CHAPTER 7

SOLUTIONS OF ELECTROLYTES

§7.01 *Characteristics of strong electrolytes*

When certain substances such as common salt are dissolved in water, the solution has a comparatively high conductivity showing that charged ions must be present. We owe to Arrhenius the suggestion that for these substances, called *strong electrolytes*, the solute is composed largely of the free ions, such as Na^+ and Cl^- in the case of common salt. Study of the optical properties by Bjerrum* led him in 1909 to the conclusion that at least in dilute solutions there are at most very few undissociated molecules and in many such cases the properties of the solution can be accurately accounted for on the assumption that no undissociated molecules are present.

It would be outside the province of this book to discuss whether a dilute solution of a strong electrolyte contains a small fraction of undissociated molecules or none at all. All that matters is that the description of a salt solution as completely dissociated into independent ions, though admittedly an oversimplification, is at least an incomparably better model than any other of equal simplicity. We shall therefore compare the properties of every real solution of strong electrolytes with an idealized solution containing independent ions.

§7.02 *Ionic mole ratios and ionic molalities*

In accordance with the programme outlined in the previous section, we describe the composition of solutions of electrolytes in terms of the ions, not in terms of the undissociated molecules. We accordingly describe the composition of a solution containing one or more electrolytes by the *mole ratio* r_i of each ionic species i defined by

$$r_i = n_i/n_1 . \qquad 7.02.1$$

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* Bjerrum, Proc. 7th Int. Cong. Pure and Appl. Chem. London 1909 Sect. 10 p. 58; Z. Elektrochem. 1918 **24** 321.

In practice it is customary instead of *mole ratios* to use *molalities* m_i defined by

$$m_i = r_i / r^\ominus \qquad 7.02.2$$

where $r^\ominus$ is a standard value of r corresponding to one mole of the ionic species per kilogramme of solvent and equal to $M_1/\text{kg mole}^{-1}$.

§7.03 *Electrical neutrality*

When we carry out our intention of describing the properties of electrolyte solutions in terms of the ionic species, we shall find that most of the formulae have a close resemblance to those for non-electrolytes. There is however one important difference, namely that the molalities m_i of all the ionic species are not independent because the solution as a whole is electrically neutral. We now proceed to express this condition mathematically.

We use the symbol z to denote the charge on an ion measured in units of the charge of a proton, so that for example

For	Na^+	$z=1$
	Ba^{2+}	$z=2$
	La^{3+}	$z=3$
	Cl^-	$z=-1$
	SO_4^{2-}	$z=-2$
	PO_4^{3-}	$z=-3$
	$FeC_6N_6^{4-}$	$z=-4$.

We call z the *charge number* of the ion.

If then m_i denotes the molality of the ionic species i having a charge number z_i, the condition for *electrical neutrality* of the solution may be written

$$\sum_i z_i m_i = 0. \qquad 7.03.1$$

Alternatively if we use the subscript $_+$ to denote positively charged ions or *cations* and $_-$ to denote negatively charged ions or *anions*, then we may write (1) in the form

$$\sum_+ z_+ m_+ = \sum_- |z_-| m_- \qquad 7.03.2$$

wherein $|z_-| = -z_-$ is a positive integer.

Owing to the condition of *electrical neutrality* (1) or (2), a solution containing c ionic species, as well as the solvent, has c not c+1, independent components.

§7.04 *Ionic absolute activities*

Since most equilibrium conditions are expressible in a general, yet convenient, form in terms of absolute activities we shall make continual use of the absolute activity λ_i of each ionic species i. By following this procedure we shall in fact obtain formulae closely resembling those already obtained for non-electrolytes. There is however one important difference. We saw in the previous section that if there are c ionic species i and so c ionic molalities m_i, then only $c-1$ are independent. There must clearly be some analogous or related property of the set of c quantities λ_i. We shall now discover this property by considering the physical significance of the λ_i's first in particular cases and then in general.

Let us consider the distribution of NaCl between two phases, of which at least one α is a solution; the other β may be a solution in a different solvent or the solid phase. We shall now determine the equilibrium condition for NaCl ab initio on the same lines as in §1.39 but in terms of Na^+ and Cl^-. We assume the temperature, but not necessarily the pressure, to be the same in the two phases. Suppose now a small quantity dn_{Na^+} of Na^+ and a small quantity dn_{Cl^-} of Cl^- to pass from the phase α to the phase β, the temperature of the whole system being kept constant. Then the increase in the Helmholtz function is given by

$$\begin{aligned} d\mathcal{F} = & -P^\alpha dV^\alpha - \mu^\alpha_{Na^+} dn_{Na^+} - \mu^\alpha_{Cl^-} dn_{Cl^-} \\ & -P^\beta dV^\beta + \mu^\beta_{Na^+} dn_{Na^+} + \mu^\beta_{Cl^-} dn_{Cl^-}. \end{aligned} \qquad 7.04.1$$

By an argument analogous to that of §1.39, if the two phases are in mutual equilibrium with respect to the NaCl, the process being considered must be reversible and so the increase in the free energy must be equal to the work done on the system. Thus

$$d\mathcal{F} = -P^\alpha dV^\alpha - P^\beta dV^\beta. \qquad 7.04.2$$

Subtracting (2) from (1) we obtain

$$(\mu^\beta_{Na^+} - \mu^\alpha_{Na^+}) dn_{Na^+} + (\mu^\beta_{Cl^-} - \mu^\alpha_{Cl^-}) dn_{Cl^-} = 0. \qquad 7.04.3$$

The condition for electrical neutrality (7.03.2) in this case takes the simple form

$$dn_{Na^+} = dn_{Cl^-} = dn. \qquad 7.04.4$$

Substituting (4) into (3) we have

$$(\mu^\beta_{Na^+} - \mu^\alpha_{Na^+} + \mu^\beta_{Cl^-} - \mu^\alpha_{Cl^-}) dn = 0 \qquad 7.04.5$$

or dividing by dn

$$\mu^\alpha_{Na^+} + \mu^\alpha_{Cl^-} = \mu^\beta_{Na^+} + \mu^\beta_{Cl^-}. \qquad 7.04.6$$

Since according to the definition of λ_i

$$\mu_i = RT \ln \lambda_i \tag{7.04.7}$$

we may rewrite (6) as

$$\ln \lambda^{\alpha}_{\mathrm{Na}^+} + \ln \lambda^{\alpha}_{\mathrm{Cl}^-} = \ln \lambda^{\beta}_{\mathrm{Na}^+} + \ln \lambda^{\beta}_{\mathrm{Cl}^-} \tag{7.04.8}$$

or

$$\lambda^{\alpha}_{\mathrm{Na}^+} \lambda^{\alpha}_{\mathrm{Cl}^-} = \lambda^{\beta}_{\mathrm{Na}^+} \lambda^{\beta}_{\mathrm{Cl}^-}. \tag{7.04.9}$$

We thus see that any phase equilibrium relating to NaCl involves only the sum

$$\mu_{\mathrm{Na}^+} + \mu_{\mathrm{Cl}^-} \tag{7.04.10}$$

or the product

$$\lambda_{\mathrm{Na}^+} \lambda_{\mathrm{Cl}^-}. \tag{7.04.11}$$

In the same way an equilibrium relating to $BaCl_2$ would involve only the sum

$$\mu_{\mathrm{Ba}^{2+}} + 2\mu_{\mathrm{Cl}^-} \tag{7.04.12}$$

or the product

$$\lambda_{\mathrm{Ba}^{2+}} \lambda^2_{\mathrm{Cl}^-} \tag{7.04.13}$$

and an equilibrium relating to $LaCl_3$, only the sum

$$\mu_{\mathrm{La}^{3+}} + 3\mu_{\mathrm{Cl}^-} \tag{7.04.14}$$

or the product

$$\lambda_{\mathrm{La}^{3+}} \lambda^3_{\mathrm{Cl}^-} \tag{7.04.15}$$

and so on.

But it might be asked what about an equilibrium relating to the chloride ion by itself? The answer is that the transfer of a chloride ion, or any other ion alone from one phase to another involves a transfer of electrical charge, that is to say an electric current. We shall consider such processes in detail in the following chapter on *electrochemical systems.* Meanwhile as long as we exclude processes involving an electric current, and in this chapter we do so, we shall meet the μ_i's and λ_i's only in combinations corresponding to zero net electric charge. We can express this mathematically by stating that the only linear combinations

$$\sum_i \nu_i \mu_i \tag{7.04.16}$$

and the only products

$$\prod_i (\lambda_i)^{\nu_i} \tag{7.04.17}$$

which will occur will be those in which the ν_i's satisfy the relation

$$\sum_i \nu_i z_i = 0. \qquad 7.04.18$$

This means that, apart from electrochemical flow of charge, with which we are not concerned in this chapter, we could in each phase assign an arbitrary value to the absolute activity λ_i of one ionic species, for instance the chloride ion. The λ_i's of the remaining ions would then be unambiguously determined. Nothing is however gained by thus arbitrarily fixing the values of the λ_i's. We can just as well leave the arbitrary factor in the λ_i's undetermined, knowing that only those combinations (17) of the λ_i's satisfying (18) will ever occur and that in these combinations the arbitrary factors cancel.

§7.05 *Ideal dilute and real solutions*

It would be rational, as in the case of non-electrolytes, first to define an ideal dilute solution of electrolytes and thereafter to compare the properties of real solutions with ideal dilute solutions. Since however no solution of a strong electrolyte is even approximately ideal dilute even at the highest dilution at which accurate measurements can be made, there seems no point in devoting space to such solutions. We therefore pass straight to real solutions, of which ideal dilute solutions constitute an idealized limiting case.

