ELECTROMOTIVE FORCES OF CONCENTRATION CELLS

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The problem

For the electromotive force of a concentration cell of the type

Helmholtz, in 1882, under certain simplifying assumptions, deduced the equation

$$(1) \quad A_{\text{I}} - A_{\text{II}} = q.r_2\theta \int_{h_{\text{II}}}^{h_{\text{I}}} h \frac{\partial \log p_1}{\partial h} \partial h.$$

Here q denotes the mass of salt dissolved on the passage of unit current in unit time, r_2 the specific gas-constant of water vapor, θ the absolute temperature, $h = M_2/M_1$ the mass of water per unit mass of salt in the solution, and $p_1(\theta, h)$ the vapor pressure of the solution.

For comparison with experiment, Helmholtz evaluated the integral in (1) by means of an empirical relation giving the vapor pressure of solutions of zinc chloride as a function of the concentration at constant temperature. The object of the present note is to integrate Helmholtz's differential equation under the assumption that the relation between vapor pressure and concentration is given by the equation of the theory of dilute solutions,

$$\log \frac{p_0}{p_1} = (1 + \alpha) \frac{n_1}{n_2},$$

together with Ostwald's dilution law

$$k \frac{1-\alpha}{U} = \left(\frac{\alpha}{U}\right)^2;$$

and to determine how the result is altered when Ostwald's equation is replaced by van't Hoff's modification

$$K \left(\frac{1-\alpha}{U}\right)^2 = \left(\frac{\alpha}{U}\right)^3$$

of the form proposed by Rudolphi for the dilution law. In these equations, $p_o(\theta)$ denotes the vapor pressure of water, n_1/n_2 the number of mols of salt in the solution per mol of water, α the degree of electrolytic dissociation of the (binary) salt, and U the volume of the solution per mol of salt.

The electromotive force of the cell

For the purpose of making apparent the assumptions involved by (1), I shall begin by deducing the general thermodynamic equation for the electromotive force of the cell. Let $F(p, \theta, M_1, M_2)$ be the free energy of the solution composed of the masses M_1, M_2 of salt and water under the pressure p at the temperature θ . The change of the free energy of the system composed of these masses, when the separated masses at p, θ reversibly or irreversibly form the solution stable at p, θ , is

$$\Delta F = F - M_1 f_1 - M_2 f_2,$$

where $f_j(p, \theta)$ is the specific free energy of the j -th component. Since this function ΔF of the variables p, θ, M_1, M_2 is homogeneous and of the first degree in M_1, M_2 , we have

$$\Delta F = M_1 \frac{\partial \Delta F}{\partial M_1} + M_2 \frac{\partial \Delta F}{\partial M_2};$$

whence, differentiating with regard to either M_1 or M_2 ,

$$(2) \quad \frac{\partial}{\partial h} \frac{\partial \Delta F}{\partial M_1} + h \frac{\partial}{\partial h} \frac{\partial \Delta F}{\partial M_2} = 0.$$

This general equation may be employed to connect the electromotive force of the concentration cell with the concentrations of the two solutions. For $\partial \Delta F / \partial M_1$ may be

expressed by means of the electromotive force of the single cell, two of which constitute the concentration cell; and $\partial\Delta F/\partial M_2$ may be expressed by means of the vapor pressure of the solution and thus by means of the concentration; wherefore integration between the two concentrations of the double cell will yield the relation desired.

Let the current in the single cell flow from the metal M to the mercury. When the current J flows in the time dt , the electromotive force A does the work $AJdt$. The work added to the solution is $-AJdt$. This work may also be expressed as $\partial\Delta F/\partial M_1 \cdot Jqdt$. This work being exclusively electrical work,

$$\begin{aligned} -AJdt &= \frac{\partial\Delta F}{\partial M_1} Jqdt \\ \frac{\partial\Delta F}{\partial M_1} &= -\frac{A}{q} \\ (3) \quad \frac{\partial}{\partial h} \frac{\partial\Delta F}{\partial M_1} &= -\frac{1}{q} \frac{\partial A}{\partial h}, \end{aligned}$$

as was shown by Helmholtz.

