3. Ideal Solution

(Dissolution Equilibrium of Gas)

In dissolution equilibrium state of gas into water, $A(g) \rightleftharpoons A(aq)$:

$$\mu(g) = \mu(aq) \tag{3.1}$$

For an ideal gas and an ideal solution [from (0.6) and (0.7)]:

$$-\Delta_{\text{sol}}G^{\circ} = \mu^{\circ}(g) - \mu^{\circ}(aq) = RT \ln K_{\text{sol}} \qquad \text{where} \quad K_{\text{sol}} \equiv \frac{b/b^{\circ}}{p/p^{\circ}}$$
(3.2)

(Solution Phase Chemical Equilibrium)

The CO₂(aq) dissociates in solution phase as,

$$CO_2(aq) + H_2O(1) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$
 [a1]

$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$$
 [a2]

The respective acid-dissociation constants are,

$$-\Delta_{al}G^{\circ} = RT \ln K_{al}$$
 where $K_{al} \equiv \frac{[H^{+}][HCO_{3}^{-}]}{[CO_{2}(aq)]}$ (3.3)

$$-\Delta_{a2}G^{\circ} = RT \ln K_{a2}$$
 where $K_{a2} \equiv \frac{[H^{+}][CO_{3}^{2-}]}{[HCO_{3}^{-}]}$ (3.4)

where $[H^+] \equiv b[H^+(aq)] / b^\circ$, etc.

The "apparent" dissolution equilibrium constant, $K_{\text{sol, app}} = \frac{[\text{CO}_2(\text{aq})] + [\text{HCO}_3^-] + [\text{CO}_3^2]}{p(\text{CO}_2)/p^\circ}$, for a given [H⁺] is,

$$K_{\text{sol, app}} = \left\{ \left(\frac{K_{\text{a2}}}{[H^+]} + 1 \right) \frac{K_{\text{a1}}}{[H^+]} + 1 \right\} K_{\text{sol}}$$
(3.5)

Exercise 3.1

1) Compute the dissolution equilibrium constant of CO_2 into water, K_{sol} , and subsequent acid-dissociation constants, K_{a1} and K_{a2} , from the following standard Gibbs energies.

$\Delta_{ m f} G$	°(298 K) / kJ m	ol ⁻¹
$CO_2(g)$	-394.4	
$CO_2(aq)$	-386.0	
$H_2O(1)$	-237.1	
$HCO_3^-(aq)$	-586.8	
$H^+(aq)$	0 *	* zero by definition
$CO_3^{2-}(aq)$	-527.8	

2) Calculate $K_{\text{sol, app}} / K_{\text{sol}}$ for pH = 4 and 8.

Solution to Exercise 3.1

1)
$$\Delta_{\text{sol}}G^{\circ} = -386.0 - (-394.4) = 8.4 \text{ kJ mol}^{-1}.$$

$$K_{\text{sol}} = \exp(-\Delta_{\text{sol}}G^{\circ} / RT) = \exp[-8400 / (8.3145 \times 298)] = 3.37 \times 10^{-2} \text{ [-] (or mol kg}^{-1} \text{ bar}^{-1})$$

$$\Delta_{\text{al}}G^{\circ} = -586.8 - (-386.0 - 237.1) = 36.3 \text{ kJ mol}^{-1} \rightarrow K_{\text{al}} = 4.34 \times 10^{-7} \text{ [-]}$$

$$\Delta_{\text{a2}}G^{\circ} = -527.8 - (-586.8) = 59.0 \text{ kJ mol}^{-1} \rightarrow K_{\text{a2}} = 4.56 \times 10^{-11} \text{ [-]}$$

2) pH = 4:
$$\frac{K_{\text{sol, app}}}{K_{\text{sol}}} = \left(\frac{4.56 \cdot 10^{-11}}{10^{-4}} + 1\right) \frac{4.34 \cdot 10^{-7}}{10^{-4}} + 1 = 1.004 [-].$$

pH = 8:
$$\frac{K_{\text{sol, app}}}{K_{\text{sol}}} = \left(\frac{4.56 \cdot 10^{-11}}{10^{-8}} + 1\right) \frac{4.34 \cdot 10^{-7}}{10^{-8}} + 1 = 44.6 \text{ [-]}.$$

