

2. Chemical and Phase Equilibrium

⟨Gas-phase Chemical Equilibrium⟩

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

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

For an ideal gas, by using (0.6),

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

$$\text{where } K \equiv \frac{p_C / p^\circ}{(p_A / p^\circ)(p_B / p^\circ)}$$

Exercise 2.1

- 1) Calculate the equilibrium constant $K = \frac{p(\text{H}_2\text{O}) / p^\circ}{[p(\text{H}_2) / p^\circ][p(\text{O}_2) / p^\circ]^{1/2}}$ at 3000 K for the reaction, $\text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightleftharpoons \text{H}_2\text{O}(g)$, from the following data.

T / K	$\Delta_r G^\circ[\text{H}_2\text{O}(g)] / \text{kJ mol}^{-1}$ [CEA2]
3000	-77.49

- 2) Calculate $p(\text{O}_2)$ in equilibrium with H_2O of partial pressure 0.1 bar at 3000 K, by assuming $p(\text{H}_2) = 2p(\text{O}_2)$. Also, calculate the relative extent of the reaction $\xi_r = \frac{p(\text{H}_2\text{O})}{p(\text{H}_2) + p(\text{H}_2\text{O})}$.

Solution to exercise 2.1

- 1) $K = \exp(-\Delta_r G^\circ / RT) = \exp[77.49 \times 1000 / (8.3145 \times 3000)] = 22.35$ [-] (or $\text{bar}^{-1/2}$)
 2) Let $x = p(\text{O}_2) / p^\circ$. $\rightarrow x = (0.05 / K)^{2/3} = 0.0171$, $p(\text{O}_2) = 0.0171$ bar, $\xi_r = 0.745$

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,

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

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,

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

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, $\Delta_{\text{fus}} H^\circ = 6.008 \text{ kJ mol}^{-1}$, at 0°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.

	$\rho(273.15 \text{ K}, 1 \text{ bar}) / \text{g cm}^{-3}$
$\text{H}_2\text{O}(l)$	0.9998
$\text{H}_2\text{O}(s)$	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) $\Delta_{\text{fus}}V^\circ = (18.02/0.9998) - (18.02/0.9168) = -1.632 \text{ cm}^3 \text{ mol}^{-1} = -1.632 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$
 $dT / dp = -1.632 \times 10^{-6} / 22.00 = -7.418 \times 10^{-8} \text{ K Pa}^{-1} = -7.418 \times 10^{-3} \text{ K bar}^{-1}$
 $dT = -7.418 \times 10^{-3} \times (136 - 1) = -1.00 \text{ K}$ よつて $T_{\text{fus}}(136 \text{ bar}) \sim -1.00 \text{ }^\circ\text{C}$ (272.15 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.
 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.

(298 K)	$\Delta_{\text{f}}H^\circ / \text{kJ mol}^{-1}$	$S_{\text{m}}^\circ / \text{J K}^{-1} \text{ mol}^{-1}$	$C_{p, \text{m}}^\circ / \text{J K}^{-1} \text{ mol}^{-1}$
H ₂ O(l)	-285.8	69.9	75.3
H ₂ O(g)	-241.8	188.8	33.6

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), $V_{\text{m}}(p - p^\circ) = 1.8 \times 10^{-5}(3160 - 100000) = -1.7 \text{ J mol}^{-1}$, which is smaller than the smallest significant digit of $\Delta_{\text{f}}G^\circ$.
 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!)

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

$$\Delta_{\text{vap}}H^\circ(T) = \Delta_{\text{vap}}H^\circ(T^*) + \Delta_{\text{vap}}C_{p, \text{m}}^\circ (T - T^*) \quad (2.8)$$

$$\Delta_{\text{vap}}S^\circ(T) = \Delta_{\text{vap}}S^\circ(T^*) + \Delta_{\text{vap}}C_{p, \text{m}}^\circ \ln\left(\frac{T}{T^*}\right) \quad (2.9)$$

where T^* is a reference temperature.

Exercise 2.4

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

Solution to exercise 2.4

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