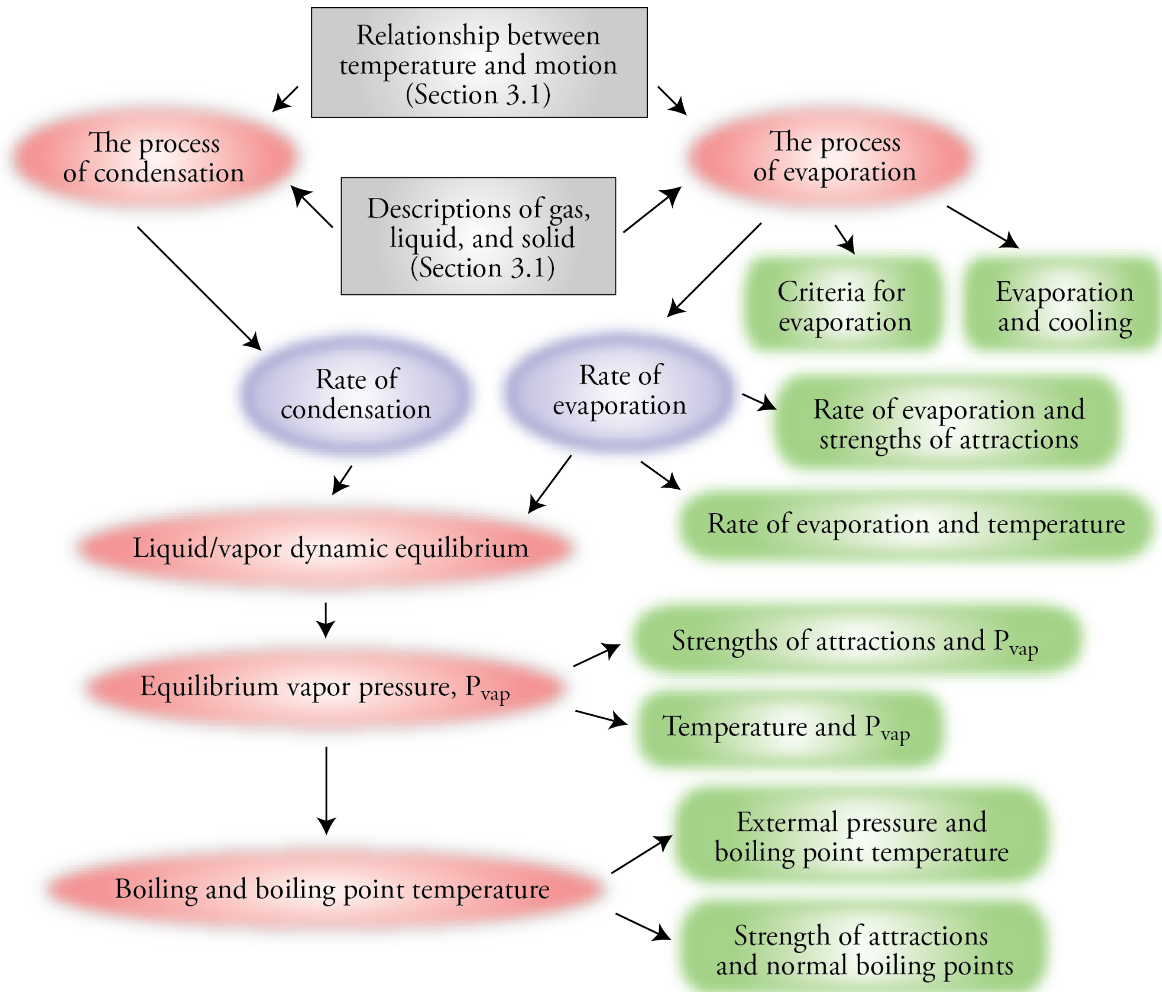
Chapter 12
Liquids: Condensation, Evaporation, and Dynamic Equilibrium

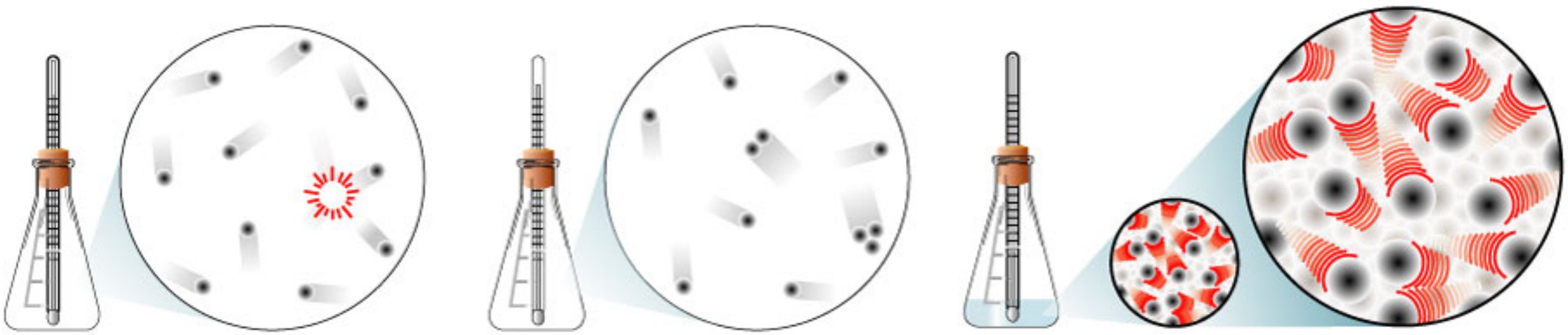
An Introduction to Chemistry

by Mark Bishop

Chapter Map


Relationship between temperature and motion (Section 3.1)
The process of condensation
The process of evaporation
Descriptions of gas, liquid, and solid (Section 3.1)
Criteria for evaporation
Evaporation and cooling
Rate of condensation
Rate of evaporation
Rate of evaporation and strengths of attractions
Rate of evaporation and temperature
Liquid/vapor dynamic equilibrium
Strengths of attractions and P_{vap}
Equilibrium vapor pressure, P_{vap}
Temperature and P_{vap}
Extermal pressure and boiling point temperature
Boiling and boiling point temperature
Strength of attractions and normal boiling points

Condensation (Gas to Liquid)

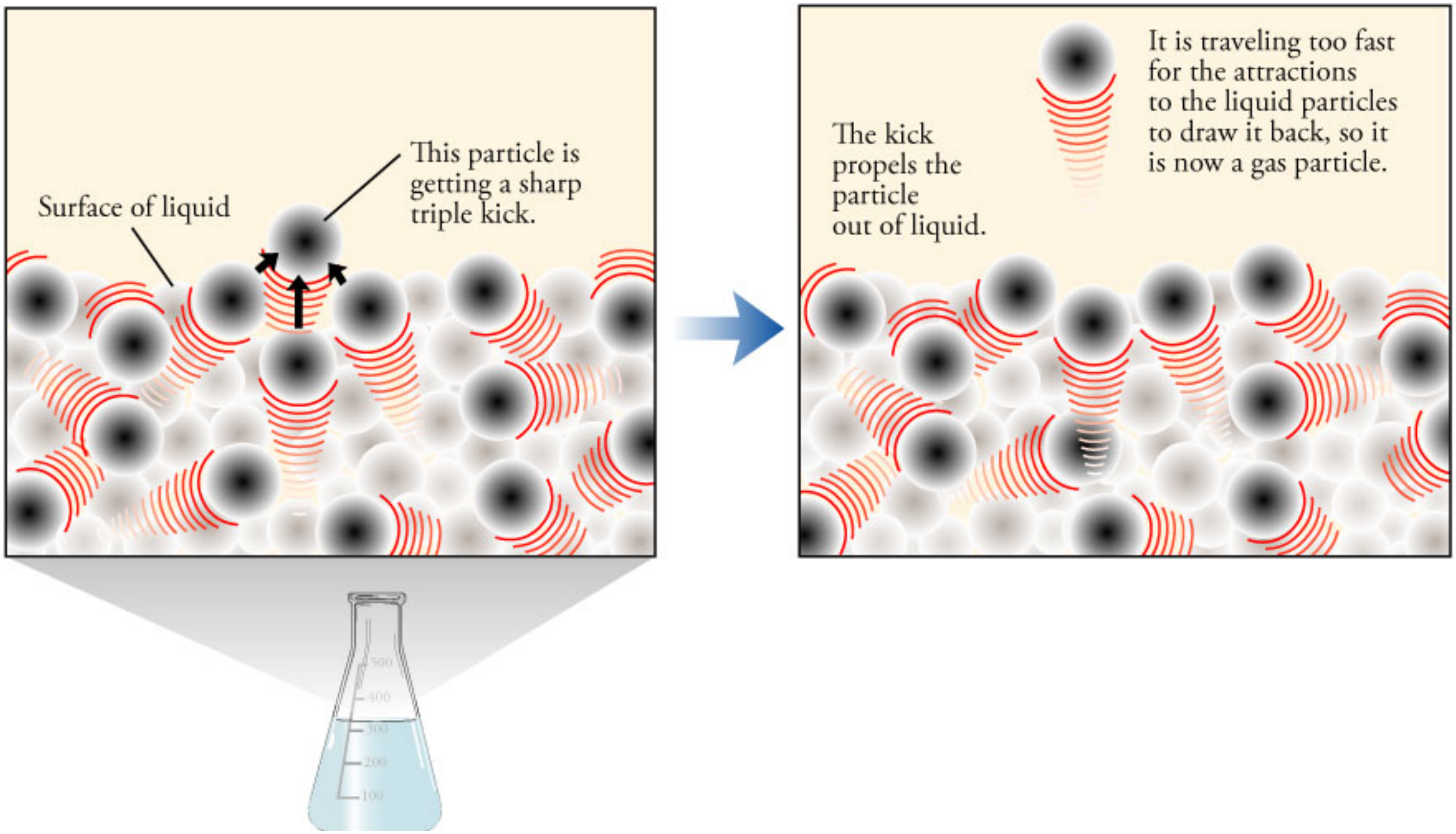


At a high temperature, there are no significant attractions between the particles.

As the temperature is lowered, attractions between particles lead to the formation of very small clusters that remain in the gas phase.

As the temperature is lowered further, the particles move slowly enough to form clusters so large that they drop to the bottom of the container and combine to form a liquid.

Evaporation



Particle Escape

- For a particle to escape from the surface of the liquid, it must meet the following criteria.
  - The particle must be at the liquid's surface.
  - Its direction of motion must take it beyond the liquid's surface.
  - Its momentum must be great enough to take it beyond the backward pull of the other particles at the surface.

Rate of Evaporation

- The rate of evaporation is the number of particles moving from liquid to gas per second.
- It is dependent on the following:
  – Surface area of the liquid
  – Strength of attractions between the particles in the liquid
  – Temperature

Relative Rates of Evaporation

Weaker attractions between particles

↓

Lower momentum necessary for particles to escape the liquid

↓

At a constant temperature, a greater percentage of particles that have the momentum necessary to escape

