Thermodynamics of Redox and Solubility Equilibria Based on Hydration and Partial Dissociation of Electrolytes

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Abstract

Thermodynamic treatments of properties of strong electrolytes in aqueous solutions based on the idea of complete dissociation and activity coefficients became too complicated to be meaningful. Therefore, on systematically re-investigating the existing data, it became evident that the earlier ideas of partial dissociation and hydration were correct. The degrees of dissociation and hydration numbers evaluated from vapor pressures or osmotic coefficients could explain many thermodynamic properties quantitatively (from zero to saturation for electrolytes like NaCl). This paper presents simple thermodynamic relations for redox and solubility equilibria in terms of ionic molalities and hydration. Lewis and Randall's results for a classical electrochemical cell have been used for demonstrating the new approach.

Key words: Partial dissociation, Strong electrolytes, Solubility, Nernstian redox, Transfer coefficients, Solution thermodynamics

1. Introduction

Lewis and Randall's classical paper[1] on solution thermodynamics introduced into physical chemistry the arbitrary concepts of activity and activity coefficients despite concern among contemporary scientists. A historical account[2,3a] shows that even the survival of the Journal of Physical Chemistry was at stake due to the concentration/activity controversy.

This paper brings out the simple thermodynamic relations pertaining to the physical chemistry and electrochemistry of reversible reactions based on ionic association/dissociation and hydration. For explaining the present approach, considered here are the processes in a classical cell of the type,[1,4-6]

H_2 ; HCl ; AgCl/Ag (or Hg_2Cl_2 /Hg) [1]

The cell consists of a normal hydrogen electrode and a silver-silver chloride electrode (or calomel electrode, CE for short) dipping in a solution of HCl of molality m.

At the hydrogen electrode, the hydrogen ions of HCl and H_2 (gas) establish the reversible redox equilibrium,

$$1/2\ H_2(g) <==> H^+ + e^- \qquad [2]$$

and the potential of the hydrogen electrode, E_H is given by[4-6]

$$E_H - E^o_H = k\ln[H^+]/[1/2\ H_2] \qquad [3a]$$

$$= k\ln[H^+] \qquad [3b]$$

where $k = RT/F = 0.02568$ V at 25 ^{o}C and E^{o}_{H} is the standard potential of the hydrogen electrode. For a normal hydrogen electrode, $H_2(g)$ is maintained at a constant pressure of one atmosphere and therefore, E_H is directly proportional to $\ln[H^+]$ as per Eq. 3b.

At the Ag, AgCl electrode, the Cl^- ions of HCl establish the reversible equilibrium with AgCl (s),

$$AgCl\ (s) + e^- <==> Ag\ (s) + Cl^- \qquad [4]$$

and the potential, E_{AgCl} is given by

$$E_{AgCl} – E^{o}_{AgCl} = k \ln[AgCl]_s /[Ag]_s[Cl^-] \qquad [5a]$$

$$= -k\ln[Cl^-] \qquad [5b]$$

where E^{o}_{AgCl} is the standard potential of the Ag, AgCl electrode. The solid (s) components do not contribute to the E.M.F. and hence E_{AgCl} is directly proportional to $–\ln [Cl^-]$, see Eq. 5b.

The measured E.M.F., E of the cell (see Eq.1) corresponds the difference,

$$E = E_{AgCl} - E_H \qquad [6a]$$

$$= (E^{o}_{AgCl} - E^{o}_{H}) - k \ln[H^+] – k \ln[Cl^-] \qquad [6b]$$

$$= E^{o} - k\ln[H^+] - k\ln[Cl^-] \qquad [6c]$$

where the difference (E^o_{AgCl} - E^o_H) = E^o_{AgCl} = E^o is the standard potential of the silver/silver chloride electrode with reference to E^o_H (which is defined as zero). The difference $\Delta E = (E - E^o)$ thus depends on $\ln[H^+][Cl^-]$. If one uses a calomel electrode (CE) then E and E^o will refer to CE in the above equations,[6] but this will not alter the difference, ΔE. (For the latest work on the absolute potentials, see Heyrovska[3h].)

