

3. Ideal Solution

⟨Dissolution Equilibrium of Gas⟩

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

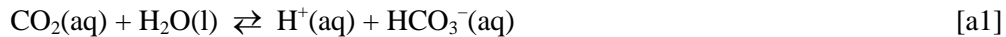
$$\mu(g) = \mu(aq) \quad (3.1)$$

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 $[\text{H}^+] \equiv b[\text{H}^+(\text{aq})] / b^\circ$, 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 $[\text{H}^+]$ is,

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

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.

	$\Delta_f G^\circ(298 \text{ K}) / \text{kJ mol}^{-1}$	
$\text{CO}_2(\text{g})$	-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 *	* zero by definition
$\text{CO}_3^{2-}(\text{aq})$	-527.8	

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

Solution to Exercise 3.1

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

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

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

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

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

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

Heat of Solution and Temperature Dependence

The eq. (3.2) can be rewritten as,

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

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 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_{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, $K_{\text{sol}, 283} = 7.81 \cdot 10^{-4} \times 1.094 = \underline{8.54} \times 10^{-4}$ [-] (or $\text{mol kg}^{-1} \text{ bar}^{-1}$).
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, $\text{AB(s)} \rightleftharpoons \text{A}^+(\text{aq}) + \text{B}^-(\text{aq})$, should be written with the mean activity coefficient, γ , as,

$$\begin{aligned} -\Delta_r G^\circ &= \mu^\circ[\text{AB(s)}] - \mu^\circ[\text{A}^+(\text{aq})] - \mu^\circ[\text{B}^-(\text{aq})] \\ &= RT \ln \left(\frac{\gamma b[\text{A}^+(\text{aq})] \gamma b[\text{B}^-(\text{aq})]}{b^\circ} \right) \end{aligned} \quad (3.7)$$

Exercise 3.3

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

	$\Delta_r G^\circ(298 \text{ K}) / \text{kJ mol}^{-1}$
KCl(s)	-409.1
$\text{K}^+(\text{aq})$	-283.3
$\text{Cl}^-(\text{aq})$	-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) $\Delta_r G^\circ = (-283.3) + (-131.2) - (-409.1) = -5.4 \text{ kJ mol}^{-1}$
 $b[\text{K}^+(\text{aq})]b[\text{Cl}^-(\text{aq})] = \exp(-\Delta_r G^\circ / RT) = \exp[5.4 \times 1000 / (8.3145 \times 298)] = 8.84 \text{ mol}^2 \text{ kg}^{-2}$
 $S_{\text{ideal}} = (8.84)^{1/2} = \underline{2.97} \text{ mol kg}^{-1}$

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

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