↓

Higher rate of evaporation

Temperature and Rate of Evaporation

Increased temperature

↓

Increased velocity and momentum of the particles

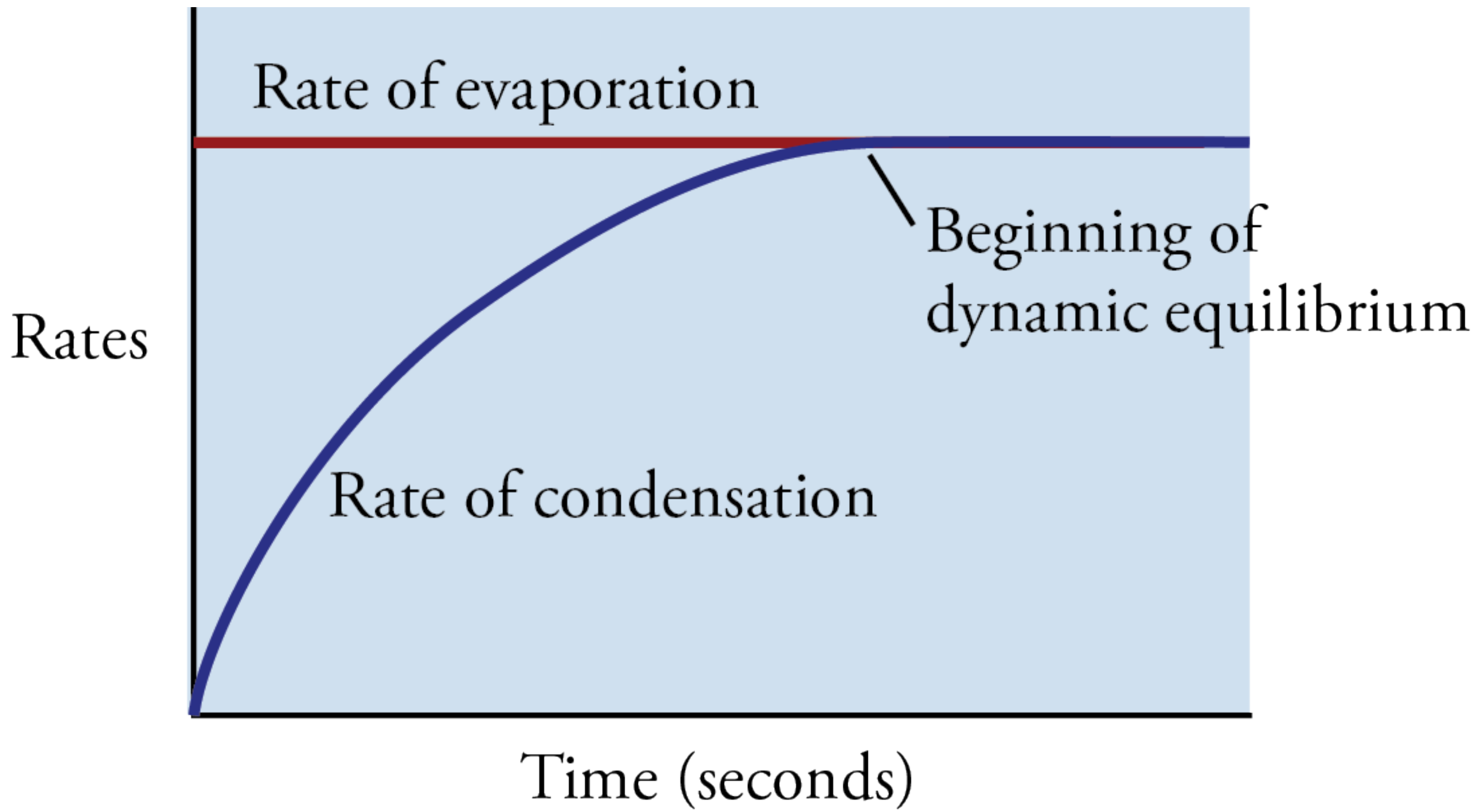
↓

Increased percentage of particles that have the minimum momentum to escape

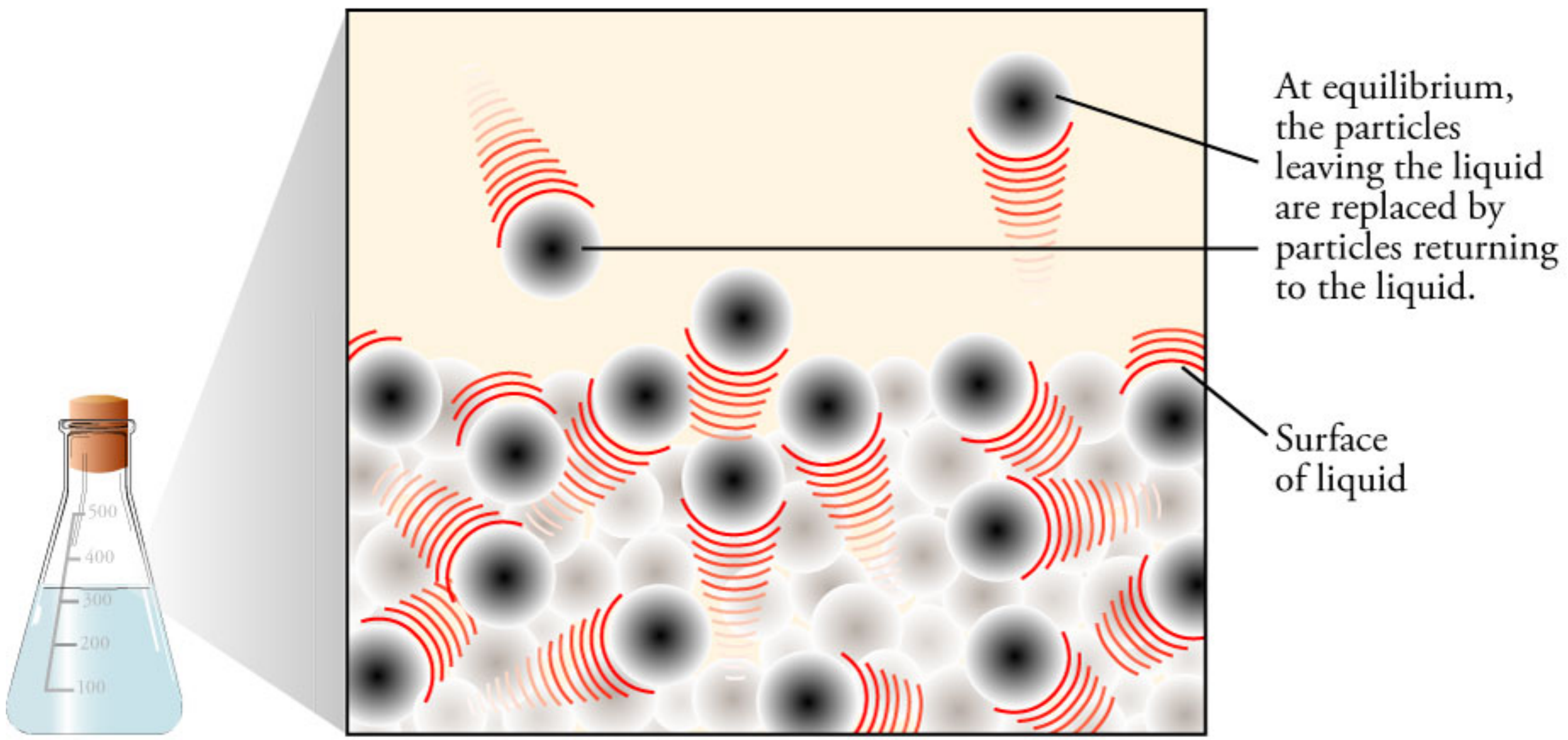
↓

Increased rate of evaporation

Dynamic Equilibrium and Rates of Evaporation and Condensation



Liquid-Vapor Equilibrium



Relative Equilibrium Vapor Pressures

Weaker attractions between particles in a liquid → Higher rate of evaporation

↓

Higher rate of condensation needed for equilibrium

↓

Higher concentration of vapor particles necessary to create the higher rate of condensation

← Higher equilibrium vapor pressure, P_{vap}

Temperature Effect On Equilibrium Vapor Pressure

Increased temperature → Increased rate of evaporation

↓

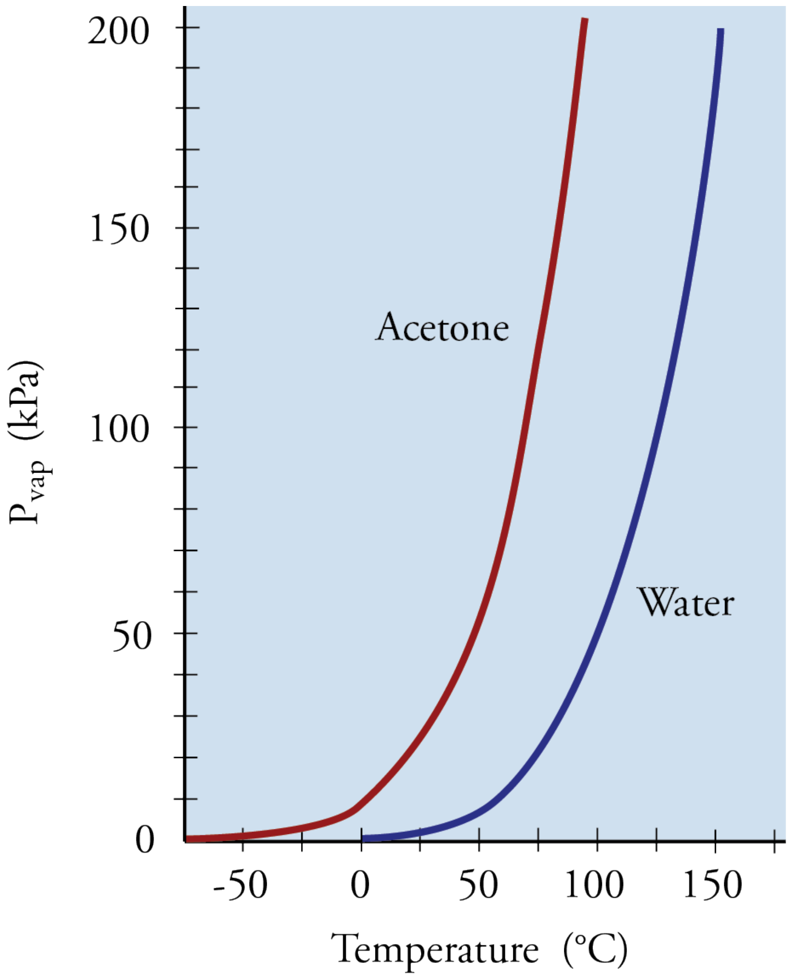
Increased rate of condensation needed for equilibrium

↓

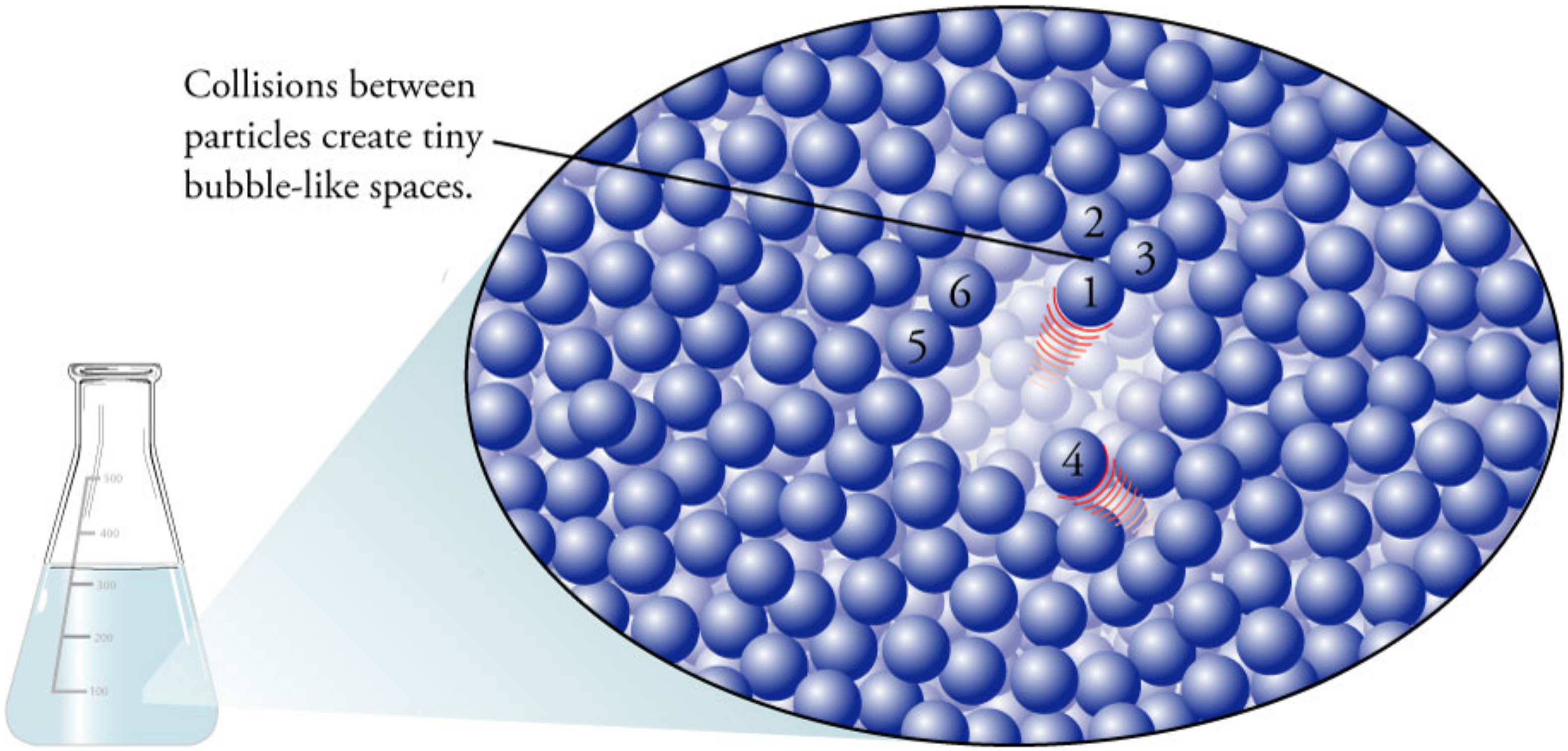
Increased concentration of vapor particles necessary to bring the rate of condensation to the higher level → Increased equilibrium vapor pressure, P_{vap}