§7.06 *Osmotic coefficient of the solvent*

We can define the *osmotic coefficient* ϕ of the solvent in complete analogy with the case where the solute species are non-electrolytes merely replacing r_s by r_i the mole ratio of an ionic species, or m_s by m_i the molality of an ionic species. For electrolyte solutions (5.10.1) becomes

$$-\ln(\lambda_1/\lambda_1^0) = -\ln(p_1/p_1^0) = \phi \sum_i r_i = \phi r^{\ominus} \sum_i m_i. \qquad 7.06.1$$

We shall use (1) to describe the several equilibrium properties of the solvent. Before doing so we however point out that if the solution contains non-electrolytes as well as electrolytes, the former may be included formally inside the summation Σ_i. We merely treat an electrically uncharged species as if it were an ionic species with $z=0$.

§7.07 *Freezing point and boiling point*

Formula (5.17.11) relating the freezing point T of a solution to the freezing point T^0 of the pure solvent, becomes

$$\phi\sum_i r_i=\phi r^\ominus\sum_i m_i=\phi(M_1/\text{kg mole}^{-1})\sum_i m_i=\langle\Delta_f H_1^0\rangle(1/RT-1/RT^0) \quad 7.07.1$$

where $\langle\Delta_f H_1^0\rangle$ denotes the value of the proper enthalpy of fusion $\Delta_f H_1^0$ of the pure solvent averaged over the reciprocal temperature range $1/T^0$ to $1/T$. In (1) the value of ϕ is that at the freezing point of the solution.

The relation (5.18.1) between the boiling point T of a solution of involatile solutes and the boiling point T^0 of the pure solvent becomes

$$\phi\sum_i r_i=\phi r^\ominus\sum_i m_i=\phi(M_1/\text{kg mole}^{-1})\sum_i m_i=\langle\Delta_e H_1^0\rangle(1/RT^0-1/RT) \quad 7.07.2$$

where $\langle\Delta_e H_1^0\rangle$ denotes the value of the proper enthalpy of evaporation $\Delta_e H_1^0$ of the pure solvent averaged over the reciprocal temperature range $1/T$ to $1/T^0$. In (2) the value of ϕ is that at the boiling point of the solution.

§7.08 *Osmotic pressure*

Formula (5.16.2) for the osmotic pressure Π becomes for a solution of electrolytes

$$\Pi\langle V_1\rangle/RT=\phi\sum_i r_i. \quad 7.08.1$$

§7.09 *Ionic activity coefficient*

In analogy with (5.09.1) and (5.09.2) the activity coefficient γ_i of the ionic species i is related to the absolute activity λ_i by

$$\lambda_i=\lambda_i^\ominus m_i\gamma_i \quad 7.09.1$$

$$\gamma_i\to 1 \quad \text{as} \quad \sum_i m_i\to 0. \quad 7.09.2$$

The proportionality constant $\lambda_i^\ominus$ depends on the solvent and the temperature. Furthermore, as explained in §7.04 *in each solution* an arbitrary value may be assigned to λ_i for any one ionic species; the values for the remaining ionic species are then determined in that solution.

§7.10 *Mean activity coefficient of electrolyte*

Let us consider an electrolyte which consists of ν_+ cations R of charge number z_+ and ν_- anions X of charge number z_- so that according to the condition of electrical neutrality $\nu_+z_++\nu_-z_-=0$. The absolute activity $\lambda_{R,X}$

of the electrolyte $R_{\nu_+}X_{\nu_-}$ is then related to the absolute activities of the two ionic species by

$$\lambda_{R,X}=\lambda_R^{\nu_+}\lambda_X^{\nu_-}. \tag{7.10.1}$$

Substituting (7.09.1) into (1) we have

$$\lambda_{R,X}=(\lambda_R^{\ominus}m_R\gamma_R)^{\nu_+}(\lambda_X^{\ominus}m_X\gamma_X)^{\nu_-} \tag{7.10.2}$$

and in the limit of infinite dilution

$$\lambda_{R,X}\to(\lambda_R^{\ominus}m_R)^{\nu_+}(\lambda_X^{\ominus}m_X)^{\nu_-} \quad \text{as} \quad \sum_i m_i\to 0. \tag{7.10.3}$$

Since $\lambda_{R,X}$ and m_R and m_X are all well defined quantities it is clear from (3) that in spite of the indefiniteness in $\lambda_R^{\ominus}$ and $\lambda_X^{\ominus}$ separately, the product $(\lambda_R^{\ominus})^{\nu_+}(\lambda_X^{\ominus})^{\nu_-}$ is completely defined. Returning now to (2) since $\lambda_{R,X}$, m_R, m_X, and, as we have just seen, the product $(\lambda_R^{\ominus})^{\nu_+}(\lambda_X^{\ominus})^{\nu_-}$ are all well defined, it follows that the product $\gamma_R^{\nu_+}\gamma_X^{\nu_-}$ is also well defined.

We now introduce a quantity $\gamma_{R,X}$ called the *mean activity coefficient* of the electrolyte, related to γ_R and γ_X by

$$\gamma_{R,X}^{\nu_++\nu_-}=\gamma_R^{\nu_+}\gamma_X^{\nu_-}. \tag{7.10.4}$$

Substituting (4) into (2) we have

$$\lambda_{R,X}=(\lambda_R^{\ominus})^{\nu_+}(\lambda_X^{\ominus})^{\nu_-}m_R^{\nu_+}m_X^{\nu_-}\gamma_{R,X}^{\nu_++\nu_-}. \tag{7.10.5}$$

Since $\gamma_{R,X}$ is well defined, while γ_R and γ_X individually are not, it would be wrong to regard (4) as a definition of $\gamma_{R,X}$ in terms of γ_R and γ_X. Nevertheless formula (4) does contain something of physical significance. For let us consider a solution containing two cations R, R′ and two anions X, X′ from which we can form four different electrolytes, for each of which we can write a relation of the form (4). What these relations together tell us is that the four mean activity coefficients are not independent. We can best illustrate the point by a simple example. Let us consider the two cations Na^+, K^+ and the two anions Cl^-, NO_3^-. Then we have formally

$$\gamma_{Na,Cl}^2=\gamma_{Na^+}\gamma_{Cl^-} \tag{7.10.6}$$

$$\gamma_{K,Cl}^2=\gamma_{K^+}\gamma_{Cl^-} \tag{7.10.7}$$

$$\gamma_{Na,NO_3}^2=\gamma_{Na^+}\gamma_{NO_3^-} \tag{7.10.8}$$

$$\gamma_{K,NO_3}^2=\gamma_{K^+}\gamma_{NO_3^-}. \tag{7.10.9}$$

In a given solution each of the quantities on the left of formulae (6) to (9) is well defined, while the individual factors on the right are not. But these four formulae together lead to the physically significant result

$$\gamma_{\mathrm{Na,Cl}}/\gamma_{\mathrm{K,Cl}}=\gamma_{\mathrm{Na,NO_3}}/\gamma_{\mathrm{K,NO_3}}. \qquad 7.10.10$$

§7.11 *Temperature dependence*

Just as for non-ionic species, we have according to (5.03.10)

$$\partial \ln \lambda_i/\partial T=-H_i/RT^2 \qquad 7.11.1$$

so that according to (7.09.1)

$$\partial \ln(\lambda_i^{\ominus}\gamma_i)/\partial T=-H_i/RT^2. \qquad 7.11.2$$

Proceeding to the limit of infinite dilution (2) becomes

$$\partial \ln \lambda_i^{\ominus}/\partial T=-H_i^{\infty}/RT^2 \qquad 7.11.3$$

where H_i^{∞} denotes the limiting value of H_i when $\Sigma_i m_i \to 0$. Now subtracting (3) from (2) we find

$$\partial \ln \gamma_i/\partial T=-(H_i-H_i^{\infty})/RT^2. \qquad 7.11.4$$

For reasons previously given, only linear combinations of these formulae will occur of the type defined by (7.04.18). In particular for an electrolyte composed of ν_+ cations R and ν_- anions X, we have according to (1)

$$\partial \ln \lambda_{\mathrm{R,X}}/\partial T=-H_{\mathrm{R,X}}/RT^2 \qquad 7.11.5$$

where

$$H_{\mathrm{R,X}}=\nu_+H_{\mathrm{R}}+\nu_-H_{\mathrm{X}} \qquad 7.11.6$$

is the *partial enthalpy* of the electrolyte. Similarly from (4) we deduce

$$(\nu_++\nu_-)\partial \ln \gamma_{\mathrm{R,X}}/\partial T=-(H_{\mathrm{R,X}}-H_{\mathrm{R,X}}^{\infty})/RT^2 \qquad 7.11.7$$

where $H_{\mathrm{R,X}}^{\infty}$ denotes the limiting value of $H_{\mathrm{R,X}}$ as $\Sigma_i m_i \to 0$.

