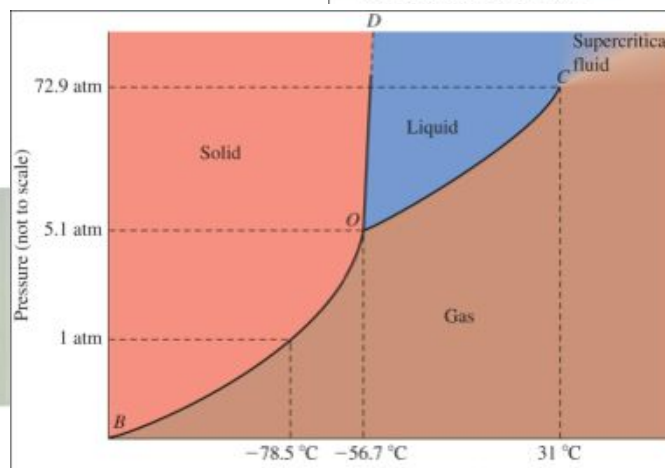
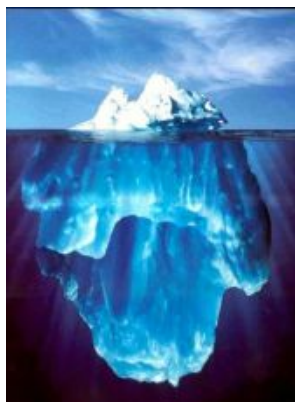


CHEM 1AA3: Intro. Chemistry II

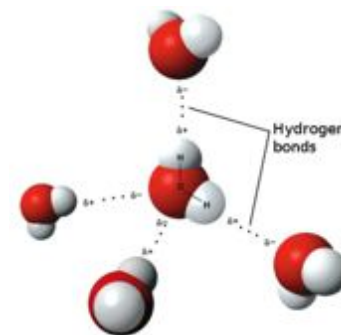
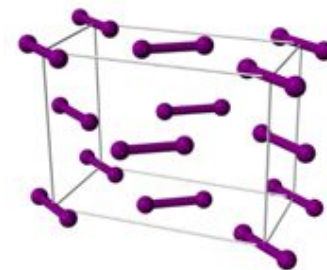
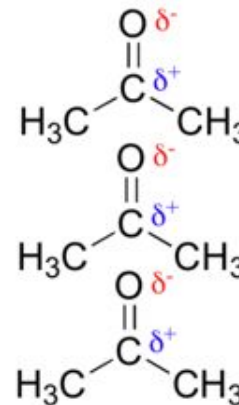
Ch.12: Liquids, Solids & Intermolecular Forces (12.1-12.4)



12.1: Intermolecular Forces

In pure substances:

- London (dispersion) forces e.g. iodine
- Dipole-dipole forces e.g. acetone
- Hydrogen-bonding forces e.g. water



wikimedia

In solutions we also see:

- Ion-dipole forces e.g., hydrated ions
- Ionic interactions e.g., hydrated ions

London (dispersion) forces

- Also called **induced dipole-induced dipole** forces
 - nonpolar molecule,
 - experiences an instantaneous dipole,
 - which induces a dipole in its neighbour.

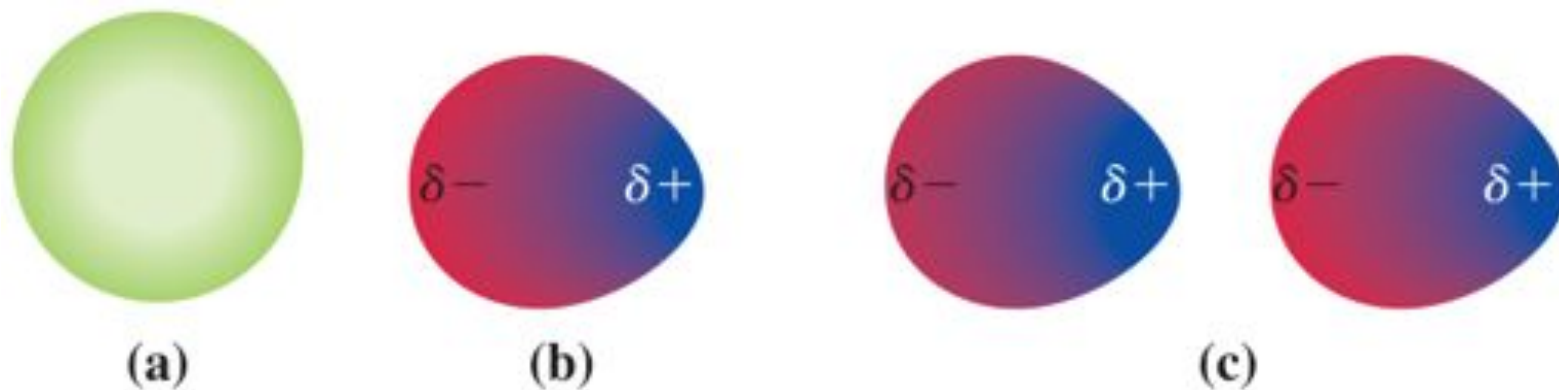


Fig. 12-2, p. 499

- Instantaneous dipoles propagate throughout the sample
- Force strength depends on **polarizability** (the tendency for charge separation to occur).

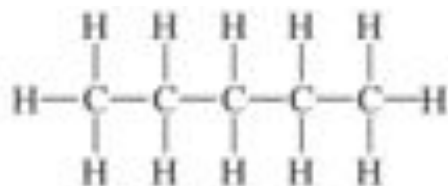
London (dispersion) forces

- Forces strength increases with:
 - atomic number and size of the molecule (because of polarizability):

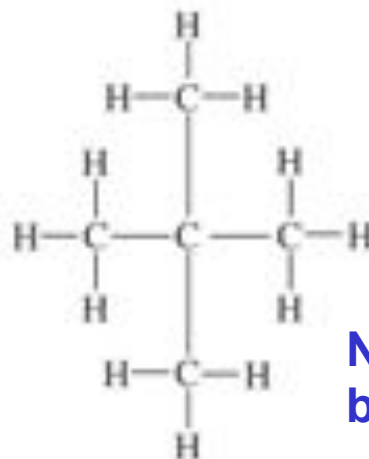
Molecule	Melting point
Cl_2	172 K
I_2	387 K

