Review of Intermolecular Forces & Liquids (Chapter 12)

CHEM 102
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READING

- We will very briefly review the underlying concepts from Chapters 12 on intermolecular forces since it is relevant to Chapter 14 (Solutions).
- The subject of Colligative Properties (large section 14.4) will be delayed until we do Chapter 19 (Thermodynamics).
- By next Monday (perhaps before) we'll start on thermodynamics (Chapter 15).

Intermolecular Forces

- Deviations from ideal gas behavior in real gases:
  - effects of the volume of gas molecules
  - Effects of forces acting between the molecules.
- Like bonding, intermolecular forces are based on Coulomb forces (but cancelation effects lead to other labels for this)
- Much weaker than ionic or covalent chemical bonds
- Types we will consider:
  - Strong: Ion-ion, ion-dipole, dipole-dipole forces
  - dispersion forces
  - hydrogen bonding

Ion-Ion Forces

- The potential energy, $E_{\text{ion-ion}}$, of ion-ion interactions (Coulomb forces), has the longest range of forces that affect chemistry.

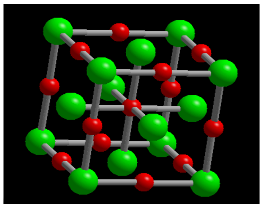
$$E_{\text{ion-ion}} \propto q_1 q_2 / r_{12}$$

- These strong, long-range forces are responsible for ionic bonds.

$q_1 = -1$ $q_2 = +1$

Ion-Ion Potential Energy

The potential energy law that govern charged particles are defined by Coulomb's law.



$$U = k \times \frac{q^{+} \times q^{-}}{r}$$

q = the charges on the cation and anion
r = the distance between ions
k = a constant

Greater charge = stronger attraction

Greater distance = weaker attraction

These are the strong forces that lead to salts with high melting temperatures.

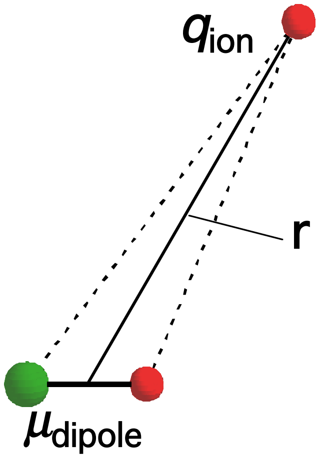
H_2O, mp = 0 °C NaCl, mp = 800 °C MgO, mp = 2800 °C

Ion-Dipole Energies

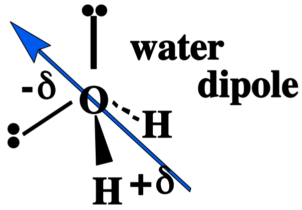
- Because "both ends" of a dipole interact with a nearby ion, there is a lot of cancellation of the net Coulomb $E_{ion\text{-}ion}$, of ion-ion interactions.

$$E_{ion\text{-}dipole} \propto |q_{ion}| \bullet \mu_{dipole} / r^2$$

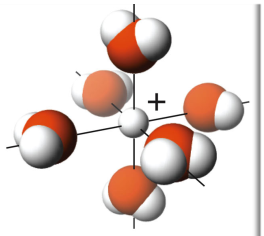
- These are weaker, but still one of the strongest of intermolecular forces.



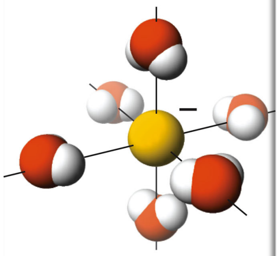
Attractions Between Ions & Permanent Dipoles



The polar nature of water provides for attractive forces between ions and water.

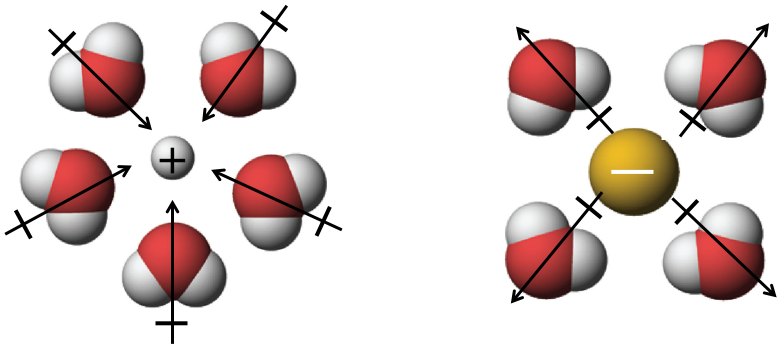


water surrounding a cation



water surrounding an anion

Solvation of Ions



When a *cation* exists in solution, it is surrounded by the *negative* dipole ends of water molecules.

