

4. Surface and Particle Equilibria

⟨Reactive Condensation⟩

In the equilibrium state of $AB(s) \rightleftharpoons A(g) + B(g)$,

$$\mu[AB(s)] = \mu[A(g)] + \mu[B(g)] \quad (4.1)$$

By ignoring the pressure dependence of $\mu[AB(s)]$ and using (0.6),

$$-\Delta_r G^\circ = \mu^\circ[AB(s)] - \mu^\circ[A(g)] - \mu^\circ[B(g)] = RT \ln K \quad (4.2)$$

$$\text{where } K \equiv \frac{p_A}{p^\circ} \frac{p_B}{p^\circ}$$

Exercise 4.1

1) Compute the equilibrium constant for $NH_4NO_3(s) \rightleftharpoons NH_3(g) + HNO_3(g)$ from the following data.

$\Delta_f G^\circ(298 \text{ K}) / \text{kJ mol}^{-1}$	
$NH_4NO_3(s)$	-183.9
$NH_3(g)$	-16.5
$HNO_3(g)$	-73.9 [JANAF]

2) Calculate the minimum p at which $NH_4NO_3(s)$ starts to form for the case $p(NH_3) = p(HNO_3) = p$.

Solution to Exercise 4.1

$$1) \Delta_r G^\circ = (-16.5) + (-73.9) - (-183.9) = 93.5 \text{ kJ mol}^{-1}.$$

$$K = \exp(-93.5 \times 1000 / 8.3145 \cdot 298) = 4.09 \times 10^{-17}.$$

$$2) p = K^{1/2} = 6.4 \times 10^{-9} \text{ bar } (\sim 6.3 \text{ ppb})$$

⟨Surface Tension⟩

A work dW necessary to increase the surface area by $d\sigma$ is given as,

$$dW = \gamma d\sigma \quad (4.3)$$

where γ is the surface tension with a unit of $\text{J m}^{-2} = \text{N m}^{-1}$. The difference between the pressure inside a spherical droplet (radius r), $p_{l, \text{droplet}}$, and the ambient pressure, p_a , is given by,

$$p_{l, \text{droplet}} - p_a = \frac{2\gamma}{r} \quad (\text{Laplace equation}) \quad (4.4)$$

Exercise 4.2

1) Compute the pressure difference, $p_{l, \text{droplet}} - p_a$, for water droplets with radii 0.1 μm and 10 nm from the following value.

$\gamma(298 \text{ K}) / \text{N m}^{-1}$	
water	7.2×10^{-2}

2) Estimate the depression of the freezing point of these water droplets by using the results of Exercise 2.2 ($dT_{\text{fus}} / dp = -7.418 \times 10^{-3} \text{ K bar}^{-1}$). Assume γ is independent of temperature.

Solution to Exercise 4.2

$$1) r = 0.1 \mu\text{m}: p_{l, \text{droplet}} - p_a = (2 \times 7.2 \times 10^{-2}) / 0.1 \times 10^{-6} / 1 \times 10^5 = 14.4 \text{ bar.}$$

$$r = 10 \text{ nm}: p_{l, \text{droplet}} - p_a = (2 \times 7.2 \times 10^{-2}) / 10 \times 10^{-9} / 1 \times 10^5 = 144 \text{ bar.}$$

$$2) \text{ By using the result of exercise 2.2, } dT / dp = -7.418 \times 10^{-3} \text{ K bar}^{-1},$$

$$r = 0.1 \mu\text{m}: \Delta T_f = -7.418 \times 10^{-3} \times 14.4 = -0.107 \text{ K}$$

$$r = 10 \text{ nm}: \Delta T_f = -7.418 \times 10^{-3} \times 144 = -1.07 \text{ K}$$

* The freezing point depression of water droplet comes from the fact $V_m(s) > V_m(l)$.

For most of the metals, $V_m(s) < V_m(l)$ and the freezing point depression cannot be explained by surface tension.

〈Vapor Pressure above Droplet Surface〉

Below, p^* and p denote the vapor pressures above a plane surface and the droplet surface, respectively. By equating the chemical potentials in liquid and gas phases, and using (0.9) and (0.6),

$$V_m \frac{2\gamma}{r} = RT \ln \left(\frac{p}{p^*} \right) \quad (4.5)$$

where V_m is the molar volume of the liquid. By a transformation one can obtain,

$$\frac{p}{p^*} = \exp \left(\frac{2\gamma V_m}{rRT} \right) \quad (\text{Kelvin equation}) \quad (4.6)$$

Exercise 4.3

Compute the supersaturation [%] = 100 ($p/p^* - 1$) of the water vapor above the surfaces of water droplet of radii 0.1 μm and 10 nm. Use the density of water $\rho = 0.997 \text{ g cm}^{-3}$.

Solution to Exercise 4.3

$$V_m = 18.02 / 0.997 = 18.07 \text{ cm}^3 \text{ mol}^{-1} = 1.807 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$$

$$r = 0.1 \mu\text{m}: p/p^* = \exp[2 \times 7.2 \times 10^{-2} \times 1.807 \times 10^{-5} / (0.1 \times 10^{-6} \times 8.3145 \times 298)] = 1.0106$$

supersaturation: 1.06 %

$$r = 10 \text{ nm}: p/p^* = \exp[2 \times 7.2 \times 10^{-2} \times 1.807 \times 10^{-5} / (10 \times 10^{-9} \times 8.3145 \times 298)] = 1.111$$

supersaturation: 11.1 %

* homogeneous nucleation is expected to require very large supersaturation such as > 200%.

〈Cloud Condensation〉

In the atmosphere, cloud is formed from nuclei (aerosols). For water-soluble nuclei, the vapor pressure above the droplet is also affected by the Raoult's law,

$$p = p^* (1 - x) \quad (4.7)$$

where p^* is the vapor pressure of pure solvent and x is the mole fraction of solute. By combining with the Kelvin effect (4.6),

$$\frac{p}{p^*} = (1 - x) \exp \left(\frac{2\gamma V_m}{rRT} \right) \quad (4.8)$$

Exercise 4.4

Compute the supersaturation (%) of the water vapor above the surface of water droplet of radius 0.1 μm containing sulfuric acid by mole fraction 1.0%. Assume the same γ , and V_m , as water and the complete dissociation of sulfuric acid.

Solution to Exercise 4.4

$$p/p^* = [1 - 3/(99+1 \times 3)] \exp[2 \times 7.2 \times 10^{-2} \times 1.807 \times 10^{-5} / (0.1 \times 10^{-6} \times 8.3145 \times 298)] = 0.9808$$

supersaturation: -1.92 %

* This droplet can grow at humidity > 98.1%, non-supersaturation condition.