Acetone/Water

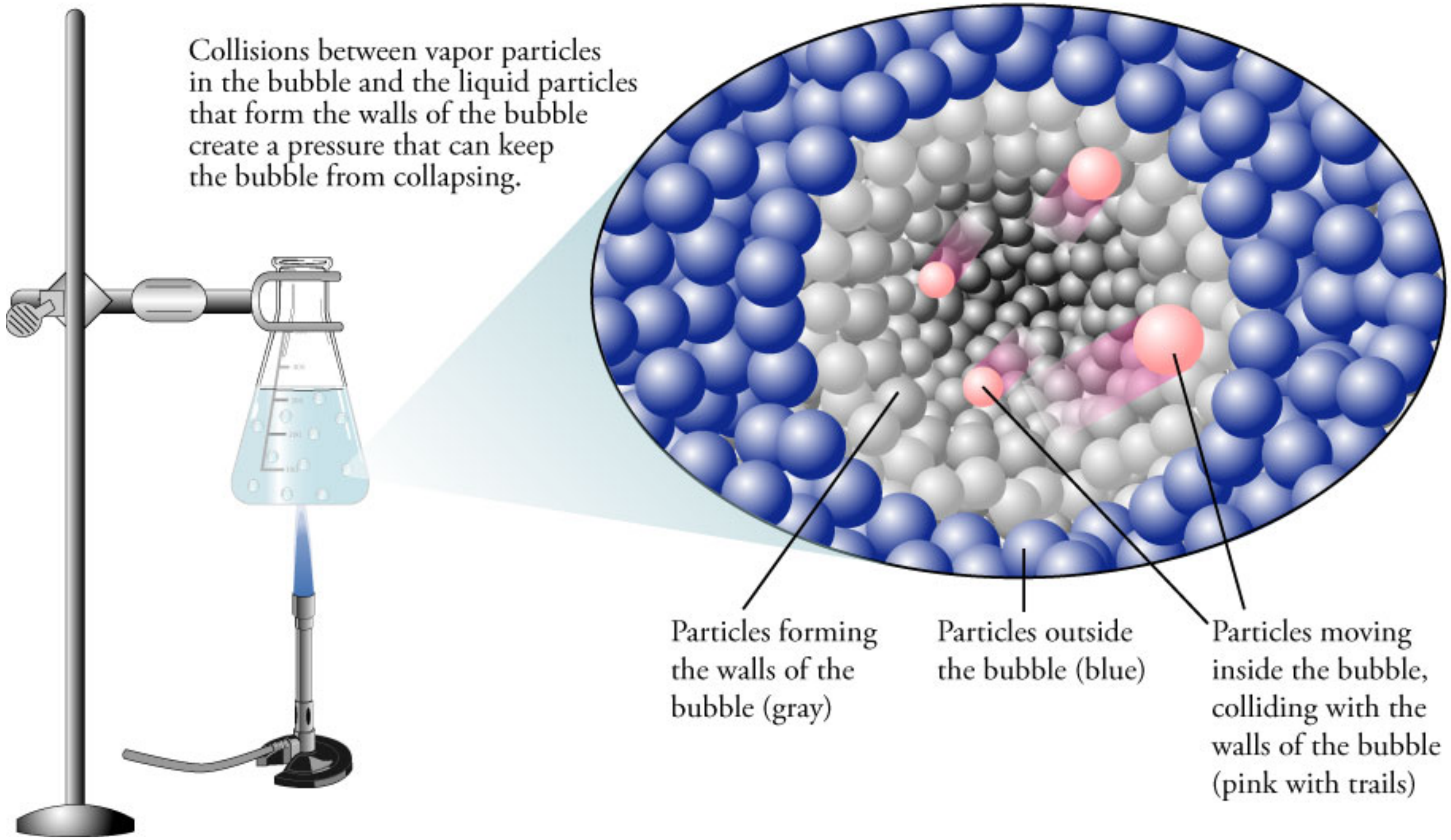
P_{vap} vs. T



Spaces in Liquids



Bubble in Liquid

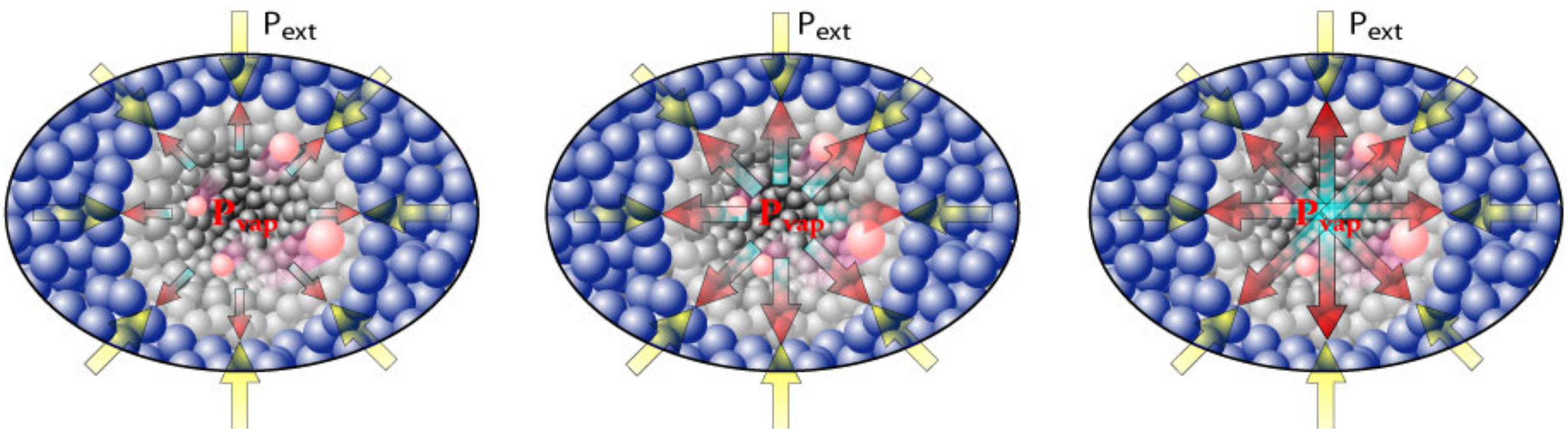


Bubble Formation

$P_{vap} < P_{ext}$
Bubble collapses

$P_{vap} = P_{ext}$
Bubble maintains its volume

$P_{vap} > P_{ext}$
Bubble expands



Pressure and Boiling Points

Decreased external pressure above liquid water

↓

Decreased vapor pressure necessary to allow bubbles to form

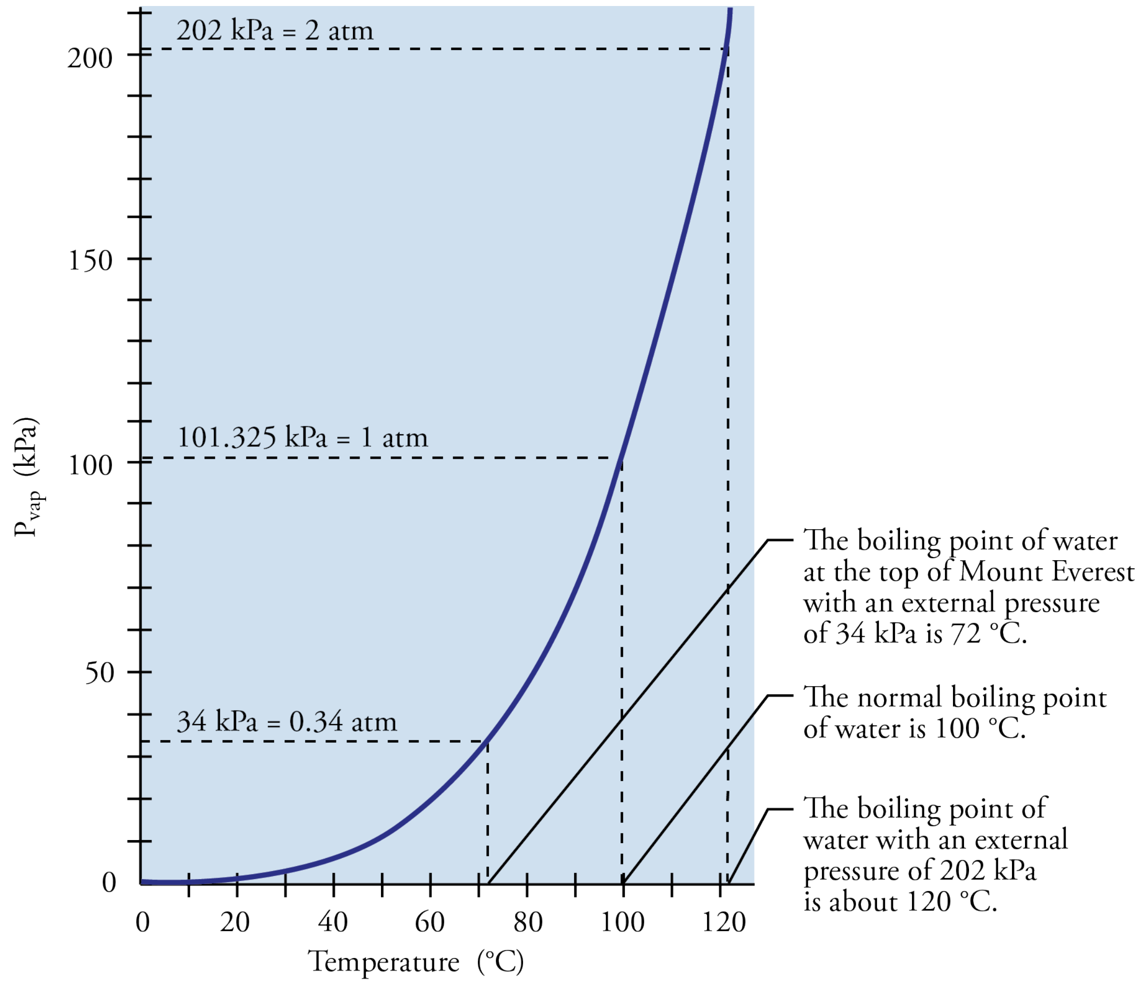
↓

Decreased temperature necessary to reach this lower vapor pressure

↓

Decreased boiling-point temperature

Pressure and Boiling Point for Water



Strengths of Attractions and Boiling Point

Increased strength of attractions

↓

Decreased rate of evaporation

↓

Decreased rate of condensation at equilibrium

↓

Lower concentration of vapor necessary to reach lower rate of condensation

↓

Lower vapor pressure at any given temperature

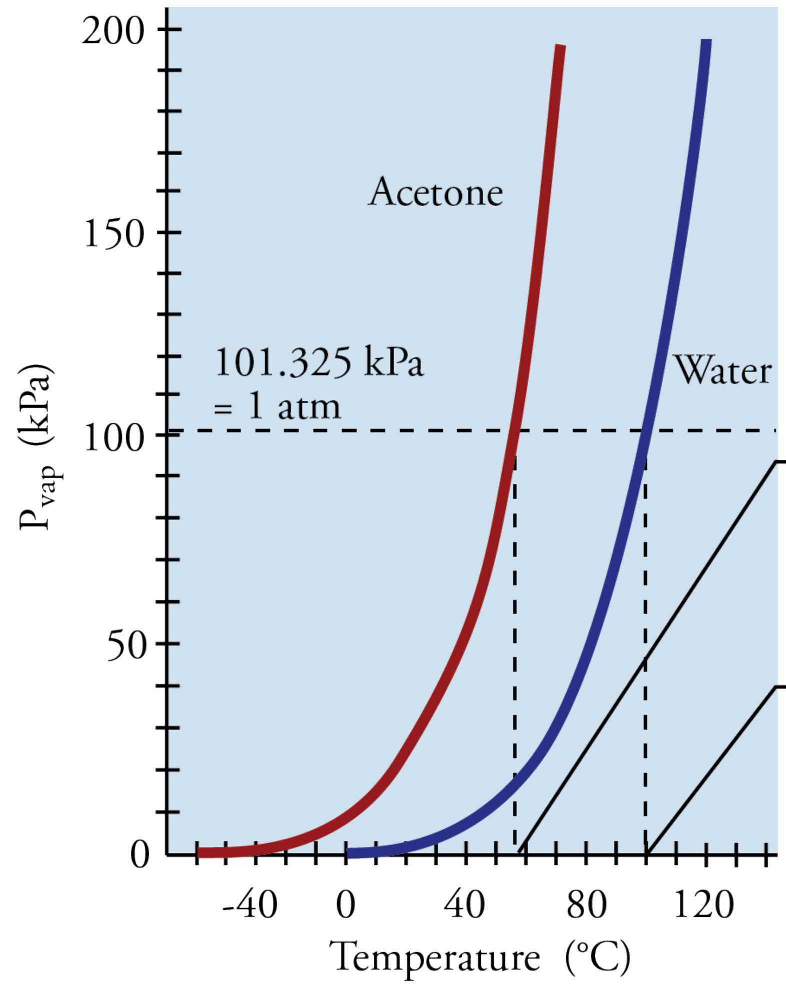
↓

Higher temperature necessary to bring the vapor pressure to the external pressure

↓

Increased boiling-point temperature

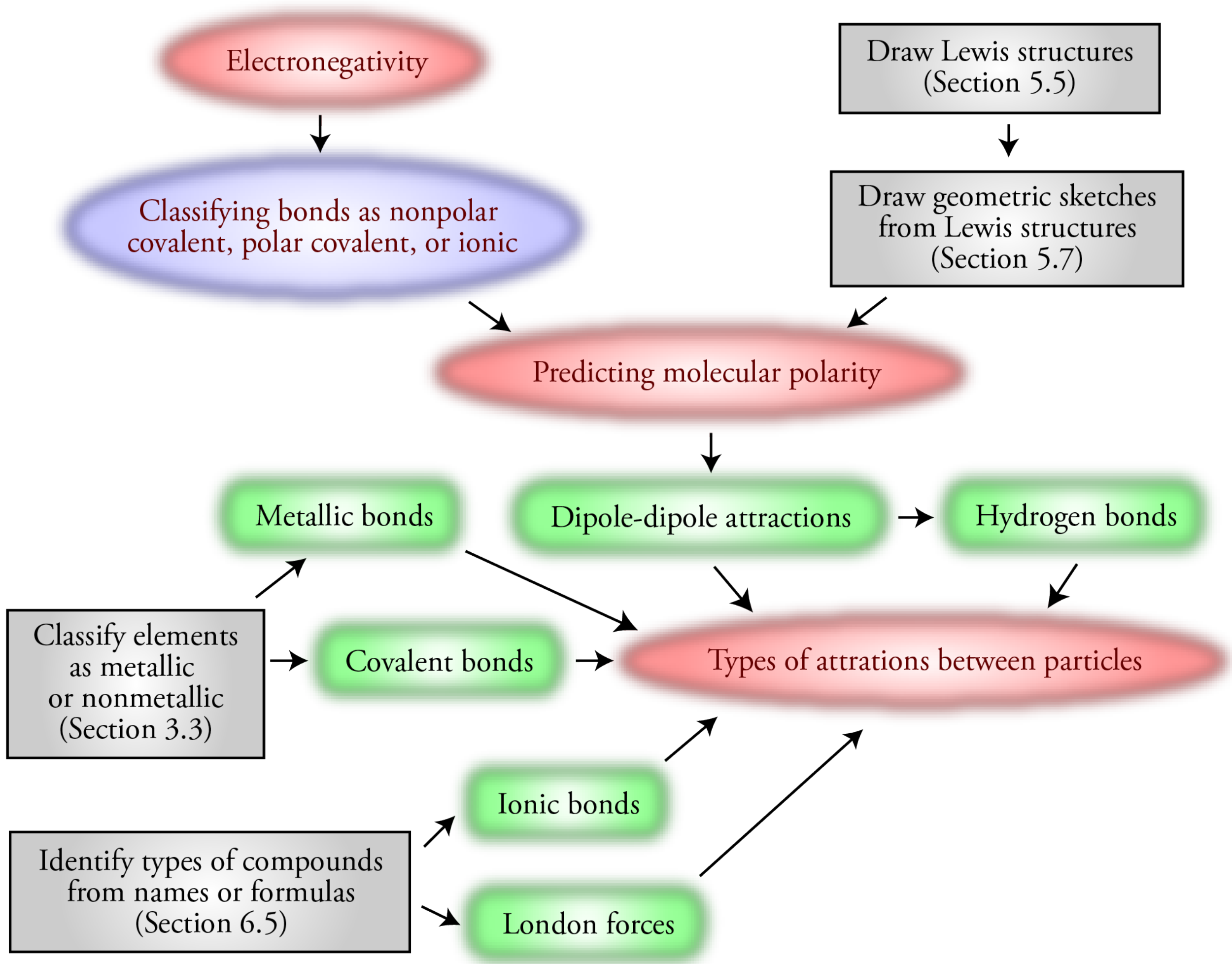
Normal Boiling Points



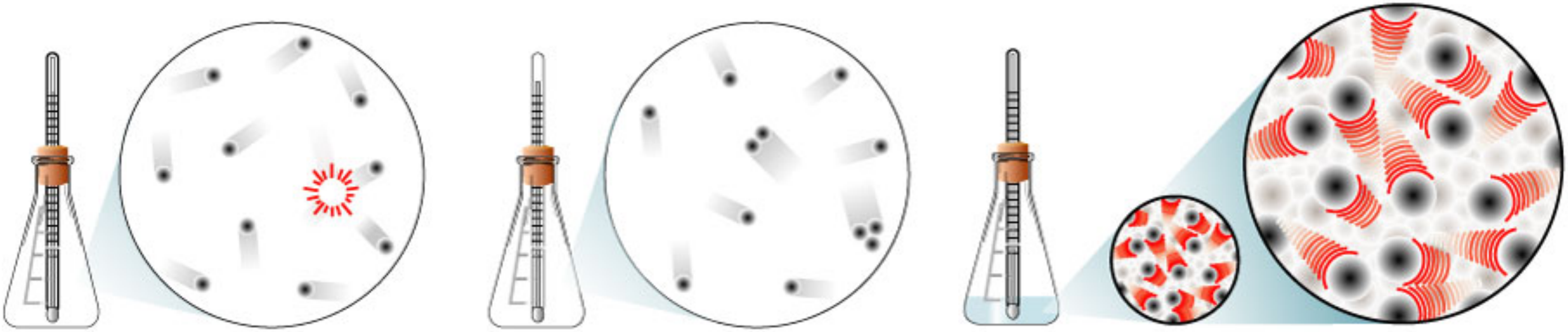
The normal boiling point of acetone is 56.5 °C.

The normal boiling point of water is 100 °C.

More Chapter 12



Condensation (Gas to Liquid)



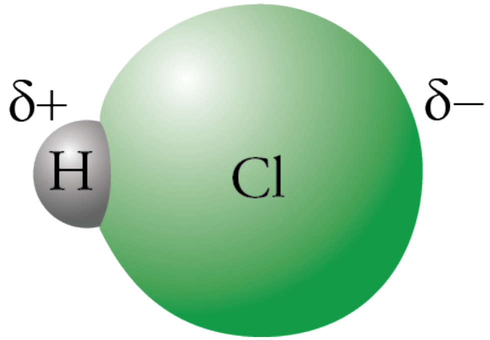
At a high temperature, there are no significant attractions between the particles.