When as *anion* exists in solution, it is surrounded by the *positive* dipole ends of water molecules.

Enthalpies of Hydration: A Measure of Ion-Dipole Forces

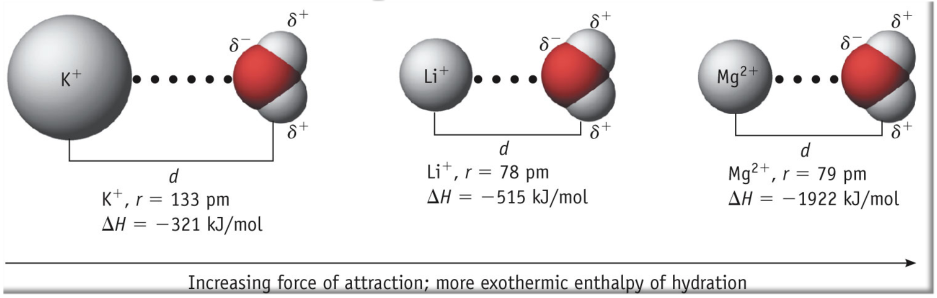
Table 12.1 **Radii and Enthalpies of Hydration of Alkali Metal Ions**

Cation	Ion Radius (pm)	Enthalpy of Hydration (kJ/mol)
Li^+	78	−515
Na^+	98	−405
K^+	133	−321
Rb^+	149	−296
Cs^+	165	−263

As the size of the ion increases, the exothermicity of the process decreases.

This is due to the weaker ion-dipole forces.

Enthalpies of Hydration: A Measure of Ion-Dipole Forces



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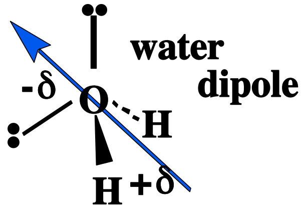
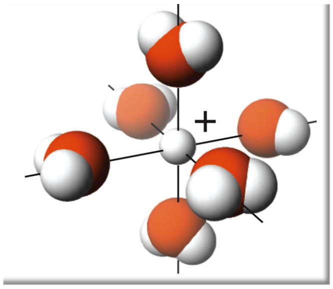
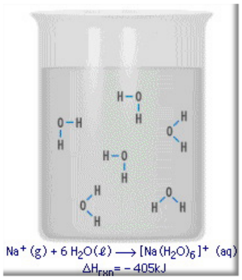
Attraction Between Ions & Permanent Dipoles





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



$Na^+(g) + 6\ H_2O(\ell) \longrightarrow [Na(H_2O)_6]^+\ (aq)$

$\Delta H_{rxn} = -405kJ$

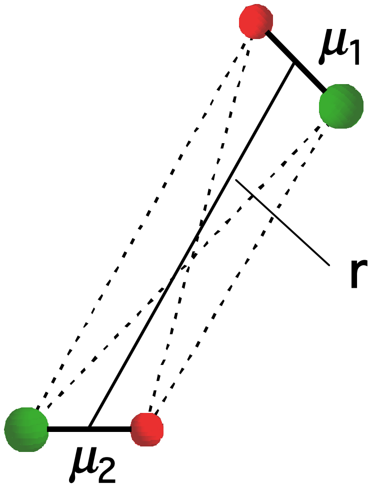
Dipole-Dipole Forces

Here, "both ends" of both dipoles interact with each other via Coulomb interactions.

$$E_{\text{dipole-dipole}} \propto -(\mu_{\text{dipole}})^2/r^3$$

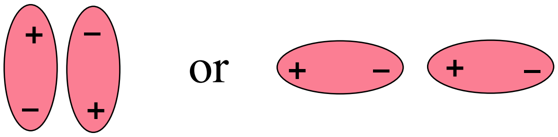
Weaker still, but still stronger than the case when molecules have no dipole moment:

$$E_{\text{dispersion}}(\text{gas}) \propto -\alpha_1{}^2\,\alpha_2{}^2/r^6$$



Dipole Forces

- In a collection of dipoles, oppositely charged ends of the dipoles will attract each other. Similarly charged ends will repel.
- These forces will cause dipoles to line up with one another and “stick together.”