§7.12 *Distribution of electrolyte between two solvents*

The equilibrium condition for the distribution of an electrolyte consisting of ν_+ cations R and ν_- anions X between two solvents α and β can be written either in terms of the electrolytes as

$$\lambda_{\mathrm{R,X}}^{\alpha}=\lambda_{\mathrm{R,X}}^{\beta} \qquad 7.12.1$$

or in terms of the ions as

$$(\lambda_{\mathrm{R}}^{\alpha})^{\nu_+}(\lambda_{\mathrm{X}}^{\alpha})^{\nu_-}=(\lambda_{\mathrm{R}}^{\beta})^{\nu_+}(\lambda_{\mathrm{X}}^{\beta})^{\nu_-}. \qquad 7.12.2$$

According to (7.10.1) the two conditions are equivalent. Substituting (7.10.5) into (1) we obtain

$$\frac{[m_{\mathrm{R}}^{\nu_+} m_{\mathrm{X}}^{\nu_-} \gamma_{\mathrm{R,X}}^{\nu_+ + \nu_-}]^{\beta}}{[m_{\mathrm{R}}^{\nu_+} m_{\mathrm{X}}^{\nu_-} \gamma_{\mathrm{R,X}}^{\nu_+ + \nu_-}]^{\alpha}} = l_{\mathrm{R,X}}^{\alpha\beta} \qquad 7.12.3$$

where

$$l_{\mathrm{R,X}}^{\alpha\beta} = (\lambda_{\mathrm{R}}^{\ominus\alpha}/\lambda_{\mathrm{R}}^{\ominus\beta})^{\nu_+} (\lambda_{\mathrm{X}}^{\ominus\alpha}/\lambda_{\mathrm{X}}^{\ominus\beta})^{\nu_-} \qquad 7.12.4$$

and according to (7.11.3) we have

$$\partial \ln l_{\mathrm{R,X}}^{\alpha\beta}/\partial T = (H_{\mathrm{R,X}}^{\infty\beta} - H_{\mathrm{R,X}}^{\infty\alpha})/RT^2 \qquad 7.12.5$$

We notice that the numerator of the right side is the limiting value as $\Sigma_i m_i \to 0$ of the *partial enthalpy of transfer of the electrolyte* from the solvent α to the solvent β.

§7.13 *Solubility*

For the equilibrium between the solid electrolyte composed of the ions R, X and a solution containing R, X and possibly other electrolytes, we have

$$\lambda_{\mathrm{R,X}} = \lambda_{\mathrm{R,X}}^{\mathrm{S}} \qquad 7.13.1$$

where we denote the solid phase by the superscript $^{\mathrm{S}}$ and the solution by no superscript.

Substituting from (7.10.5) into (1) we obtain

$$m_{\mathrm{R}}^{\nu_+} m_{\mathrm{X}}^{\nu_-} \gamma_{\mathrm{R,X}}^{\nu_+ + \nu_-} = s_{\mathrm{R,X}}^{\nu_+ + \nu_-} \qquad 7.13.2$$

where

$$s_{\mathrm{R,X}}^{\nu_+ + \nu_-} = \lambda_{\mathrm{R,X}}^{\mathrm{S}}/(\lambda_{\mathrm{R}}^{\ominus})^{\nu_+}(\lambda_{\mathrm{X}}^{\ominus})^{\nu_-} \qquad 7.13.3$$

is called the *solubility product* of the electrolyte and $s_{\mathrm{R,X}}$ is called the *mean solubility* of the electrolyte. Since

$$\partial \ln \lambda_{\mathrm{R,X}}^{\mathrm{S}}/\partial T = -H_{\mathrm{R,X}}^{\mathrm{S}}/RT^2 \qquad 7.13.4$$

we have, using this and (7.11.3) in (3)

$$\partial \ln s_{\mathrm{R,X}}/\partial T = (H_{\mathrm{R,X}}^{\infty} - H_{\mathrm{R,X}}^{\mathrm{S}})/(\nu_+ + \nu_-)RT^2. \qquad 7.13.5$$

We notice that the numerator on the right of (5) is the limiting value as $\Sigma_i m_i \to 0$ of the *enthalpy of dissolution of the solid electrolyte* in the given solvent.

§7.14 *Chemical reactions*

If we consider the chemical reaction

$$0=\sum_i \nu_i \mathrm{B}_i \qquad 7.14.1$$

where some or all of the species B_i may be ionic, the condition of equilibrium, in the notation defined in §6.01 is according to (6.13.3)

$$\prod(m_i)\prod(\gamma_i)=K_m(T). \qquad 7.14.2$$

The fact that some or all of the reacting species may be ions has no effect on the form of (2). It is however of interest to notice that, owing to the conservation of net electric charge, it follows from (1) that

$$\sum_i \nu_i z_i=0 \qquad 7.14.3$$

and so

$$\ln \prod(\gamma_i) \qquad 7.14.4$$

conforms to the type of product which is physically well defined according to the condition (7.04.18).

We shall illustrate the point by an example. Consider the reaction

$$0=2\mathrm{Fe}^{2+}+\mathrm{Sn}^{4+}-2\mathrm{Fe}^{3+}-\mathrm{Sn}^{2+}. \qquad 7.14.5$$

According to (2) the equilibrium condition is

$$\frac{m^2_{\mathrm{Fe}^{2+}}\, m_{\mathrm{Sn}^{4+}}\, \gamma^2_{\mathrm{Fe}^{2+}}\, \gamma_{\mathrm{Sn}^{4+}}}{m^2_{\mathrm{Fe}^{3+}}\, m_{\mathrm{Sn}^{2+}}\, \gamma^2_{\mathrm{Fe}^{3+}}\, \gamma_{\mathrm{Sn}^{2+}}}=K_m \qquad 7.14.6$$

wherein the *activity coefficients product* is well defined. It can in fact be expressed in terms of mean activity coefficients as follows

$$\frac{\gamma^2_{\mathrm{Fe}^{2+}}\, \gamma_{\mathrm{Sn}^{4+}}}{\gamma^2_{\mathrm{Fe}^{3+}}\, \gamma_{\mathrm{Sn}^{2+}}}=\frac{\gamma^2_{\mathrm{Fe}^{2+}}\, \gamma_{\mathrm{Sn}^{4+}}\, \gamma^8_{\mathrm{Cl}^-}}{\gamma^2_{\mathrm{Fe}^{3+}}\, \gamma_{\mathrm{Sn}^{2+}}\, \gamma^8_{\mathrm{Cl}^-}}=\frac{\gamma^6_{\mathrm{Fe}^{2+},\mathrm{Cl}^-}\, \gamma^5_{\mathrm{Sn}^{4+},\mathrm{Cl}^-}}{\gamma^8_{\mathrm{Fe}^{3+},\mathrm{Cl}^-}\, \gamma^3_{\mathrm{Sn}^{2+},\mathrm{Cl}^-}}. \qquad 7.14.7$$

For the temperature dependence of K_m we have (6.14.2)

$$\mathrm{d}\ln K_m/\mathrm{d}T=\Delta H^\infty/RT^2 \qquad 7.14.8$$

where ΔH^∞ denotes the *enthalpy of reaction* at infinite dilution.

§7.15 *Gibbs–Duhem relation for electrolyte solutions*

For any phase whatever we have the Gibbs–Duhem relation (1.30.2). For a solution of electrolytes in a solvent 1 this becomes

$$S\mathrm{d}T - V\mathrm{d}P + n_1\mathrm{d}\mu_1 + \sum_i n_i\mathrm{d}\mu_i = 0 \qquad 7.15.1$$

or considering variations of composition at constant temperature and pressure

$$n_1\mathrm{d}\mu_1 + \sum_i n_i\mathrm{d}\mu_i = 0 \qquad (T, P \text{ const.}). \qquad 7.15.2$$

We may rewrite (2) in terms of absolute activities λ_i as

$$n_1\mathrm{d}\ln\lambda_1 + \sum_i n_i\mathrm{d}\ln\lambda_i = 0 \qquad (T, P \text{ const.}). \qquad 7.15.3$$

According to the definition of mole ratios and molalities given in §5.02 and extended to ions in §7.02 we have

$$n_i/n_1 = r_i = r^{\ominus}m_i = (M_1/\text{kg mole}^{-1})m_i. \qquad 7.15.4$$

If then we divide (2) and (3) throughout by n_1 and use (4) we obtain

$$\mathrm{d}\mu_1 = -\sum_i r_i\mathrm{d}\mu_i = -(M_1/\text{kg mole}^{-1})\sum_i m_i\mathrm{d}\mu_i \qquad (T, P \text{ const.}) \qquad 7.15.5$$

$$\mathrm{d}\ln\lambda_1 = -\sum_i r_i\mathrm{d}\ln\lambda_i = -(M_1/\text{kg mole}^{-1})\sum_i m_i\mathrm{d}\ln\lambda_i \qquad (T, P \text{ const.}). \qquad 7.15.6$$

As explained in §7.03 all variations of composition of an electrolyte solution are subject to the condition for electrical neutrality

$$\sum_i z_i m_i = 0 \qquad 7.15.7$$

so that

$$\sum_i z_i\mathrm{d}m_i = 0. \qquad 7.15.8$$

The variations in formulae (1), (2), (3), (5), (6) are all subject to the condition (8); but for variations satisfying (8) these formulae hold just as well for electrolyte solutions as for other solutions.

We now recall the definition of the osmotic coefficient (7.06.1)

$$-\ln(\lambda_1/\lambda_1^0) = \phi\sum_i r_i = \phi(M_1/\text{kg mole}^{-1})\sum_i m_i \qquad 7.15.9$$

and the definition of ionic activity coefficients γ_i by (7.09.1)

$$\lambda_i = \lambda_i^{\ominus} m_i \gamma_i. \qquad 7.15.10$$

Differentiating (9) with respect to changes of composition at constant temperature and pressure we obtain

$$\mathrm{d}\ln\lambda_1 = -(M_1/\text{kg mole}^{-1})\mathrm{d}(\phi\sum_i m_i) \qquad (T, P \text{ const.}). \qquad 7.15.11$$

Taking logarithms of (10) and differentiating we obtain

$$\mathrm{d}\ln\lambda_i = \mathrm{d}\ln m_i + \mathrm{d}\ln\gamma_i \qquad (T, P \text{ const.}). \qquad 7.15.12$$

Now substituting (11) and (12) into (6) we obtain

$$\mathrm{d}\{(\phi-1)\sum_i m_i\} = \sum_i m_i \mathrm{d}\ln\gamma_i \qquad (T, P \text{ const.}) \qquad 7.15.13$$

of the same form as formula (5.11.2) and due to Bjerrum*.

