General Chemistry II

Chem 102

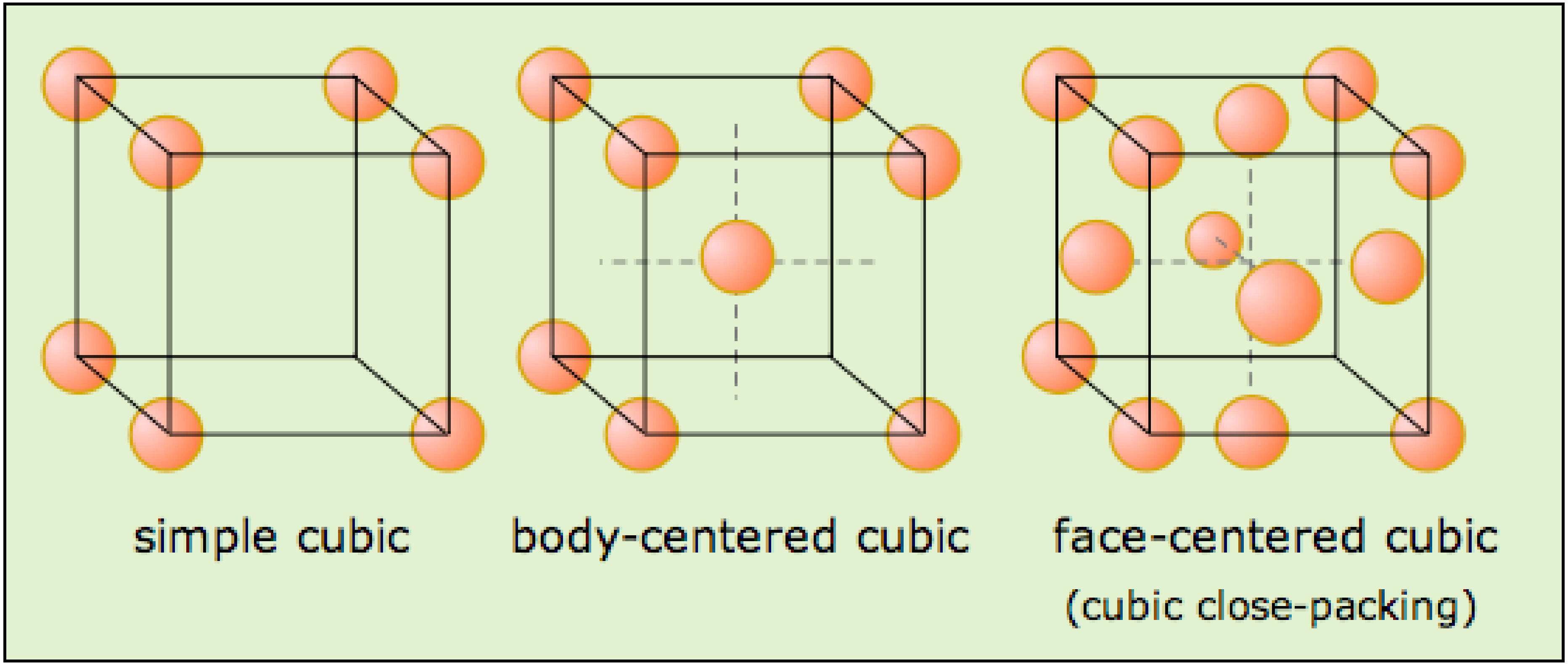
Lecture 5

Solids_Cont.

States'Conversions

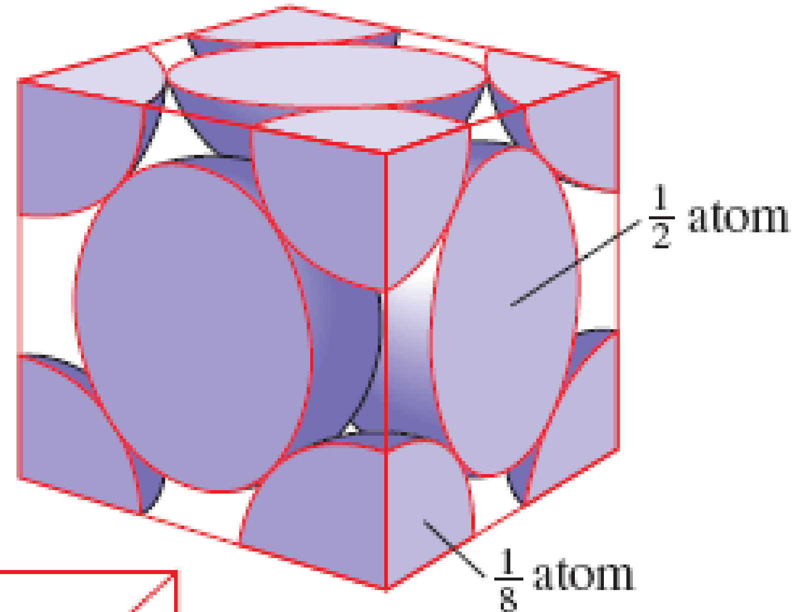
Ahmad Alakraa

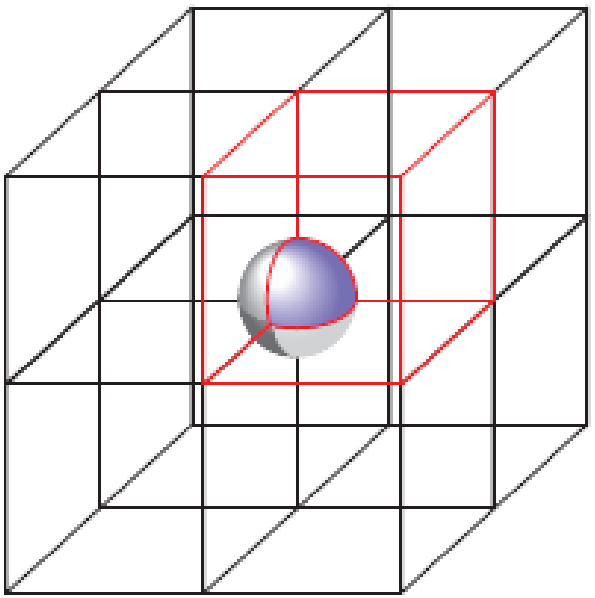
3 types of cubic lattices

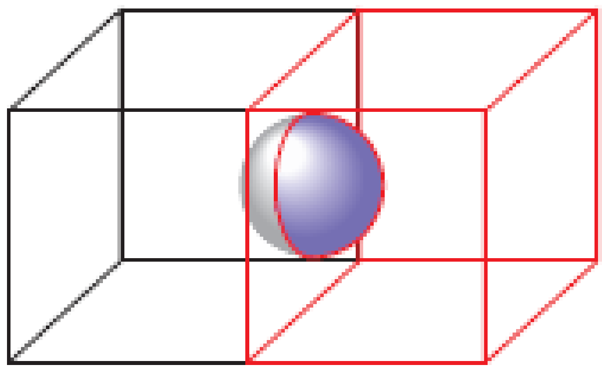


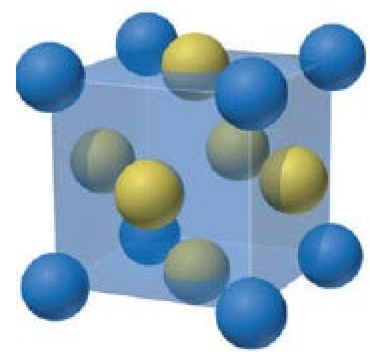
Net number of spheres (atoms) in fcc unit cells

- centers of the spheres on the cube's corners + spheres at the center of each face.









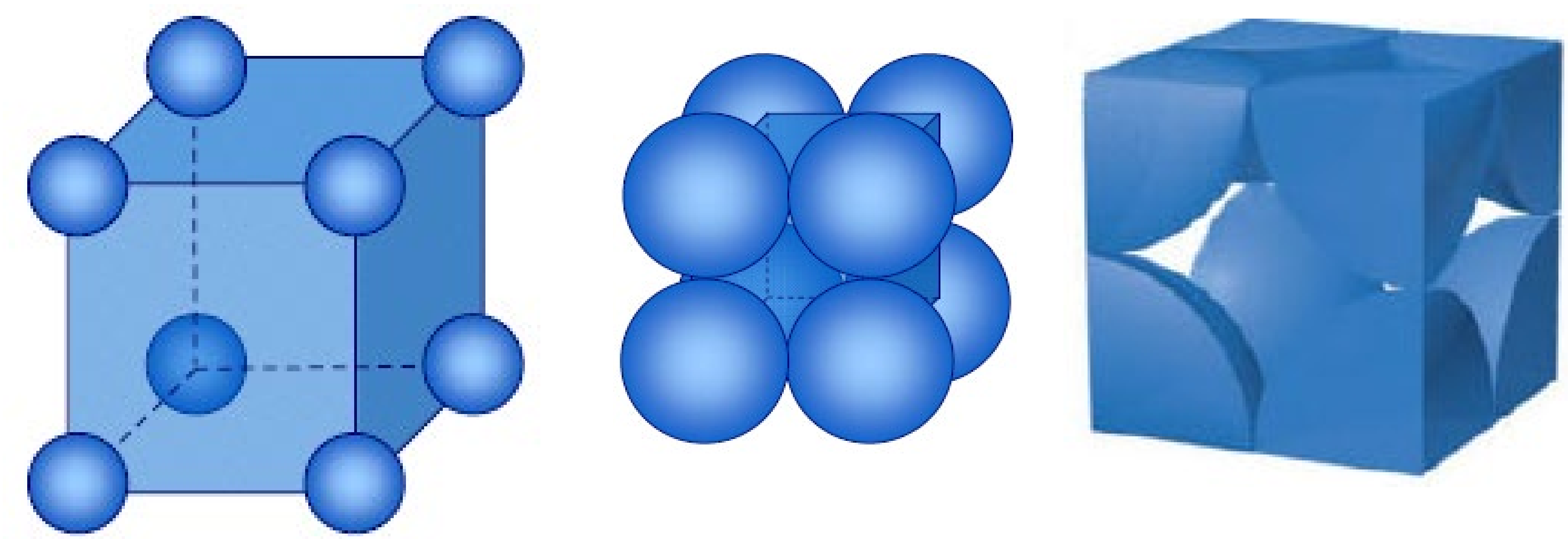
$$\textbf{Total spheres} = \left(8 \times \frac{1}{8}\right) + \left(6 \times \frac{1}{2}\right) = 4$$

Position of atoms and fraction in a single UC

Position of Atom in the Unit Cell	# of adjacent cells sharing atom	Fraction contained within a single unit cell
Cube Corner	8	1/8
Edge	4	1/4
Face	2	1/2
Internal (bulk)	1	1

