

1412 - E1  
CH 10 - Liquids & Solids (IMFs)  
Notes

10

# CHAPTER 10 LIQUIDS AND SOLIDS (IMFs)

## Intermolecular Forces [10.1]

Question: *¿ What makes something a solid, liq, gas?  
¿ " " " viscous, and something else not?  
¿ What govern physical properties in general?*

Answer: *Relative proportions of IMF & KE.*

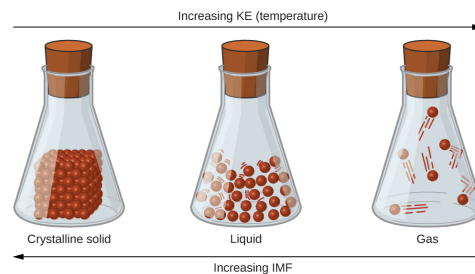
### IMF (Intermolecular Forces) vs KE (Kinetic Energy)

#### INTERMOLECULAR FORCES OF ATTRACTION

- vehicle through which atoms and molecules interact
- they are often pulled toward each other (analogous to the moon and the earth)
- vehicle through which they "feel" the presence of one another

#### KINETIC ENERGY (KE)

- provides the energy to overcome attractive forces



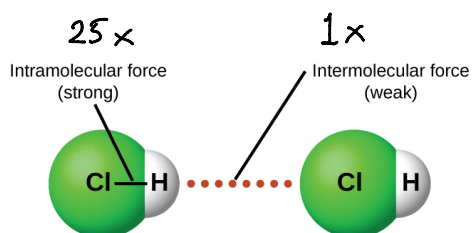
## Forces Between Molecules

### VAN DER WAALS

- collective term for all attractive forces between neutral species
- there are three “types” of van der Waals forces.

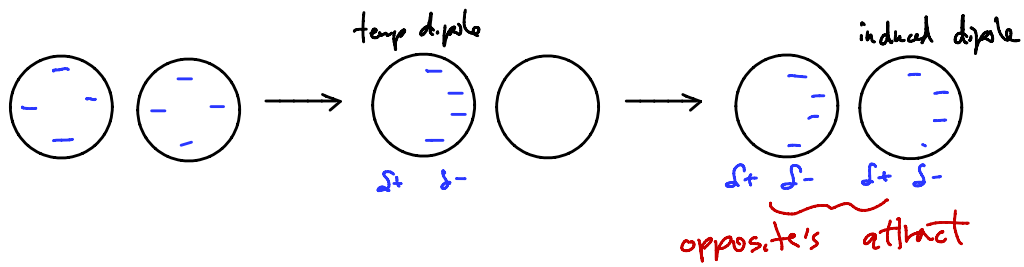
### THREE TYPES OF van der WAALS FORCES

- Dispersion Forces (aka London Forces) — these are the weakest
- Dipole–Dipole — these are intermediate in strength
- Hydrogen Bonding — these are the strongest



(NOTE: a fourth oft-discussed force is ION-ION, but these are not van der Waals, as the species are not neutral.)

## Dispersion Forces



- Dispersion forces are fleeting, but nevertheless significant... as soon as they disappear, they re-appear
- Extremely weak, but ever-present

(EX) ¿For the halogens shown in the following tabl, explain the BP and FP trends interms of intermolecular forces (IMF's)?

Melting and Boiling Points of the Halogens

Halogen	Molar Mass	Atomic Radius	Melting Point	Boiling Point
fluorine, F <sub>2</sub>	38 g/mol	72 pm	53 K	85 K
chlorine, Cl <sub>2</sub>	71 g/mol	99 pm	172 K	238 K
bromine, Br <sub>2</sub>	160 g/mol	114 pm	266 K	332 K
iodine, I <sub>2</sub>	254 g/mol	133 pm	387 K	457 K
astatine, At <sub>2</sub>	420 g/mol	150 pm	575 K	610 K

Table 10.1

The size of the halogens ↑ from top to bottom; as indicated by both MM and AR... ↑ size, ↑ opportunity for Temporary Dipole interaction ... ↑ int, ↑ BP, MP.

