

Ch. 11 Liquids, Solids, and Materials**Ch. 9.5,6 Molecular Polarity and Intermolecular Forces**with
answers**Types of Bonds/Binding Forces**

1. Covalent (strong)
2. Ionic (strong)
3. Metallic (strong)
 - 1-3 are Full Bonds (strong!):
4. Intermolecular Forces: Noncovalent Interactions between molecules (weak)

Intermolecular Forces between Molecules

1. H-Bonding (O-H, N-H, or F-H bonds). Way strongest.
2. Dipole-Dipole (polar, but without O-H, N-H, or F-H bonds)
3. London (only thing that nonpolar molecules have, but applies to all)

Recognizing Polarity (Necessary for recognizing/evaluating intermolecular forces)

1. AB_m Nonpolar If no lone pairs on central, and all outside atoms same, nonpolar.
2. AB_mL_N Polar. If lone pairs on central atom.
3. AB_mL_n Weakly polar No lone pairs on central atom, but attached atoms not same.
4. Hydrocarbons Nonpolar
5. Halocarbons Very weakly polar

Network vs Molecular Substances

1. Network (usually identifiable by presence of a metal!)
 - a. Ionic
 - b. Metallic
 - c. Network Covalent (diamond)
2. Molecular (usually identifiable by absence of a metal)
 - Network binding forces are strong, molecular binding forces are relatively weak

Ranking substances in terms of relative binding forces:

1. Identify network substances versus molecular substances (Key: are there any metals in formula?)
2. For molecular substances:
 - a. H-bonding? (yes or no. If no, proceed to question b. If yes, go to question 3)
 - b. Polar? (yes or no)
3. For molecular substances, what is the molecular weight? Greater molecular weight gives greater binding force.
 - Note: when molecular weight effects counteract H-bonding or polar effects (such as methanol versus acetone versus hexane) you are not expected to be able to predict which has stronger binding forces, except for special cases like H₂O. But normally H-bonding is more important than molecular weight.

Predictable Properties that Depend on Binding Forces

- | | | |
|-----------------------------------|-----------------|---|
| 1 melting point | mp | higher binding force → higher mp |
| 2 boiling point | bp | higher binding force → higher bp |
| 3 evaporation rate ("volatility") | | higher binding force → lower evaporation rate |
| 4 vapor pressure | | higher binding force → lower vapor pressure |
| 5 heat of fusion (melting) | ΔH _f | higher binding force → higher ΔH _f |
| 6 heat of vaporization (boiling) | ΔH _v | higher binding force → higher ΔH _v |
| 7 viscosity | | higher binding force → higher viscosity |
| 8 surface tension | | higher binding force → higher surface tension |
| 9 solubility | | higher solute/solvent binding force → higher solubility |

Ch. 11 Liquids, Solids, and Materials

A. Intro: Substances, Phases, and Attractive/Binding Forces

1. 3 Phases: (Show T-84, Brown)

a. Crystalline Solid-

- **complete order** (Show T75 Gillespie)
- held closely together by strong forces
- no "molecular flow"

b. Liquid-

- limited disorder
- -held together, but not fixed; free "molecular flow"

c. Gas-

- **complete disorder** (Show T2, Fig 1.5, Brown)
- Not held together at all, far apart

Gases can be compressed; Solids/liquids are "condensed" states, can't be compressed

2. The state of a given substance depends on balance between **attractive binding forces** (hold together) versus **kinetic energy** (pull particles apart)

- When energy increases, organization is overcome, particles pull apart
- **Temperature:** When binding force is the same, but temperature changes:
 - Raising temp increases KE → increased disorder
 - Raising temp: solid → liquid → gas
- **Binding Force:** At a given temperature, but different substances have different binding forces:
 - Raising binding force → reduces movement → reduces disorder
 - Raising binding force → increasing likelihood of being solid, decreasing likelihood of being gas
 - As attraction grows: gas → liquid → solid

Key: recognizing nature, strength of binding is key to predicting resultant properties

3. **Predictable Properties that Depend on Binding Forces**

| | | |
|----------------------------------|--------------|---|
| 1 melting point | mp | higher binding force → higher mp |
| 2 boiling point | bp | higher binding force → higher bp |
| 3 evaporation rate | | higher binding force → lower evaporation rate |
| 4 vapor pressure | | higher binding force → lower vapor pressure |
| 5 heat of fusion (melting) | ΔH_f | higher binding force → higher ΔH_f |
| 6 heat of vaporization (boiling) | ΔH_v | higher binding force → higher ΔH_v |
| 7 viscosity | | higher binding force → higher viscosity |
| 8 surface tension | | higher binding force → higher surface tension |
| 9 solubility | | higher solute/solvent binding force → higher solubility |

B. Types of Bonds/Binding Forces (Section 9.6)

1. Covalent (strong)
2. Ionic (strong)
3. Metallic (strong)
 - 1-3 are Full Bonds (strong!):
4. Intermolecular Forces: Non-covalent Interactions between molecules (**weak**)
 - a. these do not involve full bonds. (Show T-2, Brown Fig 1.5)
 - b. weaker interactions,
 - c. <10% of a full bond,
 - d. easier to overcome (ex bp, etc.)
 - e. "Intermolecular forces" attract different molecules
 - f. "Intramolecular forces" involve the same principles, but attract and organize otherwise remote parts of the same molecule (key in biology: hydrophobic, hydrophilic, hydrogen-bonding, etc.)
 - g. "IMF"

C. Intermolecular Forces (IMF): Non-covalent forces between molecules(Section 9.6)

- Forces between different molecules
- If there were no IMF attracting molecules to other molecules, all molecular substances would be gases
- Some attractive forces are needed in order to have molecular liquids or molecular solids
- Like all bonds, IMF are based on charge-charge attractions
- Key: Don't forget the difference between non-covalent IMF and true covalent bond: (draw H₂O molecules)
 - a. H-O in water itself: covalent
 - b. One water to another water: noncovalent, IMF