Net number of spheres in simple cubic unit cell

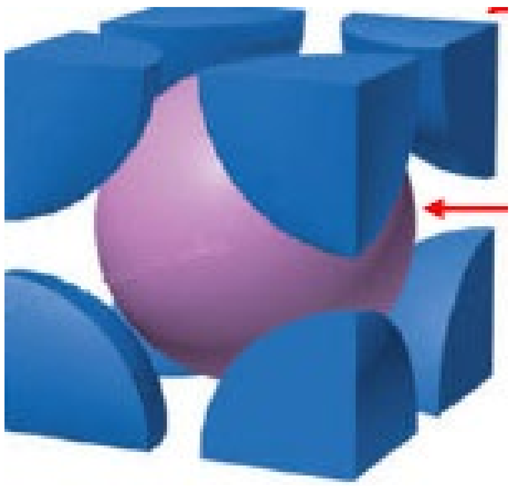
centers of the spheres on the cube’s corners

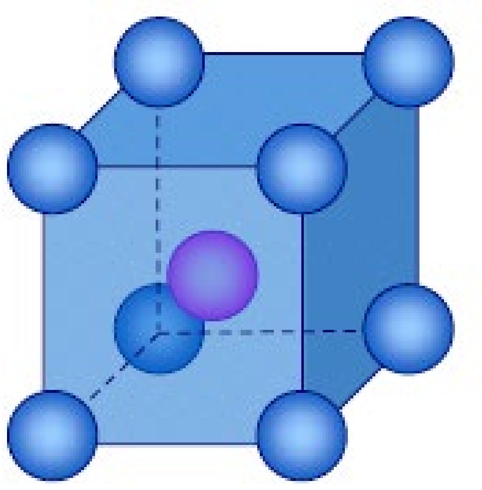


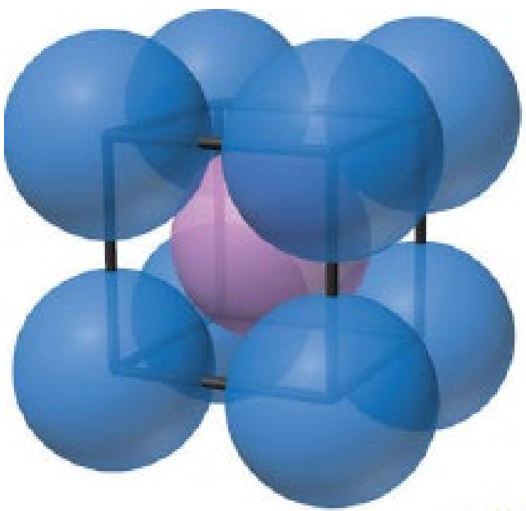
$$\textbf{Total spheres} = \left(8 \times \frac{1}{8}\right) = 1$$

Net number of spheres in bcc unit cell

centers of the spheres on the cube’s corners + 1 sphere in the center





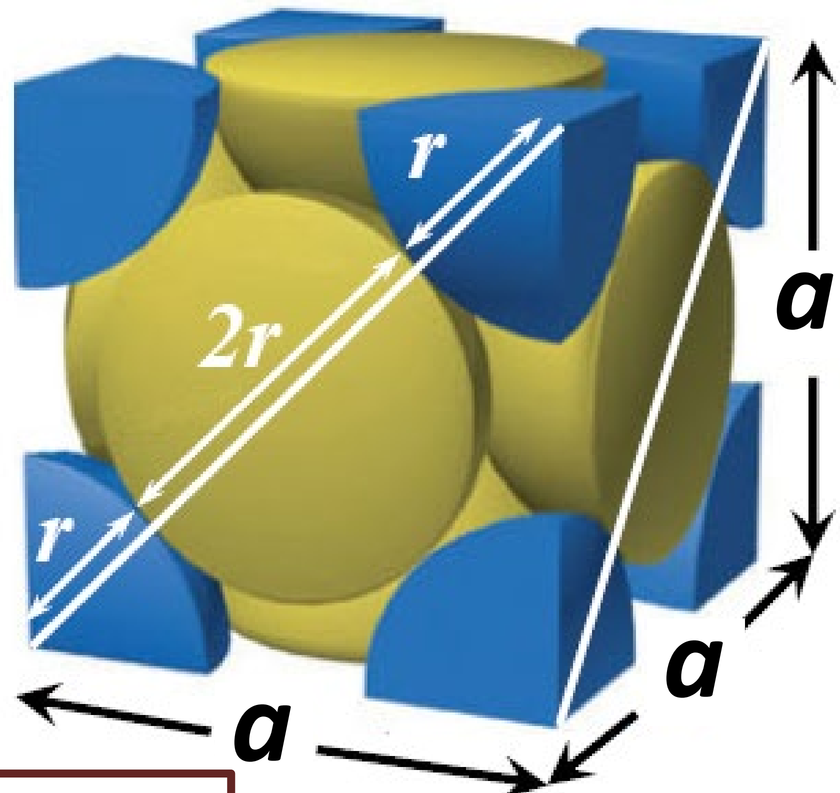


$$\textbf{Total spheres} = \left(8 \times \frac{1}{8}\right) + (1 \times 1) = 2$$

Density of a Closest Packed Solid

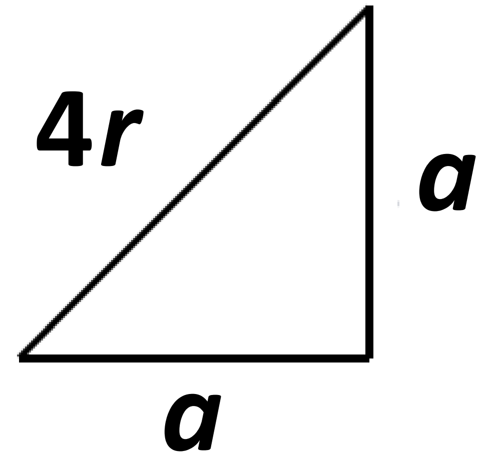
Silver crystallizes in a cubic closest packed structure. The radius of a silver atom is 1.44 Å (1 Å = 10^{-8} cm). Calculate the density of solid silver.

- The structure is ccp, which means the unit cell is face-centered cubic.
- Find the volume of this unit cell for silver and the net number of atoms it contains.
- Atoms touch along the diagonals for each face and not along the edges of the cube.



Diagonal length = r+2r+r = 4r

- Find the length of the edge of the cube by the Pythagorean theorem



$$(4r)^2 = a^2 + a^2 = 2a^2$$

$$a^2 = 8r^2$$

$$a = r\sqrt{8}$$

radius of a silver atom is 1.44 Å.

$$a = r\sqrt{8} = 1.44\ \mathring{A}\sqrt{8} = 4.07\ \mathring{A}$$

V (unit cell) = $a^3 = 67.4\left(\mathring{A}\right)^3 = 6.74\times10^{-23}\,cm^3$

$$4\ Ag\ atoms\ \ occupy\ \ 6.74\times 10^{-23}\, cm^3$$

$$\text{Atomic } mass \text{ of Ag} = \frac{107.9\, g}{mol} = \frac{107.9\, g}{6.022\times 10^{23}\, atoms}$$

- **Calculate the mass of 4 atoms existing in the fcc unit cell**

$$mass \text{ of Ag unit cell} = \frac{107.9\, g}{6.022\times 10^{23}\, atoms}\times 4\, atoms = 71.7\times 10^{-23}\, g$$

$$density \text{ of Ag} = \frac{mass}{volume} = \frac{71.7\times 10^{-23}\, g}{6.74\times 10^{-23}\, cm^3} = 10.6\, g\, cm^{-3}$$

Generally

$$\text{density (d)} = \frac{Z \times M}{a^3 \times N_A}$$

d = Density (g/cm^3) Z = number of atoms per unit cell

M = Molar mass in g/mol a = Edge length in cm

N_A = Avogadro number $= 6.022 \times 10^{23}$ atoms/mol

Value of Z
- simple cubic = 1
- bcc = 2
- ccp or fcc = 4

Relationship between atomic radius and edge length

Simple cubic

$$r = \frac{a}{2}$$

BCC

$$r = \frac{a\sqrt{3}}{4}$$

FCC

$$r = \frac{a\sqrt{2}}{4}$$

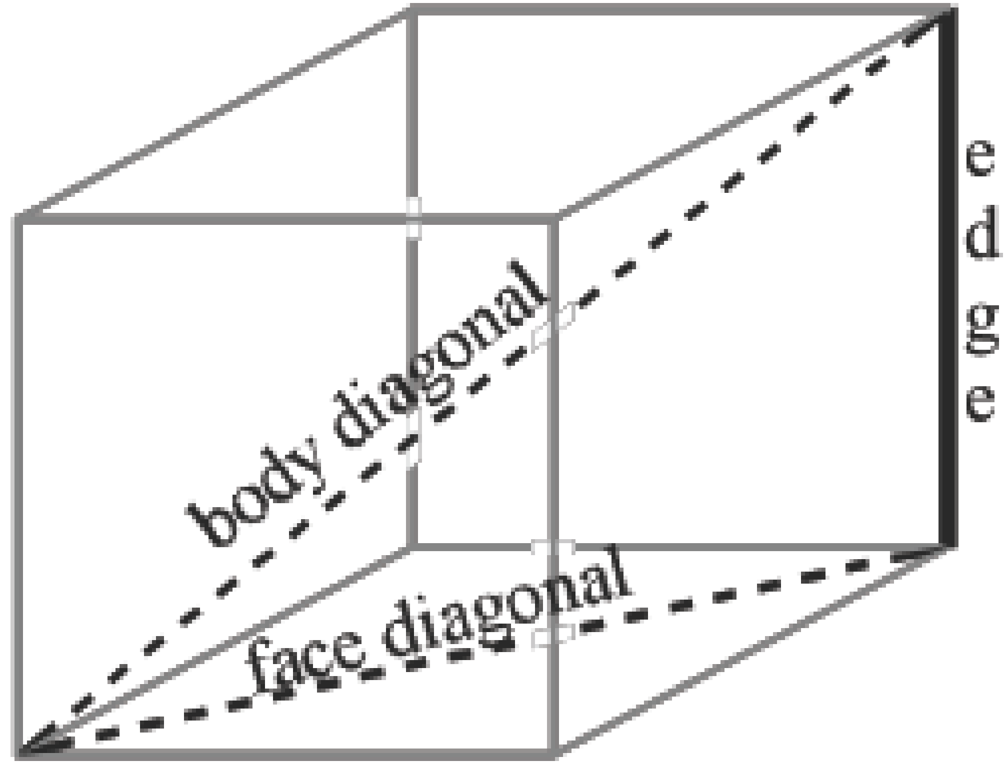
$$a = r\sqrt{8}$$

Usually

$$fd^2 = a^2 + a^2 = 2\,a^2$$

$$bd^2 = fd^2 + a^2$$

$$= a^2 + a^2 + a^2 = 3\,a^2$$



- The length of the cell edge is represented by a.
- The direction from a corner of a cube to the farthest corner is called body diagonal (bd).
- The face diagonal (fd) is a line drawn from one vertex to the opposite corner of the same face.
- If the edge is a, then we have

- If atoms touch each other along the body diagonal (bd), thus, the body diagonal has a length that is four times the radius of the atom, r, i.e., bd = 4 r

