Chapter 11
Liquids & Solids

I) Kinetic-Molecular Description

A) Intermolecular Attractive Forces

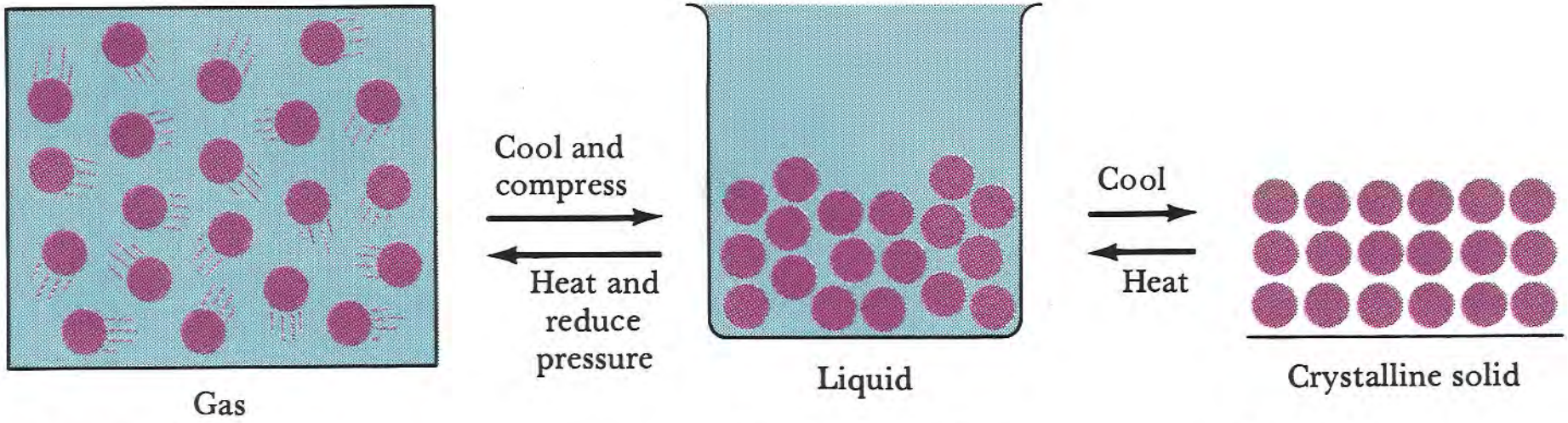
Attractive electrostatic interactions between particles that hold them together

KMT of gases: forces of attraction are negligible

High P &/or low T attractive forces are not negligible

Transparency 77

Figure 11.1 Molecular-level order of solids, liquids, and gases



Gas

Total disorder; much empty space; particles have complete freedom of motion owing to separation and ineffective attractive forces.

Liquid

Disorder; particles or clusters of particles are free to move relative to each other; particles close together.

Crystalline solid

Ordered arrangement; particles can vibrate, but are in fixed positions; particles close together.

CHEMISTRY: THE CENTRAL SCIENCE
by Brown/Le May/Bursten

II) IAF & Phase Changes

A) Ion - Ion Interactions

thought of as both intra- and intermolecular bonding

- Ionic bonding
- very strong

$$F \propto \frac{q^+ q^-}{d^2}$$

$$E \propto \frac{q^+ \cdot q^-}{d}$$

relatively high m.p. & b.p.