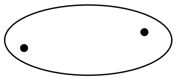
Dispersion Forces

- Non-polar molecules also form condensed phases. H_2 is a liquid below 20 K, and He is a liquid below 4.2 K (at 1 atm pressure)
- Forces?
- “Dispersion forces” due to <u>induced dipoles</u>
- Arise because electrons are not static
- Present in <u>all</u> molecules

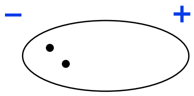
Transient Dipoles - H_2 example

- H_2 molecule: average e^- density is symmetric
- But at any given instant, the 2 e^-'s may both be on the same "end" of the molecule, creating a transient dipole.
- The transient dipole in one molecule will influence other molecules, so that the induced dipoles will "line up" just like "real" or permanent dipoles.

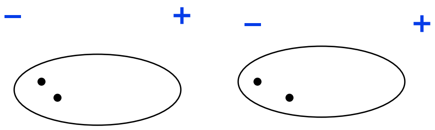
Transient Dipoles - H_2 example



H_2, one e^- on each end



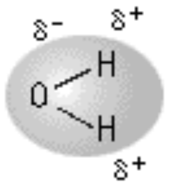
H_2, both e^-'s on same end, producing temporary dipole



Transient dipole sets up similar dipoles in nearby molecules, and molecules line up to maximize attractive forces.

“Induced” Dipoles

dipole—induced dipole



induced-dipole—induced dipole

Distance dependence of Intermolecular Potential energies

$V_{\text{Coulomb}}(r) \sim \frac{1}{r}$	Ionic bonds
$V_{\text{ion-dipole}}(r) \sim \frac{1}{r^2}$	Solvation of ions in solution
$V_{\text{dipole-dipole}}(r) \sim \frac{1}{r^3}$	Intermolecular forces in polar compounds
$V_{\text{dispersion}}(r) \sim \frac{1}{r^6}$	Intermolecular forces in non-polar compounds

Strength of Intermolecular Forces

- Strength of forces between molecules determines physical state (solid, liq., gas)
- Strength of dispersion forces increases as molecules become larger; **scale with the "surface area" of each molecule involved**

more e^-'s in larger, more "deformable" orbitals

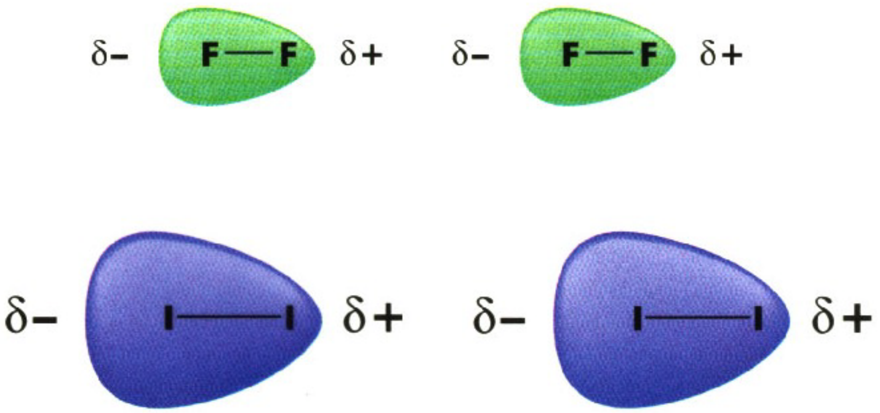
→ more "polarizable"

- Stronger intermolecular forces lead to higher melting & boiling points.