2. Interpretation of E.M.F. based on complete dissociation

The ideal value of ΔE expected for complete dissociation of the electrolyte,

$$\begin{array}{ll} HCl \dashrightarrow H^+ + Cl^- & [7] \\ (m-m) \quad m + m & \end{array}$$

is $-2k \ln m$, where m is the molality of either ion. However experiments always give an excess E.M.F., ($\Delta E + 2k \ln m$). This excess is converted into the arbitrary non-ideality parameter, defined[1] as the mean molal ionic activity coefficient, $\gamma_{+/-}$

$$E - E^o = -2k \ln m - 2k \ln\gamma_{+/-} = -2k \ln a_{+/-} \qquad [8]$$

where $a_{+/-}$ (= $m\gamma_{+/-}$ = a_{H+} = a_{Cl-}) is defined[1] as the mean molal ionic activity. For evaluating $\gamma_{+/-}$ from the measured values of E, it is necessary to know the value of E^o (when $a_{+/-} = 1$). This is usually done[4-6] by using the approximation for $\ln \gamma_{+/-}$ from the Debye-Huckel theory for moderate concentrations that,

$$\ln \gamma_{+/-} = Am^{1/2} + Bm \qquad [9]$$

where A and B are constants related to the dielectric constant, temperature and charge of the ions. On substituting Eq. 9 for $\ln\gamma_{+/-}$ in Eq. 8, one gets,

$$E + 2k(\ln m + Am^{1/2}) = E^o - 2k\,Bm \qquad [10]$$

The left hand side of this equation is then plotted against m and the value of E^o is found as the intercept at m = 0 ($\ln\gamma_{+/-} = 0$ at m = 0). Harned and Ehlers[7] thus obtained a value of 0.22239 V for E^o at 25 °C. This value of E^o is used in Eq. 8 to evaluate γ_+ from the measured values of E at various molalities m.

3. The standard potentials E^o_{AgCl} and $E^o_{Ag,Ag+}$ and the solubility of AgCl

The standard potential E^o_{AgCl} (see Eq. 5a) of the Ag, AgCl electrode is actually the sum of two terms corresponding to the solubility equilibrium established by the Cl^- ions from HCl with AgCl (Eq. 11a) and the Ag, Ag^+ redox equilibrium (Eq. 11b),[4-6]

$$AgCl(s) \Longleftrightarrow Ag^+ + Cl^- \qquad [11a]$$

$$Ag^+ + e^- \Longleftrightarrow Ag(s) \qquad [11b]$$

$$AgCl(s) + e^- \Longleftrightarrow Ag(s) + Cl^- \qquad [11a] + [11b] = [4]$$

Therefore, E^o_{AgCl} in Eq. 5 is the sum of two terms,

$$E^o_{AgCl} = k \ln\{[Ag^+]^o[Cl^-]^o/[AgCl]^o_s + k \ln\{[Ag]^o_s/[Ag^+]^o\} \qquad [12a]$$

$$= k \ln K^o_{so} + E^o_{Ag,\,Ag+} \qquad [12b]$$

where $E^o_{Ag,Ag+}$ = 0.799 V, is the standard redox potential (E^o_H = 0) of the Ag, Ag^+ redox couple (which can be measured or obtained as the sum of the heat of sublimation, heat of solution, ionization potential and electron affinity),[6] $[Ag^+]$ = $K^o_{so}/[Cl^-]$ is the concentration of silver ions in equilibrium with $[Cl^-]$ from HCl, K^o_{so} = $[Ag^+]\ [Cl^-] = a_{+/-}^2 = 1.763 \times 10^{-10}$ is the solubility product of AgCl in pure water and $a_{+/-} = 1.33 \times 10^{-5}$ (mean ionic activity of Ag^+ or Cl^-). Therefore, E^o_{AgCl} = 0.799 - 0.577 = 0.222 V. (All values are for 25 °C from Ref. 5). It can be seen that this agrees well with the value (0.2224 V) obtained by by the EMF method by Harned and Ehlers.[7]

On using the above relations in Eqs. 5 and 6, one gets,

$$E_{AgCl} - E^o_{Ag,Ag+} = k\ln\,[Ag^+] \qquad [13]$$

$$E = E^o_{Ag,Ag+} + k\ \ln\,[Ag^+] - k\ \ln\,[H^+] \qquad [14]$$

Thus, Eq. 14 shows the dependence of E on the $[Ag^+]$ and $[H^+]$. If one uses a calomel electrode (see Eq. 1) instead of AgCl electrode, Eq. 14 would have $E^o_{Hg,Hg+}$ (= 0.799 V) which happens to have the same value as $E^o_{Ag,Ag+}$. (Note: Hg^+ actually stands for $(1/2)Hg_2^{++}$.)

