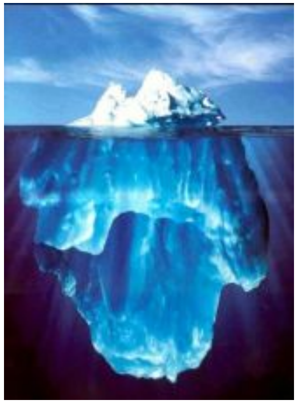
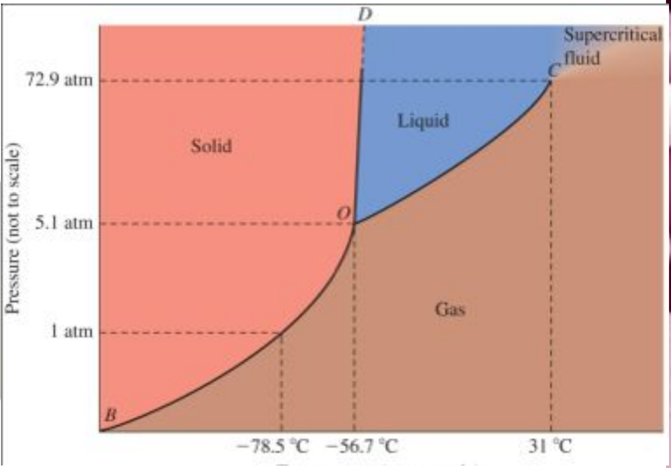
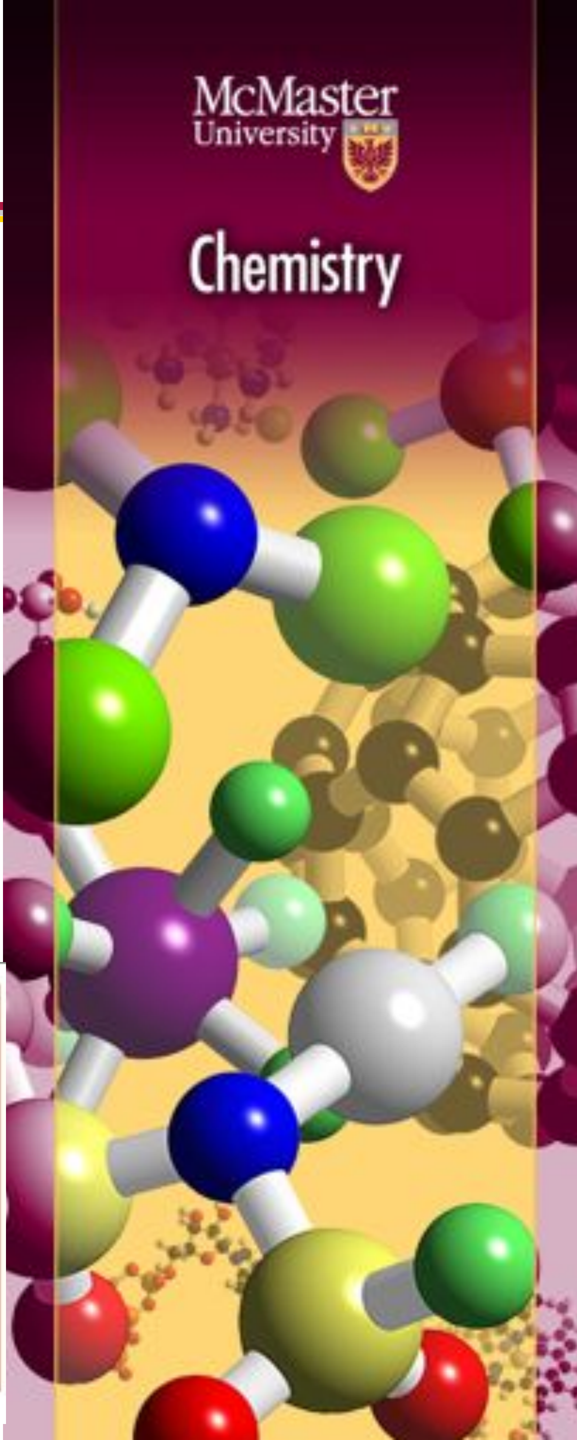
# CHEM 1AA3: Intro. Chemistry II

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







# 12.1: Intermolecular Forces

In pure substances:

- van der Waals forces
- Dipole-dipole forces
- Hydrogen-bonding forces

In solutions we also see:

- Ion-dipole forces
- Ionic interactions

# London (dispersion) forces

- Also called induced dipole-induced dipole forces
  (a) nonpolar molecule,
  (b) experiences
  (c) which induces a

(a)

Fig. 12-2, p. 499

- Instantaneous dipoles propagate
- 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** |
|---|---|
| $Cl_2$ | |
| $I_2$ | |

Table 9-5 (p. 381)