In particular for a solution of a single electrolyte having ν_+ cations R and ν_- anions X, formula (13) becomes

$$(\nu_+ + \nu_-)\partial\{(1-\phi)m\}/\partial m = -\nu_+ m\partial\ln\gamma_{\mathrm{R}}/\partial m - \nu_- m\partial\ln\gamma_{\mathrm{X}}/\partial m \qquad 7.15.14$$

where m denotes the *molality of the electrolyte*. The mean activity coefficient $\gamma_{\mathrm{R,X}}$ of the electrolyte is related to the ionic activity coefficients γ_{R} and γ_{X} by (7.10.4)

$$\gamma_{\mathrm{R,X}}^{\nu_+ + \nu_-} = \gamma_{\mathrm{R}}^{\nu_+}\gamma_{\mathrm{X}}^{\nu_-}. \qquad 7.15.15$$

We now divide (14) throughout by $(\nu_+ + \nu_-)m$ and use (15) obtaining

$$-\partial\ln\gamma_{\mathrm{R,X}}/\partial m = m^{-1}\partial\{(1-\phi)m\}/\partial m \qquad 7.15.16$$

or integrating from 0 to m

$$-\ln\gamma_{\mathrm{R,X}} = \int_0^m \frac{\partial\{(1-\phi)m\}}{\partial m}\,\frac{\mathrm{d}m}{m}. \qquad 7.15.17$$

Just as in a solution of a single solute non-electrolyte, formula (16) or (17) may be used to determine either of the quantities γ or ϕ if the other is known as a function of composition at all molalities less than m. On the other hand the more general relation (13) should not be used in this manner, but rather as a check on the self-consistency of assumed formulae for ϕ and the γ_i's because it is also necessary for the γ_i's to satisfy the relations of the type

$$\partial\ln\gamma_i/\partial m_k = \partial\ln\gamma_k/\partial m_i. \qquad 7.15.18$$

As an example of (17) suppose

$$1-\phi = am^t \qquad (a, t \text{ const.}). \qquad 7.15.19$$

Then substituting (19) into (17) we obtain

$$-\ln\gamma_{\mathrm{R,X}} = (1+t^{-1})am^t = (1+t^{-1})(1-\phi). \qquad 7.15.20$$

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* Bjerrum, Z. Physik. Chem. 1923 **104** 406.

§7.16 *Limiting behaviour at high dilutions*

It was already proved* over fifty years ago that deviations from ideality due to the long-range electrostatic interactions between ions in highly dilute electrolyte solutions are quite different from the deviations in non-electrolyte solutions.

The distinction can for a single solute be expressed in the form

$$1-\phi \propto m \quad \text{as} \quad m \to 0 \quad \text{(non-electrolyte)} \tag{7.16.1}$$

$$1-\phi \propto m^t \quad \text{as} \quad m \to 0 \quad (t<1) \quad \text{(electrolyte).} \tag{7.16.2}$$

This distinction is most strikingly expressed in the form

$$\mathrm{d}(1-\phi)/\mathrm{d}m \to \text{finite limit} \quad \text{as} \quad m \to 0 \quad \text{(non-electrolyte)} \tag{7.16.3}$$

$$\mathrm{d}(1-\phi)/\mathrm{d}m \to \infty \quad \text{as} \quad m \to 0 \quad \text{(electrolyte).} \tag{7.16.4}$$

The latter behaviour is shown graphically in figure 7.1 which is of historical interest being taken from a paper by Bjerrum† written as early as 1916.

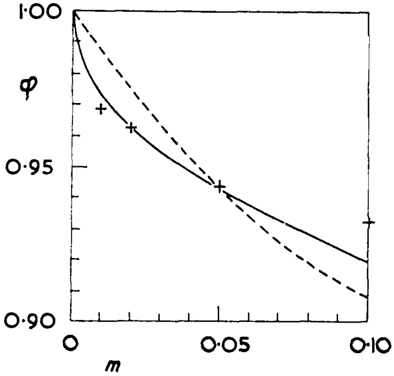

Fig. 7.1. Osmotic coefficients in aqueous solutions of potassium chloride. + + Freezing-point measurements. ——— Electrostatic interaction according to Milner. - - - - Incomplete dissocation ignoring electrostatic interaction

Milner* in 1912 had shown by statistical methods that the theoretical value of t is near $\frac{1}{2}$. Various values of t in (2) were used empirically in the period around 1922, some authors using different values of t for different electrolytes. Brønsted‡ pointed out in 1922 that in the limit of high dilutions

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* Milner, Phil. Mag. 1912 **23** 551.

† Bjerrum, 16te Skand. Naturforskermøte 1916 p. 229.

‡ Brønsted, J. Amer. Chem. Soc. 1922 **44** 938.

the value of t and likewise the proportionality factor in (2) must be the same for all electrolytes of the same charge type. For 1–1 electrolytes Brønsted proposed $t=\frac{1}{2}$. Finally in 1923 Debye and Hückel* determined by a statistical treatment the theoretical law valid in the limit $m\rightarrow 0$. According to this law $t=\frac{1}{2}$ and the proportionality constant in (2) is also determined by the theory.

§7.17 *Limiting law of Debye and Hückel*

As already mentioned the behaviour of a strong electrolyte in the limit of high dilution is given quantitatively by the formulae due to Debye and Hückel.* We shall now specify these formulae. All the deviations from ideality are most concisely expressed in terms of two characteristic lengths denoted by s and κ^{-1}. The definition of s is

$$s=e^2/4\pi\varepsilon_0\varepsilon_r kT \qquad 7.17.1$$

where e is the elementary charge, ε_0 is the rationalized permittivity of empty space (so that $4\pi\varepsilon^0$ is the unrationalized permittivity of empty space), ε_r is the relative permittivity ('dielectric constant') of the solvent and k is the Boltzmann constant. The other characteristic length κ^{-1} is defined by

$$\kappa^2=8\pi L\varrho s\sum_i \tfrac{1}{2}z_i^2 n_i/n_1 M_1 \qquad 7.17.2$$

where L is the Avogadro constant, ϱ is the density of the solvent, and M_1 is the proper mass of the solvent.

If G denotes the Gibbs function of the solution and G^{id} denotes the Gibbs function of an ideal dilute solution of the same composition, then at high dilutions

$$(G-G^{\mathrm{id}})/RT=-\tfrac{1}{3}\sum_i n_i z_i^2\kappa s. \qquad 7.17.3$$

Differentiating (3) with respect to n_1 and noting that $\kappa\propto n_1^{-\frac{1}{2}}$ we obtain

$$(1-\phi)\sum_i n_i/n_1=(\mu_1-\mu_1^{\mathrm{id}})/RT=\tfrac{1}{6}\sum_i n_i z_i^2\kappa s/n_1 \qquad 7.17.4$$

so that

$$1-\phi=\tfrac{1}{6}(\sum_i n_i z_i^2/\sum_i n_i)\kappa s. \qquad 7.17.5$$

Differentiating (3) with respect to n_i and noting that $\kappa\propto(\Sigma_i n_i z_i^2)^{\frac{1}{2}}$ we obtain

$$-\ln\gamma_i=\tfrac{1}{2}z_i^2\kappa s. \qquad 7.17.6$$

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* Debye and Hückel, Phys. Z. 1923 **24** 185.

We readily verify that Bjerrum's condition (7.15.13)

$$\mathrm{d}\{(1-\phi)\sum_i m_i\} = -\sum_i m_i \mathrm{d} \ln \gamma_i \qquad (T, P \text{ const.}) \tag{7.17.7}$$

is satisfied when used with (7.15.20) and $t=\frac{1}{2}$.

We now rewrite the above formulae for numerical calculations. We recall that the molality m_i of an ionic species i is defined by

$$m_i = r_i/r_i^{\ominus} = r_i/(M_1/\text{kg mole}^{-1}) = n_i/n_1 M_1 \text{ mole kg}^{-1}. \tag{7.17.8}$$

We also define the *ionic strength*, following Lewis and Randall*, by

$$I = \tfrac{1}{2}\sum_i z_i^2 m_i. \tag{7.17.9}$$

We further define a dimensionless parameter α depending on the nature of the solvent and on the temperature, by

$$\alpha = (2\pi L \varrho s^3 \text{ mole kg}^{-1})^{\frac{1}{2}} \tag{7.17.10}$$

and we observe that

$$\tfrac{1}{2}\kappa s = \alpha I^{\frac{1}{2}}. \tag{7.17.11}$$

We can now rewrite (3) as

$$(G-G^{\mathrm{id}})/RT = -\tfrac{2}{3}\alpha \sum_i z_i^2 n_i I^{\frac{1}{2}} \tag{7.17.12}$$

and (5) as

$$1-\phi = \tfrac{1}{3}\alpha\Big(\sum_i z_i^2 m_i \Big/ \sum_i m_i\Big) I^{\frac{1}{2}} \tag{7.17.13}$$

and (6) as

$$-\ln \gamma_i = \alpha z_i^2 I^{\frac{1}{2}}. \tag{7.17.14}$$

In the simple case of a single electrolyte composed of ν_+ cations of charge number z_+ and ν_- anions of charge number z_- formula (13) becomes

$$1-\phi = \tfrac{1}{3}\alpha\{(\nu_+ z_+^2 + \nu_- z_-^2)/(\nu_+ + \nu_-)\} I^{\frac{1}{2}}. \tag{7.17.15}$$