4. Interpretation based on partial dissociation and hydration

Although one gets the right value for E^o_{AgCl} by using Eq. 10, the significance and interpretation of the activity coefficient, $\gamma_{+/-}$ based on the idea of complete dissociation has remained obscure and complicated[4,8] from the time of its arbitrary conception.[1] Eventually, the idea of complete dissociation was abandoned.[3b-g]

The thermodynamic properties of strong electrolytes, including the E.M.F. of concentration cells, have since been quantitatively interpreted[3b-e] based on the earlier[9,10] idea of hydration and partial dissociation of electrolytes,[9]

$$HCl \; <==> H^+ + Cl^- \qquad [15]$$

$$(m - \alpha m) \qquad \alpha m + \alpha m$$

where α is the degree of dissociation. Thus note that the molality of either ion (H^+ or Cl^-) is αm, molality of the ion pair is $(1-\alpha)m$ and that the total number of moles of solute is not 2m as for complete dissociation but is given by $im = (1- \alpha)m + 2\alpha m = (1+\alpha)m$, where i is the van't Hoff factor. The available data on vapor pressures (or the related solvent activity, a_A or osmotic coefficients, ϕ) were used to evaluate α and the hydration numbers. All the details of the method and Tables of data for nearly fifty 1:1 strong electrolytes can be found in Refs.3b-e.

On the basis of hydration and partial dissociation of the electrolyte, E is proportional to ln r, where r is the ionic molality per mole of free water.[3b,d,e] The ion pair does not contribute to E. Hence, instead of Eq. 8 one has,

$$E - E^o = \Delta E = - 2k\delta_A \ln [(\alpha m/n_{Af})/r^o] \qquad [16a]$$

$$= - 2k\delta_A \ln (r/r^o) \qquad [16b]$$

where $n_{Af} = 55.51 - mn_s$ is the molality of free water, n_s is the hydration number, $r = (\alpha m/n_{Af})$, $r^o = (\alpha m/n_{Af})^o$ when $\Delta E = 0$ (corresponds to $a_{+/-} = 1$ in Eq. 8) and δ_A is a constant close to unity (discussed later in this paper) and is obtained from the slope of the linear dependence of E on ln (r). From the intercept at $E = E^o$ ($= E^o_{AgCl} = 0.2224$ V), one gets the mole ratio r^o. Alternately, since the measured values of E are stored in the literature extensively in the coverted form of $\gamma_{+/-}$ using Eq. 8, one can plot ln ($a_{+/-}$) vs ln (r) and obtain ln (r^o) from the intercept of the line at ln (a_+) = 0.

The linear dependence of E on ln (r) is shown in Fig.1, where the data on γ_+ for HCl(aq) at 25 ^oC given by Lewis and Randall[1] (see Table 1, this paper) were used to calculate E for the AgCl electrode ($E^o = 0.2224$V) and for the calomel electrode (CE, $E^o = 0.268$ V). The α and n_s values (evaluated from osmotic coefficients) from Ref. 3e (also given in Table 1 here) have been used for obtaining the mole ratio r. From the slope and intercept, one gets $\delta_A = 0.963$ and $r^o = 0.0217$. The values of r^o and δ_A obtained by using more recent γ_+ data have been tabulated[3b.d.e] for many 1:1 electrolytes. For HCl,[3e] $\delta_A = 0.980$ and $r^o = 0.0216$ when $\Delta E = 0$. (Note that in Eq. 8, by the arbitrary use[1] of $a_{+/-}$ and $\gamma_{+/-}$, the information about the two quantities r^o and δ_A is lost).

Thus, Eqs. 16 based on the mole ratio r replace Eq. 8 based on the idea of complete dissociation and mean ionic activity and activity coefficient.

Since the ratio r can be obtained from vapor pressure or osmotic coefficient data, and since ln (r/r^o) and the difference in E.M.F., ΔE are proportional to each other, one can use in general, any other convenient reference value E_{ref} (instead of E^o) corresponding to the mole ratio r_{ref} and write Eq. 16b as,

$$E - E_{ref} = \Delta E = -2k\, \delta_A \log (r/ r_{ref}) \qquad [17]$$

For getting a better insight into the significance of r^o and δ_A (of Eq.16), some basic thermodynamic relations have been reconsidered here in terms of the mole ratios r.

