697. *The Thermodynamics of Thermocells with Redox Electrodes.*

By H. J. V. TYRRELL.

Expressions for the initial and steady-state thermoelectric powers of cells with redox electrodes have been derived from non-equilibrium thermodynamics, and the difficulties which arise in the interpretation of such results, except in special cases, are pointed out.

ALTHOUGH all electrode systems can strictly be regarded as redox electrodes, this paper is principally concerned with those which consist of a noble metal immersed in a solution containing a dissolved species in two oxidation states. A recent paper[1] dealt with measurement of the initial thermoelectric power of iodine–iodide thermocells, and in this, the theoretical treatment was confined to a particular case. A more general treatment is now presented since such cells may attract further attention in the future.

It is not difficult to show[2] that, with the convention that the heated electrode is externally positive, the thermoelectric power ε is given by:

$$(z_O - z_R)F\varepsilon = -(z_O - z_R)\bar{\bar{S}}_{el} + (s_R - s_O) + (z_O - z_R)F \text{ grad } \psi/\text{grad } T, \qquad (1)$$

where z, s represent, respectively, the valency, and the partial molar entropy, of the reduced and oxidised species, these being distinguished by the suffixes R and O. $\bar{\bar{S}}_{el}$ is the transported entropy of the electron in the conductor leading from the electrode to the potentiometer. grad ψ is the gradient of potential in the electrolytic conductor. When the temperature gradient, grad T, is first applied, grad ψ is written (grad $\psi)_0$ and given by $[-\sum_k(t_kS_k^*/z_kF)$ grad $T]$, where S_k^* is the entropy of transfer of the k'th ion, as defined by

---

[1] Tyrrell and Wilson, *J.*, 1961, 5390.

[2] *E.g.*, Tyrrell, " Diffusion and Heat Flow in Liquids," Butterworths, London, 1961.

Eastman,[3,4] and the sum is taken over all the ion species present. When the steady state has been set up, all material flows become zero, and, for all values of k,

$$z_k F(\text{grad } \psi)_{\text{stat.}} + (\text{grad } \mu_k)_{T,P,\text{stat.}} + S_k{}^* \text{ grad } T = 0, \tag{2}$$

where μ_k is the chemical potential of species k (cf. ref. 2, Chap. 4). The suffix " stat." indicates that the stationary state has been attained. Both $(\text{grad } \psi)_{\text{stat.}}$ and $(\text{grad } \mu_k)_{T,P,\text{stat.}}$ can be expressed in terms of $S_k{}^*$ alone by utilising the electroneutrality condition (N_k, mole fraction):

$$\sum_k z_k \text{ grad } N_k = 0; \tag{3}$$

but, in this case, it is more useful to combine equations of the form (2) for the oxidised and reduced species to give:

$$(z_\text{O} - z_\text{R})F(\text{grad } \psi)_{\text{stat.}} = (\text{grad } \mu_\text{R})_{T,P,\text{stat.}} - (\text{grad } \mu_\text{O})_{T,P,\text{stat.}} + (S_\text{R}{}^* - S_\text{O}{}^*) \text{ grad } T$$

$$\text{or} \quad (z_\text{O} - z_\text{R})F\left(\frac{\text{grad } \psi}{\text{grad } T}\right)_{\text{stat.}} = \boldsymbol{R}T\left\{(\partial/\partial N_\text{R} \ln a_\text{R})_{N_\text{O},T,P}\left(\frac{\text{grad } N_\text{R}}{\text{grad } T}\right)_{\text{stat.}} - (\partial/\partial N_\text{O} \ln a_\text{O})_{N_\text{R},T,P}\left(\frac{\text{grad } N_\text{O}}{\text{grad } T}\right)_{\text{stat.}}\right\} + (S_\text{R}{}^* - S_\text{O}{}^*). \tag{4}$$