B) Strength of IAF

Properties (m.p., b.p.) depend on strength of IAF

NOT as strong as chem. bonds

$\approx$ 1 - 10 kJ/mol

chem. bonds: 100 - 1000 kJ/mol

C) Four Types of IAF

Ion - Dipole

London (Dispersion)
Dipole - Dipole
} van der Waals forces

H - Bonding

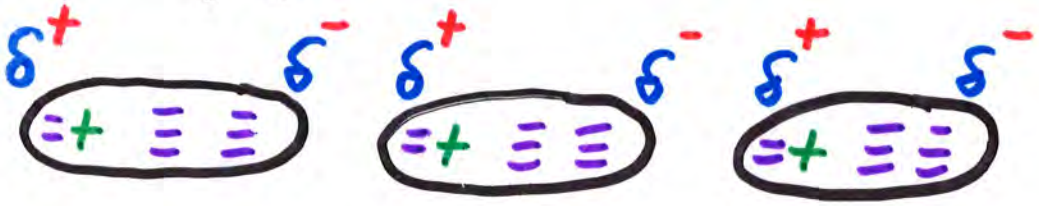
D) London (Dispersion) Forces

Due to small instantaneous induced dipoles due to motion of e^-

$$F \propto \frac{1}{d^7} \quad , \quad E \propto \frac{1}{d^6}$$

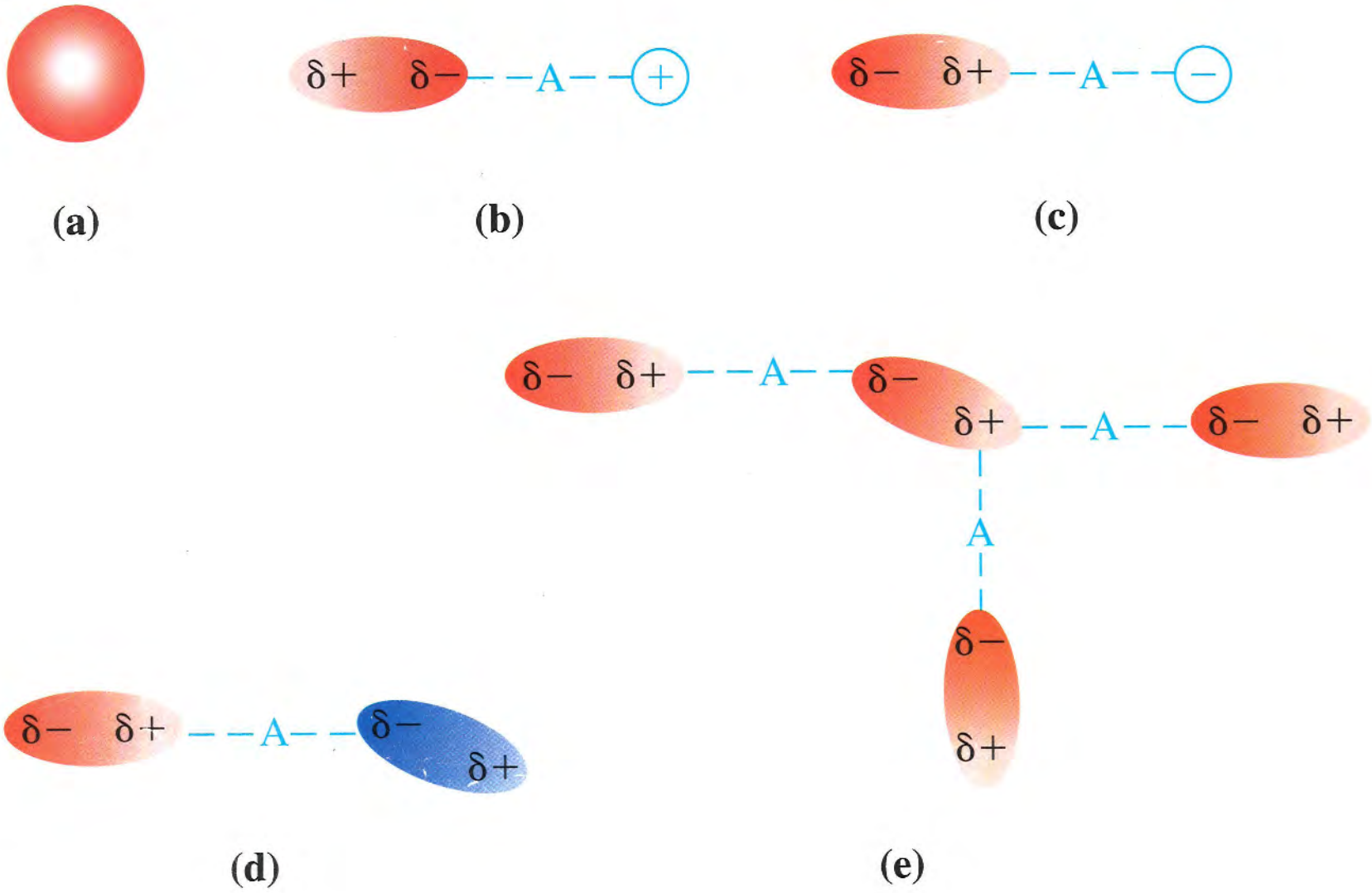
on average: 

