Lecture 4

States' Conversions

Evaporation

The (endothermic) transformation process from the liquid state to the gaseous state. The opposite process is called condensation.

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, 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.*
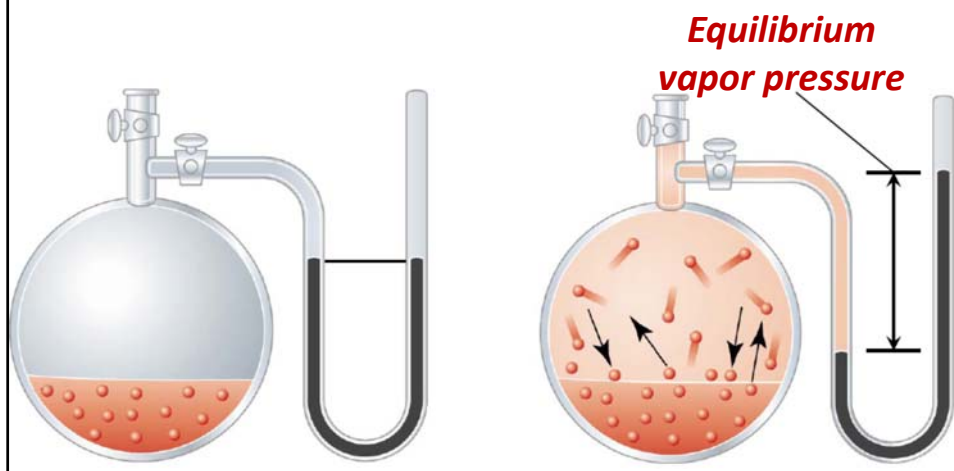
Equilibrium vapor pressure: is the maximum vapor pressure a liquid exerts at a given temperature. It is constant at a constant T

Liquids with high vapor pressure are said to be volatile.
The vapor pressure increases with temperature.
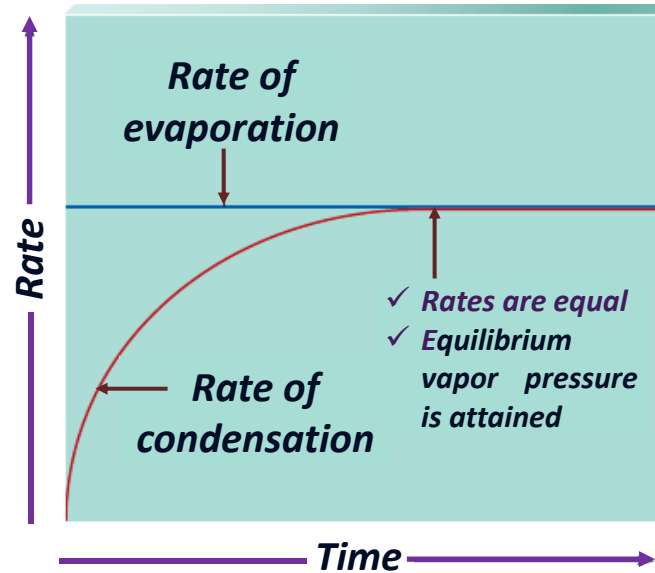