Table 9-5 (p. 381)

- linear versus branched structures (because of increased intermolecular contact area):



Pentane,
b.p. = 36.1 °C



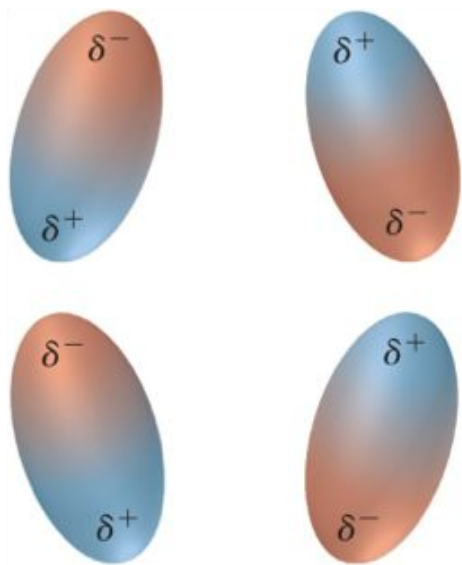
Neopentane,
b.p. = 9.5 °C

Fig. 12-3



Dipole-dipole forces

- Occur in polar molecules (molecules with permanent dipoles)
 - polar molecules have bond dipoles and asymmetric shape (e.g. acetone is polar, while carbon dioxide is not polar)
- Being polar increases b.p. over dispersion forces alone
 - e.g., N₂ (77K), NO (121 K), O₂ (90 K)



e.g.: acetone

p. 502

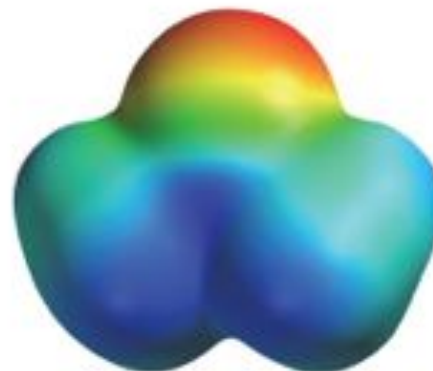
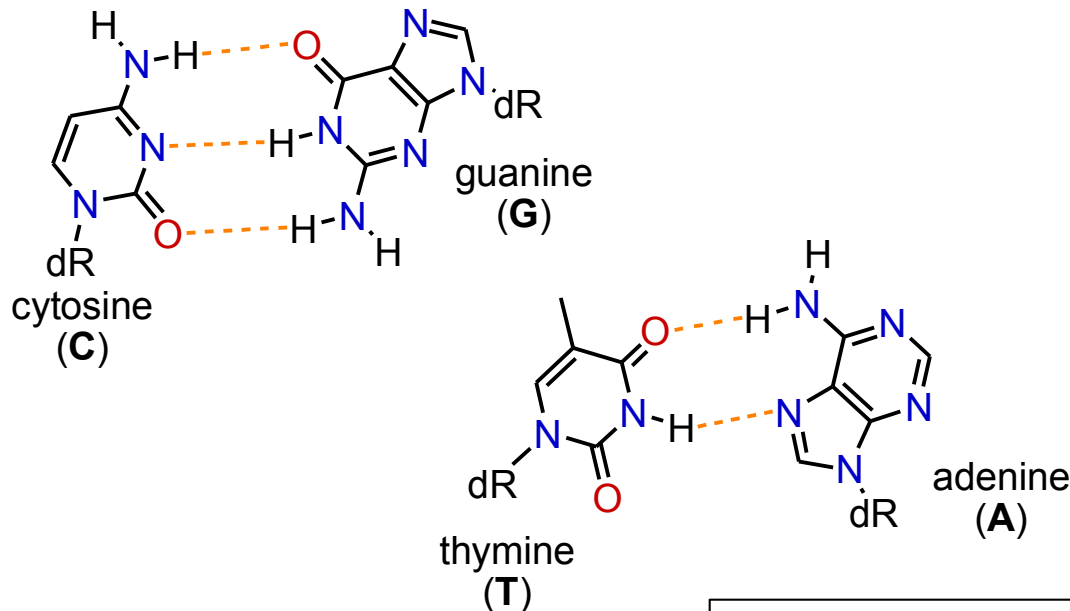


Fig. 12-4

Hydrogen bonding

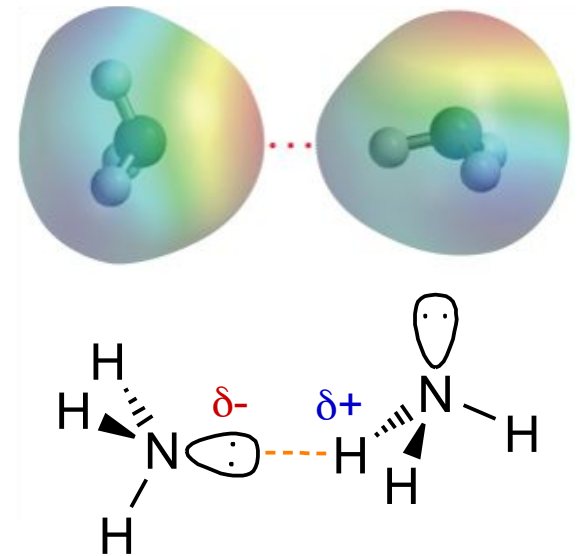
- Between an H atom in a polar bond (i.e., H-N, H-O, or H-F) and another electronegative atom (i.e., N, O, or F)
- One H-bond is small, but many are mighty.

Base-pairing in DNA



----- = hydrogen bond
dR = deoxyribose

Base-pairing in ammonia



p. 495
(9th ed.)

