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Investigations [1 to 3] have shown that the temperature coefficient of the alternating component of the diffusion current is in many cases less than the coefficient of the constant component, and that its absolute value depends on the temperature.

In order to estimate the precision of measurements, achievable with instruments of the type KAP-225u, the vector polarograph TsLA, and concentration meters, it is desirable to establish the relation between the active component of the cell current and temperature.

In the case of reversible reactions, the mean value of the active component during the life of the drop can be determined from Matsuda's equation [4], which may be written:

$$\bar{i}_a = am^{1/2} \tau^{1/2} D^{1/2} \cdot \frac{1}{T} \operatorname{sech}^2 \xi, \quad (1)$$

where m is the mercury flow rate; τ is the drop time; D is the diffusion coefficient; T is the absolute temperature; a is a constant, incorporating terms which are independent of temperature; $\xi = (nF/RT)(U - U_p)$, where U is the existing value of the voltage and U_p is the voltage corresponding to the peak potential.

Differentiating Eq. (1) with respect to temperature, we have

$$\gamma = \frac{d\bar{i}_a}{\bar{i}_a dT} = \frac{2}{3m} \frac{dm}{dT} + \frac{2}{3\tau} \frac{d\tau}{dT} - \frac{1}{T} + \frac{1}{2D} \frac{dD}{dT} + \tanh \xi \operatorname{sech} \xi \frac{d\xi}{dT}. \quad (2)$$

We will consider first the case of measurement with a complete polarogram, when the value of the last term may be neglected.

According to [5], the temperature coefficients of the rate of mercury flow and of the drop time are:

$$\frac{dm}{m dT} = -\varepsilon \quad (3)$$

and

$$\frac{d\tau}{\tau dT} = \varepsilon + \varphi, \quad (4)$$

where ε and φ are the temperature coefficients of the viscosity and surface tension of mercury respectively.

The diffusion coefficient is given by the equation:

$$D = \frac{RT}{nF^2} \lambda_{\infty}, \quad (5)$$

where λ_{∞} is the equivalent electrical conductivity at infinite dilution, so that the temperature coefficient of diffusion can be expressed in the form:

$$\frac{dD}{D dT} = \frac{1}{T} + \frac{1}{\lambda_{\infty}} \frac{d\lambda_{\infty}}{dT}. \quad (6)$$

We may neglect φ which is small (about 0.04% per degree at 25°C). Then, substituting (3), (4), and (6) in (2), we obtain:

$$\gamma = 1/2 \left(\frac{d\lambda_{\infty}}{\lambda_{\infty} dT} - \frac{1}{T} \right). \quad (7)$$

TABLE 1. Variation of ν and γ with Temperature

Temp. interval, °C	$\nu \cdot 10^2$, cP/deg	γ , %/deg
20-30	-2,2	0,94
30-40	-2,0	0,80
40-50	-1,71	0,70
50-60	-1,56	0,63
60-70	-1,45	0,58
70-80	-1,30	0,51
80-90	-1,20	0,46
90-100	-1,10	0,42

TABLE 2. Temperature Coefficient of the Active Component of the Diffusion Current

Element	Supporting electrolyte	H_p , mm	T , °C	ΔT , °C	γ , %/deg
Cd	2 M ZnSO ₄	135	24		
		148	35	11	0,8
		155	45	10	0,5
		165	55	10	0,6
		171	65	10	0,4
Co	1M. NH ₄ Cl, 8M NH ₃ , 10 ⁻² M K ₃ Fe(CN) ₆	103	16,9		
		116	26,7	9,8	1,2
		128	37,5	10,8	0,9
		137	47,3	9,8	0,7
Cu	Nickel electrolyte*	63	24,2		
		68	34,5	10,3	0,8
		74	49,7	15,2	0,6
		81	73,1	23,4	0,4
		83	86,1	13,1	0,2

*The composition of this electrolyte, in g-ion/liter, was Ni²⁺ 80, Na⁺ 20, Cl⁻ 35, and SO₄²⁻ 150; the pH was 2.5.

For aqueous solutions, the temperature coefficient of the equivalent electrical conductivity is given [5] by:

$$\frac{1}{\lambda_{\infty}} \frac{d\lambda_{\infty}}{dT} = -\frac{1}{\eta} \frac{d\eta}{dT} = \nu, \quad (8)$$

where η is the viscosity of water.

Equation (7) then has the form:

$$\gamma = -1/2 \left(\nu + \frac{1}{T} \right). \quad (9)$$

The temperature coefficient of the viscosity of water, at 10° intervals, in the range 20 to 100°C, was determined from the equation:

$$\eta_{T_2} = \eta_{T_1} e^{\nu(T_2 - T_1)}, \quad (10)$$

where η_{T_2} and η_{T_1} are the viscosities of water at temperature T_2 and T_1 [6].

