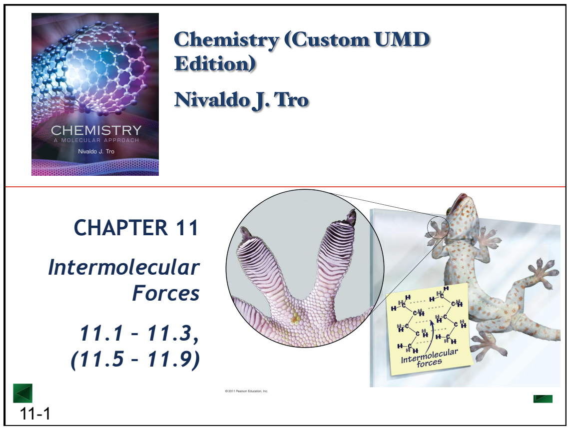


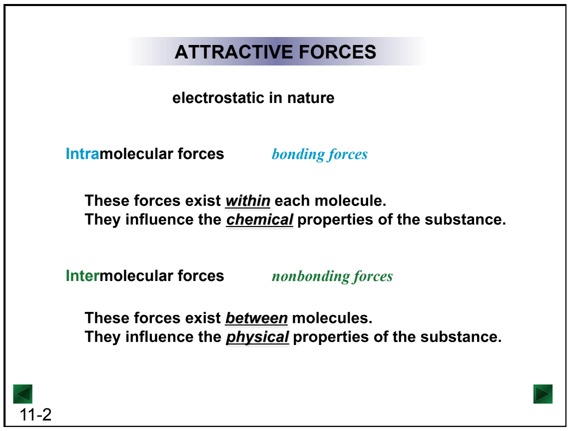
Chemistry (Custom UMD Edition)

Nivaldo J. Tro

CHAPTER 11

Intermolecular Forces

11.1 - 11.3, (11.5 - 11.9)



ATTRACTIVE FORCES

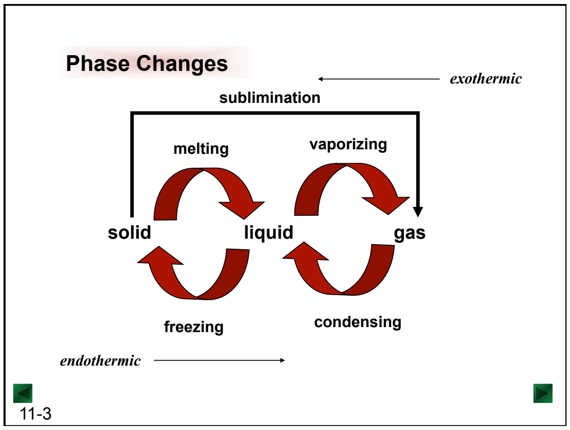
electrostatic in nature

Intramolecular forces *bonding forces*

These forces exist ***within*** each molecule.
They influence the ***chemical*** properties of the substance.

Intermolecular forces *nonbonding forces*

These forces exist ***between*** molecules.
They influence the ***physical*** properties of the substance.



Phase Changes

← *exothermic*

endothermic →

Changes of State

At the phase-change temperature, all the energy goes into changing the state of the substance and, therefore, *the temperature remains* constant during a phase change. For melting, energy goes into the system; for freezing, energy leaves the system.

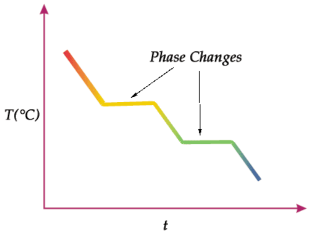
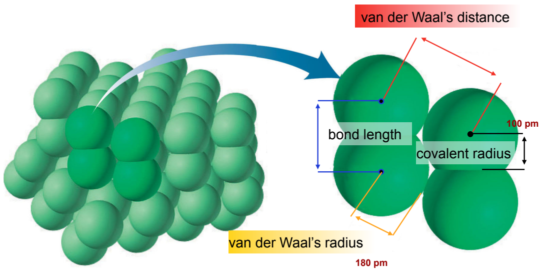


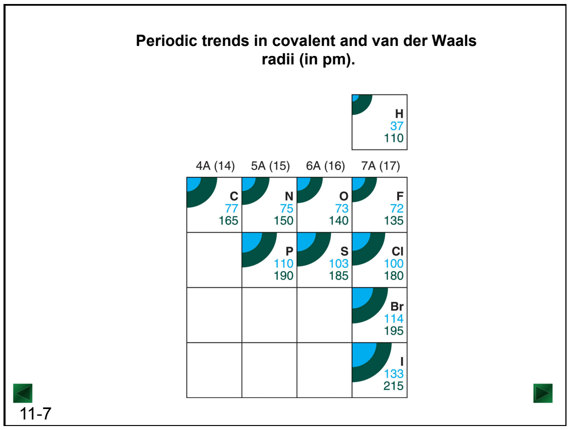
Table 12.1

A Macroscopic Comparison of Gases, Liquids, and Solids

State	Shape and Volume	Compressibility	Ability to Flow
Gas	Conforms to shape and volume of container	high	high
Liquid	Conforms to shape of container; volume limited by surface	very low	moderate
Solid	Maintains its own shape and volume	almost none	almost none

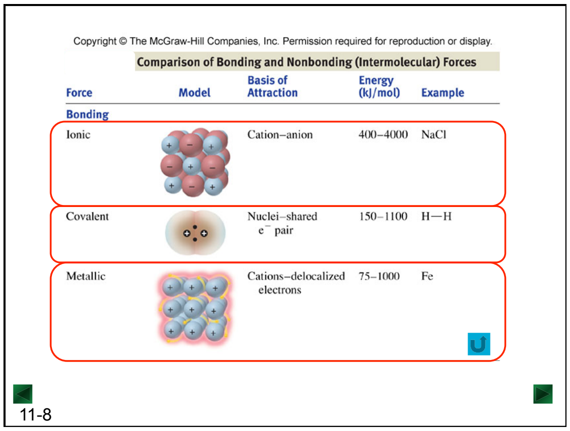
Figure 12.10 **Covalent and van der Waals radii.**





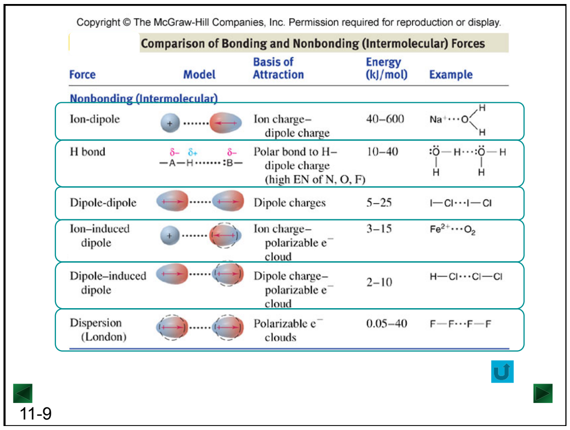
Periodic trends in covalent and van der Waals radii (in pm).

