CHAPTER 8

ELECTROCHEMICAL SYSTEMS

§8.01 *Electrically charged phases*

In the previous chapter we saw how a solution containing ions can be treated by means of the same formulae as one containing only electrically neutral molecules. In particular the formula

$$dG = -S\,dT + V\,dP + \sum_i \mu_i\,dn_i \qquad 8.01.1$$

from which follows

$$\mu_i = (\partial G/\partial n_i)_{T,\,P,\,n_j} \qquad 8.01.2$$

are applicable. The only significant difference in our treatment of ions was the imposition of the condition for electrical neutrality

$$\sum_i n_i z_i = 0 \qquad 8.01.3$$

where z_i is the charge number of the ionic species i. We shall now consider what happens if we try to relax the condition (3).

To obtain a clear picture of what happens it is useful to begin with some simple numerical calculations. The charge e on a proton is given by

$$e = 1.6021 \times 10^{-19}\ \mathrm{C}. \qquad 8.01.4$$

Consequently the proper electric charge, associated with an ionic species having a charge number 1, called the *Faraday constant* and denoted by F is given by

$$F = Le = 0.96487 \times 10^{5}\ \mathrm{C\ mole^{-1}}. \qquad 8.01.5$$

Let us now consider a single phase surrounded by a vacuum and thus electrically insulated. Let us further imagine that this phase, instead of satisfying the condition of electrical neutrality (3), contains an excess of 10^{-10} moles of an ionic species with charge number $+1$. Then most, if not all, the excess electrical charge will accumulate at the surface of the phase. For simplicity let us suppose that the phase is spherical with a radius one centimetre. The electrical potential ψ of a charged sphere of radius r in vacuo is determined by

$$\psi = Q/4\pi\varepsilon_0 r \qquad 8.01.6$$

where Q is the charge on the sphere and ε_0 is the rational permittivity of a vacuum. Substituting the values

$$\begin{aligned} Q &= 10^{-10}\ F\ \text{mole} = 0.96 \times 10^{-5}\ \text{C} \\ 4\pi\varepsilon_0 &= 1.11 \times 10^{-10}\ \text{C V}^{-1}\ \text{m}^{-1} \\ r &= 10^{-2}\ \text{m} \end{aligned} \qquad 8.01.7$$

into (6), we obtain

$$\psi = (0.96 \times 10^{-5}/1.11 \times 10^{-10} \times 10^{-2})\text{V} = 0.86 \times 10^{7}\ \text{V}. \qquad 8.01.8$$

From this example we have reached the striking conclusion that a departure from the condition of electrical neutrality corresponding to a quantity of ions far too small to be detected chemically corresponds to an electrostatic potential which could be encountered only in specialized high tension laboratories. Any other numerical example would lead to the same conclusion.

§8.02 *Phases of identical composition*

The above general result leads to the use of the following terminology. We speak of two phases having the *same chemical content*, but *different electrical potentials*. Actually two such phases differ in chemical content but the difference is too small to be detectable by chemical means, or any other means, except electrical. For example suppose we mention two spheres of copper each containing precisely one gramme differing in electrical potential by 200 V. If this electrical potential difference is ascribed to an excess of copper ions Cu^{2+} with a charge number $+2$, then the amount of this excess is about 3.5×10^{-16} moles or 2×10^{-14} grammes. This excess is so small as to be entirely negligible except in its electrical effect. Consequently it is of no importance or interest whether the electrical charge is in fact due to an excess of Cu^{2+} ions or to an equivalent deficiency of electrons or even to some extraneous kind of ion such as H_3O^+, present as an impurity.

Similar considerations apply to a pair of phases of different size but of the same chemical composition.

§8.03 *Electrochemical potentials*

Having agreed as to what we mean when we speak of two phases having the same chemical composition but different electrical potentials, we see that the μ_i's occurring in the formulae mentioned in §8.01 have values depending on the electrical state of the phase as well as on its chemical composition. To stress this fact we call the μ_i of an ionic species its *electrochemical potential.**

The difference of the electrochemical potential μ_i between two phases of *identical chemical composition* will clearly be proportional to the proper electrical charge $z_i F$ associated with the species in question but independent of all its other individual characteristics. Hence for any two phases α and β of identical chemical composition we may write for any ionic species i

$$\mu_i^\beta - \mu_i^\alpha = z_i F(\psi^\beta - \psi^\alpha) \qquad 8.03.1$$

where $\psi^\beta - \psi^\alpha$ is the *electrical potential difference* between the two phases. Formula (1) may be regarded as the thermodynamic definition of the electrical potential difference between two phases of *identical chemical composition.* The equilibrium condition for a given ionic species between two phases of identical composition is that the two phases should be at the same electrical potential. In fact the laws of mathematical electrostatics are applicable to any ionic species, in particular to electrons, only in so far as differences in chemical composition between several phases are excluded or ignored.

For the distribution of the ionic species i between two phases α, β of different chemical composition the equilibrium condition is equality of the electrochemical potential μ_i, that is to say

$$\mu_i^\alpha = \mu_i^\beta. \qquad 8.03.2$$

Any splitting of $\mu_i^\beta - \mu_i^\alpha$ into a chemical part and an electrical part is in general arbitrary and without physical significance.

As long ago as 1899 Gibbs wrote:[†] 'Again, the consideration of the electrical potential in the electrolyte, and especially the consideration of the difference of potential in electrolyte and electrode, involve the consideration of quantities of which we have no apparent means of physical measurement, while the difference of potential in pieces of metal of the same kind attached to the electrodes is exactly one of the things which we can and do measure.' This principle was however ignored or forgotten until rediscovered and reformulated thirty years later as follows:* 'The electric potential difference between two points in different media can never be measured and has not yet been defined in terms of physical realities. It is therefore a conception which has no physical significance.' The electrostatic potential difference

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* Guggenheim, J. Phys. Chem. 1929 **33** 842.

[†] Gibbs, Collected Works, Longmans, vol. 1, p. 429.

between two points is admittedly defined in *electrostatics*, the mathematical theory of an imaginary fluid *electricity*, whose equilibrium or motion is determined entirely by the electric field. *Electricity* of this kind does not exist. Only electrons and ions have physical existence and these differ fundamentally from the hypothetical fluid *electricity* in that their equilibrium is *thermodynamic* not *electrostatic*.

Although the above considerations seem almost obvious to anyone who has thought about the matter, there has in the past been considerable confusion due to misleading terminology. It therefore seems worth while considering in more detail some simple examples. Consider a potentiometer wire made of copper and in particular two sections of the wire α' and α'' between which the electrical potential difference $\psi''-\psi'$ is say 2 V. Since α' and α'' are both in copper, there is no ambiguity in the meaning of $\psi''-\psi'$. If two pieces of copper wire are attached to α' and α'', then the electrical potential difference between these two is also $\psi''-\psi'=2\text{ V}$. If instead of copper wire we attach two pieces of silver wire β' and β'' to α' and α'' respectively, then the difference of electrical potential between β' and β'' is likewise 2 V. The electrical potential difference between a piece of copper and a piece of silver is however not defined. The silver wire β' and the copper wire α' are in equilibrium with respect to electrons, so that

$$\mu^{\alpha'}_{\text{el}^-}=\mu^{\beta'}_{\text{el}^-} \tag{8.03.3}$$

where the subscript $_{\text{el}^-}$ denotes electrons. Likewise

$$\mu^{\alpha''}_{\text{el}^-}=\mu^{\beta''}_{\text{el}^-}. \tag{8.03.4}$$

Thus the situation is completely described by (3) or (4) together with

$$\mu^{\alpha''}_{\text{el}^-}-\mu^{\alpha'}_{\text{el}^-}=\mu^{\beta''}_{\text{el}^-}-\mu^{\beta'}_{\text{el}^-}=-F(\psi''-\psi'). \tag{8.03.5}$$

Suppose further that the two pieces of silver wire β', β'' be dipped respectively into two solutions γ', γ'' both having the same composition and both containing a silver salt. Then between each piece of silver wire and the solution with which it is in contact there will be equilibrium with respect to silver ions Ag^+. Hence

$$\mu^{\gamma'}_{\text{Ag}^+}=\mu^{\beta'}_{\text{Ag}^+} \tag{8.03.6}$$

$$\mu^{\gamma''}_{\text{Ag}^+}=\mu^{\beta''}_{\text{Ag}^+}. \tag{8.03.7}$$

At the same time

$$\mu^{\gamma''}_{\text{Ag}^+}-\mu^{\gamma'}_{\text{Ag}^+}=\mu^{\beta''}_{\text{Ag}^+}-\mu^{\beta'}_{\text{Ag}^+}=F(\psi''-\psi')=F\times 2\text{ V}. \tag{8.03.8}$$

If the two solutions γ', γ'' are contained in insulating vessels and the silver wires are removed without otherwise touching or disturbing the two solutions then the relations (8) remain valid until one solution is touched by some other electrically charged or electrically conducting body. From this it is clear that the value of μ_{Ag^+} in a solution of a silver salt depends not only on the composition of the solution but also on its, usually accidentally determined, electrical state. If the solutions also contain nitrate ions NO_3^- then, since both solutions have the same composition,

$$\mu^{\gamma''}_{NO_3^-} - \mu^{\gamma'}_{NO_3^-} = -F(\psi'' - \psi'). \qquad 8.03.9$$

Adding (8) and (9), we obtain

$$\mu^{\gamma'}_{Ag^+} + \mu^{\gamma'}_{NO_3^-} = \mu^{\gamma''}_{Ag^+} + \mu^{\gamma''}_{NO_3^-} \qquad 8.03.10$$

the electrical terms cancelling. We accordingly speak of the *chemical potential* of a salt, for example $\mu_{AgNO_3} = \mu_{Ag^+} + \mu_{NO_3^-}$, but of the *electrochemical potentials* of ions, for example μ_{Ag^+} and $\mu_{NO_3^-}$.

§8.04 *Absolute activities of ions*

Since the absolute activity λ_i is related to μ_i by

$$\mu_i = RT \ln \lambda_i \qquad 8.04.1$$

it is clear that the absolute activity of an ionic species contains a factor depending on the, usually accidentally determined, electrical state of the system. The same applies to the activity coefficient of an ionic species. As already emphasized in the previous chapter all such indeterminacy disappears in formulae relating to electrically neutral combinations of ions, in particular to salts.

