

Gibbs Function and Work

- Start with the First Law of Thermodynamics and some standard thermodynamic relations.

$$dU = dq + dw$$

$$dq = T dS$$

$$dw = -P dV + dw_{\text{electrical}}$$

$$dU = T dS - P dV + dw_{\text{electrical}}$$

$$dH_P = dU_P + P dV$$

$$dG_T = dH_T - T dS$$

$$= dU_{T,P} + P dV - T dS$$

$$= \cancel{T dS} - \cancel{P dV} + dw_{\text{electrical}} + \cancel{P dV} - \cancel{T dS}$$

$$dG_{T,P} = dw_{\text{electrical}}$$

Gibbs function is also at the heart of electrochemistry, for it identifies the amount of work we can extract electrically from a system.

Thermodynamics of Galvanic Cells

Helmholtz 'free' energy

$$dU = T dS + dw$$

$$dU - T dS = dw$$

$$d(U - TS) = dw$$

$$A = U - TS$$

At constant T

$$dA_T \leq dw$$

Gibbs 'free' energy

$$H = U + pV$$

$$dH = dU + p dV + V dp$$

$$dU = T dS - p dV + dw_{\text{non-}pV}$$

$$dH = T dS - p dV + dw_{\text{non-}pV} + p dV + V dp$$

$$dH - T dS = dw_{\text{non-}pV} + V dp$$

$$d(H - TS) = dw_{\text{non-}pV}$$

$$dG_{p,T} \leq dw_{\text{non-}pV}$$

$$dG_{p,T} = dw_{\text{electrical}}$$

Gibbs energy change is equal to the maximum non- pV work that can be done by an electrochemical cell.

Gibbs Free Energy

The free energy function is the key to assessing the way in which a chemical system will spontaneously evolve.

$$dG = -SdT + VdP + \sum \mu_i dn_i + \gamma dA + f dl$$

constant T

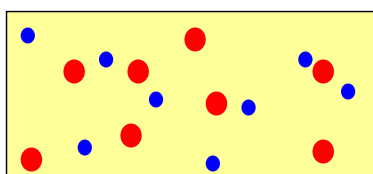
constant P

No surface effect

No extension

$$dG = \sum \mu_i dn_i$$

Thermodynamic Properties of Ions in Solutions



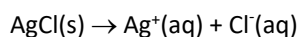
• cation

• anion

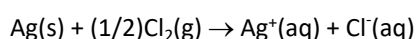
- Thermodynamic functions of formation
- Ion activities

The standard enthalpy and Gibbs energy of a reaction involving ions in solution are expressed in terms of standard enthalpies and Gibbs energies of formation, which are used exactly the same as those for neutral compounds.

Examples:



$$\Delta_r G^\ominus = \Delta_f G^\ominus(\text{Ag}^+, \text{aq}) + \Delta_f G^\ominus(\text{Cl}^-, \text{aq}) - \Delta_f G^\ominus(\text{AgCl, s})$$



$$\Delta_r H^\ominus = \Delta_f H^\ominus(\text{Ag}^+, \text{aq}) + \Delta_f H^\ominus(\text{Cl}^-, \text{aq})$$

The enthalpies of formation of ions

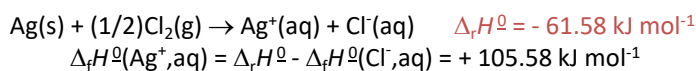
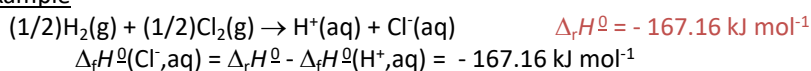


Define that H^+ has zero standard enthalpy of formation:

$$*\Delta_f H^\ominus(\text{H}^+, \text{aq}) = 0 \text{ at all temperatures}$$

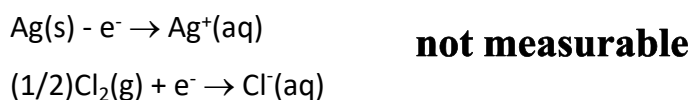
This definition adjusts the actual values of the enthalpies of ions all by a fixed amount. The adjusted enthalpies of ions may then be determined from the standard enthalpies of reaction

Example



The Gibbs energies of formation of ions

The Gibbs energy of individual ion formation reactions, e.g.