- The larger the size, the easier it is to distort the electron cloud
- The ease (or unease) with which an electron cloud distorts is known as POLARIZABILITY  
... "more polarizable" means the electron cloud is more easily distorted, and hence readily participates in Temp Dipole-Induced Dipole interactions

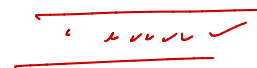
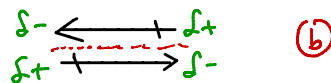
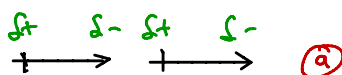
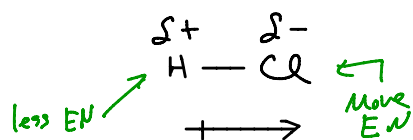


## So, just how does a Gecko work?

Besides selling insurance, they can walk upside down on a ceiling, despite gravity. How do they do it?

- Toes  $\Rightarrow$  Hairs (setae)  $\Rightarrow$  branched tips (spatulae)
- Surface area is enough to hold Gecko in place
- "Unsticks" by folding-in tips,  $\downarrow$  area,  $\downarrow$  Load.

## Dipole-Dipole Attractions



### Case Study: HCl vs. F<sub>2</sub>

i @ 150°C, HCl & F<sub>2</sub> have (a) similar MM, (b) same # atoms, (c) same KE  
 but ... bp (HCl) = 188 K vs. bp (F<sub>2</sub>) = 85 K. Why?

ANS: HCl has both Dispersion & Dipole-Dipole forces,  
 whereas F<sub>2</sub> only Dispersion forces.

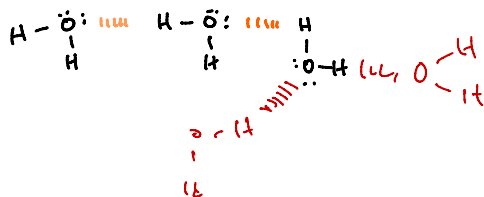
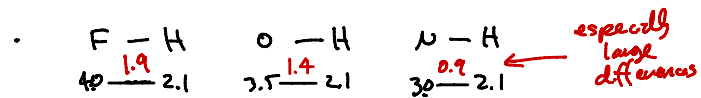
### Relative Strengths

dispersion < polar



# Hydrogen Bonds

- F-H O-H N-H
- particularly strong variant of dipole-dipole.



## Relative Strengths

dispersion < polar < H-bonding < ion

(EX) Arrange the following in order of increasing BP: HBr, HF, HI, HCl?

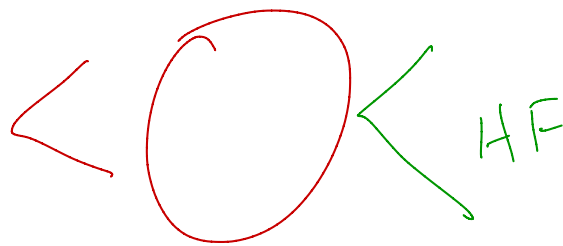
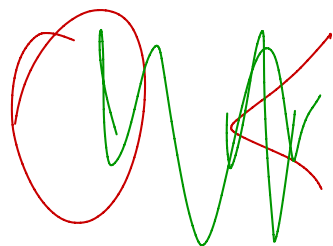
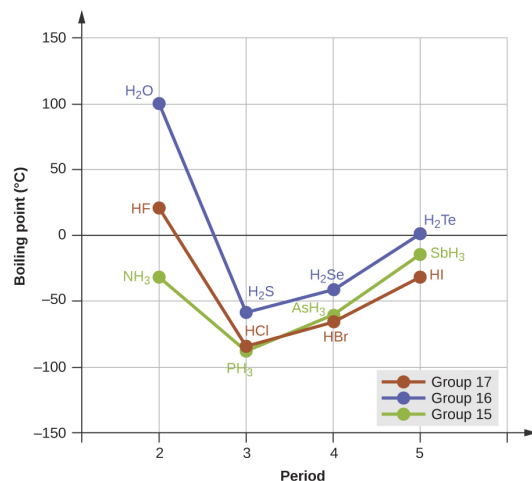
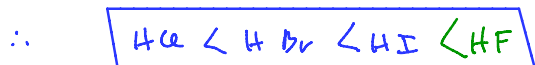


① these represent a Homologous series. (1-differs)

② as go from top to bottom, polarity ↑ a little, but size a lot, so, London forces still rule:



However... unlike the others, HF can participate in very strong H-bonding, which overrules Dispersion force,