5. Chemical and electrochemical aspects of redox equilibria

For a simple reversible redox equilibrium involving an oxidised (O) and reduced (R) form and a single electron,

$$O + e^- <==> R \qquad [18]$$

the chemical equilibrium is attained when the concentrations (these will be replaced by mole ratios (r) later in the final equations) attain the equilibium values, $[O]^o$ and $[R]^o$ and the rates of reduction and oxidation become equal:

$$k_O[O]^o = k_R[R]^o \qquad [19]$$

where k_O and k_R are the rate constants for reduction and oxidation respectively. The equilibrium constant K^o is obtained from Eq.19 as the ratio,

$$K^o = k_O / k_R = [R]^o/[O]^o = \exp(- \Delta G^o/RT) \qquad [20]$$

where ΔG^o is the corresponding standard free energy of the redox process.

Since redox equilibria involve transfer of charge, the concentrations, $[O]^o$ and $[R]^o$ can be changed/perturbed by electrochemical oxidation/reduction. In accordance with the Le Chatelier principle, new equilibrium values of [O] and [R] are established depending on the value of the applied E.M.F., E. The electrochemical equilibria are described by the equality of the rates,[6]

$$k_O\,[O]\exp(-\alpha_O E/k) = k_R\,[R]\exp(\alpha_R E/k) = i^o/F \qquad [21]$$

where α_O and α_R are the electron transfer coefficients, which add up to unity for a reversible process yielding the Nernst equation, and i^o is measured as the exchange current density, see e.g., Ref.11. In Eq. 21 the following relations hold:

$$[O]^o = [O]\exp(-\ \alpha_O E/k) \text{ and } [R]^o = [R]\exp(\alpha_R E/k) \qquad [22a]$$

$$\alpha_O E = k \ln [O]/[O]^o \text{ and } \alpha_R E = k \ln [R]^o/[R] \qquad [22b]$$

$$(\alpha_O + \alpha_R)E = k \ln K^o + k \ln [O]/[R] \qquad [22c]$$

$$(\alpha_O + \alpha_R) = 1 \qquad \text{(Nernst equilibrium)} \qquad [22d]$$

When $E = E^o$, the following relations hold:

$$[O] = [R] = ([O]^o + [R]^o)/2 = [O]^o(1+K^o)/2 = [R]^o(1+K^o)/2K^o \qquad [23a]$$

$$[O] = [O]^o \exp(\alpha_O E^o/k) = [R] = [R]^o \exp(-\alpha_R E^o/k) \qquad [23b]$$

$$\alpha_O E^o = k \ln [O]/[O]^o = k \ln [(1+K^o)/2] \qquad [23c]$$

$$\alpha_R E^o = k \ln [R]^o/[R] = k \ln [2K^o/(1+K^o)] \qquad [23d]$$

$$(\alpha_O + \alpha_R)E^o = E^o = k \ln K^o \qquad [23c] + [23d] + [22d] = [23e]$$

$$\alpha_O \ln K^o = \ln [(1+K^o)/2] \text{ and } \alpha_R \ln K^o = \ln [2K^o/(1+K^o)] \qquad [23f]$$

From Eqs. 22c, d and 23e, one obtains the Nernst equation,

$E = E^o + k \ln [O]/[R]$ (Nernst equation) [24]

The free energy relation corresponding to the redox equilbrium, Eqs. 22a and the Nernst equation, Eq. [24] is:

$\Delta G^o = \{RT\ln [R] + \alpha_R FE\} - \{RT\ln[O] - \alpha_O FE\}$ [25]

where $\Delta G^o = -RT \ln K^o = -FE^o$ and $\Delta G = -FE$ is the (electrical) free energy corresponding to the E.M.F. E. Thus, when $K^o > 1$, E^o is positive, ΔG^o is negative, and vice versa.

