

Chemical Equilibrium

1. Standard Thermodynamic Functions

≡ Thermodynamic functions at a pressure p° ($\equiv 1$ bar) or at a molality b° ($\equiv 1$ mol kg⁻¹), relative to the reference states of elements

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

≠ molarity (mol dm⁻³)
 solution
 solvent

⟨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:

$$E^\circ = -\frac{\Delta_r G^\circ}{\nu F} \quad (1.1)$$

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

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

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

| | $\Delta_f G^\circ$ (298 K) / kJ mol ⁻¹ |
|-----------------------------|---|
| $\text{Zn}^{2+}(\text{aq})$ | -147.1 |
| $\text{Cu}^{2+}(\text{aq})$ | 65.5 |

Solution to Exercise 1.1

1) $E^\circ = 0.34 - (-0.76) = 1.10$ V

2) $E^\circ = -\Delta_r G^\circ / \nu F = -(-147.1 - 65.5) \times 1000 / (2 \times 96485) = 1.102$ 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: $\text{H}_2(\text{g}) + 0.5 \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g})$, $\nu = 2$] operating at 300 K and 1000 K from the following data.

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

Solution to Exercise 1.2

$$E^\circ = -\Delta_r G / \nu F = 228.5 \times 1000 / (2 \times 96485) = 1.18 \text{ V (300 K)},$$

$$= 192.6 \times 1000 / (2 \times 96485) = 1.00 \text{ V (1000 K)}$$

* 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 $\text{H}_2(\text{g}) + 0.5 \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$ is usually called as the "theoretical emf of hydrogen fuel cell".

⟨Solubility of Electrolyte⟩

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

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

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

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

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

Applying these to (1.2) gives,

$$\begin{aligned} -\Delta_r G^\circ &= \mu^\circ[\text{AB}(\text{s})] - \mu^\circ[\text{A}^+(\text{aq})] - \mu^\circ[\text{B}^-(\text{aq})] \\ &= RT \ln \left(\frac{b[\text{A}^+(\text{aq})] b[\text{B}^-(\text{aq})]}{b^\circ} \right) \end{aligned} \quad (1.3)$$

Exercise 1.3

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

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

Solution to Exercise 1.3

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

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

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

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 $K_w = b[\text{H}^+(\text{aq})]b[\text{OH}^-(\text{aq})]$ from the following data.

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

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

Solution to Exercise 1.4

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

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

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

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

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

$$K_w = \exp(-\Delta_r G^\circ / RT) = \exp[-83.88 \times 1000 / (8.3145 \times 348)] = 2.6 \times 10^{-13} \text{ mol}^2 \text{ kg}^{-2}$$