Comparison of alkane b.p.s

n-alkane	boiling points
CH_4	– 161.6 °C
CH_3CH_3	– 89 °C
$CH_3CH_2CH_3$	– 42.1 °C
$CH_3(CH_2)_2CH_3$	– 0.5 °C
$CH_3(CH_2)_3CH_3$	36.1 °C
$CH_3(CH_2)_4CH_3$	69 °C

F_2 vs. I_2: Polarizability Differences

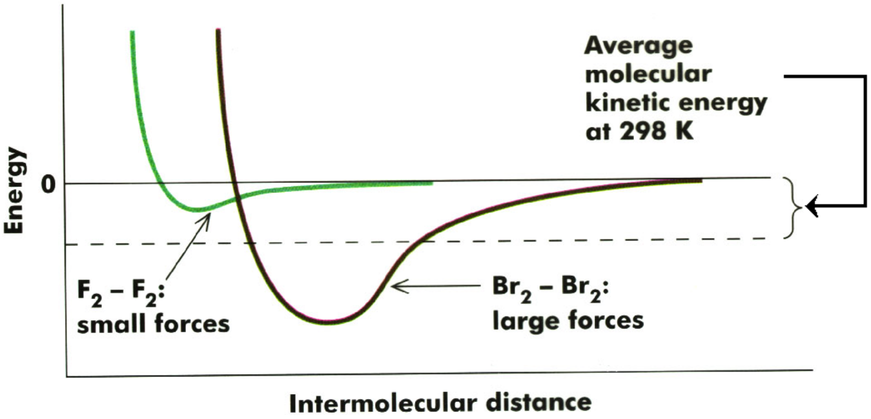


Intermolecular forces & physical state

V-d-W constants

F_2: $a = 1.154$ atm-L^2-mol^{-2} , $b = 0.02896$ L-mol^{-1}

Br_2: $a = 9.61$ atm-L^2-mol^{-2} , $b = 0.0591$ L-mol^{-1}



Comparison of Halogen b.p.s

	boiling points	
F_2	-188 ˚C	greenish gas
Cl_2	-34 ˚C	yellow-green gas
Br_2	59 ˚C	blood-red liquid
I_2	185 ˚C	purple solid

Iodine Sublimation

Strength of Intermolecular Forces

- Big, polarizable molecules tend to have high boiling points.
- Polar molecules tend to have higher boiling points than non-polar molecules with similar size & shape.

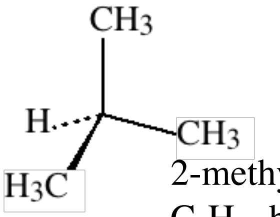
Polar Molecules

- Many molecules have a dipole moment due to polarity of bonds & shape of molecule
- The strength of intermolecular forces between polar molecules will be influenced by dipolar forces.
- Examples for dipole moments:

HF vs. BeF_2 vs. BF_3 vs. CH_2F_2 vs. CF_4

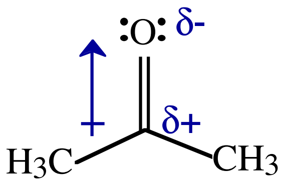
Dipole Moments (see Sec. 8.4)

- Both polarity of bonds and molecular shape (symmetry) are important
- Polar molecules tend to have higher boiling points than non-polar molecules with similar size & shape:



2-methylpropane

C_4H_{10} b.p. -12 ˚C

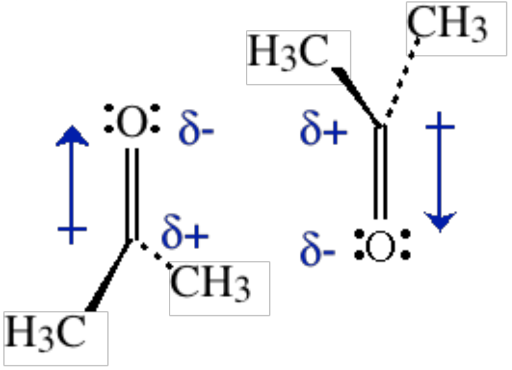


acetone

C_3H_6O b.p. 56 ˚C

Dipole-dipole interactions

- Dipole-dipole interactions hold polar molecules together more strongly than non-polar molecules with similar size & shape:



Effect of Molecular Shape & Symmetry

Which compound has the highest boiling point?

$CH_3{-}C{\equiv}N{:}$

acetonitrile

$\underset{\cdot\cdot}{\ddot{O}}{=}C{=}\underset{\cdot\cdot}{\ddot{O}}$

carbon dioxide

Effect of Molecular Shape & Symmetry

Which compound has the highest boiling point?