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

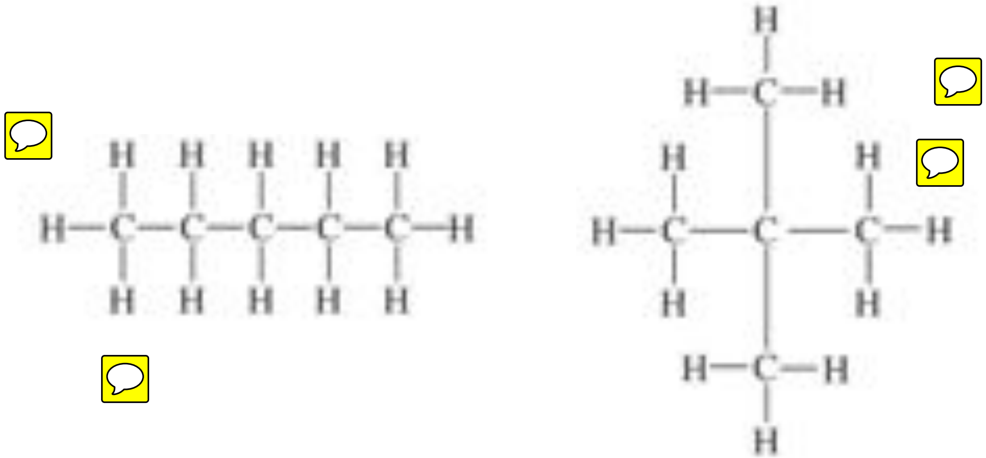


Fig. 12-3

# 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., $N_2$ (77K), NO (121 K), $O_2$ (90 K)

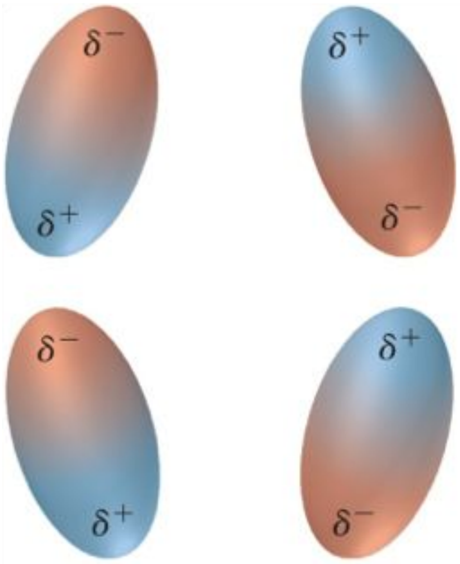
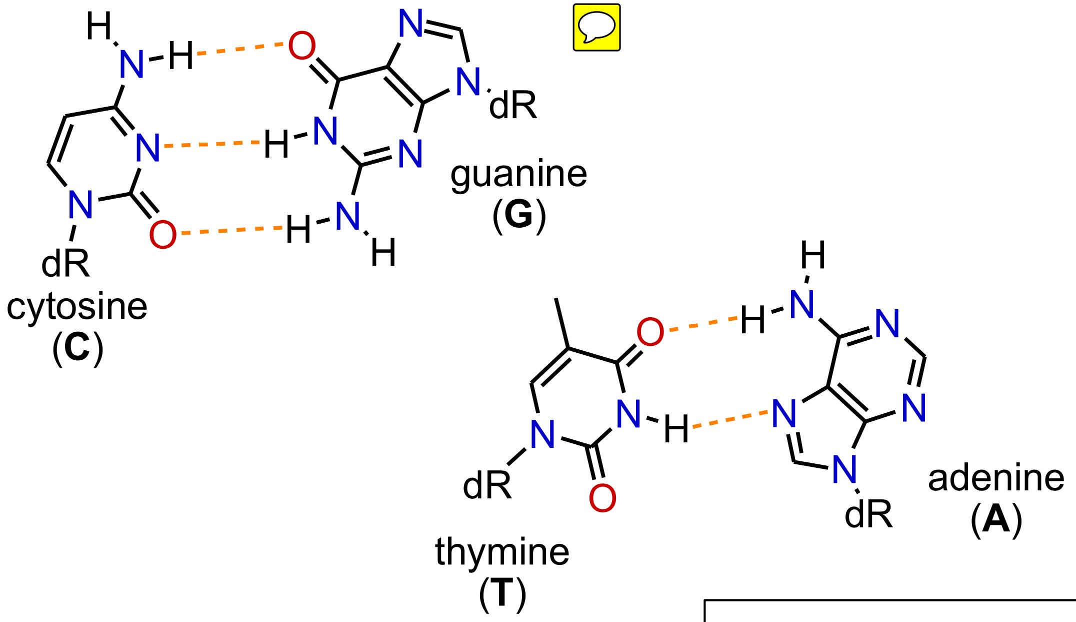


Fig. 12-4

# Hydrogen bonding

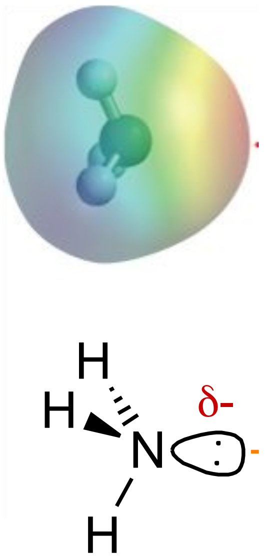
- Between an H atom in a polar bond (i.e., H-N, H-O, or H-F) and another electronegative atom (i.e., N, O, or F)
- One H-bond is small, but many are mighty.

**Base-pairing in DNA**



- - - - = hydrogen bond
dR = deoxyribose

**Base-pairing in ammonia**



p. 495
(9th ed.)

