STATES OF MATTER

Degrees of Freedom

- *Translational freedom* is the ability to move from one position in space to another.

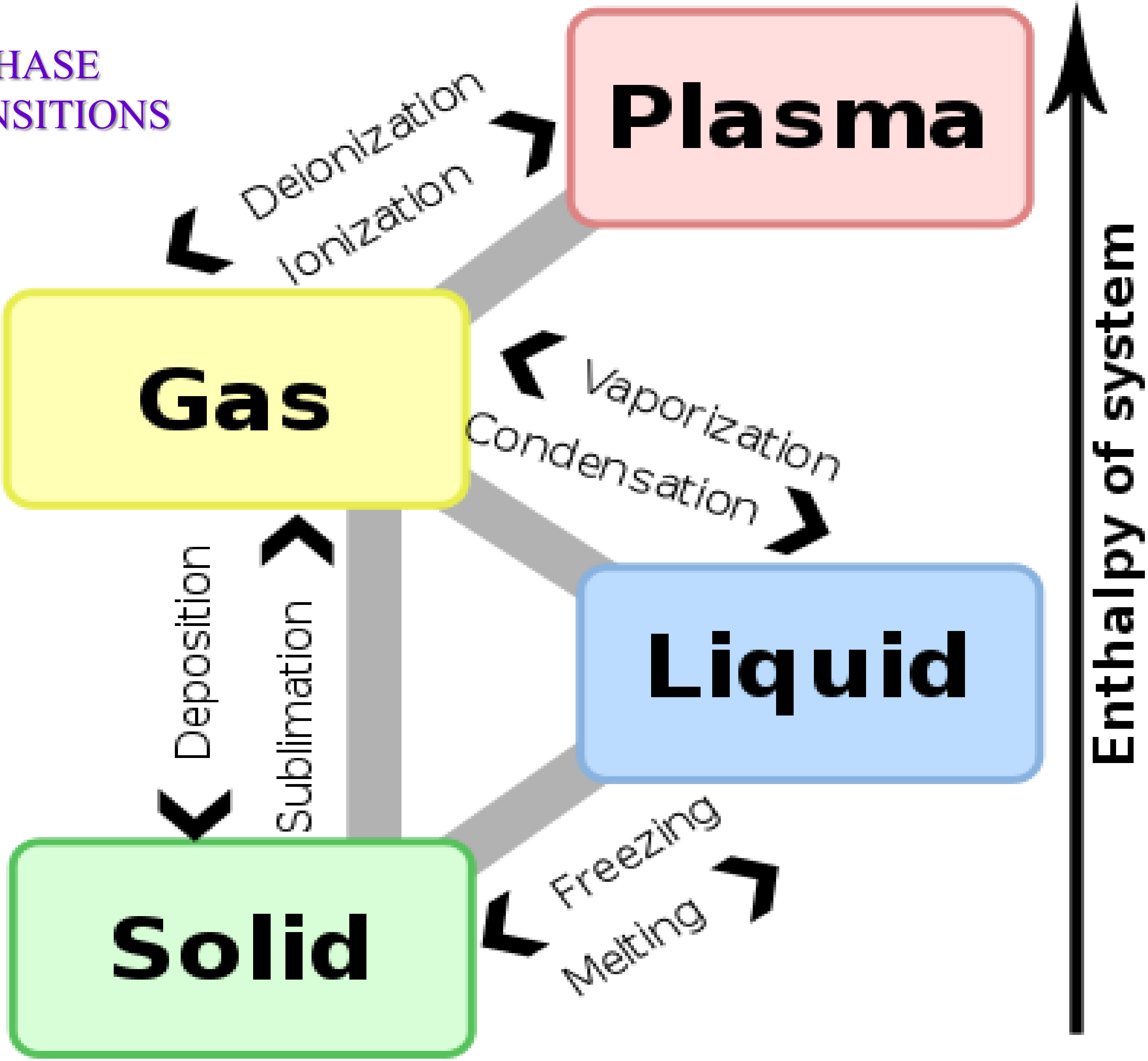
- *Rotational freedom* is the ability to reorient the particle's direction in space.

- *Vibrational freedom* is the ability to oscillate about a particular point in space.

States and Degrees of Freedom

- The molecules in a gas have complete freedom of motion.
  - *Their kinetic energy overcomes the attractive forces between the molecules.*
- The molecules in a solid are locked in place; they cannot move around.
  - *Though they do vibrate, they don't have enough kinetic energy to overcome the attractive forces.*
- The molecules in a liquid have limited freedom—they can move around a little within the structure of the liquid.
  - *They have enough kinetic energy to overcome some of the attractive forces, but not enough to escape each other.*