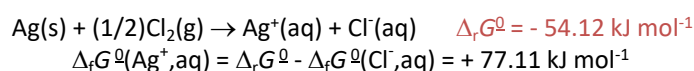
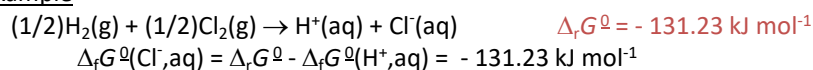


Define that H^+ has zero standard Gibbs energy of formation:

$$*\Delta_f G^\ominus(\text{H}^+, \text{aq}) = 0 \text{ at all temperatures}$$

This definition adjusts the actual values of the Gibbs energies of formation of ions all by a fixed amount. The adjusted Gibbs energies of ions may then be determined from the standard Gibbs energies of reactions

Example



The entropies of ions in solution

Define that H^+ has zero standard entropy:

$$S^0(H^+,aq) = 0 \text{ at all temperatures}$$

This definition adjusts the actual values of the entropies of ions all by a fixed amount. Thus, the entropies may be either positive or negative.

Molar ion entropies vary as expected on the basis that they are related by the degree to which the ions order water molecules around them in the solution.

Small, highly charged ions induce local structure of water, and disorder is decreased more than in the case of large, singly charged ions.

Thermodynamics of Galvanic Cells

If $d\xi$ is the extent of cell reaction

$$\Delta G_r = \left(\frac{\partial G}{\partial \xi} \right)_{p,T}$$

$$dG_{p,T} = \Delta G_r d\xi = dw_{\text{non } pV, \text{rev}}$$

$$dG_{p,T} = dw_{\text{electrical}}$$

$dw_{\text{electrical}} = \text{charge} \times \text{potential difference}$

$$= \nu d\xi (-eN_A) \times E$$

$$= -\nu F E d\xi$$

$\nu d\xi$ moles of electrons are getting transferred in a cell with cell potential E

$$\Delta G_r = -\nu F E$$

$$\begin{aligned} \Delta G_r &= \Delta G_r^0 + RT \ln \prod_i a_i^{\nu_i} \\ &= \Delta G_r^0 + RT \ln Q = -\nu F E \end{aligned}$$

Equilibrium Conditions in Electrochemical Systems

A system with multiple phases with electric potentials:

$$dU^\alpha = TdS^\alpha - pdV^\alpha + \mu_i^\alpha dn_i^\alpha + V_{el}^\alpha$$

$$V_{el}^\alpha = \phi^\alpha dQ_i^\alpha = \phi^\alpha (z_i F dn_i^\alpha)$$

$$dU^\alpha = TdS^\alpha - pdV^\alpha + (\mu_i^\alpha + z_i F \phi^\alpha) dn_i^\alpha$$

$$= TdS^\alpha - pdV^\alpha + \tilde{\mu}_i^\alpha dn_i^\alpha$$

Electrochemical potential

is the sum of chemical potential and molar electrostatic potential energy ϕ of species i in phase α .

$$dU^\alpha = TdS^\alpha - pdV^\alpha + \sum_i \tilde{\mu}_i^\alpha dn_i^\alpha$$

Phase Equilibrium and Reaction Equilibrium:

(In electrochemical systems)

$$(\mu_i^\alpha + z_i F \phi^\alpha) = (\mu_i^\beta + z_i F \phi^\beta)$$

$$\mu_i^\alpha - \mu_i^\beta = z_i F (\phi^\beta - \phi^\alpha)$$

Chemical potential difference between two phases increase with increase in electric potential difference.

$$\tilde{\mu}_i^\alpha = \tilde{\mu}_i^\beta$$

$$\sum_i \nu_i \tilde{\mu}_i = 0$$

Equilibrium Conditions in Electrochemical Systems

$$dU^\alpha = TdS^\alpha - pdV^\alpha + \sum_i \tilde{\mu}_i^\alpha dn_i^\alpha$$

$$\tilde{\mu}_i^\alpha = \tilde{\mu}_i^\beta \quad \sum_i \nu_i \tilde{\mu}_i = 0$$

IUPAC Conventions:

T	E	I	E'	T'
=====			=====	
Left half cell			Right half cell	
ϕ_L			ϕ_R	
Oxidation			Reduction	
Loss of e^-			Gain of e^-	
Anode			Cathode	

Cell Potential (electromotive force):

$$E = \phi_R - \phi_L$$

$E > 0$ Cell reaction occurs spontaneously

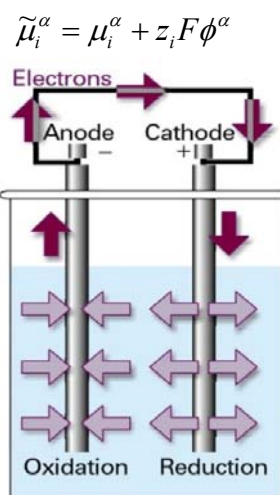


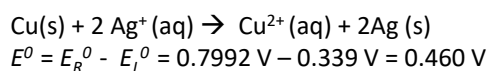
Figure 7-11
Atkins Physical Chemistry, Eighth Edition
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$$\Delta G_r = -\nu FE$$