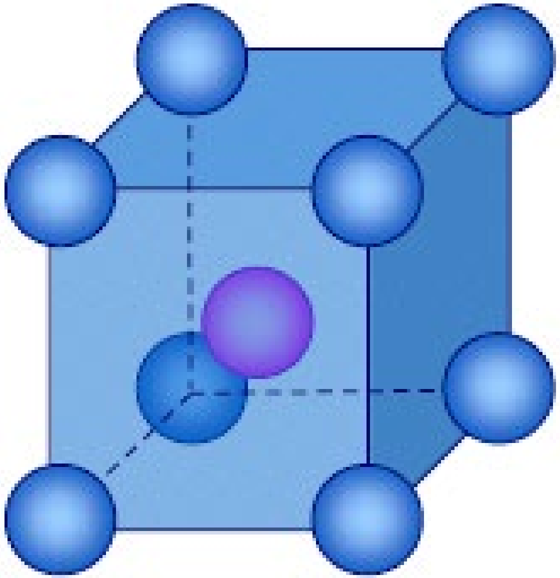
$$(4r)^2 = 2a^2 + a^2 = 3a^2$$

$$4r = a\sqrt{3}$$

$$a = \frac{4r}{\sqrt{3}}$$

$$r = \frac{a\sqrt{3}}{4}$$

Packing fraction for a bcc packed structure



$$r = \frac{a\sqrt{3}}{4} \Rightarrow a = \frac{4r}{\sqrt{3}}$$

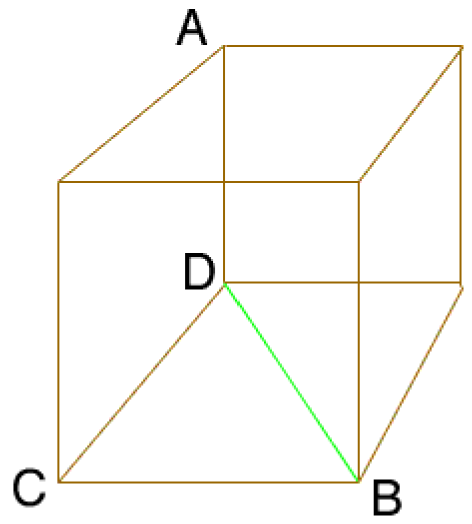
$$\textit{Packing fraction} = \frac{V_{sphere}}{V_{unit\ cell}} = \frac{2 \times \frac{4}{3}\pi r^3}{\left(\frac{4r}{\sqrt{3}}\right)^3} = \frac{\sqrt{3}\,\pi}{8} = 0.6802$$

The packing fractions are

fcc and hcp	bcc	simple cubic
74.05 %	68.02 %	52%

Packing fraction of fcc lattice = 0.74

- Atoms are touched along the face diagonal (fd).
- For spheres of radius r, the diagonal of the cube face is equal to 4r, and is also equal to √2 a, where a is the dimension of the unit cell.



$$|DB|^2 = |DC|^2 + |CB|^2$$

As there are 6 atoms in the faces and half of each is in the unit cell:

$$r = \frac{a\sqrt{2}}{4}$$

$$6 \times \frac{1}{2} \times \frac{4}{3}\pi r^3 = 4\pi\left(\frac{a\sqrt{2}}{4}\right)^3 = 0.55536\, a^3$$

There are also 8 atoms in the corners of the unit cell, and 1/8 of each is in the cell:

$$8 \times \frac{1}{8} \times \frac{4}{3}\pi r^3 = \frac{4}{3}\pi\left(\frac{a\sqrt{2}}{4}\right)^3 = 0.18512\,a^3$$

The volume of the unit cell is a^3 and the total volume of the spheres in the unit cell is

$$V(spheres) = (0.5536 + 0.18512) = 0.74048\,a^3$$

$$Packing\ fraction = \frac{0.74048\,a^3}{a^3} = 0.74048$$

States' Conversions


Evaporation

Water vapor
Evaporation
Liquid water

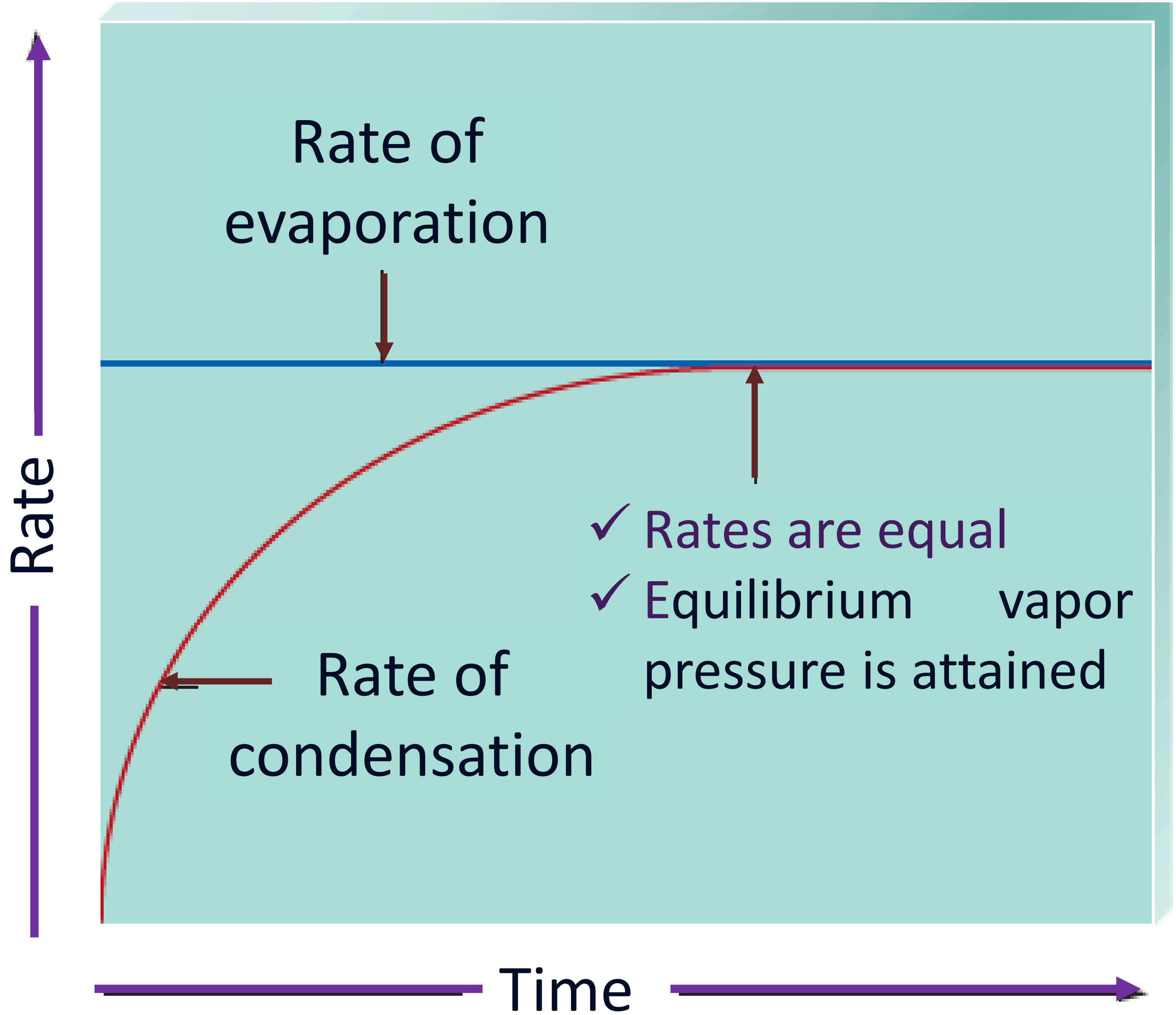
Vaporization/Evaporation

- At any temperature, a certain no. of molecules in a liquid possess a sufficient KE to escape (vaporize) from the surface.
- Evaporation is **endothermic** because energy is required to overcome the relatively strong intermolecular forces in the liquid.
- When a liquid evaporates in a closed vessel, its gaseous molecules exert a vapor pressure on the liquid surface.
- As vaporization proceeds, the concentration of gaseous molecules increase and their tendency to return back (**condense**) to the liquid state increases.
- The rate of evaporation is constant at a given temperature.

- The rate of condensation increases with the concentration of gases molecules until becoming equal to the evaporation rate.
- At this moment, a state of dynamic equilibrium is attained and the vapor pressure exerted therefore is called the **equilibrium vapor pressure** or simply notes **vapor pressure**.

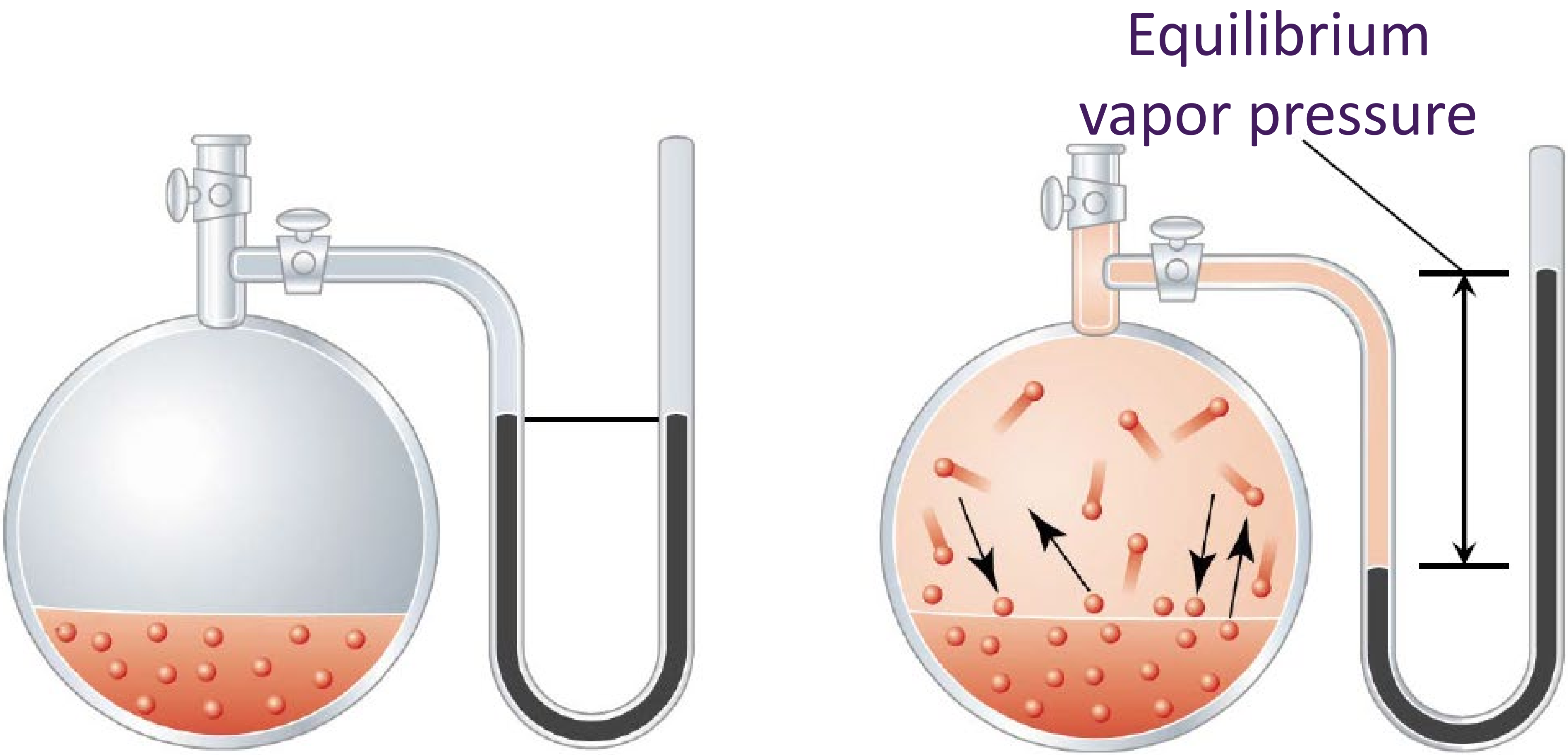
Equilibrium vapor pressure

- is the maximum vapor pressure a liquid exerts at a given temperature.
- It is constant at a **constant T**
- Liquids with high vapor pressure are said to be **volatile**.