Using the condition for electrical neutrality

$$\nu_+ z_+ + \nu_- z_- = 0 \tag{7.17.16}$$

we can rewrite (15) as

$$1-\phi = \tfrac{1}{3}\alpha z_+ |z_-| I^{\frac{1}{2}}. \tag{7.17.17}$$

From (14) it follows that the mean activity coefficient $\gamma_\pm$ of an electrolyte composed of ν_+ cations of charge number z_+ and ν_- anions of charge

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* Lewis and Randall, J. Amer. Chem. Soc. 1921 **43** 1141.

number z_- is given by

$$-\ln \gamma_{\pm} = \alpha\{(\nu_+ z_+^2 + \nu_- z_-^2)/(\nu_+ + \nu_-)\} I^{\frac{1}{2}}. \qquad 7.17.18$$

Using (16) we can rewrite (18) as

$$-\ln \gamma_{\pm} = \alpha z_+ |z_-| I^{\frac{1}{2}}. \qquad 7.17.19$$

§7.18 *Aqueous solutions*

We now illustrate the formulae of the previous section by giving numerical values for water. At 0 °C we have

$$L = 0.60225 \times 10^{24}\ \text{mole}^{-1}$$
$$\varrho = 0.9999 \times 10^{3}\ \text{kg m}^{-3}$$
$$e = 1.6021 \times 10^{-19}\ \text{C}$$
$$4\pi\varepsilon_0 = 8.85416 \times 10^{-12}\ \text{C V}^{-1}\ \text{m}^{-1}$$
$$k = 1.3805 \times 10^{-23}\ \text{J K}^{-1}$$
$$T = 273.15\ \text{K}$$
$$\varepsilon_r = 88.23.$$

As usual we take $r^{\ominus} = M_1/\text{kg mole}^{-1}$. These values lead to

$$s = 6.935\ \text{Å} \qquad \alpha = 1.123. \qquad 7.18.1$$

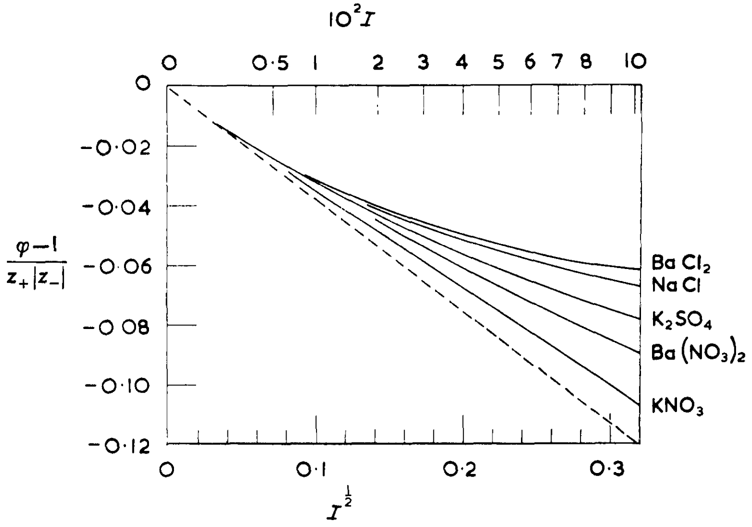

Fig. 7.2. Osmotic coefficients of electrolytes of various charge types at 0 °C

Similarly for water at 25 °C we have

$$\varrho = 0.9971 \times 10^3 \text{ kg m}^{-3}$$
$$T = 298.15 \text{ K}$$
$$\varepsilon_r = 78.54.$$

These lead to

$$s = 7.134 \text{ Å} \qquad \alpha = 1.171. \qquad 7.18.2$$

Figure 7.2 gives a plot of $(\phi - 1)/z_+|z_-|$, determined by freezing-point measurements, against $I^{\frac{1}{2}}$ for several electrolytes of various charge types. The tangent at the origin shown as a broken line has the theoretical slope $\frac{1}{3}\alpha$ according to formula (7.17.17).

§7.19 *Less dilute solutions*

The limiting law of Debye and Hückel described in the previous two sections is most valuable in providing a reliable means of extrapolating experimental data to infinite dilution, since experimental measurements determine only ratios of the values of γ in the several solutions. To determine values of γ itself in the several solutions some assumption has to be made concerning the value of γ in at least one such solution, for example the most dilute. The limiting law of Debye and Hückel provides the necessary assumption.

On the other hand this limiting law is accurate only at very high dilutions. For example when the solvent is water it is accurate enough at $I = 10^{-3}$, but already at $I = 10^{-2}$ deviations are experimentally detectable and at $I = 10^{-1}$ deviations are serious. In other solvents having smaller permittivities deviations from the limiting law appear at correspondingly lower ionic strengths.

For less dilute solutions various formulae can be used, all reducing to the limiting formula of Debye and Hückel at high dilutions and all more or less empirical at less high dilutions. Two of these will be described in the succeeding sections.

§7.20 *Formulae of Debye and Hückel*

We saw in §7.17 how the limiting law of Debye and Hückel can be conveniently and succinctly expressed in terms of two lengths s and κ^{-1}, the former being completely determined by the solvent and the temperature, and the latter being inversely proportional to the square root of the ionic strength. The formulae for less dilute solutions contain another characteristic length a

representing an average distance of closest approach between pairs of ions and therefore called the *ionic diameter.*

Formula (7.17.3) of the limiting law is replaced by*

$$(G-G^{\text{id}})/RT=-\tfrac{1}{3}\sum_i n_i z_i^2 \kappa s\{\tfrac{3}{2}(1+\kappa a)^{-1}-\tfrac{1}{2}\sigma(\kappa a)\} \qquad 7.20.1$$

where $\sigma(y)$ is a tabulated function† defined by

$$\sigma(y)=3y^{-3}\{1+y-(1+y)^{-1}-2\ln(1+y)\} \qquad 7.20.2$$

or when $y<1$

$$\sigma(y)=1+3\sum_{t=1}^{\infty}(t+1)(t+3)^{-1}(-y)^t \qquad (y<1). \qquad 7.20.3$$

By differentiating (1) with respect to n_1 and noting that $\kappa \propto n_1^{-\frac{1}{2}}$ we deduce for the osmotic coefficient

$$\begin{aligned}(1-\phi)\sum_i n_i/n_1 &= (\mu_1-\mu_1^{\text{id}})/RT=-\tfrac{1}{2}\kappa \mathrm{d}\{(G-G^{\text{id}})/RT\}/\mathrm{d}\kappa \\ &= \tfrac{1}{6}\sum_i n_i z_i^2 \kappa s n_1^{-1}\sigma(\kappa a) \qquad 7.20.4\end{aligned}$$

so that

$$1-\phi=\tfrac{1}{6}(\sum_i n_i z_i^2/\sum_i n_i)\kappa s\sigma(\kappa a). \qquad 7.20.5$$

By differentiating (1) with respect to n_i and noting that $\kappa^2 \propto \Sigma_i n_i z_i^2$ we obtain

$$-\ln \gamma_i=\tfrac{1}{2}z_i^2 \kappa s(1+\kappa a)^{-1}. \qquad 7.20.6$$

As in §7.17 we now rewrite the above formulae for numerical calculations in terms of the ionic strength I and the dimensionless parameter α. Formula (1) becomes

$$(G-G^{\text{id}})/RT=-\tfrac{2}{3}\alpha\sum_i z_i^2 n_i I^{\frac{1}{2}}\{\tfrac{3}{2}(1+2\alpha I^{\frac{1}{2}}a/s)^{-1}-\tfrac{1}{2}\sigma(2\alpha I^{\frac{1}{2}}a/s)\}. \qquad 7.20.7$$

Formulae (5) and (6) become respectively

$$1-\phi=\tfrac{1}{3}\alpha(\sum_i z_i^2 m_i/\sum_i m_i)I^{\frac{1}{2}}\sigma(2\alpha I^{\frac{1}{2}}a/s) \qquad 7.20.8$$

$$-\ln \gamma_i=\alpha z_i^2 I^{\frac{1}{2}}(1+2\alpha I^{\frac{1}{2}}a/s)^{-1}. \qquad 7.20.9$$

For solutions containing only a single electrolyte composed of ν_+ cations of charge number z_+ and ν_- anions of charge number z_- these formulae, when we use the condition of electrical neutrality,

$$\nu_+ z_+ + \nu_- z_- = 0 \qquad 7.20.10$$

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* Debye and Hückel, Phys. Z. 1923 **24** 185.

† Harned and Owen, Physical Chemistry of Electrolyte Solutions, Reinhold 2nd ed. 1950 p. 597.

reduce to

$$1-\phi=\tfrac{1}{3}\alpha z_{+}|z_{-}|I^{\frac{1}{2}}\sigma(2\alpha I^{\frac{1}{2}}a/s) \qquad 7.20.11$$

$$-\ln\gamma_{\pm}=\alpha z_{+}|z_{-}|I^{\frac{1}{2}}(1+2\alpha I^{\frac{1}{2}}a/s)^{-1}. \qquad 7.20.12$$

§7.21 *Specific interactions*

The formulae of Debye and Hückel enunciated in the previous section contain a single adjustable parameter a. By ad hoc adjustment of the value assigned to a it is usually possible to account for the behaviour of a solution containing a single electrolyte at ionic strengths not exceeding 0.1. In a mixture of several electrolytes these formulae predict the same value of $\gamma_{\pm}$ for all electrolytes of the same charge type and this contradicts the experimental facts. To conform with these facts further adjustable parameters are essential. We shall describe the use of a simple and convenient set of such parameters. For the sake of brevity and simplicity we shall here consider solutions containing only ions of charge number ± 1.