$CH_3{-}C{\equiv}N{:}$

acetonitrile

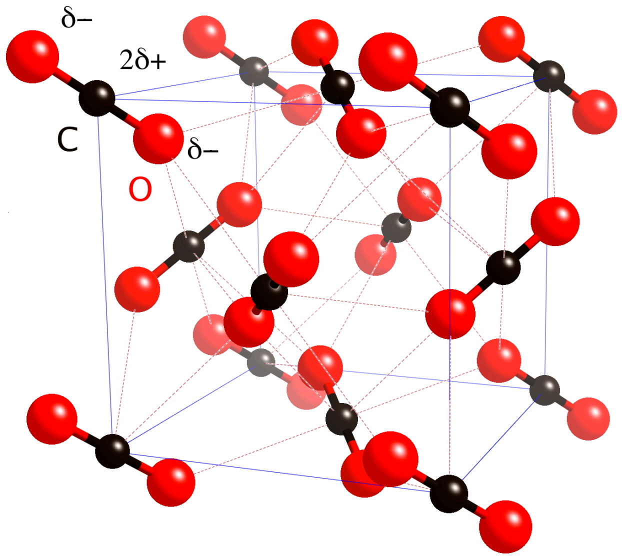
b.p. 82 ˚C

$\underset{\cdot\cdot}{\ddot{O}}{=}C{=}\underset{\cdot\cdot}{\ddot{O}}$

carbon dioxide

sublimes @ -78 ˚C
(no liquid at 1 atm.)

Solid CO_2 (dry ice)



$\chi(O) = 3.5$
$\chi(C) = 2.5$

Is carbon monoxide an exception?

Why does CO have such a low boiling point? It is little different from N_2.

$:C\equiv O:$	$:N\equiv N:$
b.p. –191.5 ˚C	b.p. –195.8 ˚C

$\chi(O) = 3.5$
$\chi(C) = 2.5$ CO dipole moment = 0.122 D
$\chi(H) = 2.2$ HCl dipole moment = 1.05 D
$\chi(Cl) = 3.2$ b.p. –85.1 ˚C

Hydrogen Bonding

- Special case of dipole-dipole interaction
- Occurs only in molecules containing H bound to a very electronegative atom (F, O, or N)
- Stronger than usual due to small size of H-atom (more concentrated positive charge)
- H “end” of one molecule is attracted to the electronegative “end” of another molecule

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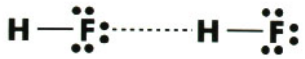
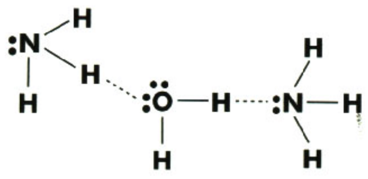
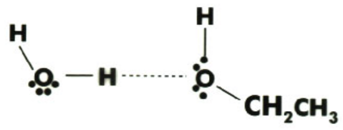
Examples of Hydrogen Bonds