Standard Electrode Potentials at 25 °C and 1 bar

Half-cell reaction	$\mathcal{E}^\circ/\text{V}$	Half-cell reaction	$\mathcal{E}^\circ/\text{V}$
$\text{K}^+ + \text{e}^- \rightarrow \text{K}$	-2.936	$2\text{D}^+ + 2\text{e}^- \rightarrow \text{D}_2$	0.01
$\text{Ca}^{2+} + 2\text{e}^- \rightarrow \text{Ca}$	-2.868	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	0
$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$	-2.714	$\text{AgBr(c)} + \text{e}^- \rightarrow \text{Ag} + \text{Br}^-$	0.073
$\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}$	-2.360	$\text{AgCl(c)} + \text{e}^- \rightarrow \text{Ag} + \text{Cl}^-$	0.2222
$\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$	-1.677	$\text{Hg}_2\text{Cl}_2(\text{c}) + 2\text{e}^- \rightarrow 2\text{Hg(l)} + 2\text{Cl}^-$	0.2680
$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-$	-0.828	$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	0.339
$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$	-0.762	$\text{Cu}^+ + \text{e}^- \rightarrow \text{Cu}$	0.518
$\text{Ga}^{3+} + 3\text{e}^- \rightarrow \text{Ga}$	-0.549	$\text{I}_2(\text{c}) + 2\text{e}^- \rightarrow 2\text{I}^-$	0.535
$\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$	-0.44	$\text{Hg}_2\text{SO}_4(\text{c}) + 2\text{e}^- \rightarrow 2\text{Hg(l)} + \text{SO}_4^{2-}$	0.615
$\text{Cd}^{2+} + 2\text{e}^- \rightarrow \text{Cd}$	-0.402	$\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$	0.771
$\text{PbI}_2(\text{c}) + 2\text{e}^- \rightarrow \text{Pb} + 2\text{I}^-$	-0.365	$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	0.7992
$\text{PbSO}_4(\text{c}) + 2\text{e}^- \rightarrow \text{Pb} + \text{SO}_4^{2-}$	-0.356	$\text{Br}_2(\text{l}) + 2\text{e}^- \rightarrow 2\text{Br}^-$	1.078
$\text{Sn}^{2+} + 2\text{e}^- \rightarrow \text{Sn(white)}$	-0.141	$\text{O}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$	1.229
$\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$	-0.126	$\text{Cl}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^-$	1.360
$\text{Fe}^{3+} + 3\text{e}^- \rightarrow \text{Fe}$	-0.04	$\text{Au}^+ + \text{e}^- \rightarrow \text{Au}$	1.69

Example



Cu has thermodynamic tendency to **reduce** Ag^+ in aqueous solution

Cell Potential at Equilibrium and the Nernst Equation

At equilibrium,

$$\Delta G_r(T) = \Delta G_r^0(T) + RT \ln K = 0$$

$$\Delta G_r^0(T) = -RT \ln K$$

$$\Delta G_r^0(T) = -vFE^0$$

$$K = \left[\prod_i a_i^{v_i} \right]_{\text{equilibrium}}$$

E^0 Standard Cell Potential

$$E = -\frac{\Delta G_r^0}{vF} - \frac{RT}{vF} \ln Q$$

$$= E^0 - \frac{RT}{vF} \ln Q$$

Nernst Equation

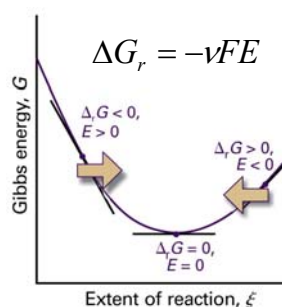


Figure 7-14
Physical Chemistry, Eighth Edition
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For a cell at equilibrium,