We begin by choosing a real or hypothetical single electrolyte as a standard with which to compare other electrolytes either alone or in a mixed solution. We shall find that it does not matter how this standard electrolyte is prescribed provided it resembles a typical real electrolyte. We shall mention alternative convenient choices of the standard electrolyte:

1. Some real electrolyte, say NaCl.
2. A hypothetical electrolyte accurately described by the formulae ot Debye and Hückel with $2\alpha a/s=1$ which corresponds to $a\approx 3$Å in water.
3. A hypothetical electrolyte accurately described by the formulae of Debye and Hückel with $2a/s=1$ which corresponds to $a\approx 3.5$Å in water.

We use the superscript $^{\ominus}$ to denote the standard electrolyte and we repeat that what follows is independent of the choice of standard.

We assume that the Gibbs function G of a solution containing n_{R} cations R and n_{X} anions X is related to the Gibbs function $G^{\ominus}$ of a solution of the standard electrolyte at the same total molality m by

$$(G-G^{\ominus})/RT=n_1\sum_{\mathrm{R}}\sum_{\mathrm{X}}2\beta_{\mathrm{R,X}}m_{\mathrm{R}}m_{\mathrm{X}}. \qquad 7.21.1$$

The outstanding feature of this formula is that there is a single *interaction parameter* $\beta_{\mathrm{R,X}}$ for every combination of a cation R and an anion X, that is to say one parameter for each electrolyte. The formula contains no parameter for interaction between two cations, nor between two anions. This is the essence of a principle enunciated by Brønsted* in 1921 and called by him the *principle of specific interaction of ions*. According to this principle two ions of the same sign will so rarely come close to each other in dilute solution that their mutual interactions may be assumed to be determined by their charges, but otherwise to be non-specific. Ions of the opposite sign on the other hand often come close to each other and their mutual interactions are therefore specific depending on their sizes, shapes, polarizabilities, and so on. When this principle is introduced into a statistical treatment† it leads to parameters of the type $\beta_{R,X}$ but none of the type $\beta_{R,R'}$ or $\beta_{X,X'}$.

By differentiating (1) with respect to n_1 noting that $m_R \propto n_1^{-1}$ and $m_X \propto n_1^{-1}$ we obtain

$$\left(\sum_R n_R + \sum_X n_X\right)(\phi^\ominus - \phi) = -\sum_R \sum_X 2\beta_{R,X} m_R m_X \qquad 7.21.2$$

so that

$$\phi - \phi^\ominus = \sum_R \sum_X \beta_{R,X} m_R m_X / m \qquad 7.21.3$$

where

$$m = \sum_R m_R = \sum_X m_X. \qquad 7.21.4$$

By differentiating (1) with respect to n_R noting that $m_R \propto n_R$ we obtain

$$\ln(\gamma_R/\gamma^\ominus) = 2\sum_{X'} \beta_{R,X'} m_{X'}. \qquad 7.21.5$$

Similarly

$$\ln(\gamma_X/\gamma^\ominus) = 2\sum_{R'} \beta_{R',X} m_{R'}. \qquad 7.21.6$$

Consequently the mean activity coefficient $\gamma_{R,X}$ of RX is given by

$$\ln(\gamma_{R,X}/\gamma^\ominus) = \sum_{X'} \beta_{R,X'} m_{X'} + \sum_{R'} \beta_{R',X} m_{R'}. \qquad 7.21.7$$

In a solution of a single electrolyte RX these formulae reduce to

$$\phi - \phi^\ominus = \beta_{R,X} m$$
$$\ln(\gamma_{R,X}/\gamma^\ominus) = 2\beta_{R,X} m. \qquad 7.21.8$$

We see that every parameter $\beta_{R,X}$ can be determined by measurements on solutions of the single electrolyte RX. Thus the properties of all solutions of mixed electrolytes can be predicted from the properties of solutions of single electrolytes.

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* Brønsted, J. Amer. Chem. Soc. 1922 **44** 938.

† Guggenheim, Phil. Mag. 1935 **19** 588; Guggenheim, Applications of Statistical Mechanics, Clarendon Press 1966 chapter 9.

The *principle of specific interaction* leads to a number of conclusions concerning mixtures of electrolytes which have been confirmed experimentally by Brønsted*. We shall not give details, but shall merely mention one illustrative example of the usefulness of the principle.

From formula (7) it follows that the mean activity of NaCl present as a trace in a solution of HCl at $m=10^{-1}$ is equal to that of HCl present as a trace in a solution of NaCl at $m=10^{-1}$. The latter can be measured electrometrically, as we shall see in the next chapter, while there is no convenient experimental method for determining the former. Hence the former is best determined by measuring the latter.

TABLE 7.1

Interaction coefficients

Values of $\beta_{\mathrm{R,X}}-\beta_{\mathrm{Na,Cl}}$ at 25 °C

		NaF	−0.08	KF	−0.02		
HCl	0.12	NaCl	0.00	KCl	−0.05	RbCl	−0.09
HBr	0.18	NaBr	0.02	KBr	−0.04	RbBr	−0.10
HI	0.21	NaI	0.06	KI	0.00	RbI	−0.11
$HClO_4$	0.15	$NaClO_3$	−0.05	$KClO_3$	−0.19	$RbNO_3$	−0.29
		$NaClO_4$	−0.02			RbAc	0.11
LiCl	0.07	$NaBrO_3$	−0.14	$KBrO_3$	−0.22	CsCl	−0.15
LiBr	0.11			KIO_3	−0.22	CsBr	−0.15
LiI	0.20	$NaNO_3$	−0.11	KNO_3	−0.26	CsI	−0.16
						$CsNO_3$	−0.30
$LiClO_4$	0.19	NaAc	0.08	KAc	0.11	CsAc	0.13
$LiNO_3$	0.06	NaCNS	0.05	KCNS	−0.06	$AgNO_3$	−0.29
		NaH_2PO_4	−0.21	KH_2PO_4	−0.31	$TlClO_4$	−0.32
LiAc	0.03					$TlNO_3$	−0.51
						TlAc	−0.19

Values of the parameter $\beta_{\mathrm{R,X}}$ are known for a large number of 1 : 1 electrolytes in water. The values of $\beta_{\mathrm{R,X}}$ of course depend on the choice of standard electrolyte, but the difference between the values for any two electrolytes is almost independent of this choice. For this reason we give[†] in table 7.1 values of $\beta_{\mathrm{R,X}}-\beta_{\mathrm{Na,Cl}}$ at 25 °C. The values for HCl, NaCl, and KCl are obtained from electromotive-force measurements by use of the theory given in the following chapter. These values are probably accurate to ± 0.02. The remaining values are obtained by the isopiestic measurements

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[*] Brønsted, Kgl. Danske Videnskab. Selskab Mat.-Fys. Medd. 1921 **4**(4); J. Amer. Chem. Soc. 1922 **44** 877; 1923 **45** 2898.

[†] Guggenheim and Turgeon, Trans. Faraday Soc. 1955 **51** 747.

relative to NaCl or KCl of Robinson and Stokes*. Some of the β values may be uncertain by as much as ± 0.1 but most of them are probably more accurate than this.

§7.22 *Chemical reactions involving solvent*

In §7.14 we obtained the condition for equilibrium in a chemical reaction between solute ionic species, including non-ionic species as if they were ionic with $z=0$. We shall now consider how in dilute solution this condition can be extended to include chemical reactions involving the solvent.

A reaction involving the solvent is called *solvolysis* with the exception of simple addition called *solvation*. In particular if the solvent is water it is called *hydrolysis*.

For the sake of brevity we shall consider not the general case, but a specific example. We choose the hydrolysis of chlorine

$$\mathrm{Cl_2+2H_2O \rightarrow H_3O^+ + Cl^- + HOCl}. \qquad 7.22.1$$

The equilibrium condition in its most general form is

$$\lambda_{\mathrm{H_3O^+}}\lambda_{\mathrm{Cl^-}}\lambda_{\mathrm{HOCl}}/\lambda_{\mathrm{Cl_2}}\lambda^2_{\mathrm{H_2O}}=1 \qquad 7.22.2$$

which we rewrite as

$$\lambda_{\mathrm{H_3O^+}}\lambda_{\mathrm{Cl^-}}\lambda_{\mathrm{HOCl}}/\lambda_{\mathrm{Cl_2}}=\lambda^2_{\mathrm{H_2O}}. \qquad 7.22.3$$

According to (7.06.1) we have

$$\lambda_{\mathrm{H_2O}}/\lambda^0_{\mathrm{H_2O}}=\exp(-\phi\sum_i r_i). \qquad 7.22.4$$

In dilute solution it is sufficiently accurate to replace (4) by the approximation

$$\lambda_{\mathrm{H_2O}}/\lambda^0_{\mathrm{H_2O}}=1 \qquad 7.22.5$$

with an accuracy depending on the composition of the solution. As a typical example in an aqueous solution of 1 : 1 electrolytes at a total molality one tenth, we have approximately

$$\sum_i r_i \approx 3.6\times 10^{-3}$$

$$\phi\approx 0.92$$

so that

$$\lambda_{\mathrm{H_2O}}/\lambda^0_{\mathrm{H_2O}}\approx \exp(-3.3\times 10^{-3})\approx 0.997. \qquad 7.22.6$$

Hence we may usually replace (3) by

$$\lambda_{\mathrm{H_3O^+}}\lambda_{\mathrm{Cl^-}}\lambda_{\mathrm{HOCl}}/\lambda_{\mathrm{Cl_2}}=\lambda^{02}_{\mathrm{H_2O}}. \qquad 7.22.7$$

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* Robinson and Stokes, Trans. Faraday Soc. 1949 **45** 612.

