2. Chemical and Phase Equilibria

⟨Gas-phase Chemical Equilibrium⟩

In the equilibrium state of a gas-phase reaction, $A(g) + B(g) \rightleftarrows C(g)$,

$$\mu[C(g)] = \mu[A(g)] + \mu[B(g)] \tag{2.1}$$

The chemical potential of an ideal gas A at a partial pressure p_A is,

$$\mu[A(g)] = \mu°[A(g)] + RT \ln \frac{p_A}{p°} \tag{0.6}$$

Similar relation holds for gas B and C.   The standard Gibbs energy change of this reaction is

$$\Delta_r G° = \mu°[C(g)] - \mu°[A(g)] - \mu°[B(g)] \tag{2.2}$$

Exercise 2.1

1) Derive an equation for the relation among p_A, p_B, p_C, and $-\Delta_r G$ for $A(g) + B(g) \rightleftarrows C(g)$.

2) Calculate the equilibrium constant for the reaction, $H_2(g) + \frac{1}{2}O_2(g) \rightleftarrows H_2O(g)$, at 3000 K from the following data.

T / K	$\Delta_f G°[H_2O(g)]$ / kJ mol^{-1} [JANAF]
3000	−77.2

Solution to Exercise 2.1
1) Substitution of (0.6) to (2.1) and transformation gives

$$RT \ln \frac{p_C / p°}{(p_A / p°)(p_B / p°)} = \mu°[A(g)] + \mu°[B(g)] - \mu°[C(g)]$$

By using (2.2), $RT \ln K = -\Delta_r G°$, where $K \equiv \dfrac{p_C / p°}{(p_A / p°)(p_B / p°)}$

2) $K = \exp(-\Delta_r G° / RT) = \exp[77.2\times1000 / (8.3145\times3000)] = 22.09$ [-] (or bar$^{-1/2}$)

⟨Phase Equilibrium between Condensed Phases⟩

On the boundary between phase 1 and 2 in p–T plane,

$$d\mu(1) = d\mu(2) \tag{2.3}$$

From (0.3) and (0.4), one obtains $V_m(1)dp - S_m(1)dT = V_m(2)dp - S_m(2)dT$, and then,

$$\frac{dp}{dT} = \frac{\Delta_{trs} S}{\Delta_{trs} V} \quad \text{(Clapeyron equation)} \tag{2.4}$$

where $\Delta_{trs} S = S_m(2) - S_m(1)$, $\Delta_{trs} V = V_m(2) - V_m(1)$

From the definition of the entropy,

$$\Delta_{trs} S = \frac{\Delta_{trs} H}{T_{trs}} \tag{2.5}$$

Exercise 2.2
1) Calculate the standard entropy of fusion $\Delta_{fus} S°$ of the ice from the standard enthalpy of fusion, $\Delta_{fus} H° = 6.008$ kJ mol^{-1}, at 0 °C.
2) Estimate the melting point of ice at a pressure 136 bar from the $\Delta_{fus} S$ above and the following densities of ice and water.   Ignore the pressure dependence of $\Delta_{fus} S$ and density.

	$\rho(273.15$ K, 1 bar$)$ / g cm^{-3}
$H_2O(l)$	0.9998
$H_2O(s)$	0.9168

Solution to Exercise 2.2
1) $\Delta_{fus}S° = 6.008 \times 1000 / 273.15 = 22.00$ J K^{-1} mol^{-1}
2) $\Delta_{fus}V° = (18.02/0.9998) - (18.02/0.9168) = -1.632$ cm^3 mol^{-1} $= -1.632 \times 10^{-6}$ m^3 mol^{-1}
   $dT / dp = -1.632 \times 10^{-6} / 22.00 = -7.418 \times 10^{-8}$ K Pa^{-1} $= -7.418 \times 10^{-3}$ K bar^{-1}
   $dT = -7.418 \times 10^{-3} \times (136 - 1) = -1.00$ K　よって　$T_{fus}(136$ bar$) \sim -1.00$ °C (272.15 K)

⟨Phase Equilibrium between Gas and Condensed Phases⟩

On the boundary between a condensed phase 1 and a gas phase,

$$\mu(1) = \mu(g) \tag{2.6}$$

By ignoring the small pressure dependence of the chemical potential of a condensed phase, and using (0.6),

$$-\Delta_{vap}G° = \mu°(1) - \mu°(g) = RT \ln(p / p°) \tag{2.7}$$

Exercise 2.3
1) Calculate the vapor pressure of water at 298 K from the following data.

(298 K)	$\Delta_f H°$ / kJ mol^{-1}	$S_m°$ / J K^{-1} mol^{-1}
$H_2O(l)$	−285.8	69.9
$H_2O(g)$	−241.8	188.8

2) Estimate the vapor pressure of water at 100 °C (= 373 K) assuming that $\Delta_{vap}H°$ and $\Delta_{vap}S°$ are independent of temperature.

Solution to Exercise 2.3
1) $\Delta_{vap}H° = -241.8 - (-285.8) = 44.0$ kJ mol^{-1}, $\Delta_{vap}S° = 188.8 - 69.9 = 118.9$ J K^{-1} mol^{-1}
   $\Delta_{vap}G° = \Delta_{vap}H° - T\Delta_{vap}S° = 44.0 - 298 \cdot 118.9/1000 = 8.57$ kJ mol^{-1}
   $p / p° = \exp(-8.57 \times 1000 / 8.3145 \cdot 298) = 3.15 \times 10^{-2}$, thus $p = 0.0315$ bar

   * The pressure dependence of $\mu[H_2O(l)]$ is, from (0.9), $V_m(p - p°) = 1.8 \times 10^{-5}(3160-100000) = -1.7$ J mol^{-1}, which is smaller than the smallest significant digit of $\Delta_f G°$.

2) $\Delta_{vap}G° = \Delta_{vap}H° - T\Delta_{vap}S° = 44.0 - 373 \cdot 118.9/1000 = -0.35$ kJ mol^{-1}
   $p / p° = \exp(+0.35 \times 1000 / 8.3145 \cdot 373) = 1.119$, thus $p = 1.119$ bar (10% higher than 1 atm!)