Eqs. 23c,d,f show that the transfer coefficients depend on K^o and can be calculated from a knowledge of K^o or the standard redox potentials, E^o. The following three cases of Eq. 23f depend on K^o as shown:

$K^o = 1$; $E^o = 0$; $[R]^o = [O]^o$; $\alpha_O = \alpha_R = (0/0)$ [26a]

$K^o >> 1$; $E^o >> k$; $[R]^o >> [O]^o$; $\alpha_O \ln K^o = \ln (K^o/2) > \alpha_R \ln K^o = \ln 2$ [26b]

$K^o << 1$; $E^o << k$; $[R]^o << [O]^o$; $\alpha_O \ln K^o = -\ln 2 < \alpha_R \ln K^o = \ln (2K^o)$ [26c]

The above equations show that α_O is small for large and negative values of E^o and follows an S-shaped curve as E^o increases from -ve to positive values, with an inflexion point at $E^o = 0$. The reverse trend holds for α_R. For an earlier thermodynamic explanation of the transfer coefficients treating O and R as consisting of holes and electrons respectively, see Ref. 3f.

The value of $E^o_H = 0$ (see Eq. 3) for the normal hydrogen electrode corresponds to Eq. 26a. For $E^o_{Ag,Ag+} = 0.799$ V (= $E^o_{Hg,Hg+}$); $K^o = 3.255 \times 10^{13}$ and from Eq. 26b, α_O (Ag^+) = α_O(Hg^+) = 30.421 /31.114 =0.978 and α_R (Ag) = α_R (Hg) = 0.693/31.114 = 0.022. For $E^o_{AgCl} = 0.2224$, $K^o = 5.77 \times 10^3$ and again from Eq. 26b, α_R (Cl^-) = 0.693/8.660 = 0.08 and α_O (Cl) = 0.92. However, this is a composite equilibrium consisting of a redox and a solubility process (see Eqs. 12). The Na,Na^+ redox with $E^o = -2.714$ V and $K^o = 1.263 \times 10^{-46}$ is an example of the last case, Eq. 26c with α_O (Na^+) =0.007 and α_R (Na) = 0.993. When $\alpha_O > \alpha_R$, there is a higher tendency for the oxidised form to accept the electron, as in the case of Ag, Ag^+, Hg, Hg^+ and Cl^-, Cl couples, than vice versa. The Na, Na^+ couple is an example of the opposite case with $\alpha_O < \alpha_R$.

The linear dependence of E on ln (r) shown in Fig.1 and represented by Eq.16b, show that the concentration terms in square brackets [ ] in the above thermodynamic relations actually refer to the mole ratio r and that r^o, the mole ratio when $\Delta E = 0$ is a thermodynamic quantity.

On using Eqs. 23c,d for the two equilibria (Eqs. 2 and 4) involving $H^+/(1/2)H_2$ and Cl^- /Cl, and r for the concentration terms, Eqs. 6b and 16b become,

$$(\alpha_{H+} + \alpha_{Cl-}) (E - E^o) = k \ln (r/r^o) \qquad [27a]$$

$$\delta_A = 1/(\alpha_{H+} + \alpha_{Cl}-) \qquad [27b]$$

Thus, Eq. 27b gives δ_A a thermodynamic significance. For the value of $\delta_A = 0.963$ (slope of the line in Fig.1), the sum of the transfer coefficients is $1/\delta_A = 1.039$. On using the value obtained above for α_{Cl}^- (= 0.08), one finds that $\alpha_{H+} = 0.959$. Note that H^+ and Cl^- are the oxidised and reduced forms of two different redox couples and therefore the sum of the transfer coefficients need not add up to unity, (as for the Nernstian equation for a single redox).

6. The dependence of $[Ag^+]$ and $[Hg^+]$ on E, and the mole ratio r

On using Eq. 12b for E^o_{AgCl} in Eq. 16b, one gets,

$$E = (E^o_{Ag,Ag+} + k\ln K^o_{so}) - 2k\delta_A \ln(r/r^o) \qquad [28]$$

Since the silver ion (or chloride ion) activity in pure water[5], $a_+ = (K^o_{so})^{1/2}$, on replacing a_+ by the mole ratios and writing $r_{Ag+}r_{Cl-} = (K'_{so})$, where $K'_{so} = (K^o_{so})^{1/\delta A} = 7.433 \times 10^{-11}$ (with $\delta_A = 0.963$ for HCl, obtained from the slope in Fig.1) one finds that E and the mole ratios r_{Cl-} (= r of Eqs. 16) and r_{Ag+} depend on each other by the relations,

$$r_{Cl-} = (K'_{so}/r_{Ag+}) = r^o_{Cl-} \exp[-(E-E^o)/2k\delta_A] \qquad [29a]$$