# Effects of Hydrogen bonding

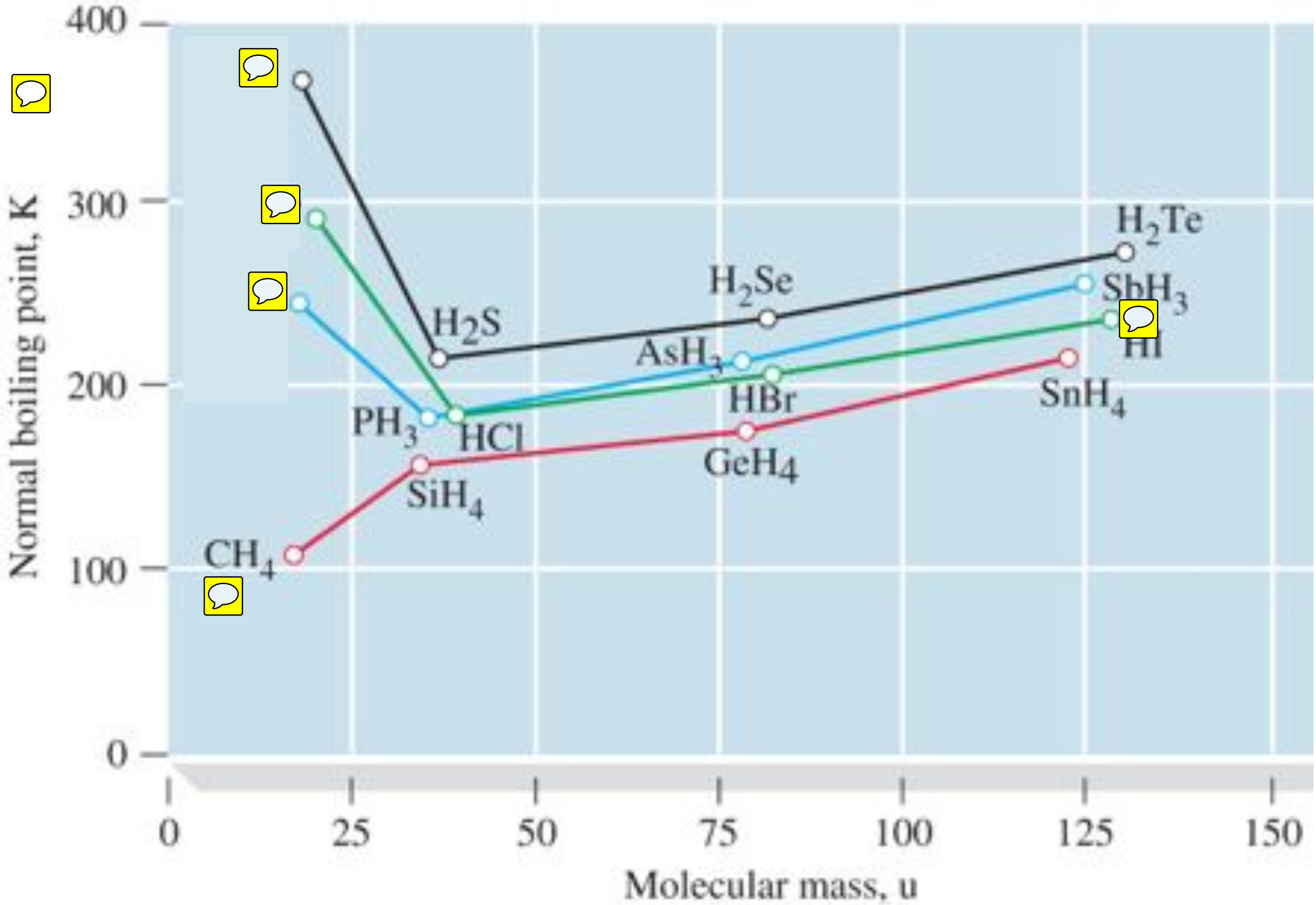


Fig. 12-5

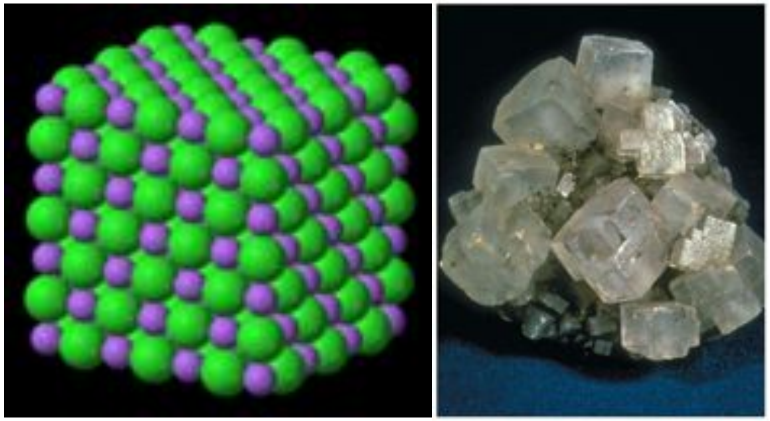
# How mighty are those H-bonds?