# PROPERTIES OF LIQUIDS [10.2]

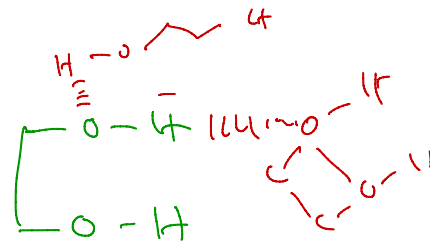
## Viscosity

- resistance to flow -  $\uparrow$  IMF,  $\uparrow$  Viscosity
- det'd by COHESIVE FORCES, IMF's between IDENTICAL molecules.  
(ADHESIVE FORCES = IMF's between DIFFERENT TYPES of molecules)
- Logic: Stronger Cohesive Forces, more resistance to flow,  $\uparrow$  Viscosity

Viscosities of Common Substances at 25 °C

Substance	Formula	Viscosity (mPa·s)
water	H <sub>2</sub> O	0.890
mercury	Hg	1.526
ethanol	C <sub>2</sub> H <sub>5</sub> OH	1.074
octane	C <sub>8</sub> H <sub>18</sub>	0.508
ethylene glycol	CH <sub>2</sub> (OH)CH <sub>2</sub> (OH)	16.1
honey	variable	~2,000-10,000
motor oil	variable	~50-500

Table 10.2

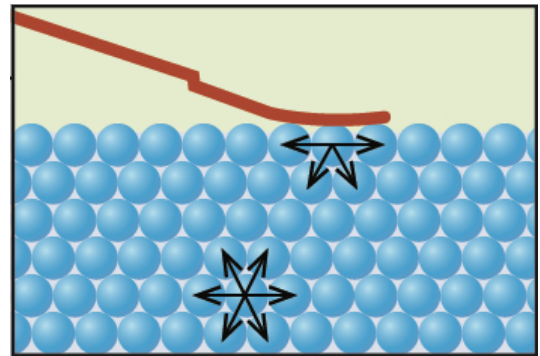


## Surface Tension

- energy required to  $\uparrow$  surface area of liquid.
- surface molecules have higher energy than internal molecules.

- Unbalanced  $\rightarrow$  Higher Energy  
Minimize surface  $\leftarrow$

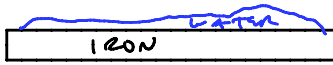
- RESULT: "tough skin"
  - $\hookrightarrow$  needle will float
  - $\hookrightarrow$  insects will not sink



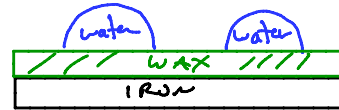
# Waxing True

## Cohesive and Adhesive Forces

- SETUP: 2 different substances in contact, have competing forces: COHESIVE vs. ADHESIVE

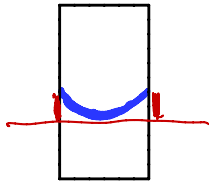


Cohesive (W-W) < Adhesive (W-Fe)  
"water likes Fe more than water"

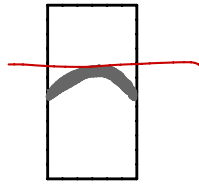


Cohesive (W-W) > Adhesive (W-wax)  
"water likes water more than wax"

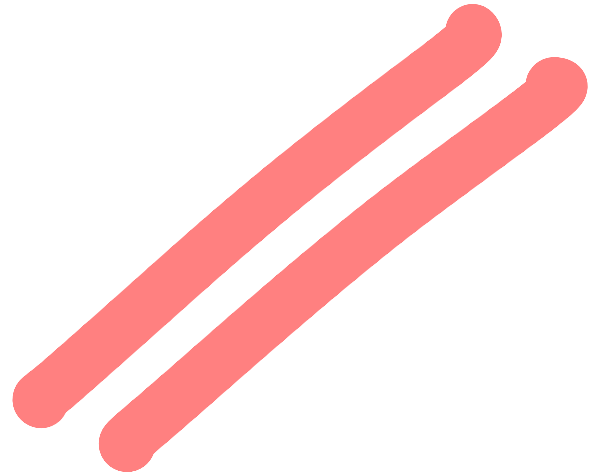
# Capillary Action



Adhesion  $>$  Cohesion



Adhesion  $<$  Cohesion



## Calculation: Height of Liquid Rise

$$h = \frac{2T \cos \theta}{r \rho g}$$

Annotations for the equation:

- surface tension  $\rightarrow T$
- contact angle  $\rightarrow \theta$
- gravitational acceleration  $\rightarrow g = 9.8 \text{ m/s}^2$
- density of liquid  $\rightarrow \rho$
- tube radius  $\rightarrow r$

(EX) You want 25°C water to rise 8.4 cm. What diameter capillary tube do you need?

