3. Ideal Solution

⟨Solution Equilibrium of Gas⟩

In a solution equilibrium state of a gas into water, $A(g) \leftrightarrows A(aq)$:

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

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

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

$$\text{where} \quad K_{sol} \equiv \frac{b/b°}{p/p°}$$

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, $K_{sol} = (b/b°)/(p/p°)$, from the following standard Gibbs energies.

	$\Delta_f G°(298\ K) / kJ\ mol^{-1}$
$CO_2(g)$	–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) $\Delta_{sol}G° = -386.0 - (-394.4) = 8.4\ kJ\ mol^{-1}$.
> $K_{sol} = \exp(-\Delta_{sol}G°/RT) = \exp[-8400/(8.3145 \times 298)] = 3.37 \times 10^{-2}$ (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,

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

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 $\Delta_{sol}H° = -4.2\ kJ\ mol^{-1}$ 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
>
> $$\frac{K_{sol,283}}{K_{sol,298}} = \exp\left[-\frac{\Delta_{sol}H°}{R}\left(\frac{1}{283} - \frac{1}{298}\right)\right] = \exp\left[-\frac{-4.2 \times 1000}{8.3145}\left(\frac{1}{283} - \frac{1}{298}\right)\right] = 1.094$$
>
> Then, $K_{sol,283} = 7.81 \cdot 10^{-4} \times 1.094 = \underline{8.5}_4 \times 10^{-4}$ mol kg^{-1} bar^{-1}.
>   *cf.*) experimental $= \underline{8.72} \times 10^{-4}$ mol kg^{-1} bar^{-1}
> 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 $\Delta_{sol}S°$,
$\Delta_{sol}G°(283$ K$) = -4.2 - 283 \times (-73.59) / 1000 = 16.63$ kJ mol^{-1}
$K_{sol} = \exp(-\Delta_{sol}G° / RT) = \exp[-16630 / (8.3145 \times 283)] = 8.5_2 \times 10^{-4}$ 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,

$$-\Delta_r G° = \mu°[AB(s)] - \mu°[A^+] - \mu°[B^-]$$
$$= RT \ln\left(\frac{\gamma b[A^+]}{b°} \frac{\gamma b[B^-]}{b°}\right) \tag{3.6}$$

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}
$b[A^+(aq)]b[B^-(aq)] = \exp(-\Delta_r G° / RT) = \exp[5.4 \times 1000 / (8.3145 \times 298)] = 8.84$ 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.