at any given moment:



Occurs in ALL molecules

- Only IAF between nonpolar molecules


δ+ δ− A +
δ− δ+ A −
(a)
(b)
(c)
δ− δ+ A δ− δ+ A δ− δ+
A
δ−
δ+
δ− δ+ A δ− δ+
(d)
(e)

Inc. w. polarizability of molecule

– Larger molecules are more polarizable

(e^- cloud more easily distorted)

∴ L.F. tend to inc. in strength w. inc. in M.W.

	He	Ne	Ar	Kr	Xe
b.p. (°C)	-269	-246	-186	-153	-108

CH_4 < CH_3CH_3 < $CH_3CH_2CH_3$

-162 -89 -42

Stronger forces ⇒

Higher m.p., b.p., $\Delta H_{vap.}$, ΔH_{fus}

Lower vapor pressure

E) Dipole - Dipole Forces

IAF between permanent dipoles

- polar molecules

$F \propto \frac{1}{d^4}$ $E \propto \frac{1}{d^3}$

More polar the molec. the stronger the IAF

	SiH_4	PH_3	H_2S
# e^-	18	18	18
geom.	tetrah.	trig. pyr.	bent
dipole moment	0.0 D	0.55 D	1.1 D
b.p.	-111.8	-87.4	-61.8