$$E = E^o - 2k\delta_A \ln (K'_{so}/r^o_{Cl-}\, r_{Ag+}) \qquad [29b]$$

$$= E^o + 2k\delta_A \ln (r_{Ag+}/r^o_{Ag+}) \qquad [29c]$$

Therefore, it follows from Eqs. 29a and 29c that at $E = E^o_{AgCl} = 0.2224$ V, r^o is the mole ratio of the chloride ion in equlibrium with AgCl, and $r^o_{Ag+} = K'_{so}/r^o$. For HCl at 25°C, $r^o = 0.0217$ (obtained from the intercept, see Fig. 1) and hence, $r^o_{Ag+} = 8.124 \times 10^{-9}$, which is about 10^{-3} times less than the value in pure water, $(K'_{so})^{1/2} = 8.621 \times 10^{-6}$, due to the common ion effect.[5,6]

Note that since the ratio r/r^o depends only on ΔE, if instead of the silver chloride electrode, a calomel electrode ($E^o_{CE} = 0.268$ V) is used, then $r^o_{Cl-} = (K'_{so}/r^o_{Hg+}) = 0.0217$ (intercept of Fig.1), where $K'_{so} = (10^{-17.88})^{1/\delta A} = 2.690 x 10^{-19}$ (with $\delta_A = 0.963$, see Fig.1) is the solubility product of (Hg_2Cl_2). $r^o_{Hg+} = 1.24 x 10^{-17}$ corresponds to the mercuorus ions (Hg_2^{++}), which is far less than the value in pure water, 5.186×10^{-9}, due to the common ion effect.

Fig. 1 is also a representation of the dependence of E (AgCl) and E (CE) on ln r_{Ag+} and $\ln r_{Hg+}$. The good agreement of calculated values of E as per Eq. 16b (for a silver-slver chloride electrode as well as a calomel electrode) with those calculated from activity coefficients (see Table 1 and Fig. 1) shows that Eq. 16b based on partial dissociation and hydration explains quantitatively the EMF of the cell (Eq. 1).

Since for very small values of m, the molality of free water, $n_{Af} \sim 55.51$, the values of the ionic molalities, $m(Ag^+) = 55.51\ r_{Ag+}$ and $m(Hg^+) = 55.51\ r_{Hg+}$ have also been been presented in Table 1. Fig. 2 shows the molalities of silver ions (when Ag, AgCl electrode is used) and of mercurous ions (when CE is used) in the solution at various molalities of HCl.

7. The charge balance in the solution

Finally, it is also necessary to consider the charge balance[5] in the solution since there are four ions to be considered: H^+ from HCl (in equilibrium with OH^- of water (ionic product = $[H^+][OH^-] = K^o_w = 10^{-14}$), Cl^- from HCl which is in equilibrium with AgCl(s) ($K^o_{so} = [Ag^+][Cl^-] = 1.763 \times 10^{-10}$), OH^- from water and the Ag^+ ions. Thus,

$$[Cl^-] + [OH^-] = [H^+] + [Ag^+] \qquad [30a]$$

$$[Cl^-] + K^o_w/[H^+] = [H^+] + K^o_{so}/[Cl^-] \qquad [30b]$$

$[Cl^-] (1 - K^o_{so} /[Cl^-]^2) = [H^+] (1 - K^o_w/[H^+]^2)$ [30c]

As $K^o_w < K^o_{so}$ for the AgCl electrode, $[Cl^-] > [H^+]$ for very dilute solutions when [ ] = $r \sim (K^o_{so})^{1/2} \sim 10^{-5}$ and the second term in the left half of Eq. 30c would become appreciable. For higher values of r, $[Cl^-] = [H^+]$ in the solution. When one uses the calomel electrode, note that $K^o_w > K^o_{so}$ and hence $[Cl^-] < [H^+]$ for dilute solutions with values of $r \sim (K^o_w)^{1/2} \sim 10^{-7}$, and the second term in the right half of Eq. 30c would become appreciable.