On p. 399 of a paper¹ on the thermodynamic theory of solutions, I have shown, equation (15a), that

$$\frac{\partial\Delta F}{\partial M_2} = p^2 \frac{\partial}{\partial p} \frac{1}{p} \left\{ \int_{p_1}^{p_0} \left(v_a - \frac{\partial V}{\partial M_2} \right) dp + \int_{p_0}^p \left(v_2 - \frac{\partial V}{\partial M_2} \right) dp \right\},$$

where $v_a(p, \theta)$ is the specific volume of saturated water vapor, $v_2(p, \theta)$ is the specific volume of liquid water, and $V(p, \theta, M_1, M_2)$ is the volume of the solution of M_1 in M_2 . Executing the indicated differentiation,

$$\frac{\partial\Delta F}{\partial M_2} = p \left(v_2 - \frac{\partial V}{\partial M_2} \right) - \int_{p_1}^{p_0} \left(v_a - \frac{\partial V}{\partial M_2} \right) dp - \int_{p_0}^p \left(v_2 - \frac{\partial V}{\partial M_2} \right) dp;$$

whence

$$\begin{aligned} (4) \quad \frac{\partial}{\partial h} \frac{\partial\Delta F}{\partial M_2} &= -p \frac{\partial}{\partial h} \frac{\partial V}{\partial M_2} - \frac{\partial}{\partial h} \int_{p_1}^{p_0} \left(v_a - \frac{\partial V}{\partial M_2} \right) dp \\ &\quad - \frac{\partial}{\partial h} \int_{p_0}^p \left(v_2 - \frac{\partial V}{\partial M_2} \right) dp. \end{aligned}$$

¹ This Journal, 10, 392 (1906).

Substituting (3) and (4) in the general equation (2), solving for $\partial A/\partial h$, and integrating between h_{II} and h_I , where $h_I > h_{II}$,

$$(5) \quad A_I - A_{II} = -q \int_{h_{II}}^{h_I} h \frac{\partial}{\partial h} \frac{\partial V}{\partial M_2} dh - q \int_{h_{II}}^{h_I} h \frac{\partial}{\partial h} \int_{p_1}^{p_0} \left(v_a - \frac{\partial V}{\partial M_2} \right) dp \cdot dh \\ - q \int_{h_{II}}^{h_I} h \frac{\partial}{\partial h} \int_{p_0}^{p_1} \left(v_2 - \frac{\partial V}{\partial M_2} \right) dp \cdot dh.$$

This is the wholly general thermodynamic equation for the electromotive force of the concentration cell at p, θ . When the cell functions under the pressure $p = p_0$, the last of the three terms of the second member disappears.

Helmholtz's equation

If we assume that $p = p_0$, and also that $\partial V/\partial M_2$ is independent of h and is negligible in comparison with v_a , the equation (5) becomes

$$A_I - A_{II} = -q \int_{h_{II}}^{h_I} h \frac{\partial}{\partial h} \int_{p_1}^{p_0} v_a dp \cdot dh.$$

If we further assume that the saturated water vapor may be regarded as an ideal gas, *i. e.*, that $v_a = r_2 \theta / p$, we find

$$(5a) \quad A_I - A_{II} = q \cdot r_2 \theta \int_{h_{II}}^{h_I} h \frac{\partial \log p_1}{\partial h} dh,$$

which is Helmholtz's equation as cited at the beginning of this article.

Integration of Helmholtz's equation

Our present problem is to effect the integration of (5a), under the assumption that the form of $p_1(\theta, h)$ is given by

$$(6) \quad \log \frac{p_0}{p_1} = (1 + \alpha) \frac{n_1}{n_2},$$

where the form of $\alpha(\theta, h)$ is to be obtained from

$$(7) \quad k \frac{1 - \alpha}{U} = \left(\frac{\alpha}{U} \right)^2.$$

We thus require to find the form of $\partial \log p_1 / \partial h$ in h , through elimination of α between (6), (7), and determination of the forms of the functions n_1/n_2 and U .

Solving (7) for α ,

$$\alpha = -\frac{kU}{2} + \left\{ kU + \left(\frac{kU}{2} \right)^2 \right\}^{\frac{1}{2}}.$$

Here, both k and U being positive, the positive square root must be taken to make α positive. Eliminating α ,

$$(8) \quad -\log \frac{p_0}{p_1} = -\frac{n_1}{n_2} + \frac{kU}{2} \frac{n_1}{n_2} - \frac{n_1}{n_2} \left\{ kU + \left(\frac{kU}{2} \right)^2 \right\}^{\frac{1}{2}}.$$

It remains to express n_1/n_2 and U in terms of h . Writing w_j for the molecular weight of the j -th component of the solution,

$$(9) \quad \frac{n_1}{n_2} = \frac{M_1}{M_2} \frac{w_2}{w_1} = \frac{w_2}{w_1} \frac{1}{h}.$$

Identifying the volume V of the solution with the mass of water in the solution, $V = M_2$; whence U , the volume of the solution per mol of salt, becomes

$$(10) \quad U = \frac{V}{M_1/w_1} = \frac{w_1 M_2}{M_1} = w_1 h.$$

Eliminating n_1/n_2 and U , (8) becomes

$$(11) \quad -\log \frac{p_0}{p_1} = -\frac{w_2}{w_1} \frac{1}{h} + \frac{k w_2}{2} - \frac{w_2}{w_1} \frac{1}{h} \left\{ k w_1 h + \left(\frac{k w_1 h}{2} \right)^2 \right\}^{\frac{1}{2}}.$$