As the temperature is lowered, attractions between particles lead to the formation of very small clusters that remain in the gas phase.

As the temperature is lowered further, the particles move slowly enough to form clusters so large that they drop to the bottom of the container and combine to form a liquid.

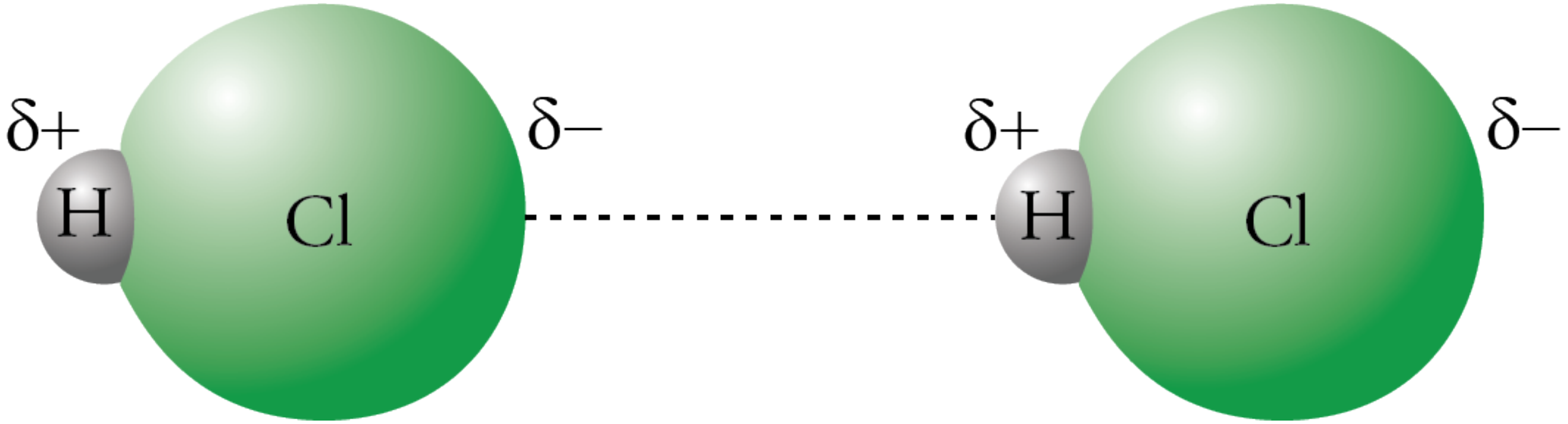
Hydrogen Chloride Molecule

- The hydrogen atom and the chlorine atom in an HCl molecule are held together by a polar covalent bond. Because chlorine atoms attract electrons more strongly than hydrogen atoms, some of the hydrogen atom's electron cloud is pulled toward the chlorine atom, making the hydrogen atom partially positive and the chlorine atom partially negative.
- We call this separation of positive and negative charges a **dipole**.



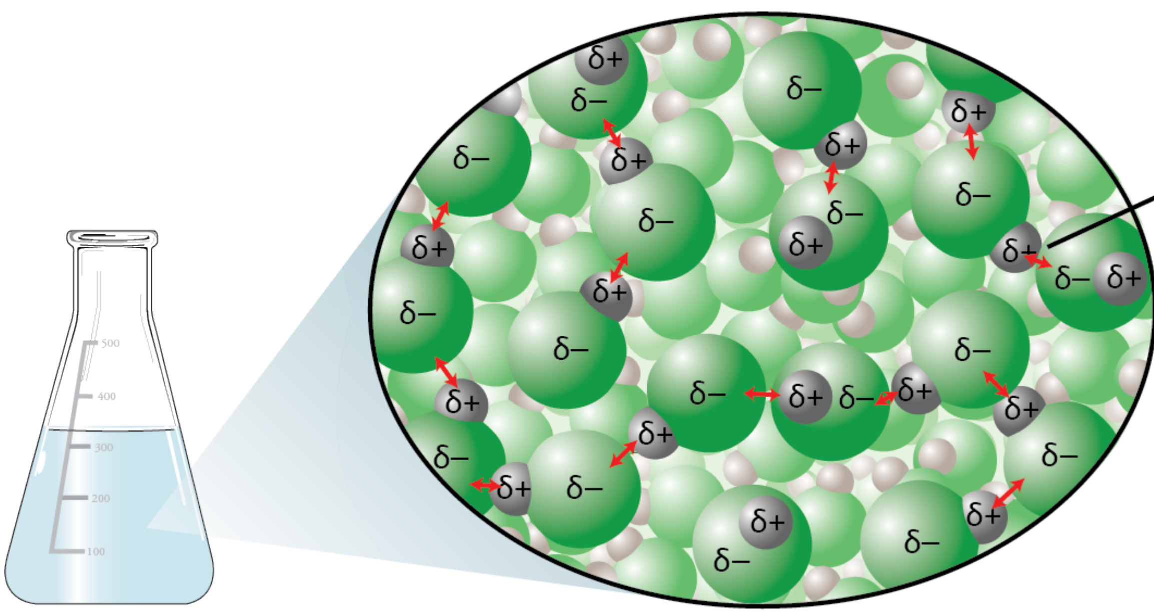
Dipole-Dipole Attractions

- The partial negative end of one HCl molecule is attracted to the partial positive end of another HCl molecule.
- This attraction is called a **dipole-dipole attraction**.



Dipole-Dipole Attractions in a Liquid

- When hydrogen chloride is cooled and/or compressed enough to convert it into a liquid, dipole-dipole attractions hold the HCl molecules together.
- It is dipole-dipole attractions that would be broken and reformed as HCl molecules move throughout the liquid, and it is dipole-dipole attractions that are broken when liquid HCl is converted into a gas.



The polar molecules are held together by dipole-dipole atractions, which are broken and re-formed as the molecules travel throughout the liquid.

Polar Molecules

- Polar molecules have a separation of charge with one end of the molecule more positive and one end more negative.
- For a molecule to be polar, it must have
  - at least one polar covalent bond
  - and an asymmetrical (unbalanced) distribution of the polar bonds.

Nonpolar Molecules

- A nonpolar molecule has no separation of charge, either because
  - it has no polar bonds,
  - or it has a symmetrical distribution of its polar bonds.

Electronegativity

- **Electronegativity** is a measure of the electron attracting ability of atoms in chemical bonds.
  - Based on experimental evidence, the atoms of each element are assigned a number that represents its electron attracting ability.
  - The higher the number is, the stronger the atom's attraction for electrons.

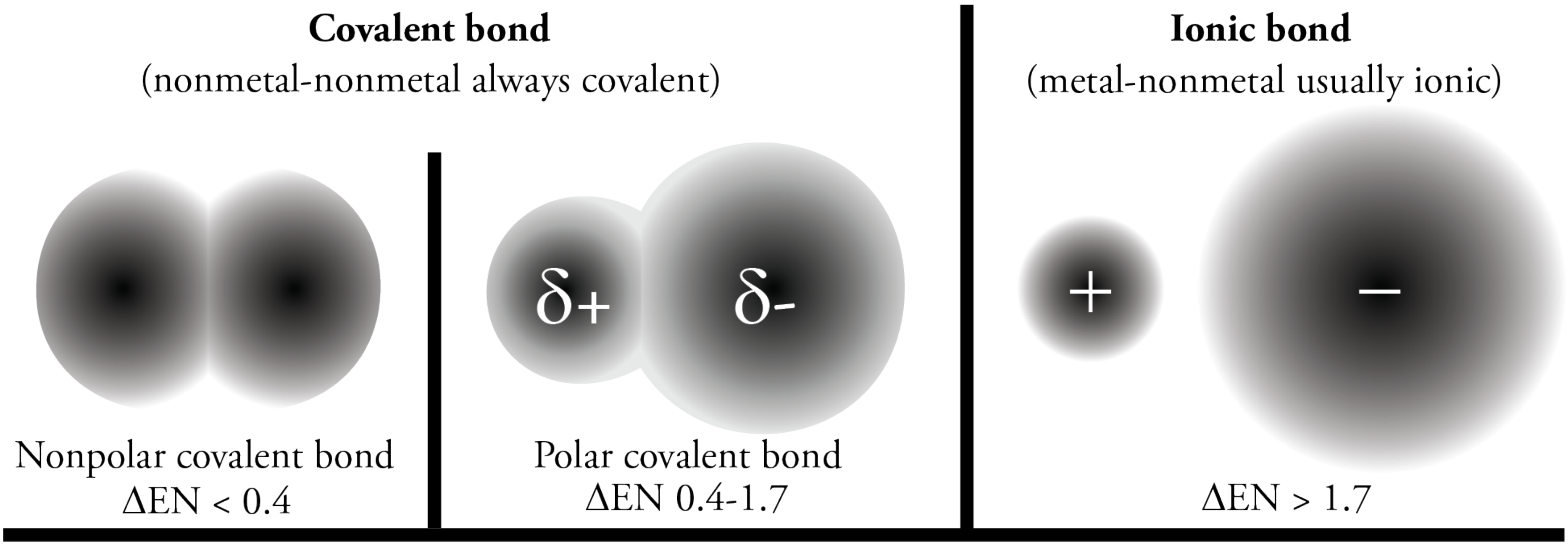
Electronegativities

	1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9 8B	10 8B	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1	2.20 H																	
2	0.98 Li	1.57 Be											2.04 B	2.55 C	3.04 N	3.44 O	3.98 F	
3	0.93 Na	1.31 Mg											1.61 Al	1.90 Si	2.19 P	2.58 S	3.16 Cl	
4	0.82 K	1.00 Ca	1.36 Sc	1.54 Ti	1.63 V	1.66 Cr	1.55 Mn	1.83 Fe	1.88 Co	1.91 Ni	1.90 Cu	1.65 Zn	1.81 Ga	2.01 Ge	2.18 As	2.55 Se	2.96 Br	3.00 Kr
5	0.82 Rb	0.95 Sr	1.22 Y	1.33 Zr	1.6 Nb	2.16 Mo	1.9 Tc	2.2 Ru	2.28 Rh	2.20 Pd	1.93 Ag	1.69 Cd	1.78 In	1.96 Sn	2.05 Sb	2.1 Te	2.66 I	2.6 Xe
6	0.79 Cs	0.89 Ba	1.27 Lu	1.3 Hf	1.5 Ta	2.36 W	1.9 Re	2.2 Os	2.20 Ir	2.28 Pt	2.54 Au	2.00 Hg	1.62 Tl	2.33 Pb	2.02 Bi	2.0 Po	2.2 At	
7	0.7 Fr	0.9 Ra																

Electronegativity

- Electronegativity values can be used to predict
  - whether a chemical bond is nonpolar covalent, polar covalent, or ionic.
  - which atom in a polar covalent bond is partial negative and which is partial positive.
  - which atom in an ionic bond forms the cation and which forms the anion.
  - and which of two covalent bonds are more polar.

Bond Types



Covalent bond
(nonmetal-nonmetal always covalent)
Ionic bond
(metal-nonmetal usually ionic)
δ+
δ-
+
–
Nonpolar covalent bond
ΔEN < 0.4
Polar covalent bond
ΔEN 0.4-1.7
ΔEN > 1.7

Electronegativities

	1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9 8B	10 8B	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
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7	0.7 Fr	0.9 Ra																

Which atom in a polar covalent bond is partially negative and which is partially positive?

higher electronegativity

↓

greater attraction for electrons

↓

partial negative charge

lower electronegativity

↓

lesser attraction for electrons

↓

partial positive charge

Which of two bonds is more polar?

- The greater the difference in electronegativity (ΔEN) is, the larger the partial negative and partial positive charges on the atoms and the more polar the bond.
  - ΔEN for C-O is 0.89
  - ΔEN for C-N is 0.49
  - The C-O bond has larger the partial negative and partial positive charges and is more polar.

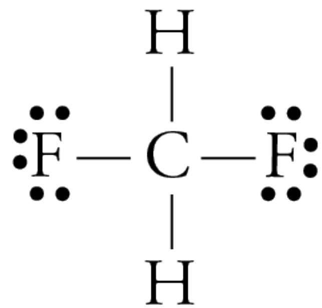
Predicting Molecular Polarity

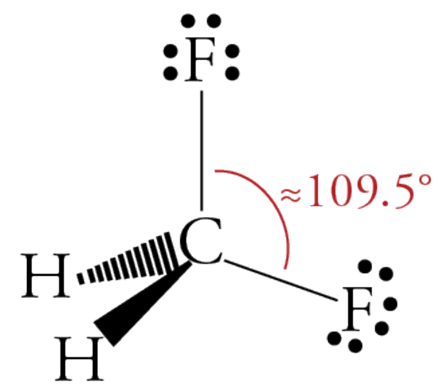
- Three questions will help you predict whether substances are composed of polar or nonpolar molecules.
  - *Is the substance molecular?* (all nonmetallic atoms and no ammonium)
  - *If the substance is molecular, do the molecules contain polar covalent bonds?* (You can see the bonds from the Lewis structure, and you predict polarity from electronegativities.)
  - *If the molecules contain polar covalent bonds, are these bonds asymmetrically arranged?* (This may involve sketching the molecular geometry.)