F) Hydrogen Bonding

Special type of fairly strong D-D attraction

chem. bonds $>$ H-bonds $>$ L.F. D-D

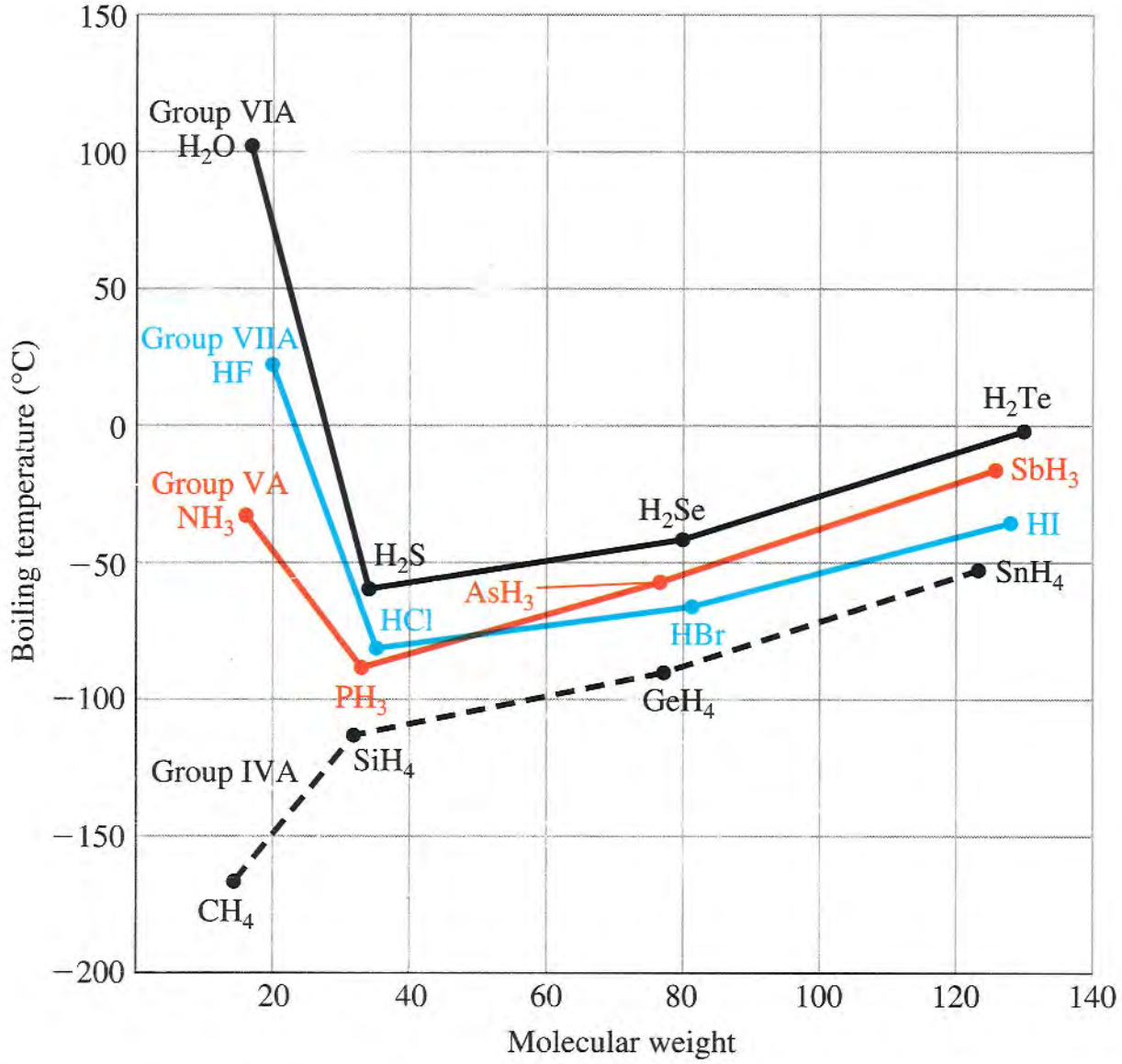
10x

-100x

10x

Must have H covalently bonded to a small atom of high electronegativity having at least one unshared pair of e^-.