[ex 10.4b]

$$T_w = \frac{71.99 \text{ mN}}{\text{m}}, \quad \rho = \frac{1.0 \text{ g}}{\text{cm}^3}$$

$$h = \frac{2T \cos \theta}{r \rho g} \rightarrow r = \frac{2T \cos \theta}{h \rho g}$$

water spreads on glass, so  $\theta = 0^\circ$   
 $\therefore \cos(0) = 1$

$$\frac{\text{g m}}{\text{mN s}^2} \leftarrow \frac{\text{kg m}}{\text{N s}^2} \leftarrow \mu = \frac{\text{kg m}}{\text{s}^2}$$

$$r = \frac{\square \text{ cm}}{1} = \frac{2}{1} \left| \frac{71.99 \text{ mN}}{\text{m}} \right| \frac{1}{8.4 \text{ cm}} \left| \frac{\text{cm}^3}{1.0 \text{ g}} \right| \frac{\text{s}^2}{9.8 \text{ m}} \left| \frac{\text{g m}}{\text{mN s}^2} \right| \frac{1 \text{ m}}{100 \text{ cm}}$$

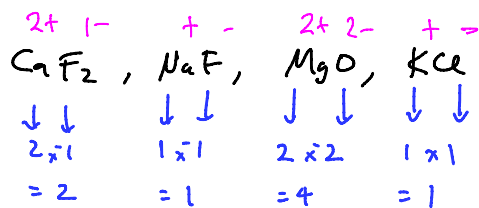
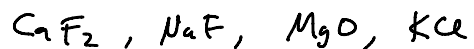
$$r = 0.017 \text{ cm} \xrightarrow{\times 2} \boxed{d = 0.035 \text{ cm}} = \boxed{0.35 \text{ mm}}$$

book answer

## Ionic Strength: Rule of Thumb Det'n

RECALL:  
dispersion < polar < H-bonding < ion

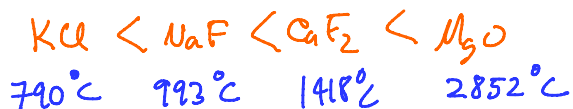
(EX) ¿Arrange in order of increasing melting point?



smaller, so  
force is greater:

$$F \propto \frac{1}{\text{distance}}$$

Force falls off  
with distance!





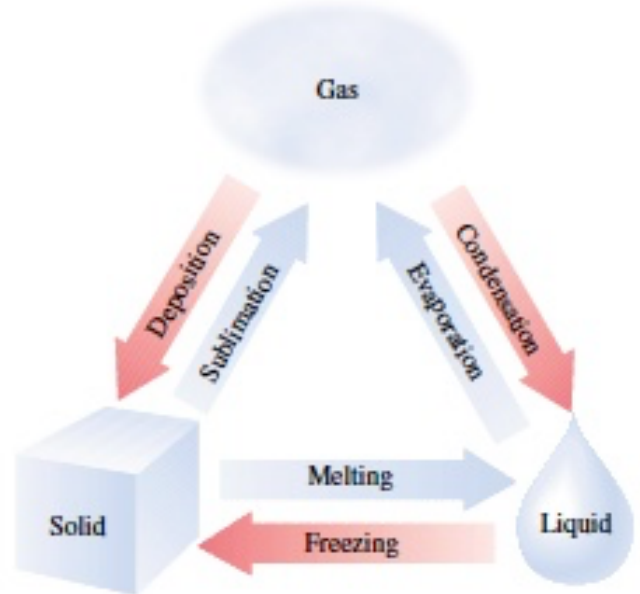
# PHASE TRANSITIONS [10.3]

## 6 Phase Transitions

### Vaporization & Condensation

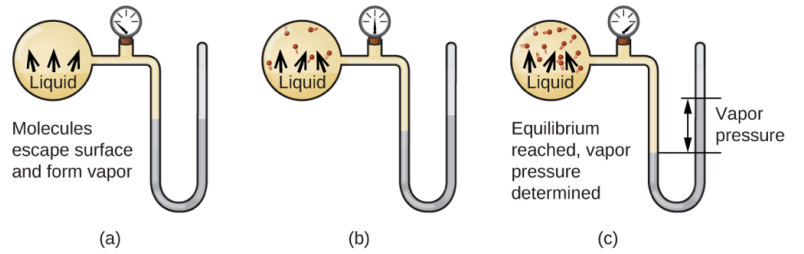
Equilibrium...

