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),

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

For an ideal gas, by using (0.6),

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

where $\quad K \equiv \dfrac{p_C / p°}{(p_A / p°)(p_B / p°)}$

Exercise 2.1

1) Calculate the equilibrium constant $\quad K = \dfrac{p(H_2O)/p°}{[p(H_2)/p°][p(O_2)/p°]^{1/2}}\quad$ at 3000 K for the reaction,

 $H_2(g) + \frac{1}{2}O_2(g) \rightleftarrows H_2O(g)$, from the following data.

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

2) Calculate $p(O_2)$ in equilibrium with H_2O of partial pressure 0.1 bar at 3000 K, by assuming $p(H_2)$ = $2p(O_2)$.   Also, calculate the relative extent of reaction $\quad \xi_r = \dfrac{p(H_2O)}{p(H_2) + p(H_2O)}$.

> Solution to Exercise 2.1
> 1) $K = \exp(-\Delta_r G° / RT) = \exp[77.2 \times 1000 / (8.3145 \times 3000)] = 22.09$ [-] (or bar$^{-1/2}$)
> 2) Let $x = p(O_2)/p°$. $\rightarrow x = (0.05 / K)^{2/3} = 0.0172$, $p(O_2) = 0.0172$ bar, $\xi_r = 0.744$
>   At high temperatures, the reaction cannot be "completed" even in the equilibrium state.

⟨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.

	ρ(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} = -1.632×10^{-6} m^3 mol^{-1}
   $dT / dp = -1.632 \times 10^{-6} / 22.00 = -7.418 \times 10^{-8}$ K Pa^{-1} = -7.418×10^{-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}	$C_{p, m}°$ / J K^{-1} mol^{-1}
H$_2$O(l)	–285.8	69.9	75.3
H$_2$O(g)	–241.8	188.8	33.6

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$_2$O(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!)

Better approximation can be achieved by taking into account the temperature dependence of $\Delta_{vap}H°$ and $\Delta_{vap}S°$, but assuming constant $\Delta_{vap}C_{p, m}° = C_{p, m}°(g) - C_{p, m}°(1)$.

$$\Delta_{vap}H°(T) = \Delta_{vap}H°(T*) + \Delta_{vap}C_{p, m}° (T - T*) \tag{2.8}$$

$$\Delta_{vap}S°(T) = \Delta_{vap}S°(T*) + \Delta_{vap}C_{p, m}° \ln\left(\frac{T}{T*}\right) \tag{2.9}$$

where $T*$ is a reference temperature.

Exercise 2.4
Estimate the vapor pressure of water at 100 °C (= 373 K) by using $C_{p, m}°$ shown in the table of Exercise 2.3.

Solution to Exercise 2.4
$\Delta C_p = 33.6 - 75.3 = -41.7$ J K^{-1} mol^{-1}.
$\Delta_{vap}H° = 44.0 - 41.7 \times (373 - 298) / 1000 = 40.87$ kJ mol^{-1}.
$\Delta_{vap}S° = 118.9 - 41.7 \ln(373 / 298) = 109.54$ J K^{-1} mol^{-1}.
$\Delta_{vap}G° = 40.87 - 373 \times 109.54 / 1000 = 0.012$ kJ mol^{-1}.
$p / p° = \exp(-0.012 \times 1000 / 8.3145 \cdot 373) = 0.996$, thus $p = 0.996$ bar (1.7% smaller than 1 atm)