Effects of Hydrogen bonding

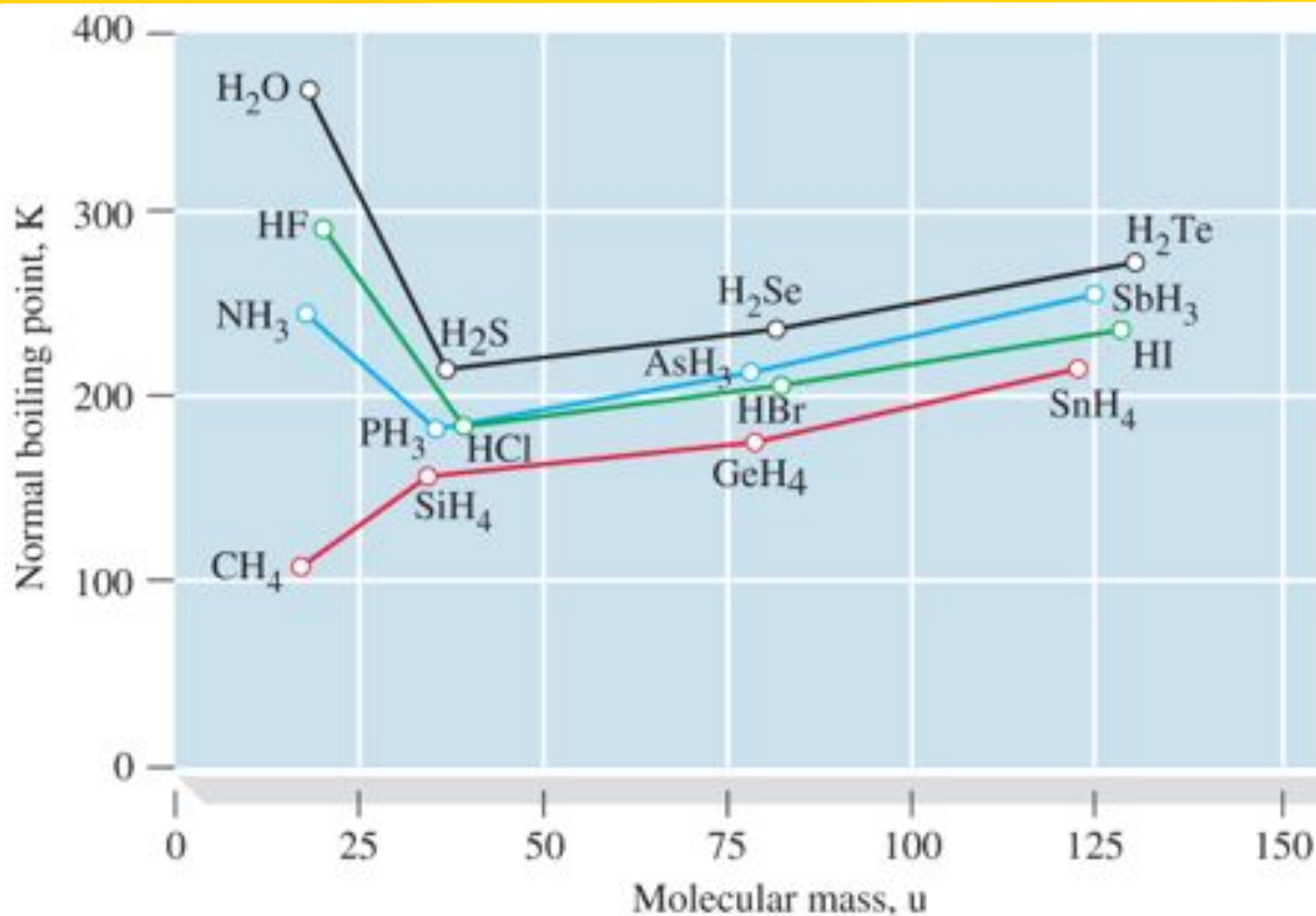


Fig. 12-5

How mighty are those H-bonds?

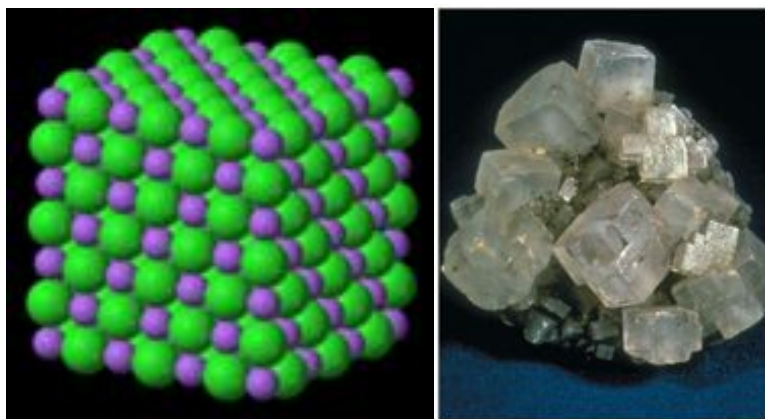
- Demonstration: 2 magazines with pages interwoven
- Mythbusters video of phone books:
<http://www.wimp.com/themyth/>
- They are very mighty!
(8000 lb force to separate the phone books)



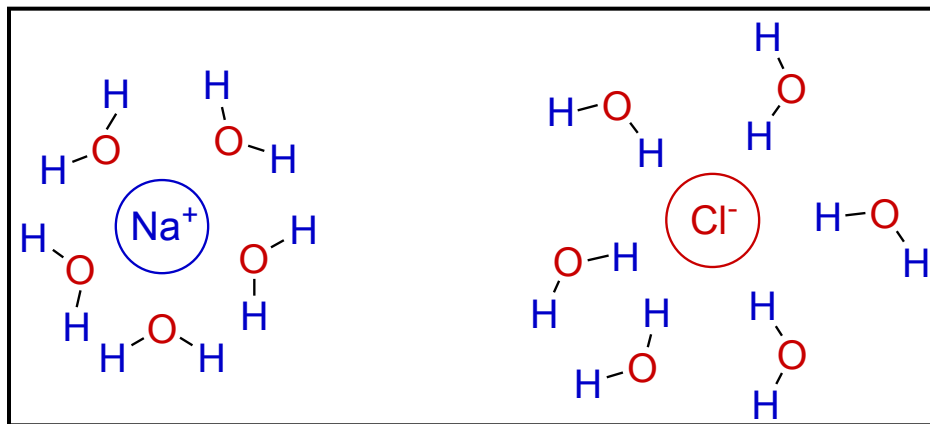
Ionic Interactions

- Ionic interactions are very favourable in solids, but are weaker in solution, and can even be unfavourable in water, where solvation of the individual ions by water can be more favourable than the ionic interactions