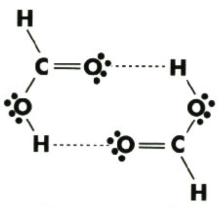
Hydrogen fluoride



Ammonia-water

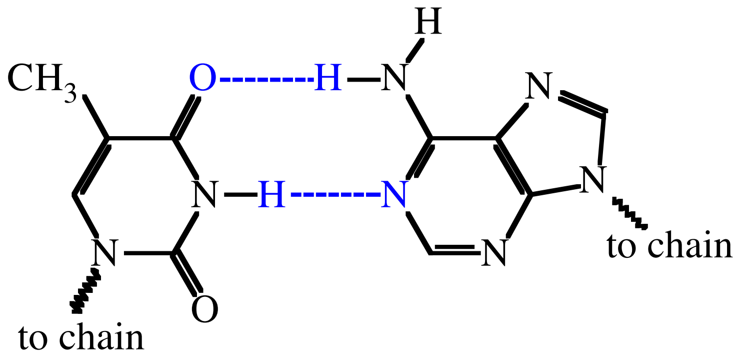


Water-ethanol



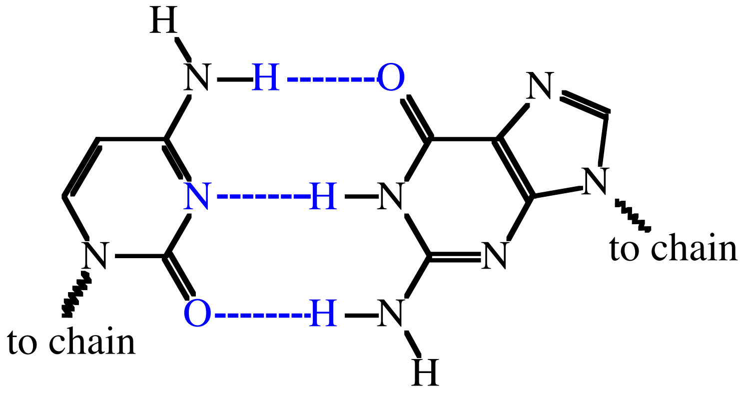
Formic acid

H-bonded “base pair” in DNA



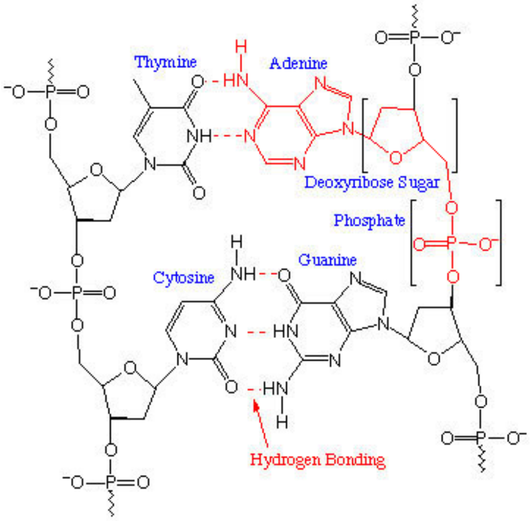
Thymine Adenine

Another DNA “base pair”

