12.2 Quantitative Aspects of Phase Changes

- **Heating-cooling curves** – show the variation of the temperature of a sample as it is heated or cooled at a constant rate
- **Regions in the heating-cooling curves**
  - **Sloped regions** – correspond to temperature changes in the pure solid, liquid or gas phases (slope depends on the heat capacity of each phase; $E_k$ of molecular motion changes)
  - **Flat regions** – correspond to phase changes (temperature remains constant; $E_p$ of intermolecular attraction changes)

\[
q = nC_{\text{water(g)}} \Delta T \quad q = nC_{\text{water(l)}} \Delta T \quad q = nC_{\text{water(s)}} \Delta T
\]

$n$ – number of moles of water; $C$ – molar heat capacity

The Equilibrium Nature of Phase Changes

- **Liquid-gas equilibria (liquid ↔ gas)**
  - At constant temperature in a closed container a **dynamic equilibrium** is established between vaporization and condensation
  - At equilibrium the rate of vaporization equals the rate of condensation

- **Vapor pressure ($P_v$)** – the pressure exerted by the vapors over a liquid at equilibrium
  - $P_v$ depends only on the nature of the liquid and $T$ (if $P_v$ is disturbed by compression or expansion, the equilibrium shifts to restore the original $P_v$)
  - In the presence of other gases over the liquid, $P_v$ is the **partial pressure** of the vapors

- $P_v$ increases with decreasing the strength of the intermolecular forces ($IF$)
  - In order to vaporize, a molecule must escape the forces of attraction, $IF$, between the molecules in the liquid
• \( P_v \) increases with increasing temperature
  - In order to vaporize, a molecule must have enough kinetic energy to escape the liquid
  - Increasing \( T \) increases the fraction of molecules having enough kinetic energy to escape the liquid

- Maxwell distribution

- Examples:
  - The \( IF \) in water are stronger than in diethyl ether \( \Rightarrow \) the \( P_v \) of water is lower than that of diethyl ether at a given temperature (20°C)
  - The \( P_v \) of all three liquids increases exponentially with increasing the temperature

- Clausius-Clapeyron equation – relates \( P_v \), \( T \) and \( \Delta H_{vap} \):
  \[
  \ln P_v = -\frac{\Delta H_{vap}}{R} \left( \frac{1}{T} \right) + \text{const.}
  \]
  - A plot of \( \ln P_v \) versus \( (1/T) \) should yield a straight line with slope \(-\Delta H_{vap}/R\)
  \( \Rightarrow \) Can be used to determine \( \Delta H_{vap} \) by measuring \( P_v \) at different \( T \)s

- Boiling – in an open container a liquid starts boiling (forming bubbles inside) when \( P_v \) reaches the external pressure, \( P_{atm} \)
  - Boiling point \( (T_b) \) – the \( T \) at which \( P_v = P_{atm} \)
  \( \Rightarrow T_b \) increases with increasing \( P_{atm} \) since at higher \( P_{atm} \), higher \( P_v \) must be achieved for boiling to occur, so higher \( T \) is needed
  - Normal boiling point – the \( T_b \) at \( P_{atm} = 760 \text{ torr} \)
**Example:** Estimate the $T_b$ (boiling temperature) of water on Mt. Everest where $P_{atm}$ is ~270 torr, if its $\Delta H_{vap}$ is 40.7 kJ/mol. 

→ Use the Clausius-Clapeyron equation for two $T$s:

Normal boiling point $\rightarrow T_1 = 100^\circ C$ $\rightarrow P_1 = 760$ torr

Boiling point Everest $\rightarrow T_2 = ???$ $\rightarrow P_2 = 270$ torr

\[
\ln \frac{270 \text{ torr}}{760 \text{ torr}} = \frac{-40.7 \text{ kJ/mol}}{8.314 \times 10^{-3} \text{ kJ/mol} \cdot \text{K}} \left( \frac{1}{T_2} - \frac{1}{373 \text{ K}} \right)
\]

\[
\frac{1}{T_2} - \frac{1}{373} = \frac{8.314 \times 10^{-3}}{-40.7} \ln \frac{270}{760} = 2.11 \times 10^{-4}
\]

\[
\frac{1}{T_2} = 2.11 \times 10^{-4} + \frac{1}{373} = 2.89 \times 10^{-3} \quad T_2 = 346 \text{ K} = 73^\circ C
\]

**Phase Diagrams**

- Specify the stability of the various phases at different $T$ and $P$
  - Solid lines – phase boundaries
  - Between the lines – one stable phase
  - On the lines – two phases in equilibrium
  - At the triple point – three phases in equilibrium
  - Critical point – the end of the liquid/gas phase boundary

- Solid-liquid equilibria (solid ↔ liquid)
  - At constant temperature a dynamic equilibrium is established as the rate of melting equals the rate of freezing
  - *Melting* (freezing) point ($T_m$) – pressure affects $T_m$ only very slightly

- Solid-gas equilibria (solid ↔ gas)
  - At constant temperature a dynamic equilibrium is established as the rate of sublimation equals the rate of deposition
  - Since the vapor pressure of solids is typically quite low, solid-gas equilibria are not very common at normal $T$ and $P$ conditions

- The slope of the solid/liquid boundary is normally positive, but in a few cases like H$_2$O, it’s negative $\Rightarrow$ ice melts at lower $T$ when the $P$ is higher

  - **Critical temperature** ($T_c$) – vapors can’t be liquefied at any $P$ if $T$ is greater than $T_c$

  - **Critical pressure** ($P_c$) – $P$ at the critical point

  - **Supercritical fluid** – above $T_c$ and $P_c$ – the liquid and vapor merge into a single phase (resembles both phases)