8. Relation between the solvent and solute free energies

On using mole fractions in Eq. 16b, the free energy relation becomes:

$$\Delta G = [-RT(\ln a_A+\ln N_{H+}) + \alpha_{H+}F(E - E^o)] + [-RT(\ln a_A+\ln N_{Cl-}) + \alpha_{Cl-}F(E -E^o)] + 2RT\ln(r^o) = 0 \quad [31]$$

where $N_i = \alpha m/(n_{Af} + im)$ and $a_A = n_{Af}/(n_{Af} + im)$ are the mole fractions of ions (H^+ or Cl^-) and free solvent respectively[3], $(N_i/a_A) = r$ and $(N^o_i/a^o_A) = r^o$ is the value of r for $E = E^o$. Eq. 31 shows the relation between the free energies of the solvent (ΔG_A, the first term), ions (ΔG_i, the second term) and the associated electrical contribution, ΔG_{el} (the third term) at equilibrium.

9. The Gibbs-Duhem relation

On substituting the mole ratio r for $m\gamma_+$ (= a_+) in the Gibbs-Duhem relation[1,4,12] (see Eq. 32a below) between the free energies of the solvent and solute for a 1:1 electrolyte, one gets

$$-55.51\ \mathrm{dln}\,(a_A) = 2m\mathrm{dln}(a_+) \qquad \text{(complete dissociation)} \qquad [32a]$$

$$= 2m\delta_A \mathrm{dln}(r) \qquad \text{(partial dissociation)} \qquad [32b]$$

Therefore, the Gibbs-Duhem Eq. 32a which is written assuming complete dissociation (and is used for converting solvent and ionic activities into each other by performing complicated integrations)[1,4,12] actually amounts to,

$$-(55.51 + 2m\delta_A)\mathrm{dln}\ a_A = 2m\delta_A \mathrm{dln}\ N_i \qquad [33]$$

in terms of the mole ratio r (= N_i/a_A) for the ions.

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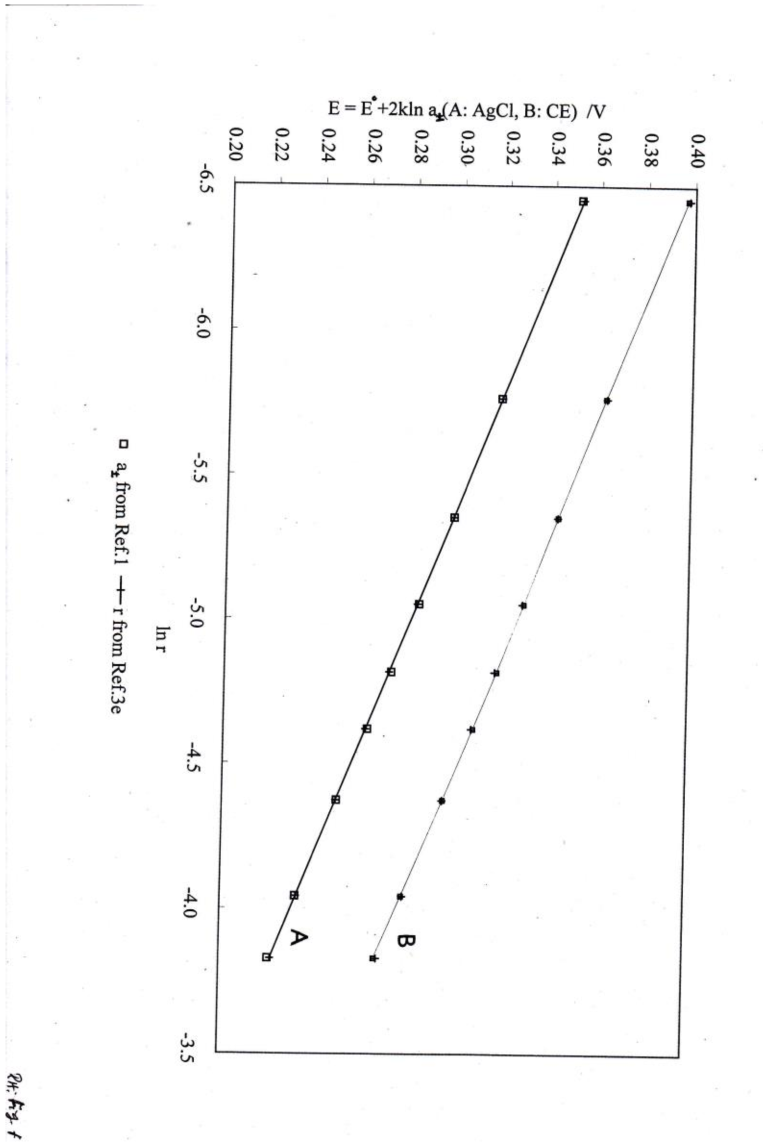