- Demonstration: 2 magazines with pages interwoven
- Mythbusters video of phone books: http://www.wimp.com/themyth/

# Ionic Interactions

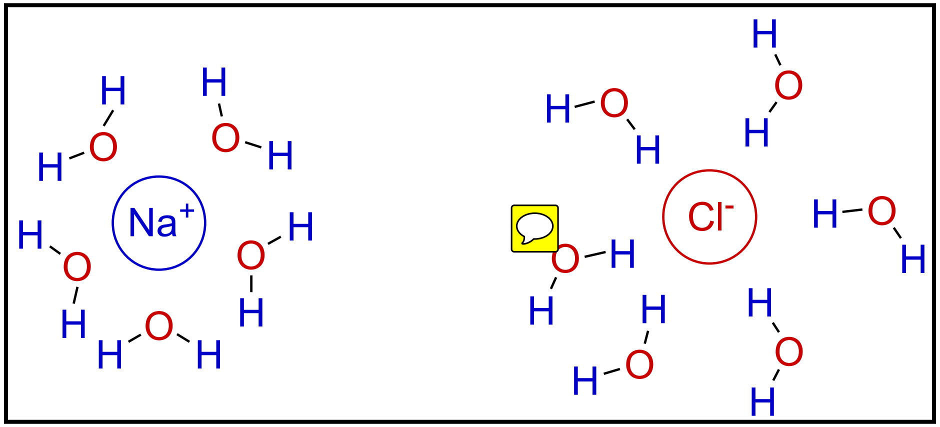
- Ionic interactions are very favourable in solids, but are weaker in solution, and can even be unfavourable in water, where solvation of the individual ions by water can be more favourable than the ionic interactions

Solid NaCl



Melting point = 801 °C

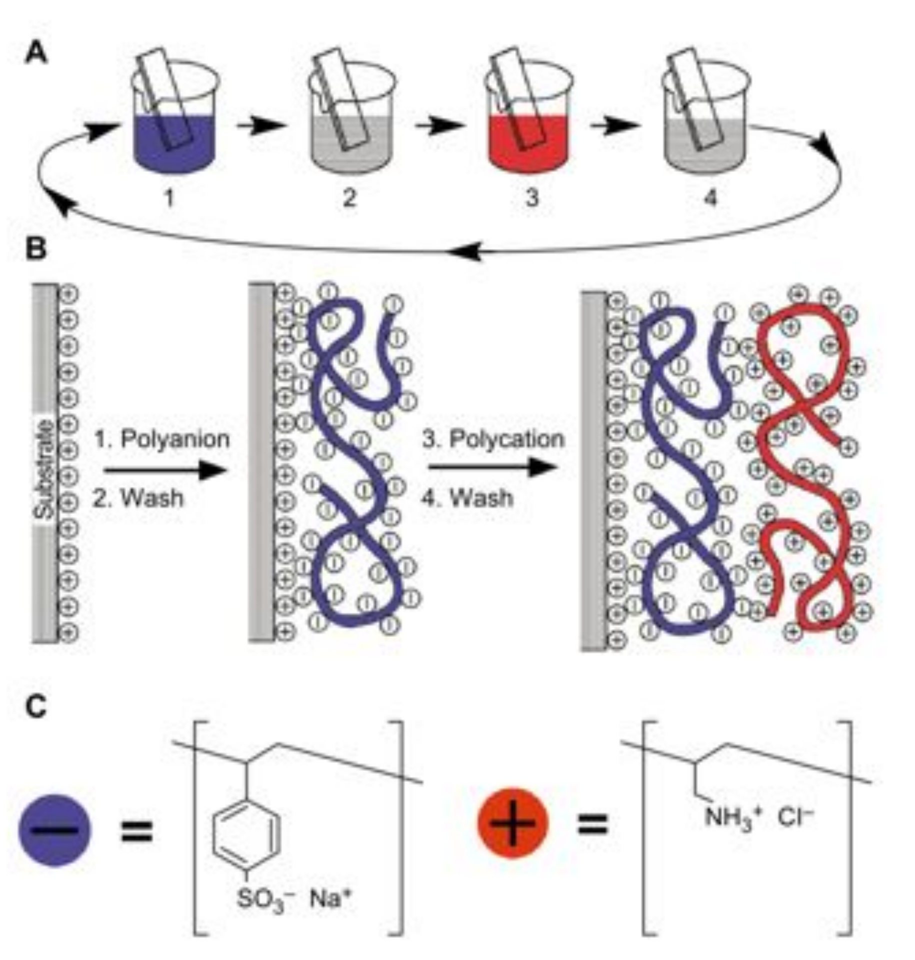
Aqueous NaCl solution



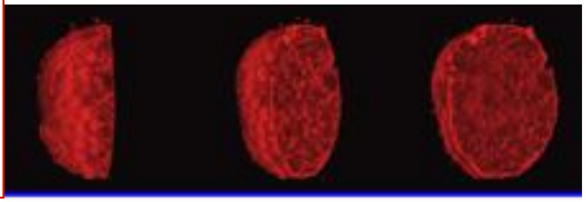
http://www.ck12.org/flexr/chapter/2325/ & JLM Visuals

