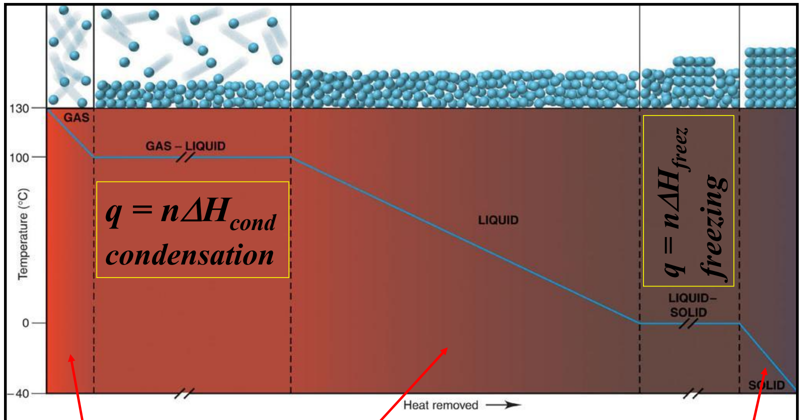
12.2 Quantitative Aspects of Phase Changes

- **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)



$q = n\Delta H_{cond}$ ***condensation***

$q = n\Delta H_{freez}$ ***freezing***

$q = nC_{water(g)}\Delta T$ ***cooling gas***

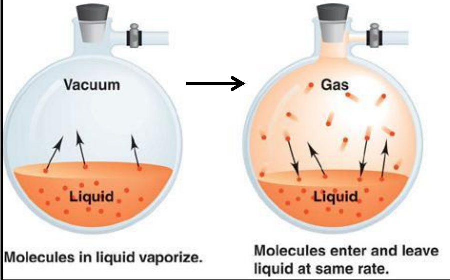
$q = nC_{water(l)}\Delta T$ ***cooling liquid***

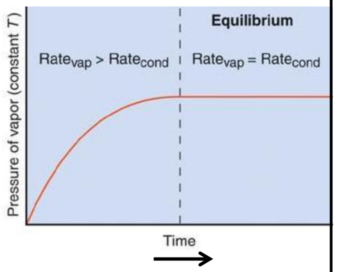
$q = nC_{water(s)}\Delta T$ ***cooling solid***

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

The Equilibrium Nature of Phase Changes

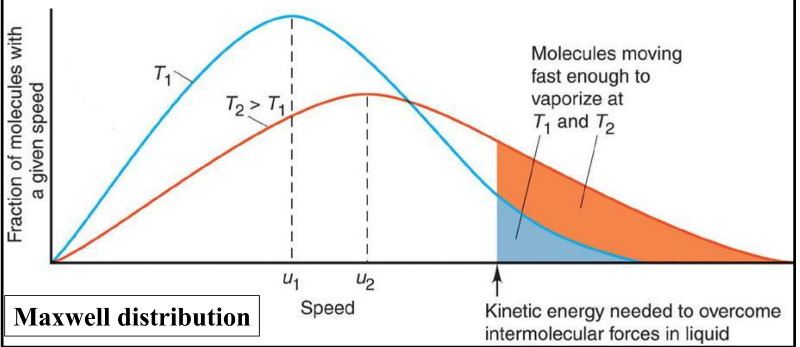
- Liquid-gas equilibria (**liquid ↔ gas**)
  - At constant temperature in a closed container a **dynamic equilibrium** is established between vaporization and condensation
  - At equilibrium the rate of vaporization equals the rate of condensation



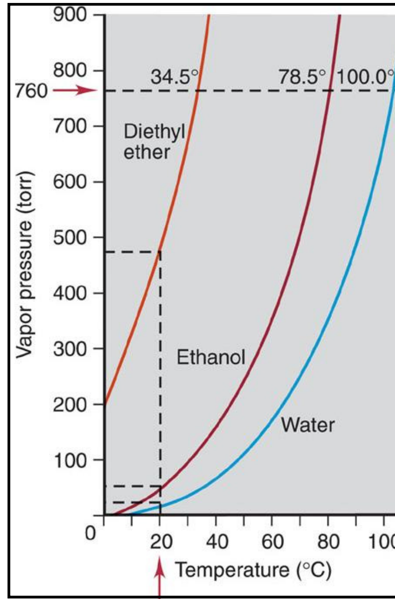


- **Vapor pressure** (***P**$_v$*) – the pressure exerted by the vapors over a liquid at equilibrium
  - P_v depends only on the nature of the liquid and ***T*** (if P_v is disturbed by compression or expansion, the equilibrium shifts to restore the original P_v)
  - In the presence of other gases over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



