

# Chemical Equilibrium

## 1. Standard Thermodynamic Functions

≡ thermodynamic functions at a pressure  $p^\circ$  ( $\equiv 1$  bar) or the molality  $b^\circ$  ( $\equiv 1$  mol kg<sup>-1</sup>), relative to the reference states of elements

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

### ⟨EMF⟩

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

Standard emf  $E^\circ$  in terms of the reaction Gibbs energy  $\Delta_r G^\circ$  for the overall cell reaction involving  $\nu$  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:  $\text{Zn} \rightarrow \text{Zn}^{2+} + 2 e^-$ , cathode:  $\text{Cu}^{2+} + 2 e^- \rightarrow \text{Cu}$ ) from the following standard potentials.

reduction half-reaction	$E^\circ$ (298 K) / V
$\text{Zn}^{2+} + 2 e^- \rightarrow \text{Zn}$	-0.76
$\text{Cu}^{2+} + 2 e^- \rightarrow \text{Cu}$	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 <sup>-1</sup>
$\text{Zn}^{2+}(\text{aq})$	-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 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.

$T / \text{K}$	$\Delta_f G^\circ[\text{H}_2\text{O}(\text{g})] / \text{kJ mol}^{-1}$ [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  $\Delta_f G^\circ = -237.1$  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 solution equilibrium of the 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)],

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

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

Applying these to (1.2) gives,

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

### Exercise 1.3

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

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

#### Solution to exercise 1.3

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

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

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

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

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

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

#### Solution to exercise 1.4

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

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

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

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

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

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