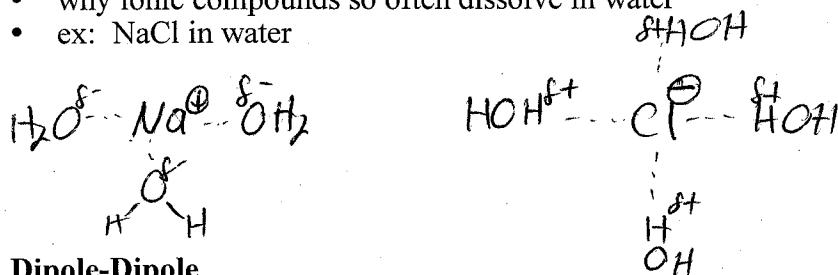
-molecular substances with weak IMF => easy to disorganize (solid → liquid → gas)
 one molecule can be removed from others without breaking full bond

Summary of Intermolecular Forces between Molecules

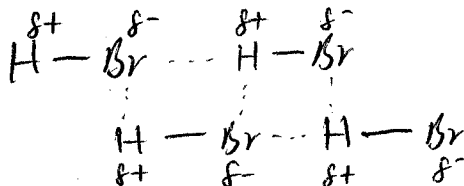
- | | | | |
|---|------------------|--|---------------|
| 1 | Hydrogen-Bonding | O-H, N-H, or F-H bonds present | Strongest IMF |
| 2 | Dipole-Dipole | Molecule is polar , but without O-H, N-H, or F-H bonds | |
| 3 | London | Increasing molecular weight → increased London force. All molecules, whether H-bonders or polar or nonpolar all have London force. But London force is the only intermolecular force that can act between nonpolar molecules. | Weakest IMO |
| 4 | Ion-Dipole | Doesn't really belong here, because not truly "intermolecular". But involves the attraction between a charged ion and a polar molecule. | |

1. Ion Dipole

- not literally an intermolecular force, but illustrative of the principle and important
- between an ion (full charge) and partial charge of polar solvent (water especially)
- why ionic compounds so often dissolve in water
- ex: NaCl in water

2. Dipole-Dipole

- Between polar molecules
 - Involve attraction between opposite δ^+ and δ^- partial charges
- Ex: HBr

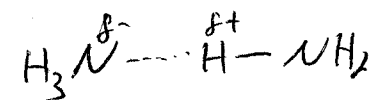
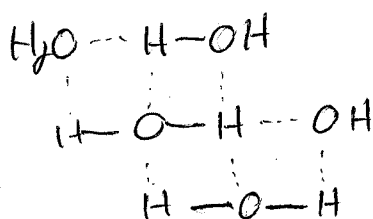


- Hydrogen-bonding molecules (with OH or NH bonds) are also polar, and hydrogen-bonding really is an extreme form of dipole-dipole interaction. But hydrogen-bonding is so much stronger that it is given its own name and consideration (see below)
- Polarity can vary widely, so the importance of dipole-dipole attractions can vary widely from one polarized molecule to another
- In general, increasing polarity \rightarrow stronger dipole-dipole force

| | polarity \downarrow | Dipole | BP (K) | boiling point \downarrow |
|----------------------------------|-----------------------|--------|--------|----------------------------|
| CH ₃ OCH ₃ | | 1.3 | 248 | |
| CH ₃ CHO | | 2.7 | 294 | |
| CH ₃ CN | | 3.9 | 355 | |

3. Hydrogen Bonding

- Requires the presence of an O-H, N-H, or F-H bond
 - Ultra-strong dipole-dipole interaction
 - δ^+ Charge on O-H or N-H hydrogens is quite strong, and very attractive to lone pairs on oxygen or nitrogen; the δ^- charge on OH or NH oxygens or nitrogens is also strong, and attractive to the δ^+ hydrogens.
 - Why water is so wonderful
 - H-bonding (\rightarrow "hydrophilic") a dominating factor in biological organization
 - While probably 10 times stronger than most dipole-dipole interactions, hydrogen bonding is still $<10\%$ of the strength of a full covalent bond
- Ex: H₂O



4. **London Force** (alias London Dispersion Force, Dispersion Force, or VanderWaal's Interactions)

- Why would a non-polar molecule have any attraction to another non-polar molecule? But if they didn't have at least some, why wouldn't all non-polars be gases?
 - Cl_2 (gas) Br_2 (liquid) I_2 (solid)
- Nonpolar molecules lack permanent dipole, but electron flow \rightarrow Temporary dipoles
- These temporary, non-permanent dipoles can still cause charge-charge attractions, analogous to regular dipole-dipole attractions. (Show Brown, 11.5)
 - "Polarizability": ease of electron distortion
 - Larger molecules with more electrons can more easily and to greater degree distort their electrons \rightarrow larger temporary dipoles \rightarrow large London force

Key: *Larger mw = larger molecules \Rightarrow more London force*

| | Molecular Weight | BP (K) | IMF |
|---------------|------------------|--------|-----|
| F_2 | | 85 | |
| Cl_2 | | 239 | |
| Br_2 | | 332 | |
| I_2 | | 458 | |

- While London force is the only IMF in nonpolar molecules, it is also important in polar molecules
 - Electron distortion can reinforce existing dipoles and amplify charge attractions
- Key: London force is a great tie-breaker for things with comparable H-bonding or dipole-dipole attraction
 - It can even override polarity or hydrogen bonding.