Solid NaCl



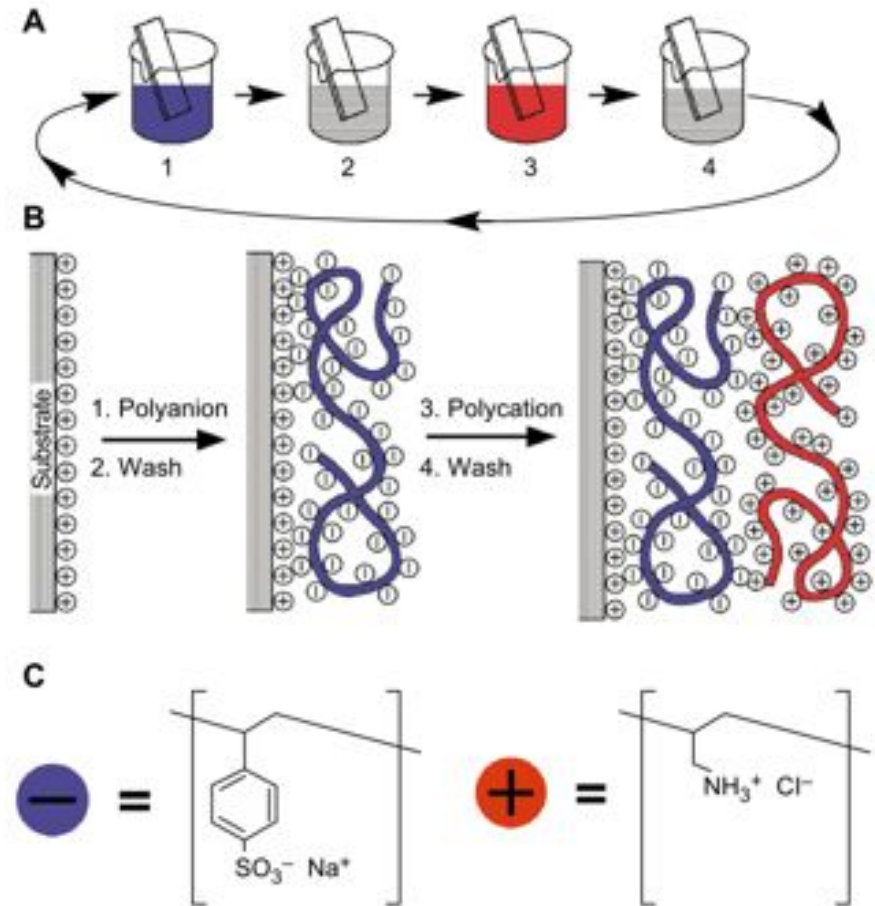
Aqueous NaCl solution



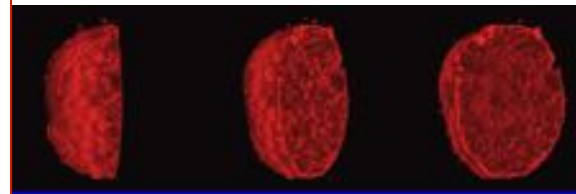
Melting point = 801 °C

Ionic Interactions: Applications

Layer-by-layer polyelectrolyte deposition



Analogous polymer shells may one day be used to protect transplanted donor cells from the hosts immune system: Encapsulated Islets of Langerhans for Type 1 diabetics. They can produce and release insulin, but are protected from immune rejection.



Relative Strengths of IMFs: A summary

- All molecules have dispersion (London) forces
- The range of strength for each force type overlaps, but approximately:

Dispersion < Dipole < H-bonding < Ionic/Covalent

Interaction	Interaction energy (kJ/mol)*
Dispersion	0.05 – 40
Dipole	5 – 25
Hydrogen bonding	10 – 40 (per bond)
Ionic	400 – 4000
C-C covalent bond	350 (per bond)

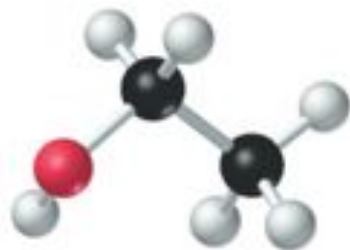
*values from p. 507, Petrucci 10th ed.



12.2: Impact of IMF Strength in Liquids

Physical property	Effect of increasing IMF
Boiling point (b.p.)	increases
Vapour pressure	decreases
Melting Point (m.p.)	increases
Viscosity	increases

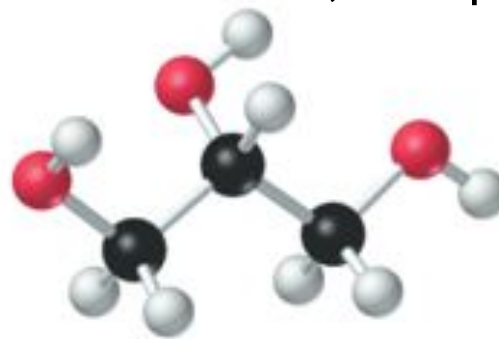
e.g., more H-bonding = higher viscosity (measured in cP, centipoise)



Ethanol
1.2 cP



Ethylene glycol
20 cP



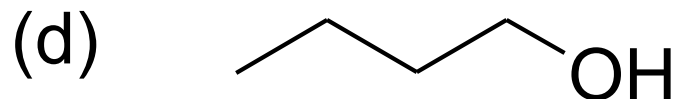
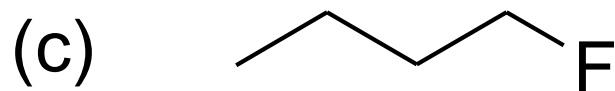
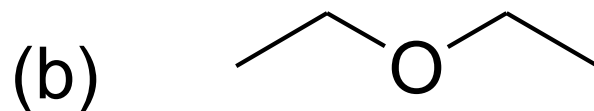
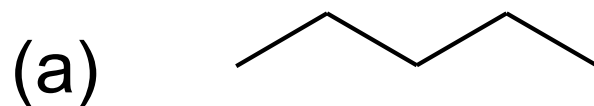
Glycerol
1500 cP

p. 504



iClicker Question #1

Which compound will have the highest boiling point?



