Chapter 10 Electrolyte Solution

Solutes in electrolyte solution exists in solvated ions (+ or - ions).

Nonelectrolyte solution (Chap 4);

$\Delta H_f^o \equiv 0, \Delta G_{f,}^o \equiv 0$ for pure substance (1bar) ....(a)

→Calculate $\Delta H_f^o, \Delta G_f^o$ for compound.

Electrolyte solution; Long range electrostatic (Coulombic) interactions exist btn the ions↔van der Walls force btn the neutral solutes (intermolecular interactions). So, in addition to (a)

→$\Delta G_f^o(H^+, aq) \equiv 0$ → Calculate $\Delta H_f^o, \Delta G_{f,}^o S^o$ for ions.

10.1 Enthalpy, entropy, Gibbs energy of ion formation in solution

Electrolytes: Substances that dissociate into positively and negatively charged mobile solvated ions in solvent (water in our text).

Consider the following overall reaction in water:

$$1/2H_2(g) + 1/2Cl_2(g) \rightarrow H^+(aq) + Cl^-(aq) ...... (1)$$

$H^+(aq)$, $Cl^-(aq)$=Solvated, charged ions and their associated hydration shell. The hydration shell lowers the energy of ions, thereby making the reaction spontaneous. Although energy flow into the system is required to dissociate and ionize the hydrogen and chlorine, more energy is gained in the orientation of the dipolar water molecular around the ion in the solvation wall.

→$\triangle H_R$=-167.2 kJ/mole @ Constant pressure (for rxn 1) (Exothermic)

(What about gas phase rxn?)

The standard state enthalpy (heat of formation) for the reaction can be written in terms of formation enthalpies;

$\triangle H_R = \triangle H_f^o(H^+, aq) + \triangle H_f^o(Cl^-, aq) - 0 - 0$ (2)

(Note that $\triangle H_f^o$ for pure element in its standard state = 0)

$\triangle H_f^o(H^+, aq)$ and $\triangle H_f^o(Cl^-, aq)$ are measured together (by formula unit), not by the individual ion since the solution must remain electrically neutral, and hence any dissociation reactions of neutral solute must produce both anions and cations.

How can the formation enthalpy, entropy, and Gibbs energy for individual solvated cation and anion are obtained?

This can be done by making an appropriate choice for the zero of ΔH_f^o, ΔG_f^o, and S^o.

By convention

$\Delta G_f^o(H^+, aq) \equiv 0$ for all T (3)

Then, from dG = -SdT + Vdp and G =H-TS

$$S^0(H^+,aq) = -\left(\frac{\partial \triangle G_f^0(H^+,aq)}{\partial T}\right)_P = 0 \quad \text{and}$$

$$\triangle H_f^0(H^+,aq) = \triangle G_f^0(H^+,aq) + T\triangle S^0(H^+,aq) = 0 \qquad (4)$$

Based on this, the numerical values for ΔH_f^o, ΔG_f^o, and S^o for other ions can be assigned as shown later.

ΔH_R^o = Measured using calorimeter (=$C_p\Delta T$). Then,

ΔG_R^o = -RT ln K (b)

(K is determined by measuring the degree of dissociation.)

And ΔS_R is determined by

$$\Delta S_R^o = \frac{\Delta H_R^o - \Delta G_R^o}{T} \text{.......(c)}$$

Then, from eq (2) and convention for ΔH_f^o and ΔG_f^o = 0 for element;

$\Delta H_R^o = \triangle H_f^o(Cl^-, aq) + 0 - 0 - 0 = \triangle H_f^o(Cl^-, aq)$,

$\Delta G_R^o = \triangle G_f^o(Cl^-, aq) + 0 - 0 - 0 = \triangle G_f^o(Cl^-, aq)$

$\Delta S_R^o = S^o(Cl^-, aq) + 0 - \frac{1}{2}S^o(H_2, g) - \frac{1}{2}S^o(Cl_2, g)$

In this way the following are obtained.