Predicting Molecular Polarity – Example 1

Difluoromethane, CH_2F_2

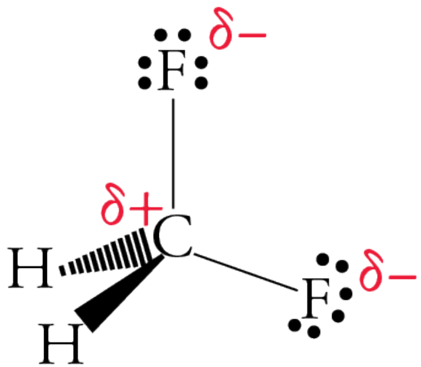
- All nonmetals and no ammonium – molecular
- You need a Lewis structure to see bonds.
- The carbon-fluorine bonds are polar.
- You need a geometric sketch to predict the symmetry.
- Asymmetrical - polar

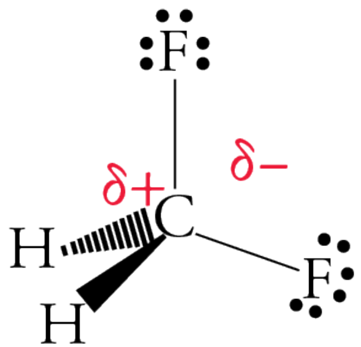




Ways to Predict Symmetry

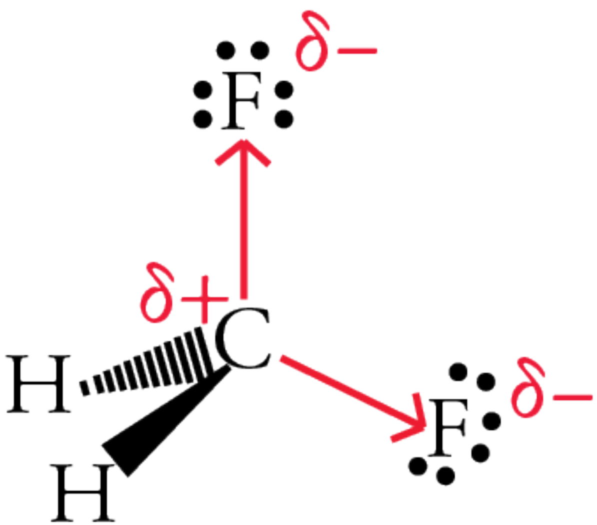
- Is the center of the partial negative charge in a different place than the center of the positive charge?
  - If yes, polar
  - If no, nonpolar





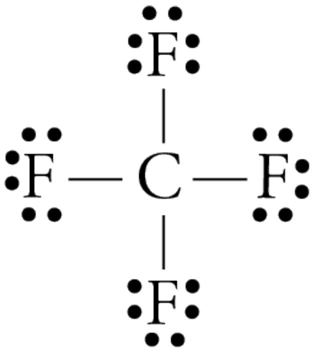
Ways to Predict Symmetry

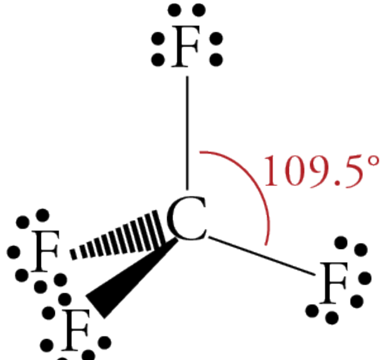
- If we describe the movement of electrons in the polar bonds with arrows, and if we think of the arrows as forces, would the molecule move?
  - If yes, polar
  - If no, nonpolar



Predicting Molecular Polarity – Example 2

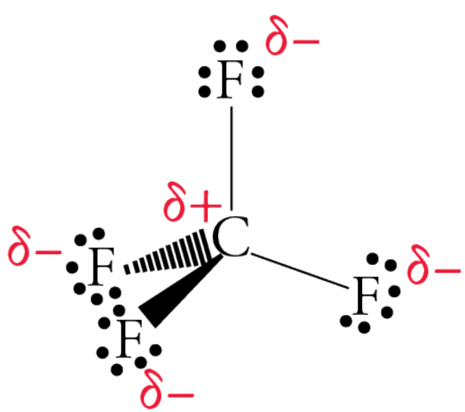
- **Tetrafluoromethane, CF_4**
- All nonmetals and no ammonium – molecular
- You need a Lewis structure to see bonds.
- The carbon-fluorine bonds are polar.
- You need a geometric sketch to predict the symmetry.
- Symmetrical – nonpolar

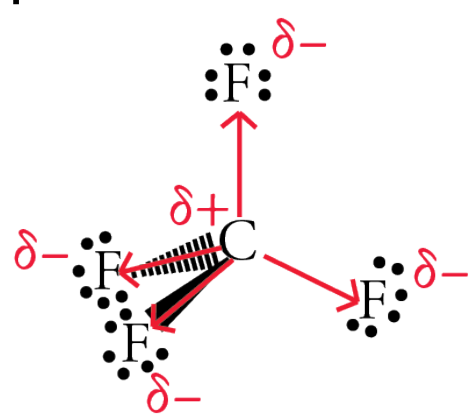




Ways to Predict Symmetry

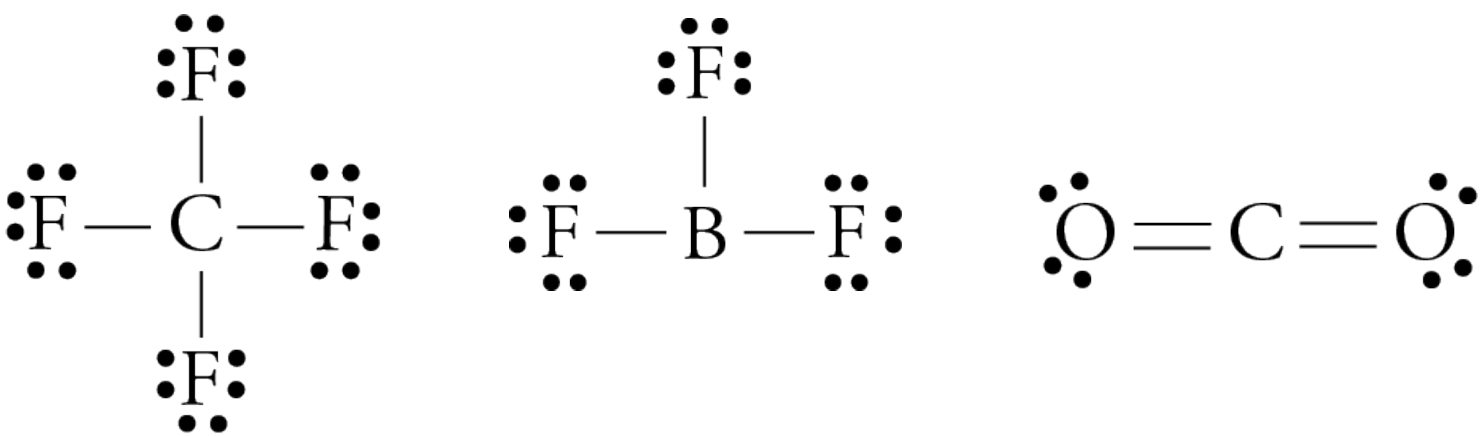
- The center of the partial plus and partial minus are both at the carbon.
- If the arrows showing the shift of electrons were forces, the molecule would not move.
- So the molecule has a symmetrical distribution of polar bonds and is nonpolar.





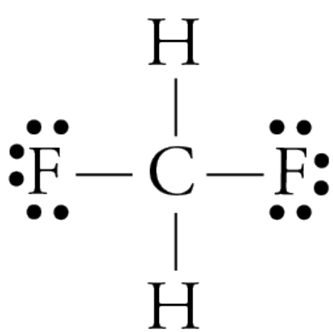
Shortcuts

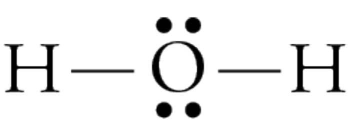
- If all of the groups around the central atom are identical, e.g. all bond groups to atoms of the same element and no lone pairs on the central atom, the molecule is nonpolar.

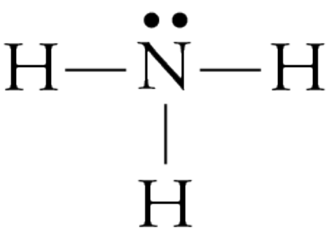


Shortcuts

- If a molecule has at least one polar bond, and if the groups around the central atom are not identical, e.g. bonds to atoms of different elements or a mixture of bonds and lone pairs, it is *almost* certainly polar.

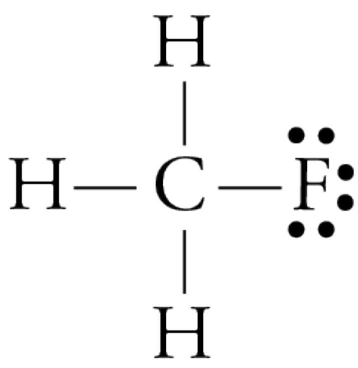


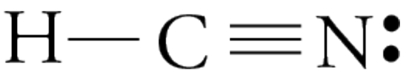




Shortcuts

- If there is only one polar bond, the molecule is polar.





Examples of Polar and Nonpolar Molecules

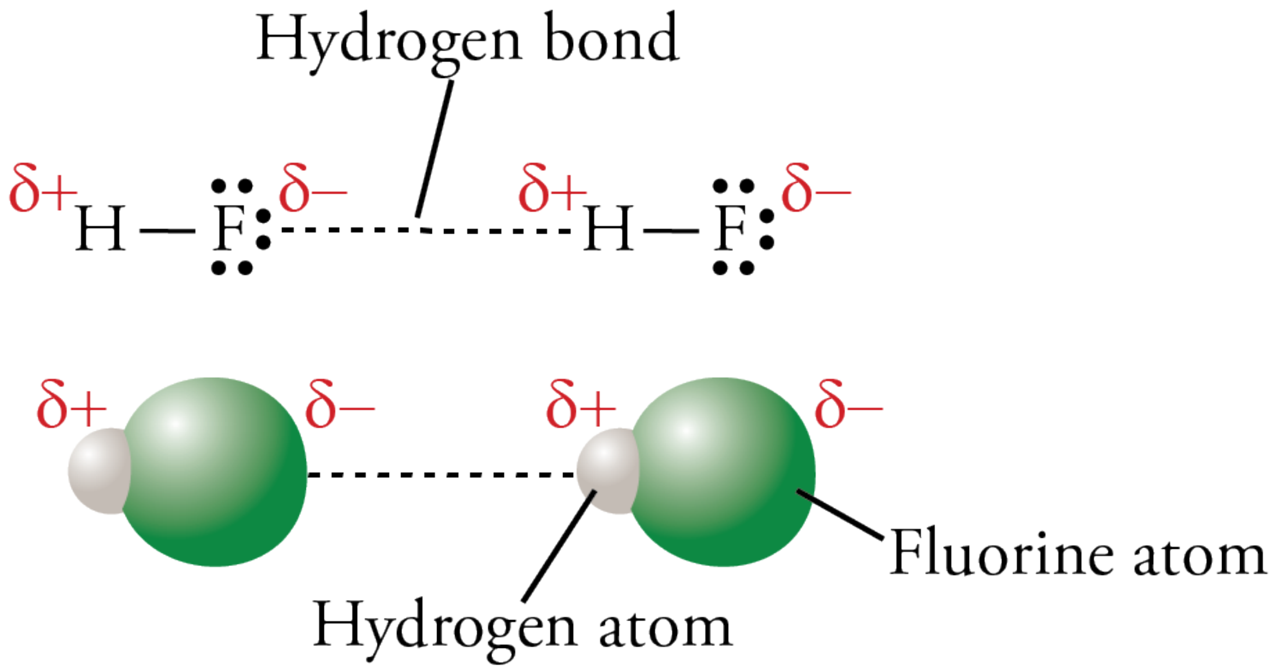
- Polar
  - H_2O, NH_3
  - Acids (HNO_3, H_2SO_4, and $HC_2H_3O_2$)
  - Hydrogen halides: HF, HCl, HBr, and HI
  - Alcohols: CH_3OH, C_2H_5OH
- Nonpolar
  - Elements composed of molecules: H_2, N_2, O_2, F_2, Cl_2, Br_2, I_2, P_4, S_8, Se_8
  - CO_2
  - Hydrocarbons, C_aH_b

Hydrogen Bonds

- **Hydrogen bonds** are attractions between a nitrogen, oxygen, or fluorine atom of one molecule and a hydrogen atom attached to a nitrogen, oxygen, or fluorine atom of another molecule.
- Hydrogen bonds are generally stronger than normal dipole-dipole attractions.

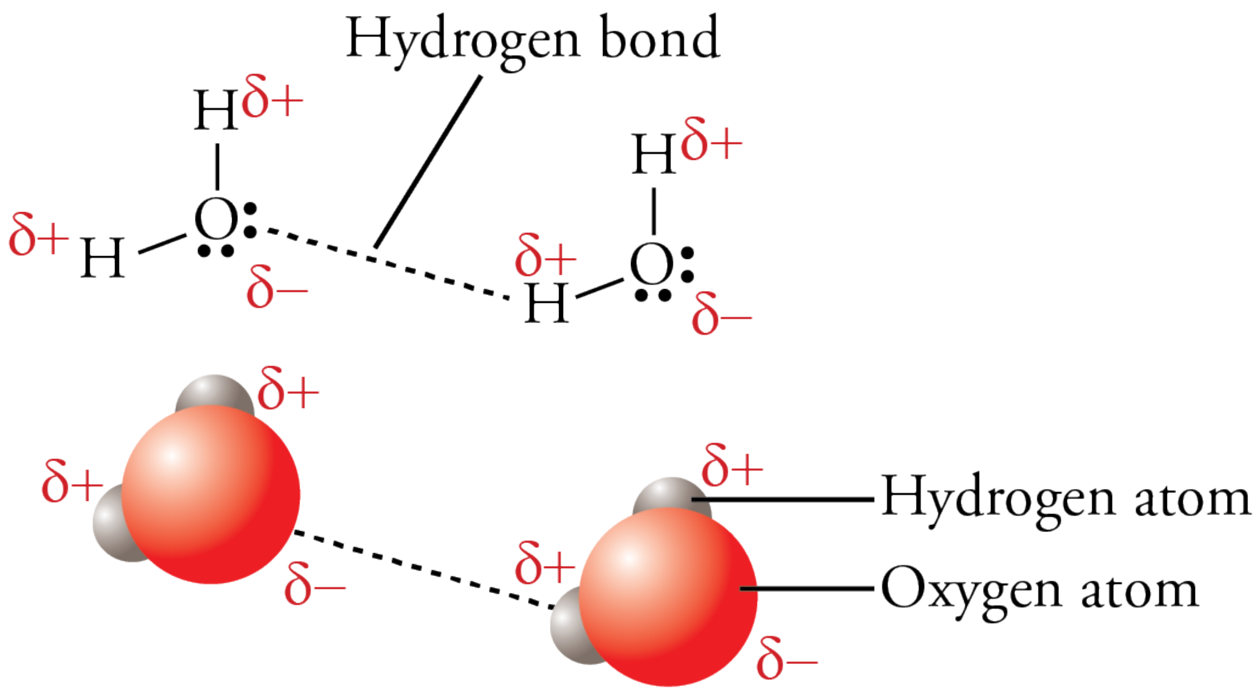
Hydrogen Bonds in HF

In HF, the hydrogen bond is between the partial positive H of one HF molecule and the partial negative F of another HF molecule.