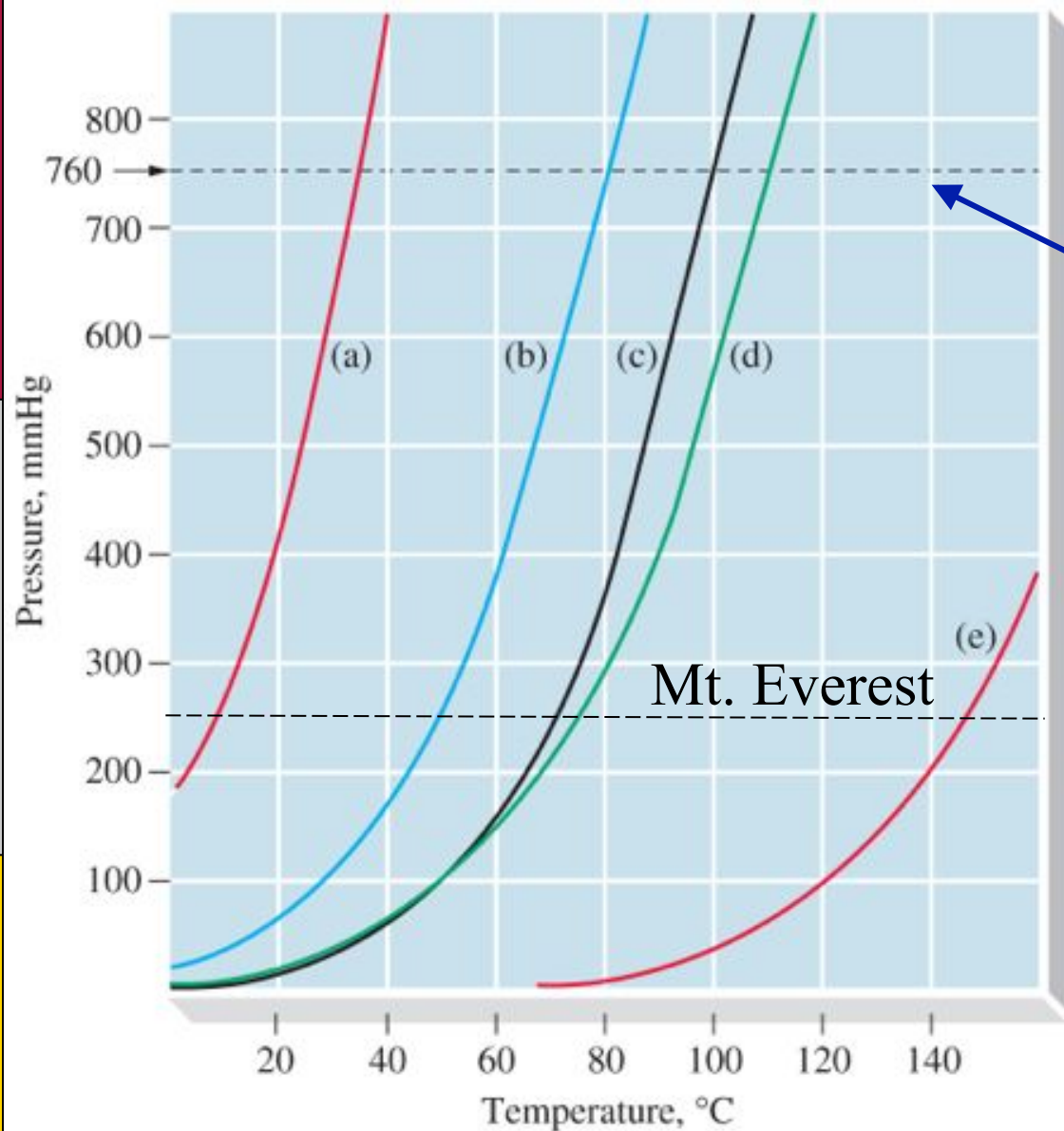
Vapours/Solids/

- IMFs do not have a significant effect on gases, as molecules are well separated
- Melting point of a solid is also impacted by IMF strength
- Vaporizing from a liquid to a vapour *is* impacted by IMF strength
- Vapour pressure vs. T plots give boiling/condensation points at different pressures

(Note: You are not responsible for Clausius-Clapeyron eq., p. 516)



P_{vap} vs T



Normal boiling point
when $P_{\text{vap}} = 1 \text{ atm}$

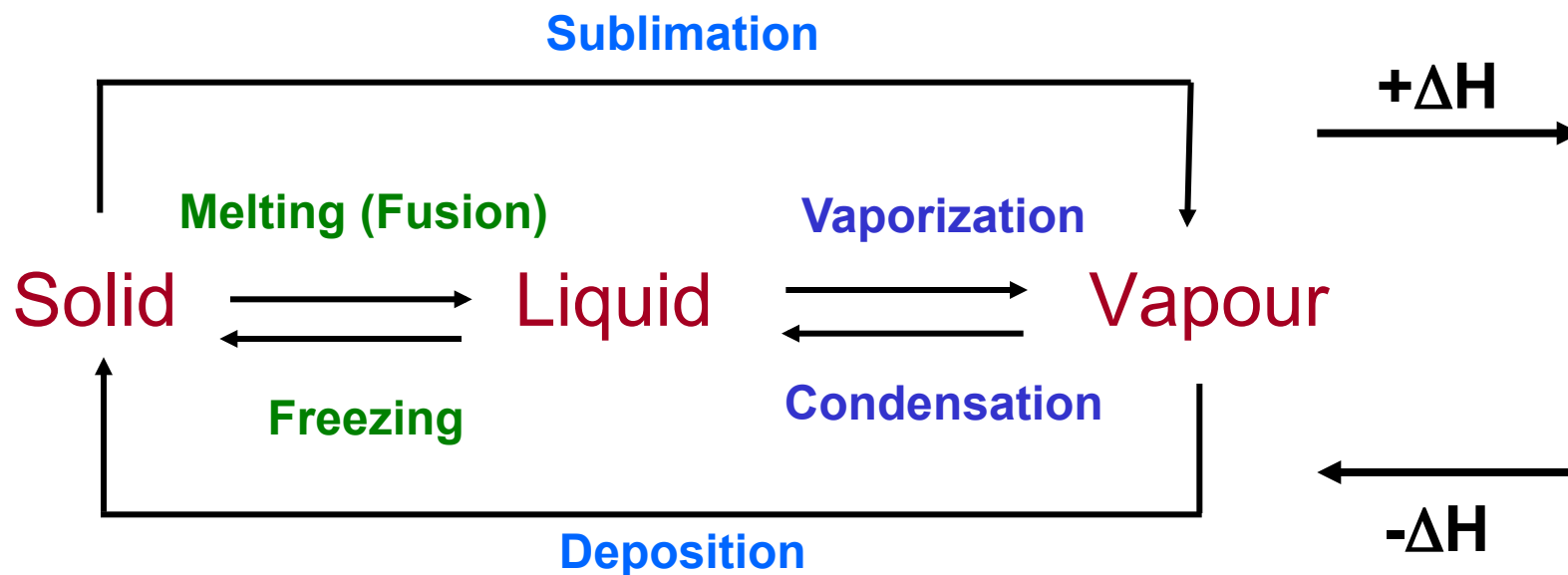
- (a) Diethyl ether, $(\text{CH}_3\text{CH}_2)_2\text{O}$
- (b) Benzene, C_6H_6
- (c) Water, H_2O
- (d) Toluene, $\text{C}_6\text{H}_5\text{-CH}_3$
- (e) Aniline, $\text{C}_6\text{H}_5\text{-NH}_2$