§8.05 *Dilute solutions in common solvent*

According to (7.09.1) the absolute activity λ_i of an ionic species i is related to its molality m_i and its activity coefficient γ_i by

$$\lambda_i = \lambda_i^{\ominus} m_i \gamma_i \qquad 8.05.1$$

where $\lambda_i^{\ominus}$ depends on the solvent and temperature and moreover contains a partly undetermined factor, which however cancels in all applications to processes not involving a net transfer of electric charge. Correspondingly the electrochemical potential μ_i has the form

$$\mu_i = RT \ln \lambda_i^{\ominus} + RT \ln m_i + RT \ln \gamma_i \qquad 8.05.2$$

and includes an undetermined additive term which cancels in all applications to processes not involving a net transfer of electrical charge. We shall investigate this term in greater detail.

Let us formally write

$$\mu_i = z_i F\psi + RT\ln l_i^{\ominus} + RT\ln m_i + RT\ln\gamma_i \qquad 8.05.3$$

where $l_i^{\ominus}$ is independent of the electrical state of the phase and ψ is the electrical potential of the phase. Let us now apply (3) to two phases denoted by a single and a double dash respectively and then subtract. We obtain

$$\mu_i'' - \mu_i' = z_i F(\psi'' - \psi') + RT\ln(l_i^{\ominus\prime\prime}/l_i^{\ominus\prime}) + RT\ln(m_i''/m_i') + RT\ln(\gamma_i''/\gamma_i'). \qquad 8.05.4$$

We now re-examine the condition for the term containing $\psi'' - \psi'$ to be physically defined.

The easiest case is when the two phases have the same chemical composition so that

$$l_i^{\ominus\prime\prime} = l_i^{\ominus\prime} \qquad 8.05.5$$

$$m_i'' = m_i' \qquad 8.05.6$$

$$\gamma_i'' = \gamma_i'. \qquad 8.05.7$$

Formula (4) then reduces to

$$\mu_i'' - \mu_i' = z_i F(\psi'' - \psi'). \qquad 8.05.8$$

Since $\mu_i'' - \mu_i'$ is always well defined, formula (8) in this special case defines $\psi'' - \psi'$.

We now consider the extreme opposite case of two solutions in different solvents or two different pure phases. In this case there is no means of distinguishing in (4) between the term containing $\psi'' - \psi'$ and the term containing $\ln(l_i^{\ominus\prime\prime}/l_i^{\ominus\prime})$. The splitting into these two terms has in this case no physical significance. These remarks merely repeat and confirm what has already been stated in the preceding sections.

We have still to consider the intermediate case of two solutions of different composition in the same solvent, of course at the same temperature. We then have

$$l_i^{\ominus\prime\prime} = l_i^{\ominus\prime} \qquad 8.05.9$$

so that (4) reduces to

$$\mu_i'' - \mu_i' = z_i F(\psi'' - \psi') + RT\ln(m_i''/m_i') + RT\ln(\gamma_i''/\gamma_i'). \qquad 8.05.10$$

Since $\mu_i'' - \mu_i'$ is well defined and m_i'', m_i' are measurable, the question whether

$\psi''-\psi'$ is determinate depends on our knowledge of γ_i''/γ_i'. If both the solutions are so dilute that we can evaluate γ_i by an explicit formula such as (7.20.9), then we may consider that (10) defines $\psi''-\psi'$. If on the other hand either solution is so concentrated that our knowledge of the value of γ_i is incomplete, then the value of $\psi''-\psi'$ becomes correspondingly indefinite.

§8.06 *Volta potentials*

It is outside the province of this book to consider thermionic phenomena. In case however any reader may be puzzled by the fact that the so-called *Volta potential difference* or *contact potential difference* between two metals can be determined, it seems worth while stressing that the only measurable potential difference of this kind is that between two regions in free space immediately *outside* the two metals respectively.

§8.07 *Membrane equilibrium (non-osmotic)*

Suppose two solutions α and β at the same temperature and pressure in the same solvent be separated by a membrane permeable to some ions, but not to others, nor to the solvent. We call this a *non-osmotic membrane equilibrium*. Then for every permeant ion we have the equilibrium condition

$$\mu_i^\alpha=\mu_i^\beta. \qquad 8.07.1$$

If for example one of the permeant ions is the Ag^+ ion, we have

$$\mu_{Ag^+}^\alpha=\mu_{Ag^+}^\beta. \qquad 8.07.2$$

If then we place in each of the two solutions a piece of silver wire since each piece of wire is, with respect to Ag^+, in equilibrium with the solution in which it dips, the equality of μ_{Ag^+} also holds between the two pieces of silver wire. Hence the two pieces of silver wire have equal electrical potentials, as could be verified by connecting them to a potentiometer or electrometer.

We have yet to consider what, if anything, can be said concerning the electrical potential difference between the two solutions. Since the solvent is the same in both solutions, we may in accordance with (8.05.10) replace (2) by

$$F(\psi^\beta-\psi^\alpha)+RT\ln(m_{Ag^+}^\beta/m_{Ag^+}^\alpha)+RT\ln(\gamma_{Ag^+}^\beta/\gamma_{Ag^+}^\alpha)=0. \qquad 8.07.3$$

Supposing that m_{Ag^+} has been measured in both solutions, the determination of $\psi^\beta-\psi^\alpha$ reduces to that of the values of γ_{Ag^+} in the two solutions. If the solutions are so dilute that accurate or at least approximate, formulae for the activity coefficients γ are available then the electrical potential difference $\psi^{\beta}-\psi^{\alpha}$ can be evaluated with greater or less accuracy as the case may be. If either solution is so concentrated that γ_{Ag^+} cannot be evaluated, then no more can $\psi^{\beta}-\psi^{\alpha}$.

If there are several permeant ions, then the relations of the form (1) can be combined into relations corresponding to processes involving no net flow of electric charge. For example for a salt composed of ν_+ cations R of charge number z_+ and ν_- anions X of charge number z_-, both permeant, the equilibrium condition is

$$\nu_+ \mu_{\mathrm{R}}^{\alpha} + \nu_- \mu_{\mathrm{X}}^{\alpha} = \nu_+ \mu_{\mathrm{R}}^{\beta} + \nu_- \mu_{\mathrm{X}}^{\beta} \qquad 8.07.4$$

which can be written in the equivalent form

$$(m_{\mathrm{R}}^{\alpha})^{\nu_+}(m_{\mathrm{X}}^{\alpha})^{\nu_-}(\gamma_{\mathrm{R,X}}^{\alpha})^{\nu_+ + \nu_-} = (m_{\mathrm{R}}^{\beta})^{\nu_+}(m_{\mathrm{X}}^{\beta})^{\nu_-}(\gamma_{\mathrm{R,X}}^{\beta})^{\nu_+ + \nu_-}. \qquad 8.07.5$$

§8.08 *Osmotic membrane equilibrium*

In the preceding section we assumed that the membrane was impermeable to the solvent. The more usual case when the membrane is permeable to the solvent, called *osmotic membrane equilibrium*, is less simple. In this case equilibrium as regards the solvent between two phases separated by the membrane, will generally require a pressure difference between the two phases, the *osmotic pressure difference*, and this pressure difference complicates the exact conditions of equilibrium for the solute ions. We shall consider only the case of one and the same solvent on both sides of the membrane.

The conditions for membrane equilibrium can be written in the general form

$$\mu_1^{\alpha} = \mu_1^{\beta} \qquad 8.08.1$$

for the solvent and

$$\mu_i^{\alpha} = \mu_i^{\beta} \qquad 8.08.2$$

for each permeant ionic species.

We have now to take account of how each μ depends on the pressure, but for the sake of brevity we shall neglect the compressibility of the solutions. We have then in accordance with (7.06.1)

$$\begin{aligned}\mu_1(P) &= \mu_1^0(P) - RT\phi \sum_i r_i \\ &= \mu_1^{0\ominus} + PV_1^0 - RT\phi \sum_i r_i \qquad 8.08.3\end{aligned}$$

where $\mu_1^0(P)$ is the value of μ_1 for the pure solvent at the pressure P, while $\mu_1^{0\ominus}$ is the value for the pure solvent in the limit of zero pressure.

Similarly for each ionic species i we replace (8.05.3) by

$$\mu_i = PV_i + z_i F\psi + RT\ln(l_i^{\ominus} m_i \gamma_i) \qquad 8.08.4$$

where $l_i^{\ominus}$ is independent of the pressure.

Using (3) in (1) we obtain for the equilibrium value of the pressure difference

$$P^\beta - P^\alpha = RT(\phi^\beta \sum_i r_i^\beta - \phi^\alpha \sum_i r_i^\alpha)/V_1^0. \qquad 8.08.5$$

Using (4) in (2) we obtain

$$RT\ln(m_i^\beta \gamma_i^\beta / m_i^\alpha \gamma_i^\alpha) + z_i F(\psi^\beta - \psi^\alpha) = (P^\alpha - P^\beta)V_i. \qquad 8.08.6$$

Finally substituting (5) into (6) we have

$$\ln(m_i^\beta \gamma_i^\beta / m_i^\alpha \gamma_i^\alpha) + z_i F(\psi^\beta - \psi^\alpha)/RT = V_i(\phi^\alpha \sum_i r_i^\alpha - \phi^\beta \sum_i r_i^\beta)/V_1^0. \qquad 8.08.7$$

Whether formula (7) by itself has any physical significance depends, as explained in §8.05, on whether values of γ_i can be computed. If they can, then from formula (7) the value of $\psi^\beta - \psi^\alpha$ can be computed, since all the other quantities occurring in (7) are measurable. In any case the term containing $\psi^\beta - \psi^\alpha$ can be eliminated by applying (7) to several ionic species together forming an electrically neutral combination. Thus for the equilibrium distribution of a permeant electrolyte consisting of ν_+ cations R and ν_- anions X we obtain

$$\frac{(m_R^\beta)^{\nu_+}(m_X^\beta)^{\nu_-}(\gamma_{R,X}^\beta)^{\nu_+ + \nu_-}}{(m_R^\alpha)^{\nu_+}(m_X^\alpha)^{\nu_-}(\gamma_{R,X}^\alpha)^{\nu_+ + \nu_-}} = \exp\{(\nu_+ V_R + \nu_- V_X)(\phi^\alpha \sum_i r_i^\alpha - \phi^\beta \sum_i r_i^\beta)/V_1^0\}. \qquad 8.08.8$$

At high dilutions when all $r_i \ll 1$ the quantity within the { } on the right side of (8) may be so small that it can be neglected. Under such conditions (8) reduces to

$$(m_R^\beta)^{\nu_+}(m_X^\beta)^{\nu_-}(\gamma_{R,X}^\beta)^{\nu_+ + \nu_-} = (m_R^\alpha)^{\nu_+}(m_X^\alpha)^{\nu_-}(\gamma_{R,X}^\alpha)^{\nu_+ + \nu_-} \qquad 8.08.9$$

of the same form as (8.07.5) for a non-osmotic membrane equilibrium.

