

2. Chemical and Phase Equilibria

〈Gas-phase Chemical Equilibrium〉

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

$$\mu[C(g)] = \mu[A(g)] + \mu[B(g)] \quad (2.1)$$

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

$$\mu[A(g)] = \mu^\circ[A(g)] + RT \ln \frac{p_A}{p^\circ} \quad (0.6)$$

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

$$\Delta_r G^\circ = \mu^\circ[C(g)] - \mu^\circ[A(g)] - \mu^\circ[B(g)] \quad (2.2)$$

Exercise 2.1

- 1) Derive an equation for the relation among p_A , p_B , p_C , and $-\Delta_r G$ for $A(g) + B(g) \rightleftharpoons C(g)$.
- 2) Calculate the equilibrium constant for the reaction, $H_2(g) + \frac{1}{2} O_2(g) \rightleftharpoons H_2O(g)$, at 3000 K from the following data.

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

Solution to Exercise 2.1

- 1) Substitution of (0.6) to (2.1) and transformation give

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

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

- 2) $K = \exp(-\Delta_r G^\circ / RT) = \exp[77.2 \times 1000 / (8.3145 \times 3000)] = 22.09 [-]$ (or $bar^{-1/2}$)

〈Phase Equilibrium between Condensed Phases〉

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

$$d\mu(1) = d\mu(2) \quad (2.3)$$

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,

$$\left. \frac{dp}{dT} \right|_{\text{phase boundary}} = \frac{\Delta_{\text{trs}} S}{\Delta_{\text{trs}} V} \quad (\text{Clapeyron equation}) \quad (2.4)$$

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

From the definition of the entropy,

$$\Delta_{\text{trs}} S = \frac{\Delta_{\text{trs}} H}{T_{\text{trs}}} \quad (2.5)$$

Exercise 2.2

- 1) Calculate the standard entropy of fusion $\Delta_{\text{fus}} S^\circ$ of the ice from the standard enthalpy of fusion, $\Delta_{\text{fus}} H^\circ = 6.008 kJ mol^{-1}$, at $0^\circ C$.
- 2) Estimate the melting point of ice at a pressure 136 bar from the $\Delta_{\text{fus}} S$ above and the following densities of ice and water. Ignore the pressure dependence of $\Delta_{\text{fus}} S$ 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) $\Delta_{\text{fus}}S^\circ = 6.008 \times 1000 / 273.15 = 22.00 \text{ J K}^{-1} \text{ mol}^{-1}$
 2) $\Delta_{\text{fus}}V^\circ = (18.02/0.9998) - (18.02/0.9168) = -1.632 \text{ cm}^3 \text{ mol}^{-1} = -1.632 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$
 $dT / dp|_{\text{boundary}} = -1.632 \times 10^{-6} / 22.00 = -7.418 \times 10^{-8} \text{ K Pa}^{-1} = -7.418 \times 10^{-3} \text{ K bar}^{-1}$
 $dT = -7.418 \times 10^{-3} \times (136 - 1) = -1.00 \text{ K}$ よつて $T_{\text{fus}}(136 \text{ bar}) \sim -1.00 \text{ }^\circ\text{C} (272.15 \text{ K})$

Phase Equilibrium between Gas and Condensed Phases

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

$$\mu(1) = \mu(\text{g}) \quad (2.6)$$

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

$$-\Delta_{\text{vap}}G^\circ = \mu^\circ(1) - \mu^\circ(\text{g}) = RT \ln(p / p^\circ) \quad (2.7)$$

Exercise 2.3

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

(298 K)	$\Delta_f H^\circ / \text{kJ mol}^{-1}$	$S_m^\circ / \text{J K}^{-1} \text{ mol}^{-1}$
H ₂ O(l)	-285.8	69.9
H ₂ O(g)	-241.8	188.8

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

Solution to Exercise 2.3

- 1) $\Delta_{\text{vap}}H^\circ = -241.8 - (-285.8) = 44.0 \text{ kJ mol}^{-1}$, $\Delta_{\text{vap}}S^\circ = 188.8 - 69.9 = 118.9 \text{ J K}^{-1} \text{ mol}^{-1}$
 $\Delta_{\text{vap}}G^\circ = \Delta_{\text{vap}}H^\circ - T\Delta_{\text{vap}}S^\circ = 44.0 - 298 \cdot 118.9/1000 = 8.57 \text{ kJ mol}^{-1}$
 $p / p^\circ = \exp(-8.57 \times 1000 / 8.3145 \cdot 298) = 3.15 \times 10^{-2}$, thus $p = 0.0315 \text{ bar}$
 * The pressure dependence of $\mu[\text{H}_2\text{O}(l)]$ is, from (0.9), $V_m(p - p^\circ) = 1.8 \times 10^{-5}(3160 - 100000) = -1.7 \text{ J mol}^{-1}$,
 which is smaller than the smallest significant digit of $\Delta_f G^\circ$.
- 2) $\Delta_{\text{vap}}G^\circ = \Delta_{\text{vap}}H^\circ - T\Delta_{\text{vap}}S^\circ = 44.0 - 373 \cdot 118.9/1000 = -0.35 \text{ kJ mol}^{-1}$
 $p / p^\circ = \exp(+0.35 \times 1000 / 8.3145 \cdot 373) = 1.119$, thus $p = 1.119 \text{ bar}$ (10% higher than 1 atm!)