A Calorimetric Method for Determination of $\varDelta S$ for a Chemical Reaction from Measurements on an Electrochemical Cell

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An equation is derived which may be used for the calculation of $\varDelta S$ for a chemical reaction from rather simple calorimetric measurements on an electrochemical cell. This equation is experimentally exemplified for the lead accumulator. Further application of the method, notably the determination of Peltier heats for electrodes, is discussed.

THEORY

Consider an electrochemical cell operating at the temperature T and pressure p and at a certain voltage e and current i that may be defined as positive for an electrolyzer and as negative for a galvanic cell. e is related to η, the overpotential of the cell, by

$$\eta = e - E \tag{1}$$

where E denotes the electromotive force. η is consequently > 0 when $i > 0$ and *vice versa*. During the time of current flow dt, the energy U of the system is changed by an amount

$$dU = \delta q - p dV + e dQ \tag{2}$$

where dQ is the change of charge $i \cdot dt$, d means a complete differential and δ a differential depending upon the means chosen in order to achieve a certain change of state. If, however, the same change is performed quasistatically, we have that

$$dU = T dS - p dV + E dQ \tag{3}$$

because it is then sufficient to consider only reversible energy increments. Now eqns. (2) and (3) must both be applicable assuming that all independently occurring self-discharge reactions are negligible.
Hence,

$$\delta q + e dQ = T dS + E dQ \tag{4}$$

This equation may also be rewritten in other more convenient forms. Introduction of (1) and the definition

$$dS = \delta_e S + \delta_i S \tag{5}$$

where $T\delta_e S = \delta q$ and $T\delta_i S$ equals the Clausius uncompensated heat leads to the well-known formula [1]

$$\eta i = T\sigma = P \tag{6}$$

Here σ is the entropy production $\delta_i S/dt$ in the cell and P is the "power of irreversibility", a concept introduced by de Donder and Van Rysselberghe [2]. From the second law it follows that

$$P \geq 0 \tag{7}$$

Another formulation of (4) may be attained by dividing by dQ or by combining (5) and (6), namely

$$\dot{q}/i = T(dS/dQ) - \eta \tag{8}$$

where $\dot{q}$ denotes the rate of heat absorption $\delta q/dt$. We now define the cell reaction as the reaction which *proceeds* when a discharging current is withdrawn. dQ can thus be expressed by

$$dQ = -nF d\xi \tag{9}$$

where ξ is the extent of the cell reaction, n the participating number of moles of electrons and F the Faraday constant. However, for given T and p, dS equals $\Delta S d\xi$ and thus eqn. (8) reduces to the differential equation

$$-\dot{q}/i = T\Delta S/nF + \eta \tag{10}$$

This equation is generally valid for the system considered, *i.e.* it holds for any construction of the electrochemical cell. An equation similar although not identical to (10), has been derived by Van Rysselberghe [3]. Using eqn. (10), it is obviously possible to evaluate ΔS for the cell reaction from simultaneous measurements of the rate of heat absorption, the overvoltage and the current. Since ΔS for a reaction is a constant at fixed initial and final states, the quotient $-\dot{q}/i$ should vary linearly with η provided T, p, and the composition variables are held constant. However, a current flow generally causes both a temperature change and variations in the compositions. But it is well-known that the temperature-dependence of ΔS for a reaction is usually rather small at ordinary temperatures and so a slight change in temperature is permissible. This small change may be used for the determination of $\dot{q}$ under adiabatic conditions if a sensitive temperature-measuring device like a thermistor is utilized. In actual experiments it is also possible to maintain approximately constant compositions if the time of current flow is short enough and the amounts of electrolyte and electrodes are comparatively large.

Consider now especially the discharge of a galvanic cell at a certain resistance in the cell circuit. At the time $t = 0$, the current starts to flow and the rate of decrease of the overpotential is large. After a short time, η decreases only slowly. However, as η is a function of time, $\dot{q}$ and i are also time-dependent. Because the thermal effects at the electrodes usually have different signs and

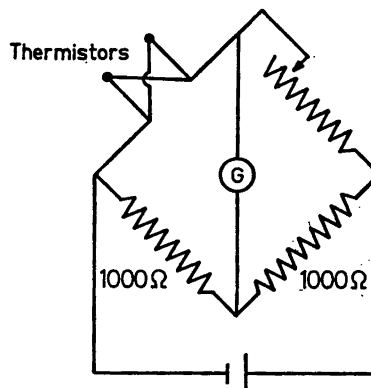Thermistors

$1000\,\Omega$ $1000\,\Omega$

Fig. 1. The bridge system used for the determination of small temperature changes.