The thermodynamic methods of Gibbs were first applied to osmotic membrane equilibria by Donnan. Such an equilibrium is accordingly called a *Donnan membrane equilibrium*.

§8.09 *Contact equilibrium*

The most important and simplest example of non-osmotic equilibrium is that of two phases with one common ion, the surface of separation being in effect a membrane permeable to the common ion but impermeable to all others. This may be called *contact equilibrium.*

We have already met several examples of contact equilibrium. For example, for two metals say Cu and Ag in contact there is equilibrium between the metals as regards electrons, but not as regards the positive ions Cu^{2+} or Ag^{+}. This equilibrium is expressed by

$$\mu^{\mathrm{Cu}}_{\mathrm{el}^-}=\mu^{\mathrm{Ag}}_{\mathrm{el}^-} \tag{8.09.1}$$

the subscript $_{\mathrm{el}^-}$ denoting electrons and the superscripts denoting the two phases.

Likewise for a piece of metal M of say Cu dipping into a solution S containing ions of the metal, in this case Cu^{2+}, the contact equilibrium is completely described by

$$\mu^{\mathrm{M}}_{\mathrm{Cu}^{2+}}=\mu^{\mathrm{S}}_{\mathrm{Cu}^{2+}} \tag{8.09.2}$$

the metal and solution being in mutual equilibrium as regards the metallic ions only.

In neither of these cases is any contact electrical potential difference thermodynamically definable.

§8.10 *Examples of galvanic cell*

We shall now introduce the subject of galvanic cells by the detailed study of a simple example in terms of the electrochemical potentials. At a later stage we shall proceed to derive more general formulae applicable to all galvanic cells.

We describe a cell symbolically by writing down in order a number of phases separated by vertical lines, each phase being in contact with the phases written down immediately to its left and right. For example

$$\begin{array}{c|c|c|c|c|c} \mathrm{Cu} & \mathrm{Zn} & \begin{array}{c}\text{Solution I}\\ \text{containing }\mathrm{Zn}^{2+}\end{array} & \begin{array}{c}\text{Solution II}\\ \text{containing }\mathrm{Ag}^{+}\end{array} & \mathrm{Ag} & \mathrm{Cu} \end{array} \tag{8.10.1}$$

may be regarded as denoting a copper *terminal* attached to a zinc *electrode* dipping into a solution I containing zinc ions; this solution is in contact with another solution II containing silver ions in which there is dipping a silver electrode attached to another copper terminal. We shall use the following superscripts to denote the several phases:

$'$	the copper terminal on the left
$^{\mathrm{Zn}}$	the zinc electrode
$^{\mathrm{I}}$	the solution on the left
$^{\mathrm{II}}$	the solution on the right
$^{\mathrm{Ag}}$	the silver electrode
$''$	the copper terminal on the right.

In the metal phases, since there is equilibrium between electrons, metallic ions, and the metal atoms, we have

$$\tfrac{1}{2}\mu'_{\mathrm{Cu}^{2+}}+\mu'_{\mathrm{el}^-}=\tfrac{1}{2}\mu''_{\mathrm{Cu}^{2+}}+\mu''_{\mathrm{el}^-}=\tfrac{1}{2}\mu^{\mathrm{Cu}}_{\mathrm{Cu}} \qquad 8.10.2$$

$$\tfrac{1}{2}\mu^{\mathrm{Zn}}_{\mathrm{Zn}^{2+}}+\mu^{\mathrm{Zn}}_{\mathrm{el}^-}=\tfrac{1}{2}\mu^{\mathrm{Zn}}_{\mathrm{Zn}} \qquad 8.10.3$$

$$\mu^{\mathrm{Ag}}_{\mathrm{Ag}^+}+\mu^{\mathrm{Ag}}_{\mathrm{el}^-}=\mu^{\mathrm{Ag}}_{\mathrm{Ag}}. \qquad 8.10.4$$

The contact equilibrium conditions are

$$\mu'_{\mathrm{el}^-}=\mu^{\mathrm{Zn}}_{\mathrm{el}^-} \qquad 8.10.5$$

$$\mu^{\mathrm{Zn}}_{\mathrm{Zn}^{2+}}=\mu^{\mathrm{I}}_{\mathrm{Zn}^{2+}} \qquad 8.10.6$$

$$\mu^{\mathrm{II}}_{\mathrm{Ag}^+}=\mu^{\mathrm{Ag}}_{\mathrm{Ag}^+} \qquad 8.10.7$$

$$\mu^{\mathrm{Ag}}_{\mathrm{el}^-}=\mu''_{\mathrm{el}^-}. \qquad 8.10.8$$

From (5) and (8) we deduce

$$\mu''_{\mathrm{el}^-}-\mu'_{\mathrm{el}^-}=\mu^{\mathrm{Ag}}_{\mathrm{el}^-}-\mu^{\mathrm{Zn}}_{\mathrm{el}^-} \qquad 8.10.9$$

and so using (3) and (4)

$$\mu''_{\mathrm{el}^-}-\mu'_{\mathrm{el}^-}=\mu^{\mathrm{Ag}}_{\mathrm{Ag}}-\tfrac{1}{2}\mu^{\mathrm{Zn}}_{\mathrm{Zn}}-\mu^{\mathrm{Ag}}_{\mathrm{Ag}^+}+\tfrac{1}{2}\mu^{\mathrm{Zn}}_{\mathrm{Zn}^{2+}} \qquad 8.10.10$$

and then using (6) and (7)

$$\mu''_{\mathrm{el}^-}-\mu'_{\mathrm{el}^-}=\mu^{\mathrm{Ag}}_{\mathrm{Ag}}-\tfrac{1}{2}\mu^{\mathrm{Zn}}_{\mathrm{Zn}}-\mu^{\mathrm{II}}_{\mathrm{Ag}^+}+\tfrac{1}{2}\mu^{\mathrm{I}}_{\mathrm{Zn}^{2+}}. \qquad 8.10.11$$

We may further write

$$\mu''_{\mathrm{el}^-}-\mu'_{\mathrm{el}^-}=-F(\psi''-\psi') \qquad 8.10.12$$

where $\psi''-\psi'$ denotes the electrical potential difference between the two copper terminals. It is evident from relations (5) and (8) that the value of (12) would be the same if both copper terminals were replaced by any other metal provided both were of the same metal. Thus $\psi''-\psi'$ is determined by the nature of the two electrodes and of the two solutions. The electric potential difference $\psi''-\psi'$ is called the *electromotive force* of the cell and is denoted by E. We accordingly replace (12) by

$$\mu''_{\mathrm{el}^-}-\mu'_{\mathrm{el}^-}=-FE. \qquad 8.10.13$$

Substituting (13) into (11) we then obtain

$$-FE=\mu^{\mathrm{Ag}}_{\mathrm{Ag}}-\tfrac{1}{2}\mu^{\mathrm{Zn}}_{\mathrm{Zn}}-\mu^{\mathrm{II}}_{\mathrm{Ag}^+}+\tfrac{1}{2}\mu^{\mathrm{I}}_{\mathrm{Zn}^{2+}}\,. \qquad 8.10.14$$

We shall now assume that there is at least one anion, say NO_3^- present in both solutions I and II so that

$$\tfrac{1}{2}\mu^{\mathrm{I}}_{\mathrm{Zn}^{2+}}=\tfrac{1}{2}\mu^{\mathrm{I}}_{\mathrm{Zn(NO_3)_2}}-\mu^{\mathrm{I}}_{\mathrm{NO}_3^-} \qquad 8.10.15$$

$$\mu^{\mathrm{II}}_{\mathrm{Ag}^+}=\mu^{\mathrm{II}}_{\mathrm{AgNO_3}}-\mu^{\mathrm{II}}_{\mathrm{NO}_3^-}\,. \qquad 8.10.16$$

Using (15) and (16) we can rewrite (14) as

$$\begin{aligned} FE=&\{\tfrac{1}{2}\mu^{\mathrm{Zn}}_{\mathrm{Zn}}-\tfrac{1}{2}\mu^{\mathrm{I}}_{\mathrm{Zn(NO_3)_2}}+RT\ln m^{\mathrm{I}}_{\mathrm{NO}_3^-}\}\\ &+\{\mu^{\mathrm{I}}_{\mathrm{NO}_3^-}-\mu^{\mathrm{II}}_{\mathrm{NO}_3^-}+RT\ln(m^{\mathrm{II}}_{\mathrm{NO}_3^-}/m^{\mathrm{I}}_{\mathrm{NO}_3^-})\}\\ &-\{\mu^{\mathrm{Ag}}_{\mathrm{Ag}}-\mu^{\mathrm{II}}_{\mathrm{AgNO_3}}+RT\ln m^{\mathrm{II}}_{\mathrm{NO}_3^-}\}. \end{aligned} \qquad 8.10.17$$

We have now a formula for E containing three terms in { } of which the first relates only to the Zn electrode and the solution around this electrode and the last relates only to the Ag electrode and the solution around this electrode. The middle term on the other hand is independent of the nature of the electrodes and relates to an anion present in both solutions. One might be inclined to call the first of these three terms the *electrode potential* of the Zn electrode, the second the *liquid–liquid junction potential*, and the last the *electrode potential* of the silver. Such a procedure is harmless provided it is realized that

(a) this decomposition of E into three terms is affected by our arbitrary choice of the anion NO_3^- for use in our formulae;
(b) other alternative decompositions of E into three terms can be obtained by the arbitrary choice of some other ion instead of NO_3^- in our formulae;
(c) any such decomposition of E is no more nor less fundamental than another;
(d) there is in general no means of decomposing E into three terms which is less arbitrary than the one described.

