Chemical Equilibrium

1. Standard Thermodynamic Functions

≠ molarity (mol dm⁻³)

- ≡ Thermodynamic functions at a pressure p° (≡ 1 bar) or at a molality b° (≡ 1 mol kg⁻¹), relative to the reference states of elements
- $\cdot \Delta_f H^{\circ}, \Delta_f G^{\circ}, S_m^{\circ}, etc. \rightarrow \text{thermodynamic database}$

⟨EMF⟩

Electromotive force (emf) = maximum non-expansion work = Gibbs energy

Standard emf E° in terms of reaction Gibbs energy $\Delta_r G^{\circ}$ for overall cell reaction involving ν electrons:

$$E^{\circ} = -\frac{\Delta_{\rm r} G^{\circ}}{\nu F} \tag{1.1}$$

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: $Zn \rightarrow Zn^{2+} + 2e^-$, cathode: $Cu^{2+} + 2e^- \rightarrow Cu$) from the following standard potentials.

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

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

$$\frac{\Delta_{\rm f} G^{\rm o}(298~{\rm K}) \, / \, {\rm kJ~mol}^{-1}}{{\rm Zn}^{2+}({\rm aq}) \qquad -147.1} \\ {\rm Cu}^{2+}({\rm aq}) \qquad \qquad 65.5$$

Solution to Exercise 1.1

- 1) $E^{\circ} = 0.34 (-0.76) = 1.10 \text{ V}$
- 2) $E^{\circ} = -\Delta_{\rm r} G^{\circ} / \nu F = -(-147.1 65.5) \times 1000 / (2 \times 96485) = 1.102 \text{ V}$
 - * Rather, the $\Delta_f G^{\circ}$'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: $H_2(g) + 0.5 O_2(g) \rightarrow H_2O(g)$, $\nu = 2$] operating at 300 K and 1000 K from the following data.

| T/K | $\Delta_f G^{\circ}[H_2O(g)] / kJ \text{ mol}^{-1}$ | [JANAF] |
|------|---|---------|
| 300 | -228.5 | |
| 1000 | -192.6 | |

Solution to Exercise 1.2

$$E^{\circ} = -\Delta_{\rm r}G / vF = 228.5 \times 1000/(2 \times 96485) = 1.18 \text{ V } (300 \text{ K}),$$

= 192.6×1000/(2×96485) = 1.00 V (1000 K)

- * Theoretical emf depends on the overall cell reaction only.
- * The $E^{\circ}=1.23$ V derived from the room temperature $\Delta_r G^{\circ}=-237.1$ for $H_2(g)+0.5$ $O_2(g) \rightarrow H_2O(l)$ is usually called as the "theoretical emf of hydrogen fuel cell".

(Solubility of Electrolyte)

Upon the dissolution equilibrium of an electrolyte, $AB(s) \rightarrow A^{+}(aq) + B^{-}(aq)$,

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

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

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

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

Applying these to (1.2) gives,

$$-\Delta_{r}G^{\circ} = \mu^{\circ}[AB(s)] - \mu^{\circ}[A^{+}(aq)] - \mu^{\circ}[B^{-}(aq)]$$

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

Exercise 1.3

Calculate the solubility S (mol kg⁻¹) of AgCl(s) from the following standard Gibbs energies of formation.

| | $\Delta_{\rm f}G^{\circ}(298~{ m K}) / { m kJ~mol}^{-1}$ |
|----------------------|--|
| AgCl(s) | -109.8 |
| $Ag^+(aq)$ | 77.1 |
| Cl ⁻ (aq) | -131.2 |

Solution to Exercise 1.3

$$\Delta_{\rm r}G^{\circ} = 77.1 + (-131.2) - (-109.8) = 55.7 \text{ kJ mol}^{-1}$$

 $b[{\rm A}^{+}({\rm aq})]b[{\rm B}^{-}({\rm aq})] = \exp(-\Delta_{\rm r}G^{\circ} / RT) = \exp[-55.7 \times 1000 / (8.3145 \times 298)] = 1.725 \times 10^{-10} \text{ mol}^{2}$
 ${\rm kg}^{-2}$

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

hardly soluble salt \rightarrow 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) | $\Delta_{\rm f} H^{\circ} / { m kJ~mol}^{-1}$ | $S_{\rm m}^{\circ}$ / J K ⁻¹ mol ⁻¹ | -1 |
|----------------------|---|---|----------------------|
| $H_2O(1)$ | -285.8 | 69.9 | |
| $H^+(aq)$ | 0 * | 0 * | * zero by definition |
| OH ⁻ (aq) | -230.0 | -10.8 | |

2) Estimate the autoprotolysis constant $K_{\rm w}$ at 75 °C (= 348 K) assuming that $\Delta_{\rm r} H^{\circ}$ and $\Delta_{\rm r} S^{\circ}$ are independent of temperature. cf.) experimental $K_{\rm w}$ (75 °C) = 2.0×10^{-13} mol² 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.

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

$$\Delta_r H^\circ = (-230.0) - (-285.8) = 55.8 \text{ kJ mol}^{-1}$$
. $\Delta_r S^\circ = -10.8 - 69.9 = -80.7 \text{ J K}^{-1} \text{ mol}^{-1}$. $\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ = 55.8 - 298 \times (-80.7) / 1000 = 79.85 \text{ kJ mol}^{-1}$

$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ = 55.8 - 298 \times (-80.7) / 1000 = 79.85 \text{ kJ mol}^2$$

 $K_w = \exp(-\Delta_r G^\circ / RT) = \exp[-79.85 \times 1000 / (8.3145 \times 298)] = 1.01 \times 10^{-14} \text{ mol}^2 \text{ kg}^{-2}$

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

$$K_{\rm w} = \exp(-\Delta_{\rm r} G^{\circ} / RT) = \exp[-83.88 \times 1000 / (8.3145 \times 348)] = 2.6 \times 10^{-13} \,\rm mol^2 \, kg^{-2}$$