Equilibrium vapor pressure

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

Equilibrium vapor pressure

Equilibrium vapor pressure

❑ *Liquids with high vapor pressure are said to be* *volatile.*

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

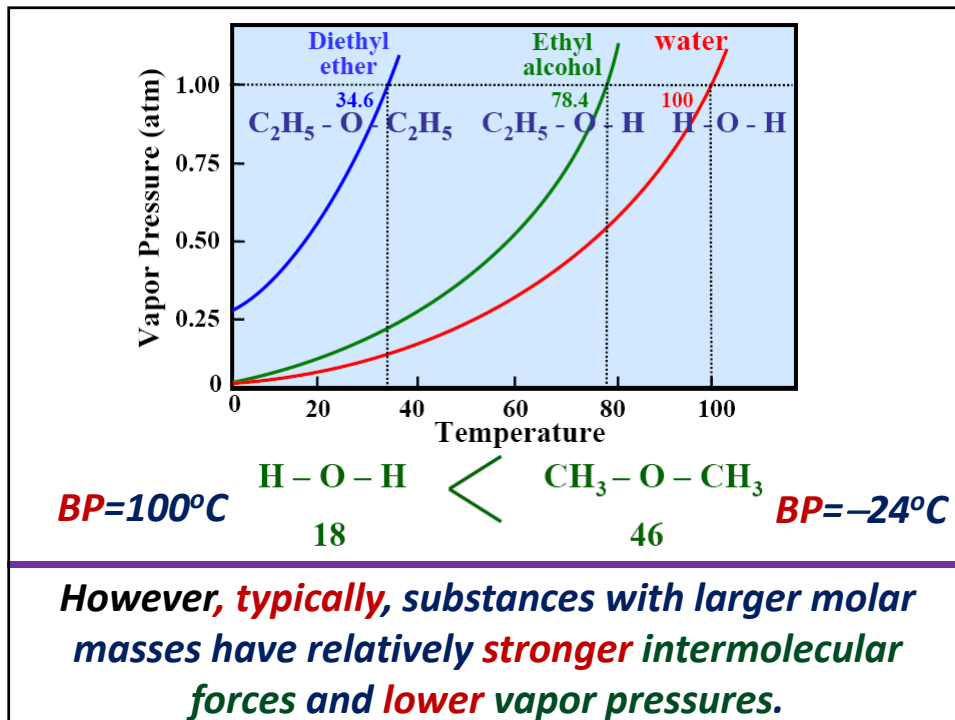*Strong intermolecular forces* → *Low equilibrium vapor pressure*
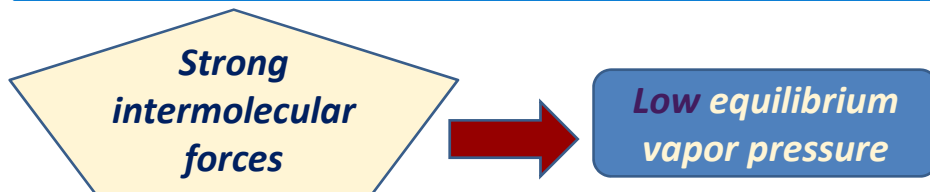
Rate of evaporation

is increased by

❑ *Heating (holding the liquid/solution at high temperature)*

❑ *Increasing the exposed surface area*

Vapor Pressure (atm) vs **Temperature**

Diethyl ether — 34.6 — $C_2H_5 - O - C_2H_5$

Ethyl alcohol — 78.4 — $C_2H_5 - O - H$

water — 100 — $H - O - H$

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

*the energy (**usually in kJ**) required to vaporize one <u>mole</u> 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

*the energy (**usually in kJ**) required to vaporize one <u>gram</u> of a liquid*

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

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

the energy (*amount of heat*) absorbed when one <u>mole</u> of a solid melts

Specific Heat of fusion, ------ ΔH_s

the energy (*amount of heat*) absorbed when one <u>gram</u> of a solid melts

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

Boiling Point, BP

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

Normal Boiling Point

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

As the strength of Intermolecular forces ↑, ΔH_{vap} ↑, BP ↑
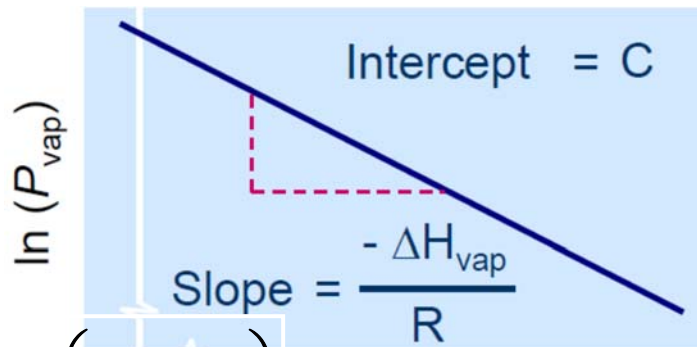
Normal Melting Point / Freezing point

the *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)