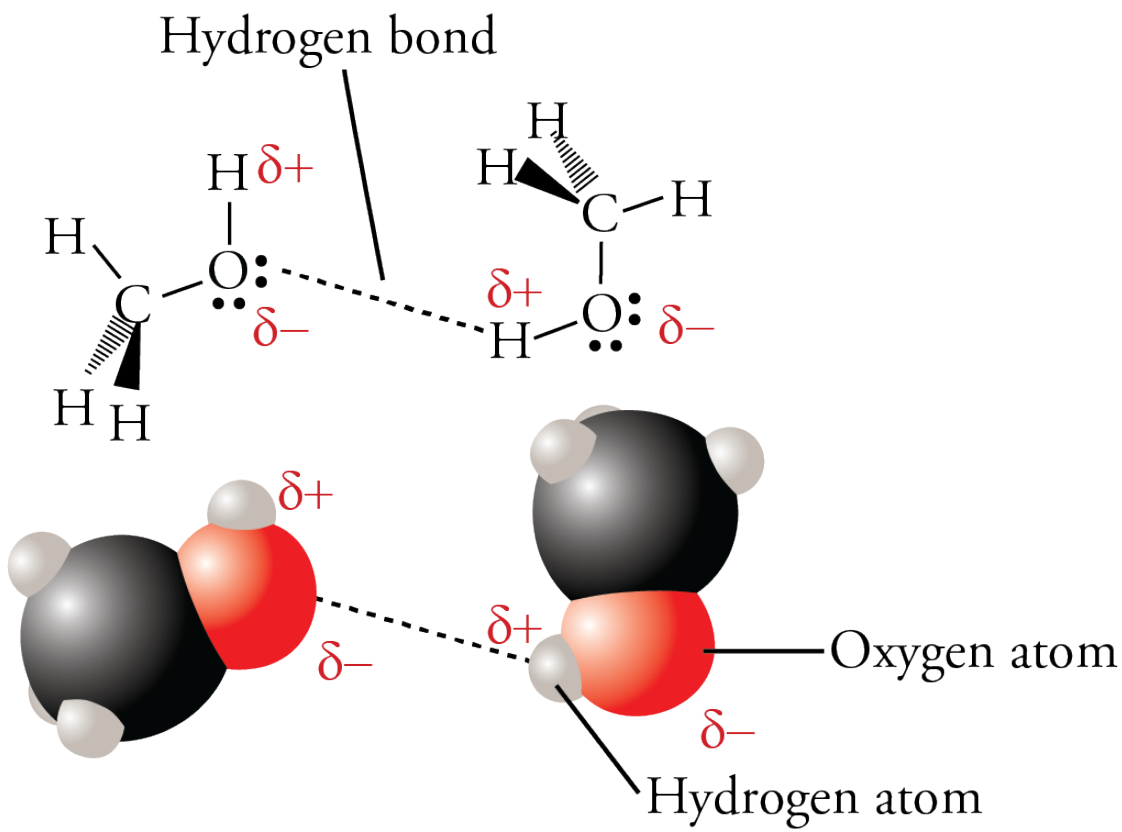
Hydrogen Bonds in Water

In H_2O, the hydrogen bond is between a partial positive H of one H_2O molecule and the partial negative O of another H_2O molecule.



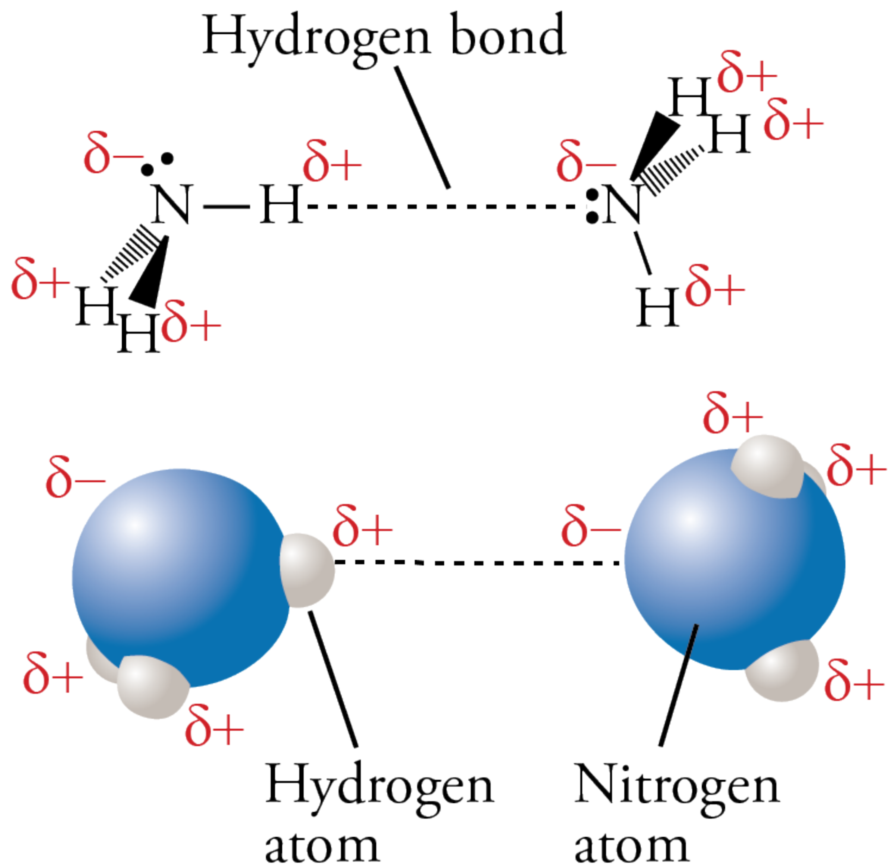
Hydrogen Bonds in Methanol

In CH_3OH, the hydrogen bond is between the partial positive H of one CH_3OH molecule and the partial negative O of another CH_3OH molecule.



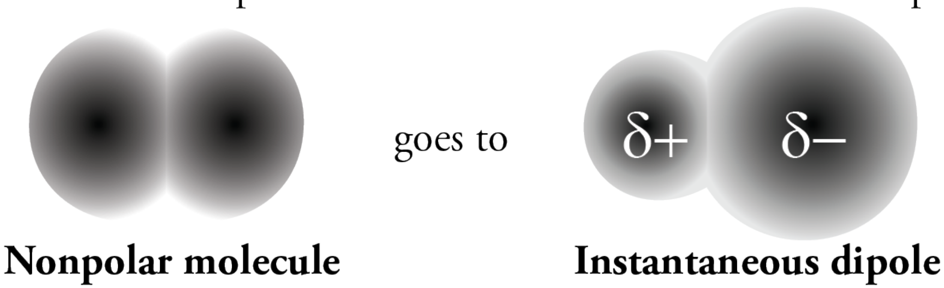
Hydrogen Bonds in Ammonia

In NH_3, the hydrogen bond is between a partial positive H of one NH_3 molecule and the partial negative N of another NH_3 molecule.

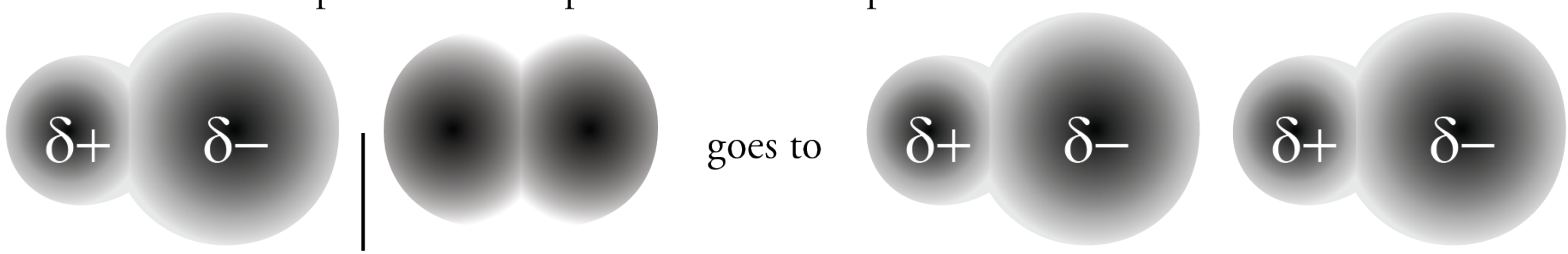


London Forces

1. Chance or collisions cause nonpolar molecules to form instantaneous dipoles.



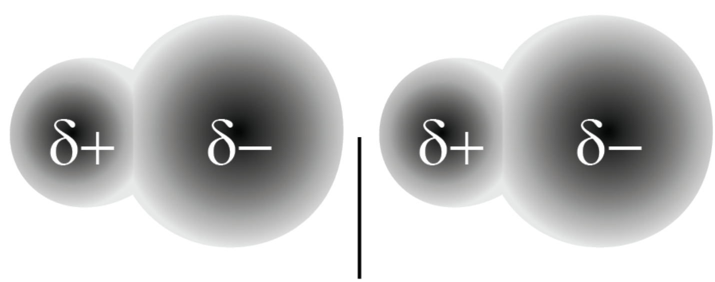
2. Instantaneous dipoles induce dipoles in other nonpolar molecules.



Induced dipole

Repulsion between the partial negative charge of the instantaneous dipole and the negative charge of the electrons in the nonpolar molecule pushes the electrons in the nonpolar molecule to the right, forming an induced dipole.

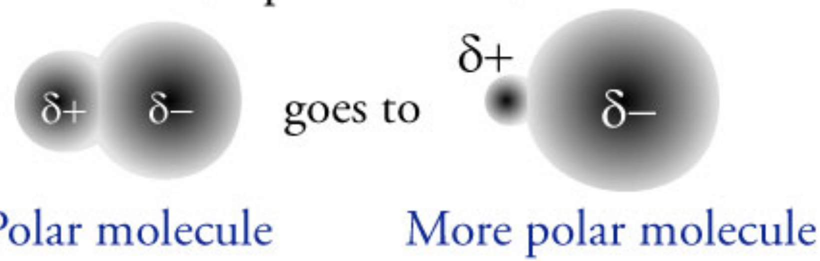
3. Induced dipoles can induce dipoles in other nonpolar molecules, resulting in many molecules with partial charges. London forces are the attractions between the partial positive and partial negative charges in these instantaneous and induced dipoles.



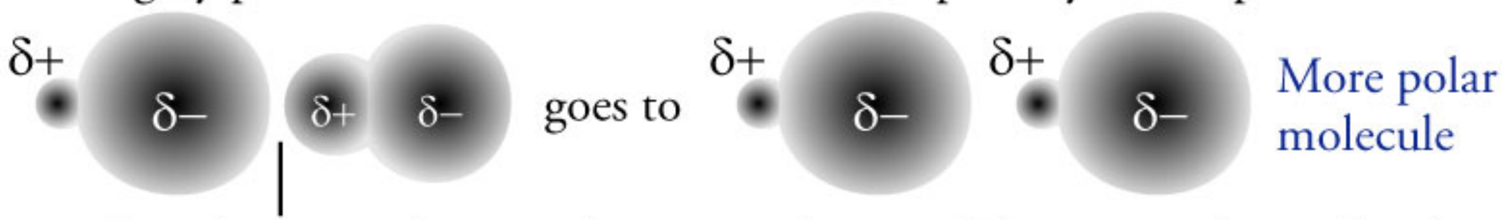
London force

London Forces in Polar Molecules

1. Chance or collisions cause polar molecules to become more polar.

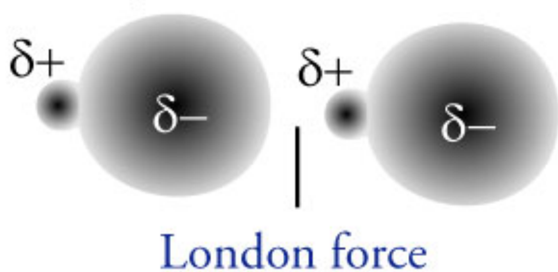


2. More highly polar molecules induce increases in polarity in less polar molecules.



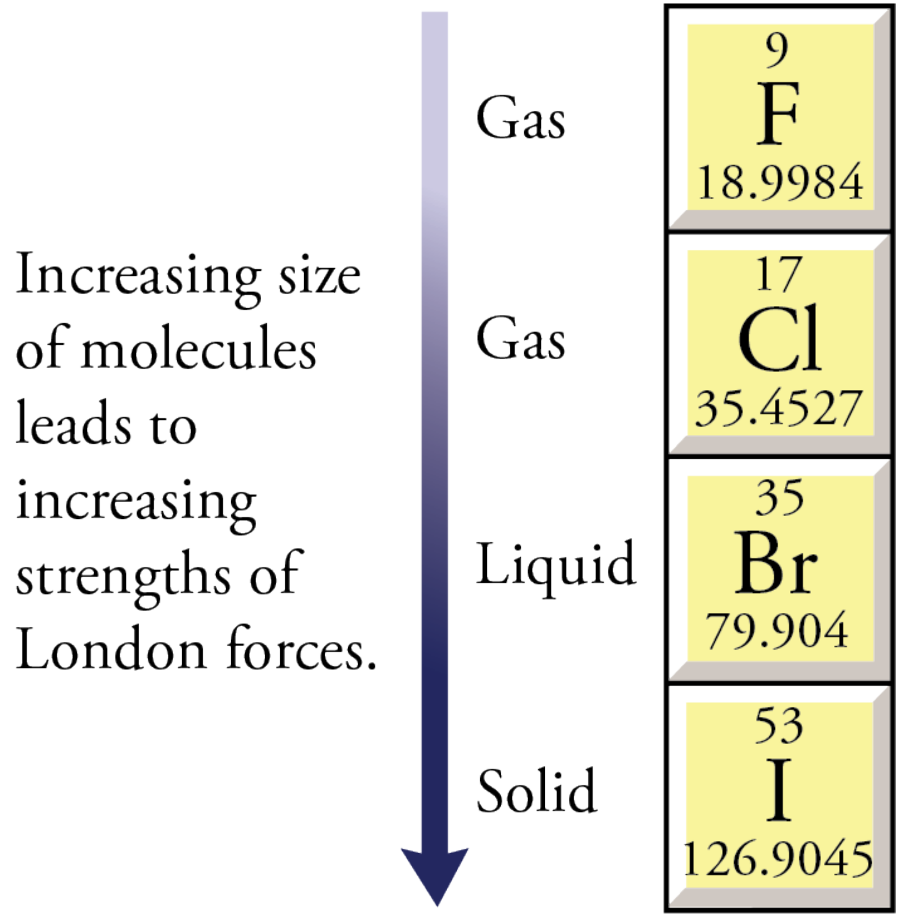
Repulsion between the partial negative charge of the more polar molecule and the negative charge of the electrons in the less polar molecule pushes the electrons in the less polar molecule to the right, leading to an induced increase in polarity.

3. The more polar molecules can induce increases in polarity in other less polar molecules, resulting in many molecules with larger partial charges. London forces are the attractions between the partial positive and partial negative charges in these instantaneously increased dipoles and induced increases in dipoles.