- occurs when  $\text{rate(VAP)} = \text{rate(COND)}$
- Liq and Vap are said to be “in equilibrium”
- dynamic: no net change, but lots of movement



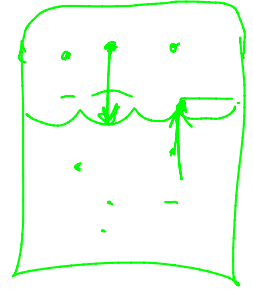
# Vapor Pressure

• pressure exerted by a gas on its liquid surface



- VP used as proxy for IMF

↑ IMF, ↑ difficulty to escape liquid, ↓ VP (fewer molecules in vapor)

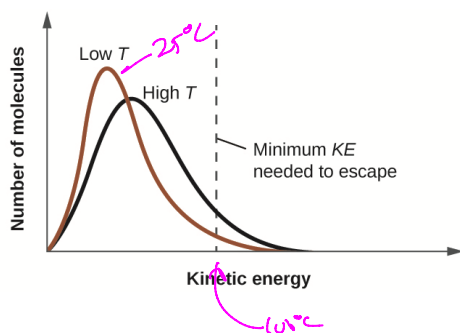


Remember: ↑ IMF

- ① ↑ size/MM of molecule (Larger)
- ② ↑ dipole moment (POLARITY)
- ③ ↑ # N-H, O-H's (H-BONDING)

## Affect of Kinetic Energy, KE

Prompt: Why does water evaporate at room temp., which is  $75^{\circ}\text{C}$  below the BP?

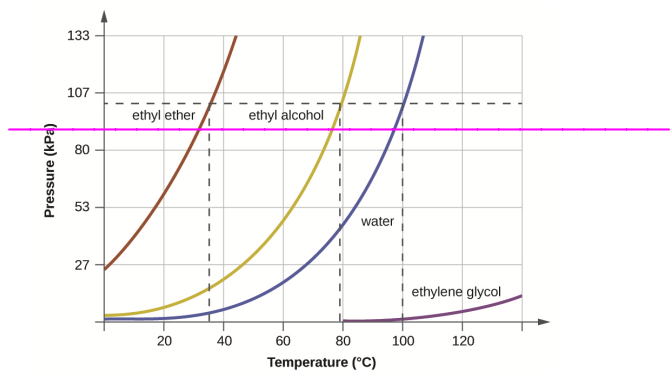


Answer: even at  $25^{\circ}\text{C}$ , a small number of molecules have "escape velocity".

# Boiling Points, and their Relation to VP

Def: BP is temp at which Equilibrium Vapor Pressure is equal to the pressure exerted on the liquid by its gaseous SURROUNDINGS.  $VP_{lig} = VP_{ext}$

Def: Normal BP is the BP when surrounding pressure is equal to 1 atm (101.3 kPa)



NOTE:  $VP_{Liq}$  only a function of  $T_{Liq}$   
 $BP_{Liq}$  " " " "  $P_{ext}$

EX: VP vs. TEMP FOR WATER

VP (torr)	5	24	95	300	760	1741
Temp (°C)	0	25	50	75	100	125

aside: Raoult

$$P_i = X_i P_T$$

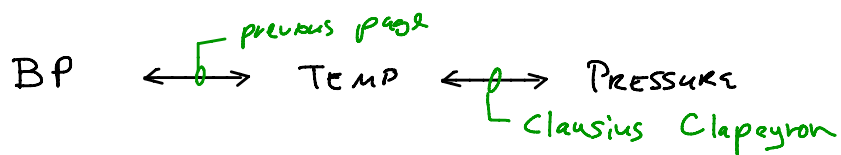
(EX) VP vs. BP

¿Will a compound with a higher VP than another have a (higher | lower | can't tell) BP?

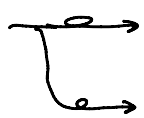
ANS: LOWER

RATIONALE: higher VP  
→ easier to get molecule into vapor  
→ ∴ lower temp (less energy) needed.

# Mathematical Relationship among BP—Temp—Pressure



$$P = A e^{-\Delta H_{\text{vap}}/RT}$$



$$\ln P_1 = -\frac{\Delta H_{\text{vap}}}{RT_1} + \ln A$$

$$\ln P_2 = -\frac{\Delta H_{\text{vap}}}{RT_2} + \ln A$$

↓ A = same (same compd / diff T)

CC Eq.