				H 37 110
	4A (14)	5A (15)	6A (16)	7A (17)
	C 77 165	N 75 150	O 73 140	F 72 135
		P 110 190	S 103 185	Cl 100 180
				Br 114 195
				I 133 215



Comparison of Bonding and Nonbonding (Intermolecular) Forces

Force	Model	Basis of Attraction	Energy (kJ/mol)	Example
Bonding				
Ionic		Cation–anion	400–4000	NaCl
Covalent		Nuclei–shared e^- pair	150–1100	H—H
Metallic		Cations–delocalized electrons	75–1000	Fe



Comparison of Bonding and Nonbonding (Intermolecular) Forces

Force	Model	Basis of Attraction	Energy (kJ/mol)	Example
Nonbonding (Intermolecular)				
Ion-dipole		Ion charge–dipole charge	40–600	$Na^+\cdots OH_2$
H bond	$\overset{\delta-}{—A}—\overset{\delta+}{H}\cdots\cdots:\overset{\delta-}{B}—$	Polar bond to H–dipole charge (high EN of N, O, F)	10–40	:Ö—H···:Ö—H (each O with H below)
Dipole-dipole		Dipole charges	5–25	I—Cl···I—Cl
Ion–induced dipole		Ion charge–polarizable e^- cloud	3–15	$Fe^{2+}\cdots O_2$
Dipole–induced dipole		Dipole charge–polarizable e^- cloud	2–10	H—Cl···Cl—Cl
Dispersion (London)		Polarizable e^- clouds	0.05–40	F—F···F—F

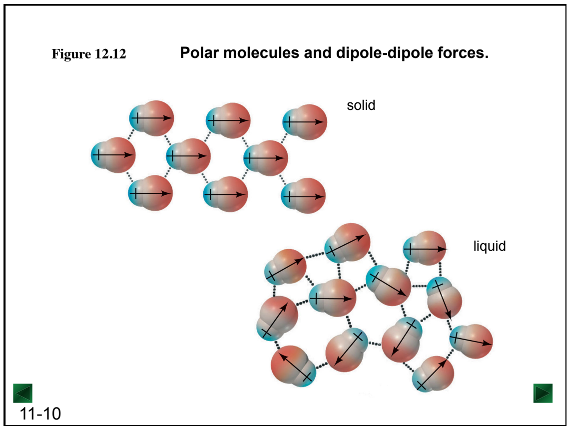
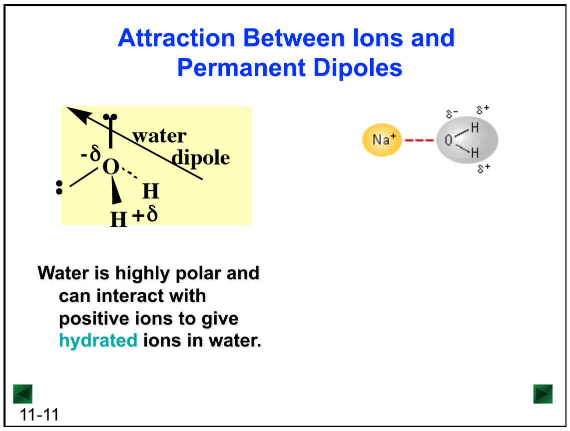


Figure 12.12 **Polar molecules and dipole-dipole forces.**

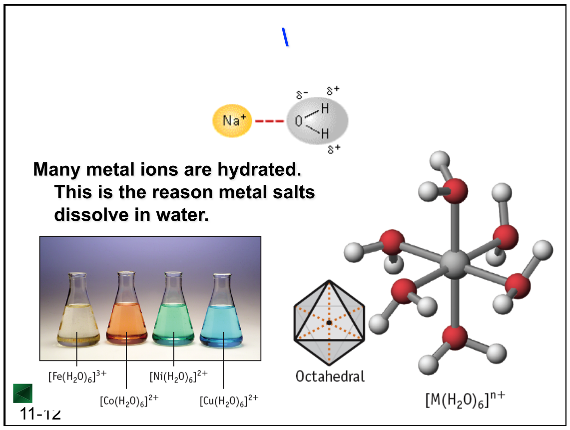
11-10



Attraction Between Ions and Permanent Dipoles

Water is highly polar and can interact with positive ions to give hydrated ions in water.

11-11



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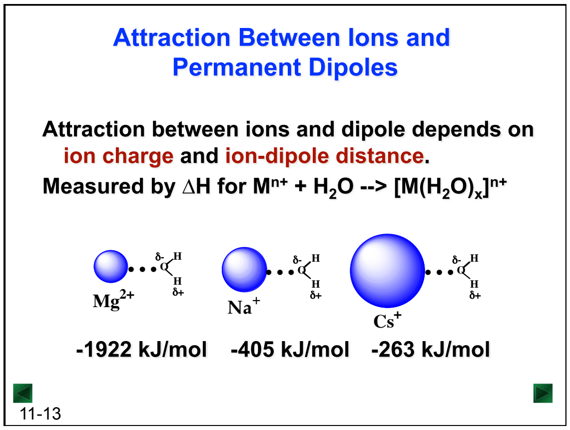
Many metal ions are hydrated. This is the reason metal salts dissolve in water.

11-12

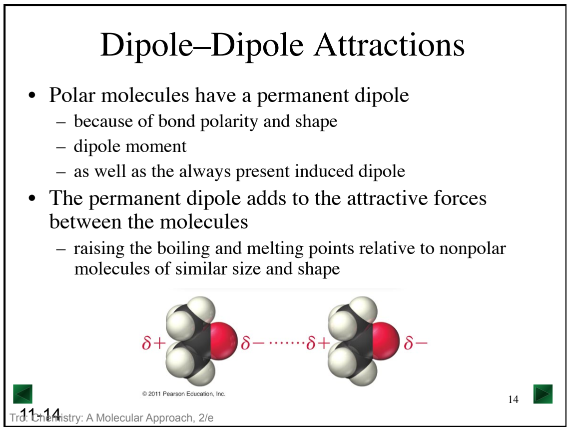


Attraction Between Ions and Permanent Dipoles

Attraction between ions and dipole depends on ion charge and ion-dipole distance.

Measured by ΔH for $M^{n+} + H_2O \dashrightarrow [M(H_2O)_x]^{n+}$

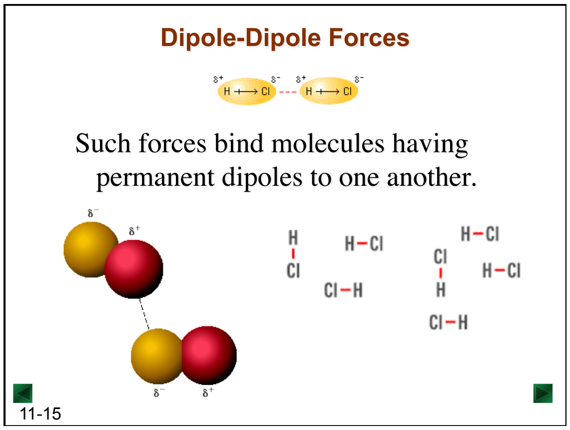
-1922 kJ/mol -405 kJ/mol -263 kJ/mol



Dipole–Dipole Attractions

- Polar molecules have a permanent dipole
  - because of bond polarity and shape
  - dipole moment
  - as well as the always present induced dipole
- The permanent dipole adds to the attractive forces between the molecules
  - raising the boiling and melting points relative to nonpolar molecules of similar size and shape

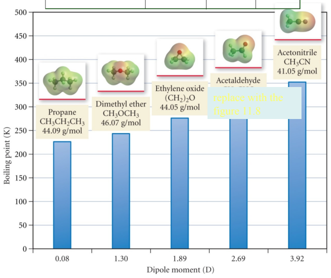
Tro: Chemistry: A Molecular Approach, 2/e



Dipole-Dipole Forces

Such forces bind molecules having permanent dipoles to one another.

