4. Surface and Particle Equilibrium

⟨Reactive Condensation⟩

In the equilibrium state of AB(s) ↔ 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),

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

where $K \equiv \dfrac{p_\mathrm{A}}{p^\circ}\dfrac{p_\mathrm{B}}{p^\circ}$

Exercise 4.1

1) Compute the equilibrium constant for NH_4NO_3(s) ↔ NH_3(g) + HNO_3(g) from the followings.

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

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) $\Delta_r G^\circ = (-16.5) + (-73.9) - (-183.9) = 93.5$ kJ mol^{-1}.
   $K = \exp(-93.5\times1000 / 8.3145\cdot298) = 4.09\times10^{-17}$.
2) $p = K^{1/2} = 6.4\times10^{-9}$ 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. 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, dT / dp = -7.418×10^{-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_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),

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

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

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

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 ρ = 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,

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

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),

$$\ln\frac{p}{p^*} = \frac{2\gamma V_\mathrm{m}}{rRT} + \ln(1 - x) \qquad (4.8)$$

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^* = [99/(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.