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

$$\leftarrow \ln P_1 + \frac{\Delta H_{\text{vap}}}{RT_1} = \ln A = \ln P_2 + \frac{\Delta H_{\text{vap}}}{RT_2}$$



## My Problem Solving Approach: "head EAST"

① "head EAST"

E = extract data

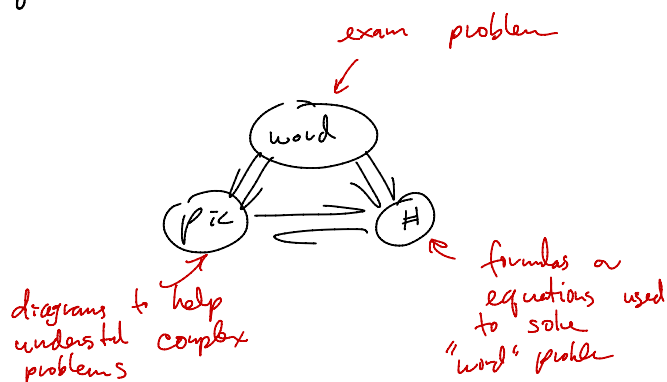
A = analysis

S = set up and solve

T = test your answer

② Need to know how to convert between three languages:

- words speak (info. spelled out in words)
- science speak (formulas, eq, numbers, units, equations)
- picture speak (diagrams)





**LECTURE STOP**

## Enthalpy of Vaporization

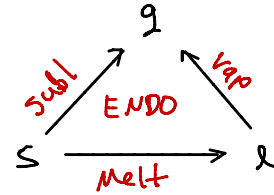
- Vaporization is ENDOthermic

$$H_v(\text{water}) = +44.01 \frac{\text{KJ}}{\text{mol}}$$

↓ requires energy

$$H_{\text{cond}}(\text{water}) = -44.01 \frac{\text{KJ}}{\text{mol}}$$

↑ gives off energy

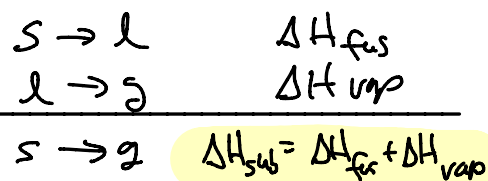
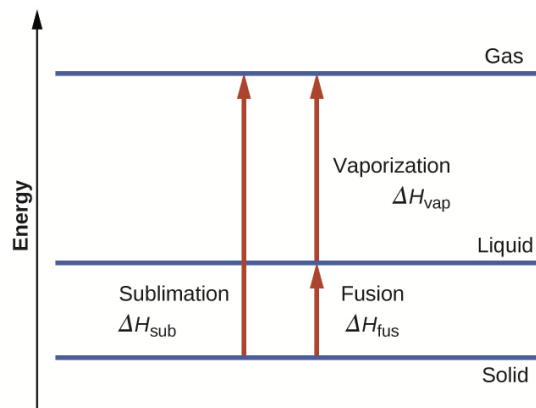
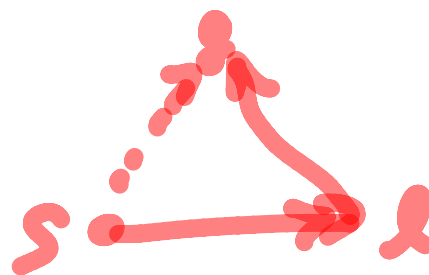


## Melting & Freezing

- As with other physical properties discussed, amt energy required/given off of IMF which must be overcome
- "Fusion" = melting
- $\Delta H_{\text{fus}}(\text{water}) = +6.01 \text{ kJ/mol}$
- $\Delta H_{\text{fz}}(\text{water}) = -6.01 \text{ kJ/mol}$

## Sublimation & Deposition

- Analogous to other phase changes
- $\Delta H_{\text{sub}}(\text{CO}_2) = 26.1 \text{ kJ/mol}$
- $\Delta H_{\text{dep}}(\text{CO}_2) = -26.1 \text{ kJ/mol}$



## Hess' Law

Hess' Law applies to combinations of phase changes

## Calculating Phase Change Energies

$$Q = m \cdot \Delta H_x$$

$$Q = m \cdot s \cdot \Delta T$$

how much

how how

how high

(EX) How much heat is required to evaporate 100.0 g of liquid ammonia (NH<sub>3</sub>), knowing  $\Delta H_v(\text{NH}_3) = 4.8 \text{ kJ/mol}$ ?