Intercept = C

$\ln (P_{vap})$

Slope $= \dfrac{-\Delta H_{vap}}{R}$

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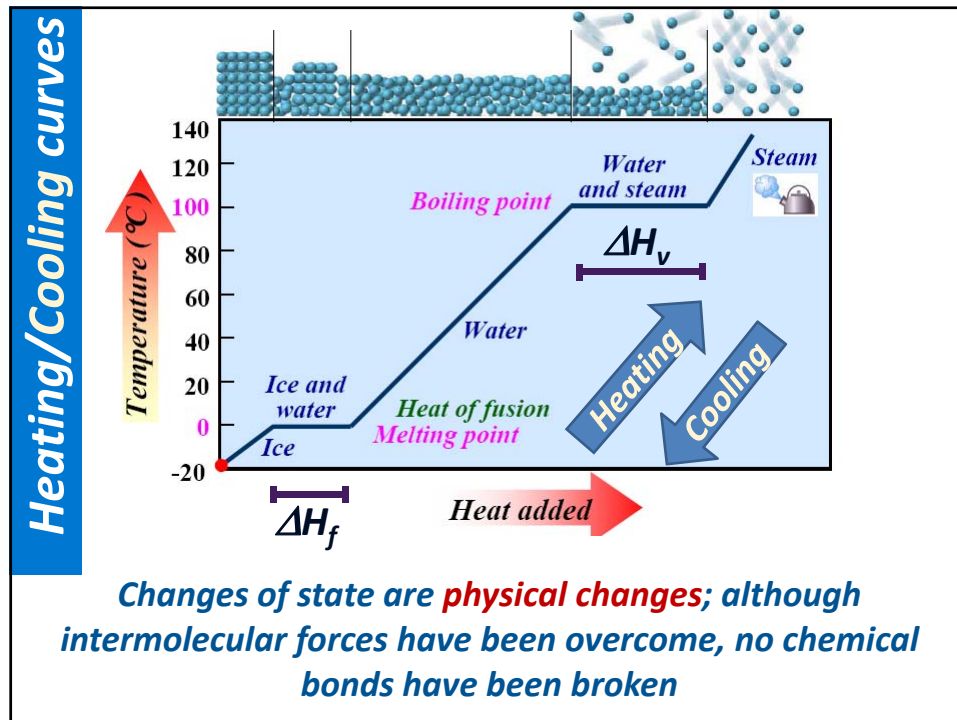
$1/T$ (K)

Exercise

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

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

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

$$\boxed{P_2 = 93.7\,torr}$$

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Heating/Cooling curves

*Changes of state are **physical changes**; 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
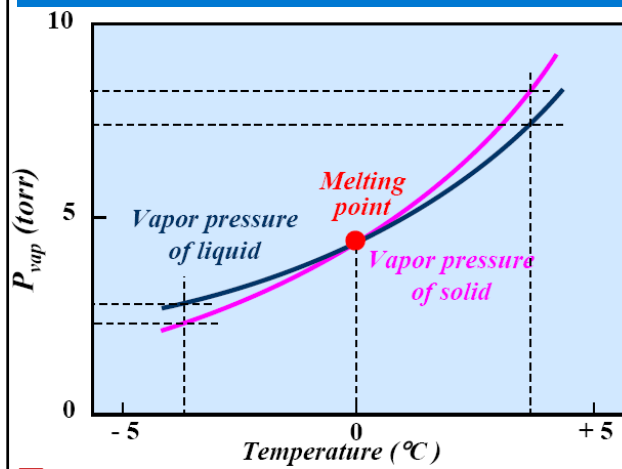
Data for liquid water below 0°C were obtained from **supercooled water.**

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 $P_{liq.H2O}$**
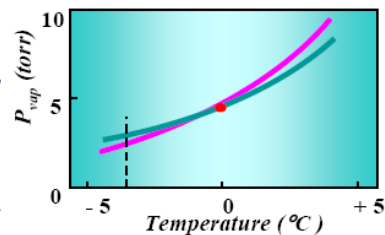
At temperatures where $P_{ice} > P_{liq.H2O}$
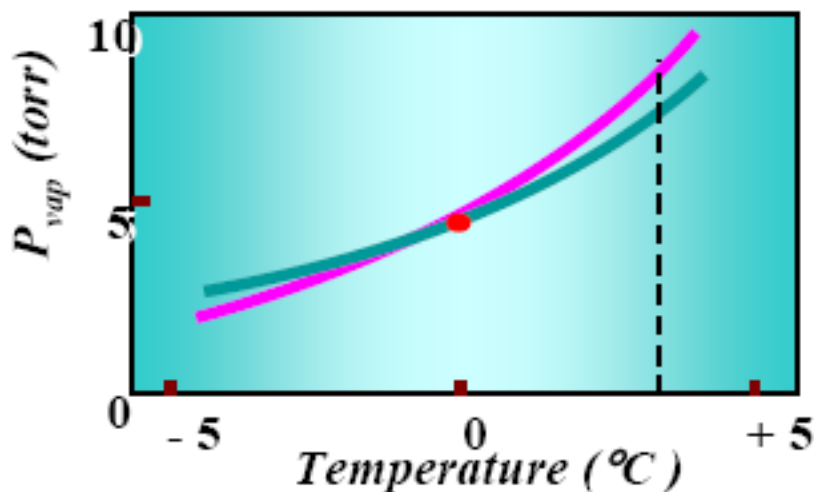
▶ **Solid requires a higher pressure than the liquid does to be in equilibrium with the vapor.**

