

## 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  $\gamma$  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  $0.1 \mu\text{m}$  and  $10 \text{ nm}$  from the following value.

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

- 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  $\gamma$  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) 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  $\mu\text{m}$  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  $\mu\text{m}$  containing sulfuric acid by mole fraction 1.0%. Assume the same  $\gamma$ , 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.