Rate of evaporation
Rate of condensation
✓ Rates are equal
✓ Equilibrium vapor pressure is attained
Rate
Time

Equilibrium vapor pressure

- When the system reaches equilibrium, the vapor pressure can be determined from the change in the height of the mercury column.



VP vs. forces

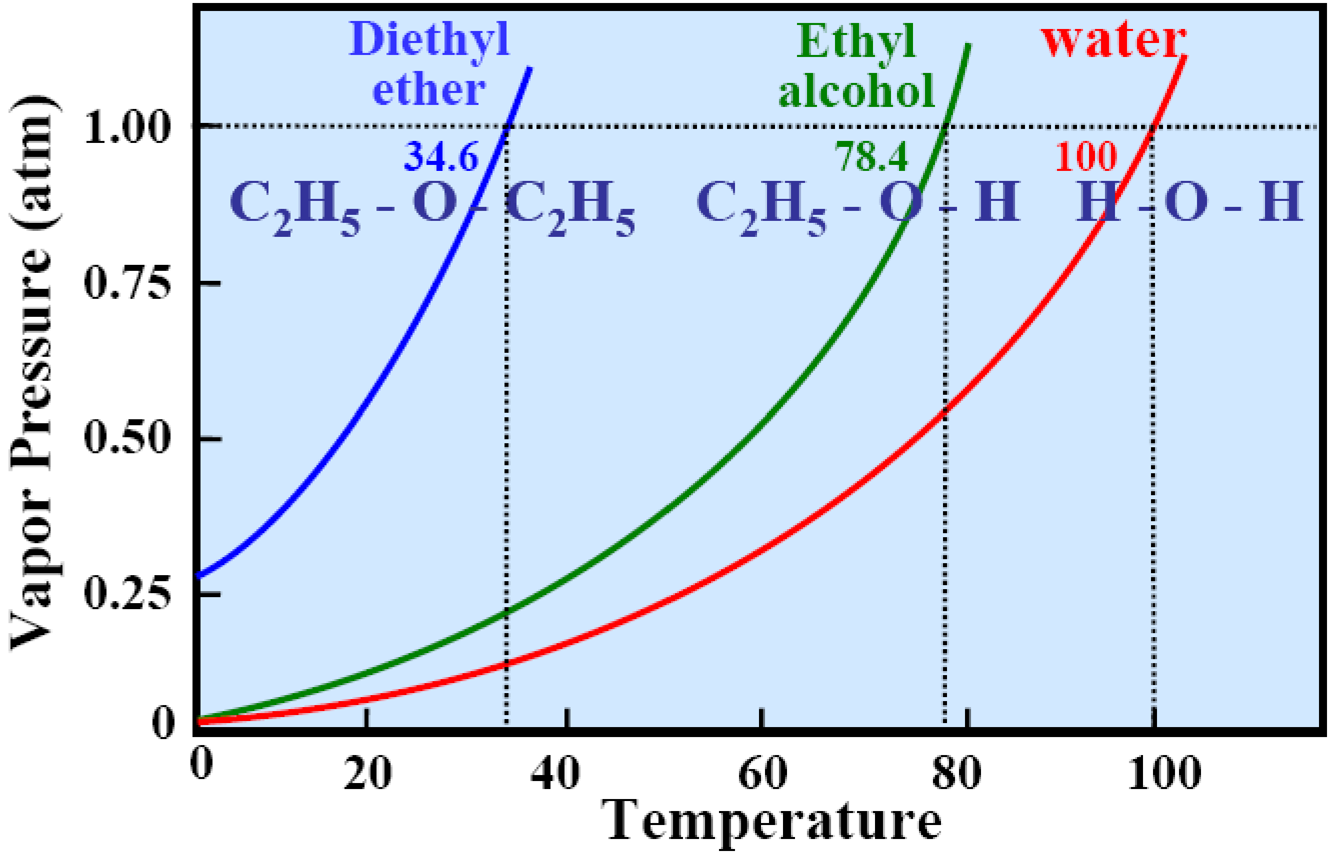
- The vapor pressure is determined by the strength of the intermolecular forces in the liquid.

Strong intermolecular forces → **Low** equilibrium vapor pressure

Rate of evaporation

is increased by

- ❑Heating
- ❑Increasing the exposed surface area



BP=100°C $H - O - H$ < $CH_3 - O - CH_3$ BP=–24°C

18 46

However, typically, substances with larger molar masses have relatively stronger intermolecular forces and lower vapor pressures.

Molar Heat of Vaporization, ΔH_{vap} ------ ΔH_m

energy (usually in kJ) required to vaporize one **mole** of a liquid

As the strength of intermolecular forces in a liquid **increases**, its vapor pressure **decreases** and ΔH_{vap} **increases**.

Specific (Latent) Heat of Vaporization ------ ΔH_s

energy (usually in kJ) required to vaporize one gram of a liquid

$$\Delta H_m \left(\frac{\text{kJ}}{\text{mol}}\right) = \Delta H_s \left(\frac{\text{kJ}}{\text{g}}\right) \times \text{molar mass} \left(\frac{\text{g}}{\text{mol}}\right)$$

Molar Heat of fusion, ΔH_f ------ ΔH_m

energy (**amount of heat**) absorbed when one **mole** of a solid melts

Specific Heat of fusion, ------ ΔH_s

energy (amount of heat) absorbed when one gram of a solid melts

$$\Delta H_m \left(\frac{\text{kJ}}{\text{mol}}\right) = \Delta H_s \left(\frac{\text{kJ}}{\text{g}}\right) \times \text{molar mass} \left(\frac{\text{g}}{\text{mol}}\right)$$

Boiling Point, BP

temperature at which the vapor pressure of a liquid equals the external pressure

Normal Boiling Point

temperature at which the vapor pressure of a liquid equals 1 atm

As the strength of Intermolecular forces ↑, ΔH_{vap} ↑, BP ↑

Normal Melting Point / Freezing point

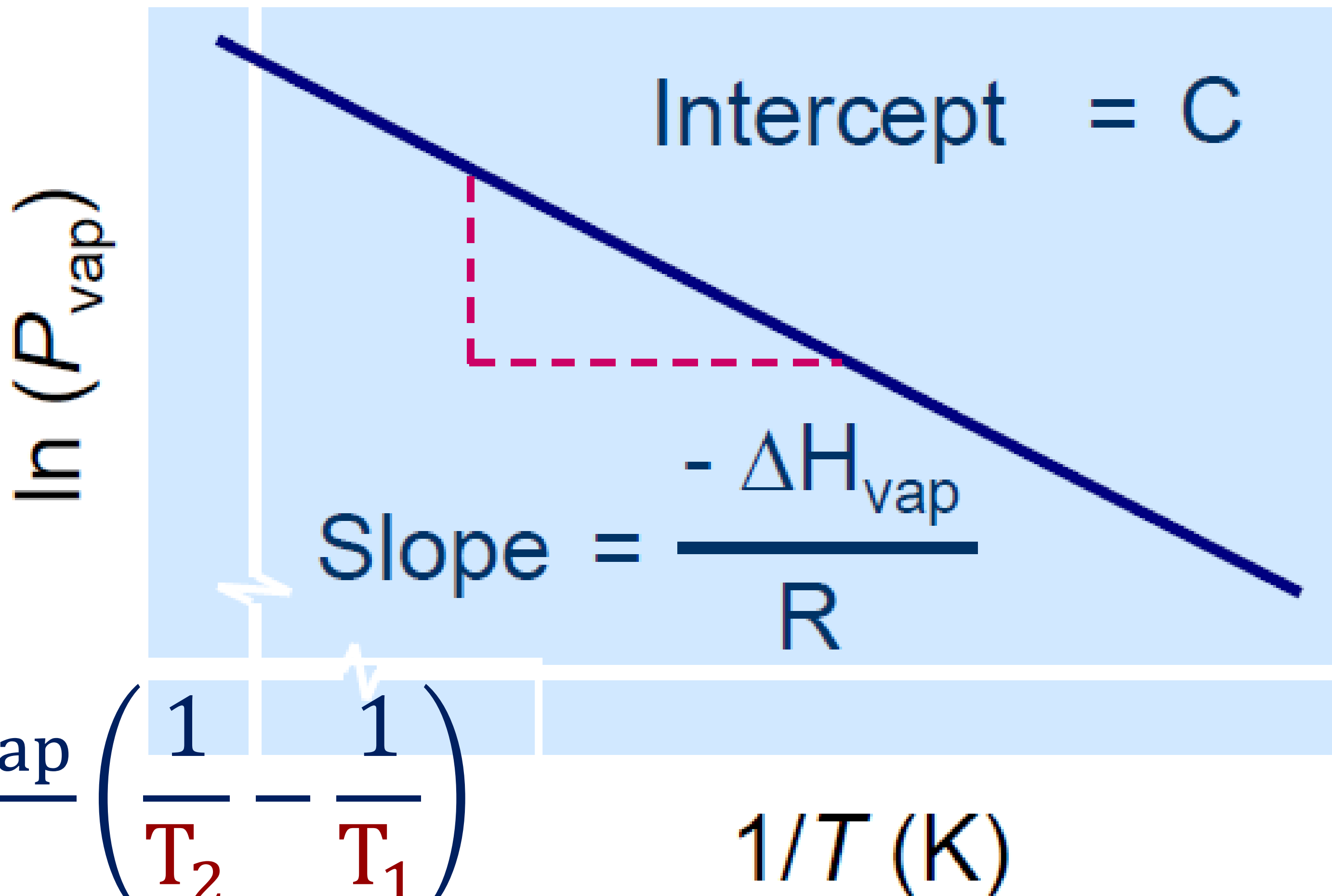
temperature at which the vapor pressure of a liquid equals the vapor pressure of its solid

Clausius-Clapeyron Equation/ideal behavior

$$\ln P = -\frac{\Delta H_{vap}}{RT} + C$$

R = 8.314 J/K. mol

C: a constant (characteristic for a given material)



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

Exercise

The vapor pressure of water at 25°C is 23.8 torr, and the heat of vaporization is 43.9 kJ/mol. Calculate the vapor pressure of water at 50°C.

