

### 3. Ideal Solution

#### ⟨Dissolution Equilibrium of Gas⟩

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

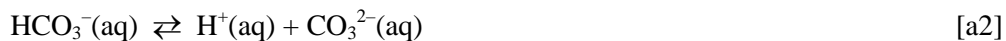
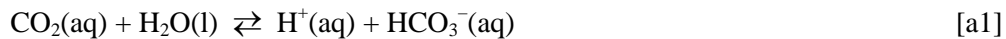
$$\mu(g) = \mu(aq) \quad (3.1)$$

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

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

#### ⟨Solution Phase Equilibrium⟩

The  $\text{CO}_2(\text{aq})$  dissociates in solution phase as,



The respective acid-dissociation constants are,

$$-\Delta_{\text{a1}}G^\circ = RT \ln K_{\text{a1}} \quad \text{where } K_{\text{a1}} \equiv \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2(\text{aq})]} \quad (3.3)$$

$$-\Delta_{\text{a2}}G^\circ = RT \ln K_{\text{a2}} \quad \text{where } K_{\text{a2}} \equiv \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \quad (3.4)$$

where  $[\text{CO}_2(\text{aq})] \equiv b[\text{CO}_2(\text{aq})] / b^\circ$ ,  $[\text{H}^+] \equiv b[\text{H}^+(\text{aq})] / b^\circ$ , etc.

#### Exercise 3.1

- 1) Compute the dissolution equilibrium constant of  $\text{CO}_2$  into water,  $K_{\text{sol}}$ , and subsequent acid-dissociation constants,  $K_{\text{a1}}$  and  $K_{\text{a2}}$ , from the following standard Gibbs energies.

$\Delta_f G^\circ(298 \text{ K}) / \text{kJ mol}^{-1}$	
$\text{CO}_2(\text{g})$	-394.4
$\text{CO}_2(\text{aq})$	-386.0
$\text{H}_2\text{O}(\text{l})$	-237.1
$\text{HCO}_3^-(\text{aq})$	-586.8
$\text{H}^+(\text{aq})$	0 *
$\text{CO}_3^{2-}(\text{aq})$	-527.8

\* zero by definition

- 2) Derive an equation for "apparent" dissolution equilibrium constant,

$$K_{\text{sol, app}} = \frac{[\text{CO}_2(\text{aq})] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]}{p(\text{CO}_2) / p^\circ}, \text{ for given } [\text{H}^+] \text{ by using } K_{\text{sol}}, K_{\text{a1}} \text{ and } K_{\text{a2}}.$$

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

#### Solution to Exercise 3.1

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

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

$$\Delta_{\text{a1}}G^\circ = -586.8 - (-386.0 - 237.1) = 36.3 \text{ kJ mol}^{-1} \rightarrow K_{\text{a1}} = 4.34 \times 10^{-7} [-]$$

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

$$2) K_{\text{sol, app}} = \left\{ \left( \frac{K_{\text{a2}}}{[\text{H}^+]} + 1 \right) \frac{K_{\text{a1}}}{[\text{H}^+]} + 1 \right\} K_{\text{sol}}$$

$$3) \text{pH} = 4: \frac{K_{\text{sol, app}}}{K_{\text{sol}}} = \left( \frac{4.56 \cdot 10^{-11}}{10^{-4}} + 1 \right) \frac{4.34 \cdot 10^{-7}}{10^{-4}} + 1 = 1.004 [-].$$

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

### Heat of Solution and Temperature Dependence

The eq. (3.2) can be rewritten as,

$$K_{\text{sol}} = \exp\left(\frac{\Delta_{\text{sol}}S^\circ}{R}\right) \exp\left(-\frac{\Delta_{\text{sol}}H^\circ}{RT}\right) \quad (3.5)$$

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  $\text{H}_2$  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  $K_{\text{sol}}$  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,  $K_{\text{sol}, 283} = 7.81 \cdot 10^{-4} \times 1.094 = 8.54 \times 10^{-4} [-]$  (or  $\text{mol kg}^{-1} \text{ bar}^{-1}$ ).

cf.) experimental =  $8.72 \times 10^{-4}$

$K_{\text{sol}}$  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,  $\text{AB(s)} \rightleftharpoons \text{A}^+(\text{aq}) + \text{B}^-(\text{aq})$ , should be written with the mean activity coefficient,  $\gamma$ , as,

$$\begin{aligned} -\Delta_r G^\circ &= \mu^\circ[\text{AB(s)}] - \mu^\circ[\text{A}^+(\text{aq})] - \mu^\circ[\text{B}^-(\text{aq})] \\ &= RT \ln \left( \frac{\gamma b[\text{A}^+(\text{aq})] \gamma b[\text{B}^-(\text{aq})]}{b^\circ} \right) \end{aligned} \quad (3.6)$$

#### Exercise 3.3

1) Assuming the ideal solution, calculate the solubility  $S_{\text{ideal}}$  ( $\text{mol kg}^{-1}$ ) of  $\text{KCl(s)}$  from the following data.

	$\Delta_f G^\circ(298 \text{ K}) / \text{kJ mol}^{-1}$
$\text{KCl(s)}$	-409.1
$\text{K}^+(\text{aq})$	-283.3
$\text{Cl}^-(\text{aq})$	-131.2

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

#### Solution to Exercise 3.3

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

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

$$S_{\text{ideal}} = (8.84)^{1/2} = 2.97 \text{ mol kg}^{-1}$$

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

Trend of solubility  $S$  against  $T$  for small  $|\Delta H|$  dissolution process often disturbed (looks reversed) by  $T$ -dep of  $\gamma$ .