$\triangle H_f^o(Cl^-, aq) = -167.2$ kJ/mole (See also Table 10.1 @298.15K)

$S^o(Cl^-, aq) = 56.5$ (See also Table 10.1 @298.15K)

$\triangle G_f^o(Cl^-, aq) = -131.2$ (See also Table 10.1 @298.15K)

These values can be used to determine the formation functions of other ions. Example:

$$NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq) \qquad (5)$$

The std rxn enthalpy, $\Delta H_R^o = +3.90$ kJ/mole (Experimental). Enthalpy change for this reaction is,

$$\triangle H_R = \triangle H_f(Cl^-, aq) + \triangle H_f(Na^+, aq) - \triangle H_f(NaCl, s) \qquad (6)$$

Tabulated data: $\Delta H_f^o(NaCl, s) = -411.2$ kJ/mol, $\triangle H_f^o(Cl^-, aq) = -167.2$ kJ/mole (calculated above)→$[\Delta H_f^o(Na^+, aq) + (-167.2)] - (-411.2)] = 3.9$ → $\Delta H_f^o(Na^+, aq) = -240.1$

See Table 10.1 for ΔH_f^o, ΔG_f^o, S^o for various aqueous ion species.

Notes

1) ΔG_f^o, ΔH_f^o, S^o for ions are defined relative to H^+ (aq).

2) $\Delta H_f^o < 0$→ More exothermic than H^+ (aq).

(Multiple charged or smaller ion is more negative due to the greater interactions btn ions and water in solvation shell.)

