3. Ideal Solution

〈Dissolution Equilibrium of Gas〉

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

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

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

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

〈Solution Phase Chemical Equilibrium〉

The CO_2(aq) dissociates in solution phase as,

$$\mathrm{CO_2(aq) + H_2O(l) \rightleftarrows H^+(aq) + HCO_3^-(aq)} \qquad [a1]$$

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

The respective acid-dissociation constants are,

$$-\Delta_{\mathrm{a1}}G^\circ = RT\ln K_{\mathrm{a1}} \qquad \text{where} \quad K_{\mathrm{a1}} \equiv \frac{[\mathrm{H^+}][\mathrm{HCO_3^-}]}{[\mathrm{CO_2(aq)}]} \tag{3.3}$$

$$-\Delta_{\mathrm{a2}}G^\circ = RT\ln K_{\mathrm{a2}} \qquad \text{where} \quad K_{\mathrm{a2}} \equiv \frac{[\mathrm{H^+}][\mathrm{CO_3^{2-}}]}{[\mathrm{HCO_3^-}]} \tag{3.4}$$

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

The"apparent" dissolution equilibrium constant, $K_{\mathrm{sol,\,app}} = \dfrac{[\mathrm{CO_2(aq)}]+[\mathrm{HCO_3^-}]+[\mathrm{CO_3^{2-}}]}{p(\mathrm{CO_2})/p^\circ}$, for a given $[\mathrm{H^+}]$ is,

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

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 K) / kJ mol^{-1}	
CO_2(g)	–394.4	
CO_2(aq)	–386.0	
H_2O(l)	–237.1	
HCO_3^-(aq)	–586.8	
H^+(aq)	0 *	* zero by definition
CO_3^{2-}(aq)	–527.8	

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

Solution to Exercise 3.1

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

$K_{\mathrm{sol}} = \exp(-\Delta_{\mathrm{sol}}G^\circ / RT) = \exp[-8400 / (8.3145\times298)] = 3.37\times10^{-2}$ [-] (or mol kg^{-1} bar^{-1})

$\Delta_{\mathrm{a1}}G^\circ = -586.8 - (-386.0-237.1) = 36.3$ kJ mol^{-1} $\rightarrow K_{\mathrm{a1}} = 4.34\times10^{-7}$ [-]

$\Delta_{\mathrm{a2}}G^\circ = -527.8 - (-586.8) = 59.0$ kJ mol^{-1} $\rightarrow K_{\mathrm{a2}} = 4.56\times10^{-11}$ [-]

2) pH = 4: $\dfrac{K_{\mathrm{sol,\,app}}}{K_{\mathrm{sol}}} = \left(\dfrac{4.56\cdot10^{-11}}{10^{-4}}+1\right)\dfrac{4.34\cdot10^{-7}}{10^{-4}}+1 = 1.004$ [-].

pH = 8: $\dfrac{K_{\mathrm{sol,\,app}}}{K_{\mathrm{sol}}} = \left(\dfrac{4.56\cdot10^{-11}}{10^{-8}}+1\right)\dfrac{4.34\cdot10^{-7}}{10^{-8}}+1 = 44.6$ [-].

⟨Heat of Solution and Temperature Dependence⟩

The eq. (3.2) can be rewritten as,

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

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 $\Delta_{\mathrm{sol}}H° = –4.2$ kJ mol^{-1} and the solution equilibrium constant is $K_{\mathrm{sol}} = 7.81\times10^{-4}$ mol kg^{-1} bar^{-1} at 298 K. Estimate K_{sol} at 10 °C (283 K).

Solution to Exercise 3.2

$$\frac{K_{\mathrm{sol,\,283}}}{K_{\mathrm{sol,\,298}}} = \exp\left[-\frac{\Delta_{\mathrm{sol}}H^\circ}{R}\left(\frac{1}{283}-\frac{1}{298}\right)\right] = \exp\left[-\frac{-4.2\times1000}{8.3145}\left(\frac{1}{283}-\frac{1}{298}\right)\right] = 1.094$$

Then, $K_{\mathrm{sol,\,283}} = 7.81\cdot10^{-4} \times 1.094 = \underline{8.5}_4 \times 10^{-4}$ [-] (or mol kg^{-1} 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) $\rightleftarrows$ A^+(aq) + B^-(aq), should be written with the mean activity coefficient, γ, as,

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

Exercise 3.3

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

	$\Delta_f G°$(298 K) / 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 $S = 4.769$ mol kg^{-1}.

Solution to Exercise 3.3

1) $\Delta_r G° = (–283.3) + (–131.2) – (–409.1) = –5.4$ kJ mol^{-1}
$b[\mathrm{K^+(aq)}]b[\mathrm{Cl^-(aq)}] = \exp(-\Delta_r G^\circ / RT) = \exp[5.4\times1000 / (8.3145\times298)] = 8.84$ mol^2 kg^{-2}
$S_{\mathrm{ideal}} = (8.84)^{1/2} = \underline{2.97}$ mol kg^{-1}

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

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