	Molar Mass	Boiling Point	Dipole Size
$CH_3CH_2CH_3$	44.09	−42°C	0.08 D
CH_3–O–CH_3	46.07	−24°C	1.30 D
CH_3–CH=O	44.05	20.2°C	2.69 D
CH_3–C≡N	41.05	81.6°C	3.92 D



Example 11.1b: Determine if dipole–dipole attractions occur between CH_2Cl_2 molecules

Given: CH_2Cl_2, EN C = 2.5, H = 2.1, Cl = 3.0

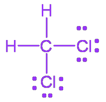
Find: If there are dipole–dipole attractions

Conceptual Plan: Formula → Lewis Structure → Bond Polarity → Molecule Polarity

EN Difference Shape

Relationships: molecules that have dipole–dipole attractions must be polar

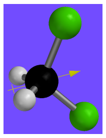
Solution:



Cl—C
3.0−2.5 = 0.5
polar

C—H
2.5−2.1 = 0.4
nonpolar

4 bonding areas
no lone pairs =
tetrahedral shape



polar bonds and tetrahedral shape = polar molecule

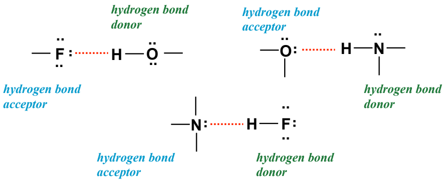
polar molecule; therefore dipole–dipole attractions

THE HYDROGEN BOND

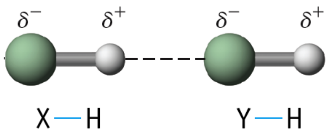
a dipole-dipole intermolecular force

A hydrogen bond may occur when an H atom in a molecule, bound to small highly electronegative atom with lone pairs of electrons, is attracted to the lone pairs in another molecule.

The elements which are so electronegative are N, O, and F.



The Hydrogen Bond

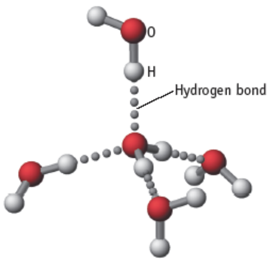


Types of Hydrogen Bonds [X—H - - - :Y]

N—H - - - :N—	O—H - - - :N—	F—H - - - :N—
N—H - - - :O—	O—H - - - :O—	F—H - - - :O—
N—H - - - :F—	O—H - - - :F—	F—H - - - :F—

H-bonding is strongest when X and Y are N, O, or F

H-Bonding in Water



H-bonding is especially strong in water because

- **the O—H bond is very polar**
- **there are 2 lone pairs on the O atom**

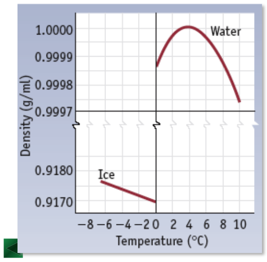
Accounts for many of water's unique properties.

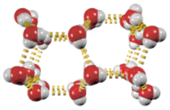
H-Bonds

- Hydrogen bonds are very strong intermolecular attractive forces
  - – stronger than dipole–dipole or dispersion forces
- Substances that can hydrogen bond will have higher boiling points and melting points than similar substances that cannot
- But hydrogen bonds are not nearly as strong as chemical bonds
  - – 2 to 5% the strength of covalent bonds

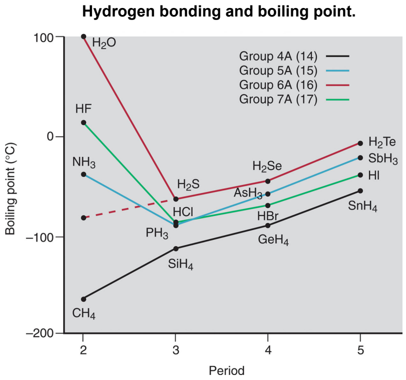
H-Bonding in Water

Ice has open lattice-like structure.
Ice density is < liquid and so solid floats on water.





One of the VERY few substances where solid is LESS DENSE than the liquid.



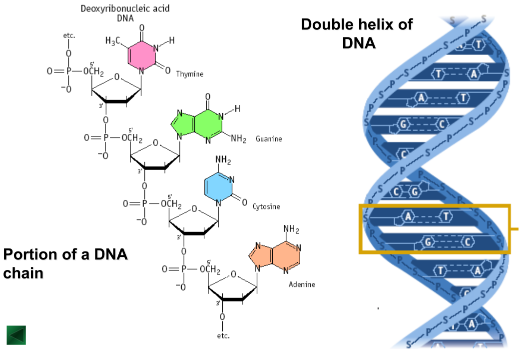
H-Bonding in Biology

H-bonding is especially strong in biological systems — such as DNA.

DNA — helical chains of phosphate groups and sugar molecules. Chains are helical because of tetrahedral geometry of P, C, and O.

Chains bind to one another by specific hydrogen bonding between pairs of Lewis bases.
- —adenine with thymine
- —guanine with cytosine

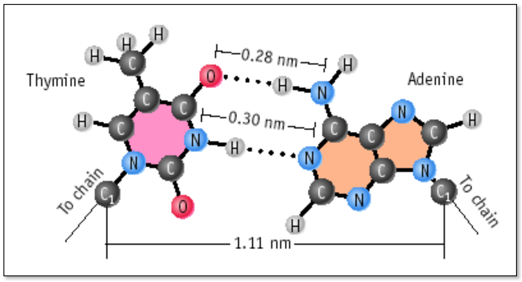
H-Bonding in DNA



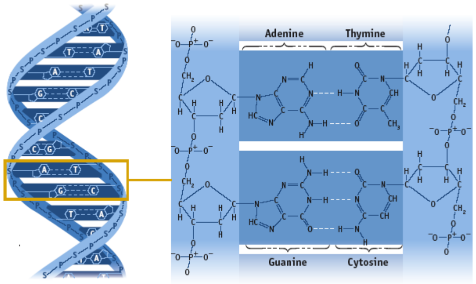
Double helix of DNA

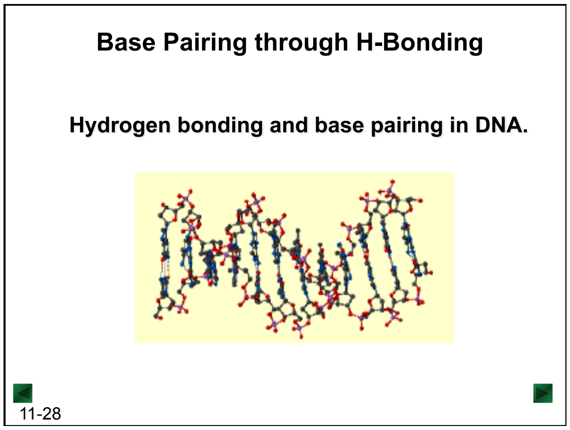
Portion of a DNA chain

Base Pairing through H-Bonding



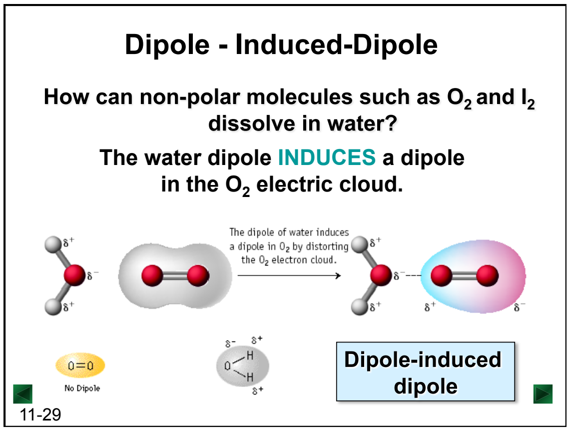
Base Pairing through H-Bonding





Base Pairing through H-Bonding

Hydrogen bonding and base pairing in DNA.



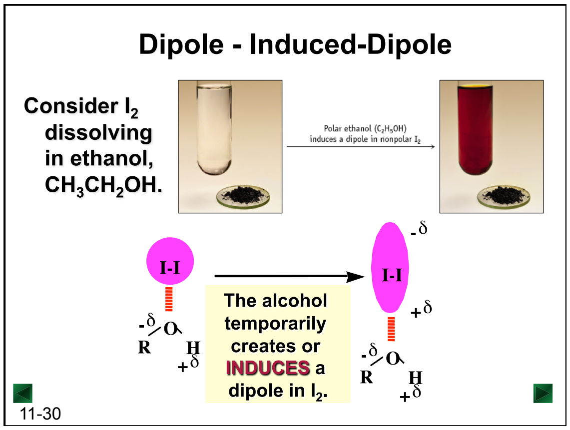
Dipole - Induced-Dipole

How can non-polar molecules such as O_2 and I_2 dissolve in water?