| | BP | IMF | | Dipole | BP | IMF |
|---------------------------------|-------|-----|--------------|--------|-------|-----|
| CH_3OH | 348 K | | HCl | 1.03 D | 190 K | |
| | | | (mw=30) | | | |
| $\text{C}_2\text{H}_5\text{OH}$ | 361 K | | HBr | 0.79 D | 206 K | |
| | | | (mw=80) | | | |

London beats dipole, in this case

- For test:
 - Assume water hydrogen bonding beats anything else
 - Assume hydrogen bonding overrides London force
 - Normally I will avoid apples-to-oranges cases unless it's involving water

5. **Recognizing Polarity** (Section 9.5)

| | |
|--|---------------------------------|
| 1 Hydrocarbons | Nonpolar |
| 2 Halocarbons | Very weakly polar (or nonpolar) |
| 3 Diatomic formula, both atoms same | Nonpolar |
| 4 Diatomic formula, two atoms different | Polar |
| 5 AB_m (multiatom, no lone pairs on center, all outside atoms same) | Nonpolar |
| 6 AB_mC_n (outside atoms aren't all the same, but still no lone pairs on central atom) | Polar (Sometimes Weakly) |
| 7 AB_mL_x or $\text{AB}_m\text{C}_n\text{L}_x$ (Lone Pairs on Central Atom) | |

Q1: Classify each of the following as polar (molecular), completely nonpolar (molecular), weakly polar (molecular), ionic, or metallic. Identify any for which hydrogen-bonding would apply.

1. CO_2 nonpolar
2. $\text{CH}_3\ddot{\text{O}}\text{H}$ polar
H-bonding
3. O_2 nonpolar
4. :NH_3 polar
H-bonding
5. CH_2Cl_2 weakly polar
6. :PCl_3 polar
7. CO polar
8. $\text{H}-\text{C}=\ddot{\text{O}}:$ polar
9. SiCl_4 nonpolar
10. Fe metallic
11. NaCl ionic

Q2: For the following four structures, rank them from 1-4 according to each of the properties

| | LiCl 42 g/mol | $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ 74 g/mol | $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ 60 g/mol | $\text{CH}_3\text{OCH}_2\text{CH}_3$ 60 g/mol |
|--------------------------------|---------------------------|---|--|--|
| Binding Strength (and why?) | ① ionic | 2 H-bonding | 3 H-bonding | 4 |
| Melting point | 1 highest | 2 | 3 | 4 |
| Boiling point | 1 highest | 2 | 3 | 4 |
| Evaporation rate | 4 | 3 | 2 | 1 highest |
| vapor pressure | 4 | 3 | 2 | 1 |
| Energy to melt | 1 most | 2 | 3 | 4 |
| Energy to Boil | 1 most | 2 | 3 | 4 |
| Viscosity | 1 thickest | 2 | 3 | 4 |
| Surface tension | 1 | 2 | 3 | 4 |

Notes:

- If you can figure out the relative binding forces at work for different substances, you can rank those substances relative to any of these physical properties
- An understanding of whether a stronger binding force causes an increase or decrease is also required

D. Molecular vs Network Substances: 2 Broad Subsets

1. Molecular

- Recognition: **Nonmetals only** in formula
- Different molecules attracted to each other only by IMF, which are relatively weak compared to full bonds
- Because attractive IMF aren't that strong \rightarrow molecular substances are relative easy to disorganize
- One molecule can be moved away from others without breaking full bonds, so the energy price is modest
 - bp, mp, ΔH_v , ΔH_f , etc. won't be too high
 - molecular substance can often be gases or liquids

2. Network

- 3 Types, all organized and held together using full bonds
 - 1) Ionic:
 - Recognition: **Metals as well as nonmetal(s)** in formula
 - 2) Covalent "Network" (rare) C (diamond), SiO₂ (quartz)
 - Recognition: Exceptionally rare, memorize diamond and quartz
 - 3) Metallic
 - Recognition: **Metal only** in formula
- a. complete 3-D lattice: can't move one atom without breaking a strong full bond
- b. Thus **network substances normally have much stronger binding forces than molecular substances** (there is variation, of course, but as a class network \gg molecular)
 - bp, mp, ΔH_v , ΔH_f , etc. will be very high
 - Always solids (almost, mercury the one exception at room temp)
- c. Terminology: "network" is often applied (book) only to covalent network, but the broader classification including metals and ionic network substances is useful

KEY Binding: Network Substance (metals involved) $\gg\gg$ Molecular Substance (nonmetals)
 \Rightarrow **molecular substances have much lower mp, bp, etc.**

Ranking substances in terms of relative binding forces:

1. Identify network substances versus molecular substances (Key: are there any metals in formula?)
2. If molecular, is their H-bonding?
3. If molecular, is it polar? (not worth asking if you've already ID'd as an H-bonder....)
4. If molecular, what is the molecular weight?

Tiebreakers for molecular substances:

- If mw = comparable, then H-bonding or polarity required to break tie
- If two things are similar in terms of H-bonding or polarity, then mw (London force) should break the tie.