$$Q = K; \Delta_r G = 0, E = 0;$$

For the cell reaction,

$$E^0 = \frac{RT}{vF} \ln K \quad K = \exp\left(\frac{vFE^0}{RT}\right)$$

Standard Molar Entropy (and Enthalpy) Change in a Cell

$$\Delta G_r^0 = -vFE^0$$

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

$$\left[\frac{\partial(\Delta G_r^0)}{\partial T}\right]_p = -\Delta S_r^0$$

$$\Delta S_r^0 = vF \left(\frac{\partial E^0}{\partial T}\right)_p$$

Change in standard state molar entropy during the cell reaction

$$\Delta H_r^0 = \Delta G_r^0 + T\Delta S_r^0$$

Non-calorimetric determination of enthalpy change of a (cell) reaction

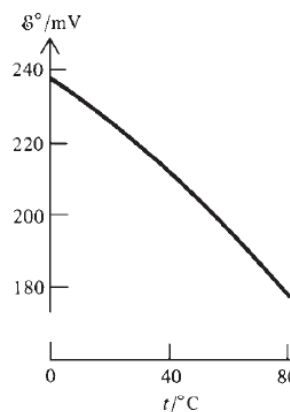


Figure 13.14

E° versus temperature at 1 bar for the cell (13.31), consisting of a hydrogen electrode and an Ag–AgCl electrode.

The definition of activity

The chemical potential of a solute:

$$\mu = \mu^0 + RT \ln a$$

Activity and its coefficient: $a = \gamma m / m^0$

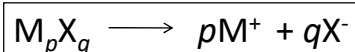
The activity coefficient γ depends on the composition, molality and temperature of the solution.

At low molalities, the activity coefficient γ tends towards 1

$$\gamma \rightarrow 1 \text{ and } a \rightarrow m / m^0 \text{ as } m \rightarrow 0$$

$$\begin{aligned} \mu &= \mu^0 + RT \ln (m / m^0) + RT \ln \gamma \\ &= \mu^{\text{id}} + RT \ln \gamma \end{aligned}$$

chemical potential of the ideal-dilute solution

Activity of salt solutions

$$\mu_{\text{salt}} = p\mu_+ + q\mu_-$$

$$\mu_+ = \mu_+^0 + RT \ln a_+$$

$$\mu_- = \mu_-^0 + RT \ln a_-$$

$$= p(\mu_+^0 + RT \ln \gamma_+ b_+) + q(\mu_-^0 + RT \ln \gamma_- b_-)$$

$$= (p\mu_+^0 + q\mu_-^0) + RT \ln(\gamma_+^p \gamma_-^q b_+^p b_-^q)$$

$$= \mu_{\pm}^0 + RT \ln(\gamma_{\pm} b_{\pm})^{p+q}$$

where b_{\pm} is in mol/kg

$$\mu_{\text{salt}} = \mu_{\pm}^0 + RT \ln a_{\pm}$$

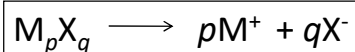
Mean activity coefficient

$$\mu_{\pm}^0 = p\mu_+^0 + q\mu_-^0$$

$$a_{\pm} = (\gamma_{\pm} b_{\pm})^{p+q}$$

$$\gamma_{\pm} = (\gamma_+^p \gamma_-^q)^{1/(p+q)}$$

$$b_{\pm} = (b_+^p b_-^q)^{1/(p+q)}$$

Activity of salt solutions

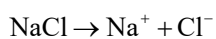
$$\mu_{\text{salt}} = p\mu_+ + q\mu_-$$

$$= p(\mu_+^0 + RT \ln a_+) + q(\mu_-^0 + RT \ln a_-)$$

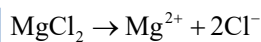
$$= p(\mu_+^0 + RT \ln \gamma_+ b_+) + q(\mu_-^0 + RT \ln \gamma_- b_-)$$

$$= (p\mu_+^0 + q\mu_-^0) + RT \ln(\gamma_+^p \gamma_-^q b_+^p b_-^q)$$

$$= \mu_{\pm}^0 + RT \ln(\gamma_{\pm} b_{\pm})^{p+q}$$

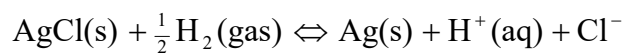
Examples:

$$\begin{aligned} \mu_{\text{NaCl}} &= (\mu_{\text{Na}}^0 + \mu_{\text{Cl}}^0) + RT \ln(\gamma_{\pm} b_{\pm})^2 \\ &= (\mu_{\text{Na}}^0 + \mu_{\text{Cl}}^0) + RT \ln(\gamma_{\text{Na}} \gamma_{\text{Cl}} b_{\text{Na}} b_{\text{Cl}}) \end{aligned}$$



$$\begin{aligned} \mu_{\text{MgCl}_2} &= (\mu_{\text{Mg}}^0 + 2\mu_{\text{Cl}}^0) + RT \ln(\gamma_{\pm} b_{\pm})^3 \\ &= (\mu_{\text{Mg}}^0 + 2\mu_{\text{Cl}}^0) + RT \ln(\gamma_{\text{Mg}} \gamma_{\text{Cl}}^2 b_{\text{Mg}} b_{\text{Cl}}^2) \end{aligned}$$