The water dipole **INDUCES** a dipole in the O_2 electric cloud.

The dipole of water induces a dipole in O_2 by distorting the O_2 electron cloud.

Dipole-induced dipole



Dipole - Induced-Dipole

Consider I_2 dissolving in ethanol, CH_3CH_2OH.

Polar ethanol (C_2H_5OH) induces a dipole in nonpolar I_2

The alcohol temporarily creates or **INDUCES** a dipole in I_2.

Dipole - Induced-Dipole

Table 13.2 The Solubility of Some Gases in Water*

Gas	Molar Mass (g/mol)	Solubility at 20 °C (g gas/100 g water)†
H_2	2.01	0.000160
N_2	28.0	0.00190
O_2	32.0	0.00434

- **Process of inducing a dipole is polarization**
- **Degree to which electron cloud of an atom or molecule can be distorted in its polarizability.**

Polarizability and Charged-Induced Dipole Forces

distortion of an electron cloud

•Polarizability increases down a group

size increases and the larger electron clouds are further from the nucleus

•Polarizability decreases left to right across a period

increasing Z_{eff} shrinks atomic size and holds the electrons more tightly

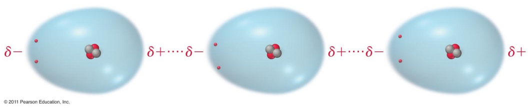
•Cations are less polarizable than their parent atom because they are smaller.

•Anions are more polarizable than their parent atom because they are larger.

Dispersion Force

Dispersion Force

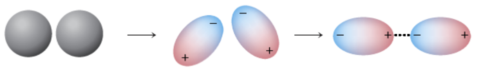
An instantaneous dipole on any one helium atom induces instantaneous dipoles on neighboring atoms, which then attract one another.



INDUCED-DIPOLE - INDUCED-DIPOLE

Formation of a dipole in two nonpolar I_2 molecules.

Induced dipole-induced dipole



Two nonpolar atoms or molecules (depicted as having an electron cloud that has a time-averaged spherical shape).

Momentary attractions and repulsions between nuclei and electrons in neighboring molecules lead to induced dipoles.

Correlation of the electron motions between the two atoms or molecules (which are now dipolar) leads to a lower energy and stabilizes the system.

INDUCED-DIPOLE - INDUCED-DIPOLE

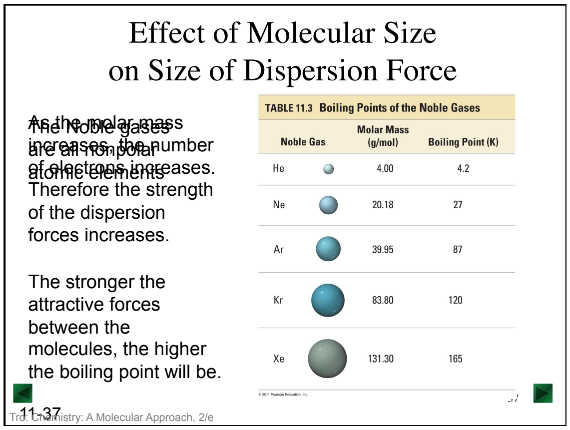
The induced forces between I_2 molecules are very weak, so solid I_2 sublimes (goes from a solid to gaseous molecules).

INDUCED-DIPOLE - INDUCED-DIPOLE

The magnitude of the induced dipole depends on the tendency to be distorted.

Higher molec. weight ---> larger induced dipoles.

Molecule	Boiling Point (°C)
CH_4 (methane)	- 161.5
C_2H_6 (ethane)	- 88.6
C_3H_8 (propane)	- 42.1
C_4H_{10} (butane)	- 0.5



Effect of Molecular Size on Size of Dispersion Force

The Noble gases are all nonpolar atomic elements

As the molar mass increases, the number of electrons increases. Therefore the strength of the dispersion forces increases.

The stronger the attractive forces between the molecules, the higher the boiling point will be.

TABLE 11.3 Boiling Points of the Noble Gases

Noble Gas	Molar Mass (g/mol)	Boiling Point (K)
He	4.00	4.2
Ne	20.18	27
Ar	39.95	87
Kr	83.80	120
Xe	131.30	165

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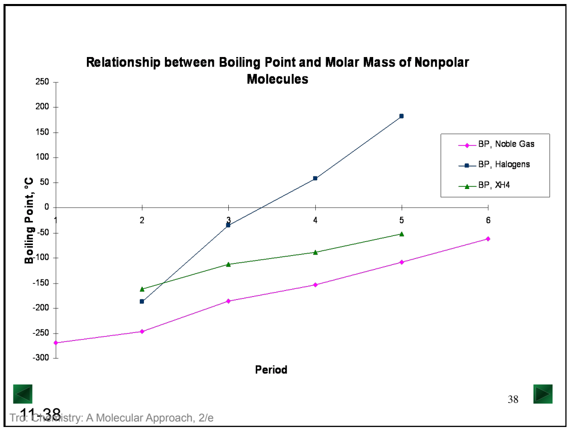
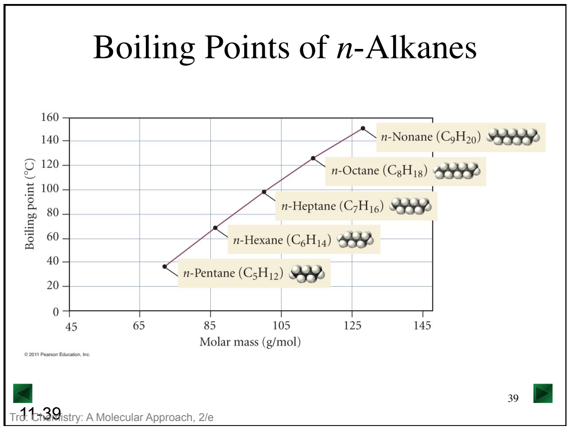


Relationship between Boiling Point and Molar Mass of Nonpolar Molecules



Boiling Points of *n*-Alkanes

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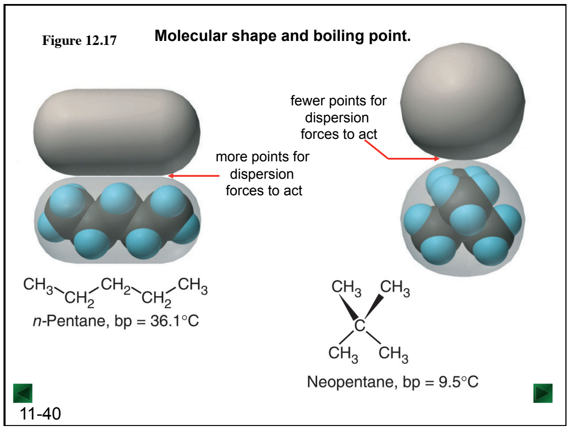
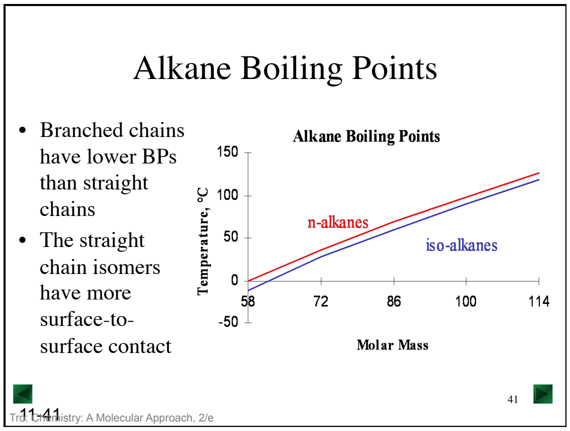