# 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:

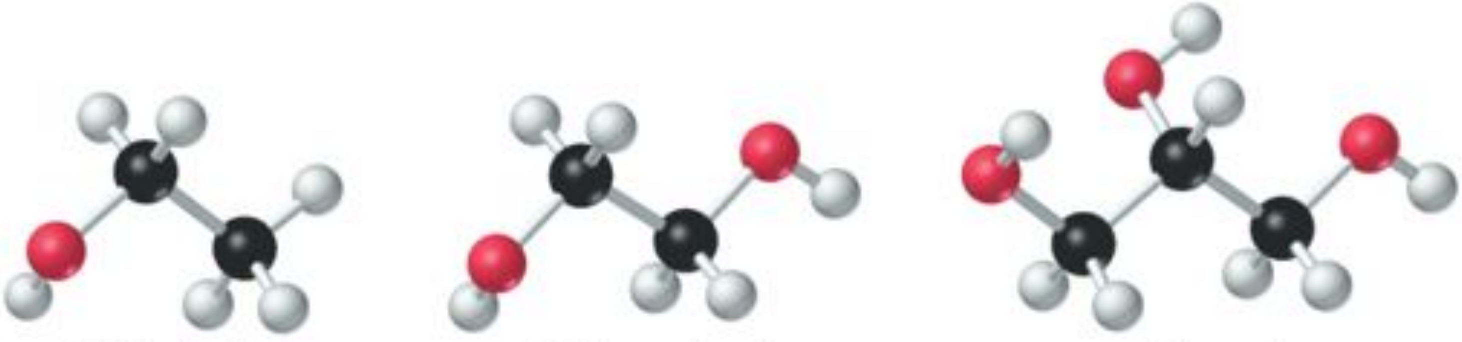
| Interaction | Interaction energy (kJ/mol)* |
|---|---|
| Dispersion | |
| Dipole | |
| Hydrogen bonding | |
| Ionic | |
| C-C covalent bond | |

*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.) | |
| Vapour pressure | |
| Melting Point (m.p.) | |
| Viscosity | |

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



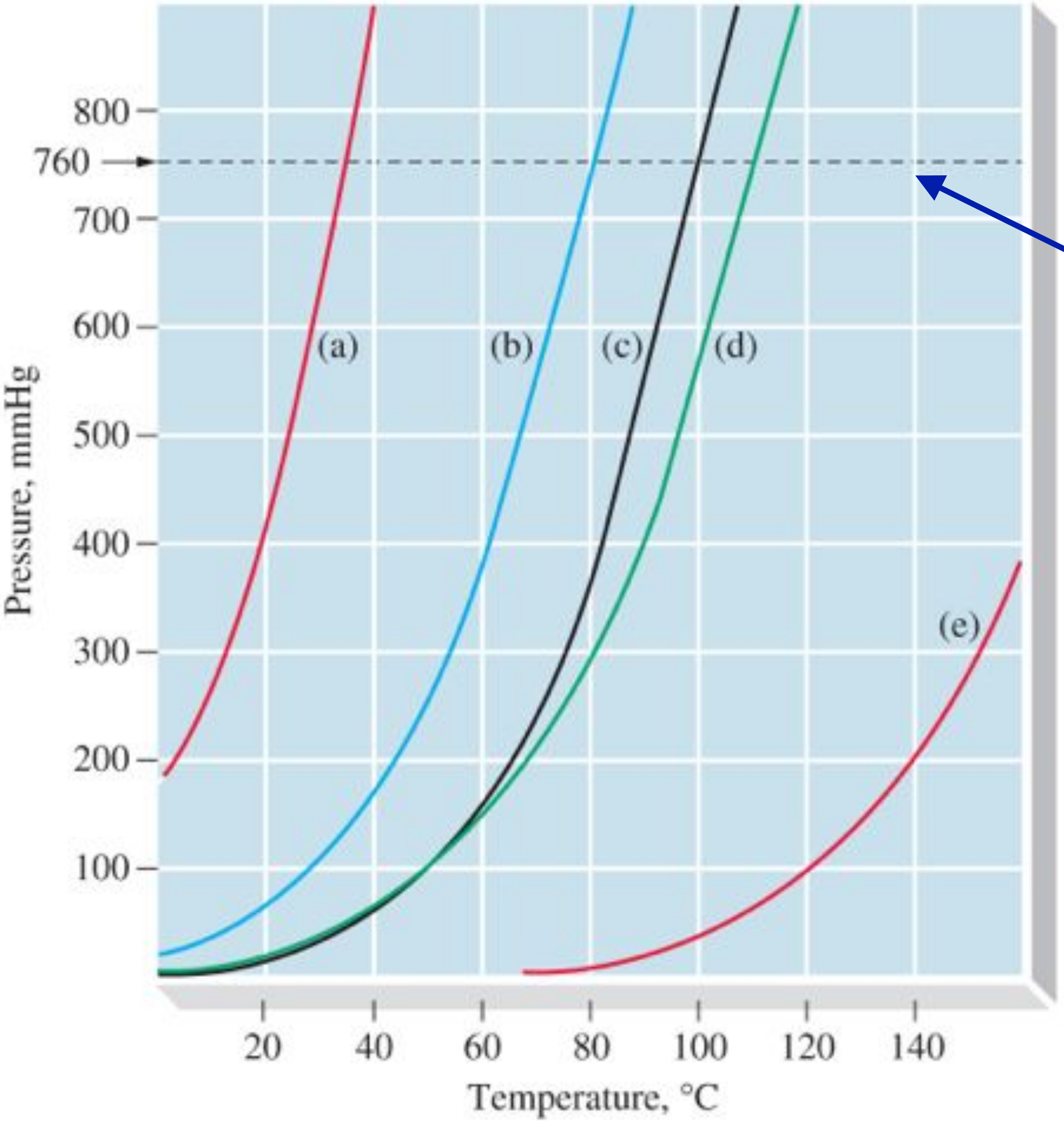
# iClicker Question #1

# Vapours/Solids/Melts

- IMFs do not have a significant effect on gases,
- Melting point of a solid is
- Vaporizing from a liquid to a vapour
- 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 $P_{vap}$ = 1 atm