Differentiating,

$$(12) \quad \frac{\partial \log p_1}{\partial h} = \frac{w_2}{w_1} \frac{1}{h^2} + \frac{w_2}{w_1} \frac{k w_1}{2 h (k w_1 h + k^2 w_1^2 / 4 h^2)^{\frac{1}{2}}}.$$

Substituting this expression in (5a), and noting that $w_2 r_2$ is the molecular gas-constant r ,

$$(13) \quad \begin{aligned} A_I - A_{II} &= \frac{q}{w_1} \cdot r \theta \cdot \log \frac{h_I}{h_{II}} + \frac{k q \cdot r \theta}{2} \int_{h_{II}}^{h_I} \frac{dh}{(k w_1 h + k^2 w_1^2 / 4 h^2)^{\frac{1}{2}}} \\ &= \frac{q}{w_1} \cdot r \theta \cdot \log h \left\{ 1 + \frac{k w_1}{2} h + \sqrt{k w_1 h + \left(\frac{k w_1 h}{2} \right)^2} \right\} \Big|_{h_{II}}^{h_I}. \end{aligned}$$

This result assumes a simpler form when the composition of the solution is expressed by means of α instead of by means of h . From (7) and (10), namely

$$kU = \frac{\alpha^2}{1-\alpha}, \quad U = w_1 h,$$

we find $h(\alpha)$ to be

$$\frac{1}{kw_1} \frac{\alpha^2}{1-\alpha}.$$

Replacing h in (13) by $h(\alpha)$, we find

$$\begin{aligned} A_I - A_{II} &= 2 \frac{q}{w_1} r \theta \cdot \log \frac{\alpha}{1-\alpha} \Big|_{a_{II}}^{a_I} \\ (13a) \quad &= 2 \frac{q}{w_1} r \theta \cdot \log \frac{\alpha_I}{\alpha_{II}} \frac{1-\alpha_{II}}{1-\alpha_I}. \end{aligned}$$

Integration with regard to the degree of electrolytic dissociation

As is indicated by the simple form of the result (13a), the above integration of Helmholtz's differential equation is more readily effected when α instead of h is employed as the concentration variable. This shall now be shown. From the general thermodynamic equation

$$\Delta F = M_1 \frac{\partial \Delta F}{\partial M_1} + M_2 \frac{\partial \Delta F}{\partial M_2},$$

by differentiation with regard to M_2 we find

$$\left(M_1 \frac{\partial}{\partial \alpha} \frac{\partial \Delta F}{\partial M_1} + M_2 \frac{\partial}{\partial \alpha} \frac{\partial \Delta F}{\partial M_2} \right) \frac{\partial \alpha}{\partial M_2} = 0.$$

Noting that $\partial \alpha / \partial M_2$ does not vanish, and that

$$\frac{M_2}{M_1} = h = \frac{1}{kw_1} \frac{\alpha^2}{1-\alpha},$$

as just shown, we obtain

$$(14) \quad \frac{\partial}{\partial \alpha} \frac{\partial \Delta F}{\partial M_1} + \frac{1}{kw_1} \frac{\alpha^2}{1-\alpha} \frac{\partial}{\partial \alpha} \frac{\partial \Delta F}{\partial M_2} = 0.$$

Now, as before

$$\frac{\partial \Delta F}{\partial M_1} = -\frac{A}{q};$$

whence

$$(15) \quad \frac{\partial}{\partial \alpha} \frac{\partial \Delta F}{\partial M_1} = -\frac{1}{q} \frac{\partial A}{\partial \alpha}.$$

Again as before, and under the same assumptions,

$$\begin{aligned} \frac{\partial \Delta F}{\partial M_2} &= - \int_{p_1}^{p_0} v_a(p, \theta) dp \\ &= - \phi(p_0(\theta), \theta) + \phi(p_1(\theta, \alpha), \theta); \end{aligned}$$

whence

$$\begin{aligned} \frac{\partial}{\partial \alpha} \frac{\partial \Delta F}{\partial M_2} &= \frac{\partial \phi}{\partial p_1} \frac{\partial p_1}{\partial \alpha} \\ &= v_a(p_1, \theta) \frac{\partial p_1}{\partial \alpha} \\ (16) \quad &= r_2 \theta \frac{\partial \log p_1}{\partial \alpha}. \end{aligned}$$

Again assuming (6), we have

$$\begin{aligned} \log \frac{p_0}{p_1} &= (1 + \alpha) \frac{n_1}{n_2} \\ &= (1 + \alpha) \frac{w_2}{w_1} \frac{1}{h} \\ &= w_2 k \frac{1 - \alpha^2}{\alpha^2} \\ \frac{\partial \log p_1}{\partial \alpha} &= \frac{2w_2 k}{\alpha^3}; \end{aligned}$$

wherefore (16) becomes

$$(16a) \quad \frac{\partial}{\partial \alpha} \frac{\partial \Delta F}{\partial M_2} = \frac{2k.w_2.r_2.\theta}{\alpha^3}.$$