Solution

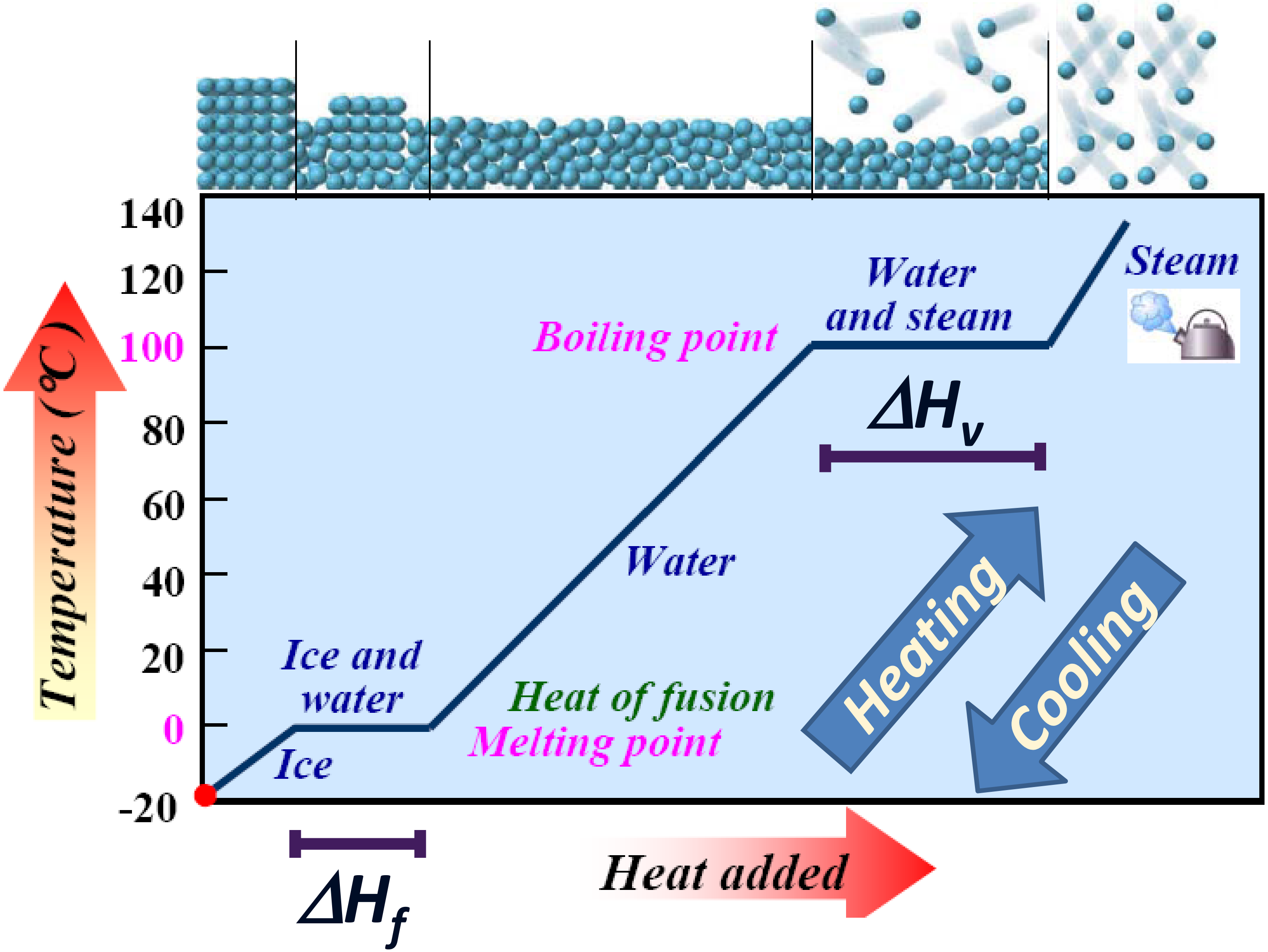
$$\ln P = -\frac{\Delta H_{vap}}{RT} + C$$

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

$$\ln \frac{23.8\ torr}{P_2} = \frac{43.9\ kJ/mol}{8.314\ J/K.mol}\left(\frac{1}{323\ K} - \frac{1}{298\ K}\right)$$

$$P_2 = 93.7\ torr$$

Heating/Cooling curves

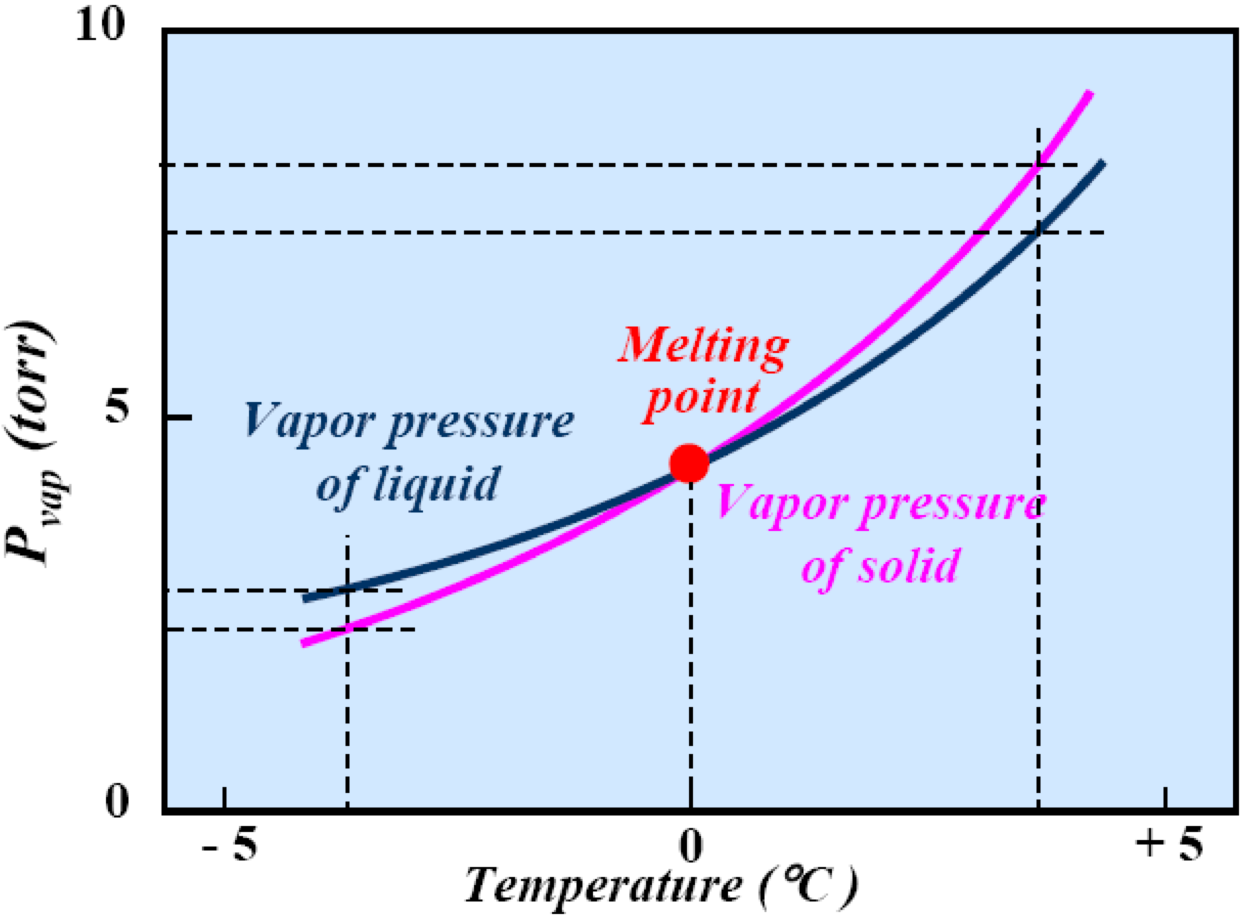


Changes of state are **<u>physical changes</u>**; although intermolecular forces have been overcome, no chemical bonds have been broken

Heating curves

- ❑ Before melting, the heat is consumed in increasing the random vibrations of the ice (water) molecules.
- ❑ At the melting point,
  - ✓ the molecules become energetic enough to overcome the lattice energy.
  - ✓ All the added energy is used to overcome the lattice energy and to break (partially) the H-bonds; damaging the ice lattice.
  - ✓ The temperature remains constant until the solid is completely changed to liquid; then it increases again.

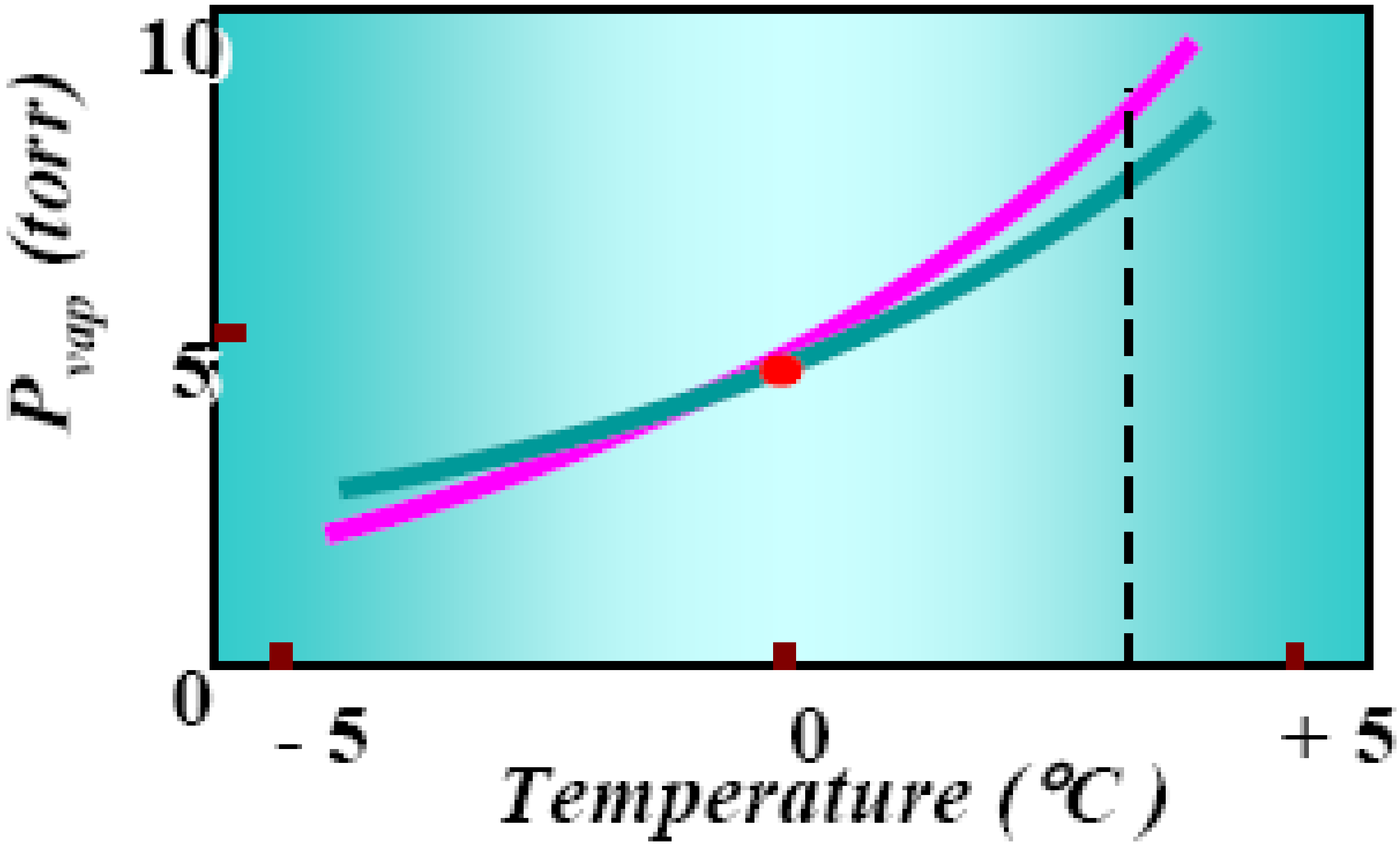
Vapor pressure of solid and liquid water



- Data for liquid water below 0°C were obtained from supercooled water.
- Data for solid water above 0°C are estimated by extrapolation of vapor pressure from below 0°C.