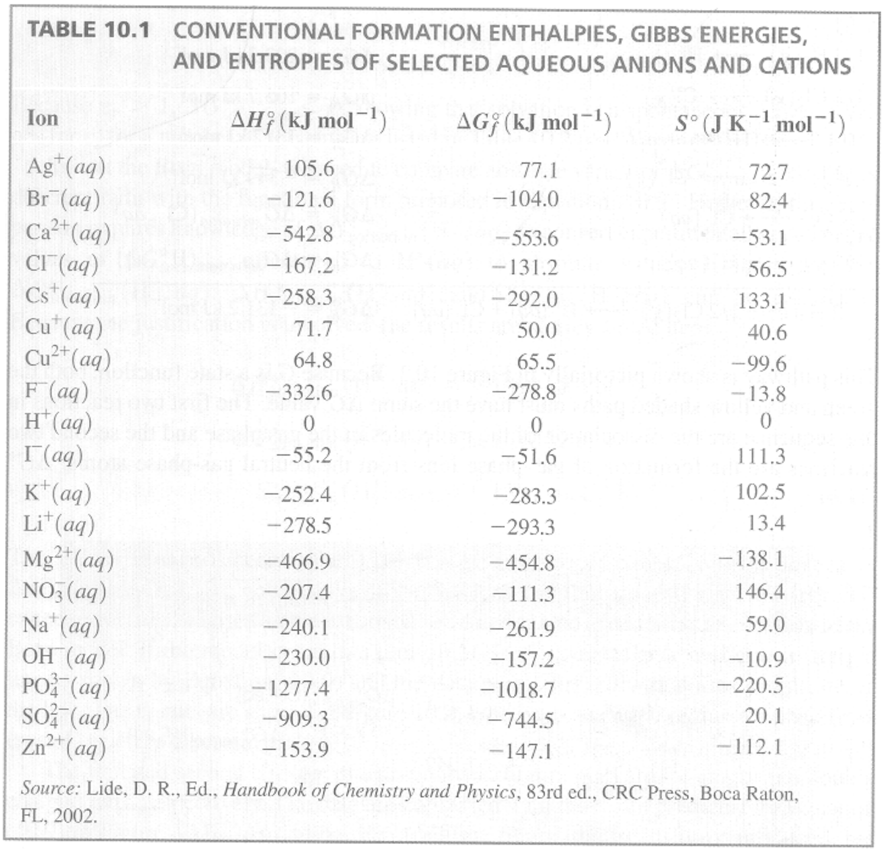


TABLE 10.1 CONVENTIONAL FORMATION ENTHALPIES, GIBBS ENERGIES, AND ENTROPIES OF SELECTED AQUEOUS ANIONS AND CATIONS

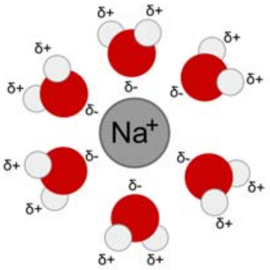
Ion	ΔH_f° (kJ mol^{-1})	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
$Ag^+(aq)$	105.6	77.1	72.7
$Br^-(aq)$	−121.6	−104.0	82.4
$Ca^{2+}(aq)$	−542.8	−553.6	−53.1
$Cl^-(aq)$	−167.2	−131.2	56.5
$Cs^+(aq)$	−258.3	−292.0	133.1
$Cu^+(aq)$	71.7	50.0	40.6
$Cu^{2+}(aq)$	64.8	65.5	−99.6
$F^-(aq)$	−332.6	−278.8	−13.8
$H^+(aq)$	0	0	0
$I^-(aq)$	−55.2	−51.6	111.3
$K^+(aq)$	−252.4	−283.3	102.5
$Li^+(aq)$	−278.5	−293.3	13.4
$Mg^{2+}(aq)$	−466.9	−454.8	−138.1
$NO_3^-(aq)$	−207.4	−111.3	146.4
$Na^+(aq)$	−240.1	−261.9	59.0
$OH^-(aq)$	−230.0	−157.2	−10.9
$PO_4^{3-}(aq)$	−1277.4	−1018.7	−220.5
$SO_4^{2-}(aq)$	−909.3	−744.5	20.1
$Zn^{2+}(aq)$	−153.9	−147.1	−112.1

Source: Lide, D. R., Ed., *Handbook of Chemistry and Physics*, 83rd ed., CRC Press, Boca Raton, FL, 2002.

3)Entropy decreases as the hydration shell is formed since water molecules are oriented in hydration shell.

►The hydration shell of an ion in water

An ion inserted into water rotates water molecules so that their polarized charges face the oppositely charged central ion while breaking their hydrogen bonds to their nearest neighbors. By doing this salt water has a lower freezing point than pure water. The group of water molecules oriented around an ion is called a hydration shell.



10.2 Understanding the thermodynamics of ion formation and solvation

ΔH_f^o, ΔG_f^o, S^o are measured for formula unit as above.

Values for individual ions can be calculated using thermodynamic model as below (Focused on ΔG_f^o).

Individual contributions to ΔG_f^o for $H^+(aq)$ and $Cl^-(aq)$ formation

$$1/2\,H_2(g) \rightarrow H(g) \qquad \triangle G_R^o = 203.3 kJmol^{-1}$$
$$1/2\,Cl_2(g) \rightarrow Cl(g) \qquad \triangle G_R^o = 105.7 kJmol^{-1}$$
$$H(g) \rightarrow H^+(g) + e^- \qquad \triangle G_R^o = 1312 kJmol^{-1}$$
$$Cl(g) + e^- \rightarrow Cl^-(g) \qquad \triangle G_R^o = -349 kJmol^{-1}$$
$$Cl^-(g) \rightarrow Cl^-(aq) \qquad \triangle G_R^o = \triangle G_{solvation}^o(Cl^-, aq)$$
$$H^+(g) \rightarrow H^+(aq) \qquad \triangle G_R^o = \triangle G_{solvation}^o(H^+, aq)$$

$$1/2\,H_2(g) + 1/2\,Cl_2(g) \rightarrow H^+(aq) + Cl^-(aq) \quad \triangle G_R^o = -131.2 kJmol^{-1}$$

The pathway is shown in Figure 10.1. Green and yellow paths gives the same ΔG (state function).

FIGURE 10.1

ΔG° in units of kJ mol^{-1} is shown pictorially for two different paths starting with $1/2\ H_2(g)$ and $1/2\ Cl_2(g)$ and ending with $H^+(aq)$ + $Cl^-(aq)$. The units for the numbers are kJ mol^{-1}. Because ΔG is the same for both paths, $\Delta G^\circ_{solvation}(H^+, aq)$ can be expressed in terms of gas-phase dissociation and ionization energies.

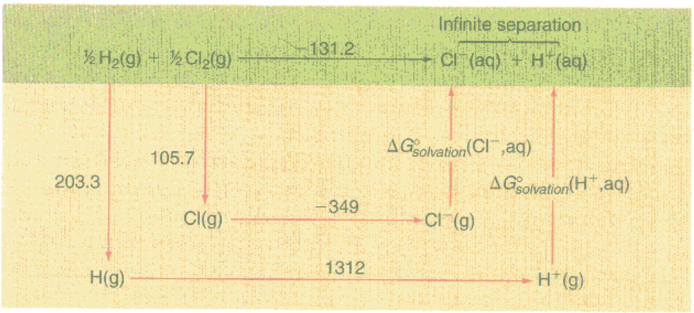


Figure 10.1(High resolution)

1st two rxns = dissociation

2nd two rxns = ionization

ΔG^o for the 4 gaseous reactions are determined experimentally.