Using the relation (7.09.1) for each reacting species other than the solvent H_2O we obtain

$$(m_{H_3O^+} m_{Cl^-} m_{HOCl}/m_{Cl_2})(\gamma_{H_3O^+} \gamma_{Cl^-} \gamma_{HOCl}/\gamma_{Cl_2}) = K_m(T) \qquad 7.22.8$$

the constant $\lambda^{02}_{H_2O}$ being absorbed as a factor of K_m.

From this typical example we see that for a chemical reaction involving the solvent, the equilibrium condition takes the approximate form in dilute solution

$$\prod{}'(m_i \gamma_i) = K_m(T) \qquad 7.22.9$$

where Π' differs from Π by the omission of factors relating to the solvent.

§7.23 *Acid–base equilibrium*

One of the most important classes of chemical processes between ions in solution, is that of the transfer of a proton from one ion or molecule to another. Any ion or molecule capable of losing a proton is called an *acid*; any ion or molecule capable of gaining a proton is called a *base*. These definitions due to Brønsted* are simpler and more rational than earlier definitions which they supersede. The acid and base which differ from each other by one proton are called a *conjugate pair*†. Obviously the electric charge number of any acid exceeds by unity that of its conjugate base. Table 7.2 gives examples of well-known conjugate pairs of acids and bases. It is clear from several examples in table 7.2 that an ion or a molecule may be both an acid and a base.

TABLE 7.2

Typical conjugate acids and bases

Acid	Base
CH_3CO_2H	$CH_3CO_2^-$
NH_4^+	NH_3
H_2O	OH^-
H_3O^+	H_2O
H_3PO_4	$H_2PO_4^-$
$H_2PO_4^-$	HPO_4^{2-}
HPO_4^{2-}	PO_4^{3-}
$H_3N^+ \cdot CH_2 \cdot CO_2H$	$H_3N^+ \cdot CH_2 \cdot CO_2^-$
$H_3N^+ \cdot CH_2 \cdot CO_2^-$	$H_2N \cdot CH_2 \cdot CO_2^-$

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* Brønsted, Rec. Trav. Chim. Pays-Bas 1923 **42** 718.

† Brønsted and Guggenheim, J. Amer. Chem. Soc. 1927 **49** 2554.

If A and B denote an acid and its conjugate base, while A′ and B′ denote another conjugate pair then the chemical reaction

$$A+B'\rightarrow B+A' \qquad 7.23.1$$

is typical of acid–base reactions. The equilibrium condition is

$$(m_B m_{A'}/m_A m_{B'})(\gamma_B \gamma_{A'}/\gamma_A \gamma_{B'})=K \qquad 7.23.2$$

where K depends on the solvent and the temperature, but not on the composition of the solution. As a typical example we have, using Ac as an abbreviation for CH_3CO_2

$$NH_4^+ + Ac^- \rightarrow NH_3 + HAc \qquad 7.23.3$$

$$(m_{NH_3} m_{HAc}/m_{NH_4^+} m_{Ac^-})(\gamma_{NH_3} \gamma_{HAc}/\gamma_{NH_4^+} \gamma_{Ac^-})=K. \qquad 7.23.4$$

Since water is both a base and an acid it can react with either an acid or a base dissolved in it. As examples of acids reacting with water, we mention

$$HAc+H_2O\rightarrow Ac^- + H_3O^+ \qquad 7.23.5$$

$$NH_4^+ + H_2O\rightarrow NH_3+H_3O^+ \qquad 7.23.6$$

$$H_2PO_4^- + H_2O\rightarrow HPO_4^{2-} + H_3O^+ \qquad 7.23.7$$

and as examples of bases reacting with water

$$H_2O+Ac^- \rightarrow OH^- + HAc \qquad 7.23.8$$

$$H_2O+NH_3\rightarrow OH^- + NH_4^+ \qquad 7.23.9$$

$$H_2O+H_2PO_4^- \rightarrow OH^- + H_3PO_4. \qquad 7.23.10$$

We note that according to the definition of *hydrolysis* given in the preceding section, reactions (5) to (10) are all examples of *hydrolysis.* On the other hand reaction (3) does not involve the solvent H_2O and is therefore not a *hydrolysis.*

The reactions (5), (6), and (7) are all examples of the general type

$$A+H_2O\rightarrow B+H_3O^+ \qquad 7.23.11$$

of which the equilibrium condition in dilute solution becomes

$$(m_B m_{H_3O^+}/m_A)(\gamma_B \gamma_{H_3O^+}/\gamma_A)=K_A \qquad 7.23.12$$

where K_A is called the *acidity constant* of A in water at the given temperature. K_A is a measure of the strength of the acid A relative to water. The reciprocal of K_A may likewise be regarded as a measure of the strength of the conjugate base B. For example the acidity constants K_{HAc} of HAc and $K_{NH_4^+}$ of NH_4^+ have the values at 25 °C

$$K_{HAc} = 1.75 \times 10^{-5} \qquad 7.23.13$$

$$K_{NH_4^+} = 6.1 \times 10^{-10}. \qquad 7.23\ 14$$

Two molecules of H_2O can react together, the one acting as an acid, the other as a base, thus:

$$H_2O + H_2O \rightarrow OH^- + H_3O^+.$$

The equilibrium is determined by

$$m_{H_3O^+} m_{OH^-} \gamma_{H_3O^+} \gamma_{OH^-} = K_w \qquad 7.23.15$$

where K_w is called the *ionization product* of water. Its values at various temperatures are as follows:

$$0\ °C \quad K_w = 0.115 \times 10^{-14} \qquad 7.23.16$$

$$20\ °C \quad K_w = 0.68 \times 10^{-14} \qquad 7.23.17$$

$$25\ °C \quad K_w = 1.01 \times 10^{-14}. \qquad 7.23.18$$

The equilibrium constants for reactions of the type

$$H_2O + B \rightarrow OH^- + A \qquad 7.23.19$$

can always be expressed in terms of an acidity constant and the ionization constant of water. For example for reaction (8) we have

$$(m_{OH^-} m_{HAc}/m_{Ac^-})(\gamma_{OH^-} \gamma_{HAc}/\gamma_{Ac^-}) = K_w/K_{HAc} \qquad 7.23.20$$

where K_{HAc} is the acidity constant K_A of HAc. Similarly for reaction (9) we have

$$(m_{OH^-} m_{NH_4^+}/m_{NH_3})(\gamma_{OH^-} \gamma_{NH_4^+}/\gamma_{NH_3}) = K_w/K_{NH_4^+} \qquad 7.23.21$$

where $K_{NH_4^+}$ denotes the acidity constant of NH_4^+.

If we apply the definition (12) of an acidity constant to H_3O^+ we obtain

$$\begin{aligned} K_{H_3O^+} &= (m_{H_2O} m_{H_3O^+}/m_{H_3O^+})(\gamma_{H_2O} \gamma_{H_3O^+}/\gamma_{H_3O^+}) \\ &= m_{H_2O} \gamma_{H_2O} \\ &\approx m_{H_2O} \approx 55.5. \qquad 7.23.22 \end{aligned}$$

From (12) and (22) we see that no molecule or ion which is a much stronger acid than H_3O^+ can exist in appreciable quantity in water. For example HCl is a much stronger acid than H_3O^+. Consequently when dissolved in water it is almost completely changed to H_3O^+ and Cl^-. Similarly H_2SO_4

is a much stronger acid than H_3O^+ and is therefore almost completely changed to H_3O^+ and HSO_4^-. On the other hand $K_{HSO_4^-} = 1.0 \times 10^{-2}$ so that HSO_4^- being a much weaker acid than H_3O^+ can exist in appreciable amount in water.

Similarly no base much stronger than OH^- can exist in appreciable quantity in water, since it would be hydrolysed to its conjugate acid and OH^-. Examples of bases too strong to exist in water are O^{2-} and NH_2^- which are hydrolysed as follows

$$H_2O + O^{2-} \rightarrow OH^- + OH^- \qquad 7.23.23$$

$$H_2O + NH_2^- \rightarrow OH^- + NH_3. \qquad 7.23.24$$

Examples of very strong bases, but not so strong that they cannot exist at all in water are S^{2-} and CN^-.

When a strongly alkaline substance such as NaOH is dissolved in water, the base present in the solution is OH^-. Often NaOH is itself referred to loosely as a base.

Similar relations hold in other solvents which can react as both base and acid. Reactions of an ion or molecule with the solvent are called *solvolysis.*

§7.24 *Weak electrolytes*

An electrically neutral molecule, not itself an electrolyte, which by hydrolysis or other reaction is partly changed into ions is often called a *weak electrolyte.* In particular an electrically neutral acid such as HAc which is partly hydrolysed according to

$$HAc + H_2O \rightarrow Ac^- + H_3O^+ \qquad 7.24.1$$

and an electrically neutral base such as NH_3 which is partly hydrolysed according to

$$H_2O + NH_3 \rightarrow OH^- + NH_4^+ \qquad 7.24.2$$

are by this definition *weak electrolytes.* For these substances the names *electrically neutral acids* and *electrically neutral bases* are sufficient and more informative.