- Below 0°C, $P_{ice} < P_{liq.H2O}$
- P_{ice} has a larger temperature dependence than $P_{liq.H2O}$
- P_{ice} increases more rapidly for a given rise in temp. than $P_{liq.H2O}$

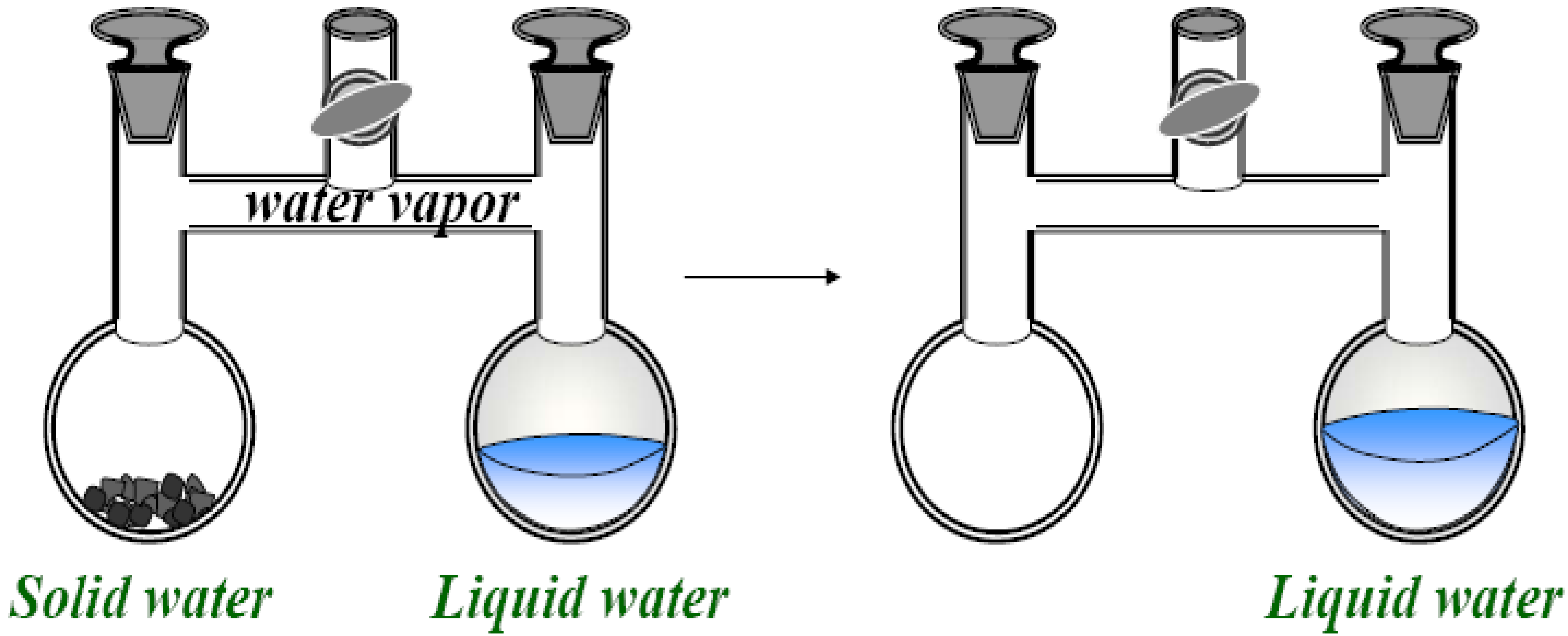
At temperatures where $P_{ice} > P_{liq.H2O}$



- Solid requires a higher pressure than the liquid does to be in equilibrium with the vapor.

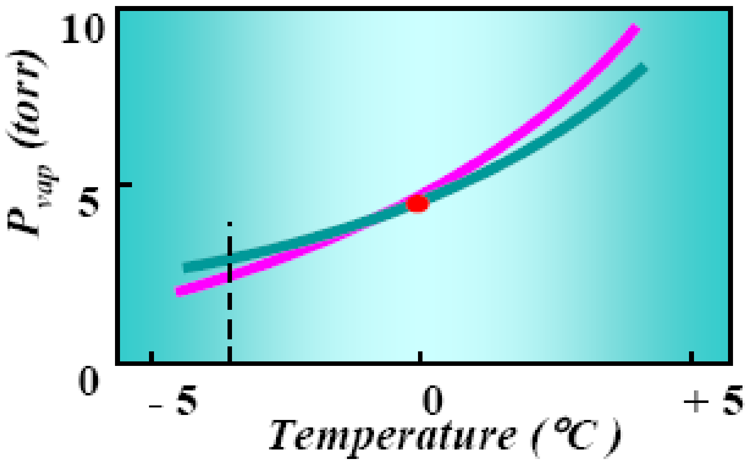
- Vapor is released from the solid to achieve equilibrium.
- Liquid will absorb vapor in an attempt to reduce its vapor pressure to its equilibrium value.
- The net effect is a conversion from solid to liquid through the vapor phase, i.e., above the melting point of ice, only the liquid state can exist.

$$P_{ice} > P_{liq.H2O}$$



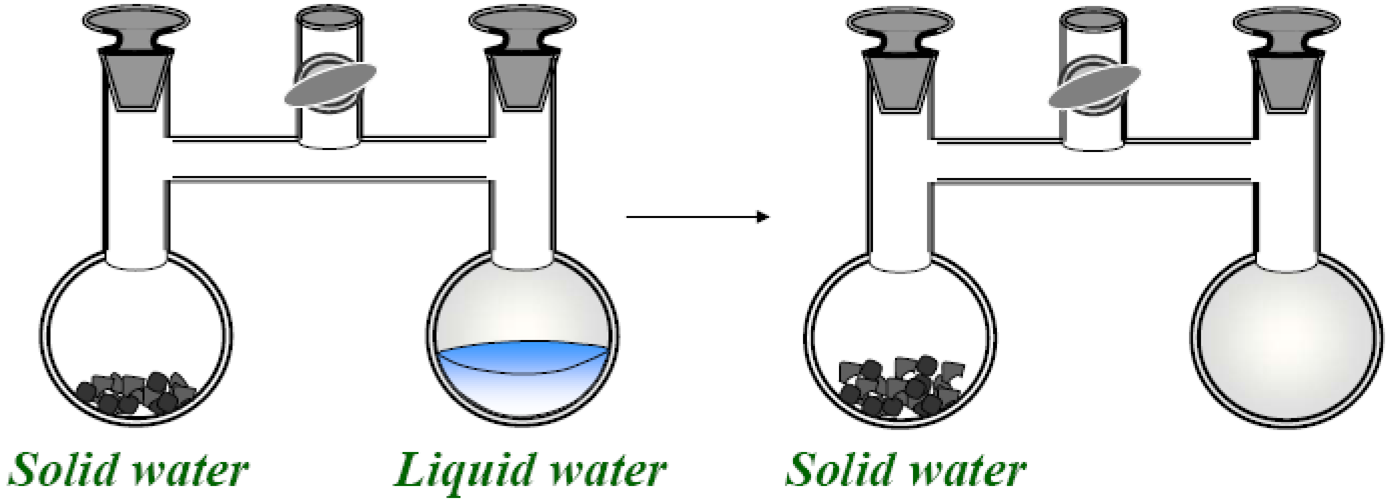
At temperatures where $P_{ice} < P_{liq.H2O}$

- A Liquid requires a **higher pressure** than a solid to be in equilibrium with the vapor. Thus, vapor is released from the liquid to achieve equilibrium.
- Solid will absorb vapor in an attempt to reduce its vapor pressure to its equilibrium value.



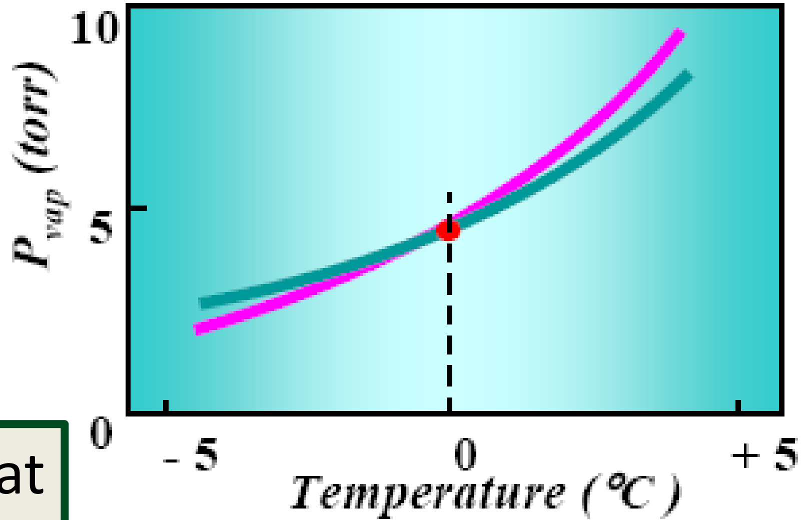
Below the melting point of ice, only the **solid** state can exist.