In view of some inevitable arbitrariness in the decomposition of the electromotive force of a cell into two *electrode potentials* and a *liquid–liquid junction potential*, we shall for the most part abandon any attempt at such a decomposition. We shall accordingly in the next section derive a general formula for the electromotive force of any cell by a more powerful method which makes no reference at all to the localization of separate terms in the electromotive force. Before proceeding to this general treatment, we shall however draw attention to a special case where the arbitrariness referred to above effectively disappears.

Reverting to formula (17), let us now consider the particular case where the molalities of Zn^{2+} and Ag^{+} in the two electrode solutions are extremely small compared with the molalities of other ions in these solutions and the compositions of the two electrode solutions are apart from their content of Zn^{2+} and Ag^{+} nearly identical. Under these particular conditions we may regard the two electrode solutions as effectively identical except with regard to the equilibrium between solution and electrode. We may accordingly drop the superscripts $^{\mathrm{I}}$ and $^{\mathrm{II}}$ so that (17) reduces to

$$FE=\{\tfrac{1}{2}\mu_{\mathrm{Zn}}^{\mathrm{Zn}}-\tfrac{1}{2}\mu_{\mathrm{Zn(NO_3)_2}}\}-\{\mu_{\mathrm{Ag}}^{\mathrm{Ag}}-\mu_{\mathrm{AgNO_3}}\} \tag{8.10.18}$$

where the μ's without superscripts refer to the solution. We may then regard the cell (1) under consideration as

$$\begin{array}{c|c|c|c|c}\mathrm{Cu} & \mathrm{Zn} & \begin{array}{c}\text{Solution containing}\\ \mathrm{Zn}^{2+}\text{ and }\mathrm{Ag}^{+}\end{array} & \mathrm{Ag} & \mathrm{Cu}\end{array} \tag{8.10.19}$$

bearing in mind that in reality the Ag^{+} must be kept away from the Zn electrode to avoid irreversible dissolution of Zn with plating out of Ag.

It is usual to describe certain cells in this manner as if containing only one solution, but in reality there must always be some real, though possibly small difference between the composition of the two electrode solutions. Consider for example the cell commonly described as

$$\mathrm{Pt,\ H_2}\,|\,\text{Aqueous solution of HCl}\,|\,\mathrm{AgCl}\,|\,\mathrm{Ag}\,|\,\mathrm{Pt} \tag{8.10.20}$$

This description implies that an electrode consisting of platinum in contact with hydrogen and another electrode consisting of a mixture of AgCl and Ag are dipping into the same solution. In fact the platinum dips into a solution saturated with H_2, but containing no AgCl, while the silver is immersed in a solution saturated with AgCl but containing no hydrogen. If in fact any part of the solution contained both hydrogen and silver chloride, these might* react irreversibly to give silver and hydrogen chloride. Thus the cell is more accurately described by

$$\begin{array}{c|c|c|c|c|c}\mathrm{Pt,\ H_2} & \begin{array}{c}\text{Solution I}\\ \text{Aqueous solution}\\ \text{of HCl saturated}\\ \text{with }\mathrm{H_2}\end{array} & \begin{array}{c}\text{Solution II}\\ \text{Aqueous solution}\\ \text{of HCl saturated}\\ \text{with AgCl}\end{array} & \mathrm{AgCl} & \mathrm{Ag} & \mathrm{Pt}\end{array} \tag{8.10.21}$$

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* Actually in the case of this cell the irreversible process will usually be too slow to affect the accuracy of the electromotive force measurements.

By an analysis of (21) similar to that applied to (1) it can be shown that the electromotive force E is given accurately by

$$FE = \tfrac{1}{2}\mu^{\mathrm{G}}_{\mathrm{H}_2} - \mu^{\mathrm{I}}_{\mathrm{H}^+} + \mu^{\mathrm{AgCl}}_{\mathrm{AgCl}} - \mu^{\mathrm{Ag}}_{\mathrm{Ag}} - \mu^{\mathrm{II}}_{\mathrm{Cl}^-} \qquad 8.10.22$$

where the superscript $^{\mathrm{G}}$ denotes the gas phase. Since however as far as the HCl is concerned we may regard the solutions I and II as essentially identical we may drop these superscripts and (22) reduces to

$$FE = \tfrac{1}{2}\mu^{\mathrm{G}}_{\mathrm{H}_2} + \mu^{\mathrm{AgCl}}_{\mathrm{AgCl}} - \mu^{\mathrm{Ag}}_{\mathrm{Ag}} - \mu_{\mathrm{HCl}} \qquad 8.10.23$$

where μ_{HCl} denotes the chemical potential of HCl in the solution.

§8.11 *General treatment of electromotive force*

We now proceed to a more general treatment applicable to any galvanic cell. We begin by describing the characteristics common to all such cells. In so doing it is convenient to assume that the system to which we refer as the *cell* is terminated at both ends by terminals of the same metal. The essential characteristic of the galvanic cell is that a process involving ions can take place in it in such a manner that the process is necessarily accompanied by a transfer of electric charge from one terminal to the other without building up any charge in any of the intermediate phases of the cell. Moreover the charge which flows from the one terminal to the other is directly proportional to the change in the extent of the process.

For example in the cell, already discussed in the previous section,

$$\mathrm{Pt},\ \mathrm{H}_2 \,|\, \text{Aqueous solution of HCl} \,|\, \mathrm{AgCl} \,|\, \mathrm{Ag} \,|\, \mathrm{Pt} \qquad 8.11.1$$

the process accompanying the flow of one mole of positive charge from the left to the right is

$$\tfrac{1}{2}\mathrm{H}_2(\mathrm{g}) + \mathrm{AgCl}(\mathrm{s}) \rightarrow \mathrm{Ag}(\mathrm{s}) + \mathrm{HCl}(\mathrm{aq}) \qquad 8.11.2$$

where (g) denotes gas, (s) denotes solid, and (aq) denotes aqueous solution.

We now suppose the two terminals of the cell to be put into contact respectively with two points of a potentiometer bridge so placed that the electric potential of the right contact exceeds that of the left contact by an amount E'. Then in general an electric current will flow through the cell and between the two points of contact with the potentiometer bridge. If either of the points of contact is moved along the bridge the current will increase or decrease and it will change sign when E' has a certain value E. When E' is slightly less than E there will be a flow of current from left to right in the cell and from right to left in the potentiometer bridge; this flow of current will be accompanied by a well-defined chemical change in the cell. When E' is slightly greater than E there will be a flow of current in the opposite direction and the accompanying chemical change in the cell will also be reversed. When E' is equal to E there will be no flow of current and no chemical change, but by a small shift in the point of contact between cell terminal and potentiometer bridge a small current can be made to flow in either direction. This is a typical and a particularly realistic example of a *reversible process*. The value E of E' at which the current changes sign is the *electromotive force* of the cell. We note that a positive value of E means that the electrode on the right is positive.

We now stipulate that $E'=E$ so that the electromotive force of the cell is balanced against the potential difference in the potentiometer bridge and we consider the flow of one mole of positive charge from left to right in the cell, the temperature being maintained constant throughout and the pressure on every phase being kept constant. The pressures on different phases will usually, but not necessarily always, be all equal. Then since, as we have seen, this process is reversible and isothermal, it follows from (1.33.5) that the work w done on the cell is equal to the increase in the Helmholtz function, that is to say

$$w=\Delta\mathcal{F}. \qquad 8.11.3$$

In the present case w consists of two distinct parts, namely

(a) the work $-\Sigma_\alpha P^\alpha \Delta V^\alpha$ done by the pressures P^α acting on the several phases α,

(b) the electrical work $-FE$ done by the potentiometer on the cell in transferring one mole of positive charge through a potential difference E.

We may therefore replace (3) by

$$-FE=\Delta\mathcal{F}+\sum_\alpha P^\alpha \Delta V^\alpha=\Delta G. \qquad 8.11.4$$

It must be emphasized that the symbol Δ in both (3) and (4) denotes the increase of a function when the process taking place is that associated with the flow in the cell of *one mole of positive charge from the left to the right*.

From (4) we see that the electrical work obtainable from a reversible isothermal process, at constant pressure on each phase, is equal to the decrease in the Gibbs function G.

§8.12 *Temperature dependence*

By combining (8.11.4) with the Gibbs–Helmholtz relation (1.49.5) we obtain*

$$F(E-T\partial E/\partial T)=-\Delta H. \qquad 8.12.1$$

By subtracting (1) from (8.11.4), or by a more direct method, we obtain

$$F(\partial E/\partial T)=\Delta S. \qquad 8.12.2$$

In both (1) and (2) the symbol Δ denotes increase when the chemical change takes place which accompanies the flow of one mole of positive charge from left to right in the cell.

It is perhaps worth while drawing attention to the physical meaning of ΔH and ΔS. If the cell is kept in a thermostat and balanced against a potentiometer so that any flow of current is reversible, then when one mole of positive charge flows from left to right in the cell

(a) the work done on the cell by the potentiometer is $-FE$
(b) the work done on the cell by external pressures is $-\Sigma_\alpha P^\alpha \Delta V^\alpha$
(c) the heat absorbed is $T\Delta S=FT(\partial E/\partial T)$
(d) the increase in the energy of the cell is the sum of the above three terms namely $\Delta U=-FE-\Sigma_\alpha P^\alpha \Delta V^\alpha+FT(\partial E/\partial T)$
(e) the increase in the enthalpy is $\Delta H=\Delta U+\Sigma_\alpha P^\alpha \Delta V^\alpha=-F\{E-T(\partial E/\partial T)\}$.