Questions

- 1) Classify as network or molecular, and identify any forces (other than London dispersion) for the following:

- | | | |
|---------------------------------------|-----------|---------------|
| a. CH ₃ OH | molecular | H-bonding |
| b. CH ₃ OCH ₃ | molec | dipole-dipole |
| c. CH ₄ | molec | |
| d. K ⁺ in H ₂ O | | ion-dipole |

Ranking substances in terms of relative binding forces:

1. Identify network substances versus molecular substances (Key: are there any metals in formula?)
2. If molecular, is their H-bonding?
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Tiebreakers for molecular substances:

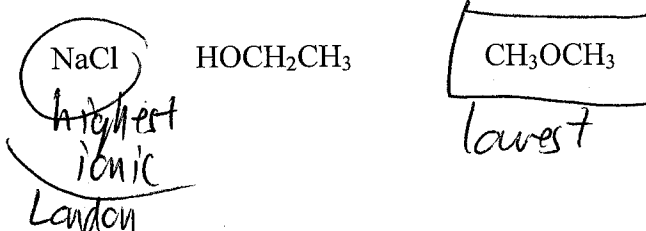
- If mw = comparable, then H-bonding or polarity required to break tie
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Questions

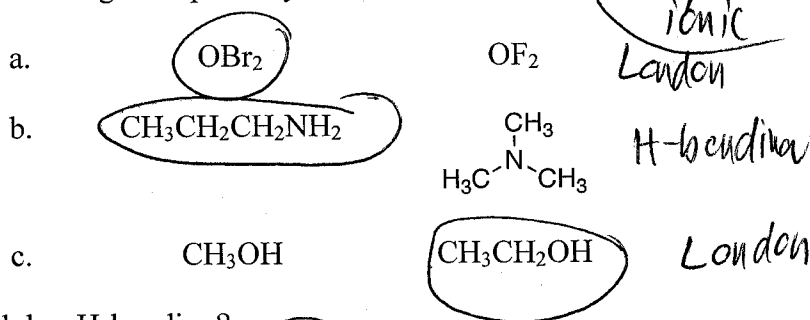
- 1) Classify as network or molecular, and identify any forces (other than London dispersion) for the following:

| | | |
|--------------|---------------|-------------------|
| e. I_2 | mcl | |
| f. $H-N=O$ | mcl | H-bonding, dipole |
| g. Fe_2O_3 | ionic network | ionic |
| h. CO | mcl | dipole-dipole |
| i. Zn | network | metallic |
| j. NH_3 | mcl | H-bonding, dipole |
| k. HCl | mcl | dipole |

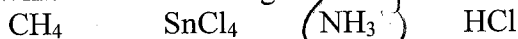
- 2) Which has highest mp? Lowest bp? (Why)



- 3) Which has highest bp? Why?



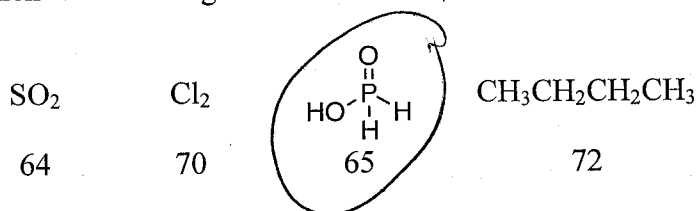
- 4) Which has H-bonding?



- 5) Which has London dispersion as ONLY IM force?



- 6) Which will have highest heat of fusion?



E. Liquid State (Section 11.1)

- At room temp, liquids are almost exclusively molecular substances
 - Mercury is the one exception
 - Molecular flow is possible
 - Binding is too weak to lock molecules into a solid
 - Binding is too strong to let the molecules all fly apart into gas phase
1. Viscosity: Resistance to flow, “thickness” of liquid
- Examples of viscous liquids: ketchup, syrup, ice-cream topping, motor oil, etc...
 - Liquids get “thick” and “viscous” when the molecules don’t want to flow, and instead want to stick together (i.e. controlled by binding force, versus kinetic energy)

Greater IMF → more viscous
Greater temp → less viscous (greater kinetic energy → better flow)

- Motor Oil issues

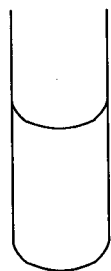
2. Surface Tension

- Water “beads up” on smooth surface, or overfilled glass
- IMF pull the molecules together, cause them to ball up, pack liquid together as if it had a skin
 - This is why water bugs can “walk” on water
 - To “cut through” the surface would require breaking hydrogen-bonds
- Mercury has much greater surface tension
- Rubbing alcohol or turpentine have much less surface tension

Greater IMF → more surface tension
Greater temp → less surface tension (greater kinetic energy → better flow)

3. Cohesive vs Adhesive Force/Attraction and Meniscus Chemistry

- “Cohesive forces” – bind like molecules together (intermolecular force)
- “Adhesive forces” – bind liquid to surface (non-covalent attractions between a liquid to a solid.)
- For water, if a surface has strong H-bonding or even ionic character, adhesive attraction (to surface) will exceed cohesive attraction (to itself). If not, cohesive attraction (to itself) will exceed adhesive attraction (to the surface)
 - The balance between adhesive vs cohesive force determines the shape of the meniscus
 - In glass tubes (glass is very strongly polar), water has a downwards meniscus
 - In plastic tubes (plastic is nonpolar), water has an upward meniscus



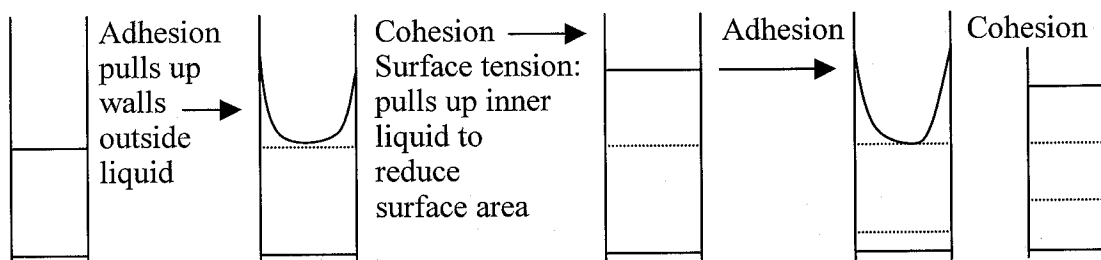
H₂O in glass (very H-bonding):
Adhesion > cohesion



Hg in glass:
Cohesion > adhesion

4. Capillary Action: Liquids climb up narrow tubes!

- Contrary to gravity
- Key to plant biology! It's the way water climbs up from the roots through the stalks/trunks and gets distributed to the leaves
- Combined adhesion/cohesion "steps" liquid up narrow tube (simplified picture)
 - 1) Adhesion pulls up "outside"
 - 2) Cohesion pulls up "inside"
- Three variable:
 - Diameter of the tube
 - Strength of the cohesive forces
 - Strength of the adhesive forces

Vapor Pressure, Volatility and Evaporation (Section 11.2)

- Why does nail polish, gas, turpentine evaporate faster than water?
- Why does "Latex" paint dries faster than oil-based gloss?
- Does Pepsi get "flat" when bottle almost empty or uncapped?