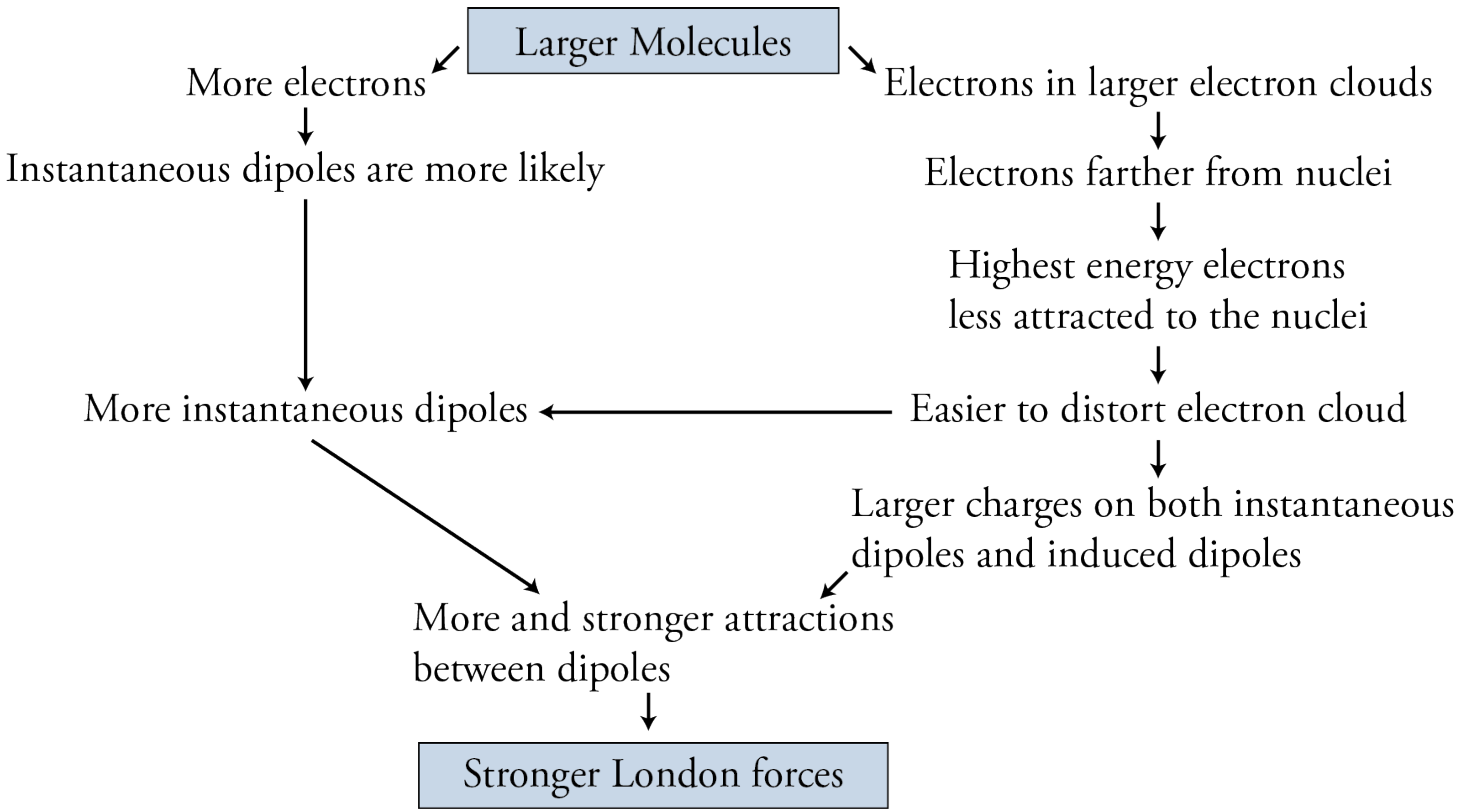


Halogens and Attractions

- Fluorine and chlorine are gases
- Bromine is a liquid.
- Iodine is a solid.



Why Larger Molecules Have Stronger London Forces



Types of Particles and Attractions - Elements

Type of element	Particles to visualize	Examples	Type of Attraction
Metals	cations in a sea of electrons	gold, Au	metallic bonds
Noble gases	atoms	xenon, Xe	London forces
Carbon (diamond)	atoms	C(dia)	covalent bonds
Other nonmetallic elements	molecules	H_2, N_2, O_2, F_2, Cl_2, Br_2, I_2, S_8, Se_8, P_4	London forces

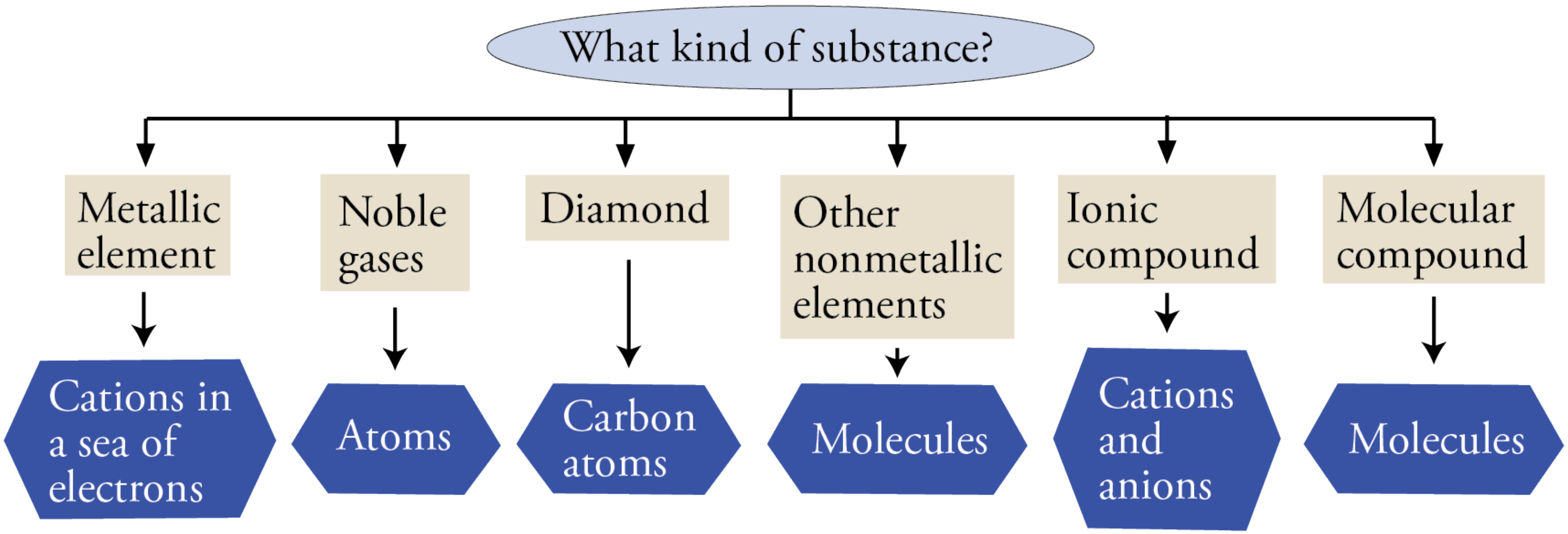
Types of Attractions – Carbon

- **Diamond -** Carbons atoms held together by covalent bonds, forming huge 3-dimensional molecules.
- **Graphite -** Carbons atoms held together by covalent bonds, forming huge 2-dimensional molecules held together by London forces.
- **Fullerenes -** Carbons atoms held together by covalent bonds, forming 3-dimensional molecules held together by London forces.

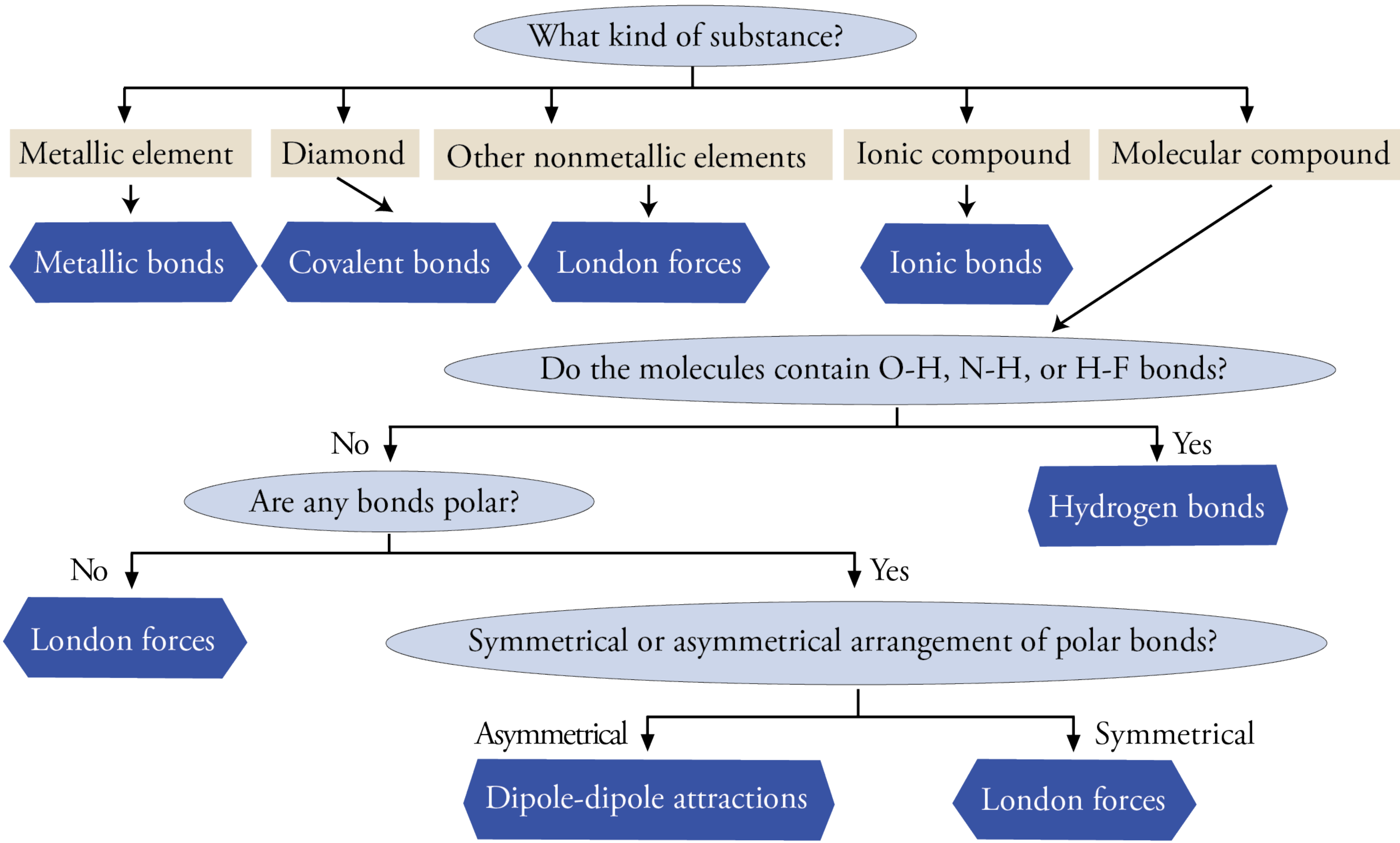
Types of Particles and Attractions - Compounds

Type of compound	Particles to visualize	Examples	Type of Attraction
Ionic	cations and anions	NaCl	ionic bonds
Nonpolar molecular	molecules	hydrocarbons	London forces
Polar molecular w/out H-F, O-H, or N-H	molecules	HCl	dipole-dipole
Polar molecular with H-F, O-H, or N-H	molecules	HF, H_2O, NH_3, alcohols	hydrogen bonds

Predicting Types of Particles



Predicting Types of Attractions

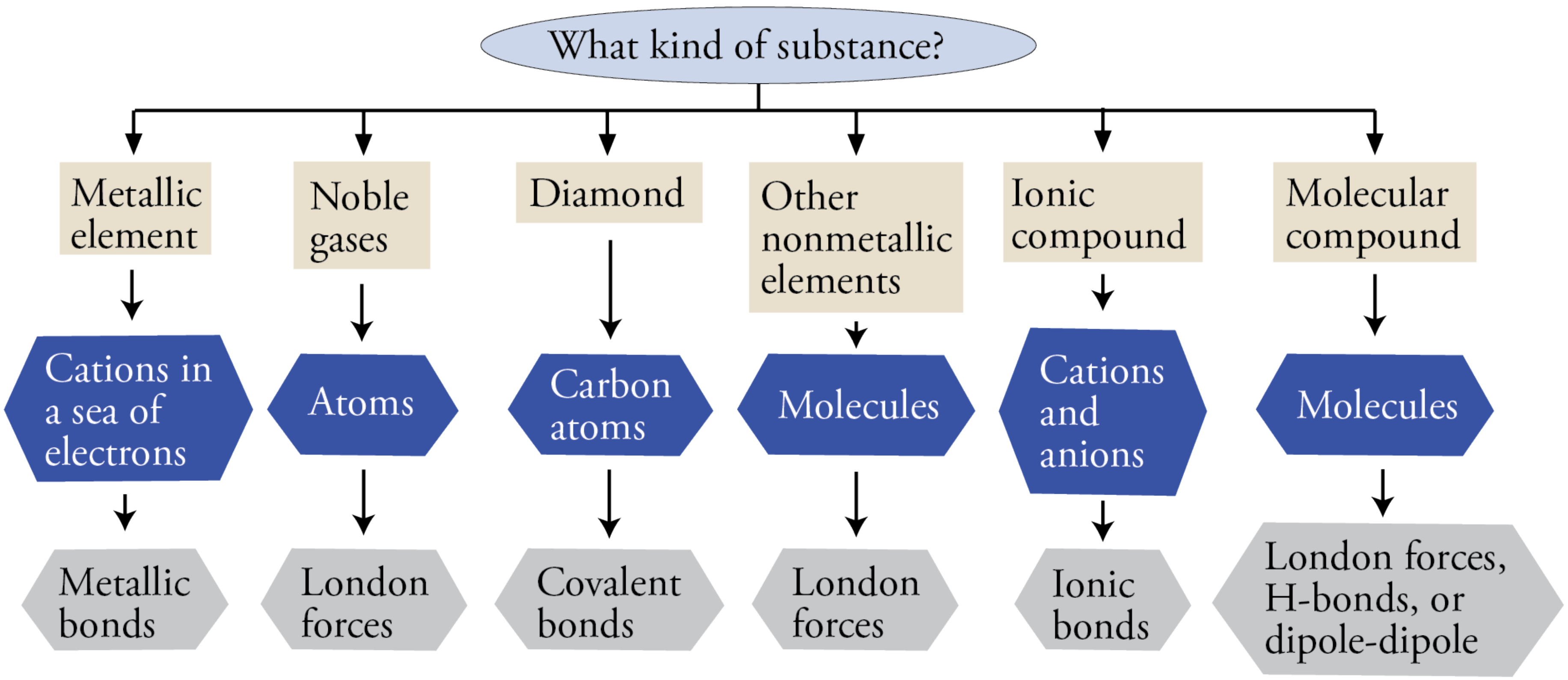


Example 1

- For iron, specify (1) the type of particle that forms the substance's fundamental structure and (2) the name of the type of attraction that holds these particles in the solid and liquid form.