Fig. 12-9

- P_{vap} is influenced by IMF strength

12.3: Solids (and Liquids & Vapours)

- If we extend the diagram by adding in solids, then we have a diagram that captures many phase transitions:



12.4: Phase diagrams

Phase diagram for CO₂

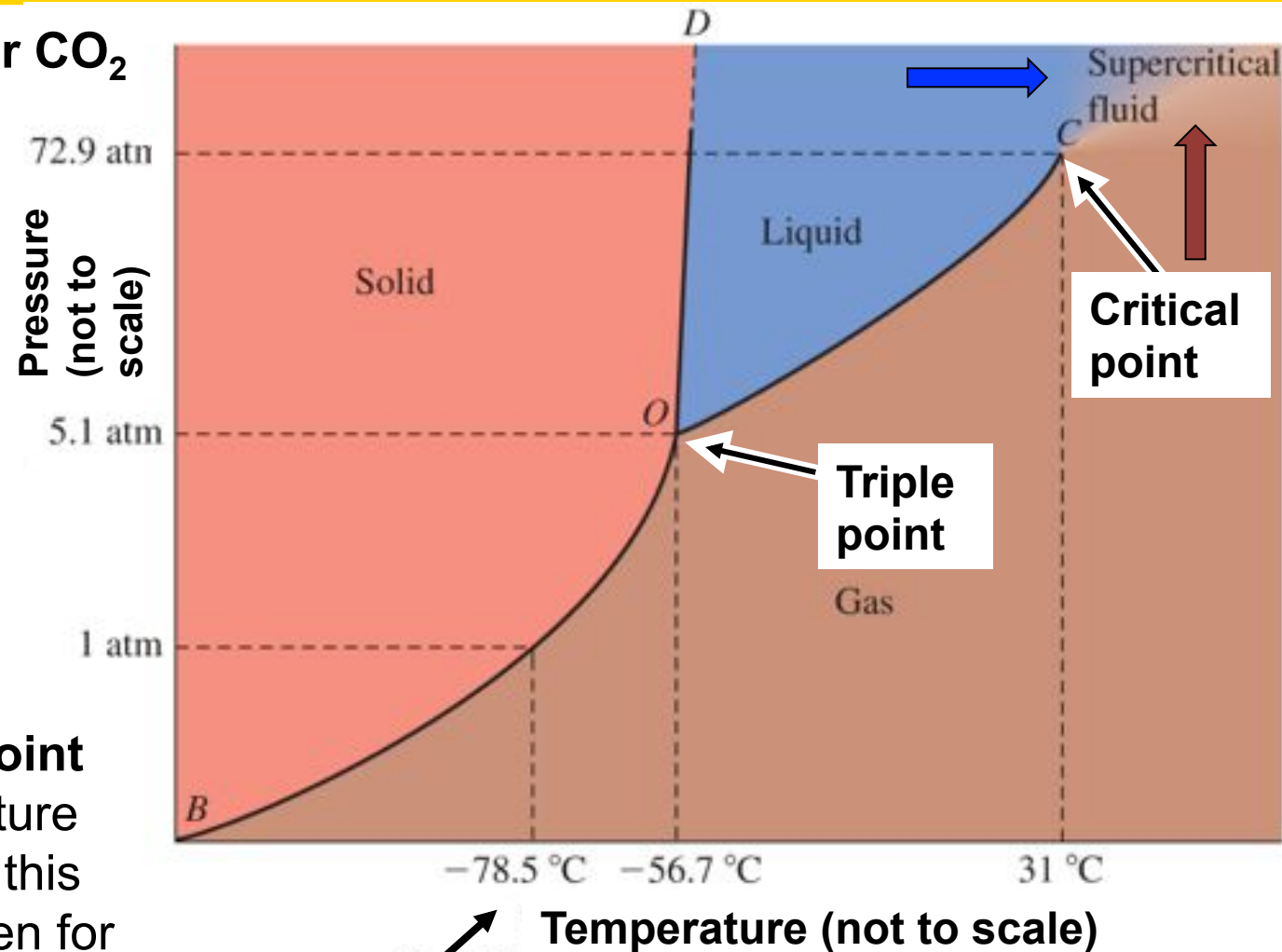
O - triple point:
all 3 phases in
equilibrium

C - critical point:
beyond C is a
supercritical fluid

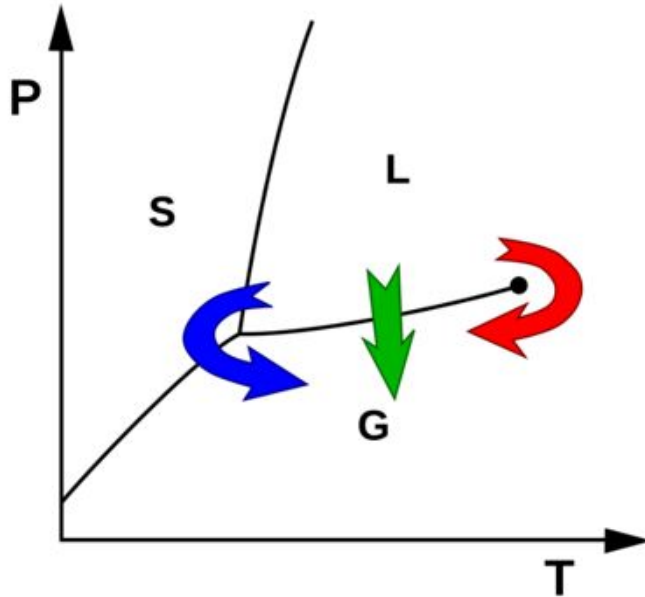
Normal melting point
is melting temperature
at 1 atm (note that this
transition is not seen for
CO₂)

Fig. 12-28

Instead, sublimation
occurs at 1 atm for CO₂



Critical Point Drying



http://en.wikipedia.org/wiki/Supercritical_drying



Jet
Propulsion
Lab

Conventional drying involves liquid-gas phase boundaries that exert huge capillary forces on samples – collapsing them.