A. Intro

- 1) **Vaporization**: When molecules break away from the liquid phase and escape into the gas phase
- 2) Temp reflects **average** kinetic energy, but some molecules are above average
- 3) Even below bp temp., some above-average molecules often have enough KE to vaporize
→ Molecules Routinely Escaping
- 4) Higher temp → Higher fraction of molecules with enough energy to escape → higher vaporization rate
- 5) At a given temp, the greater the binding force → less likely that molecules will have enough energy to escape → lower vaporization rate

Greater IMF → lower vaporization rate
 Greater temp → higher vaporization rate

B. Vaporization in Open Containers

1. Breakaway → Evaporation
2. "**Volatility**"—rate of evaporation
3. Weaker the IMF => more volatile
4. Higher the temp => more volatile

Greater IMF → lower rate of evaporation = lower volatility
 Greater temp → higher rate of evaporation = lower volatility

C. Vaporization in a **Closed Container**

1. Molecules still vaporize out of the liquid into the gas, but can't escape the container
 - The population of gas molecules increases
2. With more gas molecules flying around, a lot of them fly into the liquid and rejoin the liquid phase
 - (liquefaction or "condensation")
3. Eventually: rate of vaporization = condensation
 - Achieve "dynamic equilibrium"
 - Constant population of gas: new ones forming as fast as old ones re-liquifying
4. When gas molecules fly around and hit a surface (whether the liquid surface or the surface of the closed container), they create **pressure**
5. The **Vapor Pressure** of a substance at a given temperature is the pressure exerted by its vapor when liquid/vapor are in dynamic equilibrium.
6. The vapor pressure depends on how much vapor is present, so basically whatever is good for vaporization increases vapor pressure

Greater IMF \rightarrow lower rate of vaporization \rightarrow lower vapor pressure
 Greater temp \rightarrow higher rate of vaporization \rightarrow higher vapor pressure

Practice Problems

1. Increasing the amount of liquid in a closed container will cause vapor pressure to:
 - a) increase
 - b) decrease
 - c) remain the same
 - d) depends on the liquid
2. Increasing temperature will cause vapor pressure to:
 - a) increase
 - b) decrease
 - c) remain the same
 - d) depends on the liquid
3. Which will have highest vapor pressure? Lowest?

| | | |
|---|--------------------------------------|--|
| a) CH_3OCH_3 <i>highest</i> | b) $\text{CH}_3\text{CH}_2\text{OH}$ | c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ <i>lowest</i> |
|---|--------------------------------------|--|
4. Benzene boils at 80° . Is its vapor pressure at room temperature higher or lower than that of water? Will it's vapor pressure be higher at room temperature or *at 40° ?* *higher*
5. Hexane has higher vapor pressure than water. Which has higher bp? *water*

D. Vaporization and **Boiling Point** in the open

1. The pressure caused by the liquid substance's vapor contributes only a fraction of the total pressure operating on the surface of a liquid, especially in the open
 - Most of the external pressure comes from air (nitrogen and oxygen) in an open container
2. Boiling occurs when the vapor pressure of the escaping gas pressing up equals the total combined external pressure down
 - In a sense, the external pressure is pushing molecules down. To boil, molecules from the liquid need to be jumping into the gas phase and pushing up as hard or harder than the external pressure is pushing down.
3. **BP and External Pressure:** The boiling point is highly dependent on external pressure
 - Higher pressure \rightarrow higher boiling point (temp needs to go up for vaporization escape pressure to match external pressure)
 - Lower pressure \rightarrow lower boiling point (temp doesn't need to be that high to produce enough vaporization to match external pressure)

4. **"Normal boiling point"** = boiling temperature under normal atmospheric pressure, when external pressure = 1 atm = 760 mm Hg = 760 torr
- mostly when we refer to "boiling point", we mean the "normal boiling point"

Greater IMF \rightarrow lower rate of vaporization \rightarrow higher normal boiling point (need more temp to make up for the otherwiselow vaporization rate)

Greater external pressure \rightarrow higher boiling point (need more temp for escape pressure to match the external pressure)

Lower external pressure \rightarrow lower boiling point (need less heat to generate the escape pressure needed to match the external pressure)

Miscellany:

- Takes longer to boil an egg in Denver (higher elevation \rightarrow reduced pressure \rightarrow reduced boiling point \rightarrow boiling water isn't as hot)
- Water would boil on the moon (low external pressure), or Mercury and Venus (too hot)
- Pressure cooker cooks fast: high pressure \rightarrow higher bp for water \rightarrow hotter \rightarrow cook fast