$$Q = m \cdot \Delta H_x$$

$$\frac{\boxed{\text{kJ}}}{1} = \frac{100.0 \text{ g}}{1} \cdot \frac{4.8 \text{ kJ}}{\text{mol}} \cdot \frac{1 \text{ mol}}{17.0 \text{ g}} = \boxed{28 \text{ kJ}}$$

- given  
- CF

NH<sub>3</sub>

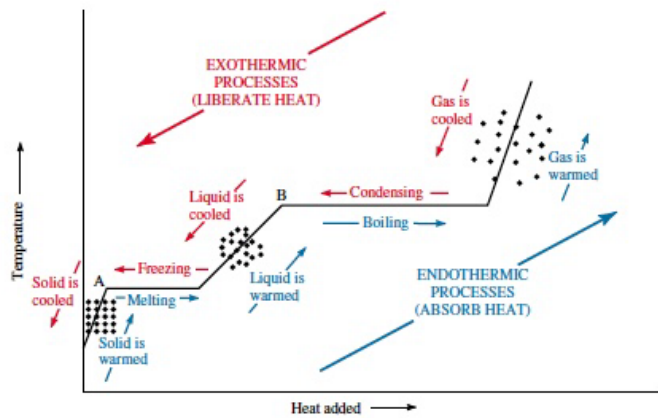
1(14) + 3(1) = 17

$$\frac{\boxed{\text{kJ}}}{1} = \frac{4.8 \text{ kJ}}{\text{mol}} \cdot \frac{100.0 \text{ g}}{1} \cdot \frac{\text{mol}}{17.0 \text{ g}} = 28.235 \text{ g} = \boxed{28 \text{ kJ}}$$

## Heating & Cooling Curves

- earlier in Thermo chapter:
- Also associated terms for Phase Changes
- **NOTE:** Temp does NOT chg w/ phase change, so no " $\Delta T$ "

$$Q = m \cdot s \cdot \Delta T$$



## Heating & Cooling Curves

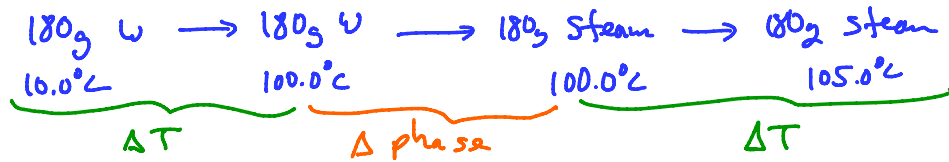
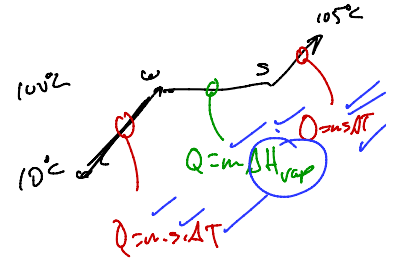
$$Q = m \cdot \Delta H_x$$

where:

$\Delta H_{\text{phase chg}}$  = # kJ needed to change 1 mol from 1 phase to another

=  $\Delta H_v$ ,  $\Delta H_{\text{cond}}$ ,  $\Delta H_{\text{melt}}$ , etc

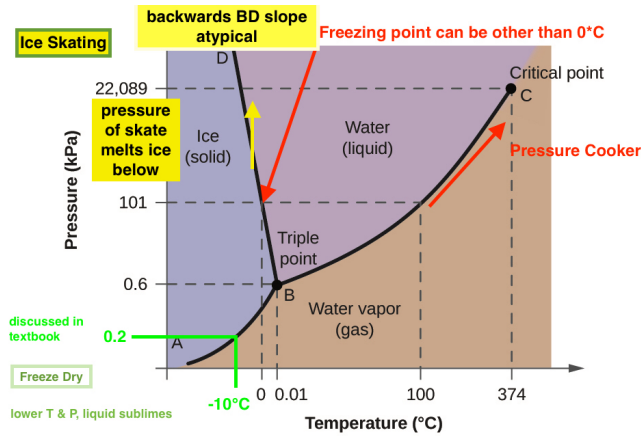
(EX) Calculate the amount of heat, in kJ, required to convert 180.0 g of water at 10.0 °C to steam at 105.0 °C?