- ▶ *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.*

water vapor

*Solid water*   *Liquid water*   *Liquid water*
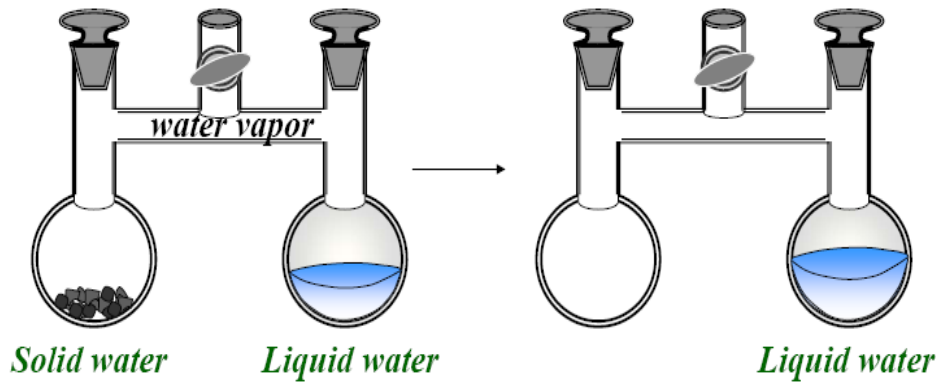
At temperatures where $P_{ice} < P_{liq.H2O}$

- ▶ *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.*

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

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

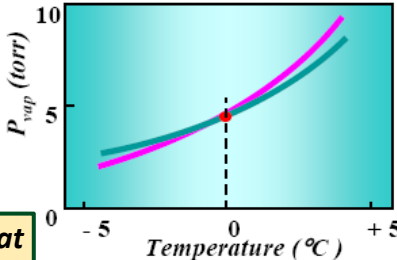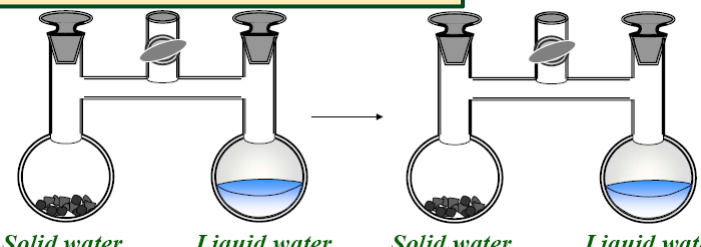*Solid water*   *Liquid water*   *Solid water*
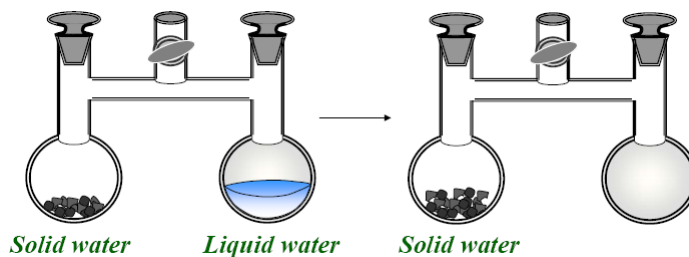
At temperatures where $P_{ice} = P_{liq.H2O}$

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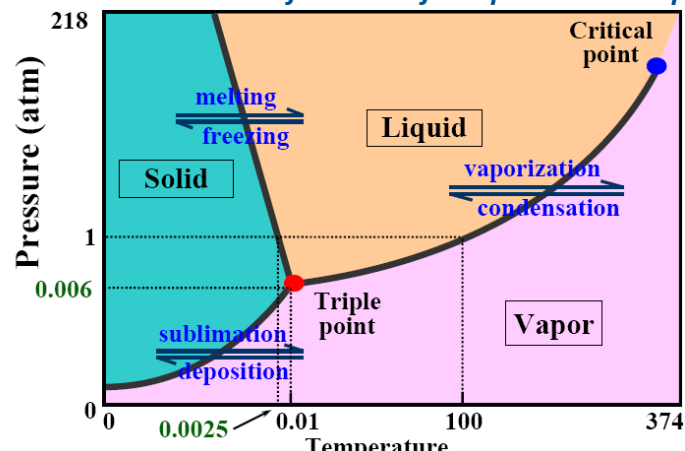
At the melting point of ice, the solid and liquid states exist.