The variation of $\gamma = f(T)$, calculated from Eq. (9), is shown in Table 1.

When carrying out continuous measurements it is necessary to take into account the effect of temperature on potential.

The adjustment of a concentration meter at a given temperature should be done in such a way as to satisfy the equation:

$$U = U' - E_a - \bar{i}_{\infty} \Sigma R = -E_p = U_p, \quad (11)$$

where U' is the voltage from the constant current generator; E_a is the anode potential; E_p is the peak potential; $\bar{i}_{\infty} \Sigma R$ is the potential drop across the resistances of the cell and the measuring circuit.

It follows from Eq. (11) that $U - U_p = 0$, so that the last term in Eq. (2) is equal to zero.

Since all the terms in Eq. (11) depend on the temperature, a change in the latter should lead to a deviation of the voltage from the value of the peak potential. Differentiating Eq. (11) with respect to T , we have:

$$\frac{dU'}{dT} - \frac{dE_a}{dT} - \frac{d\bar{i}_{\infty}}{dT} \Sigma R - \frac{d\Sigma R}{dT} \bar{i}_{\infty} = -\frac{dE_p}{dT}. \quad (12)$$

The value of dU'/dT was determined from the temperature stability of the components of the measuring circuit and was estimated to be 10^{-2} to 10^{-3} %/degree.

The temperature coefficients of the peak potentials of many metals and of the anode, if the latter is an electrode of the secondary type, are approximately the same in value (about 0.8 mV/degree [7]) and are of the same sign.

The currents measured by the polarograph were of the order 0.1 to 100 μA (ΣR were of the order of 100 Ω), and the temperature coefficients of these values were small, so that the terms $\frac{d\bar{i}_{\infty}}{dT} \Sigma R$ and $\frac{d\Sigma R}{dT} \bar{i}_{\infty}$ could be neglected.

Thus, if the anode and cathode are subjected to the same conditions, a small change in the temperature of the solution and of the surrounding medium will not lead to any deviation of the voltage from the value of the peak potential. Consequently, the effect of temperature on the potential will be zero.

If the electrodes are at different temperatures, in order to estimate the error it is necessary to assign different values of ΔT for the two electrodes. Multiplying the difference between these values by the temperature coefficient of the anode, or of the peak potential, we obtain the absolute value of the deviation of the voltage from the value of the peak potential:

$$\Delta U = U - U_p = \Delta (\Delta T) \frac{dU_p}{dT}. \quad (13)$$

The error in the potential ($\delta_{\Delta U}$), corresponding to the value of ΔU found, can be calculated from the relation: $\bar{I}_a = f(\Delta U)$ [8].

Thus, the total temperature error for a concentration meter (δ_{Σ}) can be represented by the equation:

$$\delta_{\Sigma} = \delta_{\gamma} + \delta_{\Delta U}, \quad (14)$$

where $\delta_{\gamma} = \Delta T_k \gamma$ and ΔT_k is the change in cathode temperature.

We recorded the variations with temperature for copper, cadmium, and cobalt in various supporting electrolytes. The experiments were carried out with a KAP-225u instrument, in a cell with a bottom pool mercury anode.

Temperature coefficients were calculated by means of the equation:

$$H_{p_2} = H_{p_1} e^{\gamma(T_2 - T_1)}, \quad (15)$$

where H_{p_1} and H_{p_2} are the peak heights at temperatures T_1 and T_2 .

Table 2 shows some experimental results.

The nature of the change in γ agreed well with the calculated relation.

The results of a number of investigations, obtained with polarographs using both sinusoidal and square-wave voltage forms, agreed qualitatively with ours.

Experimental determinations of the temperature error, under the conditions for a concentration meter, were carried out with the elements and supporting electrolytes listed above, over the temperature ranges ± 5 , ± 10 , and $\pm 20^\circ\text{C}$. The measurements were made with an external calomel anode, which was at room temperature.

Our experiments showed that the absolute value of the error depended on the direction of the temperature change (from the initial temperature of the setting of U_p): the error was less at higher than at lower temperatures. For the first two temperature ranges, the sign of the error was the same as the sign of ΔT_k . However, for the range $\pm 20^\circ$, the error was always negative, regardless of the sign of ΔT_k .

These results could be explained as follows. On reduction in temperature, both terms in Eq. (14) were of the same sign, so the total error was greater than in the case of an increase in temperature, when the signs of the terms were different. However, with a considerable reduction in temperature, the dominating effect was the reduction in current as the result of deviation from the peak potential, so that the error was always negative.

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