4. Surface and Particle Equilibria

⟨Reactive Condensation⟩

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

$$\mu[\mathrm{AB(s)}] = \mu[\mathrm{A(g)}] + \mu[\mathrm{B(g)}] \tag{4.1}$$

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

$$-\Delta_r G° = \mu°[\mathrm{AB(s)}] - \mu°[\mathrm{A(g)}] - \mu°[\mathrm{B(g)}] = RT \ln K \tag{4.2}$$

$$\text{where} \quad K \equiv \frac{p_\mathrm{A}}{p^\circ}\frac{p_\mathrm{B}}{p^\circ}$$

Exercise 4.1

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

	$\Delta_f G°$(298 K) / 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) $\Delta_r G° = (-16.5) + (-73.9) - (-183.9) = 93.5$ kJ mol^{-1}.
$K = \exp(-93.5\times1000 / 8.3145\cdot298) = 4.09\times10^{-17}$.

2) $p / p° = K^{1/2} = 6.4\times10^{-9}$, $p = 6.4\times10^{-9}$ bar (~ 6.3 ppb)

⟨Surface Tension⟩

A work dw necessary to increase the surface area by dσ is given as,

$$\mathrm{d}w = \gamma\, \mathrm{d}\sigma \tag{4.3}$$

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

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

Exercise 4.2

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

	γ(298 K) / 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 ($\mathrm{d}T_\mathrm{fus} / \mathrm{d}p = -7.418\times10^{-3}$ K bar^{-1}). Assume γ is independent of temperature.

Solution to Exercise 4.2

1) r = 0.1 μm: $p_\mathrm{l,\,droplet} - p_\mathrm{a} = (2 \times 7.2\times10^{-2}) / 0.1\times10^{-6} / 1\times10^{5} = 14.4$ bar.
r = 10 nm: $p_\mathrm{l,\,droplet} - p_\mathrm{a} = (2 \times 7.2\times10^{-2}) / 10\times10^{-9} / 1\times10^{5} = 144$ bar.

2) By using the result of exercise 2.2, $\mathrm{d}T / \mathrm{d}p = -7.418\times10^{-3}$ K bar^{-1},
r = 0.1 μm: $\Delta T_\mathrm{f} = -7.418\times10^{-3} \times 14.4 = -0.107$ K
r = 10 nm: $\Delta T_\mathrm{f} = -7.418\times10^{-3} \times 144 = -1.07$ K

* The freezing point depression of water droplet comes from the fact $V_\mathrm{m}(s) > V_\mathrm{m}(l)$.
For most of the metals, $V_\mathrm{m}(s) < V_\mathrm{m}(l)$ 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),

$$V_\mathrm{m} \frac{2\gamma}{r} = RT \ln\left(\frac{p}{p^*}\right) \tag{4.5}$$

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

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

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 $\rho = 0.997$ g cm^{-3}.

Solution to Exercise 4.3

V_m = 18.02 / 0.997 = 18.07 cm^3 mol^{-1} = 1.807×10^{-5} m^3 mol^{-1}

r = 0.1 μm: p / p^* = exp[2 × 7.2×10^{-2} × 1.807×10^{-5} / (0.1×10^{-6} × 8.3145 × 298)] = 1.0106

supersaturation: 1.06 %

r = 10 nm: p / p^* = exp[2 × 7.2×10^{-2} × 1.807×10^{-5} / (10×10^{-9} × 8.3145 × 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,

$$p = p^* (1 - x) \tag{4.7}$$

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),

$$\frac{p}{p^*} = (1 - x)\exp\left(\frac{2\gamma V_\mathrm{m}}{rRT}\right) \tag{4.8}$$

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+1×3)] exp[2 × 7.2×10^{-2} × 1.807×10^{-5} / (0.1×10^{-6} × 8.3145 × 298)] = 0.9808

supersaturation: –1.92 %

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