Practice Problems

1. Which will have highest bp?

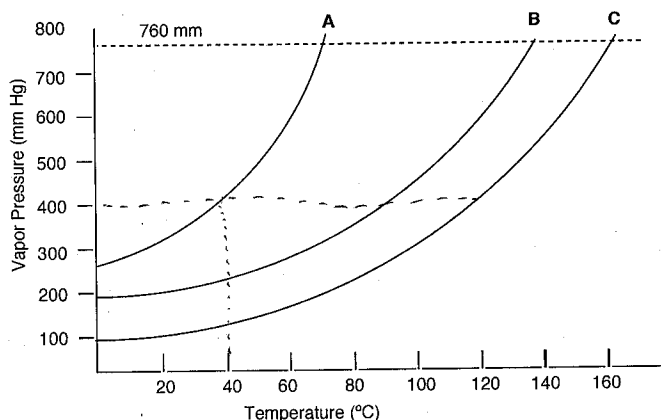
| | | | |
|---------------|--------------|----------------|---------------|
| Br_2 | F_2 | SiH_4 | CO_2 |
| 160 | 38 | 32 | 44 |

2. Which will have highest bp? Which would you guess would be lowest? Try to rank all four.

| | | | |
|--------------------------|--------------|---------------|------------------------|
| CH_3NO_2 | LiF | Cl_2 | CH_3OH |
| 61 | 26 | 70 | 32 |

lowest

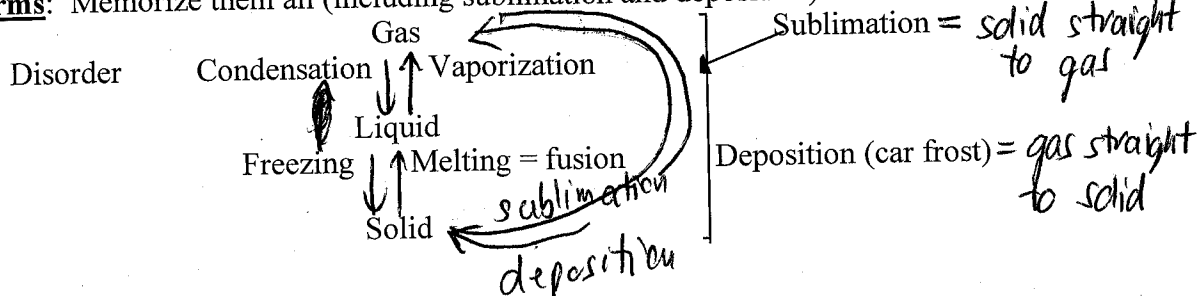
- E. **Vapor Pressure Curves:** Show the relationship between temperature and vapor pressure for different substances



For each of the following, fill in the information:

- "Normal boiling point"
- BP at 400 mmHg
- Vapor Pressures at 40°C
- Rank the three substances in terms of IMF

| | | |
|-----------|---------|---------|
| A | B | C |
| 75° | 140° | 160° |
| ~40° | ~100° | ~130° |
| ~400 mm | ~200 mm | ~100 mm |
| C > B > A | | |

Phase Changes (Section 11-3)A. **Terms:** Memorize them all (including sublimation and deposition)**B. Energy**

1. Energy is required for change to more disordered state; energy is released during change to a more ordered state

Endothermic: melting, vaporization, sublimation**Exothermic:** freezing, condensation, depositionWater as air-conditioner

- Winter heater: when water freezes, it releases heat. Without freezing water, winter temps would be 30° colder!
- Summer chiller: Evaporation absorbs heat, so instead of hitting 120° we just evaporate some lake water

Refrigeration (Evaporation is cooling!) → fridge: liquid evaporates (chills fridge/freezer) → electrical compressor resqueezes it to liquid

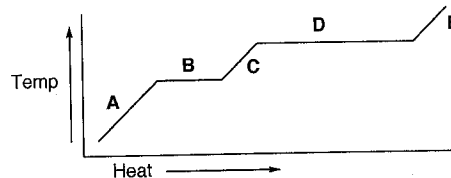
2. Quantitative Energy Calculations

- Values are given either on a per-mole or a per-gram basis
- When moles are used, you'll need to use mass-mole interconversions
- Normally $\Delta H_{\text{vap}} > \Delta H_{\text{fus}}$

| | |
|--|---|
| ΔH_{fus} : energy to melt 1 mole of solid (or 1 g) | ΔH_{vap} : energy to vaporize 1 mole of liquid (or 1 g) |
| $-\Delta H_{\text{fus}}$: energy released during freezing | $-\Delta H_{\text{vap}}$: energy released during condensation |

Greater IMF → larger ΔH_{fus} , ΔH_{vap} 3. Specific Heat Capacity: Amount of heat to raise the temperature of a solid, liquid or gas by 1°

- Applies when you are **not** at a phase change
- For a given substance, the specific heat will be different for the solid form versus the liquid form versus the gas form

4. Heating "Curves": Calculating Energy

"Horizontals" = phase change. "Diagonals" involve the heating up of a solid, liquid, or gas

| Zone | What's Happening | Phases Present | Details Needed for Energy Calculation |
|------|------------------|------------------|--|
| A | solid warming | Solid only | ΔT , grams, S.H. <u>solid</u> |
| B | solid melting | solid and liquid | ΔH_f , moles or grams |
| C | liquid warming | liquid | ΔT , grams, S.H. <u>liquid</u> |
| D | liquid boiling | liquid + gas | ΔH_{vap} , moles or grams |
| E | gas warming | gas | ΔT , grams, S.H. <u>vapor</u> |

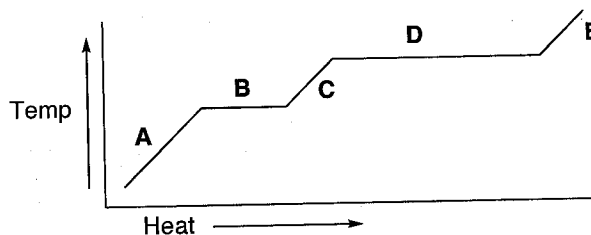
Notes:

- Temperature fixed during phase change
- Length of horizontal reflects ΔH_f , ΔH_v ($\Delta H_v > \Delta H_f$)
- "Diagonal" slopes depend on specific heat capacities of substance, which differ for each phase

Energy Calculation Problems: Calculate each portion independently. Sum them at the end.