With these values (203.9+105.7+1312−349=1272), ΔG^o for the overall process is given by;

$$\Delta G_R^o = \Delta G^o_{solvation}(Cl^-, aq) + \Delta G^o_{solvation}(H^+, aq) + 1272\, kJ/mol \qquad (7)$$

$\Delta G^o_{solvation}$ of each ion can not be determined experimentally, but can be estimated by Max Born model.

Max Born model assumes:

Solvent≡Uniform fluid with a dielectric constant, ε

Ion≡A charged sphere

At constant T and P, nonexpansion work=△G→

Difference of the reversible work for charging in solution and vacuum=

$[(A\rightarrow A^Q)_{Solution}-(A\rightarrow A^Q)_{Vacuun}]=\triangle G_{Solvation}$ (A=Neutral, A^Q=Charged by Q)

► Electrical potential around a sphere of radius r with charge Q' is given by

$\phi = Q'/4\pi\epsilon r$

Note Coulombic law

Coulombic force $F=q_1q_2/4\pi\varepsilon r^2$→Electrical field strength $E=F/q_1=q_2/4\pi\varepsilon r^2$

$E=\nabla\Phi\rightarrow\Phi=E\ r$ (Commonly E=Volt/distance)

Electric potential at a point is the electrical potential energy divided by charge (Work for unit charge). Typically measured in Volts = Joule/Coulomb.

►Work for additional charging dQ = ϕdQ.

►Then work in charging a neutral sphere in vacuum to the charge Q is

$$w = \int_0^Q \frac{Q' dQ'}{4\pi\epsilon_0 r} = \frac{1}{4\pi\epsilon_0 r}\int_0^Q Q' dQ' = \frac{Q^2}{8\pi\epsilon_0 r} \qquad (8)$$

ϵ_o= permitivity (dielectric constant) in free space

Work for the same process in solvent = $Q^2/8\pi\epsilon_o\epsilon_r r$ (8')

$\epsilon_r=\epsilon/\epsilon_o$ relative permittivity of solvent (See Table 10.2, Appendix).
Then for an ion of charge $Q=ze$ is given by ((8')-(8))

$$W=\triangle G^o_{solvation}=\frac{z^2e^2N_A}{8\pi\epsilon_0 r}\left(\frac{1}{\epsilon_r}-1\right) \qquad (9)$$

$$N_A = Avogadro's\, number,\ e = Charge\, of\, a\, proton$$

Note

$\epsilon_{r=}\epsilon/\epsilon_o>1\rightarrow\Delta G^o_{solvation}<0$: The solvation is a spontaneous process.

See Figure 10.2 to test the validity of eq 10.9.

Figure10.2a: Radius from crystal structure

Figure10.2b: r_{eff} =crystal radius+0.085 for positive ion,
=(crystal radius+0.100) for negative ion (Excellent fit)

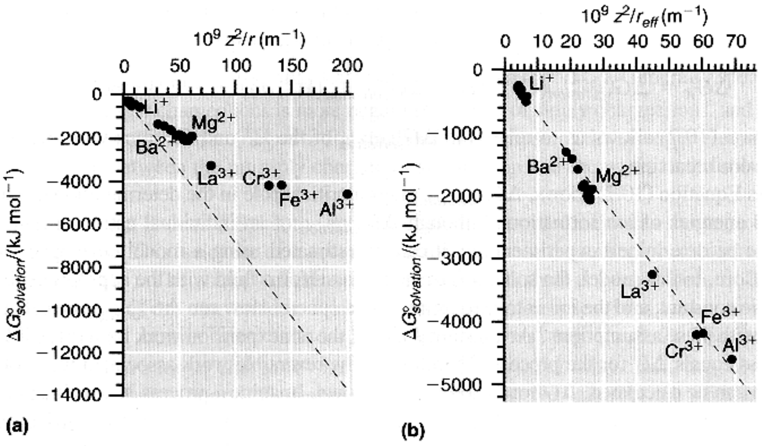


FIGURE 10.2

(a) The solvation energy calculated using the Born model is shown as a function of z^2/r. **(b)** The same results are shown as a function of z^2/r_{eff}. (See text.) The dashed line shows the behavior predicted by Equation (10.9).