Cell potential in terms of activities & Mean activity coefficients from cell potential



$$E = E^0 - \frac{RT}{F} \ln \left(\frac{[a(\text{H}^+)] [a(\text{Cl}^-)] [a(\text{Ag})]}{[a(\text{AgCl})] [a(\text{H}_2)]^{1/2}} \right)$$

$$E = E^0 - \frac{RT}{F} \ln \left(\frac{[a(\text{H}^+)] [a(\text{Cl}^-)]}{[f(\text{H}_2)/p^0]^{1/2}} \right)$$

When the pressure is near 1 bar, the activities of pure solids are 1 and the activities of H_2 gas is the fugacity in bar units

$$E = E^0 - \frac{RT}{F} \ln a_{\text{H}^+} a_{\text{Cl}^-}$$

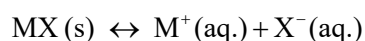
$$E = E^0 - \frac{RT}{F} \ln b^2 - \frac{RT}{F} \ln \gamma_{\pm}^2$$

$$[\text{HCl}] = b \text{ in mol kg}^{-1}$$

Mean activity coefficient

$$\ln \gamma_{\pm} = \frac{E^0 - E}{2RT/F} - \ln b$$

Solubility Product of a Sparingly Soluble Salt



$$K_s = \frac{a_{\text{M}^+} a_{\text{X}^-}}{a_{\text{MX}}} = a_{\text{M}^+} a_{\text{X}^-} = K_{sp}$$

Equilibrium constant

For the pure solid phase: $a_{\text{MX}} = 1$

$$K_{sp} = \exp \left(\frac{nFE^0}{RT} \right) \quad \text{and} \quad K_{sp} = a_{\text{M}^+} a_{\text{X}^-} = \gamma_{\pm}^2 S^2 \quad \text{Solubility Product}$$

$$S^2 = \frac{1}{\gamma_{\pm}^2} \exp \left(\frac{nFE^0}{RT} \right)$$

Solubility

S = molality of the saturated solution of MX

$$\text{For a dilute solute: } \gamma_{\pm} \approx 1 \Rightarrow K_s = S^2$$

Example: Determine the solubility of AgCl

Solubility equilibrium: $\text{AgCl(s)} \longrightarrow \text{Ag}^+(\text{aq.}) + \text{Cl}^-(\text{aq.})$

Cell : $\text{Ag(s)} \mid \text{Ag}^+(\text{aq.}) \parallel \text{HCl (aq.)} \mid \text{AgCl(s)} \mid \text{Ag(s)}$

Redn potential : $\text{AgCl(s)} + \text{e}^- \longrightarrow \text{Ag(s)} + \text{Cl}^-(\text{aq.}) \quad E_R^0 = 0.222 \text{ V}$
 $\text{Ag}^+(\text{aq.}) + \text{e}^- \longrightarrow \text{Ag(s)} \quad E_L^0 = 0.799 \text{ V}$

$$E_{\text{cell}}^0 = -0.577 \text{ V}$$

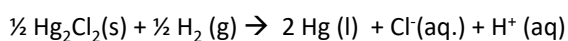
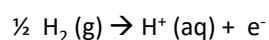
$$K_{sp}^0 = \exp (nFE^0/RT) = 1.76 \times 10^{-10}$$

Solubility : $S = 1.25 \times 10^{-5} \text{ mol kg}^{-1}$

Determination of pH

Cell : $\text{Pt(s)} \mid \text{H}_2(\text{g}, 1 \text{ bar}) \mid \text{H}^+(\text{aq.}) \parallel \text{Cl}^-(\text{aq.}, 1.0\text{M}) \mid \text{Hg}_2\text{Cl}_2(\text{s}) \mid \text{Hg (l)}$

Electrode reaction : $\frac{1}{2} \text{Hg}_2\text{Cl}_2(\text{s}) + \text{e}^- \rightarrow \text{Hg (l)} + \text{Cl}^-(\text{aq.})$
 $E^0 = 0.2680 \text{ V (calomel electrode)}$



Using Nernst equation,

$$E = E^0 - \frac{RT}{F} \ln (a_{\text{H}^+})$$

$$-\ln (a_{\text{H}^+}) = \frac{F}{RT} (E - E^0)$$

$$\text{pH} = -\log (a_{\text{H}^+}) = \frac{F}{2.303RT} (E - E^0)$$