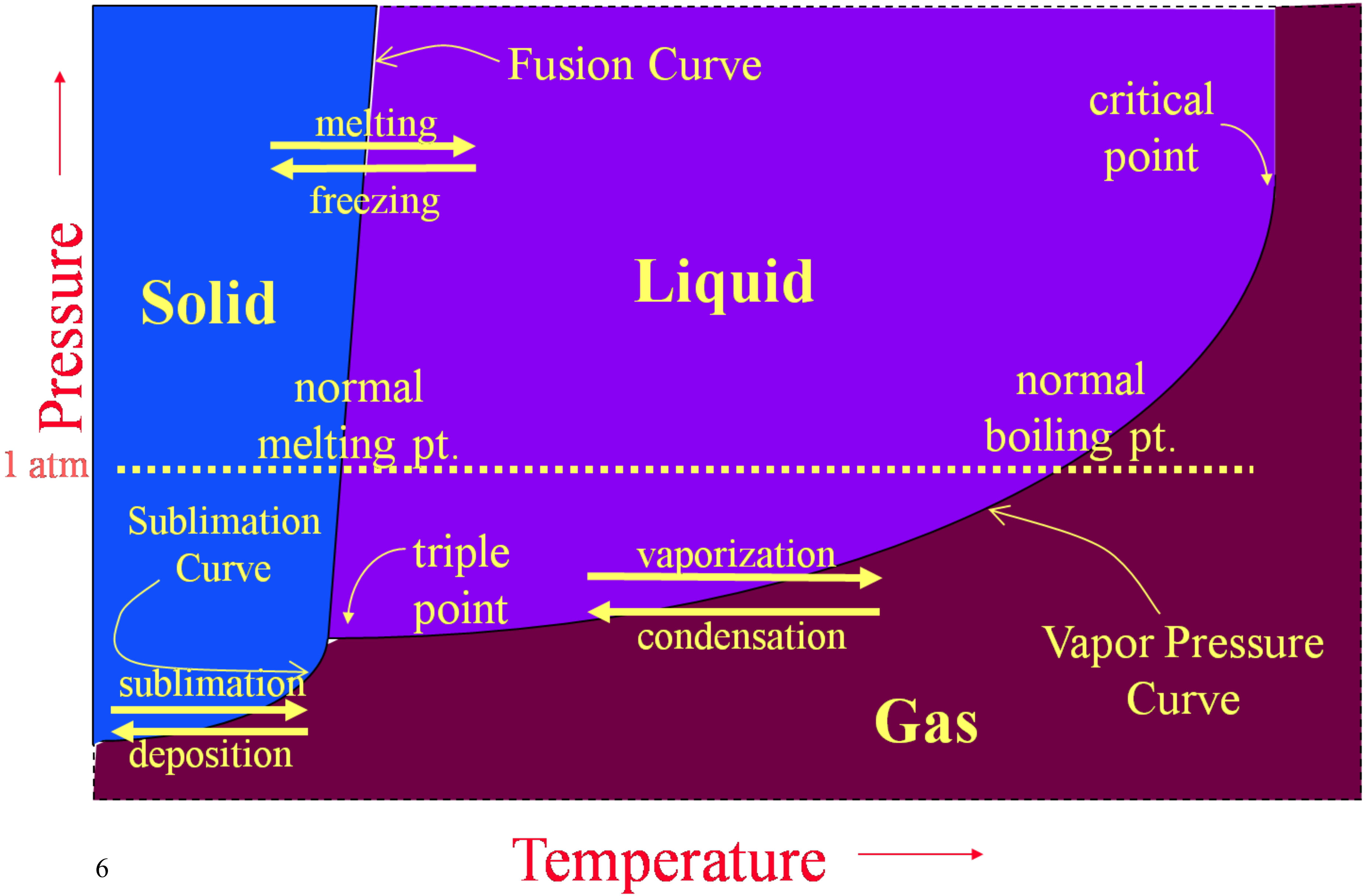
PHASE TRANSITIONS



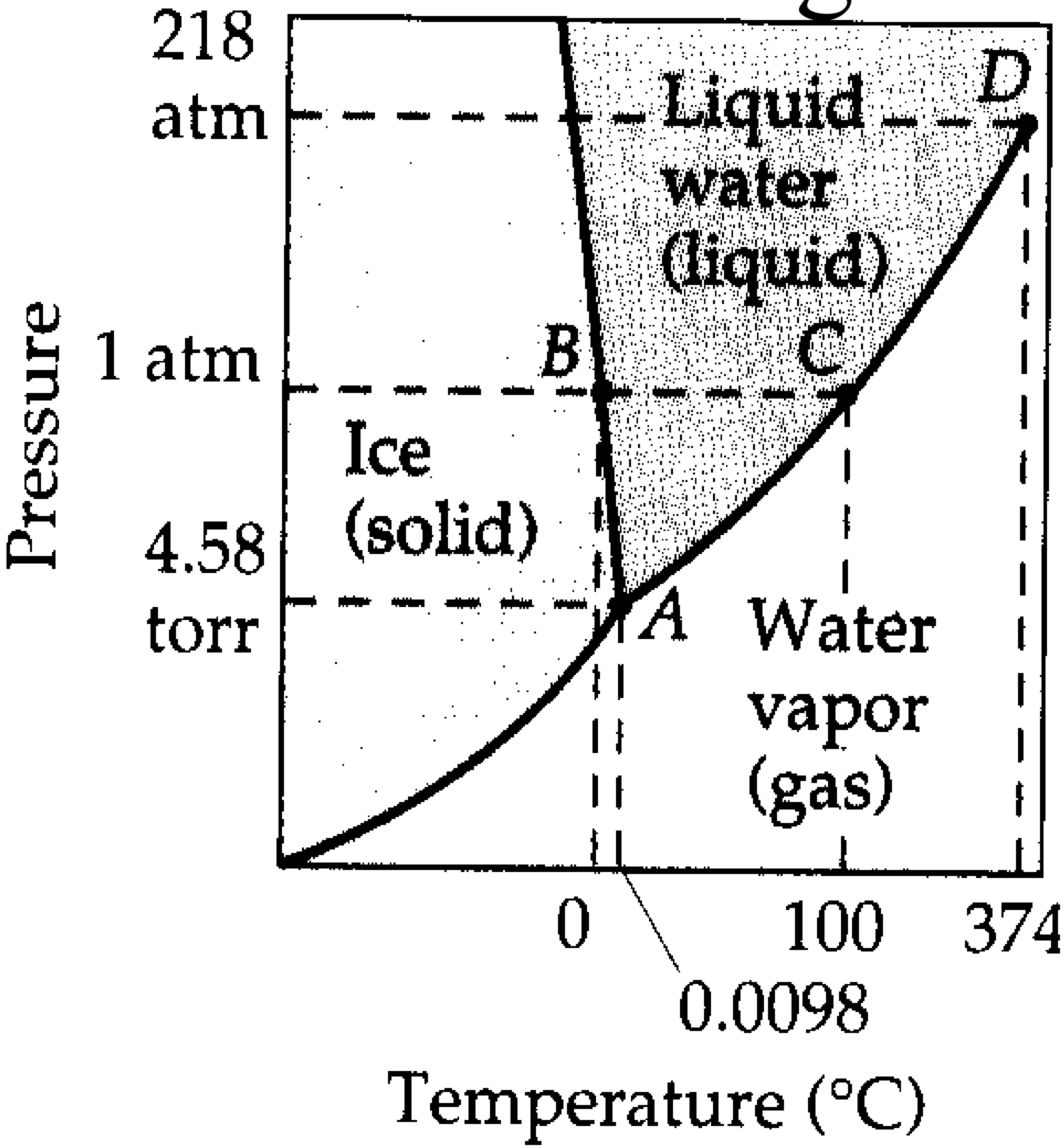
Phase Diagrams

- Phase diagrams describe the different states and state changes that occur at various temperature/pressure conditions.
- Regions represent states.
- Lines represent state changes.
  - *The liquid/gas line is the vapor pressure curve.*
  - *Both states exist simultaneously.*
  - *The critical point is the furthest point on the vapor pressure curve.*
- The triple point is the temperature/pressure condition where all three states exist simultaneously.
- For most substances, freezing point increases as pressure increases.