Figure 12.17 Molecular shape and boiling point.

n-Pentane, bp = 36.1°C

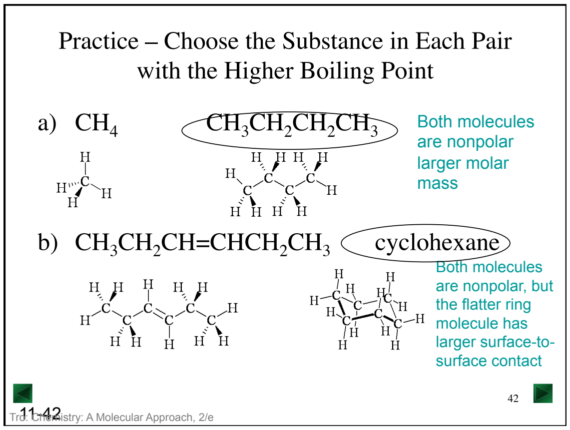
Neopentane, bp = 9.5°C

11-40



Alkane Boiling Points

- Branched chains have lower BPs than straight chains
- The straight chain isomers have more surface-to-surface contact



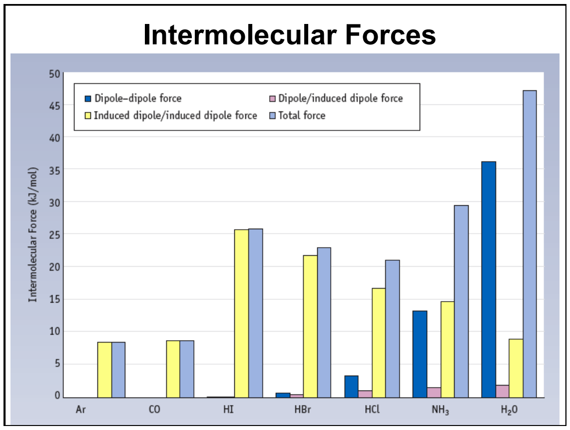
Practice – Choose the Substance in Each Pair with the Higher Boiling Point

a) CH_4 $CH_3CH_2CH_2CH_3$

Both molecules are nonpolar larger molar mass

b) $CH_3CH_2CH{=}CHCH_2CH_3$ cyclohexane

Both molecules are nonpolar, but the flatter ring molecule has larger surface-to-surface contact



Intermolecular Forces

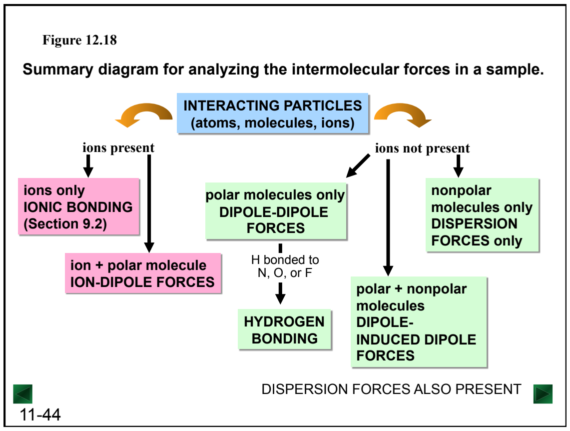


Figure 12.18

Summary diagram for analyzing the intermolecular forces in a sample.

INTERACTING PARTICLES (atoms, molecules, ions)

ions present

ions only IONIC BONDING (Section 9.2)

ion + polar molecule ION-DIPOLE FORCES

ions not present

polar molecules only DIPOLE-DIPOLE FORCES

H bonded to N, O, or F

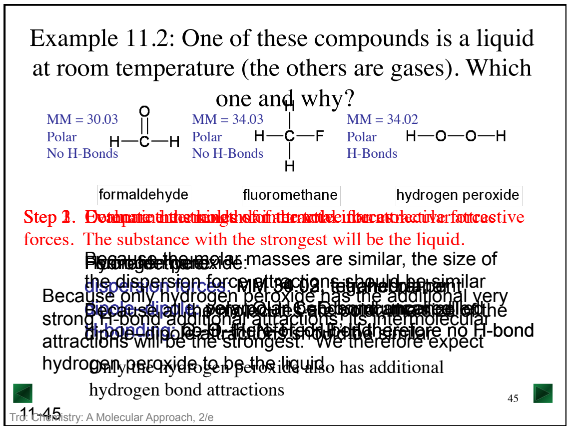
HYDROGEN BONDING

polar + nonpolar molecules DIPOLE-INDUCED DIPOLE FORCES

nonpolar molecules only DISPERSION FORCES only

DISPERSION FORCES ALSO PRESENT

11-44



Example 11.2: One of these compounds is a liquid at room temperature (the others are gases). Which one and why?

MM = 30.03
Polar
No H-Bonds

MM = 34.03
Polar
No H-Bonds

MM = 34.02
Polar
H-Bonds

formaldehyde

fluoromethane

hydrogen peroxide

Step 3. Compare the strengths of the attractive forces. The substance with the strongest will be the liquid.

Because the molar masses are similar, the size of the dispersion force attractions should be similar

Because only hydrogen peroxide has the additional very strong H-bond additional attractions, its intermolecular attractions will be the strongest. We therefore expect hydrogen peroxide to be the liquid.

Only the hydrogen peroxide also has additional hydrogen bond attractions

45

11-45

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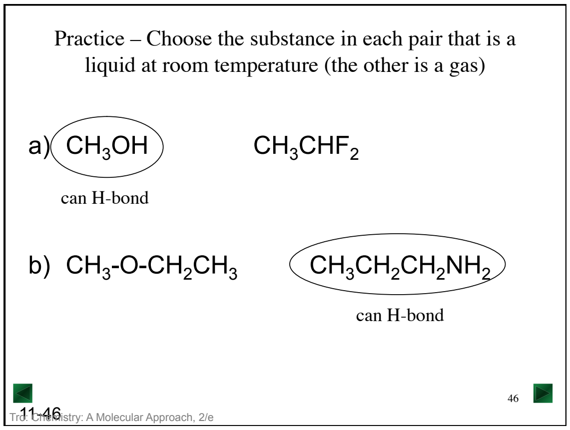

Practice – Choose the substance in each pair that is a liquid at room temperature (the other is a gas)

a) CH_3OH CH_3CHF_2

can H-bond

b) CH_3-O-CH_2CH_3 $CH_3CH_2CH_2NH_2$

can H-bond

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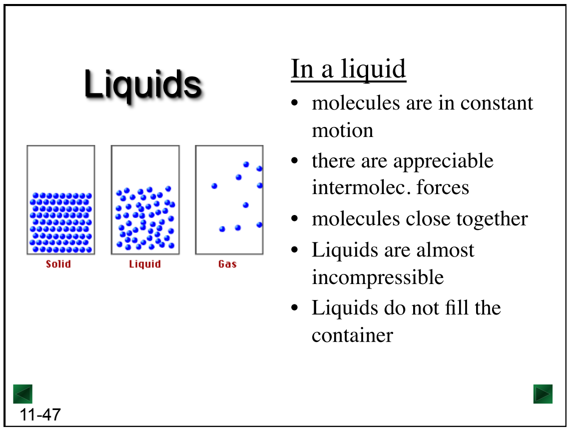
11-46

Tro: Chemistry: A Molecular Approach, 2/e

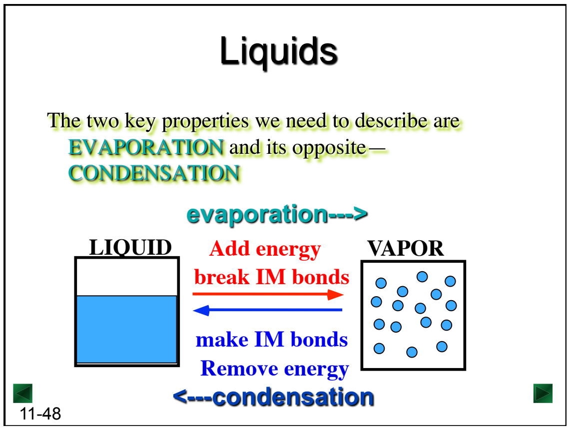


Liquids

In a liquid

- molecules are in constant motion
- there are appreciable intermolec. forces
- molecules close together
- Liquids are almost incompressible
- Liquids do not fill the container

