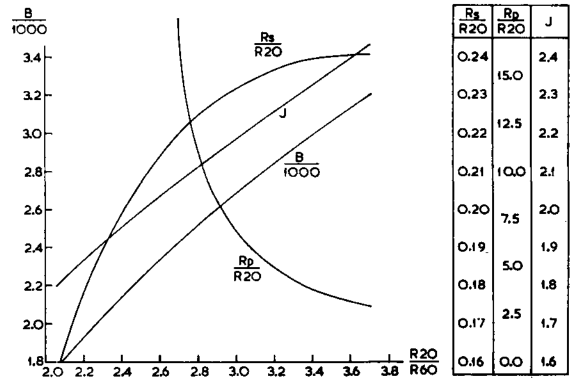


Fig. 2.—Graph of the various circuit elements.

Temperature compensation of conductivity

A. Linear conductivity versus temperature relation.—With the aid of the previous calculations, it is easy to design a thermistor resistance combination having the same temperature coefficient as the electrolyte solution to be measured.

B. Non-linear relation between conductivity and temperature.—In many cases the conductivity versus temperature curve is slightly concave. This means that if we study the temperature range from 20–60°C, the conductivity at 40°C is less than the value obtained from the average of the measurements at 20 and 60°C. The calculations for optimum compensation have now to be carried out for $R_{40+\delta}$ instead of 40°C (the average value of the conductivity between 20 and 60°C is slightly higher than the value at 40°C). For diluted NaCl solutions we found

$$K_{41\cdot 5} = \frac{K_{20} + K_{60}}{2}.$$

In so doing, very good compensation can be obtained.

Results

Following the lines above-mentioned we designed a thermistor compensator for NaCl solutions. In Fig. 3 we can see the deviation from linearity of this solution

Curve *A*

$$\Delta = K_t \bigg/ \left[K_{20} + \frac{K_{60} - K_{20}}{40} (t - 20) \right] 100\,\%.$$

Curve *B* demonstrates the relative fault of the temperature-compensated conductivity with a standard thermistor. It is clearly to be seen that com-

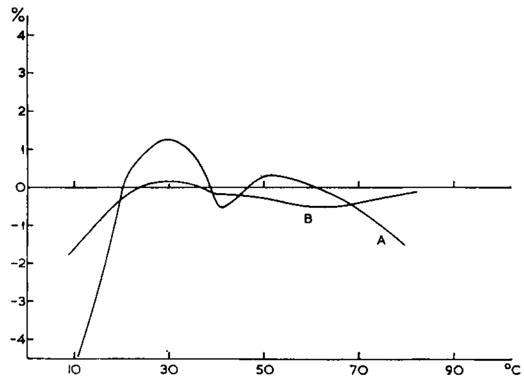


Fig. 3.—Deviation from linearity versus temperature. Curve *A*, conductivity of dilute NaCl solution; Curve *B*, solution of curve *A* temperature-compensated with thermistor.

pensation with thermistors is advantageous. Over a relatively wide temperature range high accuracies are obtainable. The technique described is very useful for producing sensitive temperature tranducers as well. The choice of the *B* value is important in such a case. A linear temperature-conductance curve may be obtained with deviations smaller than 1 per cent between 10 and 90°C. It will be clear that other temperature intervals may be chosen.

4-ELECTRODE CONDUCTIVITY PICK-UP FOR INDUSTRIAL APPLICATIONS

Introduction

To overcome the disturbing effects of either electrode deposits or polarization, the 4-electrode cell having both current and voltage-electrodes may be used. A.C. [1] as well as D.C. [2] may be used in laboratory applications; in industry the A.C. type is recommended as the measurements are not influenced by gas generation at the electrodes. The main problem is to develop a pick-up that may be used in earthed, industrial pipelines. In the following, a cell is described that is especially useful in earthed liquids and may be used as flow or immersion assembly as well.