Phase Diagrams- detailed



Challenge



Phase Diagrams

A phase diagram allows for the prediction of the state of matter at any given temperature & pressure.

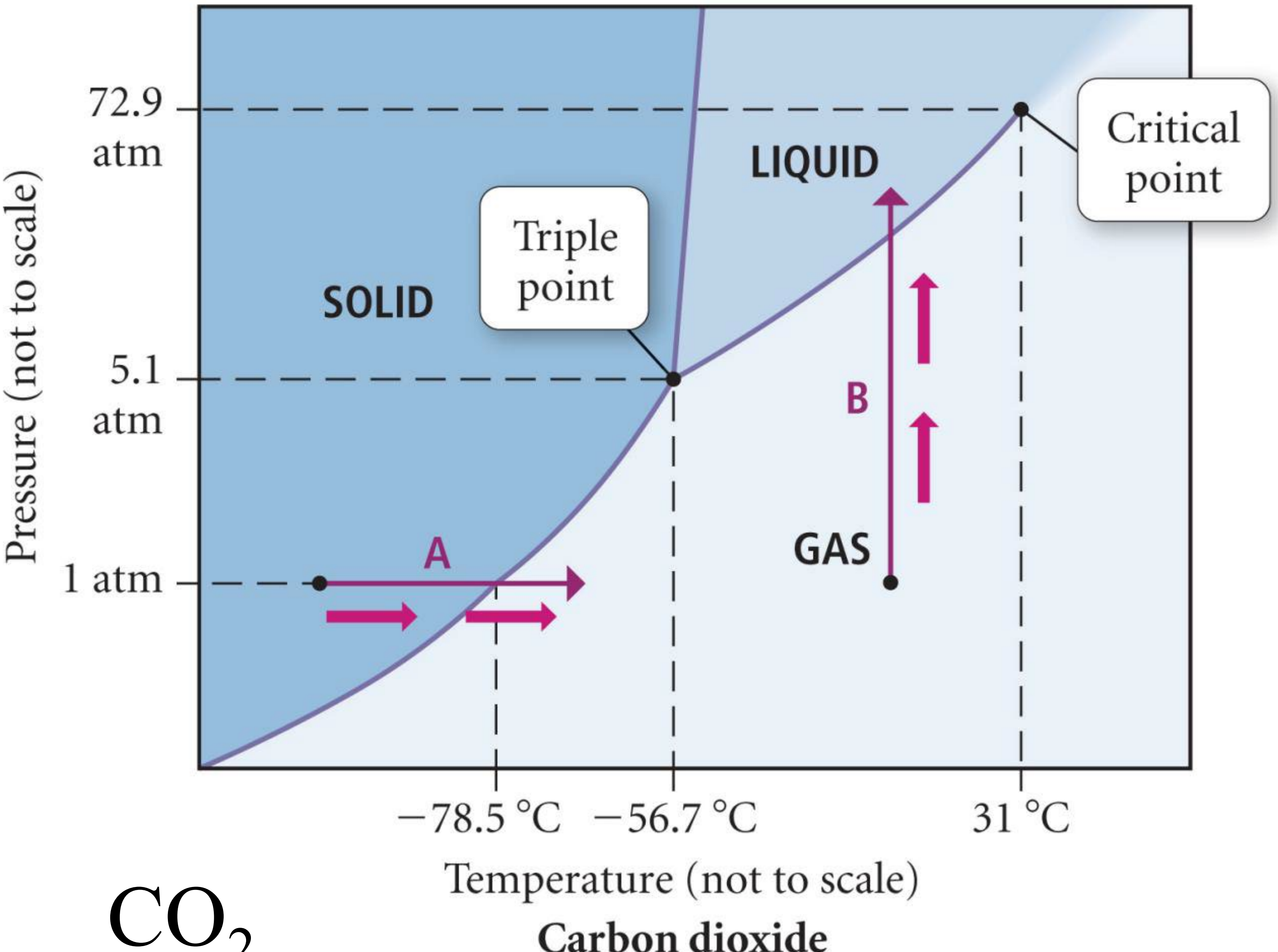
Key aspects:

-critical point*

-normal boiling point

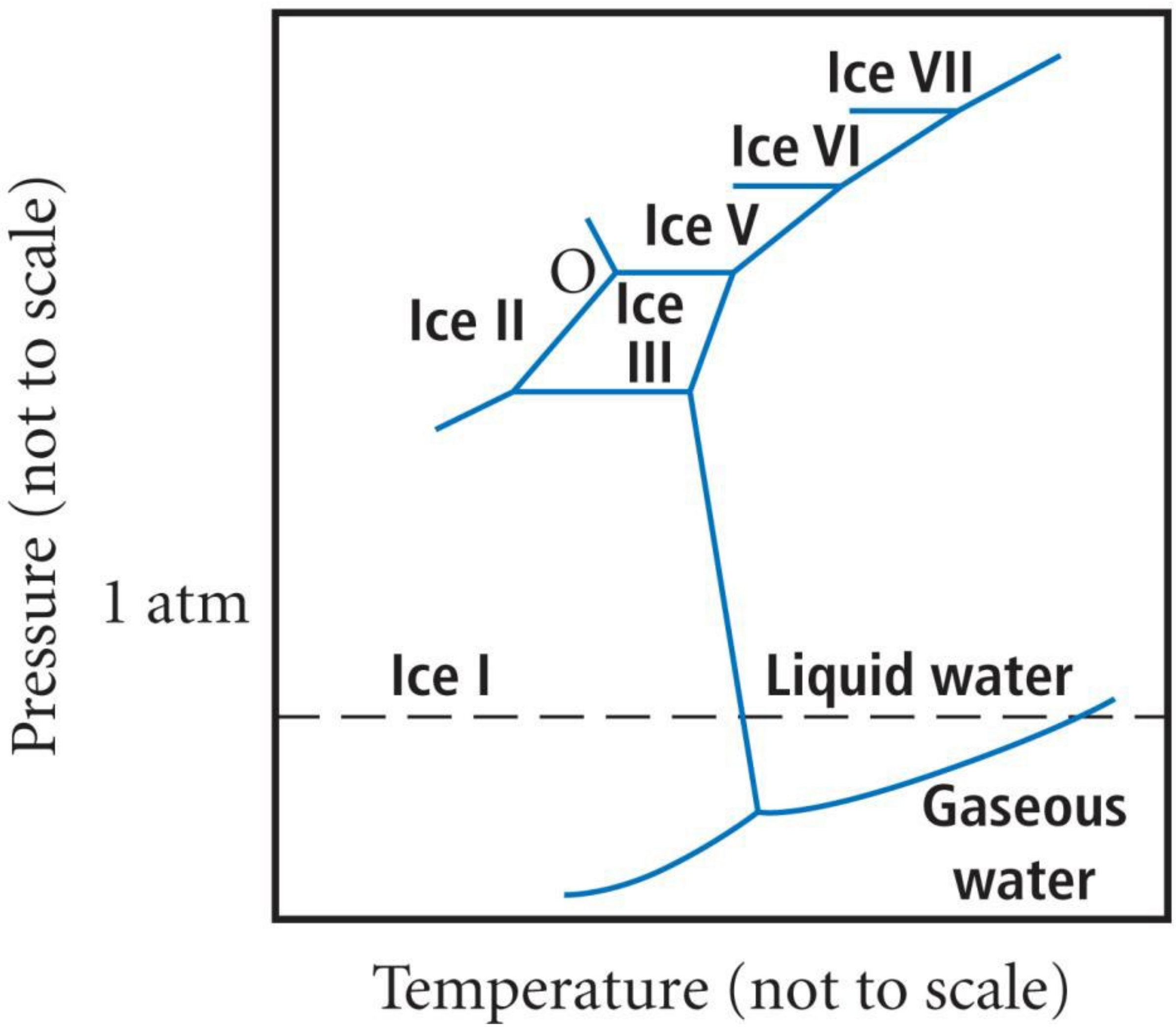
-triple point

***At the *critical temperature* or higher temperatures, the gas cannot be condensed to a liquid, no matter how high the pressure gets.**


72.9
atm
5.1
atm
1 atm
Pressure (not to scale)
SOLID
LIQUID
GAS
Triple
point
Critical
point
A
B
−78.5 °C
−56.7 °C
31 °C
Temperature (not to scale)
Carbon dioxide

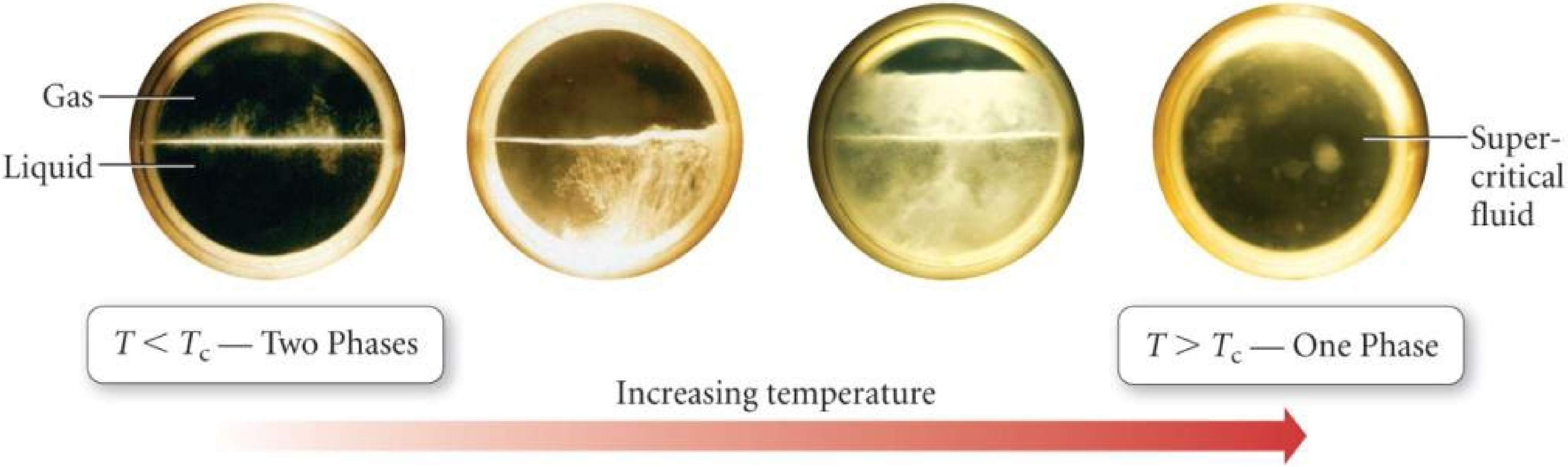
CO_2

Morphic Forms of Ice



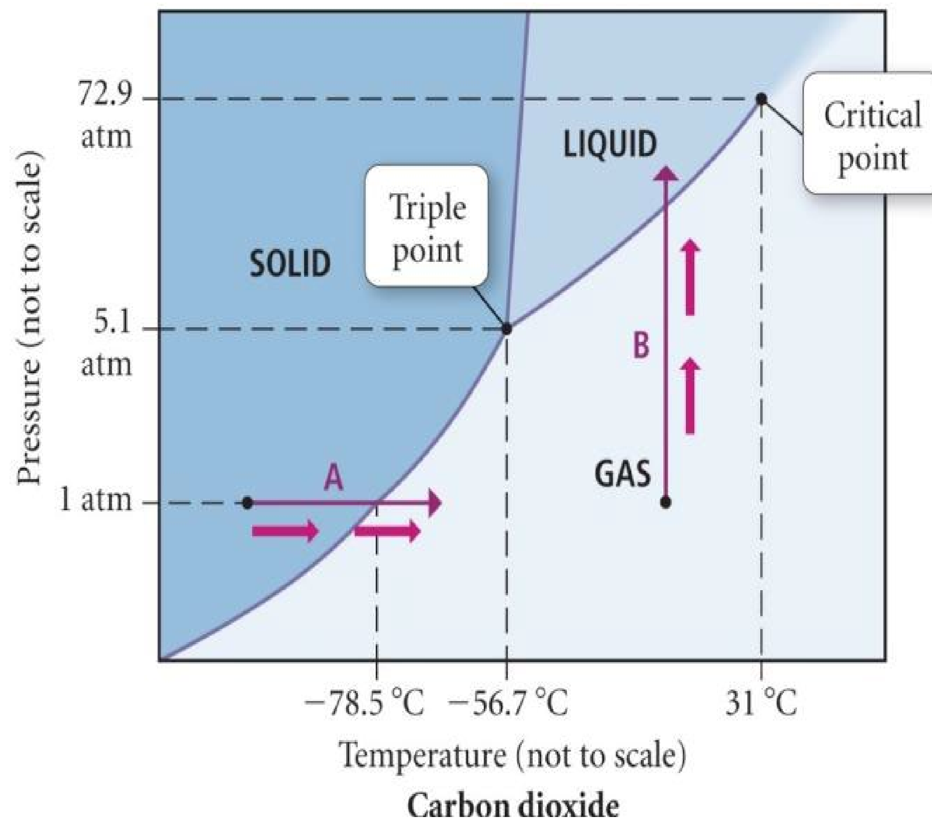
Supercritical Fluid

- As a liquid is heated in a sealed container, more vapor collects causing the pressure inside the container to rise.
  - *and the density of the vapor to increase*
  - *and the density of the liquid to decrease*
- At some temperature, the meniscus between the liquid and vapor disappears and the states commingle to form a **supercritical fluid**.
- Supercritical fluids have properties of both gas and liquid states.