Freeze-drying involves a solid-gas boundary which can still collapse fragile structures.

Supercritical Drying avoids any phase boundaries, and is hence used to dry the biological samples, and aero-gels (0.1% solid) used as heat shields on space shuttles

The critical point

- At the critical point:
 - Density of liquid and vapour are equal
 - Surface tension of liquid approaches zero
 - The interface between (l) and (g) disappears!
 - Occurs at the critical temperature (T_c) & pressure (P_c)

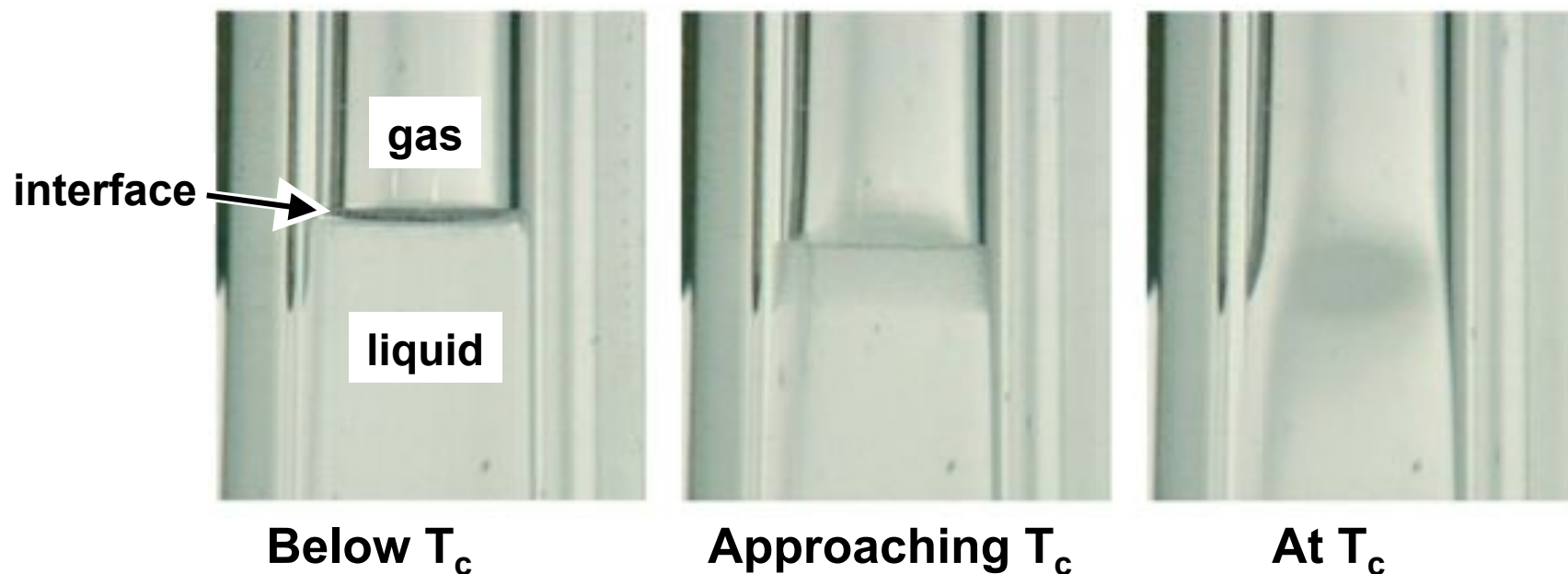


Fig. 12-11

Supercritical Fluids

Depending on path taken from vapour to liquid, the phase transition may not be visible because of critical point (e.g. supercritical drying).