§7.25 *Surface phases*

The formulae previously derived for surface phases apply just as well to solutions of electrolytes as to solutions of non-electrolytes. In particular for variations of composition at constant temperature formula (5.26.1) becomes

$$-\mathrm{d}\gamma=\sum_i(\Gamma_i-r_i\Gamma_1)\mathrm{d}\mu_i \qquad (T \text{ const.}) \qquad 7.25.1$$

where the summation Σ_i extends over all ions and other solute species. Expressed in terms of absolute activities (1) becomes

$$-\mathrm{d}\gamma=RT\sum_i(\Gamma_i-r_i\Gamma_1)\,\mathrm{d}\ln\lambda_i \qquad (T \text{ const.}). \qquad 7.25.2$$

Even if the solution is extremely dilute the term $r_i\Gamma_1$ must not be omitted for although $r_i \ll 1$ at the same time $|\Gamma_1| \gg |\Gamma_i|$.

The above relations, and in fact all the relations, for the surface of an electrolyte solution are formally analogous to those for the surface of a non-electrolyte solution. There is however a significant difference requiring careful treatment, namely counting the number of independent components. Let us consider some typical examples beginning with the simplest.

A solution of hydrochloric acid in water contains the species H_2O, H_3O^+, and Cl^-. We omit OH^-, not so much because it is present in negligible amount as because it is in any case not an independent component, since

$$OH^-=2H_2O-H_3O^+. \qquad 7.25.3$$

Of the three species H_2O, H_3O^+, and Cl^- the condition for electrical neutrality imposes the restrictions

$$m_{H_3O^+}=m_{Cl^-} \qquad 7.25.4$$

$$\Gamma_{H_3O^+}=\Gamma_{Cl^-} \qquad 7.25.5$$

so that there are only two independent components. We may take these to be H_2O on the one hand and $(H_3O^+ + Cl^-)$ on the other. More simply we may choose as independent components H_2O and HCl.

Similarly a solution of sodium hydroxide in water contains the species H_2O, OH^-, and Na^+. We omit H_3O^+ not so much because it is present in negligible amount as because it is in any case not an independent component owing to (3). The condition for electrical neutrality imposes the restrictions

$$m_{OH^-}=m_{Na^+} \qquad 7.25.6$$

$$\Gamma_{OH^-}=\Gamma_{Na^+} \qquad 7.25.7$$

so that there are only two independent components which we may take to be H_2O and NaOH. Thus for the surface tension of the solution of NaOH we have at constant temperature

$$\begin{aligned}-\mathrm{d}\gamma &= RT(\Gamma_{Na^+}-r_{Na^+}\Gamma_{H_2O})\,\mathrm{d}\ln\lambda_{Na^+}+RT(\Gamma_{OH^-}-r_{OH^-}\Gamma_{H_2O})\,\mathrm{d}\ln\lambda_{OH^-}\\ &= 2RT(\Gamma_{NaOH}-r_{NaOH}\Gamma_{H_2O})\,\mathrm{d}\ln(m_{NaOH}\gamma_{Na,OH}) \qquad 7.25.8\end{aligned}$$

where m_{NaOH} and Γ_{NaOH} are defined by, respectively,

$$m_{\mathrm{Na}^+} = m_{\mathrm{OH}^-} = m_{\mathrm{NaOH}} \tag{7.25.9}$$

$$\Gamma_{\mathrm{Na}^+} = \Gamma_{\mathrm{OH}^-} = \Gamma_{\mathrm{NaOH}}. \tag{7.25.10}$$

The reader should have no difficulty in distinguishing between γ without any subscript denoting surface tension and $\gamma_{\mathrm{Na,OH}}$ denoting the mean activity coefficient of NaOH.

Let us now consider a solution made by dissolving both hydrogen chloride and sodium hydroxide in water. Of the five species H_2O, H_3O^+, OH^-, Na^+, and Cl^- in the system only three are independent. For the equilibrium

$$H_2O + H_2O \rightarrow H_3O^+ + OH^- \tag{7.25.11}$$

imposes the restriction

$$m_{\mathrm{H_3O}^+}\, m_{\mathrm{OH}^-}\, \gamma_{\mathrm{H_3O}^+}\, \gamma_{\mathrm{OH}^-} = K_{\mathrm{w}} \tag{7.25.12}$$

and the condition for electrical neutrality imposes the restrictions

$$m_{\mathrm{Na}^+} + m_{\mathrm{H_3O}^+} = m_{\mathrm{Cl}^-} + m_{\mathrm{OH}^-} \tag{7.25.13}$$

$$\Gamma_{\mathrm{Na}^+} + \Gamma_{\mathrm{H_3O}^+} = \Gamma_{\mathrm{Cl}^-} + \Gamma_{\mathrm{OH}^-}\,. \tag{7.25.14}$$

If the hydrogen chloride is in excess, it is natural to choose as the three independent components H_2O, NaCl, and HCl. In this case m_{OH^-} is negligible compared with all the other terms in (13). If on the contrary the sodium hydroxide is in excess, it is natural to choose as the three independent components H_2O, NaCl, and NaOH. In this case $m_{\mathrm{H_3O}^+}$ is negligible compared with the other terms in (13). These remarks apply equally to the bulk of the solution and to the surface layer.

Suppose now we stipulate that precisely equivalent amounts of hydrogen chloride and sodium hydroxide are contained in the solution. Then the relation (13) is replaced by the two relations

$$m_{\mathrm{Na}^+} = m_{\mathrm{Cl}^-} \tag{7.25.15}$$

$$m_{\mathrm{H_3O}^+} = m_{\mathrm{OH}^-} \tag{7.25.16}$$

so that the solution contains only two independent components, which we naturally take to be H_2O and NaCl. But the restriction (15) which reduces by one the number of independent components in the bulk of the solution, does not imply any analogous restriction on the Γ's. In other words the surface layer can contain as well as H_2O and NaCl either an excess of HCl or an excess of NaOH. Thus the number of components necessary to describe the composition of the surface phase is still three, not two.

We shall now analyse this problem, beginning with unspecified quantities of NaCl and NaOH dissolved in water, introducing the restriction that the quantity of NaOH is zero only at a later stage. There are four ionic species Na^+, Cl^-, H_3O^+, and OH^- in the solvent H_2O. These are not independent, but are subject to the conditions for electrical neutrality

$$m_{Na^+}+m_{H_3O^+}=m_{Cl^-}+m_{OH^-} \tag{7.25.17}$$

$$\Gamma_{Na^+}+\Gamma_{H_3O^+}=\Gamma_{Cl^-}+\Gamma_{OH^-} \tag{7.25.18}$$

and to the condition for ionization equilibrium of the solvent water

$$\lambda_{H_3O^+}\lambda_{OH^-}=\lambda^2_{H_2O}=\text{const.} \tag{7.25.19}$$

For variations of the surface tension with composition at constant temperature we have the general relation of the form (2)

$$\begin{aligned}-\mathrm{d}\gamma/RT=&(\Gamma_{Na^+}-r_{Na^+}\Gamma_{H_2O})\,\mathrm{d}\ln\lambda_{Na^+}\\&+(\Gamma_{Cl^-}-r_{Cl^-}\Gamma_{H_2O})\,\mathrm{d}\ln\lambda_{Cl^-}\\&+(\Gamma_{H_3O^+}-r_{H_3O^+}\Gamma_{H_2O})\,\mathrm{d}\ln\lambda_{H_3O^+}\\&+(\Gamma_{OH^-}-r_{OH^-}\Gamma_{H_2O})\,\mathrm{d}\ln\lambda_{OH^-}.\end{aligned} \tag{7.25.20}$$

Using (17), (18), and (19) we can replace (20) by

$$\begin{aligned}-\mathrm{d}\gamma/RT=&(\Gamma_{Cl^-}-r_{Cl^-}\Gamma_{H_2O})\,\mathrm{d}\ln(\lambda_{Na^+}\lambda_{Cl^-})\\&+([\Gamma_{Na^+}-\Gamma_{Cl^-}]-[r_{Na^+}-r_{Cl^-}]\Gamma_{H_2O})\,\mathrm{d}\ln(\lambda_{Na^+}\lambda_{OH^-})\\=&(\Gamma_{Cl^-}-r_{Cl^-}\Gamma_{H_2O})\,\mathrm{d}\ln(m_{Na^+}m_{Cl^-}\gamma^2_{Na,Cl})\\&+([\Gamma_{Na^+}-\Gamma_{Cl^-}]-[r_{Na^+}-r_{Cl^-}]\Gamma_{H_2O})\,\mathrm{d}\ln(m_{Na^+}m_{OH^-}\gamma^2_{Na,OH}).\end{aligned} \tag{7.25.21}$$

Thus by studying the dependence of the surface tension on the composition by variations of the molalities of NaCl and of NaOH, provided the activity coefficients are known, we can determine the separate values of

$$\Gamma_{Cl^-}-r_{Cl^-}\Gamma_{H_2O} \tag{7.25.22}$$

and of

$$[\Gamma_{Na^+}-\Gamma_{Cl^-}]-[r_{Na^+}-r_{Cl^-}]\Gamma_{H_2O}. \tag{7.25.23}$$

The expression (22) is a measure of the adsorption of NaCl relative to H_2O, while the expression (23) is a measure of the adsorption of NaOH relative to H_2O. In particular as the molality of NaOH is made to tend to zero, so the quantity (23) tends to

$$\Gamma_{Na^+}-\Gamma_{Cl^-}. \tag{7.25.24}$$

The value of (24) then becomes the surface concentration of NaOH in a solution which in the bulk contains only NaCl and H_2O.

To recapitulate, by varying the molalities of both NaCl and NaOH and measuring surface tension we can determine separately the coefficients of the two terms on the right of (21), namely the quantities (22) and (23) of which the latter reduces to (24) in a solution containing no excess NaOH. By measuring the surface tension of solutions containing varying amounts of NaCl only without any NaOH it is not possible to separate the two terms on the right of (21) and consequently the quantity (22) can not be determined in this way.