4. Surface and Particle Equilibria

⟨Reactive Condensation⟩

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

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

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

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

where $K \equiv \dfrac{p_A}{p°} \dfrac{p_B}{p°}$

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}.
> $K = \exp(-93.5 \times 1000 / 8.3145 \cdot 298) = 4.09 \times 10^{-17}$.
> 2) $p / p° = K^{1/2} = 6.4 \times 10^{-9}$, $p = 6.4 \times 10^{-9}$ bar (~ 6.3 ppb)

⟨Surface Tension⟩

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

$$dw = \gamma\, d\sigma \tag{4.3}$$

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), $p_{l,\,droplet}$, and the ambient pressure, p_a, is given by,

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

Exercise 4.2

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

	$\gamma(298\ K)\ /\ N\ m^{-1}$
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 ($dT_{fus} / dp = -7.418 \times 10^{-3}$ K bar^{-1}).   Assume γ is independent of temperature.

> **Solution to Exercise 4.2**
> 1) $r = 0.1$ μm: $p_{l,\,droplet} - p_a = (2 \times 7.2 \times 10^{-2}) / 0.1 \times 10^{-6} / 1 \times 10^5 = 14.4$ bar.
> $r = 10$ nm: $p_{l,\,droplet} - p_a = (2 \times 7.2 \times 10^{-2}) / 10 \times 10^{-9} / 1 \times 10^5 = 144$ bar.
> 2) By using the result of exercise 2.2, $dT / dp = -7.418 \times 10^{-3}$ K bar^{-1},
> $r = 0.1$ μm: $\Delta T_f = -7.418 \times 10^{-3} \times 14.4 = -0.107$ K
> $r = 10$ nm: $\Delta T_f = -7.418 \times 10^{-3} \times 144 = -1.07$ 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),

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

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

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

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: $p\,/\,p^* = \exp[2 \times 7.2 \times 10^{-2} \times 1.807 \times 10^{-5} / (0.1 \times 10^{-6} \times 8.3145 \times 298)] = 1.0106$
> supersaturation: 1.06 %
> $r = 10$ 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,

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

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),

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

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**
> $p\,/\,p^* = [1 - 3/(99 + 1 \times 3)]\,\exp[2 \times 7.2 \times 10^{-2} \times 1.807 \times 10^{-5} / (0.1 \times 10^{-6} \times 8.3145 \times 298)] = 0.9808$
> supersaturation: –1.92 %
>
> * This droplet can grow at humidity > 98.1%, non-supersaturation condition.