$$\begin{aligned}
 q &= m \cdot s \cdot \Delta T + m \Delta H_{\text{vap}} + m \cdot s \cdot \Delta T \\
 &= m (s \cdot \Delta T + \Delta H_{\text{vap}} + s \Delta T) \\
 &= 180.0 \text{ g} \left( \frac{4.184 \text{ J}}{\text{g}^\circ\text{C}} \left| \frac{90.0^\circ\text{C}}{\text{g}^\circ\text{C}} \right. + \frac{2,260 \text{ J}}{\text{g}} + \frac{2.03 \text{ J}}{\text{g}^\circ\text{C}} \left| \frac{5.0^\circ\text{C}}{\text{g}^\circ\text{C}} \right. \right) \\
 &= 180.0 \text{ g} \left( 376.6 \text{ J/g} + 2,260 \text{ J/g} + 10.15 \text{ J/g} \right) = \frac{180.0 \text{ g} \cdot 2647 \text{ J}}{\text{g}} = \boxed{476.4 \text{ kJ}}
 \end{aligned}$$

# PHASE DIAGRAMS [10.4]

- Phase Diagram relates phases in terms of P-T.



$$PV = nRT$$

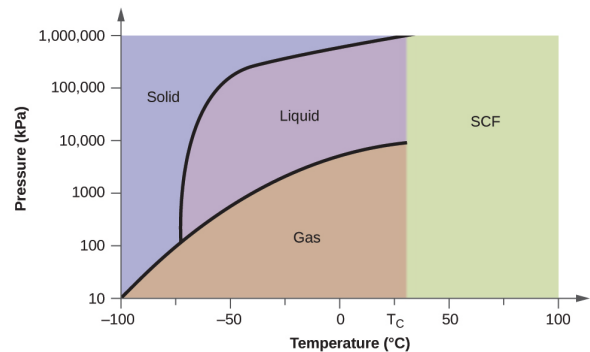
← eg WATER  
[Fig 10.31]

- Triple Point - P & T at which all 3 phases are in Equilibrium  
↳ @ P < Triple P, water cannot exist as liquid.
- Critical Point - P & T above which the material is a Super critical Fluid
- Supercritical Fluid - a single phase with properties intermediate Gas & Liquid states.



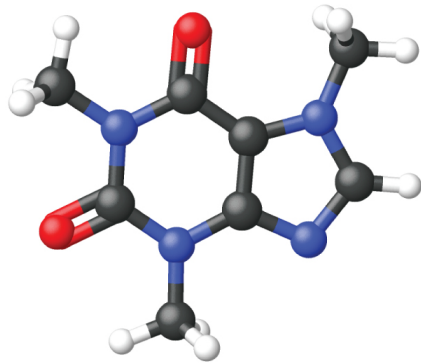
### (EX) Critical Temp Phenomenon

¿If we shake a carbon dioxide fire extinguisher on a cool day (18 °C), we can hear liquid CO<sub>2</sub> sloshing around inside the cylinder. However, the same cylinder appears to contain no liquid on a hot summer day (35 °C). Explain these observations.?

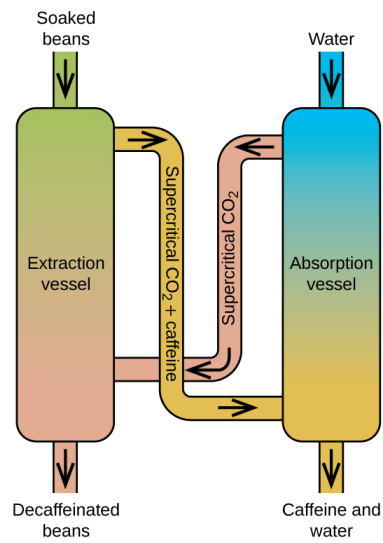


### Solution

- On the cool day, the temperature of the CO<sub>2</sub> is below the critical temperature of CO<sub>2</sub>, 304 K or 31 °C (see Table), so liquid CO<sub>2</sub> is present in the cylinder.
- On the hot day, the temperature of the CO<sub>2</sub> is greater than its critical temperature of 31 °C. Above this temperature no amount of pressure can liquefy CO<sub>2</sub> so no liquid CO<sub>2</sub> exists in the fire extinguisher.



(a)



(b)

(a) Caffeine molecules have both polar and nonpolar regions, making it soluble in solvents of varying polarities.

(b) The schematic shows a typical decaffeination process involving supercritical carbon dioxide.

# MISC BITS

**GAS**

$$PV = nRT$$

$$P_T = \sum P_i$$

$$P_i = X_{i,2} P_T$$

IGL  
Dalton

**LIQ**

$$C_i = k_i P_i$$

$$P_i = X_{i,l} P_i^0$$

$$\Delta P = X_{u,l} P_{\text{saamt}}^0$$

Henry  
Raoult