since it may be difficult to arrange stirring good enough to give a uniform temperature throughout the system, we may conclude that it is probably not easy to measure experimentally the proper value of $\dot{q}$ corresponding to given η- and i-values. Thus, it might be advantageous to use, instead of eqn. (10), its integrated form, *viz.*

$$-q/(i_{\mathrm{m}} \cdot t) = T\Delta S/nF + \eta_{\mathrm{m}} \tag{11}$$

which is valid if $T\Delta S/nF$ may be regarded as a constant during the time of current flow t. i_{m} is the mean value of the current defined by

$$i_{\mathrm{m}} = \frac{1}{t} \int_{0}^{t} i \; \mathrm{d}t \tag{12}$$

and η_{m} is given by

$$\eta_{\mathrm{m}} = \frac{|1}{i_{\mathrm{m}} \cdot t} \int_{0}^{t} \eta \cdot i \; \mathrm{d}t \tag{13}$$

Consequently, instead of measuring the rate of heat absorption, it is sufficient to determine q, the total quantity of heat absorbed during the time t. It readily appears from (11) that, if discharging experiments are performed at various cell circuit resistances and approximately constant T, p, and compositions, it is required that the quantity $-q/(i_{\mathrm{m}} \cdot t)$ shall depend linearly upon η_{m}. Disregarding the trivial case when the current is zero, q may become zero when

$$\eta_{\mathrm{m}} = -T\Delta S/nF \tag{14}$$

Thus, when $-q/(i_{\mathrm{m}} \cdot t)$ is determined as a function of η_{m}, q may in principle be measured in any arbitrary unit since the η_{m}-intercept gives directly the value of ΔS.

EXPERIMENTAL RESULTS

In order to illustrate the validity of eqn. (11) we have performed measurements at room temperature (21.3°C) when discharging a small, thermally insulated lead accumulator (type R2, Svenska Aktiebolaget Jungner). It has been shown that the lead accumulator [4] fulfils the condition that only *one* reaction, *viz.* the cell reaction $Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$, occurs at discharge. The accumulator was equipped with a magnetic stirrer and two parallel-coupled thermistors ($R_{25} \approx 2\ 600\ \Omega$) were placed in the electrolyte for the determination of the temperature changes. The thermistors were connected to an ordinary resistance-bridge (Fig. 1) and so the relative temperature could be obtained as a galvanometer reading. For sufficiently small temperature intervals, the resistance of a thermistor varies linearly with the temperature. Because the galvanometer deflection was found to depend linearly upon the resistance change in the thermistor circuit, we could consequently regard the galvanometer deflection as proportional to the temperature change. From experiments with a separate heating coil it was shown that at 21.3°C one scale division corresponded to 1.034×10^{-3} °C and that the heat capacity of the accumulator was 1 050 cal/deg. From these figures the proportionality constant between q and the galvanometer deflection was calculated to be 1.086 cal/scale division.

At various resistances in the cell circuit, the galvanometer deflection, the current i and the cell voltage e were measured as functions of the time of discharging. After correction for the heat exchange with the surroundings, the absorbed heat q could be obtained from the galvanometer readings. The cell voltage was measured with a tube voltage meter (pH-meter 22, Radiometer, Copenhagen). η_m and i_m were calculated from the experimentally given e- and i-functions. The result of our measurements appears from Fig. 2. The experimental points lie all with good accuracy on a straight line which has the slope 1 as required by the theory. The intercepts on the axes are 0.0675 V corresponding to $\Delta S = 10.6$ cal/deg. During the experiments the electromotive force E decreased from 2.046 to 2.036 V implying a slight change in the composition of the electrolyte. Thus, when calculating η_m for each separate experiment, the mean value of E before and after the discharge was used. The time of discharging chosen was 5—10 min and the maximum temperature change was always less than 0.1°C. The variation of the current i during an experiment was, as might be expected, usually negligible.

According to Beck and Wynne-Jones [4] the measurements of the comparatively small ($\approx 2 \times 10^{-4}$ V/deg) temperature coefficient of the lead accumulator made by different authors are not very consistent. An obvious reason for this fact is that there are several possible sources of irreversibility in commercial accumulators. Better agreement has been attained between measurements on electrodes carefully prepared from pure substances. The mean value for ΔS when $E = 2.041$ V of such temperature-coefficient data given by Vosburghe and Craig, Craig and Vinal, Harned and Hamer is 11.2 cal/deg at 25°C [4]. The difference between this value and ours can hardly be attributed to the small difference in the temperature at which the measurements were performed. It seems more probable that the discrepancy arises from the less good accuracy in the measurements of the rather small temperature coefficient.