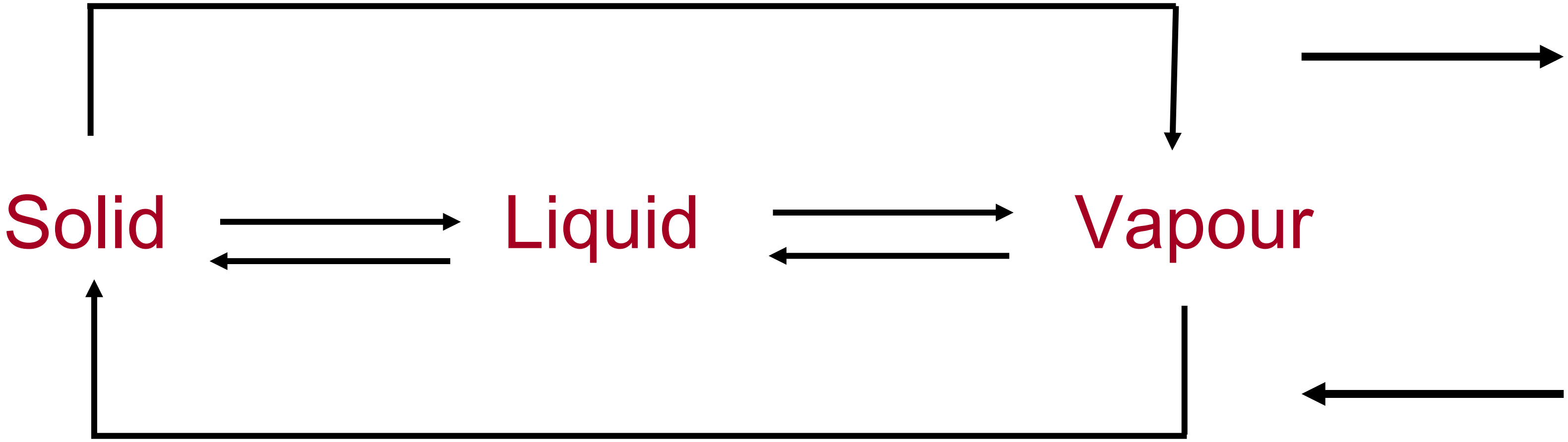
- **(a) Diethyl ether, $(CH_3CH_2)_2O$**
- **(b) Benzene, $C_6H_6$**
- **(c) Water, $H_2O$**
- **(d) Toluene, $C_6H_5$-$CH_3$**
- **(e) Aniline, $C_6H_5$-$NH_2$**

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:



Solid Liquid Vapour

# 12.4: Phase diagrams

**Phase diagram for $CO_2$**

***O* - triple point:** all 3 phases in equilibrium

***C* - critical point:** beyond *C* is a supercritical fluid

**Normal melting point**

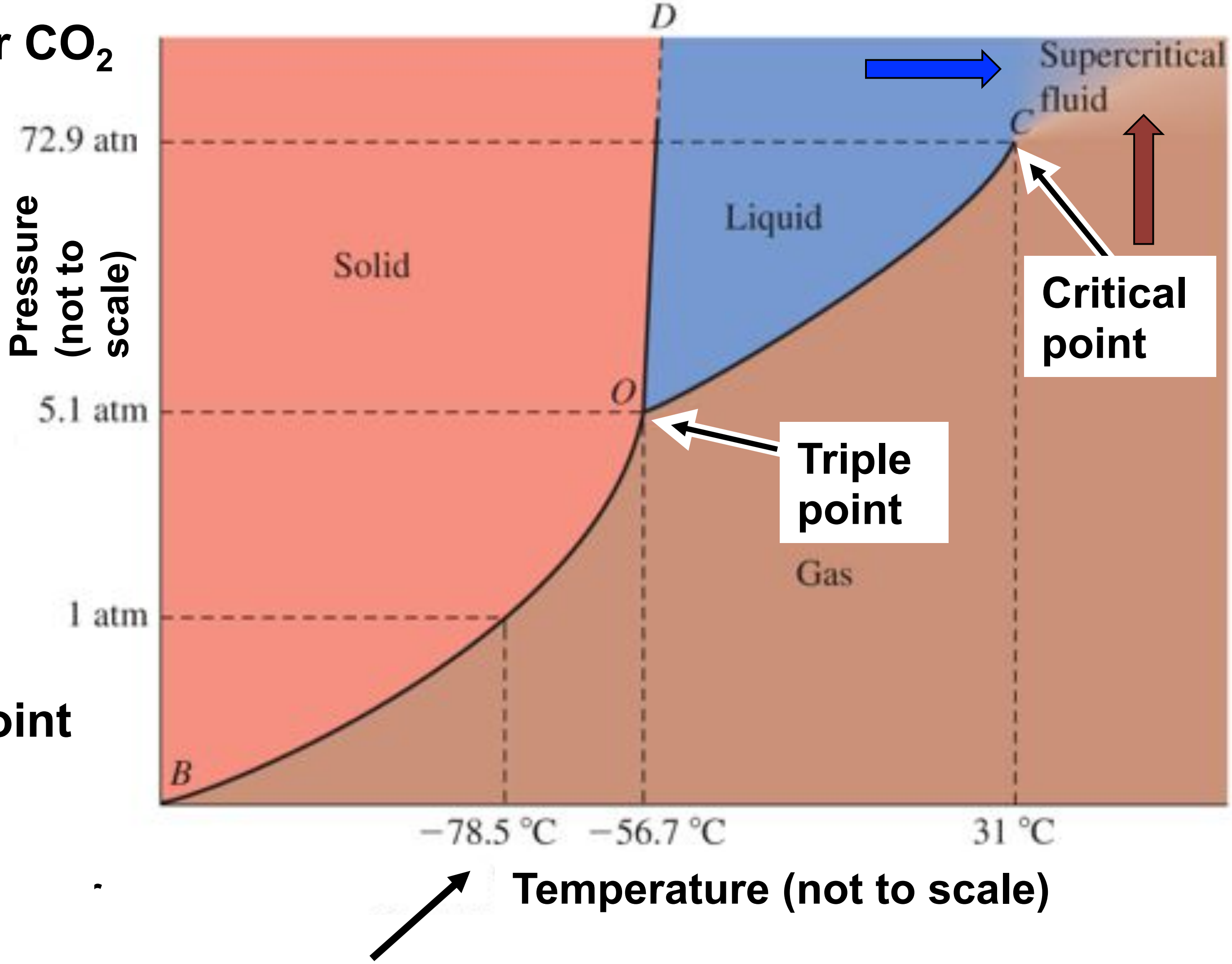
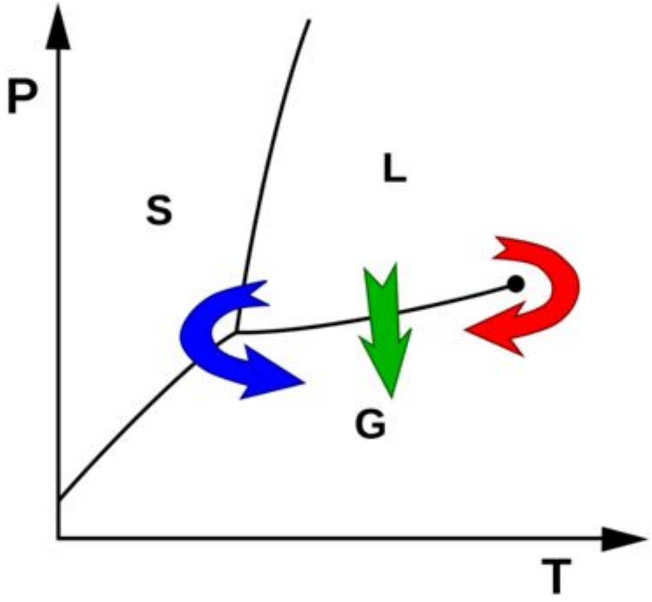


Fig. 12-28

# Critical Point Drying



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

Jet Propulsion Lab

Conventional drying involves liquid-gas phase boundaries

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 areo-gels (0.1% solid) used as heat shields on space shuttles

