Chemical Equilibrium

1. Standard Thermodynamic Functions

$\equiv$ Thermodynamic functions at a pressure $p°$ ($\equiv$ 1 bar) or at a <u>molality</u> $b°$ ($\equiv$ 1 mol kg^{-1}), relative to the reference states of elements

solution
$\neq$ molarity (mol dm^{-3})
solvent

· $\Delta_f H°$, $\Delta_f G°$, $S_m°$, *etc.* → thermodynamic database

⟨EMF⟩

Electromotive force (emf) = maximum non-expansion work = Gibbs energy
Standard emf $E°$ in terms of reaction Gibbs energy $\Delta_r G°$ for overall cell reaction involving ν electrons:

$$E° = -\frac{\Delta_r G°}{\nu F} \qquad (1.1)$$

Here F (Faraday constant) $= N_A e$ (charge of 1 mol of electrons)

Exercise 1.1

1) Calculate the emf of a Daniel cell (anode: Zn → Zn^{2+} + 2e$^-$, cathode: Cu^{2+} + 2e$^-$ → Cu) from the following standard potentials.

reduction half-reaction	$E°$ (298 K) / V
Zn^{2+} + 2e$^-$ → Zn	–0.76
Cu^{2+} + 2e$^-$ → Cu	+0.34

2) Calculate the emf of a Daniel cell [overall cell reaction: Cu^{2+}(aq) + Zn(s) → Cu(s) + Zn^{2+}(aq)] from the following standard Gibbs energies of formation.

	$\Delta_f G°$(298 K) / kJ mol^{-1}
Zn^{2+}(aq)	–147.1
Cu^{2+}(aq)	65.5

Solution to Exercise 1.1
1) $E° = 0.34 - (-0.76) = 1.10$ V
2) $E° = -\Delta_r G° / \nu F = -(-147.1 - 65.5)\times 1000 / (2\times 96485) = 1.102$ V

* Rather, the $\Delta_f G°$'s of ions in an ideal aqueous solution were calculated from the standard potentials.

Exercise 1.2

Calculate the theoretical emf of hydrogen fuel cell [overall cell reaction: H$_2$(g) + 0.5 O$_2$(g) → H$_2$O(g), ν = 2] operating at 300 K and 1000 K from the following data.

T / K	$\Delta_f G°$[H$_2$O(g)] / kJ mol^{-1} [JANAF]
300	–228.5
1000	–192.6

Solution to Exercise 1.2
$E° = -\Delta_r G / \nu F = 228.5\times 1000/(2\times 96485) = 1.18$ V (300 K),
$= 192.6\times 1000/(2\times 96485) = 1.00$ V (1000 K)

* Theoretical emf depends on the overall cell reaction only.
* The $E° = 1.23$ V derived from the room temperature $\Delta_r G° = -237.1$ for H$_2$(g) + 0.5 O$_2$(g) → H$_2$O(l) is usually called as the "theoretical emf of hydrogen fuel cell".

⟨Solubility of Electrolyte⟩

Upon the dissolution equilibrium of an electrolyte, AB(s) → A$^+$(aq) + B$^-$(aq),

$$\mu[AB(s)] = \mu[A^+(aq)] + \mu[B^-(aq)] \qquad (1.2)$$

For an ideal solution [eq. (0.7)],

$$\mu[A^+(aq)] = \mu^\circ[A^+(aq)] + RT \ln\left(\frac{b[A^+(aq)]}{b^\circ}\right) \quad \text{and}$$

$$\mu[B^-(aq)] = \mu^\circ[B^-(aq)] + RT \ln\left(\frac{b[B^-(aq)]}{b^\circ}\right)$$

Applying these to (1.2) gives,

$$-\Delta_r G^\circ = \mu^\circ[AB(s)] - \mu^\circ[A^+(aq)] - \mu^\circ[B^-(aq)]$$

$$= RT \ln\left(\frac{b[A^+(aq)]}{b^\circ}\frac{b[B^-(aq)]}{b^\circ}\right) \tag{1.3}$$

Exercise 1.3

Calculate the solubility S (mol kg^{-1}) of AgCl(s) from the following standard Gibbs energies of formation.

	$\Delta_f G^\circ$(298 K) / kJ mol^{-1}
AgCl(s)	−109.8
Ag$^+$(aq)	77.1
Cl$^-$(aq)	−131.2

Solution to Exercise 1.3

$\Delta_r G^\circ = 77.1 + (-131.2) - (-109.8) = 55.7$ kJ mol^{-1}

$b[A^+(aq)]b[B^-(aq)] = \exp(-\Delta_r G^\circ / RT) = \exp[-55.7\times1000 / (8.3145\times298)] = 1.725\times10^{-10}$ mol^2 kg^{-2}

$S = (1.725\times10^{-10})^{1/2} = 1.31\times10^{-5}$ mol kg^{-1}

hardly soluble salt → well approximated by an ideal solution

* Solubility difficult to measure can be calculated from the thermodynamic functions.

⟨Autoprotolysis Constant of Water⟩

Exercise 1.4

1) Calculate the autoprotolysis constant (or the ion product) of water $K_w = b[H^+(aq)]b[OH^-(aq)]$ from the following data.

(298 K)	$\Delta_f H^\circ$ / kJ mol^{-1}	S_m° / J K^{-1} mol^{-1}	
H$_2$O(l)	−285.8	69.9	
H$^+$(aq)	0 *	0 *	* zero by definition
OH$^-$(aq)	−230.0	−10.8	

2) Estimate the autoprotolysis constant K_w at 75 °C (= 348 K) assuming that $\Delta_r H^\circ$ and $\Delta_r S^\circ$ are independent of temperature. *cf.*) experimental K_w (75 °C) = 2.0×10^{-13} mol^2 kg^{-2}

Solution to Exercise 1.4

1) Similarly to (1.3), $-\Delta_r G^\circ = RT \ln\left(\frac{b[H^+(aq)]}{b^\circ}\frac{b[OH^-(aq)]}{b^\circ}\right)$ is obtained.

$\Delta_r H^\circ = (-230.0) - (-285.8) = 55.8$ kJ mol^{-1}. $\Delta_r S^\circ = -10.8 - 69.9 = -80.7$ J K^{-1} mol^{-1}.

$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ = 55.8 - 298\times(-80.7) / 1000 = 79.85$ kJ mol^{-1}

$K_w = \exp(-\Delta_r G^\circ / RT) = \exp[-79.85\times1000 / (8.3145\times298)] = 1.01\times10^{-14}$ mol^2 kg^{-2}

2) $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ = 55.8 - 348\times(-80.7) / 1000 = 83.88$ kJ mol^{-1}

$K_w = \exp(-\Delta_r G^\circ / RT) = \exp[-83.88\times1000 / (8.3145\times348)] = 2.6\times10^{-13}$ mol^2 kg^{-2}