DISCUSSION

Compared with the temperature-coefficient method for the determination of ΔS, the procedure developed here exhibits certain advantages. The accuracy attainable seems to be more satisfactory (optimum construction conditions have, however, not been investigated) and the experimental arrangements required are comparatively simple. For the same maximum error in ΔS, it appears that a larger error in the voltage-measurements is permissible when using our method than when the temperature-coefficient method is utilized because, if other sources of errors are neglected, it is readily demonstrated on applying $\Delta S = nF \ \mathrm{d}E/\mathrm{d}T$ that an error of 0.1 cal/deg in the ΔS-value corresponds to the error 2×10^{-6} V/deg in $\mathrm{d}E/\mathrm{d}T$ whereas the same ΔS-error from eqn. (14) would be equivalent to an error in η_m amounting to 6×10^{-4} V at room temperature. Our method is also interesting from a theoretical and pedagogical point of view and on account of its possibilities for further application. Thus, *e.g.*, it should be possible to split eqn. (10) into equations referring to different parts of the lead accumulator, *viz.*

$$T\Delta S_{+}/nF + \eta_{+} = -\dot{q}_{+}/i \tag{15}$$

$$T\Delta S_{-}/nF - \eta_{-} = -\dot{q}_{-}/i \tag{16}$$

$$T\Delta S_{\mathrm{L}}/nF + \eta_{\mathrm{L}} = -\dot{q}_{\mathrm{L}}/i \tag{17}$$

where the accumulator is imagined to be divided into two electrode spaces $(+, -)$ linked together by a tube (L) filled with the electrolyte. It should be
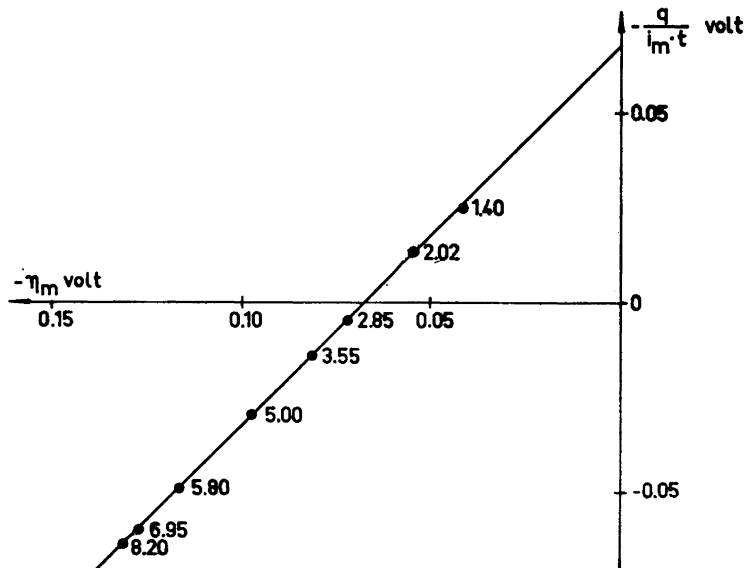

Fig. 2. $-q/(i_{\mathrm{m}} \cdot t)$ plotted against η_{m} for the lead accumulator at $E \approx 2.04$ volt and 21.3°C. The figures at the experimental points indicate the strengths of the initial currents in amp.

noticed that if the definition (1) is extended to single electrodes, we would have $\eta = \eta_+ - \eta_- + \eta_L$. Here η_L is given by $R_L \cdot i$. On inspection of the above equations it appears that $T \varDelta S_+/n$ and $T \varDelta S_-/n$ are the so-called *electrolytic Peltier heats*, usually denoted by $\varPi_+$ and $\varPi_-$, of the electrodes [5]. Such heats generally occur at isothermal reversible passage of one Faraday at the junction between an electrode and its electrolyte. When there are no interfaces between the different phases within the L-space and when approximate temperature and composition constancy is maintained, it is evident that $\varDelta S_L$ may be put equal to zero. Thus (17) is not interesting from our point of view because it only expresses the fact that the Joule-heat generated equals $R_L \cdot i^2$. It has been shown [6,7] that the electrolytic Peltier heat is given by

$$\varPi = -\sum_i t_i Q_i^*/z_i - Q_{e-}^* + T \varDelta S_j/n \qquad (18)$$

if the Soret effect is neglected. Here Q_i^* denotes the molar heat of transfer for the ion i and Q_{e-}^* the molar heat of transfer for an electron. z_i is the charge, t_i the transference number for the ion i and $\varDelta S_j$ refers to the single electrode reaction. The heats of transfer cancel when the Peltier heats for two electrodes are added resulting in $T \varDelta S/n$ for the cell reaction. The method we have developed seems to be well suited for experimental determination of electrolytic Peltier heats which have so far not been extensively measured.

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