Figure 1

The linear dependence of the E.M.F. E of the cell (see Eq. 1) at various molalities of HCl on ln (r), at 25 ^{o}C. The actvitity coefficient data in Ref. 1 was used for calculating back the E.M.F. values using Eq. 8. Line A: E^{o} (Ag, AgCl) = 0.2224 V and line B: E^{o} = 0.268 V (CE). The mole ratio r = $\alpha m/(55.51 - mn_s)$ was calculated from the α and n_s data in Ref. 3e. Points refer to data, and for the regressed lines (see Eq. 16b), slope = δ_A = 0.963 (+ 0.006); intercept at E = E^{o}, ln (r^{o}) = -3.832 (+ 0.014).

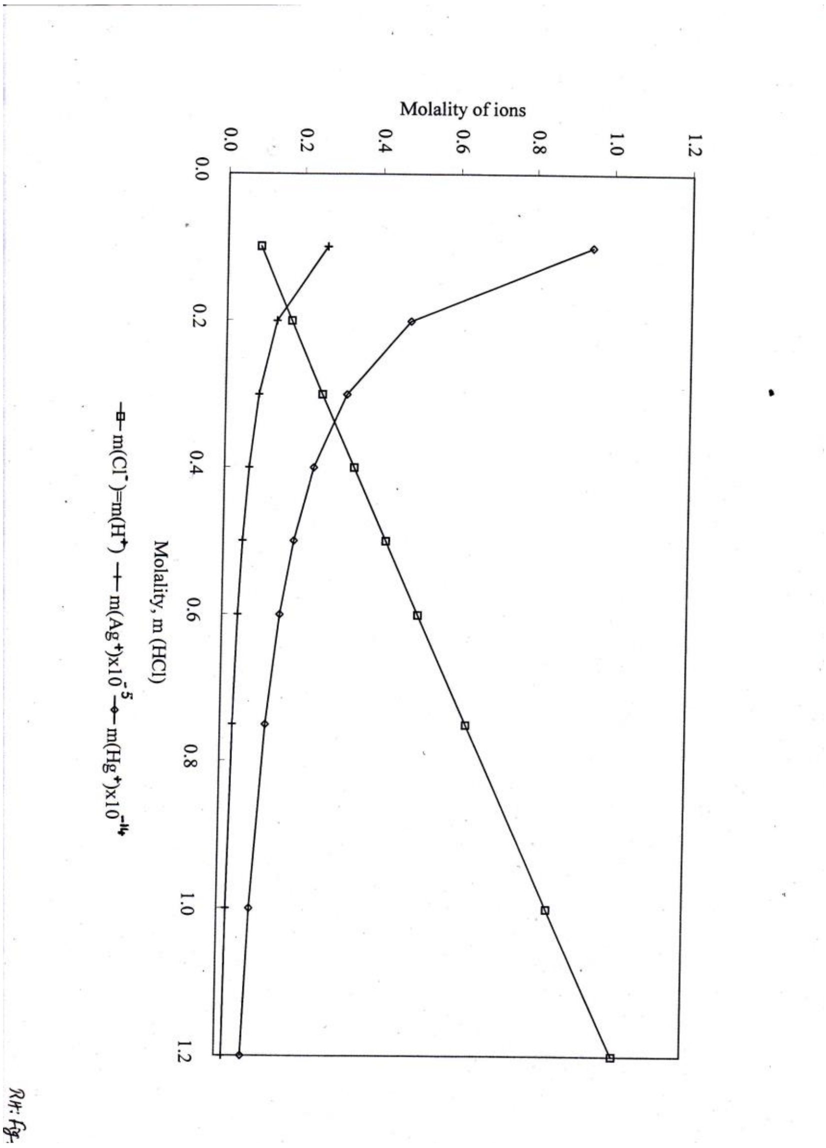

Figure 2

Concentrations of Cl^- (= H^+), Ag^+ (when silver-silver chloride electrode is used) and of $1/2Hg_2^{++}$ (when calomel electrode is used) in the cell (see Eq. 1) at various molalities of HCl, at 25 ^oC.