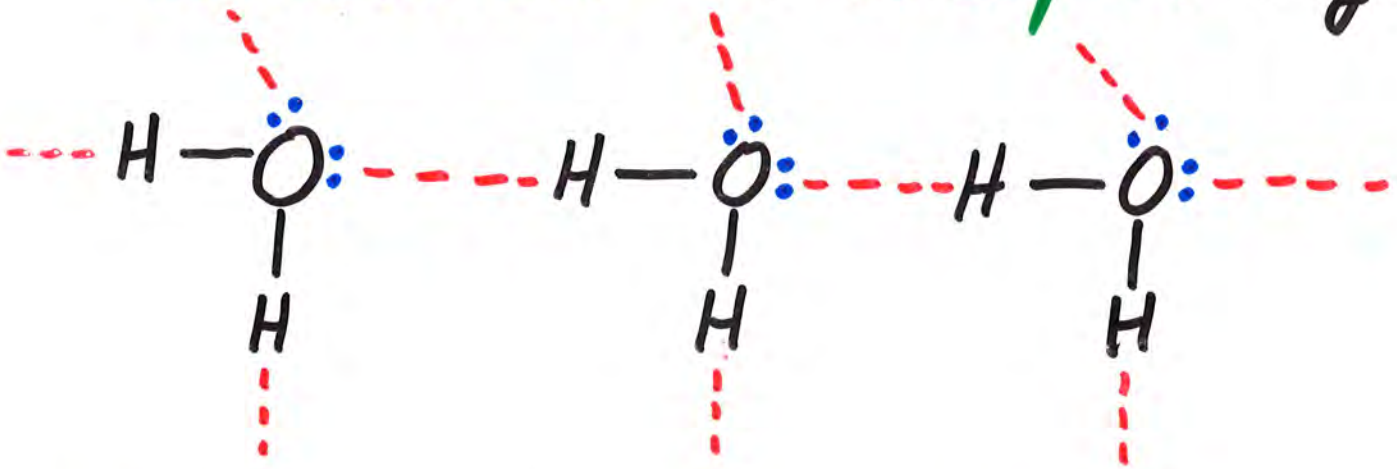
Usually, **N, O, F**


150
100
50
0
−50
−100
−150
−200
Boiling temperature (°C)
20
40
60
80
100
120
140
Molecular weight
Group VIA
H_2O
Group VIIA
HF
Group VA
NH_3
H_2S
HCl
PH_3
AsH_3
H_2Se
HBr
GeH_4
H_2Te
HI
SbH_3
SnH_4
Group IVA
CH_4
SiH_4

1) Why is b.p. $H_2O > HF > NH_3$?

HF has strongest single H-bond

neg. charge on O tends to concentrate in lone pair regions



H bridges 2 oxygens

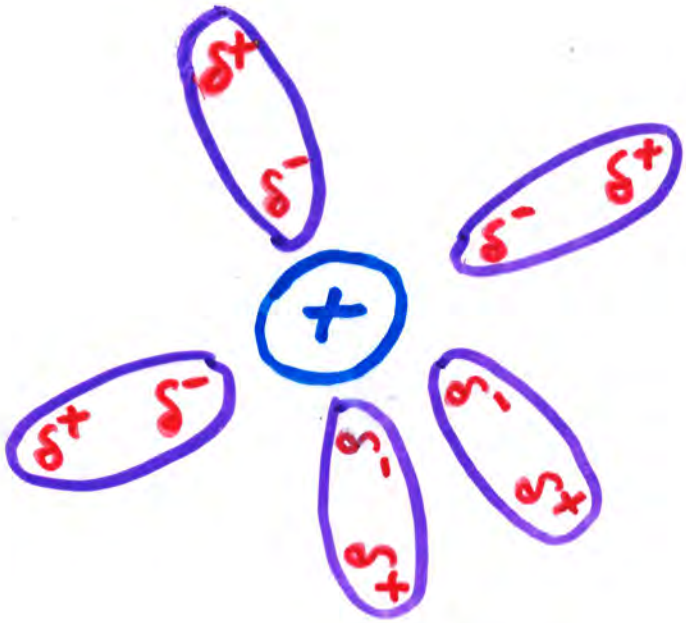
O surrounded by 4 H's

Explains why ice is less dense than liquid water

	propane	acetaldehyde	ethyl alcohol
	C_3H_8	$CH_3\underset{\underset{H}{|}}{C}=O$	CH_3CH_2OH
m.w.	44	44	46
#e^-	26	24	26
forces	LF	LF D-D	LF D-D H-bonds
b.p. (K)	231	293	351