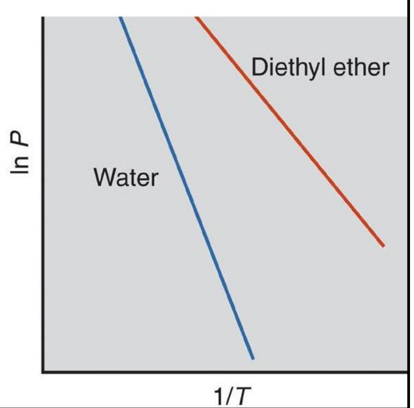
- **Examples:**
  - The ***IF*** in water are stronger than in diethyl ether ⇒ the P_v of water is lower than that of diethyl ether at a given temperature (20°C)
  - The P_v of all three liquids increases exponentially with increasing the temperature

- **Clausius-Clapeyron equation** – relates P_v, T and ΔH_{vap}:

$$\boxed{\ln P_v = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T}\right) + const.}$$

  - A plot of **ln** P_v, versus **(1/*T*)** should yield a straight line with **slope = -$\Delta H_{vap}/R$**

  ⇒ Can be used to determine ΔH_{vap} by measuring P_v at different Ts



  - If two equations are written for two different Ts, T_1 and T_2, at which the P_vs are P_1 and P_2 and the 1st equation is subtracted from the 2nd, one gets:

$$\boxed{\ln\frac{P_2}{P_1} = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

- **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 $P_v = P_{atm}$

  ⇒ 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 torr**

Example: Estimate the T_b of water on Mt. Everest where P_{atm} is ~**270 torr**, if its ΔH_{vap} is **40.7 kJ/mol**.

→ Use the Clausius-Clapeyron equation for two Ts:

Normal boiling point → T_1 **= 100°C** → P_1 **= 760 torr**

Boiling point Everest → T_2 **= ???** → P_2 **= 270 torr**

$$\ln\frac{270\ \mathbf{torr}}{760\ \mathbf{torr}} = \frac{-40.7\ \mathbf{kJ/mol}}{8.314\times10^{-3}\ \mathbf{kJ/mol\cdot K}}\left(\frac{1}{T_2}-\frac{1}{373\ \mathbf{K}}\right)$$

$$\frac{1}{T_2}-\frac{1}{373}=\frac{8.314\times10^{-3}}{-40.7}\ln\frac{270}{760}=2.11\times10^{-4}$$

$$\frac{1}{T_2}=2.11\times10^{-4}+\frac{1}{373}=2.89\times10^{-3} \qquad T_2 = 346\ \mathbf{K} = 73^\circ\mathbf{C}$$

- 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

Phase Diagrams

- Specify the stability of the various phases at different T and P

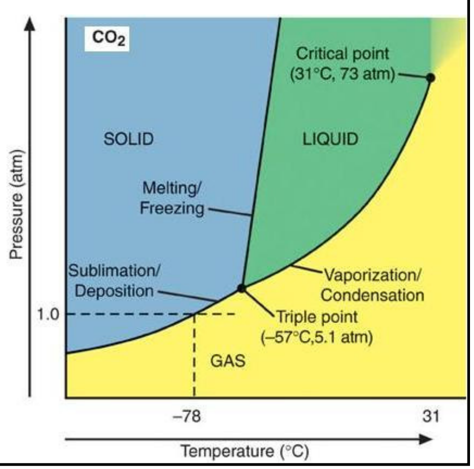
➢ Solid lines – phase boundaries

➢ 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



- The slope of the solid/liquid boundary is normally positive, but in a few cases like H_2O, it's negative ⇒ 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)