11-47



Liquids

The two key properties we need to describe are EVAPORATION and its opposite—CONDENSATION

evaporation--->

LIQUID

Add energy

break IM bonds

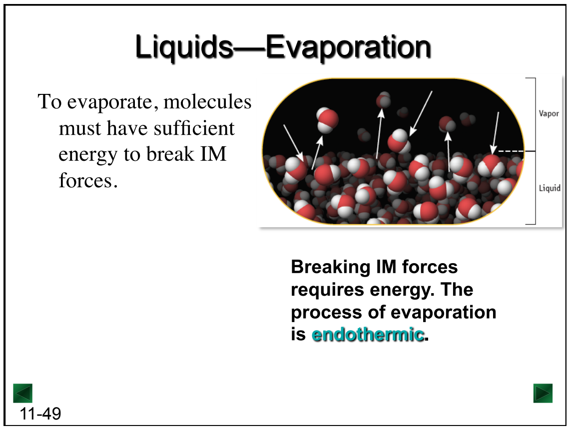
VAPOR

make IM bonds

Remove energy

<---condensation

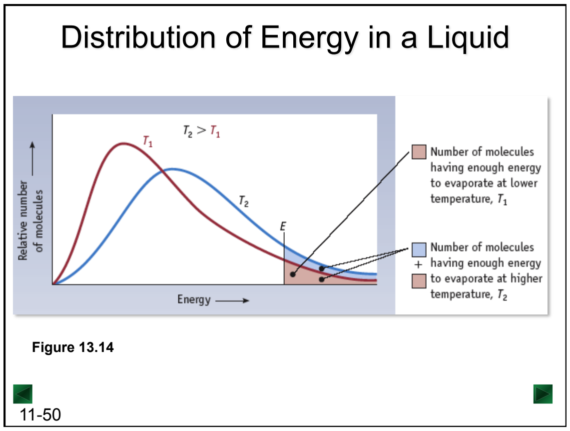
11-48



Liquids—Evaporation

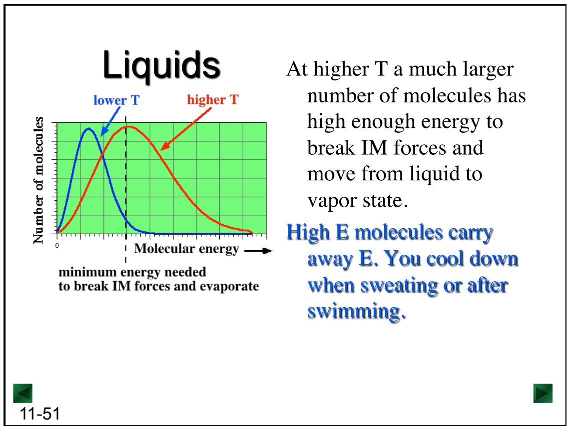
To evaporate, molecules must have sufficient energy to break IM forces.

Breaking IM forces requires energy. The process of evaporation is endothermic.



Distribution of Energy in a Liquid

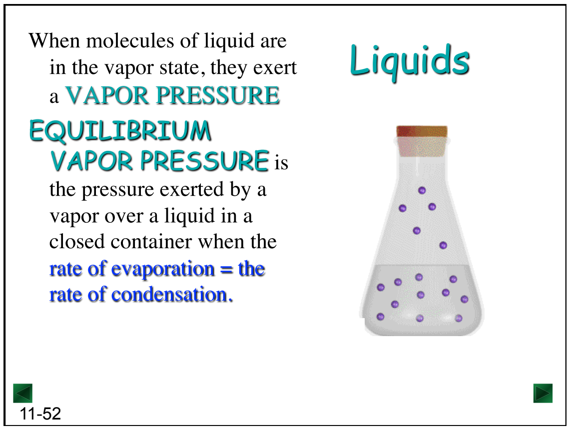
Figure 13.14



Liquids

At higher T a much larger number of molecules has high enough energy to break IM forces and move from liquid to vapor state.

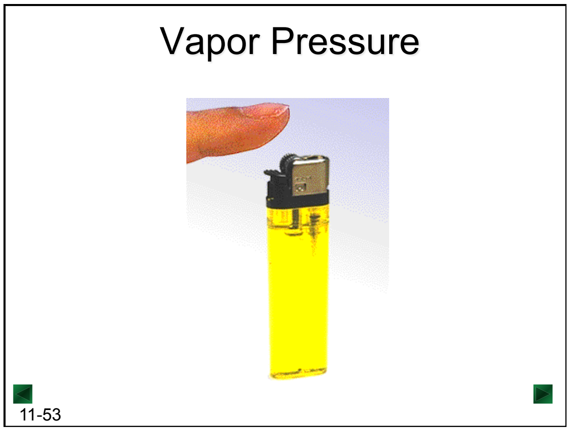
High E molecules carry away E. You cool down when sweating or after swimming.



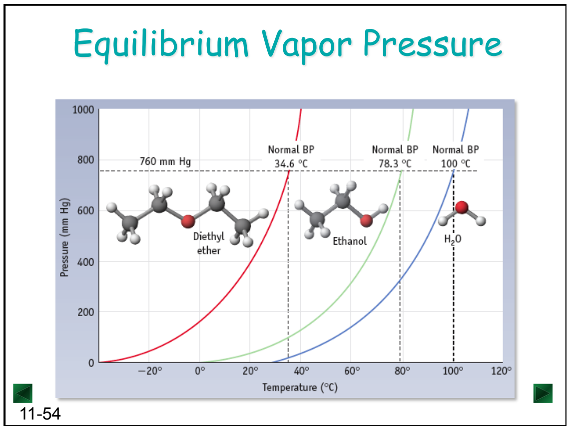
Liquids

When molecules of liquid are in the vapor state, they exert a VAPOR PRESSURE

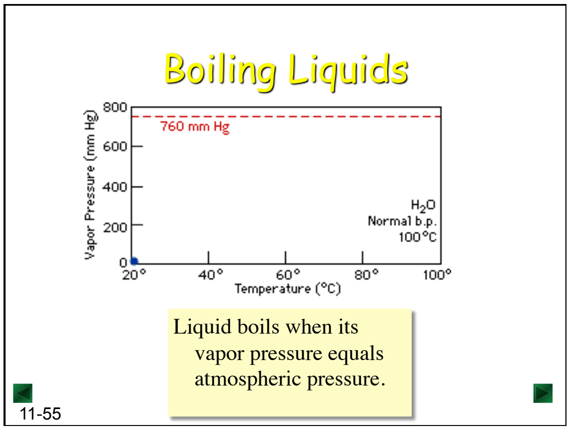
EQUILIBRIUM VAPOR PRESSURE is the pressure exerted by a vapor over a liquid in a closed container when the rate of evaporation = the rate of condensation.