If, on the other hand, the cell is kept in a thermostat and short-circuited so that the process takes place irreversibly without the performance of electrical work, then when the process takes place to the same extent as before,

(a) the electrical work done on the cell is zero
(b) the work done on the cell by external pressures is $-\Sigma_\alpha P^\alpha \Delta V^\alpha$
(c) the heat absorbed is ΔH.

§8.13 *Application of Nernst's heat theorem*

The measurement of electromotive force provides a method of determining ΔG for the accompanying chemical reaction; this can be combined with a value of ΔH, determined calorimetrically, so as to obtain the value of ΔS. Since however the magnitude of $T\Delta S$ is often small compared with those of ΔG and ΔH, the relative error in ΔS determined in this way can be large.

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* Although formula (1.49.5) is generally called the Gibbs–Helmholtz relation, it is in fact due to Gibbs, while its corollary (8.12.1) was derived by Helmholtz.

If on the other hand accurate measurements of electromotive force are made over a range of temperatures so as to give an accurate value of the temperature coefficient of the electromotive force, this provides directly the value of ΔS for the cell reaction. Values of ΔS thus obtained for any chemical reaction between only solid phases may be used to test Nernst's heat theorem, provided heat capacity data down to low temperatures are available for each substance. The procedure is illustrated by the following example.*

In the cell

$$\mathrm{Pt}\left|\mathrm{Pb}^{(\mathrm{Hg})}\right|\begin{array}{l}\text{Solution of Pb salt}\\ \text{saturated with } \mathrm{PbI_2}\end{array}\left|\mathrm{PbI_2}\right|\mathrm{I}\,\big|\,\mathrm{Pt} \qquad 8.13.1$$

where the superscript $^{(\mathrm{Hg})}$ denotes that the lead is in the form of an amalgam, the chemical process when one mole of positive charge flows from left to right is

$$\tfrac{1}{2}\mathrm{Pb}^{(\mathrm{Hg})}+\mathrm{I}\rightarrow\tfrac{1}{2}\mathrm{PbI_2}\,. \qquad 8.13.2$$

For the cell at 25 °C it is found that

$$E=893.62\ \mathrm{mV} \qquad 8.13.3$$

$$\partial E/\partial T=(-0.042\pm0.005)\ \mathrm{mV\ K^{-1}}. \qquad 8.13.4$$

In the cell

$$\mathrm{Pt}\,|\,\mathrm{Pb}^{(\mathrm{Hg})}\,|\,\mathrm{PbI_2}\,|\,\text{Solution of KI}\,|\,\mathrm{AgI}\,|\,\mathrm{Ag}\,|\,\mathrm{Pt} \qquad 8.13.5$$

where $\mathrm{Pb}^{(\mathrm{Hg})}$ denotes the same lead amalgam as in (1), the cell process accompanied by the flow of one mole of positive charge from left to right is

$$\tfrac{1}{2}\mathrm{Pb}^{(\mathrm{Hg})}+\mathrm{AgI}\rightarrow\tfrac{1}{2}\mathrm{PbI_2}+\mathrm{Ag}. \qquad 8.13.6$$

For this cell at 25 °C it is found that†

$$E=(207.8\pm0.2)\ \mathrm{mV} \qquad 8.13.7$$

$$\partial E/\partial T=(-0.188\pm0.002)\ \mathrm{mV\ K^{-1}}. \qquad 8.13.8$$

The data for neither of these cells can be used directly for testing Nernst's heat theorem owing to lack of calorimetric data for $\mathrm{PbI_2}$ down to low temperatures. However by subtracting (7) from (3) and (8) from (4) we obtain for a cell at 25 °C in which the cell process is

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* Webb, J. Phys. Chem. 1925 **29** 827.

† Gerke, J. Amer. Chem. Soc. 1922 **44** 1703.

$$\mathrm{Ag+I\rightarrow AgI} \qquad 8.13.9$$

$$E=(685.8\pm0.2)\,\mathrm{mV} \qquad 8.13.10$$

$$\partial E/\partial T=(0.146\pm0.004)\,\mathrm{mV\ K^{-1}}. \qquad 8.13.11$$

Multiplying (10) and (11) by

$$\begin{aligned} F&=0.9649\times10^{5}\ \mathrm{C\ mole^{-1}}\\ &=0.09649\ \mathrm{kJ\ mV^{-1}\ mole^{-1}} \end{aligned} \qquad 8.13.12$$

and using (8.11.4) and (8.12.2), we obtain for the process (9) at 298 K

$$\Delta G=-66.17\ \mathrm{kJ\ mole^{-1}} \qquad (T=298\ \mathrm{K}) \qquad 8.13.13$$

$$\Delta S=(14.06\pm0.4)\ \mathrm{J\ K^{-1}\ mole^{-1}} \qquad (T=298\ \mathrm{K}). \qquad 8.13.14$$

From (13) and (14) we derive incidentally

$$\begin{aligned} \Delta H&=\Delta G+T\Delta S\\ &=(-66.17+4.22)\ \mathrm{kJ\ mole^{-1}}\\ &=-61.95\ \mathrm{kJ\ mole^{-1}}\\ &=-14.81\ \mathrm{kcal\ mole^{-1}} \end{aligned} \qquad 8.13.15$$

with which may be compared the calorimetrically measured value* -14.97 kcal mole^{-1}.

We must now convert the value of ΔS at 298 K given by (14) to the corresponding value in the limit $T\rightarrow0$. The following calorimetric data are available† for $S(298\ \mathrm{K})-S(0)$.

$$\mathrm{AgI} \qquad (115.5\pm1.2)\ \mathrm{J\ K^{-1}\ mole^{-1}} \qquad 8.13.16$$

$$\mathrm{Ag} \qquad (42.5\pm0.4)\ \mathrm{J\ K^{-1}\ mole^{-1}} \qquad 8.13.17$$

$$\mathrm{I} \qquad 58.4\ \mathrm{J\ K^{-1}\ mole^{-1}}. \qquad 8.13.18$$

Although accurate calorimetric data for AgI are available down to $T=15$ K, at this temperature C/R has the exceptionally high value 1.45 which leads to the rather high uncertainty, due to the extrapolation to $T=0$, shown in (16).

Combining (16), (17), and (18) we obtain for the process (9)

$$\Delta S(298\ \mathrm{K})-\Delta S(0)=(14.6\pm1.2)\ \mathrm{J\ K^{-1}\ mole^{-1}}. \qquad 8.13.19$$

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* Webb, J. Phys. Chem. 1925 **29** 827.

† AgI, see Pitzer, J. Amer. Chem. Soc. 1941 **63** 516; Ag, see Griffiths and Griffiths, Proc. Roy. Soc. A 1914 **90** 557; I, see Lange, Z. Physik. Chem. 1924 **110** 343. Experimental data for Ag and I recomputed by Kelley, U.S. Bureau of Mines 1932 Bulletin 350.

Now comparing (19) with (14) we obtain

$$\Delta S(0) = (-0.5 \pm 1.3)\ \text{J K}^{-1}\ \text{mole}^{-1}. \qquad 8.13.20$$

so that within the experimental accuracy $\Delta S(0)=0$ in agreement with Nernst's heat theorem.

§8.14 *Cells without transference*

When a galvanic cell contains only two solutions, one surrounding each electrode, and these two solutions are so nearly alike in composition that they may be regarded as identical except with respect to the reactions at the electrodes, the cell is called a *cell without transference.* When a current flows through the cell there is in fact necessarily transference of some electrolyte from the one electrode to the other, but if the two electrode solutions are of nearly identical composition the changes in the chemical potentials of the electrolytes transferred are negligible and so this transference is without importance.

As a typical example of a *cell without transference* we again consider the cell

$$\begin{array}{l|c|c|c|c|l} & \text{Solution I} & \text{Solution II} & & & \\ \text{Pt, H}_2 & \text{Aqueous HCl} & \text{Aqueous HCl} & \text{AgCl} & \text{Ag} & \text{Pt} \\ & \text{saturated with H}_2 & \text{saturated with AgCl} & & & \end{array} \qquad 8.14.1$$

When one mole of positive charge flows from the left to the right, the following changes take place:

(a) at the left electrode

$$\tfrac{1}{2}\text{H}_2(\text{g}) \rightarrow \text{H}^+(\text{aq I}) \qquad 8.14.2$$

(b) at the right electrode

$$\text{AgCl(s)} \rightarrow \text{Ag(s)} + \text{Cl}^-(\text{aq II}) \qquad 8.14.3$$

(c) there is a simultaneous transfer of some H^+ ions from left to right and of Cl^- ions from right to left such that the net transfer of charge from left to right is one mole and that electrical neutrality is preserved in both electrode solutions.

Since however we ignore the effect on the properties of the HCl of saturating the solution with either H_2 or AgCl, we need not distinguish between the two electrode solutions. We may therefore replace (1) by

$$\text{Pt, H}_2\,|\,\text{Aqueous HCl}\,|\,\text{AgCl}\,|\,\text{Ag}\,|\,\text{Pt} \qquad 8.14.4$$

Correspondingly (a) and (b) reduce to

$$\text{(a)}\qquad \tfrac{1}{2}\mathrm{H_2(g)}\rightarrow \mathrm{H^+(aq)} \tag{8.14.5}$$

$$\text{(b)}\qquad \mathrm{AgCl(s)}\rightarrow \mathrm{Ag(s)}+\mathrm{Cl^-(aq)} \tag{8.14.6}$$

and (c) may be ignored. Thus the process accompanying the flow of one mole of charge reduces to the chemical change

$$\tfrac{1}{2}\mathrm{H_2(g)}+\mathrm{AgCl(s)}\rightarrow \mathrm{Ag(s)}+\mathrm{H^+(aq)}+\mathrm{Cl^-(aq)} \tag{8.14.7}$$

for which

$$\Delta G=\mu_{\mathrm{Ag}}^{\mathrm{Ag}}+\mu_{\mathrm{HCl}}-\tfrac{1}{2}\mu_{\mathrm{H_2}}^{\mathrm{G}}-\mu_{\mathrm{AgCl}}^{\mathrm{AgCl}} \tag{8.14.8}$$

where the superscript $^{\mathrm{G}}$ denotes the gas phase and μ_{HCl} denotes the chemical potential of HCl in the solution.