Ion-Dipole Forces

Ions & Polar molecules



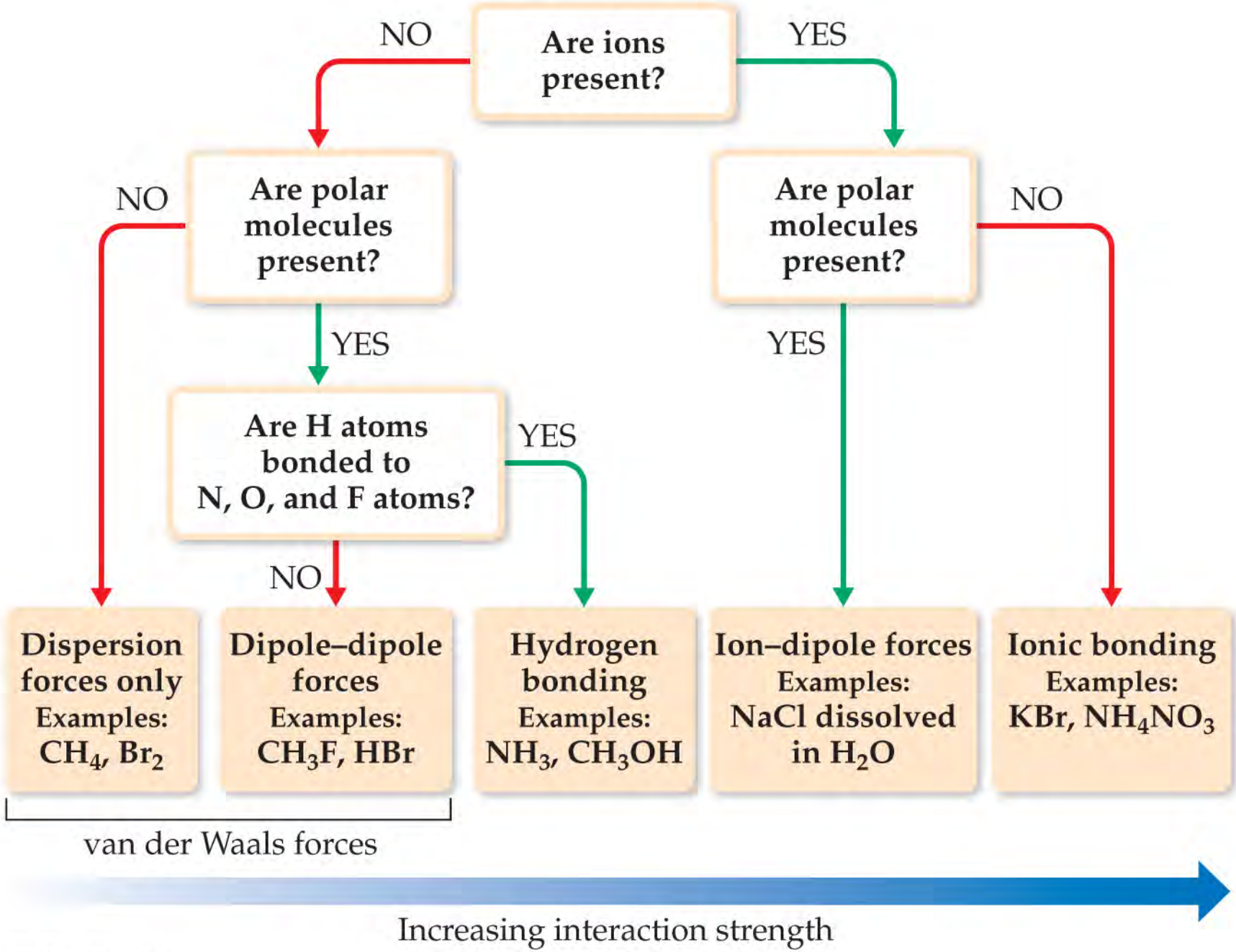
Magnitude of interaction:

$$E \propto \frac{Q\mu}{d^2}$$

$Q \equiv$ charge on ion

$\mu \equiv$ dipole moment of dipole

$d \equiv$ distance from center of ion to midpoint of dipole



III) Properties of Liquids

A) Viscosity

Resistance of liq. to flow

Depends on IAF & structural features (which cause molecules to become entangled)

Dec. w. inc. Temp.

Inc. w. inc. IAF

B) Surface Tension

Surface molecules experience net inward force

- pulls molecules from surface into interior, reducing surface area
  - forms distorted sphere

Surface Tension

energy required to inc. surface area by a unit amount

Inc. w. inc. IAF

C) Capillary Action

1) Cohesive Forces

Bind like molecules together

2) Adhesive Forces

Bind unlike molecules
(i.e. - to a surface)

H_2O - adheres to glass
- due to adhesive forces
- meniscus curved upward

Hg - cohesive forces greater than adhesive forces
- meniscus curved downward