4. Surface and Particle Equilibrium

〈Reactive Condensation〉

In the equilibrium state of \( \text{AB}(s) \leftrightarrow A(g) + B(g) \),
\[
\mu[\text{AB}(s)] = \mu[A(g)] + \mu[B(g)]
\]  
(4.1)

By ignoring the pressure dependence of \( \mu[\text{AB}(s)] \) and using (0.6),
\[
-\Delta_r G^\circ = \mu^\circ[\text{AB}(s)] - \mu^\circ[A(g)] - \mu^\circ[B(g)] = RT \ln K
\]  
(4.2)

where \( K \equiv \frac{p_A^n \, p_B^n}{p^m} \)

Exercise 4.1

1) Compute the equilibrium constant for \( \text{NH}_4\text{NO}_3(s) \leftrightarrow \text{NH}_3(g) + \text{HNO}_3(g) \) from the followings.

<table>
<thead>
<tr>
<th>Substance</th>
<th>( \Delta_r G^\circ(298 \text{ K}) ) / kJ mol(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{NH}_4\text{NO}_3(s) )</td>
<td>-183.9</td>
</tr>
<tr>
<td>( \text{NH}_3(g) )</td>
<td>-16.5</td>
</tr>
<tr>
<td>( \text{HNO}_3(g) )</td>
<td>-73.9 [NIST]</td>
</tr>
</tbody>
</table>

2) Calculate the minimum \( p \) at which \( \text{NH}_4\text{NO}_3(s) \) starts to form for the case \( p(\text{NH}_3) = p(\text{HNO}_3) = p \).

Solution to exercise 4.1

1) \( \Delta_r G^\circ = (–16.5) + (–73.9) – (–183.9) = 93.5 \text{ kJ mol}^{-1} \).
\[
K = \exp(–93.5 \times 1000 / 8.3145 \times 298) = 4.09 \times 10^{-17}.
\]

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

〈Surface Tension〉

A work \( dw \) necessary to increase the surface area by \( d\sigma \) is given as,
\[
dw = \gamma \, d\sigma
\]  
(4.3)

where \( \gamma \) is the surface tension with a unit of J m\(^{-2} \) = N m\(^{-1} \). The difference between the pressure inside a spherical droplet (radius \( r \)), \( p_\text{droplet} \), and the ambient pressure, \( p_a \), is given by,
\[
p_\text{droplet} - p_a = \frac{2\gamma}{r}
\]  
(Laplace equation)  
(4.4)

Exercise 4.2

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

<table>
<thead>
<tr>
<th>Substance</th>
<th>( \gamma(298 \text{ K}) ) / N m(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>7.2\times10^{-2}</td>
</tr>
</tbody>
</table>

2) Estimate the depression of the freezing point of these water droplets. Assume \( \gamma \) is independent of temperature.

Solution to exercise 4.2

1) \( r = 0.1 \mu \text{m} \): \( p_\text{droplet} - p_a = (2 \times 7.2\times10^{-2}) / 0.1 \times 10^{-6} / 1\times10^5 = 14.4 \text{ bar} \).
\( r = 10 \text{ nm} \): \( p_\text{droplet} - p_a = (2 \times 7.2\times10^{-2}) / 10\times10^{-9} / 1\times10^5 = 144 \text{ bar} \).

2) By using the result of exercise 2.2, \( \frac{dT}{dp} = –7.418 \times 10^{-3} \text{ K bar}^{-1} \),
\( r = 0.1 \mu \text{m} \): \( \Delta T_f = –7.418 \times 10^{-3} \times 14.4 = –0.107 \text{ K} \)
\( r = 10 \text{ nm} \): \( \Delta T_f = –7.418 \times 10^{-3} \times 144 = –1.07 \text{ K} \)

* 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.
\section*{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),

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

(4.5)

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

$$p = p^* \exp \left( \frac{2\gamma V_m}{rRT} \right)$$

(Kelvin equation)

(4.6)

\section*{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$^{-3}$.

\begin{center}
\begin{tabular}{|l|}
\hline
\textbf{Solution to exercise 4.3} \\hline
$V_m = 18.02 / 0.997 = 18.07$ cm$^3$ mol$^{-1}$ = 1.807×10$^{-5}$ m$^3$ mol$^{-1}$ \\hline
$r = 0.1$ μm: \begin{align*}
    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 \\
    \text{supersaturation: } 1.06 \% \\
    \text{supersaturation: } 11.1 \% \\
\end{align*} \\
$r = 10$ nm: \begin{align*}
    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 \\
    \text{supersaturation: } 11.1 \% \\
\end{align*} \\
\hline
\end{tabular}
\end{center}

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

\section*{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,

$$p = p^* (1 - x)$$

(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),

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

(4.8)

\section*{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 $\gamma$, and $V_m$, as water and the complete dissociation of sulfuric acid.

\begin{center}
\begin{tabular}{|l|}
\hline
\textbf{Solution to exercise 4.4} \\hline
$p / p^* = [99/(99+1\times3)] \exp[2 \times 7.2 \times 10^{-2} \times 1.807 \times 10^{-5} / (0.1 \times 10^{-6} \times 8.3145 \times 298)] = 0.9808$ \\
\text{supersaturation: } –1.92 \% \\
* This droplet can grow at humidity > 98.1%, non-supersaturation condition. \\
\hline
\end{tabular}
\end{center}