Zone Details Needed for Energy Calculation

- A ΔT , grams, S.H. solid
 B ΔH_f , moles or grams
 C ΔT , grams, S.H. liquid
 D ΔH_{vap} , moles or grams
 E ΔT , grams, S.H. vapor

**Practice Problem**

How much energy to heat 36 g of ice (18g/mol) from $-50^\circ\text{C} \rightarrow +50^\circ\text{C}$?

Given: $\Delta H_{fus} = 6.01 \text{ kJ/mol}$

Specific heat solid ice = $2.09 \text{ J/g}\cdot\text{K}$

Specific heat liquid water = $4.18 \text{ J/g}\cdot\text{K}$

Key: break it down into the different steps.

- ① Solid warming $-50^\circ \rightarrow 0^\circ$
- ② Solid melting $0^\circ \text{ solid} \rightarrow 0^\circ \text{ liquid}$
- ③ Liquid warming $0^\circ \rightarrow 50^\circ$

$$\text{① Solid warming} \quad \times \text{ J} = \left(\frac{2.09 \text{ J}}{1 \text{ g}\cdot\text{K}} \right) (36 \text{ g}) (50 \text{ K}) = 3762 \text{ J} = 3.8 \text{ kJ}$$

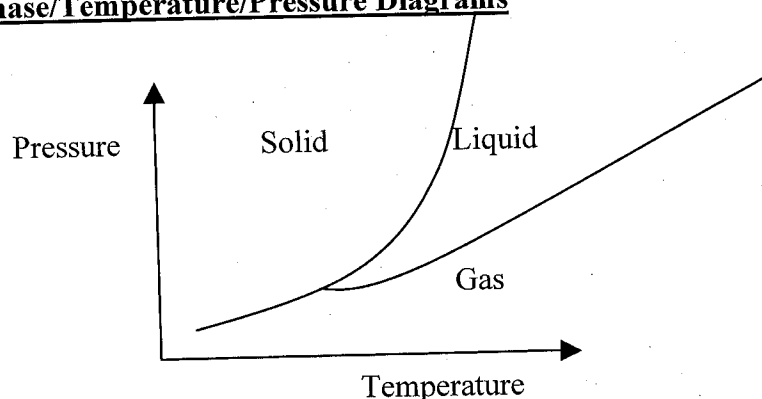
Note: 50° change in $^\circ\text{C} = 50 \text{ K}$

$$\text{② Solid melting} \quad \times \text{ kJ} = \left(\frac{6.01 \text{ kJ}}{1 \text{ mol}} \right) (20 \text{ mol}) = 12.02 \text{ kJ}$$

$$\times \text{ mol} = \frac{36 \text{ g}}{18 \text{ g}} = 20 \text{ mol}$$

$$\text{③ Liquid warming} \quad \times \text{ J} = \left(\frac{4.18 \text{ J}}{1 \text{ g}\cdot\text{K}} \right) (36 \text{ g}) (\underbrace{50^\circ - 0^\circ}_{50 \text{ K}}) = 7524 \text{ J} = 7.5 \text{ kJ}$$

$$\text{Sum: } 3.8 \text{ kJ} + 12.0 \text{ kJ} + 7.5 \text{ kJ} = \boxed{23.3 \text{ kJ}}$$

Phase/Temperature/Pressure Diagrams

- On lines: phase change situation, two phases present at once
- Triple point: unique temp/pressure situation when all 3 phases are present at once

Phases

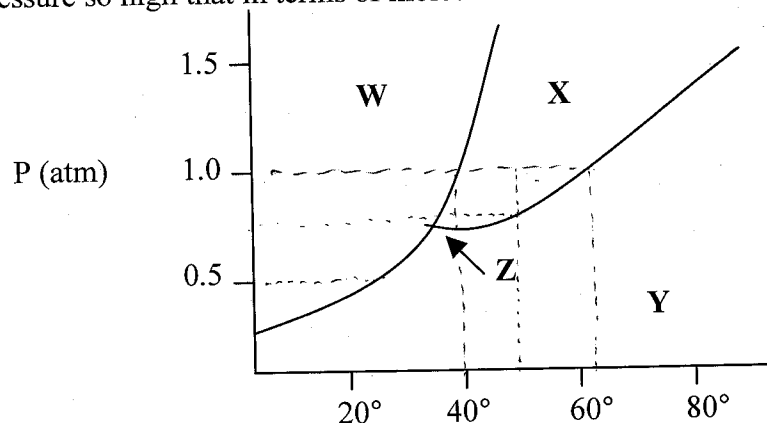
- Max temp, minimum pressure \rightarrow gas (bottom right)
- Min. temp, max pressure \rightarrow solid (upper left)
- Liquid in between

Pressure dependence: increased pressure \Rightarrow increases order (makes harder to escape)

- "Normal" Pressure: 1 atm = 760 mm Hg

Temperature dependence: increased temperature \Rightarrow increases disorder (makes easier to escape)

Critical point: (not test, but need for OWL): highest temp/pressure point where liquid and gas are distinct. Beyond this, have a "supercritical fluid": kind of like a gas in disorganization, but the pressure so high that in terms of molecular closeness and density, almost like a liquid.