# The critical point

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

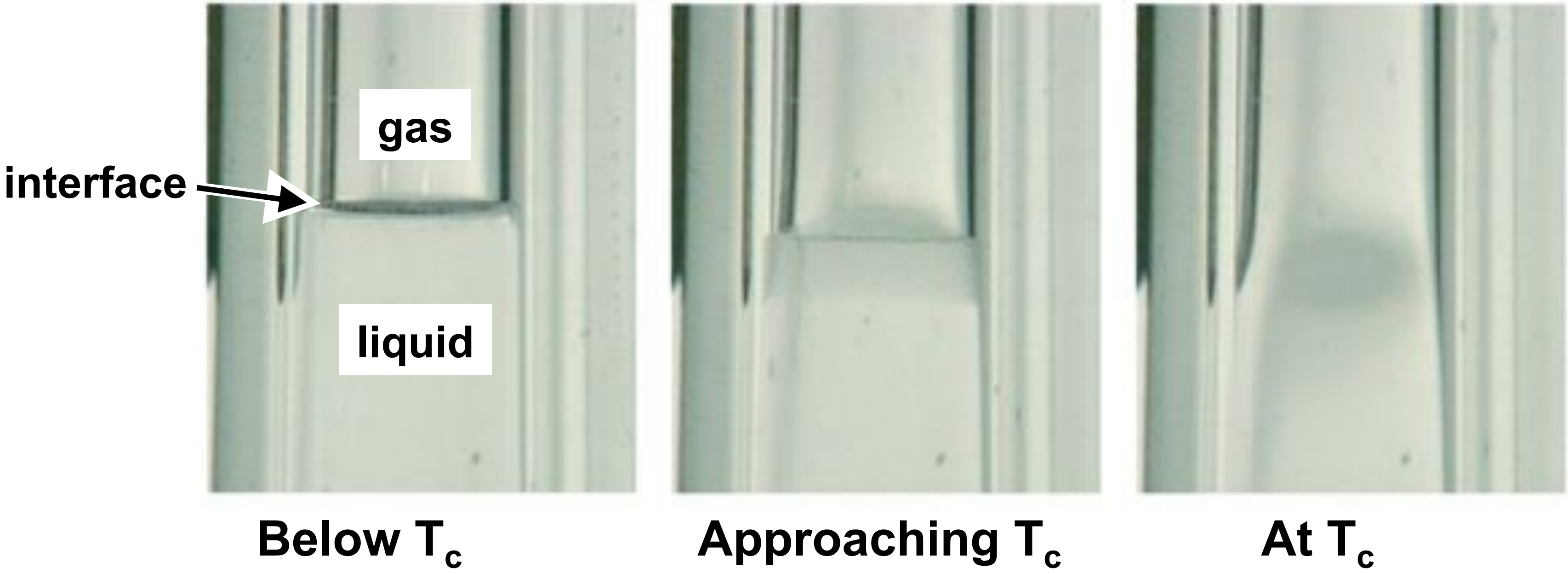


Fig. 12-11

# 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).

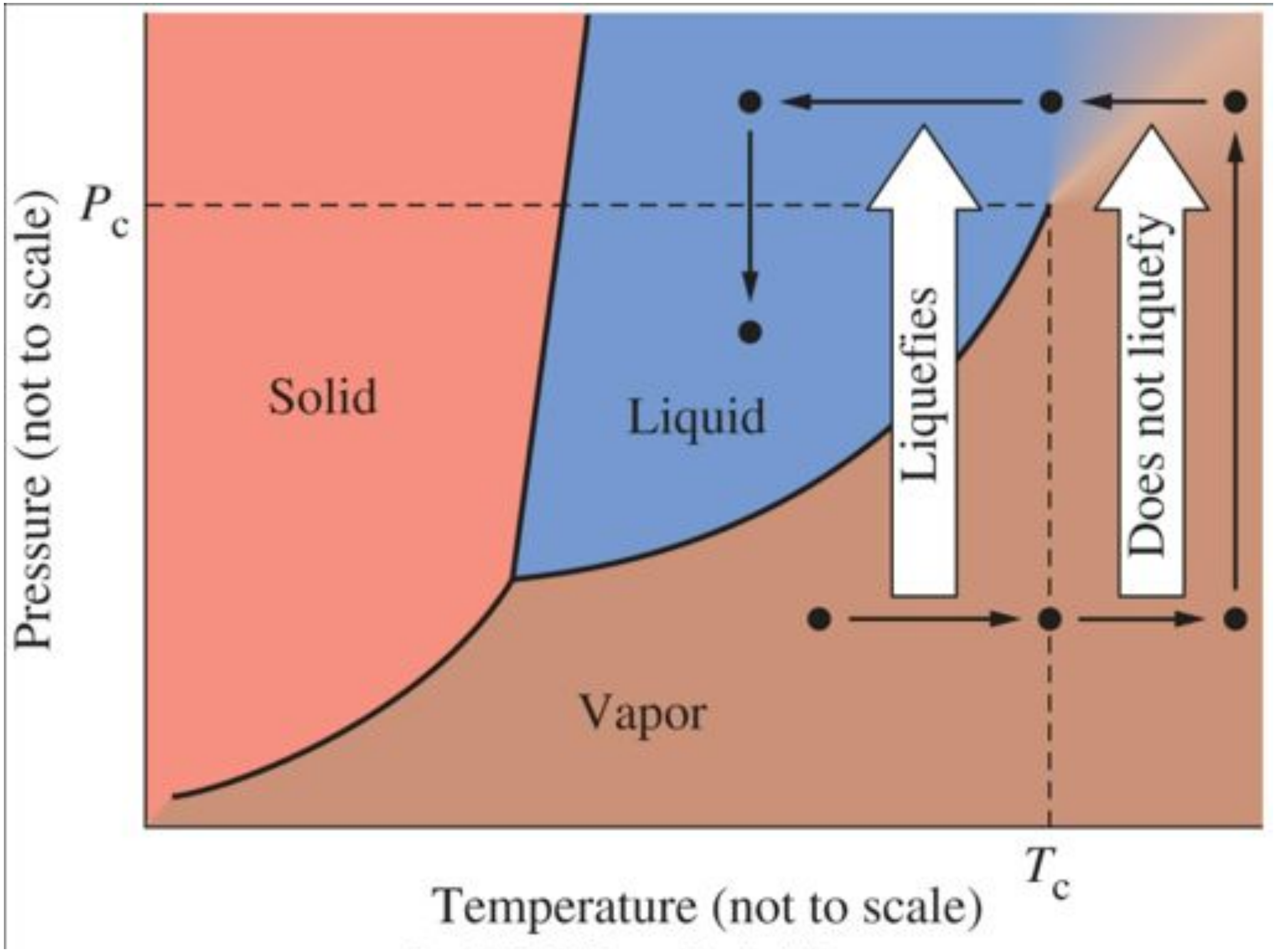


Fig. 12-29

**How does it work?** http://www.youtube.com/watch?v=yBRdBrnIlTQ

# iClicker Question #2

# Supercritical $CO_2$: 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 $CO_2$:
  - solvent for synthetic organic chemistry (*e.g.*, drug synthesis)
  - caffeine extraction from coffee (decaffeination); replaced extraction with methylene chloride

# Key concepts

- Intermolecular forces
- Vapour pressure
- Phase changes
- Phase diagrams