Practice—Consider the phase diagram of CO_2 shown. What phase(s) is (are) present at each of the following conditions?

- **20.0 °C, 72.9 atm**
- **−56.7 °C, 5.1 atm**
- **10.0 °C, 1.0 atm**
- **−78.5 °C, 1.0 atm**
- **50.0 °C, 80.0 atm**



Heat of Fusion

- The amount of heat energy required to melt one mole of the solid is called the **heat of fusion, ΔH_{fus}**.
  - *sometimes called the enthalpy of fusion*
- always endothermic, therefore ΔH_{fus} is +
- somewhat temperature dependent
- $\Delta H_{crystallization} = -\Delta H_{fusion}$
- generally much less than ΔH_{vap}
- $\Delta H_{sublimation} = \Delta H_{fusion} + \Delta H_{vaporization}$

TABLE 11.8 Heats of Fusion of Several Substances

Liquid	Chemical Formula	Melting Point (°C)	ΔH_{fus}(kJ/mol)
Water	H_2O	0.00	6.02
Rubbing alcohol (isopropyl alcohol)	C_3H_8O	−89.5	5.37
Acetone	C_3H_6O	−94.8	5.69
Diethyl ether	$C_4H_{10}O$	−116.3	7.27

SPECIFIC HEAT re-visited

The quantity of heat required to raise the temperature of one gram of a substance by one degree Celsius (or one Kelvin)

$$q = s \times m \times \Delta T$$

ENTHALPY OF A PHASE CHANGE

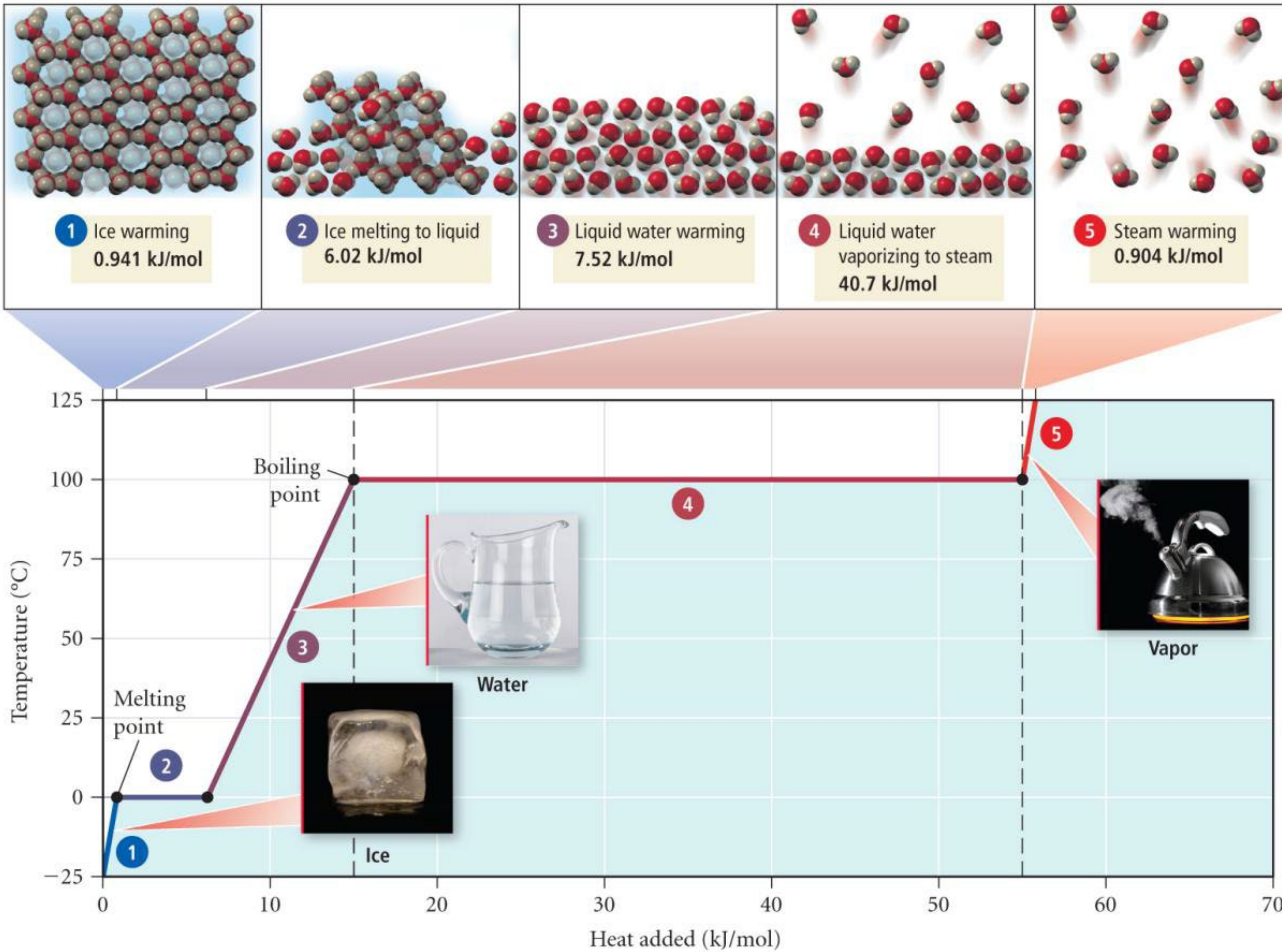
The heat energy required to undergo a change in phase occurs at constant temperature and is associated with the average change in distance between molecules.