(Heat of Solution and Temperature Dependence)

The eq. (3.2) can be rewritten as,

$$K_{\text{sol}} = \exp\left(\frac{\Delta_{\text{sol}} S^{\circ}}{R}\right) \exp\left(-\frac{\Delta_{\text{sol}} H^{\circ}}{RT}\right)$$
 (3.6)

For $\Delta H < 0$ (exothermic) $K \uparrow$ as $T \downarrow$, while for $\Delta H > 0$ (endothermic) $K \uparrow$ as $T \uparrow$. (Le Chatelier's principle)

Exercise 3.2

The enthalpy of solution of H₂ into water is $\Delta_{\text{sol}}H^{\circ} = -4.2 \text{ kJ mol}^{-1}$ and the solution equilibrium constant is $K_{\text{sol}} = 7.81 \times 10^{-4} \text{ mol kg}^{-1} \text{ bar}^{-1}$ at 298 K. Estimate K_{sol} at 10 °C (283 K).

Solution to Exercise 3.2

$$\frac{K_{\text{sol, 283}}}{K_{\text{sol, 298}}} = \exp\left[-\frac{\Delta_{\text{sol}}H^{\circ}}{R}\left(\frac{1}{283} - \frac{1}{298}\right)\right] = \exp\left[-\frac{-4.2 \times 1000}{8.3145}\left(\frac{1}{283} - \frac{1}{298}\right)\right] = 1.094$$

Then,
$$K_{\text{sol, 283}} = 7.81 \cdot 10^{-4} \times 1.094 = \underline{8.5}_{4} \times 10^{-4} \text{ [-] (or mol kg}^{-1} \text{ bar}^{-1}).$$
 $cf.$) experimental = $\underline{8.72} \times 10^{-4}$

 K_{sol} increases \uparrow as T decreases \downarrow . (consistent with $\Delta H < 0$; exothermic)

(Activity)

Except for the very dilute solution such as in exercise 1.3, the solution equilibrium of the electrolyte, $AB(s) \rightleftharpoons A^+(aq) + B^-(aq)$, should be written with the mean activity coefficient, γ , as,

$$-\Delta_{r}G^{\circ} = \mu^{\circ}[AB(s)] - \mu^{\circ}[A^{+}(aq)] - \mu^{\circ}[B^{-}(aq)]$$
$$= RT \ln \left(\frac{\gamma b[A^{+}(aq)]}{b^{\circ}} \frac{\gamma b[B^{-}(aq)]}{b^{\circ}}\right)$$
(3.7)

Exercise 3.3

1) Assuming the ideal solution, calculate the solubility S_{ideal} (mol kg⁻¹) of KCl(s) from the following data.

	$\Delta_{\rm f}G^{\circ}(298~{ m K}) / { m kJ~mol}^{-1}$
KCl(s)	-409.1
$K^+(aq)$	-283.3
Cl ⁻ (aq)	-131.2

2) Evaluate the mean activity coefficient, γ , for the saturated KCl solution by using the measured solubility $S = 4.769 \text{ mol kg}^{-1}$.

Solution to Exercise 3.3

1)
$$\Delta_r G^\circ = (-283.3) + (-131.2) - (-409.1) = -5.4 \text{ kJ mol}^{-1}$$

 $b[K^+(\text{aq})]b[Cl^-(\text{aq})] = \exp(-\Delta_r G^\circ / RT) = \exp[5.4 \times 1000 / (8.3145 \times 298)] = 8.84 \text{ mol}^2 \text{ kg}^{-2}$
 $S_{\text{ideal}} = (8.84)^{1/2} = \underline{2.97} \text{ mol kg}^{-1}$

2)
$$\gamma = S_{\text{ideal}} / S = 2.97 / 4.769 = 0.623$$

Solubility of some readily-soluble salts is determined by equilibrium between the hydrated salt and dissolved ions, for example, $CaCl_2 \cdot 6H_2O \rightleftharpoons Ca^{2+}(aq) + 2Cl^{-}(aq) + 6H_2O$.