1. Which letter represents:

a. Gas Phase

Y

b. Liquid

X

c. Solid

W

d. Triple Point

Z

2. What is the normal bp?

a) 20°

b) 40°

c) 65°

d) 80°

3. What is the normal mp?

a) 20°

b) 40°

c) 80°

4. When a liquid originally at 50° has pressure reduced, at what pressure will it vaporize?

~0.8 atm

5. When solid at 0.5 atm is warmed, does it:

a) melt

or

b) sublime

not solid \rightarrow gas
solid \rightarrow liquid

Wonderful Water: Special Properties (Section 11.4)1. Liquid Phase, and **Amazingly High Boiling Point:**

- Given small size/mass/London force, it's amazing that it's a liquid
- Liquid water essential to life

| | <u>Molar Mass</u> | <u>Bp (°C)</u> | | <u>Molar Mass</u> | <u>Bp (°C)</u> |
|-----------------|-------------------|----------------|------------------|-------------------|----------------|
| N ₂ | 28 | -196 | HF | 20 | -164 |
| O ₂ | 32 | -183 | H ₂ S | 34 | -60 |
| CO ₂ | 44 | -78 | NH ₃ | 17 | -33 |
| CH ₄ | 18 | -161 | H ₂ O | 18 | +100 |

2. "Universal Solvent": **Amazingly Good and Diverse Dissolving Power**

- Far more substances dissolve in water than in any other liquid
- Ionics, moleculars, and biologicals
- Can basically dissolve anything with nitrogens or oxygens in it (through hydrogen bonding)
- Can dissolve tons of ionics (through ion-dipole bonding)
- Solvent of the blood and of biological cells, delivers everything a body needs

3. Density (Unique Phase Diagram): **Amazingly Unusual and Beneficially Low Density of Solid Water (Ice)**

- Other solids more dense than liquids (because solids normally more organized and packed tighter) → solids sink to the bottom of liquids
- Solid water (ice) is unique in that it is **less dense** than liquid water.
 - Thus ice floats on water
 - Water underneath is insulated from winter cold, stays liquid
 - Water life is possible.
 - If solid ice fell to the bottom, whole lakes would freeze in cold winters and all biology would die
- 4°C liquid water is denser than warmer or colder liquid water, or solid ice. It sinks to the bottom → O₂ delivery and nutrient exchange

4. Water as Earth and Body Air Conditioner: **Amazingly High Heat Capacity**

- Winter heater: when water freezes, it releases heat. Without freezing water, winter temps would be 30° colder!
- Summer chiller: Evaporation absorbs heat, so instead of hitting 120° we just evaporate some lake water
- Sweat/evaporation keeps us from overheating
- Water has an extraordinarily high heat capacity for a molecular substance or for a liquid
 - A lot of energy is involved to change it's temperature by much
 - This helps to prevent wide temperature variations that are hostile to life.

5. **Amazingly High Surface Tension**

- Good for bugs, good for ships

The extraordinary Hydrogen-bonding interactions involved with water underlie all of its special properties.

Metals (Section 11.9)

- View as metal cations immersed in sea of electrons
 - The charge attraction is between the positive cations and the negative electrons
- Network substance → solid (except mercury)
- Unlike covalent bonds, where two electrons are precisely localized between two nuclei, metallic electrons are free-flowing
- Resulting properties:
 - mobile e's → **electrical** (and thermal) **conductivity**
 - variable hardness, mp
 - malleable, ductile: not brittle
 - can pound, bend, shape, draw into wires.....
 - an atom can be moved without really breaking a full bond, unlike an ionic crystal where it's really hard to move anything without breaking the bonding
 - Very high bp: you can move an atom/ion within the sea of electrons, but to remove it altogether is very difficult
- Shiny appearance

Overview: Types of Solids (Section 11.5)**Table 11.5 Structures, Bonding, and Properties of Various Types of Solid Substances**

| Type | Examples | Structural Units | Forces Holding Units Together | Typical Properties |
|------------------|---|---|---|--|
| Ionic | NaCl, K ₂ SO ₄ , CaCl ₂ , (NH ₄) ₃ PO ₄ | Positive and Negative ions (some polyatomic); no discrete molecules | Ionic bonding: attractions among charges on positive and negative ions | Hard; brittle, high melting point; poor electrical conductivity as solid, good as liquid; often water-soluble |
| Metallic | Iron, silver, copper, other metals and alloys | Metal atoms (or positive metal ions surrounded by an electron sea) | Metallic bonding; electrostatic attraction among metal ions and electrons | Malleability; ductility; good electrical conductivity in solid and liquid; good heat conductivity; wide range of hardness and melting point; low water solubility |
| Molecular | H ₂ , O ₂ , I ₂ , H ₂ O, CO ₂ , CH ₄ , CH ₃ OH, CH ₃ COOH | Molecules with covalent bonds | London forces, dipole-dipole forces, hydrogen bonds | Low to moderate melting points and boiling points; soft; poor electrical conductivity in solid and liquid; variable water solubility |
| Network Covalent | Graphite, diamond, quartz, feldspars, mica | Atoms held in an infinite two-, or three-dimensional network | Covalent bonds; directional | Variable but often very hard; variable but often very high mp; poor water solubility; low electrical conductivity |

1. Classify the following as ionic, molecular, metallic, or network covalent solids

- a. High mp, great hardness, low electrical conductivity network covalent (diamond, for example)
- b. Low mp, soft, low electrical conductivity molecular
- c. High water solubility, low electrical conductivity alone, good conductivity in water ionic
- d. High electrical conductivity \Rightarrow metallic

2. Which property is **not** characteristic of a metallic solid?

- a. Excellent thermal conductivity Yes
- b. Excellent electrical conductivity Yes
- c. Variable hardness Yes
- d. Extreme brittleness No Ionic are brittle, but metal atoms/ions can be moved without shattering metallic bonding
- e. Variable melting point