Substituting (15) and (16a) in (14),

$$\frac{\partial A}{\partial \alpha} = 2 \frac{q}{w_1} r \theta \frac{1}{(1 - \alpha)\alpha}.$$

Integrating over the difference of the concentrations in the concentration cell,

$$A_I - A_{II} = 2 \frac{q}{w_1} r \theta \log \frac{\alpha}{1 - \alpha} \Big|_{\alpha_{II}}^{\alpha_I}$$

the same result (13a) as before.

The assumptions made

From the above work it is clear that Helmholtz's differential equation (1) involves the assumptions:

- The salt is involatile ;
- The cell functions under the pressure $p_o(\theta)$;
- $\partial V/\partial M_2$ is independent of h , and negligible in comparison with v_a ;
- The form of $v_a(p, \theta)$ is $r_a \theta/p$.

And it is clear that the further assumptions made in the integration, and thereby involved in the equivalent formulations (13), (13a), are:

$$\log \frac{p_o}{p_1} = (1 + \alpha) \frac{n_1}{n_2}$$

$$k \frac{1 - \alpha}{U} = \frac{\alpha^2}{U^2}$$

$V = M_2$. I. e. the volume of the solution in cm^3 is sensibly the same as the mass of the water in grams.

It will not be overlooked that the first of these further assumptions introduces the hypothesis that the heats of dilution of the solutions are negligibly small. The general equation (5) for the electromotive force of the concentration cell involves only the assumption of the involatility of the salt.

Integration assuming the dilution law of Rudolphi-van't Hoff

It is not without interest to determine the manner in which the foregoing result is modified when the assumption of Ostwald's dilution law is replaced by that of Rudolphi's equation as modified by van't Hoff,

$$K \left(\frac{1 - \alpha}{U} \right)^2 = \left(\frac{\alpha}{U} \right)^3.$$

The formulation $U = w_1 h$ of equation (10) converts this to

$$(17) \quad h = \frac{1}{w_1 K} \frac{\alpha^3}{(1 - \alpha)^2};$$

wherefore the general relation

$$\frac{\partial}{\partial \alpha} \frac{\partial \Delta F}{\partial M_1} + h \frac{\partial}{\partial \alpha} \frac{\partial \Delta F}{\partial M_2} = 0$$

becomes

$$\frac{\partial}{\partial \alpha} \frac{\partial \Delta F}{\partial M_1} + \frac{1}{w_1 K} \frac{\alpha^3}{(1-\alpha)^2} \frac{\partial \Delta F}{\partial M_2} = 0.$$

As before, equations (15), (16), we have

$$\frac{\partial}{\partial \alpha} \frac{\partial \Delta F}{\partial M_1} = -\frac{1}{q} \frac{\partial A}{\partial \alpha}, \quad \frac{\partial}{\partial \alpha} \frac{\partial \Delta F}{\partial M_2} = r_2 \theta \frac{\partial \log p_1}{\partial \alpha};$$

wherefore

$$(18) \quad \frac{\partial A}{\partial \alpha} = \frac{q}{w_1} \frac{r_2 \theta}{K} \frac{\alpha^3}{(1-\alpha)^2} \frac{\partial \log p_1}{\partial \alpha}.$$

Now, by (6), (9), (17),

$$\begin{aligned} \log \frac{p_0}{p_1} &= w_2 K \frac{(1+\alpha)(1-\alpha)^2}{\alpha^3} \\ \frac{\partial \log p_1}{\partial \alpha} &= w_2 K \frac{(3+\alpha)(1-\alpha)}{\alpha^4}; \end{aligned}$$

which converts (18) to

$$\frac{\partial A}{\partial \alpha} = \frac{q}{w_1} r \theta \frac{3+\alpha}{(1-\alpha)\alpha};$$

wherefore; integrating between α_{II} , α_I ,

$$A_I - A_{II} = \frac{q}{w_1} r \theta \left(3 \log \frac{\alpha}{1-\alpha} + \log \frac{1}{1-\alpha} \right) \Big|_{\alpha_{II}}^{\alpha_I}.$$

This is the formulation sought. It may be written

$$\begin{aligned} (19) \quad A_I - A_{II} &= \frac{q}{w_1} r \theta \log \frac{\alpha^3}{(1-\alpha)^4} \Big|_{\alpha_{II}}^{\alpha_I} \\ &= \frac{q}{w_1} r \theta \log \frac{\alpha_I^3}{\alpha_{II}^3} \frac{(1-\alpha_{II})^4}{(1-\alpha_I)^4}. \end{aligned}$$

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