Principle

By means of two current electrodes a current is sent through the liquid to be measured. A voltage is generated between the voltage electrodes placed between the current electrodes Fig. 4. The voltmeter must have a high input impedance to overcome polarization and the influence of electrode deposits. As the current and the voltage are known, the specific conductivity may be calculated when the cell factor is known. For a direct reading instrument it would be favourable to keep the current constant and measure the voltage

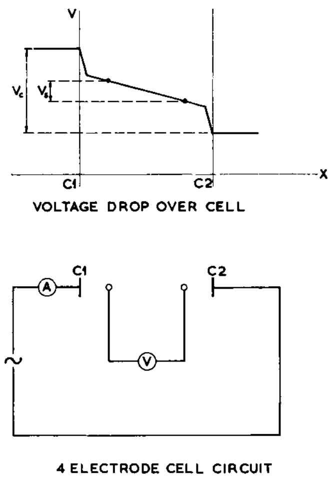


Fig. 4.

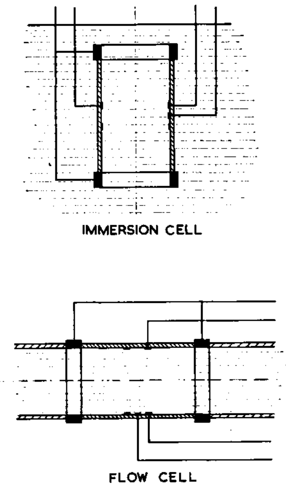


Fig. 5.

Fig. 4.—4-electrode cell circuit. C_1 and C_2, current electrodes, V_c voltage over current electrodes; and V_s voltage over sonde electrodes.
Fig. 5.—New 4-electrode cell for immersion or flow applications.

(linear ohm cm scale) or keep the voltage constant and measure the current (linear ohm^{-1} cm^{-1} scale). As the classical cell exhibits four electrodes at different potentials to the liquid, one has to be careful with earthed liquids and closed liquid loops which might destroy the measurement. It would therefore be advantageous if a cell could be designed that is screened by one of its own electrodes and preferably by an electrode that may be earthed. An earthed electrode is always interesting, due to the fact that part of the electronic amplifier and its output are then connected to earth.*

When planning for an electrode arrangement according to the previous requirements, one has to study in each case the effect of partly contaminated electrode surfaces and their influence upon the measurements. An arrangement is known in the form of a liquid Wheatstone bridge that has to be used as a flow cell. The electrodes have to be isolated from earth.

When looking for a cell[1] with one earthed electrode that may be used in flow or immersion applications, we came on a rather simple cell design. The principle of this cell is demonstrated in the next experiment.

In a plastic pipe we diametrically oppose two current electrodes, fill the pipe with liquid and measure the voltage between two diametrically opposed sonde electrodes in dependence on the distance to the former current electrodes. We discover that this measured voltage is about 0.1 per cent of the voltage applied to the current electrodes when the distance between current and

* Dutch Patent No. 234009.

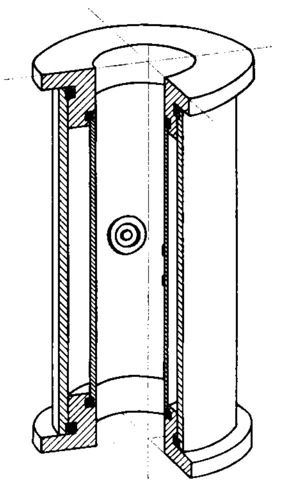


Fig. 6.—Construction of new 4-electrode cell.

voltage electrode is equal to 2 × the tube diameter. At this distance it is permissible to make the pipe conducting. This may be done at either side of the current electrodes. These two end conductors have the same potential and may be connected to each other; they act as a virtual sonde electrode somewhere in between the two current electrodes. If we now place a second voltage electrode close to one of the current electrodes, our measuring cell is complete. The advantages are clear: (*a*) Screened, earthed input and output; (*b*) Flow and immersion applications; and (*c*) Simple construction, very easily cleaned. (See Figs. 5 and 6.)

Result

The cell functions as expected. Heavily contaminated liquids do not disturb the conductivity measurement. The cell may be used between 0.3 and 1,000 m mho cm^{-1}. Temperature compensation may be carried out with a reference cell or a thermistor. A measuring voltage was applied to the cell of 80 c/s. The current was kept constant, while the voltage was measured.

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