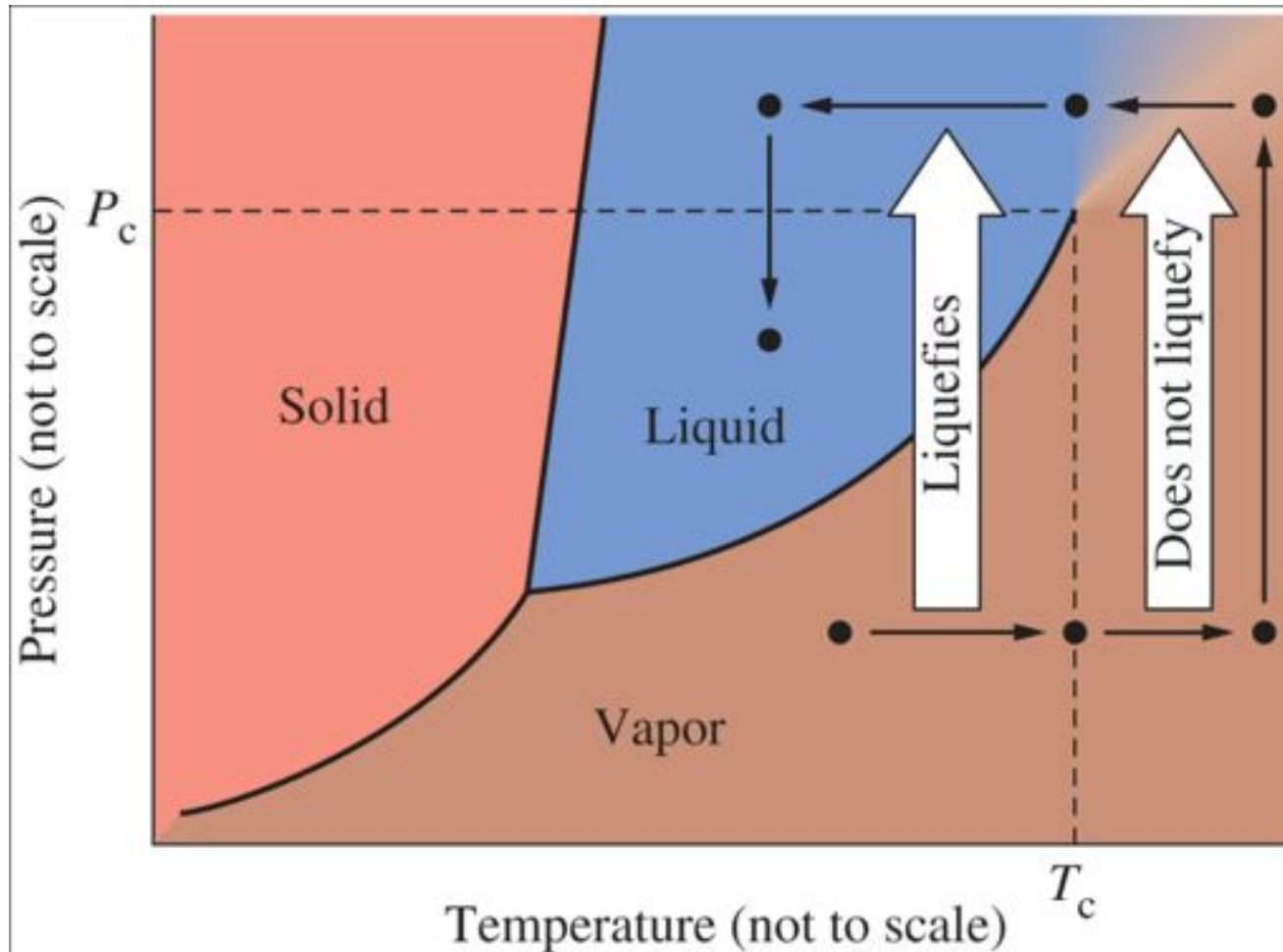
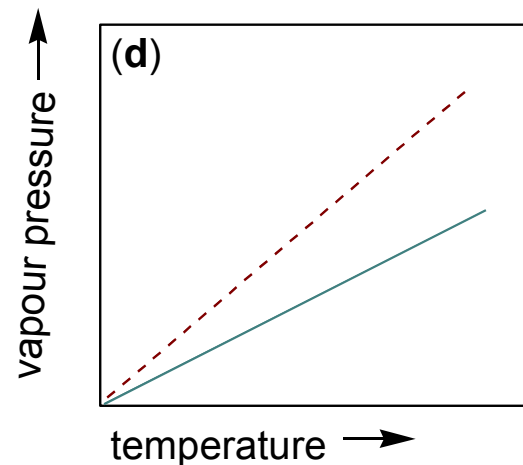
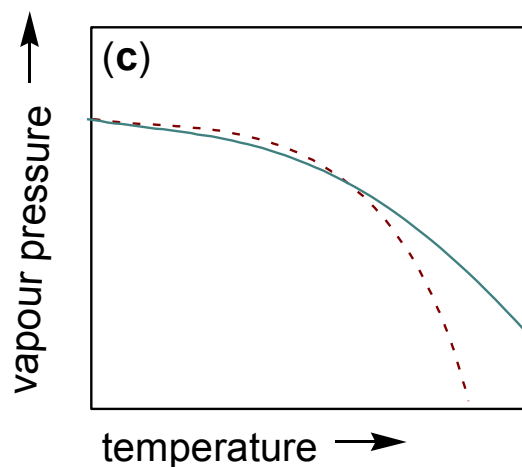
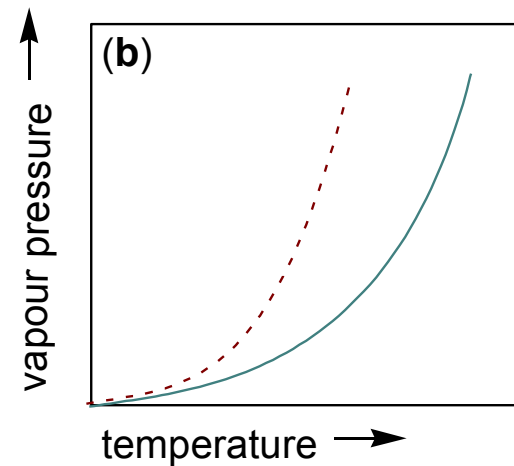
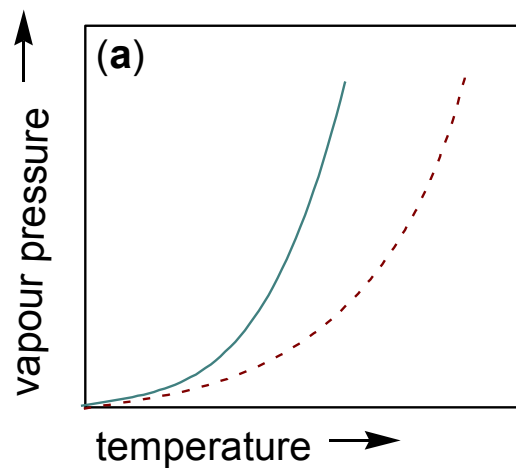
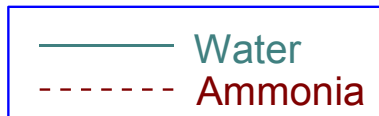


Fig. 12-29

iClicker Question #2

Which is the correct graph of temperature versus vapour pressure?



Supercritical CO₂: A “Green” Solution

- An alternative to dry cleaning solvent tetrachloroethylene
 - Problems with chlorinated solvents:
 - release of Cl-containing compounds into the atmosphere: Cl• radicals damage the ozone layer
 - tetrachloroethylene is a probable carcinogen for dry cleaning workers
- Other applications of supercritical CO₂:
 - solvent for synthetic organic chemistry (e.g., drug synthesis)
 - caffeine extraction from coffee (decaffeination); replaced extraction with methylene chloride



Key concepts

- Intermolecular forces
 - dispersion, dipole-dipole, H-bonding
- Vapour pressure
 - normal boiling point
- Phase changes
 - six to name; normal melting point
- Phase diagrams
 - regions of solid, liquid, gas, supercritical phase
 - phase changes
 - triple point, critical point

