Chemical Equilibrium

1. Standard Thermodynamic Functions

solution

≠ mola<u>r</u>ity (mol dm⁻³)

- = Thermodynamic functions at a pressure p° (= 1 bar) or at <u>a molality</u> b° (= 1 mol kg⁻¹), relative to the reference states of elements
- · $\Delta_{\rm f} H^{\circ}, \Delta_{\rm f} G^{\circ}, S_{\rm m}^{\circ}, etc. \rightarrow$ thermodynamic database

$\langle \mathsf{EMF} \rangle$

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 *v* 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	<i>E</i> ° (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.

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

Solution to Exercise 1.1

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

2) $E^{\circ} = -\Delta_r G^{\circ} / \nu F = -(-147.1 - 65.5) \times 1000 / (2 \times 96485) = 1.102 \text{ V}$

* 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	$\Delta_{f}G^{\circ}[H_{2}O(g)] \ / \ kJ \ mol^{-1} \text{[JANAF]}$
300	-228.5
1000	-192.6

Solution to Exercise 1.2

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

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

* 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)],

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

Applying these to (1.2) gives,

$$-\Delta_{\mathbf{r}}G^{\circ} = \mu^{\circ}[\mathbf{A}\mathbf{B}(\mathbf{s})] - \mu^{\circ}[\mathbf{A}^{+}(\mathbf{aq})] - \mu^{\circ}[\mathbf{B}^{-}(\mathbf{aq})]$$
$$= RT \ln\left(\frac{b[\mathbf{A}^{+}(\mathbf{aq})]}{b^{\circ}}\frac{b[\mathbf{B}^{-}(\mathbf{aq})]}{b^{\circ}}\right)$$
(1.3)

Exercise 1.3

Calculate the solubility $S \pmod{\text{kg}^{-1}}$ 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
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 $\Delta_{\rm r}G^{\circ} = 77.1 + (-131.2) - (-109.8) = 55.7 \text{ kJ mol}^{-1}$ $b[A^{+}(aq)]b[B^{-}(aq)] = \exp(-\Delta_{\rm r}G^{\circ} / RT) = \exp[-55.7 \times 1000 / (8.3145 \times 298)] = 1.725 \times 10^{-10} \text{ mol}^{2}$ 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)	$\Delta_{ m f} H^{\circ}$ / kJ mol ⁻¹	$S_{\rm m}^{\circ}$ / J K ⁻¹ mol ⁻	-1
$H_2O(l)$	-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 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.
 $\Delta_{r}H^{\circ} = (-230.0) - (-285.8) = 55.8 \text{ kJ mol}^{-1}. \Delta_{r}S^{\circ} = -10.8 - 69.9 = -80.7 \text{ J K}^{-1} \text{ mol}^{-1}.$
 $\Delta_{r}G^{\circ} = \Delta_{r}H^{\circ} - T\Delta_{r}S^{\circ} = 55.8 - 298 \times (-80.7) / 1000 = 79.85 \text{ kJ mol}^{-1}$
 $K_{w} = \exp(-\Delta_{r}G^{\circ} / RT) = \exp[-79.85 \times 1000 / (8.3145 \times 298)] = 1.01 \times 10^{-14} \text{ mol}^{2} \text{ kg}^{-2}$
2) $\Delta_{r}G^{\circ} = \Delta_{r}H^{\circ} - T\Delta_{r}S^{\circ} = 55.8 - 348 \times (-80.7) / 1000 = 83.88 \text{ kJ mol}^{-1}$
 $K_{w} = \exp(-\Delta_{r}G^{\circ} / RT) = \exp[-83.88 \times 1000 / (8.3145 \times 348)] = 2.6 \times 10^{-13} \text{ mol}^{2} \text{ kg}^{-2}$