Substituting (8) into (8.11.4) we obtain

$$FE=-\mu_{\mathrm{Ag}}^{\mathrm{Ag}}-\mu_{\mathrm{HCl}}+\tfrac{1}{2}\mu_{\mathrm{H_2}}^{\mathrm{G}}+\mu_{\mathrm{AgCl}}^{\mathrm{AgCl}} \tag{8.14.9}$$

in agreement with (8.10.23).

Explicit formulae for all cells without transference can be obtained similarly. We shall merely quote, without detailed derivation, one other example

$$\mathrm{Pt}\left|\begin{array}{c}\text{Solution containing}\\ \mathrm{Sn^{2+}}\text{ and }\mathrm{Sn^{4+}}\end{array}\right|\begin{array}{c}\text{Solution containing}\\ \mathrm{Fe^{2+}}\text{ and }\mathrm{Fe^{3+}}\end{array}\left|\mathrm{Pt}\right. \tag{8.14.10}$$

Provided that both electrode solutions contain a preponderating excess of other electrolytes and have nearly the same composition so that we may regard them as a single solution, the process accompanying the flow of one mole of positive charge from left to right is the chemical change

$$\tfrac{1}{2}\mathrm{Sn^{2+}}+\mathrm{Fe^{3+}}\rightarrow\tfrac{1}{2}\mathrm{Sn^{4+}}+\mathrm{Fe^{2+}} \tag{8.14.11}$$

for which

$$\Delta G=\tfrac{1}{2}\mu_{\mathrm{Sn^{4+}}}+\mu_{\mathrm{Fe^{2+}}}-\tfrac{1}{2}\mu_{\mathrm{Sn^{2+}}}-\mu_{\mathrm{Fe^{3+}}}\,. \tag{8.14.12}$$

Consequently

$$\begin{aligned}FE&=\tfrac{1}{2}\mu_{\mathrm{Sn^{2+}}}+\mu_{\mathrm{Fe^{3+}}}-\tfrac{1}{2}\mu_{\mathrm{Sn^{4+}}}-\mu_{\mathrm{Fe^{2+}}}\\ &=\tfrac{1}{2}\mu_{\mathrm{SnCl_2}}+\mu_{\mathrm{FeCl_3}}-\tfrac{1}{2}\mu_{\mathrm{SnCl_4}}-\mu_{\mathrm{FeCl_2}}\end{aligned} \tag{8.14.13}$$

provided there is some $\mathrm{Cl^-}$ ion in the solutions.

§8.15 *Standard electromotive force*

Let us return to the cell described by (8.14.4) and rewrite formula (8.14.9) for its electromotive force in terms of absolute activities. We have

$$FE/RT = -\ln \lambda_{\mathrm{Ag}}^{\mathrm{S}} - \ln \lambda_{\mathrm{H}^+} - \ln \lambda_{\mathrm{Cl}^-} + \tfrac{1}{2} \ln \lambda_{\mathrm{H}_2}^{\mathrm{G}} + \ln \lambda_{\mathrm{AgCl}}^{\mathrm{S}} \qquad 8.15.1$$

where we have denoted the solid phase by the superscript $^{\mathrm{S}}$, the gas phase by the superscript $^{\mathrm{G}}$, and the liquid phase by no superscript. Using (7.09.1) and (3.17.1) we can rewrite (1) as

$$FE/RT = FE^{\ominus}/RT - \ln(m_{\mathrm{H}^+} m_{\mathrm{Cl}^-} \gamma_{\mathrm{H,Cl}}^2) + \tfrac{1}{2} \ln(p_{\mathrm{H}_2}/P^{\ominus}) \qquad 8.15.2$$

where $P^{\ominus}$ denotes the standard pressure, taken to be one atmosphere, and $E^{\ominus}$ is defined by

$$FE^{\ominus}/RT = -\ln \lambda_{\mathrm{Ag}}^{\mathrm{S}} - \ln \lambda_{\mathrm{H}^+}^{\ominus} - \ln \lambda_{\mathrm{Cl}^-}^{\ominus} + \tfrac{1}{2} \ln \lambda_{\mathrm{H}_2}^{\ominus} + \ln \lambda_{\mathrm{AgCl}}^{\mathrm{S}}. \qquad 8.15.3$$

This quantity $E^{\ominus}$ is independent of the composition of the solution and independent of the pressure of the gaseous hydrogen and is called the *standard electromotive force* of cells having the specified electrodes in the specified solvent at a specified temperature.

Similarly the electromotive force of the cell described by (8.14.10) can be expressed by the formula

$$\frac{FE}{RT} = \frac{FE^{\ominus}}{RT} - \tfrac{1}{2} \ln \frac{m_{\mathrm{Sn}^{4+}} \gamma_{\mathrm{Sn}^{4+}}}{m_{\mathrm{Sn}^{2+}} \gamma_{\mathrm{Sn}^{2+}}} + \ln \frac{m_{\mathrm{Fe}^{3+}} \gamma_{\mathrm{Fe}^{3+}}}{m_{\mathrm{Fe}^{2+}} \gamma_{\mathrm{Fe}^{2+}}} \qquad 8.15.4$$

in which the standard electromotive force $E^{\ominus}$ is defined by

$$\frac{FE^{\ominus}}{RT} = -\tfrac{1}{2} \ln \frac{\lambda_{\mathrm{Sn}^{4+}}^{\ominus}}{\lambda_{\mathrm{Sn}^{2+}}^{\ominus}} + \ln \frac{\lambda_{\mathrm{Fe}^{3+}}^{\ominus}}{\lambda_{\mathrm{Fe}^{2+}}^{\ominus}}. \qquad 8.15.5$$

It can readily be verified that in all these formulae only such combinations of $\lambda^{\ominus}$'s and of γ's occur as satisfy the condition (7.04.17) with (7.04.18).

Formulae such as the above have two applications. Firstly by making measurements of E over a range of molalities as low as possible and extrapolation with the help of formulae such as those of §7.20 we can obtain the value of the standard electromotive force $E^{\ominus}$. Secondly having determined the value of $E^{\ominus}$ by extrapolation we can insert this value into the formulae and so obtain information about certain combinations of activity coefficients in solutions of given composition.

§8.16 *Numerical example*

We shall illustrate the procedure described in the previous section by an example. We choose the cell

$$\text{Pt, H}_2 \left| \begin{array}{c}\text{Aqueous HCl}\\ \text{molality } m\end{array} \right| \text{HgCl} \,\Big|\, \text{Hg} \qquad 8.16.1$$

for which there exist measurements* at 25 °C of exceptionally high accuracy. The electromotive force of this cell is given by

$$FE = FE^{\ominus} - 2RT \ln m - 2RT \ln \gamma \qquad 8.16.2$$

where m is the molality and γ the mean activity coefficient of HCl. We assume that at sufficiently high dilutions γ can be represented by

$$\ln \gamma = -\alpha m^{\frac{1}{2}}(1+m^{\frac{1}{2}})^{-1} + 2\beta m \qquad 8.16.3$$

where α has the value determined by (7.17.10) and β is an adjustable constant. We now define the experimental quantity $E^{\ominus\prime}$ by

$$E^{\ominus\prime} = E + (2RT/F) \ln m - (2RT/F)\alpha m^{\frac{1}{2}}(1+m^{\frac{1}{2}})^{-1}. \qquad 8.16.4$$

Using (3) and (4) in (2) we obtain

$$E^{\ominus\prime} = E^{\ominus} - (4RT/F)\beta m. \qquad 8.16.5$$

If then we plot $E^{\ominus\prime}$ against m, in so far as γ can be represented by formula (3), we shall obtain a straight line of slope $-4RT\beta/F$ and of intercept at $m=0$ equal to $E^{\ominus}$. This plot is shown in figure 8.1 from which we find that $E^{\ominus} = 267.96$ mV and $\beta = 0.270$. We further see from the diagram that with

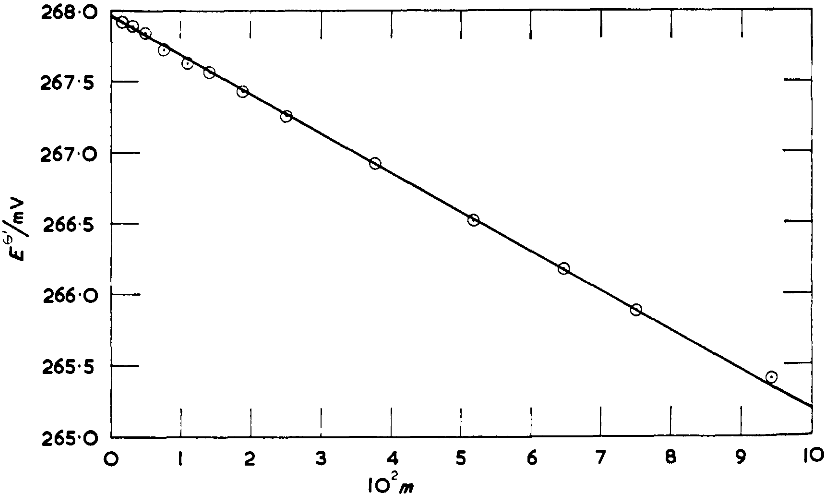

Fig. 8.1. Determination of $E^{\ominus}$ by extrapolation to $m=0$

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* Hills and Ives, J. Chem. Soc. 1951 315.

this value of β formula (3) is as accurate as the experimental measurements for all values of m up to about 0.08.