For water:

ΔH^{o}_{fus} **= 335 J/g or 6.02 kJ/mol**

ΔH^{o}_{vap} **= 2260 J/g or 40.7 kJ/mol**

Heating Curve of Water

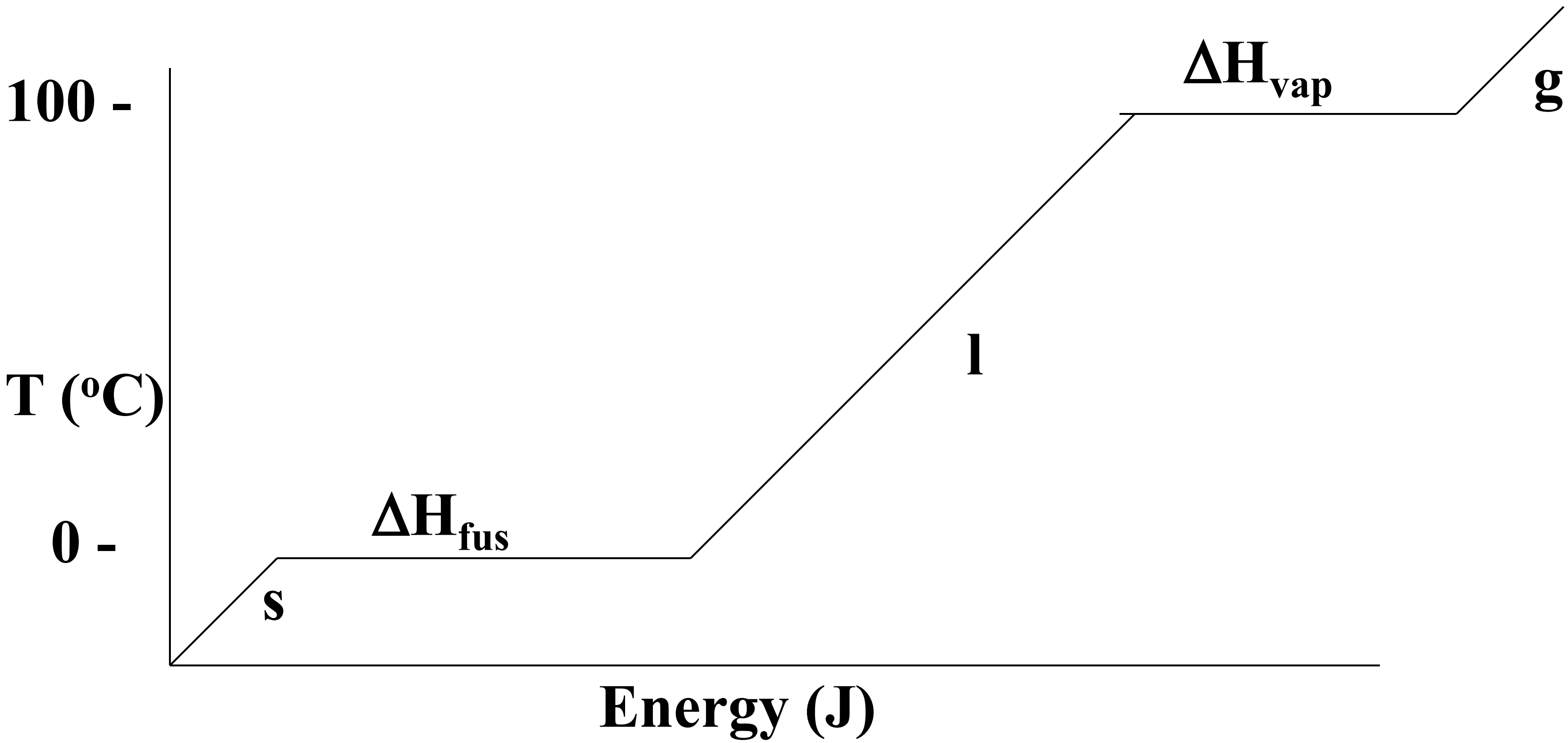


Practice—How much heat is needed to raise the temperature of a 12.0-g benzene sample from −10.0 °C to 25.0 °C?

Given:	**12.0 g benzene, seg 1 (T_1 = −10.0 °C, T_2 = 5.5 °C), seg 2 = melting, seg 3 (T_1 = 5.5 °C, T_2 = 25.0 °C)** **12.0 g benzene, seg 1 = 0.2325 kJ, seg 2 = 1.51 kJ, seg 3 = 0.3978 kJ**
Find:	**kJ**
Conceptual Plan:	Seg 1, Seg 3: $q = m \bullet C_s \bullet \Delta T$, $\frac{1\text{ kJ}}{1000\text{ J}}$ Seg 2: g → mol → kJ, $\frac{1\text{ mol}}{78.11\text{ g}}$, $\frac{9.8\text{ kJ}}{1\text{ mol}}$
Relationships:	**ΔH_{fus} 9.8 kJ/mol, 1 mol = 78.11 g, 1 kJ = 1000 J, $q = m \cdot C_s \cdot \Delta T$** **$C_s$,sol = 1.25 J/g °C, C_s,liq = 1.70 J/g °C**
Solution:	$q = m \bullet C_s \bullet \Delta T$ $= (12.0\text{ g}) \bullet (1.25\ \frac{\text{J}}{\text{g}\cdot°\text{C}}) \bullet (5.5 - (-10.0)\ °\text{C})$ $= 232.5\text{ J} = 0.2325\text{ kJ}$ $12.0\text{ g} \times \frac{1\text{ mol}}{78.11\text{ g}} \times \frac{9.8\text{ kJ}}{1\text{ mol}} = 1.51\text{ kJ}$ $q = (12.0\text{ g}) \bullet (1.70\ \frac{\text{J}}{\text{g}\cdot°\text{C}}) \bullet (25.0 - (5.5)\ °\text{C}) = 397.8\text{ J} = 0.3978\text{ kJ}$ $q_T = q_1 + q_2 + q_3$ $q = 0.2325\text{ kJ} + 1.51\text{ kJ} + 0.3978\text{ kJ}$ $q = 2.1403 = 2.1\text{ kJ}$

HEATING - COOLING CURVE

Calculate the amount of energy required to convert 15.0 g of ice at -0.5 ^oC to steam at 125.0^oC



$$q_{total} = q_{(s)} + \Delta H_{fus} + q_{(l)} + \Delta H_{vap} + q_{(g)}$$

Water and the Changes of State

Q. How many kilojoules of energy are needed to change 15.0 g of ice at -5.00 ^oC to steam at 125.0 ^oC?

The first step is to design a pathway:

$q_1 = ms\Delta T$ for ice from -5.0 to 0.0 ^oC, the specific heat of ice is 4.213 J/g ^oC

$q_2 = \Delta H_{fus}$ for ice to liquid at 0.0 ^oC

$q_3 = ms\Delta T$ for liquid 0.0 ^oC to 100.0 ^oC

$q_4 = \Delta H_{vap}$ for liquid to steam at 100.0 ^oC

$q_5 = ms\Delta T$ for steam 100.0 to 125.0 ^oC; the specific heat of steam is 1.900 J/g ^oC

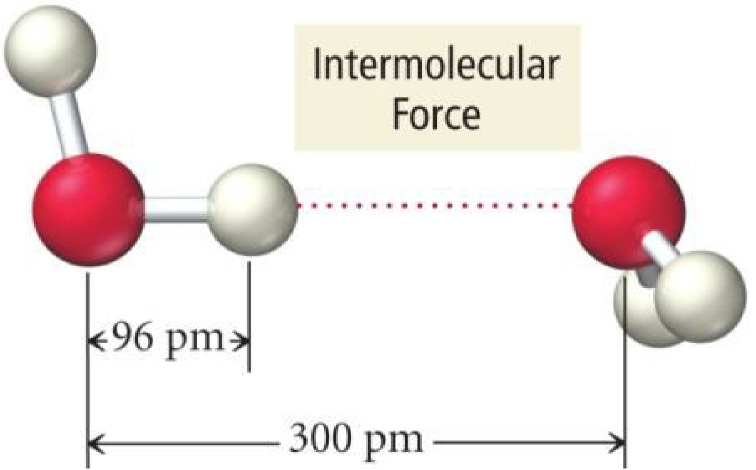
so $q_T = q_1 + q_2 + q_3 + q_4 + q_5$

The next step is to calculate each q:

INTERMOLECULAR FORCES

Why are molecules attracted to each other?

- Intermolecular attractions are due to attractive forces between opposite charges.
  - *+ ion to − ion*
  - *+ end of polar molecule to − end of polar molecule*
    - *H-bonding especially strong*
  - *Even nonpolar molecules will have temporary charges.*
- **larger the charge = stronger attraction**
- **longer the distance = weaker attraction**
- However, these attractive forces are small relative to the bonding forces between atoms.
  - *generally smaller charges*
  - *generally over much larger distances*



INTERMOLECULAR FORCES - types

INTRAMOLECULAR > INTERMOLECULAR

(covalent, ionic)
" between atoms"

(van der Waals, etc)
"between molecules"

TYPES

Neutral Molecules:

1. London Dispersion
2. Dipole-dipole forces
3. Hydrogen bonding

Ions:

1. Ion-dipole force

Intermolecular Forces- description

- **London Dispersion Forces:** Also called Induced dipole forces. An instantaneous dipole is created within the atom or molecule via the instantaneous movement of the electrons around the nucleus. All molecules have LDF.
- **Dipole-Dipole Forces:** The attractive force between molecules due to the existence of an overall dipole moment. Polar molecules have d-d forces.
- **Hydrogen Bonding:** The attractive force between a highly electronegative atom of one molecule with the hydrogen on another molecule also containing a very electronegative atom. N, O, F are the electronegative atoms.

HYDROGEN BONDING

AN INTERMOLECULAR ATTRACTION THAT EXISTS BETWEEN A ***HYDROGEN ATOM*** IN A POLAR BOND AND AN UNSHARED ELECTRON PAIR ON A NEARBY ELECTRONEGATIVE SPECIES, USUALLY

O, **F**, and **N**

NOTE: (A special type of dipole-dipole interaction)

- **stronger than dipole-dipole and London dispersion forces**

- **Accounts for water's unusual properties**
  - **high boiling point**
  - **solid Less dense than liquid**
  - **universal solvent**
  - **high heat capacity**

Example : Determine if dipole–dipole attractions occur between CH_2Cl_2 molecules.

Given: CH_2Cl_2, EN C = 2.5, H = 2.1, Cl = 3.0

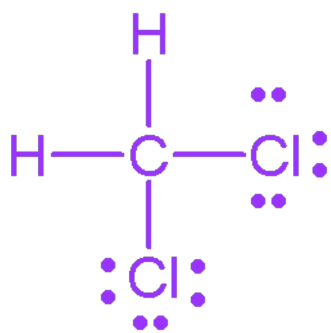
Find: Are dipole–dipole attractions present?

Conceptual Plan: Formula → Lewis Structure → Bond Polarity → Molecule Polarity

Shape EN Difference

Relationships: Molecules that have dipole–dipole attractions must be polar.

Solution:



Cl—C

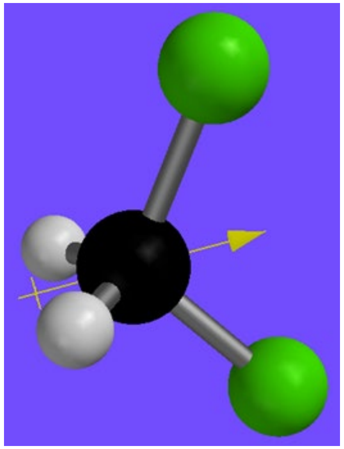
3.0 − 2.5 = 0.5

polar

C—H

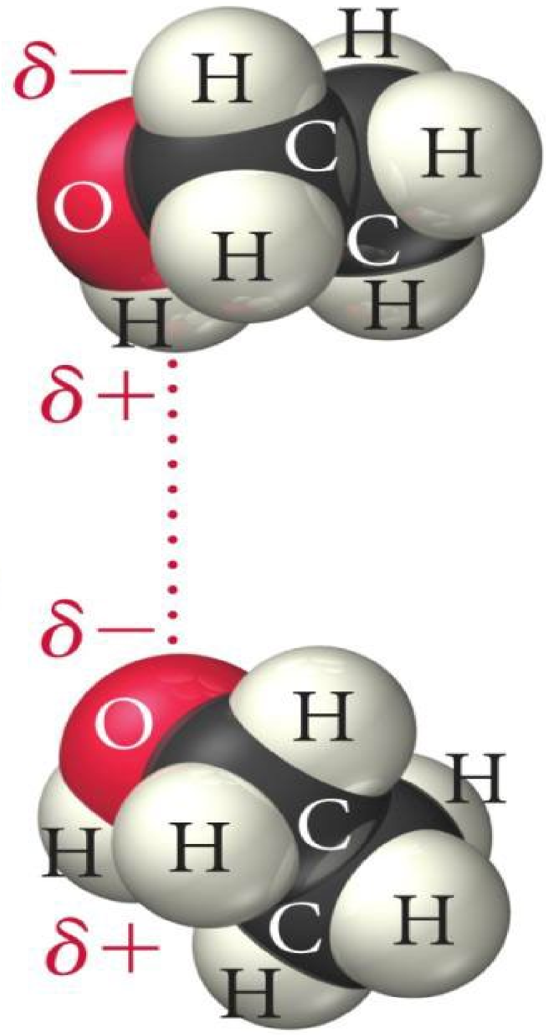
2.5 − 2.1 = 0.4

nonpolar



polar molecule; therefore dipole–dipole attractions

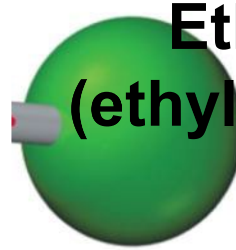
Polar Solvents



Dichloromethane (methylene chloride)

Water

Ethanol (ethyl alcohol)

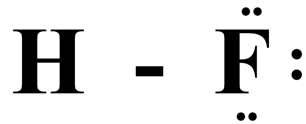


resent

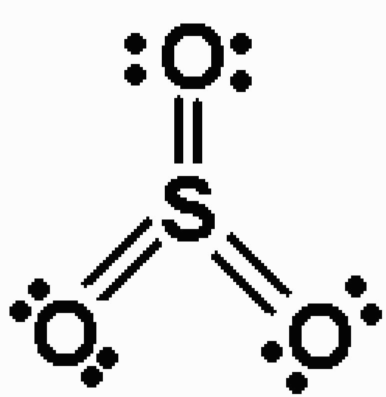
Lecture examples

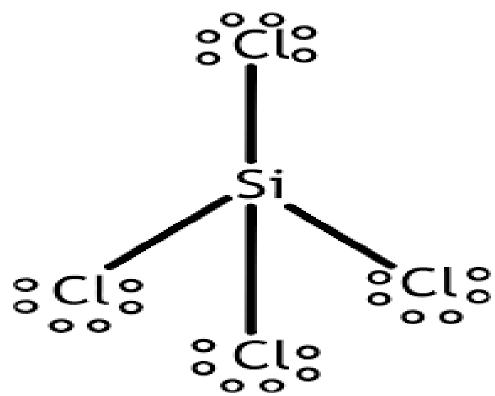
List the intermolecular force(s) that pertain to the following compounds.

a) HF **b) SO_3** **c) H_2S** **d) CO** **e) $SiCl_4$**



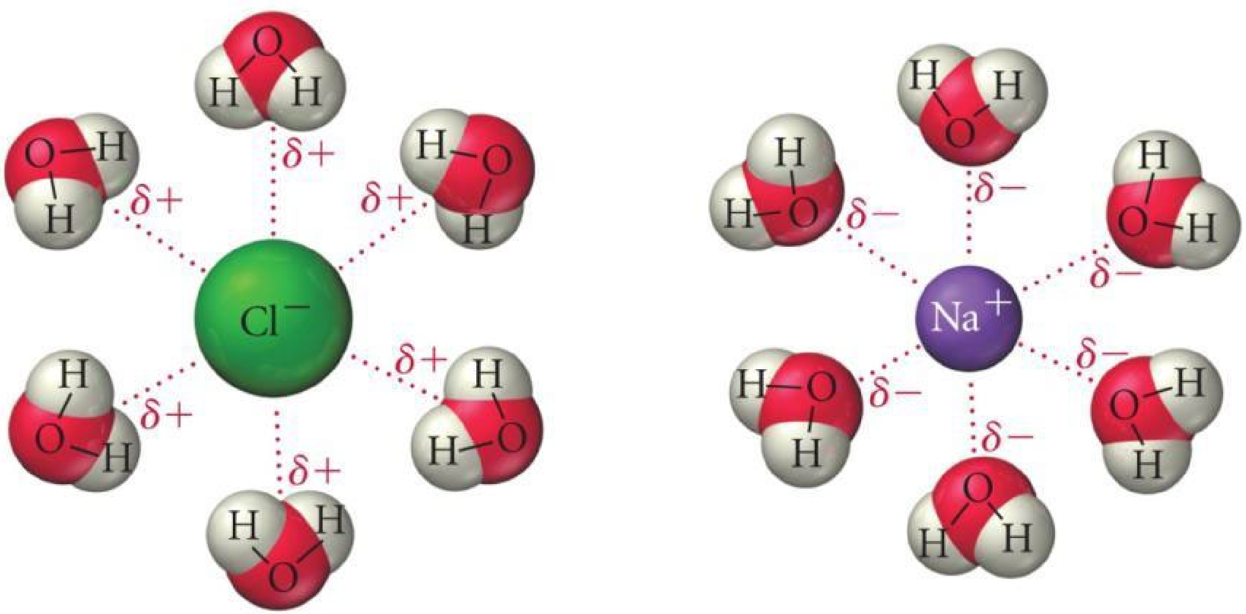
step1: draw structure
step2: determine dipole moments
step3: identify the IMF





Ion–Dipole Attraction

- In a mixture, ions from an ionic compound are attracted to the dipole of polar molecules.
- The strength of the ion–dipole attraction is one of the main factors that determines the solubility of ionic compounds in water.



FLOWCHART OF INTERMOLECULAR FORCES

Interacting molecules or ions

Are ions involved?

- **NO** → **Are polar molecules involved?**
  - **NO** → **London forces only (induced dipoles)**
    Examples: Ar(l), I_2(s)
  - **YES** → **Are hydrogen atoms bonded to N, O, or F atoms?**
    - **NO** → **Dipole-dipole forces**
      Examples: H_2S, CH_3Cl
    - **YES** → **hydrogen bonding**
      Examples liquid and solid H_2O, NH_3, HF
- **YES** → **Are polar molecules and ions both present?**
  - **Yes** → **Ion-dipole forces**
    Example: KBr in H_2O
  - **NO** → **Ionic Bonding**
    Examples: NaCl, NH_4NO_3

Van der Waals forces