Figure 10.2 (High resolution)

10.3 Activity and activity coefficients for electrolyte solutions

Activity and activity coefficient defined in Ch 9 is modified in electrolyte since Coulombic interaction (electrostatic) is dominant.
For example:

$$NaCl(s) + H_2O(l) \rightarrow Na^+(aq) + Cl^-(aq) \qquad (11)$$

Gibbs energy of solution can be written as:

$$G = n_{solvent}\mu_{solvent} + n_{solute}\mu_{solute} \qquad (12)$$

n = # of moles

If the electrolyte completely dissociates,

$$\begin{aligned} G &= n_{solvent}\mu_{solvent} + n_+\mu_+ + n_-\mu_- \\ &= n_{solvent}\mu_{solvent} + n_{solute}(\nu_+\mu_+ + \nu_-\mu_-) \qquad (13) \end{aligned}$$

$\nu =$ *stoichiometric coefficients*
$n_+ = n_{solute}\nu_+$ and $n_- = n_{solute}\nu_-$

$Ex)\ K_2SO_4 \rightarrow 2K^+ + SO_4^{-2}$
$n_{solute} = 1, \nu_+ = 2,\ \nu_- = 1$ (Produced from one mole of solute)

Letting
(12) =(13)
$\mu_{solute} = \nu_+\mu_+ + \nu_-\mu_-$ (14)

Define the mean ionic chemical potential as;

$$\mu_\pm = \frac{\mu_{solute}}{\nu} = \frac{\nu_+\mu_+ + \nu_-\mu_-}{\nu} \qquad (15)$$

where $\nu = \nu_+ + \nu_-$

The experimentally measured quantity is $\mu_{\pm}$.
(μ_{+} and μ_{-} can not be measured separately)

Chemical potential - activity coefficient relationship

$$\mu_{+} = \mu_{+}^{0} + RT\ln a_{+}, \quad \mu_{-} = \mu_{-}^{0} + RT\ln a_{-} \qquad (16)$$

Standard chemical potentials (μ_{+}^{0}, μ_{-}^{0}) are based on the Henry's law standard state.

Subing (16) into (15), $\mu_{\pm} = \frac{\mu_{solute}}{\nu} = \frac{\nu_{+}\mu_{+} + \nu_{-}\mu_{-}}{\nu}$ (15)

$$\mu_{\pm} = \frac{(\nu_{+}\mu_{+}^{0} + \nu_{-}\mu_{-}^{0}) + RT(\nu_{+}\ln a_{+} + \nu_{-}\ln a_{-})}{\nu}$$
$$= \mu_{\pm}^{0} + RT\ln a_{\pm} \qquad (17)$$

where the mean ionic activity $a_{\pm}$ is related to the individual ionic activity as,

$$\ln a_{\pm} = \frac{\nu_{+}\ln a_{+} + \nu_{-}\ln a_{-}}{\nu}$$
$$\rightarrow \ln a_{\pm}^{\nu} = \ln a_{+}^{\nu_{+}} a_{-}^{\nu_{-}}$$
$$a_{\pm}^{\nu} = a_{+}^{\nu_{+}} a_{-}^{\nu_{-}} \qquad \text{or}$$
$$a_{\pm} = (a_{+}^{\nu_{+}} a_{-}^{\nu_{-}})^{\frac{1}{\nu}} \qquad (18)$$

EXAMPLE PROBLEM 10.1

Write the mean ionic activities of NaCl, K_2SO_4, and H_3PO_4 in terms of ionic activities of the individuals anions and cations. Assume complete dissociation.