Furthermore, $$(s_\text{R} - s_\text{O}) = (s_\text{R}{}^\circ - s_\text{O}{}^\circ) + \boldsymbol{R} \ln a_\text{O}/a_\text{R} - \boldsymbol{R}T(\partial/\partial T \ln a_\text{O}/a_\text{R})_P, \tag{5}$$

and $$(\partial/\partial T \ln a_\text{O}/a_\text{R})_P = (\partial/\partial T \ln f_\text{O}/f_\text{R})_{N_\text{R},N_\text{O},P} + (\partial/\partial N_\text{O} \ln a_\text{O})_{N,T,P} \frac{\text{grad } N_\text{O}}{\text{grad } T} - (\partial/\partial N_\text{R} \ln a_\text{R})_{N_\text{R},T,P} \text{ grad } N_\text{R}/\text{grad } T, \tag{6}$$

when activity terms of the form $(\partial/ \ln a_i/\partial N_j)$ are omitted. In the initial state, grad N_k is zero for all values of k, and from equations (5) and (6) we derive:

$$s_\text{R} - s_\text{O} = (s_\text{R}{}^\circ - s_\text{O}{}^\circ) + \boldsymbol{R} \ln a_\text{O}/a_\text{R} + \boldsymbol{R}T(\partial/\partial T \ln f_\text{O}/f_\text{R})_{N_\text{O},N_\text{R},P}. \tag{7}$$

Then, from equations (1) and (7), and the value given above for the potential gradient in the electrolyte when the temperature gradient is first applied, it follows that

$$(z_\text{O} - z_\text{R})F\varepsilon_0 = -(z_\text{O} - z_\text{R})\overline{\overline{\overline{S}}}_{\text{el.}} + (s_\text{R}{}^\circ - s_\text{O}{}^\circ) + \boldsymbol{R} \ln a_\text{O}/a_\text{R} + \boldsymbol{R}T(\partial/\partial T \ln f_\text{O}/f_\text{R}) - (z_\text{O} - z_\text{R}) \sum_k t_k S_k{}^*/z_k. \tag{8}$$

Suppose, for example, the solution contains two cations derived from different oxidation states of the same element, and a common anion. Then,

$$\sum_k t_k S_k{}^*/z_k = t_\text{O} S_\text{O}{}^*/z_\text{O} + t_\text{R} S_\text{R}{}^*/z_\text{R} + t_- S_-{}^*/z_-$$

and $$t_\text{R} + t_\text{O} + t_- = 1.$$

Hence, $$\sum_k t_k S_k{}^*/z_k = \frac{t_\text{R}}{\nu_\text{R} z_\text{R}} (\nu_\text{R} S_\text{R}{}^* + \nu_- S_-{}^*) + \frac{t_\text{O}}{\nu_\text{O} z_\text{O}} (\nu_\text{O} S_\text{O}{}^* + \nu'_- S_-{}^*) + S_-{}^*/z_-, \tag{9}$$

where ν_R, ν_- are the numbers of ions of each species formed per mole of reduced cation salt,

---

[3] Eastman, *J. Amer. Chem. Soc.*, 1926, **48**, 1482; 1927, **49**, 794; 1928, **50**, 283.

[4] Agar, *Rev. Pure Appl. Chem.* (*Australia*), 1958, **8**, No. 1.

and ν_{O}, ν_-' the same quantities for the oxidised cation salt. From equations (8) and (9) and the definition [2] of standard transported ionic entropies, we then have:

$$
\begin{aligned}
(z_{\mathrm{O}} - z_{\mathrm{R}})F\varepsilon_0 = {} & -(z_{\mathrm{O}} - z_{\mathrm{R}})\bar{\bar{S}}_{\mathrm{el}} + (\bar{\bar{S}}_{\mathrm{R}}{}^{\circ} - \bar{\bar{S}}_{\mathrm{O}}{}^{\circ}) + \boldsymbol{R} \ln a_{\mathrm{O}}/a_{\mathrm{R}} + \boldsymbol{R}T(\partial/\partial T \ln f_{\mathrm{O}}/f_{\mathrm{R}}) \\
& - \frac{(z_{\mathrm{O}} - z_{\mathrm{R}})}{\nu_{\mathrm{R}} z_{\mathrm{R}}} \cdot t_{\mathrm{R}}(\nu_{\mathrm{R}} S_{\mathrm{R}}{}^* + \nu_- S_-{}^*) - \frac{(z_{\mathrm{O}} - z_{\mathrm{R}})}{\nu_{\mathrm{O}} z_{\mathrm{O}}} t_{\mathrm{O}}(\nu_{\mathrm{O}} S_{\mathrm{O}}{}^* + \nu_-' S_-{}^*) \\
& - [S_{\mathrm{R}}{}^* - S_{\mathrm{O}}{}^* + (z_{\mathrm{O}} - z_{\mathrm{R}})S_-{}^*/z_-] \qquad (10)
\end{aligned}
$$

The last term in equation (10) transforms into a combination of terms in $(\nu_{\mathrm{R}} S_{\mathrm{R}}{}^* + \nu_- S_-{}^*)$ and $(\nu_{\mathrm{O}} S_{\mathrm{O}}{}^* + \nu_-' S_-{}^*)$, as can be seen from the following:

Since $\nu_{\mathrm{R}} z_{\mathrm{R}} + \nu_- z_- = \nu_{\mathrm{O}} z_{\mathrm{O}} + \nu_-' z_- = 0,$

$$
\begin{aligned}
& 1/z_-[zS_{\mathrm{R}}{}^* - z_- S_{\mathrm{O}}{}^* + (z_{\mathrm{O}} - z_{\mathrm{R}})S_-{}^*] \\
& \qquad = 1/z_-\{z_{\mathrm{O}}/\nu_-'(\nu_{\mathrm{O}} S_{\mathrm{O}}{}^* + \nu_-' S_-{}^*) - z_{\mathrm{R}}/\nu_-(\nu_{\mathrm{R}} S_{\mathrm{R}}{}^* + \nu_- S_-{}^*)\}. \qquad (11)
\end{aligned}
$$

Substitution of equation (11) in (10) gives

$$
\begin{aligned}
(z_{\mathrm{O}} - z_{\mathrm{R}})F\varepsilon_0 = {} & -(z_{\mathrm{O}} - z_{\mathrm{R}})\bar{\bar{S}}_{\mathrm{el.}} + (\bar{\bar{S}}_{\mathrm{R}}{}^{\circ} - \bar{\bar{S}}_{\mathrm{O}}{}^{\circ}) + \boldsymbol{R} \ln a_{\mathrm{O}}/a_{\mathrm{R}} + \boldsymbol{R}T\partial/\partial T \ln f_{\mathrm{O}}/f_{\mathrm{R}} \\
& + \frac{z_{\mathrm{R}} - t_{\mathrm{R}}(z_{\mathrm{O}} - z_{\mathrm{R}})}{\nu_{\mathrm{R}} z_{\mathrm{R}}} (\nu_{\mathrm{R}} S_{\mathrm{R}}{}^* + \nu_- S_-{}^*) - \frac{z_{\mathrm{O}} + t_{\mathrm{O}}(z_{\mathrm{O}} - z_{\mathrm{R}})}{\nu_{\mathrm{O}} z_{\mathrm{O}}} \cdot (\nu_{\mathrm{O}} S_{\mathrm{O}} + \nu_-' S_-). \qquad (12)
\end{aligned}
$$

The thermoelectric power in the steady state, $\varepsilon_{\mathrm{stat.}}$, can be found from equations (1), (4), (5), and (6), and is given by

$$(z_{\mathrm{O}} - z_{\mathrm{R}})F\varepsilon_{\mathrm{stat.}} = -(z_{\mathrm{O}} - z_{\mathrm{O}})\bar{\bar{S}}_{\mathrm{el.}} + (\bar{\bar{S}}_{\mathrm{R}}{}^{\circ} - \bar{\bar{S}}_{\mathrm{O}}{}^{\circ}) + \boldsymbol{R} \ln a_{\mathrm{O}}/a_{\mathrm{R}} + \boldsymbol{R}T(\partial/\partial T \ln f_{\mathrm{O}}/f_{\mathrm{R}}).$$