§8.17 *Standard electromotive force of half-cell*

Let us consider the three cells

$$\begin{array}{l|c|c|c|c|l} \text{Pt, H}_2 & \begin{array}{c}\text{Solution}\\ \text{containing H}^+\end{array} & \begin{array}{c}\text{Solution}\\ \text{containing Cl}^-\end{array} & \text{AgCl} & \text{Ag} & \text{Pt} \end{array} \qquad 8.17.1$$

$$\begin{array}{l|c|c|l} \text{Pt, H}_2 & \begin{array}{c}\text{Solution}\\ \text{containing H}^+\end{array} & \begin{array}{c}\text{Solution}\\ \text{containing}\\ \text{Sn}^{2+}\text{ and Sn}^{4+}\end{array} & \text{Pt} \end{array} \qquad 8.17.2$$

$$\begin{array}{l|c|c|c|c|l} \text{Pt} & \begin{array}{c}\text{Solution}\\ \text{containing}\\ \text{Sn}^{2+}\text{ and Sn}^{4+}\end{array} & \begin{array}{c}\text{Solution}\\ \text{containing Cl}^-\end{array} & \text{AgCl} & \text{Ag} & \text{Pt} \end{array} \qquad 8.17.3$$

In each cell we assume that the two electrode solutions have nearly the same composition. The standard electromotive forces of the three cells are given respectively by

$$FE^{\ominus}/RT = \tfrac{1}{2}\ln\lambda^{\ominus}_{H_2} - \ln\lambda^{\ominus}_{H^+} + \ln\lambda^{S}_{AgCl} - \ln\lambda^{S}_{Ag} - \ln\lambda^{\ominus}_{Cl^-} \qquad 8.17.4$$

$$FE^{\ominus}/RT = \tfrac{1}{2}\ln\lambda^{\ominus}_{H_2} - \ln\lambda^{\ominus}_{H^+} + \tfrac{1}{2}\ln(\lambda^{\ominus}_{Sn^{4+}}/\lambda^{\ominus}_{Sn^{2+}}) \qquad 8.17.5$$

$$FE^{\ominus}/RT = -\tfrac{1}{2}\ln(\lambda^{\ominus}_{Sn^{4+}}/\lambda^{\ominus}_{Sn^{2+}}) + \ln\lambda^{S}_{AgCl} - \ln\lambda^{S}_{Ag} - \ln\lambda^{\ominus}_{Cl^-} \qquad 8.17.6$$

and we observe that the value of $E^{\ominus}$ for the third cell is equal to the difference between the values of $E^{\ominus}$ for the first and second cells. It is clear from this example that if there are available n different kinds of electrodes, although these can be paired to give $\frac{1}{2}n(n-1)$ different cells, only $n-1$ of these $E^{\ominus}$ values are independent. For example if we know the $E^{\ominus}$ values for all cells in which one of the electrodes is the Pt, H_2 electrode, then the $E^{\ominus}$ values of all other combinations can be obtained by adding and subtracting.

The $E^{\ominus}$ value of a cell consisting of an electrode α and a Pt,H_2 electrode is called the *standard electromotive force of the half-cell* α. We recall the convention that a positive value of E means that the electrode on the right is positive. We shall now illustrate by an example how this convention is extended to the electromotive force of half-cells.

We may state that the right hand half-cell

$$\text{Cl}^- \mid \text{AgCl} \mid \text{Ag} \qquad 8.17.7$$

has the standard electromotive force $E^{\ominus}_{r} = 222.5$ mV at 25 °C. This means that the cell

$$\begin{array}{l|c|c|c|l} & \text{Solution} & \text{Solution} & & \\ \mathrm{Pt,\ H_2} & \text{containing } \mathrm{H^+} & \text{containing } \mathrm{Cl^-} & \mathrm{AgCl} & \mathrm{Ag} \end{array} \qquad 8.17.8$$

has $E^{\ominus} = 222.5$ mV with the electrode on the right positive. Alternatively we may state that the left hand half-cell

$$\mathrm{Ag} \mid \mathrm{AgCl} \mid \mathrm{Cl^-} \qquad 8.17.9$$

has the standard electromotive force $E_{\mathrm{l}}^{\ominus} = -222.5$ mV at 25 °C. This means that the cell

$$\begin{array}{l|c|c|c|l} & & \text{Solution} & \text{Solution} & \\ \mathrm{Ag} & \mathrm{AgCl} & \text{containing } \mathrm{Cl^-} & \text{containing } \mathrm{H^+} & \mathrm{Pt,\ H_2} \end{array} \qquad 8.17.10$$

has $E^{\ominus} = -222.5$ mV with the electrode on the right negative. These conventions, which are unambiguous, have now been internationally agreed.*

§8.18 *Cells with transference with two similar electrodes*

Any cell which does not satisfy the conditions in the definition of a cell without transference, is called a *cell with transference*. The detailed discussion of a *cell with transference* is more involved than that of a *cell without transference*. We shall initially restrict ourselves to the case that the two electrodes are of the same chemical nature so that the chemical processes taking place at the electrodes are the converse of each other. For example we may consider the cell

$$\begin{array}{l|c|c|c|c|c|l} & & \text{Solution I} & \text{Bridge} & \text{Solution II} & & \\ \mathrm{Ag} & \mathrm{AgCl} & \text{containing} & \text{solutions} & \text{containing} & \mathrm{AgCl} & \mathrm{Ag} \\ & & \mathrm{Cl^-} & & \mathrm{Cl^-} & & \end{array} \qquad 8.18.1$$

We assume that the two electrode solutions I and II are connected by *bridge solutions* in which the composition varies continuously. It is essential to exclude any discontinuity of composition, for in that case the passage of an infinitesimal current would not be reversible and it would not then be possible to apply thermodynamic equations. Suppose for example in two solutions in contact the cation $\mathrm{Na^+}$ were present in that on the left but not that on the right, while the cation $\mathrm{K^+}$ were present in the solution on the right but not that on the left. Then an infinitesimal current from left to right would transfer $\mathrm{Na^+}$ from the left solution to the right solution. Reversal of the current would on the other hand transfer $\mathrm{K^+}$ from the right solution to the left solution. If however any two solutions in contact differ only

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* I.U.P.A.C., C.R. XVII Conference 1953 p. 83; I.U.P.A.C. Manual of Physico-chemical Symbols and Terminology, Butterworths 1959.

infinitesimally in composition, the passage of current will be reversible. It is true that simultaneously there is taking place an irreversible diffusion between the two solutions tending to equalize their compositions.

This condition of continuity of composition is the only condition imposed on the nature of the bridge solutions. In view of this condition the compositions of the outermost bridge solutions are identical respectively with those of the electrode solutions. If the bridge solutions are formed by natural mixing or interdiffusion of the two electrode solutions, then their compositions throughout will be intermediate between those of the two electrode solutions. On the other hand the middle portion of the bridge solutions may consist of a solution of entirely different composition from either electrode solution, but such solution must be connected to each electrode solution through solutions of continuously varying composition. The formulae which we are about to derive are applicable to all cases, but we begin by considering the more elementary cell

$$\mathrm{Ag}\,\Big|\,\mathrm{AgCl}\,\Big|\,\begin{matrix}\text{Solution}\\ \text{molalities } m\end{matrix}\,\Big|\,\begin{matrix}\text{Solution}\\ \text{molalities } m+\mathrm{d}m\end{matrix}\,\Big|\,\mathrm{AgCl}\,\Big|\,\mathrm{Ag} \qquad 8.18.2$$

where the two electrode solutions differ only infinitesimally in composition.

Even in the elementary cell (2) there is not thermodynamic equilibrium and there is inevitably a state of interdiffusion between the two solutions. We are consequently compelled to introduce some assumption extraneous to classical thermodynamics which applies strictly only to equilibrium conditions. Initially we make the simplest, but not the least restrictive, assumption leading to correct conclusions. In chapter 13 it will be shown how the same conclusions can be reached by a less restrictive assumption. We here assume that the flow J_i per unit area per unit time of the ionic species i is directly proportional to the gradient of its electrochemical potential μ_i. We may, for simplicity and without any loss of generality in our conclusions, assume that the gradients are in the y-direction. Our assumption thus becomes

$$J_i = -L_i \mathrm{d}\mu_i/\mathrm{d}y \qquad 8.18.3$$

where L_i may depend on the composition of the solution but is independent of the gradient of the composition and independent of the flow. We consider the condition of zero electric current which exists when the cell circuit is open or alternatively when the cell is exactly balanced against a potentiometer bridge. At each electrode we have the equilibrium

$$\mathrm{Cl^-} + \mathrm{Ag} \rightleftharpoons \mathrm{AgCl} + \mathrm{el^-} \qquad 8.18.4$$

where $\mathrm{Cl^-}$ denotes chloride ion in solution and $\mathrm{el^-}$ denotes an electron in the silver. The condition for this equilibrium is

$$z_{\mathrm{Cl}^-}^{-1}\,\mathrm{d}\mu_{\mathrm{Cl}^-} = -\mathrm{d}\mu_{\mathrm{el}^-} \qquad 8.18.5$$

since the silver has the same chemical potential at both ends and likewise the silver chloride. The charge number of the chloride ion is of course -1, but we have deliberately displayed it as z_{Cl^-} in order to facilitate generalization to other cells having electrodes reversible with respect to ions other than the chloride ion. The electromotive force $\mathrm{d}E$ of the cell (2) is then given by

$$F\,\mathrm{d}E = -\mathrm{d}\mu_{\mathrm{el}^-} = z_{\mathrm{Cl}^-}^{-1}\,\mathrm{d}\mu_{\mathrm{Cl}^-} \qquad 8.18.6$$

which we may also write as

$$F\,\mathrm{d}E/\mathrm{d}y = z_{\mathrm{Cl}^-}^{-1}\,\mathrm{d}\mu_{\mathrm{Cl}^-}/\mathrm{d}y. \qquad 8.18.7$$

The condition for zero electric current is

$$\sum_i z_i J_i = 0. \qquad 8.18.8$$

Substituting (3) into (8) we have

$$\sum_i z_i L_i \,\mathrm{d}\mu_i/\mathrm{d}y = 0. \qquad 8.18.9$$

We now multiply (7) by $\Sigma_i z_i^2 L_i$ and subtract (9) obtaining

$$\sum_i z_i^2 L_i F\,\mathrm{d}E/\mathrm{d}y = \sum_i z_i^2 L_i(-z_i^{-1}\mathrm{d}\mu_i/\mathrm{d}y + z_{\mathrm{Cl}^-}^{-1}\,\mathrm{d}\mu_{\mathrm{Cl}^-}/\mathrm{d}y) \qquad 8.18.10$$

and consequently

$$F\,\mathrm{d}E/\mathrm{d}y = \sum_i z_i^2 L_i(-z_i^{-1}\mathrm{d}\mu_i/\mathrm{d}y + z_{\mathrm{Cl}^-}^{-1}\,\mathrm{d}\mu_{\mathrm{Cl}^-}/\mathrm{d}y)/\sum_i z_i^2 L_i. \qquad 8.18.11$$

Formulae (10) and (11) in contrast to the deceptively simpler formula (7) contain only such linear combinations of $\mathrm{d}\mu_i$'s as satisfy the condition for unambiguity (7.04.18).