Vapor Pressure

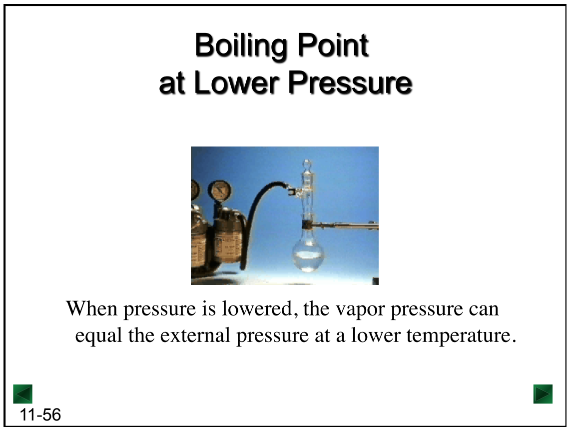


Equilibrium Vapor Pressure



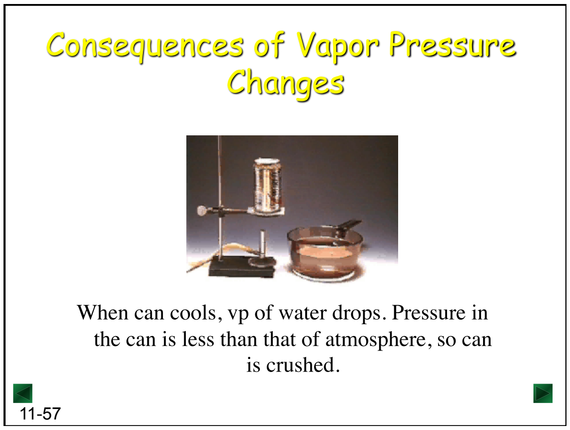
Boiling Liquids

Liquid boils when its vapor pressure equals atmospheric pressure.



Boiling Point at Lower Pressure

When pressure is lowered, the vapor pressure can equal the external pressure at a lower temperature.



Consequences of Vapor Pressure Changes

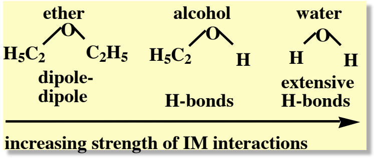
When can cools, vp of water drops. Pressure in the can is less than that of atmosphere, so can is crushed.

Liquids

VP versus T

4. If external P = 760 mm Hg, T of boiling is the **NORMAL BOILING POINT**

5. VP of a given molecule at a given T depends on IM forces. Here the VP's are in the order



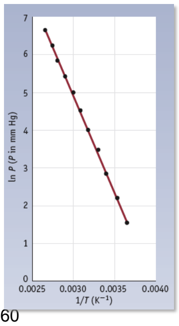
Liquids

HEAT OF VAPORIZATION is the heat req'd (at constant P) to vaporize the liquid.

LIQ + heat ---> VAP

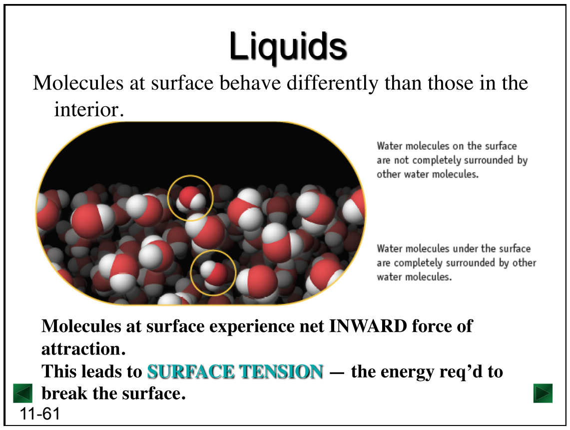
Compd.	**ΔH_{vap} (kJ/mol)**	**IM Force**
H_2O	40.7 (100 °C)	H-bonds
SO_2	26.8 (-47 °C)	dipole
Xe	12.6 (-107 °C)	induced dipole

Equilibrium Vapor Pressure & the Clausius-Clapeyron Equation



- Clausius-Clapeyron equation — used to find ΔH°_{vap}.
- The logarithm of the vapor pressure P is proportional to $\Delta H_{vaporiation}$ and to 1/T.
- $\ln P = -(\Delta H^\circ_{vap}/RT) + C$

$$\ln\frac{P_2}{P_1} = \frac{\Delta H_{vap}}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$



Liquids

Molecules at surface behave differently than those in the interior.

Water molecules on the surface are not completely surrounded by other water molecules.

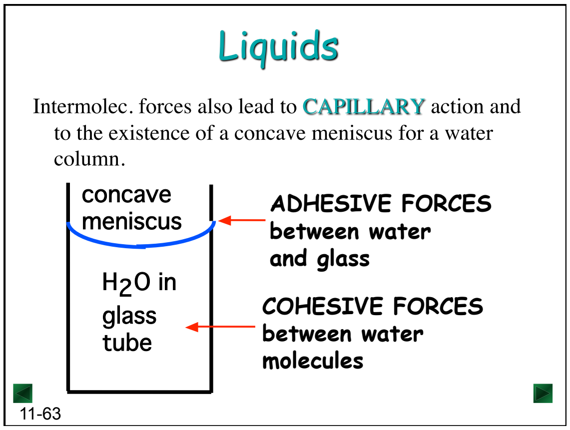
Water molecules under the surface are completely surrounded by other water molecules.

Molecules at surface experience net INWARD force of attraction.

This leads to SURFACE TENSION — the energy req'd to break the surface.

Surface Tension

SURFACE TENSION also leads to spherical liquid droplets.



Liquids

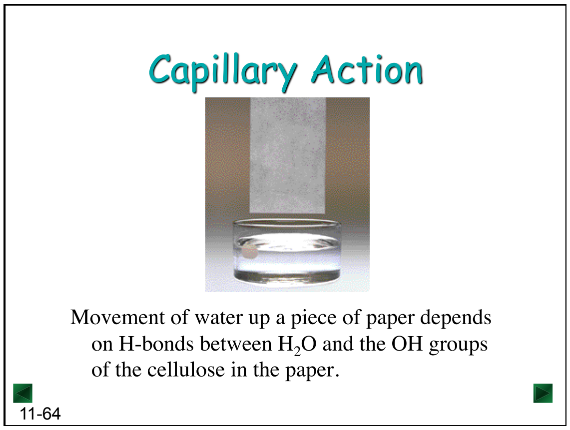
Intermolec. forces also lead to CAPILLARY action and to the existence of a concave meniscus for a water column.

concave meniscus

H_2O in glass tube

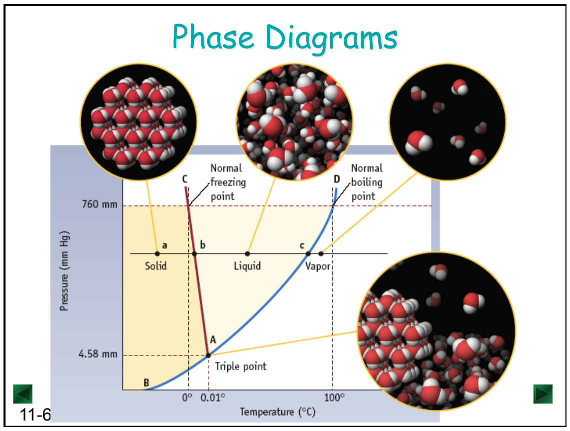
ADHESIVE FORCES between water and glass

COHESIVE FORCES between water molecules

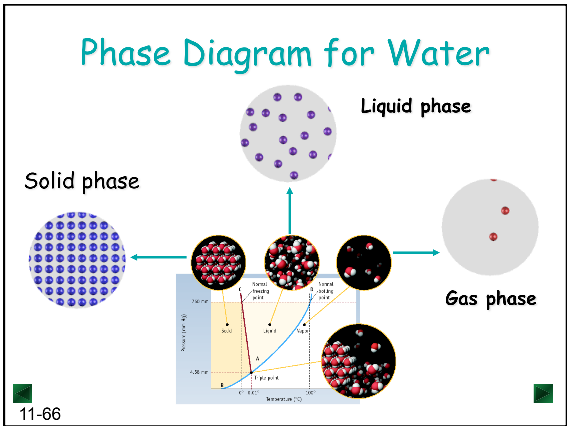


Capillary Action

Movement of water up a piece of paper depends on H-bonds between H_2O and the OH groups of the cellulose in the paper.