- The **net effect** is a conversion from **liquid** to **solid** through the vapor Phase



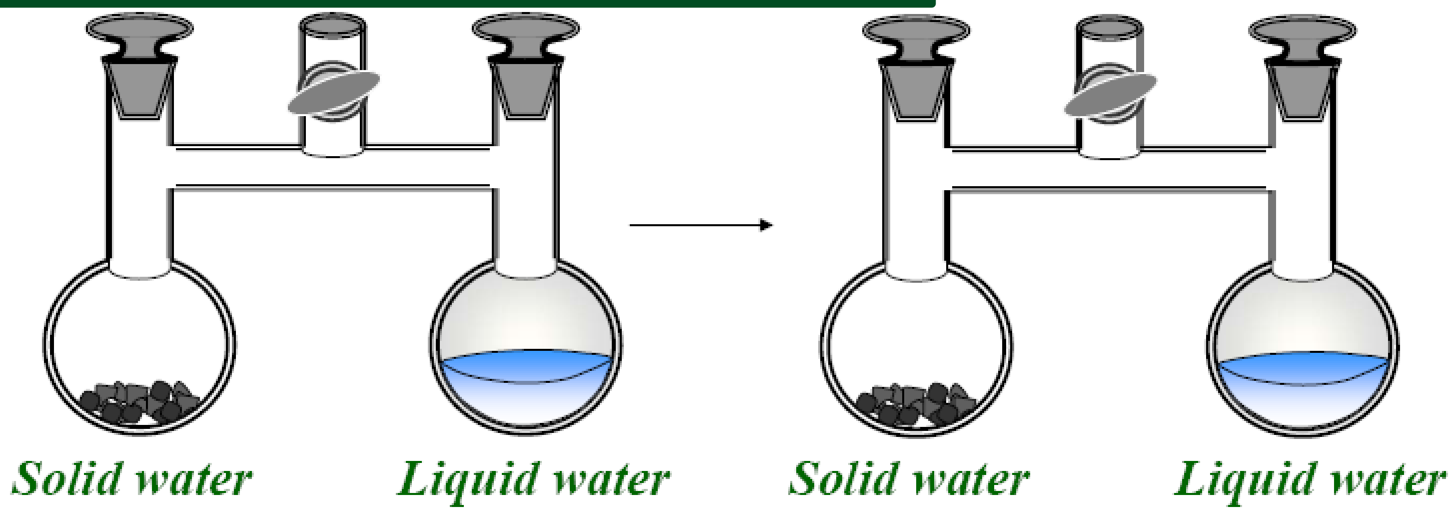
At temperatures where $P_{ice} = P_{liq.H2O}$

- Solid and liquid can **coexist** in equilibrium simultaneously with the vapor.
- This temperature represents the **freezing** (**melting**) point



Normal melting point: the temperature at which the solid and liquid states have the same vapor pressure under conditions where the total pressure is 1 atmosphere

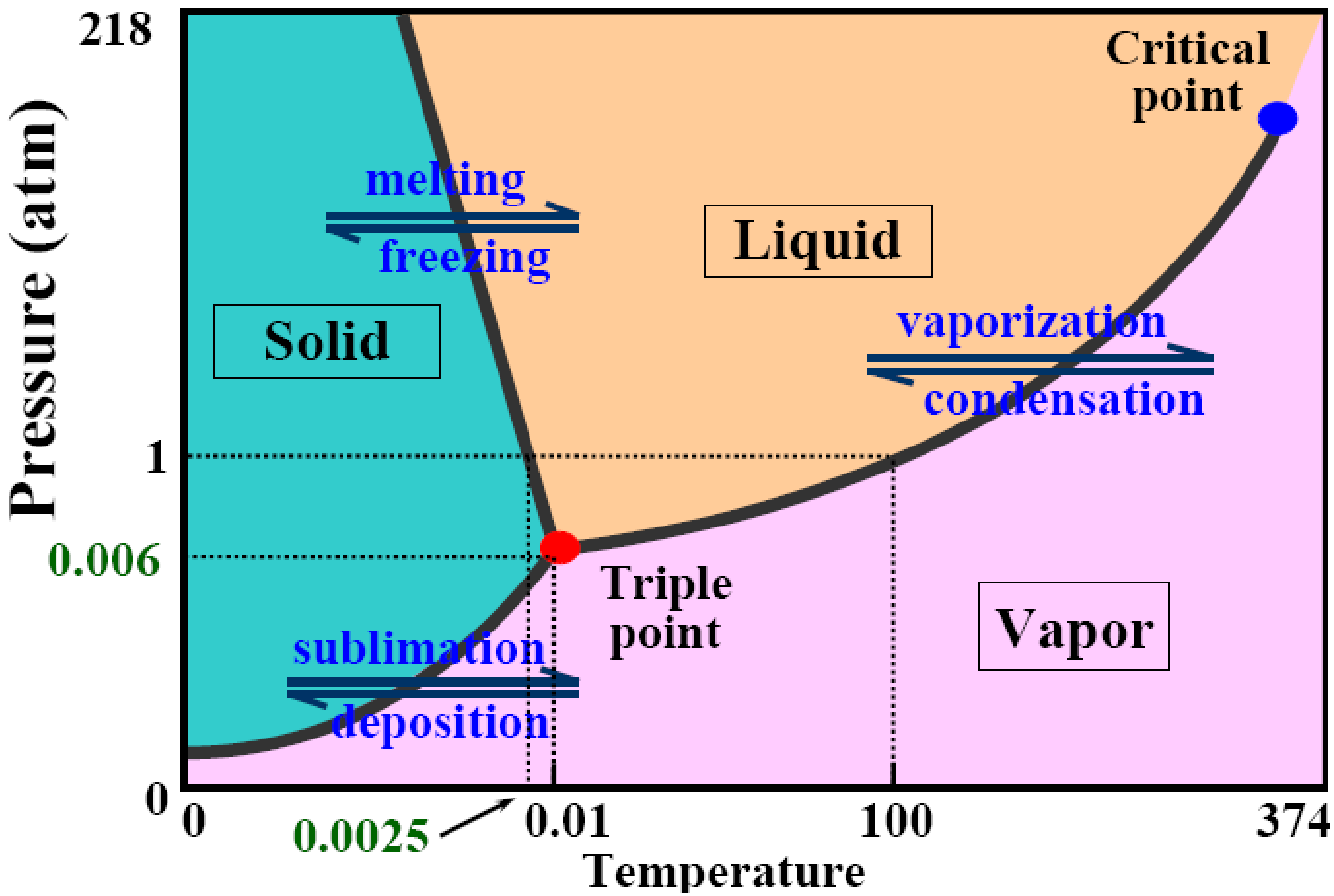
At the melting point of ice, the **solid and liquid states exist**.



Phase diagrams

is a simple **representation** for the different phases of a substance as a function of temperature and pressure.

One component systems



Phase diagram of water

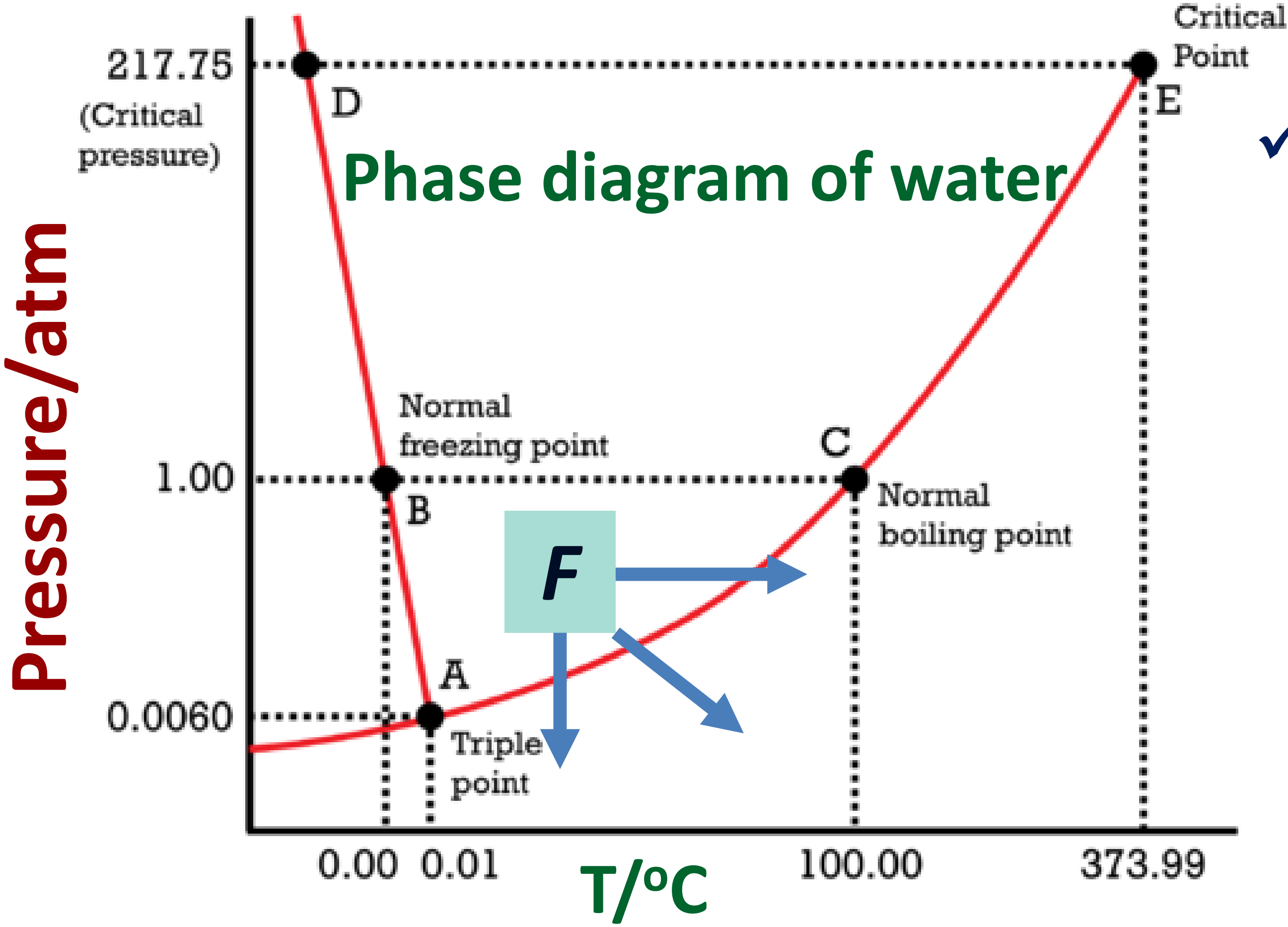
A phase diagram describes conditions and events in a closed system, where no material can escape into the surroundings and no air is present

Exercise

How can you reach the vapor state from Point F?