These equations are strictly parallel to those obtained for thermocells with cation- or anion-reversible electrodes. As in these cases, the difference $(\varepsilon_0 - \varepsilon_{\mathrm{stat.}})$ is a function of combinations of entropies of transfer. In the case of a single electrolyte these are related to the experimentally accessible Soret coefficient. For mixed electrolytes in solution they can probably be related to the Soret coefficients found at similar ionic strengths for solutions of the corresponding single electrolytes.[5] However, it is obvious from equation (12) that, even if this is so, $(\varepsilon_0 - \varepsilon_{\mathrm{stat.}})$ remains always a function of the Soret coefficients of both the oxidised and the reduced salt, and the interpretation of the results is consequently more difficult than for thermocells with electrolytes containing only one dissolved solute. If either the oxidised or the reduced species is neutral, equation (12) becomes slightly simpler. If the oxidised form is neutral, for example, z_{O} and t_{O} are zero, and the corresponding form of (12) is

$$
\begin{aligned}
-z_{\mathrm{R}} F\varepsilon_0 = {} & z_{\mathrm{R}}\bar{\bar{S}}_{\mathrm{el.}} + (\bar{\bar{S}}_{\mathrm{R}}{}^{\circ} - \bar{\bar{S}}_{\mathrm{O}}{}^{\circ}) + \boldsymbol{R} \ln a_{\mathrm{O}}/a_{\mathrm{R}} + \boldsymbol{R}T(\partial/\partial T \ln f_{\mathrm{O}}/f_{\mathrm{R}}) \\
& - \frac{t_-}{\nu_{\mathrm{R}}} (\nu_{\mathrm{R}} S_{\mathrm{R}}{}^* + \nu_- S_-{}^*) + S_{\mathrm{O}}{}^*. \qquad (13)
\end{aligned}
$$

This equation is slightly more tractable; in very dilute salt solutions at a constant concentration of oxidised species it would be reasonable to suppose that $S_{\mathrm{O}}{}^*$ is constant. This would also be true if, at a given concentration of the reduced form, values of ε_0 for different concentrations of the oxidised form were measured and extrapolated to infinite dilution of the latter. In either case, measurements of ε_0 could be used to give a series of relative values for the quantity $(\nu_{\mathrm{R}} S_{\mathrm{R}}{}^* + \nu_- S_-{}^*)$, as was done in work on iodine–iodide electrodes.[1] It is not, however, possible to determine Soret coefficients for single species from measurements on thermocells of this type, though it is conceivable that they might find some use

---

[5] Karger, *Z. phys. Chem.* (*Frankfurt*), 1955, **5**, 232.

in the study of thermal diffusion in three component systems. For this, measurements of ε_0 and $\varepsilon_{\text{stat.}}$ would be required together with Soret-coefficient data for the individual solutes.

Thermocells including fused electrolytes have attracted some attention,[6] and it has been suggested that useful results could be obtained from work on such cells with redox electrodes.[7] The interpretation of such results will be complicated by the considerations outlined here, as well as by the problems arising from the definition of transport numbers and entropies of transfer in media where there is no neutral solvent to provide a convenient frame of reference.[6] These disadvantages will probably outweigh any practical advantages which may acrue from the reproducibility and accuracy of the electrode system. They are only likely to be overcome by an adequate molecular theory of transport processes which would permit ε_0 and $\varepsilon_{\text{stat.}}$ to be formulated in terms of calculable quantities.

DEPARTMENT OF CHEMISTRY, THE UNIVERSITY, SHEFFIELD, 10. [*Received, February 2nd*, **1963**.]

---

[6] Cf. Schneebaum and Sundheim, *Discuss. Faraday Soc.*, 1961, **32**, 197.
[7] Raleigh, personal communication (1962).