Formula (11) is a complete and unambiguous formula for the electromotive force in terms of the quantities L_i defined in our assumption (3). We can however transform the expression on the right of (11) into a more perspicuous form by considering the different condition where the two electrode solutions are identical and an external potential difference $\mathrm{d}E^{\mathrm{e}}$ is applied across the electrodes. Under these conditions we have

$$z_i^{-1}\mathrm{d}\mu_i = F\,\mathrm{d}E^{\mathrm{e}} \qquad \text{(all } i\text{)}. \qquad 8.18.12$$

Hence according to (3)

$$J_i = -z_i L_i F\,\mathrm{d}E^{\mathrm{e}}/\mathrm{d}y \qquad \text{(all } i\text{)} \qquad 8.18.13$$

and the electrical current per unit cross-section carried by the ionic species i will be

$$z_i F J_i = -z_i^2 L_i F^2 \,\mathrm{d}E^{\mathrm{e}}/\mathrm{d}y. \qquad 8.18.14$$

The fraction of the total current carried by the ionic species i, called the *transport number* t_i of the species i is then given by

$$t_i = z_i^2 L_i / \sum_i z_i^2 L_i. \qquad 8.18.15$$

Comparing (11) with (15) we deduce

$$F\mathrm{d}E = \sum_i t_i(-z_i^{-1}\mathrm{d}\mu_i + z_{\mathrm{Cl}^-}^{-1}\,\mathrm{d}\mu_{\mathrm{Cl}^-}). \qquad 8.18.16$$

Returning now to cell (1) we see that this may always be regarded as several cells of type (2) in series, all electrodes other than the two extreme ones cancelling in pairs. We accordingly deduce from (16) for the electromotive force E of cell (1)

$$FE = \int \sum_i t_i(-z_i^{-1}\mathrm{d}\mu_i + z_{\mathrm{Cl}^-}^{-1}\,\mathrm{d}\mu_{\mathrm{Cl}^-}) \qquad 8.18.17$$

where the integration extends through all the bridge solutions from the left electrode solution I to the right electrode solution II.

We can rewrite (17) in terms of absolute activities as

$$FE/RT = \int \sum_i t_i(-z_i^{-1}\,\mathrm{d}\ln\lambda_i + z_{\mathrm{Cl}^-}^{-1}\,\mathrm{d}\ln\lambda_{\mathrm{Cl}^-}) \qquad 8.18.18$$

or in terms of molalities and activity coefficients as

$$FE/RT = \int \sum_i t_i\{-z_i^{-1}\,\mathrm{d}\ln(m_i\gamma_i) + z_{\mathrm{Cl}^-}^{-1}\,\mathrm{d}\ln(m_{\mathrm{Cl}^-}\gamma_{\mathrm{Cl}^-})\}. \qquad 8.18.19$$

We again stress that only such combinations of activity coefficients occur in (19) as are, in accordance with the condition (7.04.18), unambiguously defined.

§8.19 *Cells containing single electrolytes*

Formula (8.18.19) gives an explicit value of the electromotive force E, but to apply it or test it we require to know the values of the transport numbers of all cations, and all anions throughout the bridge solutions. This in turn involves a knowledge of the compositions of all the continuous series of solutions forming the bridge. Since this knowledge is usually not available, formula (8.18.19) though exact is not of much use except in specially simple cases.

The simplest and the most useful example of a cell with transference is that in which there is only one kind of cation and one kind of anion in the whole cell. Let us consider for example the cell

$$\begin{array}{c|c|c|c|c|c|c} \mathrm{Ag} & \mathrm{AgCl} & \begin{array}{c}\text{Aqueous } \mathrm{MgCl_2} \\ \text{at molality } m_1\end{array} & \begin{array}{c}\text{Transition} \\ \text{layer}\end{array} & \begin{array}{c}\text{Aqueous } \mathrm{MgCl_2} \\ \text{at molality } m_2\end{array} & \mathrm{AgCl} & \mathrm{Ag} \end{array} \qquad 8.19.1$$

We use the name *transition layer* to denote the naturally formed bridge between the two electrode solutions consisting entirely of solutions of $MgCl_2$ of intermediate compositions. For the cell (1) formula (8.18.19) reduces to

$$FE/RT = \int_{m=m_1}^{m=m_2} -t_{\mathrm{Mg}^{2+}}\{\tfrac{1}{2}\mathrm{d}\ln(m_{\mathrm{Mg}^{2+}}\gamma_{\mathrm{Mg}^{2+}})+\mathrm{d}\ln(m_{\mathrm{Cl}^-}\gamma_{\mathrm{Cl}^-})\}$$

$$= -\tfrac{1}{2}\int_{m=m_1}^{m=m_2} t_{\mathrm{Mg}^{2+}}\,\mathrm{d}\ln(m^3\gamma^3_{\mathrm{Mg,Cl}}) \qquad 8.19.2$$

where m denotes the molality and $\gamma_{\mathrm{Mg,Cl}}$ the mean activity coefficient of the electrolyte $MgCl_2$.

Since in solutions containing only the single electrolyte $MgCl_2$ the value of $t_{\mathrm{Mg}^{2+}}$ depends only on the molality, the integral in (2) is completely defined and is independent of how the molality varies across the transition layer. In particular it is independent of whether the transition layer has been formed mainly by mixing of the two electrode solutions or mainly by interdiffusion between them.

If the molalities of the two electrode solutions do not differ greatly from each other, it may be legitimate to neglect the variation of $t_{\mathrm{Mg}^{2+}}$ with composition. In this case (2) simplifies to

$$FE/RT = -\tfrac{3}{2}t_{\mathrm{Mg}^{2+}}\ln(m_2\gamma_2/m_1\gamma_1) \qquad 8.19.3$$

where γ_1, γ_2 denote the mean activity coefficients of $MgCl_2$ in solutions of molality m_1, m_2 respectively.

If the values of $\gamma_{\mathrm{Mg,Cl}}$ are known either from measurements of the electromotive force of cells without transference or by freezing-point measurements combined with use of the Gibbs–Duhem relation, then formula (2) can be used to give information concerning the transport number $t_{\mathrm{Mg}^{2+}}$. Conversely if there are independent measurements of this transport number, then formula (2) may be used to give information about the dependence of the mean activity coefficient $\gamma_{\mathrm{Mg,Cl}}$ on the molality.

§8.20 *Cells with transference having two dissimilar electrodes*

In §8.14 we discussed cells without transference and in §8.18 cells with transference having two similar electrodes. We have still to consider cells with transference having two dissimilar electrodes. These are most easily disposed of by regarding them as a combination of the two types of cell previously discussed. This will be made clear by a typical example. The cell

$$\mathrm{Pt,\ H_2}\left|\begin{array}{c}\text{Solution I}\\ \text{containing HCl}\end{array}\right|\begin{array}{c}\text{Bridge}\\ \text{solutions}\end{array}\left|\begin{array}{c}\text{Solution II}\\ \text{containing HCl}\end{array}\right|\mathrm{AgCl}\,|\,\mathrm{Ag}\,|\,\mathrm{Pt} \qquad 8.20.1$$

may be regarded as a combination of the two cells

$$\mathrm{Pt,\ H_2}\left|\begin{array}{c}\text{Solution I}\\ \text{containing HCl}\end{array}\right|\mathrm{AgCl}\,|\,\mathrm{Ag}\,|\,\mathrm{Pt} \qquad 8.20.2$$

$$\mathrm{Pt}\,|\,\mathrm{Ag}\,|\,\mathrm{AgCl}\left|\begin{array}{c}\text{Solution I}\\ \text{containing HCl}\end{array}\right|\begin{array}{c}\text{Bridge}\\ \text{solutions}\end{array}\left|\begin{array}{c}\text{Solution II}\\ \text{containing HCl}\end{array}\right|\mathrm{AgCl}\,|\,\mathrm{Ag}\,|\,\mathrm{Pt} \qquad 8.20.3$$

Consequently the electromotive force of the cell (1) is the sum of those of the cells (2) and (3). But cell (2) is without transference and, as shown in §8.14, its electromotive force E_2 is given by

$$FE_2 = -\mu^{\mathrm{Ag}}_{\mathrm{Ag}} + \tfrac{1}{2}\mu^{\mathrm{G}}_{\mathrm{H_2}} + \mu^{\mathrm{AgCl}}_{\mathrm{AgCl}} - \mu^{\mathrm{I}}_{\mathrm{HCl}} \qquad 8.20.4$$

where the superscript $^{\mathrm{I}}$ refers to the solution I. Cell (3) on the other hand has two similar electrodes and its electromotive force E_3 is given by (8.18.17)

$$\begin{aligned} FE_3 = &-\int_{\mathrm{I}}^{\mathrm{II}} \sum_{\mathrm{R}} t_{\mathrm{R}}(z_{\mathrm{R}}^{-1}\,\mathrm{d}\mu_{\mathrm{R}} - z_{\mathrm{Cl^-}}^{-1}\,\mathrm{d}\mu_{\mathrm{Cl^-}}) \\ &-\int_{\mathrm{I}}^{\mathrm{II}} \sum_{\mathrm{X}} t_{\mathrm{X}}(z_{\mathrm{X}}^{-1}\,\mathrm{d}\mu_{\mathrm{X}} - z_{\mathrm{Cl^-}}^{-1}\,\mathrm{d}\mu_{\mathrm{Cl^-}}) \qquad 8.20.5 \end{aligned}$$

wherein we recall that $z_{\mathrm{Cl^-}} = -1$ and all the z_{X} are negative integers. The electromotive force E_1 of the cell 1 is then given by

$$E_1 = E_2 + E_3 . \qquad 8.20.6$$

The accurate expressions for the electromotive force of the most general type of cell with transference were formulated by P. B. Taylor.*

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* Taylor, J. Phys. Chem. 1927 **31** 1478; Cf. Guggenheim, J. Phys. Chem. 1930 **34** 1758.