Solution

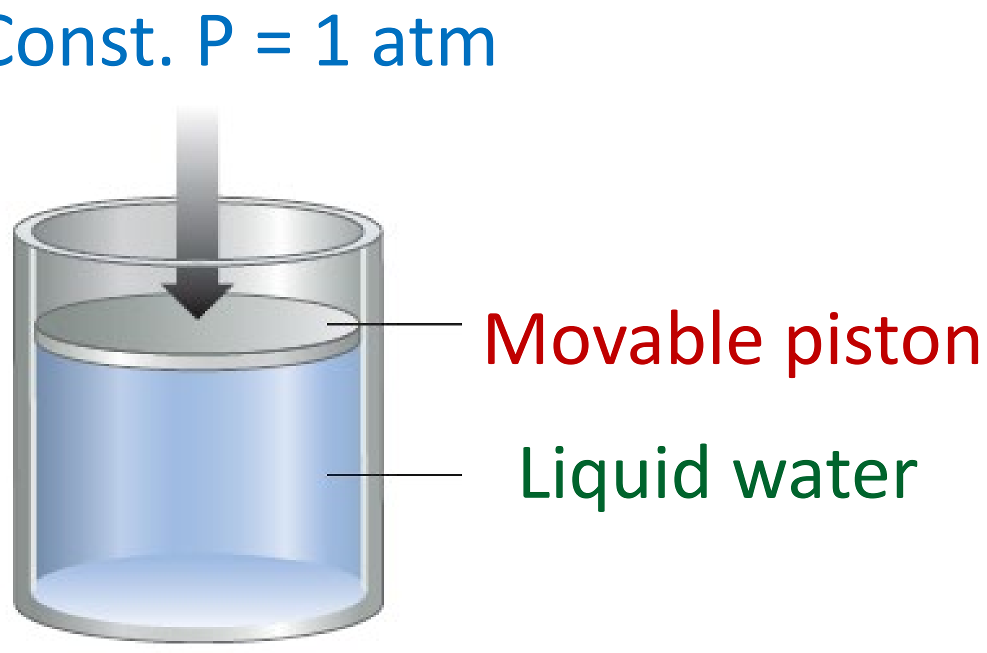
- ✓ Increasing T at constant P
- ✓ Increasing T and decreasing P simultaneously



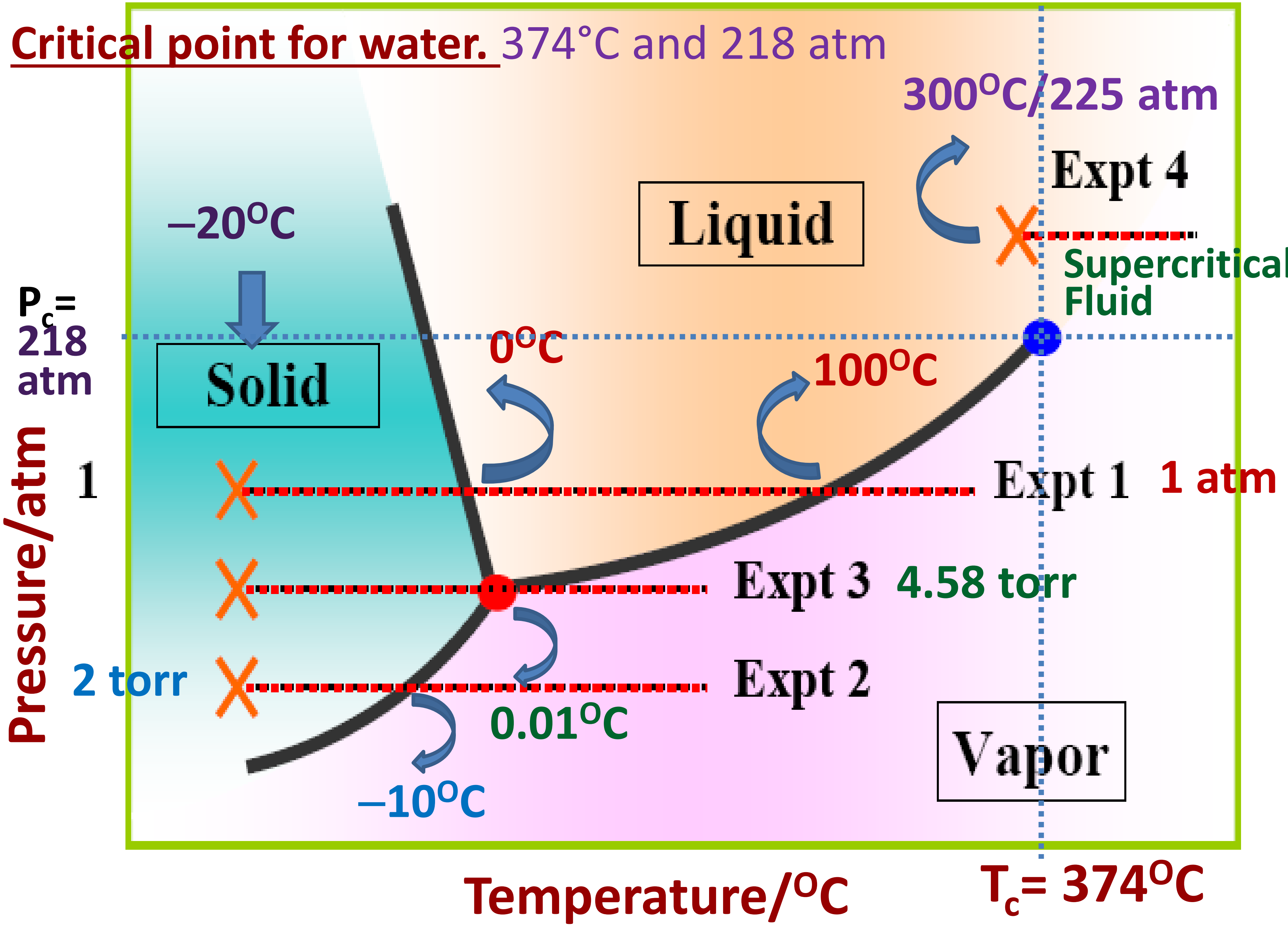
- ✓ Decreasing P at constant T

Sublimation occurs at the temperature at which the vapor pressure of ice equals the external pressure.

Heating water in a closed system



No bubbles can form within the liquid as long as the vapor pressure is less than 1 atm.



Critical point for water. 374°C and 218 atm
300°C/225 atm
Expt 4
Liquid
−20°C
Supercritical Fluid
Pc= 218 atm
0°C
Solid
100°C
Pressure/atm
1
Expt 1
1 atm
Expt 3
4.58 torr
2 torr
Expt 2
0.01°C
Vapor
−10°C
Temperature/°C
Tc= 374°C

Exp. 1

- External P = 1 atm; cylinder is completely filled with ice at –20°C.
- The vapor pressure of ice is less than 1 atm.
- The cylinder is heated; ice is the only component until the temperature reaches 0°C (normal melting point of water), where ice changes to liquid water.
- The vapor pressures of the solid and liquid are equal, but less than 1 atm.
- This is true on the solid/liquid line everywhere except at the triple point

Heating continues after complete conversion to liq. state

- Temp. reaches 100°C; the vapor pressure of liquid water = 1 atm; boiling occurs; liquid changes to vapor.

Exp. 2

- External P = 2 torr; cylinder is completely filled with ice at –20°C.
- As heating proceeds, the temperature rises to –10°C, where the ice changes directly to vapor, a process known as sublimation

Exp. 3

- External P = 4.58 torr; cylinder is completely filled with ice at –20°C.
- As heating proceeds, no new phase appears until the temperature reaches 0.01°C (273.16 K). At this point, called the triple point, solid and liquid water have identical vapor pressures of 4.58 torr (external pressure …………BOILING).
- Thus at 0.01°C (273.16 K) and 4.58 torr, all three states of water are present.

Exp. 4

- External P = 225 atm; cylinder is completely filled with liquid water at 300°C.

- This is quite unlike the behavior at lower temperatures and pressures, where the temperature remains constant while a definite phase change from liquid to vapor occurs.

- This occurs because the conditions are beyond the **critical point for water.** 374°C and 218 atm.

Critical Temperature

temperature above which the vapor cannot be liquefied no matter what pressure is applied.

Critical Pressure

pressure required to produce liquefaction at the critical temperature

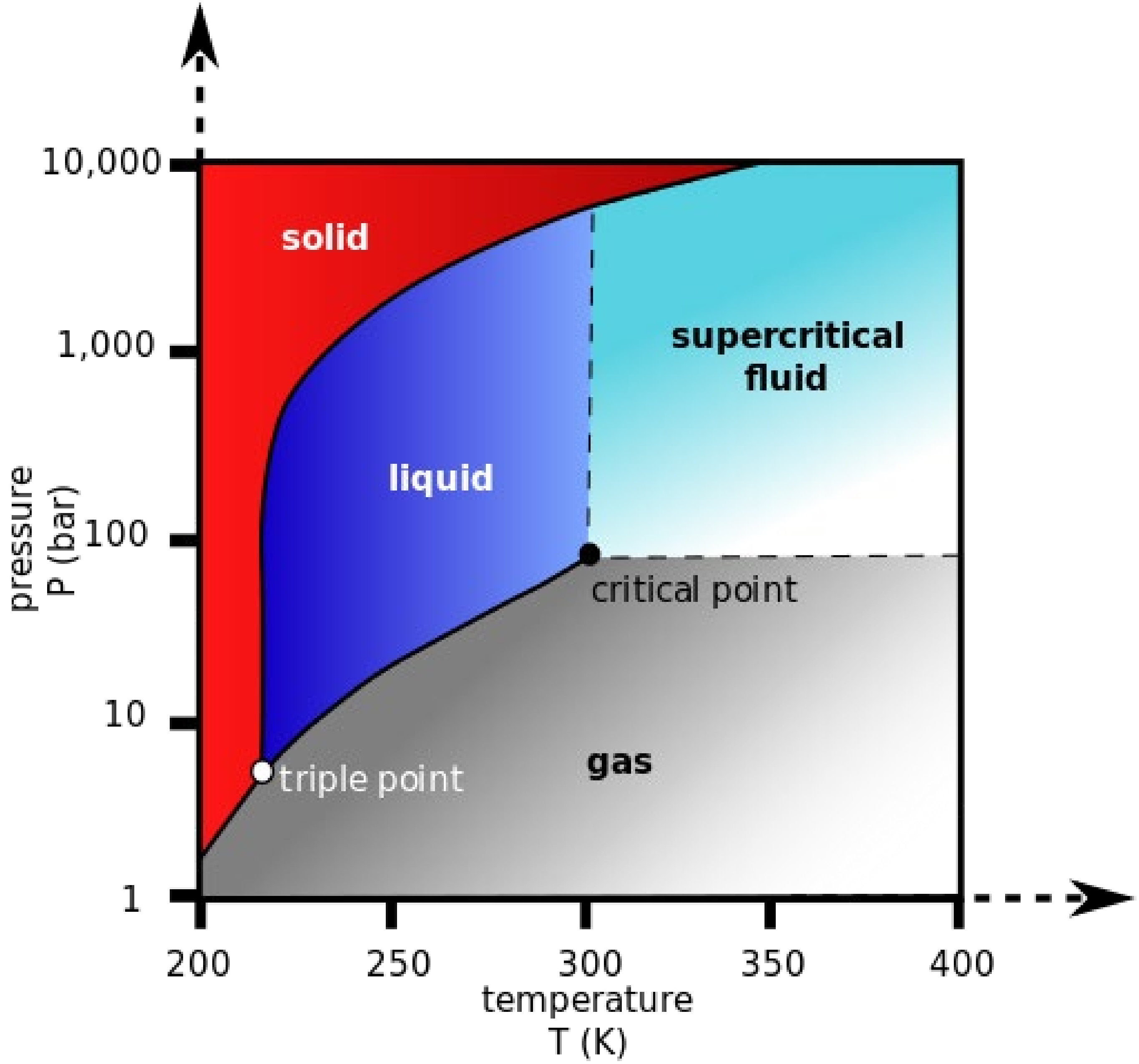
Supercritical Fluids (SCF)

- are substances at temperatures and pressures **above** their **critical points**, where distinct liquid and gas phases do not exist.

- have **properties** between those of gases and liquids.

- can **effuse** through solids (like a gas), and dissolve materials (like a liquid).

- are suitable as a substitute for **organic solvents** in a range of industrial and laboratory processes



Phase Diagram for Carbon Dioxide