Solution

$NaCl \rightarrow Na^+ + Cl^-$
$K_2SO_4 \rightarrow 2K^+ + SO_4^{2-}$
$H_3PO_4 \rightarrow 3H^+ + PO_4^{3-}$

From (18)

$$a_{NaCl}^2 = a_{Na^+} a_{Cl^-} \quad \text{or} \quad a_{NaCl} = \sqrt{a_{Na^+} a_{Cl^-}}$$
$$a_{K_2SO_4}^3 = a_{K^+}^2 a_{SO_4^{2-}} \quad \text{or} \quad a_{K_2SO_4} = (a_{K^+}^2 a_{SO_4^{2-}})^{1/3}$$
$$a_{H_3PO_4}^4 = a_{H^+}^3 a_{PO_4^{3-}} \quad \text{or} \quad a_{H_3PO_4} = (a_{H^+}^3 a_{PO_4^{3-}})^{1/4}$$

Since activity is dimensionless, the ioinic activity must be normalized by a standard state molality (m^o = 1 mole/kg) as,

$$a_+ = \frac{m_+}{m^o}\gamma_+ \text{ and } a_- = \frac{m_-}{m^o}\gamma_- \qquad (19)$$

$$m_+ = \nu^+ m \text{ and } m_- = \nu^- m$$

(Note $a_i = \frac{P_i}{P_i^*} = x_i\gamma_i = x_i$ for ideal solution)

(19) → (18)

$$a_\pm^\nu = \left(\frac{m_+}{m^o}\right)^{\nu_+}\left(\frac{m_-}{m^o}\right)^{\nu_-}\gamma_+^{\nu_+}\gamma_-^{\nu_-} \qquad (20)$$

Define mean ionic molality ($m_\pm$) and mean ionic activity coefficient ($\gamma_\pm$) as

$$m_\pm^\nu = m_+^{\nu_+} m_-^{\nu_-}$$
$$m_\pm = (m_+^{\nu_+} m_-^{\nu_-})^{\frac{1}{\nu}}$$
$$\gamma_\pm^\nu = (\gamma_+^{\nu_+}\gamma_-^{\nu_-})$$
$$\gamma_\pm = (\gamma_+^{\nu_+}\gamma_-^{\nu_-})^{\frac{1}{\nu}} \qquad (21)$$

Then

$$a_{\pm}^{\nu} = \left(\frac{m_{+}}{m^{o}}\right)^{\nu_{+}}\left(\frac{m_{-}}{m^{o}}\right)^{\nu_{-}}\gamma_{+}^{\nu_{+}}\gamma_{-}^{\nu_{-}} \qquad \text{-------} \qquad \text{(a)}$$

$$= (m_{+}^{\nu_{+}}m_{-}^{\nu_{-}})\left(\frac{1}{m^{o}}\right)^{(\nu_{+}+\nu_{-})}\gamma_{+}^{\nu_{+}}\gamma_{-}^{\nu_{-}}$$

$$= \left(\frac{m_{\pm}}{m^{o}}\right)^{\nu}\gamma_{\pm}^{\nu}$$

$$\text{or } a_{\pm} = \frac{m_{\pm}}{m^{o}}\gamma_{\pm} \qquad (22)$$

(19)~(22) relate the activity, activity coefficient, and molality of the individual ionic species to mean ionic quantities and measurable properties of the system such as molality and activity of the solute.

EX Calculate the <u>mean ionic molality</u> and <u>mean ionic activity</u> of a 0.150*m* $Ca(NO_3)_2$solutionforwhichthemeanionicactivitycoefficientis0.165.

$$m_{\pm} = \left(\nu_{+}^{\nu_{+}}\nu_{-}^{\nu_{-}}\right)^{1/\nu} m = \left(2^{2}\right)^{1/3} 0.150 \text{ mol kg}^{-1} = 0.238 \text{ mol kg}^{-1}$$

$$a_{\pm} = \left(\frac{m_{\pm}}{m^{\circ}}\right)\gamma_{\pm} = 0.238 \times 0.165 = 0.0393$$

EX) Calculate the <u>mean ionic activity</u> of a 0.0150*m* K_2SO_4 solution for which the mean activity coefficient is 0.465.

<u>Solution</u>

Use (a) and (19)-2nd line

$$a_{\pm} = \left(\frac{\left(\nu_{+}^{\nu_{+}}\nu_{-}^{\nu_{-}}\right)^{1/\nu} m}{m^{\circ}}\right)\gamma_{\pm} = \left(2^{2}\right)^{1/3} 0.0150 \times 0.465 = 0.0111$$