Phase Diagrams



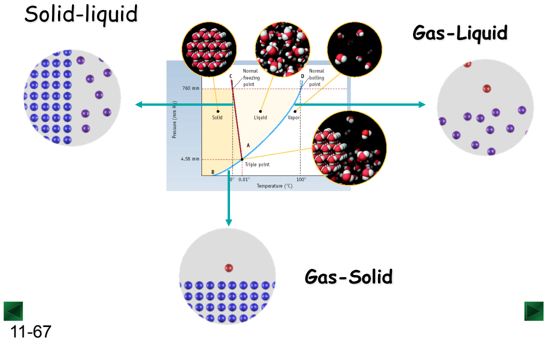
Phase Diagram for Water

Liquid phase

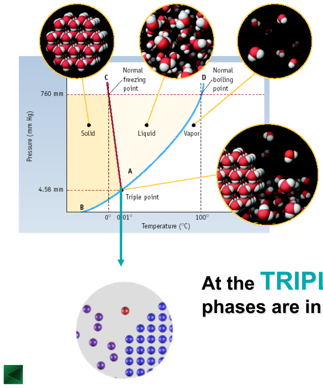
Solid phase

Gas phase

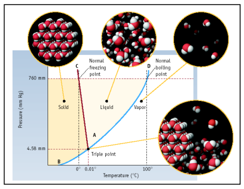
Phase Equilibria — Water



Triple Point — Water



At the TRIPLE POINT all three phases are in equilibrium.



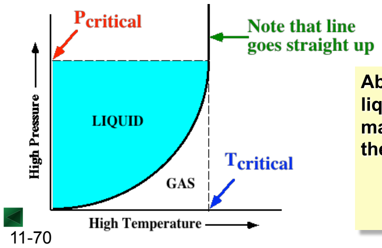
Phases Diagrams— Important Points for Water

	T(˚C)	P(mmHg)
Normal boil point	100	760
Normal freeze point	0	760
Triple point	0.0098	4.58

Critical T and P

As P and T increase, you finally reach the

CRITICAL T and P



Above critical T no liquid exists no matter how high the pressure.

Critical T and P

COMPD	T_c(°C)	P_c(atm)
H_2O	374	218
CO_2	31	73
CH_4	-82	46
Freon-12 (CCl_2F_2)	112	41

Notice that T_c and P_c depend on intermolecular forces.

Solid-Liquid Equilibria

In any system, if you increase P the DENSITY will go up.

Therefore — as P goes up, equilibrium favors phase with the larger density (or SMALLER volume/gram).

	Liquid H_2O	Solid H_2O
Density	1 g/cm³	0.917 g/cm³
cm³/gram	1	1.09

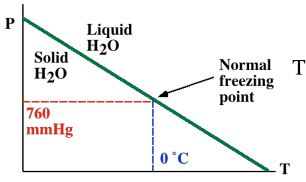
ICE $\rightleftarrows$ **LIQUID H_2O**

favored at low P — **favored at high P**

Solid-Liquid Equilibria

ICE $\rightleftharpoons$ LIQUID H_2O

favored at low P — favored at high P



Raising the pressure at constant T causes water to melt.

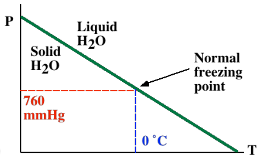
The NEGATIVE SLOPE of the S/L line is unique to H_2O. Almost everything else has positive slope.

Solid-Liquid Equilibria

The behavior of water under pressure is an example of LE CHATELIER'S PRINCIPLE

At Solid/Liquid equilibrium, raising P squeezes the solid.

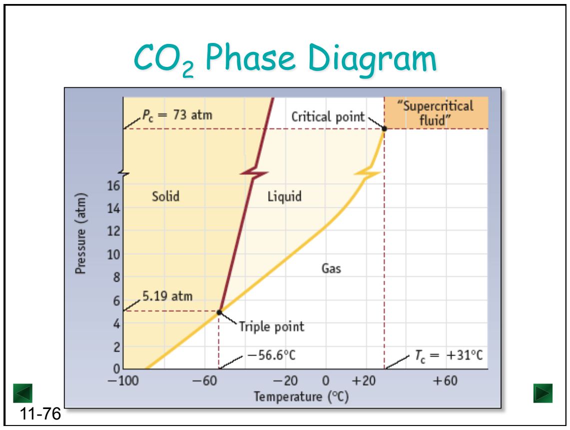
It responds by going to phase with greater density, i.e., the liquid phase.



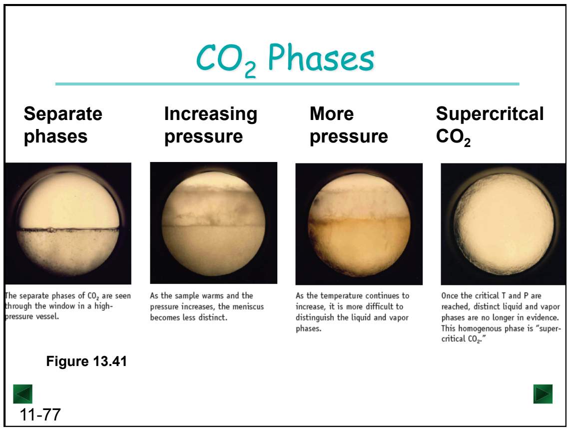
Solid-Vapor Equilibria

At $P < 4.58$ mmHg and $T < 0.0098$ ˚C solid H_2O can go directly to vapor. This process is called SUBLIMATION

This is how a frost-free refrigerator works.



CO_2 Phase Diagram



CO_2 Phases

Separate phases

The separate phases of CO_2 are seen through the window in a high-pressure vessel.

Increasing pressure

As the sample warms and the pressure increases, the meniscus becomes less distinct.

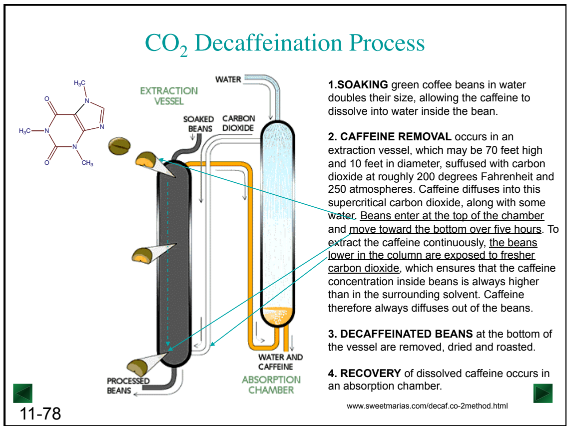
More pressure

As the temperature continues to increase, it is more difficult to distinguish the liquid and vapor phases.

Supercritcal CO_2

Once the critical T and P are reached, distinct liquid and vapor phases are no longer in evidence. This homogenous phase is "super-critical CO_2."

Figure 13.41



CO_2 Decaffeination Process

1.SOAKING green coffee beans in water doubles their size, allowing the caffeine to dissolve into water inside the bean.

2. CAFFEINE REMOVAL occurs in an extraction vessel, which may be 70 feet high and 10 feet in diameter, suffused with carbon dioxide at roughly 200 degrees Fahrenheit and 250 atmospheres. Caffeine diffuses into this supercritical carbon dioxide, along with some water. Beans enter at the top of the chamber and move toward the bottom over five hours. To extract the caffeine continuously, the beans lower in the column are exposed to fresher carbon dioxide, which ensures that the caffeine concentration inside beans is always higher than in the surrounding solvent. Caffeine therefore always diffuses out of the beans.

3. DECAFFEINATED BEANS at the bottom of the vessel are removed, dried and roasted.

4. RECOVERY of dissolved caffeine occurs in an absorption chamber.

www.sweetmarias.com/decaf.co-2method.html