Solid water — Liquid water — Solid water — Liquid water

Phase diagrams

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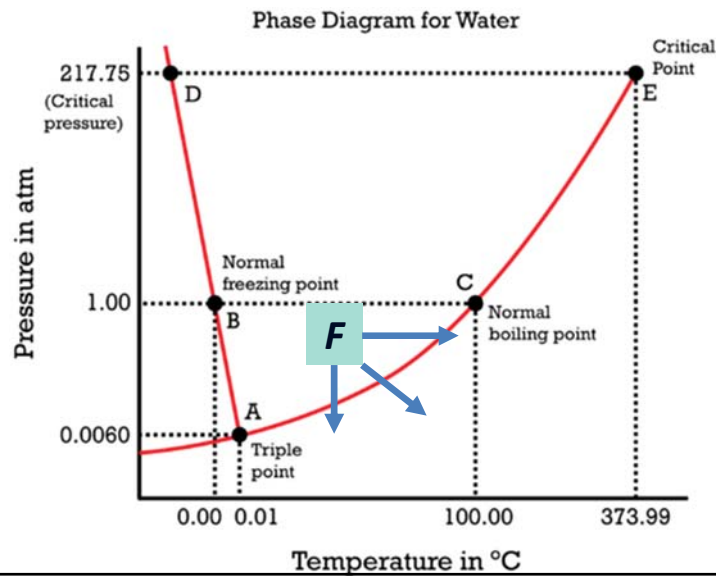
One component systems

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

► *How can you reach the vapor state from Point F?*
   ✓ *Increasing T at constant P*   ✓ *Decreasing P at constant T*
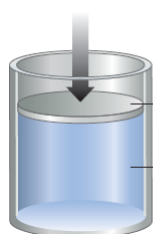   ✓ *Increasing T and decreasing P simultaneously*

Phase Diagram for Water

Sublimation

❑ *is the direct conversion from the solid state to the vapor state without passing by the liquid state.*

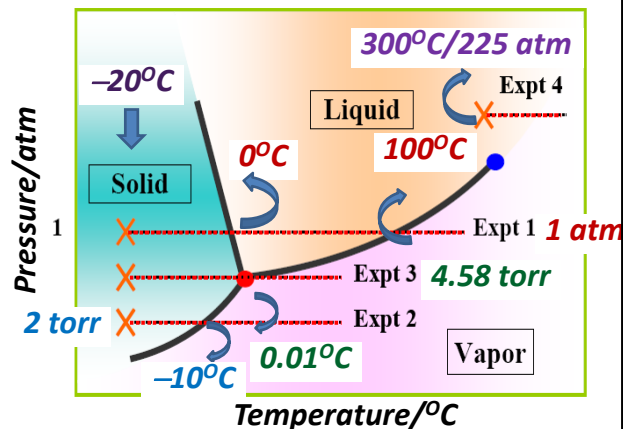❑ *occurs at the temperature at which the vapor pressure of ice equals the external pressure.*

Various heating exp. on samples of water in a closed system

Const. P = 1 atm

Movable piston

Liquid water

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

300⁰C/225 atm → $300^{0}C/225\ atm$

Expt 4

−20⁰C → $-20^{0}C$

Liquid

0⁰C → $0^{0}C$

100⁰C → $100^{0}C$

Solid

Expt 1   *1 atm*

Expt 3   *4.58 torr*

2 torr

Expt 2

0.01⁰C → $0.01^{0}C$

Vapor

−10⁰C → $-10^{0}C$

Temperature/⁰C

Pressure/atm

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 the 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 the 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.*
- *As heating proceeds, liquid gradually changes into a vapor but goes through an intermediate "fluid" region, which is neither true liquid nor vapor.*
- *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: the temperature above which the vapor cannot be liquefied no matter what pressure is applied.

Critical pressure is the pressure required to produce liquefaction at the critical temperature