Predicting Types of Attractions

Iron, Fe

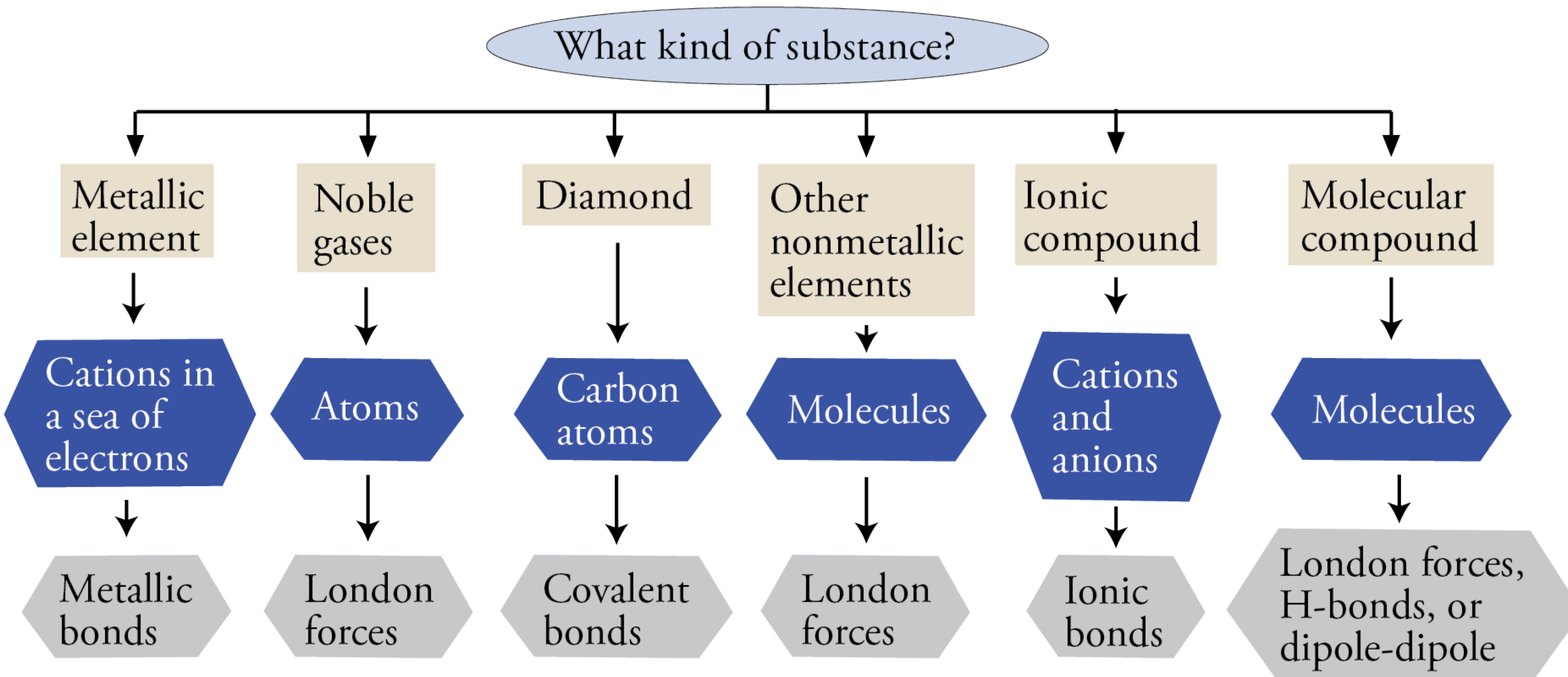


Example 2

- For iodine, specify (1) the type of particle that forms the substance's fundamental structure and (2) the name of the type of attraction that holds these particles in the solid and liquid form.

Predicting Types of Attractions

Iodine, I_2

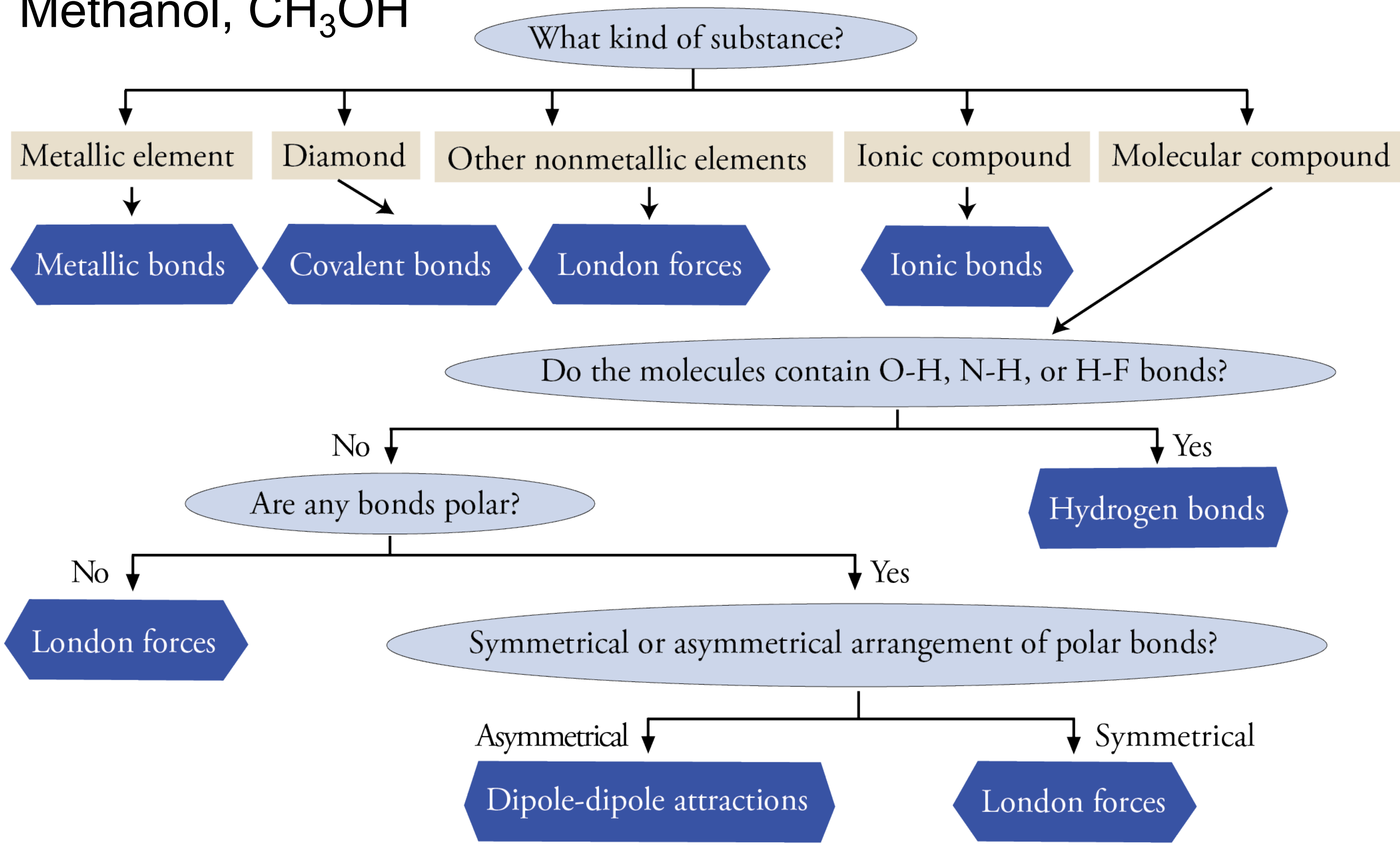


Example 3

- For methanol, CH_3OH, specify (1) the type of particle that forms the substance's fundamental structure and (2) the name of the type of attraction that holds these particles in the solid and liquid form.

Predicting Types of Attractions

Methanol, CH_3OH

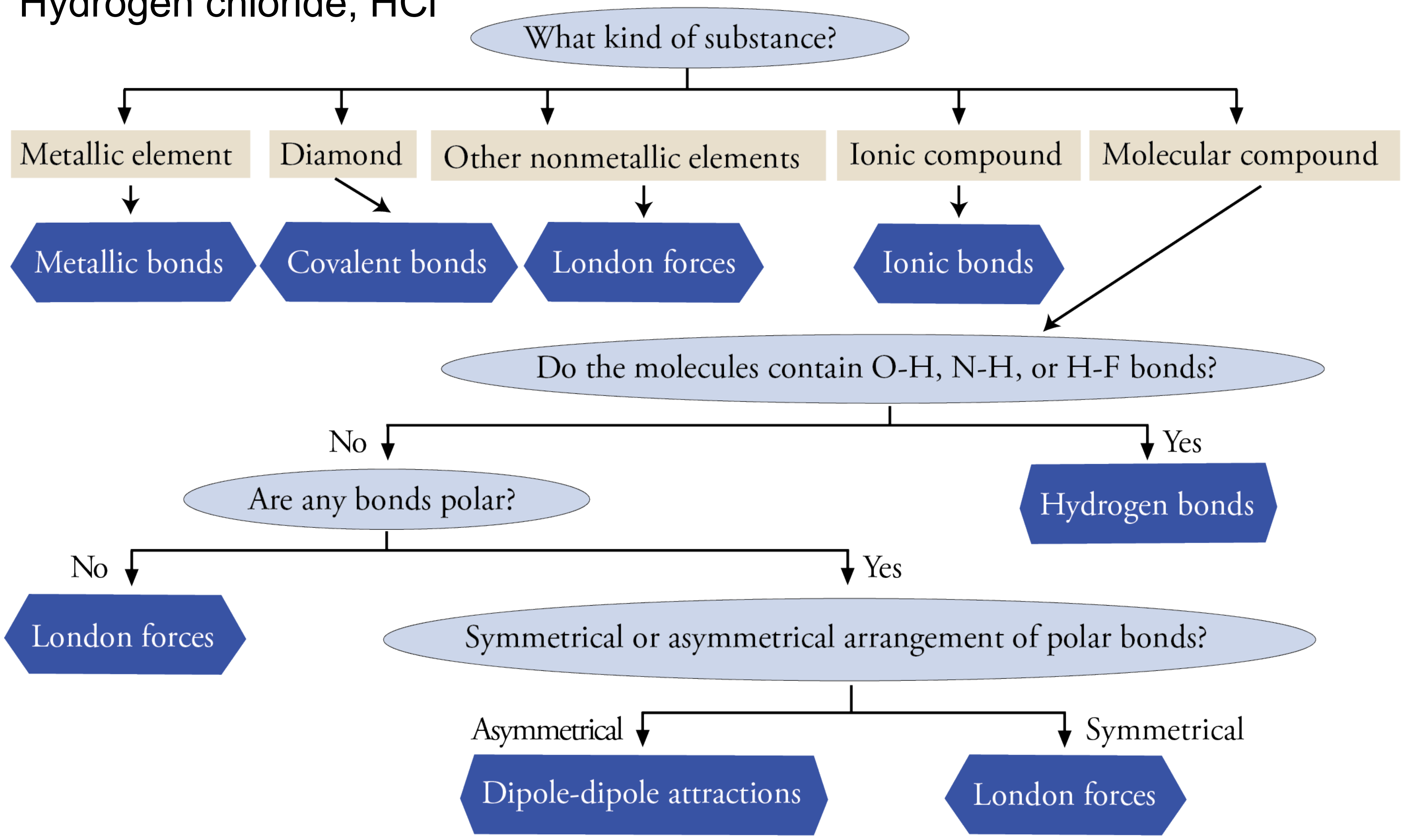


Example 4

- For hydrogen chloride, specify (1) the type of particle that forms the substance's fundamental structure and (2) the name of the type of attraction that holds these particles in the solid and liquid form.

Predicting Types of Attractions

Hydrogen chloride, HCl

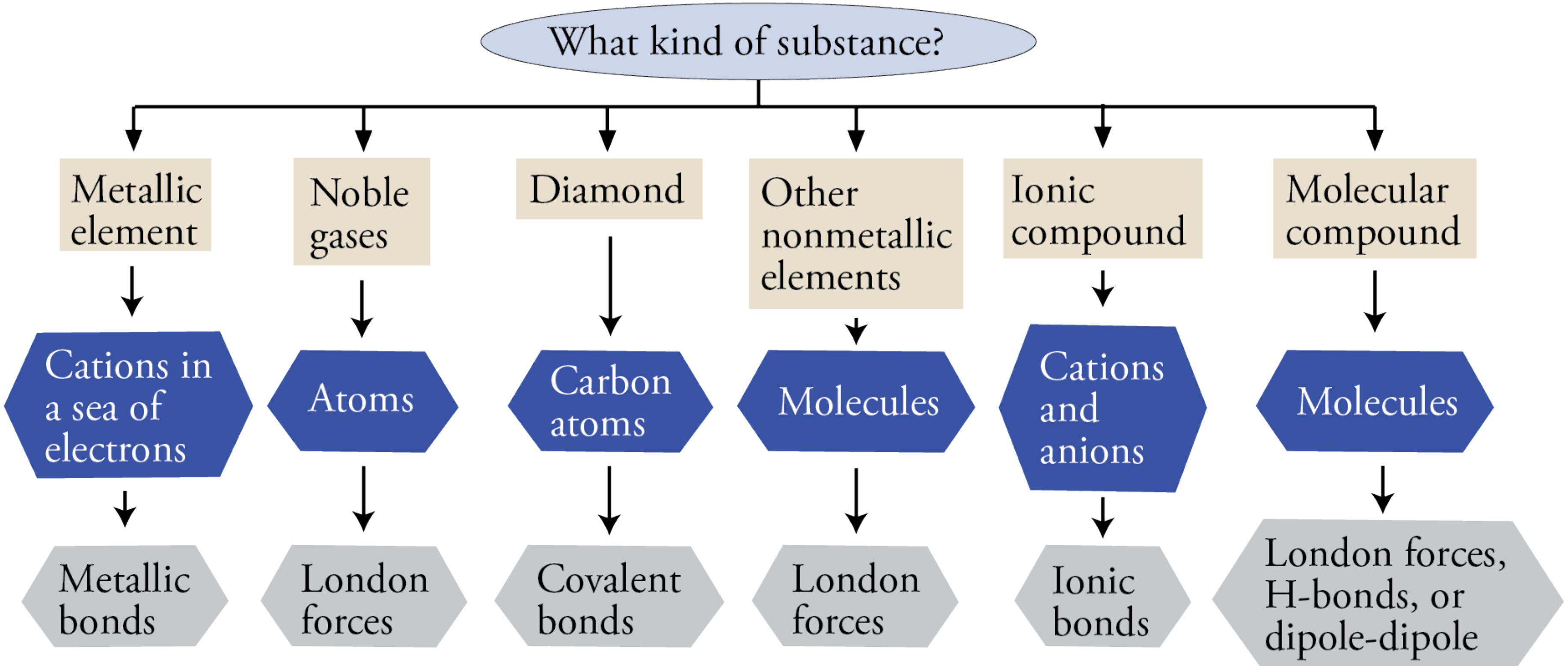


Example 6

- For potassium fluoride, specify (1) the type of particle that forms the substance’s fundamental structure and (2) the name of the type of attraction that holds these particles in the solid and liquid form.

Predicting Types of Attractions

Potassium fluoride, KF



Example 7

- For carbon in the diamond form, specify (1) the type of particle that forms the substance’s fundamental structure and (2) the name of the type of attraction that holds these particles in the solid and liquid form.

Predicting Types of Attractions

Carbon (diamond)