3. Ideal Solution

⟨Dissolution Equilibrium of Gas⟩

In dissolution equilibrium state of gas into water, $A(g) \rightleftarrows A(aq)$:
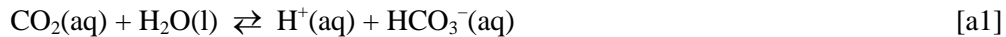
$$\mu(g) = \mu(aq) \tag{3.1}$$

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

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

⟨Solution Phase Chemical Equilibrium⟩

The $CO_2(aq)$ dissociates in solution phase as,

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

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

The respective acid-dissociation constants are,

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

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

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

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

given $[H^+]$ is,

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

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.

	$\Delta_f G°$(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 $K_{sol, app} / K_{sol}$ for pH = 4 and 8.

Solution to Exercise 3.1

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

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

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

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

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

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

⟨Heat of Solution and Temperature Dependence⟩

The eq. (3.2) can be rewritten as,

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

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

Solution to Exercise 3.2

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

Then, $K_{sol,\,283} = 7.81\cdot10^{-4} \times 1.094 = \underline{8.5}_4 \times 10^{-4}$ [-] (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,

$$-\Delta_r G^\circ = \mu^\circ[AB(s)] - \mu^\circ[A^+(aq)] - \mu^\circ[B^-(aq)]$$

$$= RT\ln\left(\frac{\gamma b[A^+(aq)]}{b^\circ}\frac{\gamma b[B^-(aq)]}{b^\circ}\right) \tag{3.7}$$

Exercise 3.3

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

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

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

   Solubility of some readily-soluble salts is determined by equilibrium between the hydrated salt and dissolved ions, for example, CaCl$_2$•6H$_2$O $\rightleftarrows$ Ca^{2+}(aq) + 2Cl$^-$(aq) + 6H$_2$O.