3. Ideal Solution

⟨Solution Equilibrium of Gas⟩

In a solution equilibrium state of a 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)]:

$$-\Delta_{sol}G^\circ = \mu^\circ(g) - \mu^\circ(aq) = RT \ln K_{sol} \tag{3.2}$$

where $K_{sol} \equiv \dfrac{b / b^\circ}{p / p^\circ}$

The Henry's law constant, K_H, is often defined in the reverse way as,

$$p = K_H b \tag{3.3}$$

$$K_H = K_{sol}^{-1} \tag{3.4}$$

Exercise 3.1

1) Compute the solution equilibrium constant of CO_2 into water, $K_{sol} = (b / b^\circ) / (p / p^\circ)$, 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

2) Compare the result with the well established Henry's law constant, $K_H = 30.1$ bar kg mol^{-1}.

Solution to exercise 3.1

1) $\Delta_{sol}G^\circ = -386.0 - (-394.4) = 8.4$ kJ mol^{-1}.
   $K_{sol} = \exp(-\Delta_{sol}G^\circ / RT) = \exp[-8400 / (8.3145 \times 298)] = 3.37 \times 10^{-2}$ [-] (or mol kg^{-1} bar^{-1})
2) K_H from thermo data, $K_H = K_{sol}^{-1} = 29.7$ bar kg mol^{-1}, agrees well with the given $K_H = 30.1$.

⟨Heat of Solution and Temperature Dependence⟩

The eq. (3.2) can be rewritten as,

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

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 H_2 into water is $\Delta_{sol}H^\circ = -4.2$ kJ mol^{-1} and the solution equilibrium constant is $K_{sol} = 7.81 \times 10^{-4}$ mol kg^{-1} bar^{-1} at 298 K. Estimate K_{sol} at 10 °C (283 K).

Solution to exercise 3.2

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

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

(alternative solution)

$\Delta_{sol}G° = -RT \ln K_{sol} = -8.3145 \cdot 298 \ln(7.81 \times 10^{-4}) = 17.73$ kJ mol^{-1}.

$\Delta_{sol}S° = (\Delta_{sol}H° - \Delta_{sol}G°) / T = (-4.2 - 17.73) \times 1000 / 298 = -73.59$ J K^{-1} mol^{-1}.

By assuming constant $\Delta_{sol}H°$ and $\Delta_{sol}S°$,

$\Delta_{sol}G°(283 \text{ K}) = -4.2 - 283 \times (-73.59) / 1000 = 16.63$ kJ mol^{-1}

$K_{sol} = \exp(-\Delta_{sol}G° / RT) = \exp[-16630 / (8.3145 \times 283)] = 8.5_2 \times 10^{-4}$ [-] (or mol kg^{-1} bar^{-1}).

Exercise 3.3

Estimate the solubility S (mol kg^{-1}) of AgCl(s) at 50 °C from the following data.

(298 K)	$\Delta_f H°$ / kJ mol^{-1}	$S_m°$ / J K^{-1} mol^{-1}
AgCl(s)	–127.1	96.2
Ag$^+$(aq)	105.6	72.7
Cl$^-$(aq)	–167.2	56.5

Solution to exercise 3.3

$\Delta_{sol}H° = (105.6 - 167.2) - (-127.1) = 65.5$ kJ mol^{-1},

$\Delta_{sol}S° = (72.7 + 56.6) - 96.2 = 33.0$ J K^{-1} mol^{-1}.

at 50 °C, $S = \exp[(-65500 / 8.3145 / 323 + 33.0 / 8.3145) / 2] = \underline{3.68 \times 10^{-5}}$ mol kg^{-1}

at 25 °C, $S = \underline{1.31 \times 10^{-5}}$ ($\rightarrow$ exercise 1.3)

cf.) experimental: $\underline{3.81 \times 10^{-5}}$ (50 °C), $\underline{1.35 \times 10^{-5}}$ (25°C)

Solubility S increases↑ as T increases↑. (consistent with $\Delta H > 0$; endothermic)

⟨Activity⟩

Except for the very dilute solution such as in exercise 3.3, the solution equilibrium of the electrolyte, AB(s) ⇄ A$^+$(aq) + B$^-$(aq), should be written with the mean activity coefficient, γ, as,

$$-\Delta_r G° = \mu°[\text{AB(s)}] - \mu°[\text{A}^+\text{(aq)}] - \mu°[\text{B}^-\text{(aq)}]$$

$$= RT \ln\left(\frac{\gamma b[\text{A}^+\text{(aq)}]}{b°} \frac{\gamma b[\text{B}^-\text{(aq)}]}{b°} \right) \qquad (3.6)$$

Exercise 3.4

1) Assuming the ideal solution, calculate the solubility S (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 3.4

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

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

$S = (8.84)^{1/2} = \underline{2.97}$ mol kg^{-1}

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

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