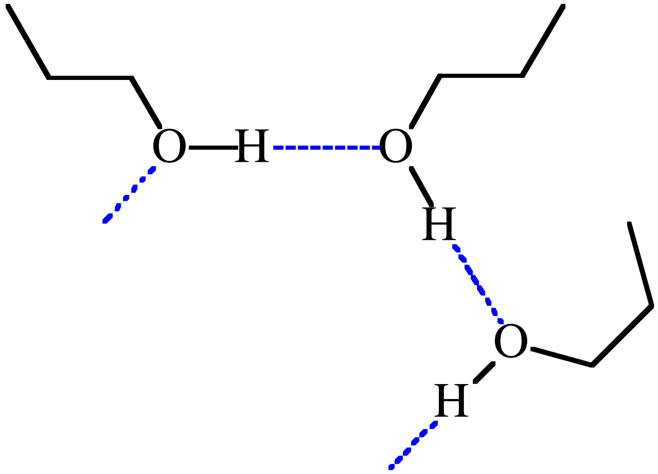


Cytosine Guanine

Schematic DNA Construction

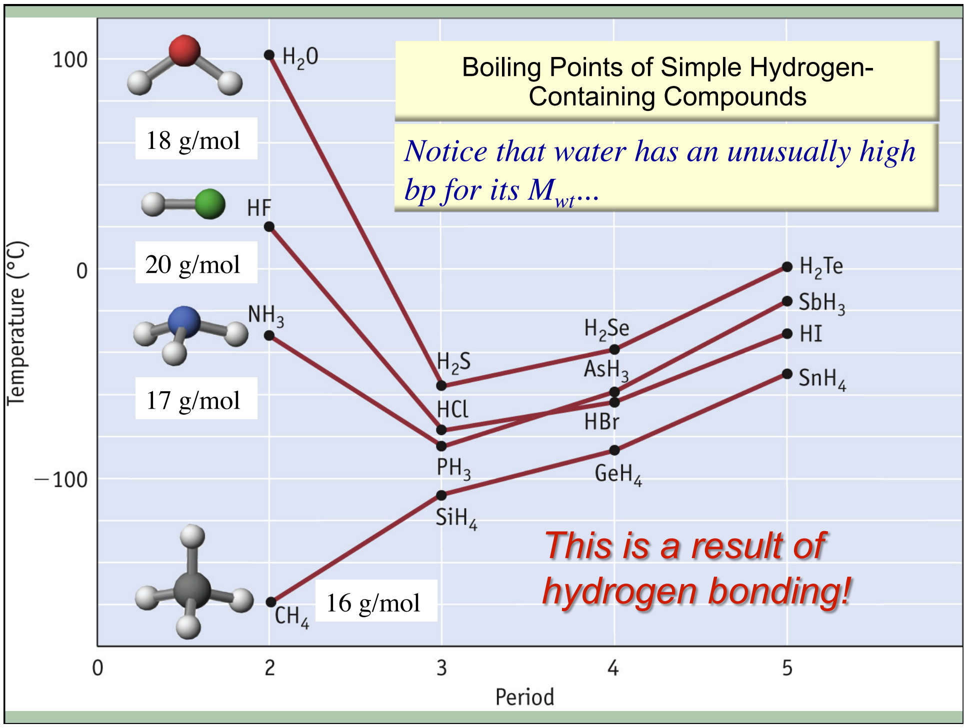


1-propanol; H-bonding



Hydrogen bonds and water

- H-bonds give water some special properties:
  - high melting & boiling points, essential for our existence
  - structure of ice is very "open" and very stable
  - density of water <u>increases</u> slightly on melting, so ice floats
- H-bonds also important in structure of bio-molecules like proteins, DNA, ...

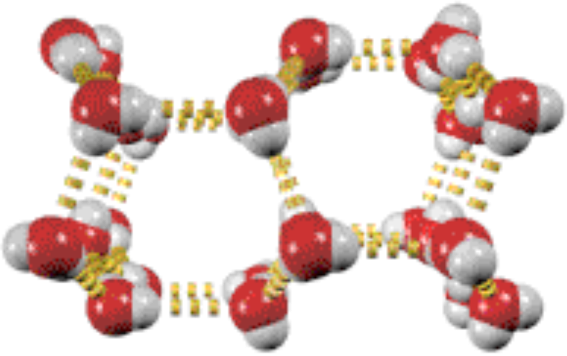


Boiling Points of Simple Hydrogen-Containing Compounds

Notice that water has an unusually high bp for its M_{wt}...

This is a result of hydrogen bonding!

Hydrogen bonding in Ice



Ice has a very "open" diamond-like structure. In liquid H_2O collapse occurs when a few H-bonds break. Liquid H_2O is therefore denser than ice.

Properties of Liquids

- Of the three states of matter, liquids are the most difficult to describe precisely.
- Under ideal conditions the molecules in a gas are far apart and are considered to be independent of one another.
- The structures of solids can be described easily because the particles that make up solids are usually in an orderly arrangement.
- The particles of a liquid interact with their neighbors, like the particles in a solid, but, unlike in solids, there is little long-range order.

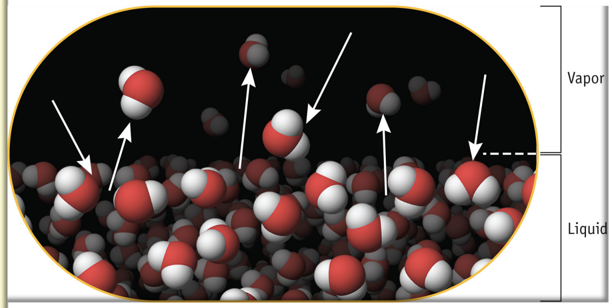
Properties of Liquids

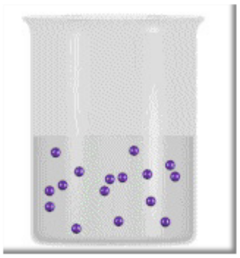
Liquids

- Particles are in constant motion.
- Particles are in close contact.
- Liquids are almost incompressible
- Liquids do not fill the container.
- ◆ Intermolecular forces are relevant.

Liquids: Vaporization

In order for a liquid to vaporize, sufficient energy must be available to overcome the intermolecular forces.





Breaking IM forces requires energy.

The process of vaporization is therefore endothermic.

Liquids: Enthalpy of Vaporization

The *HEAT OF VAPORIZATION* is the heat required to vaporize the liquid at constant P.

$$\Delta_{vap}H$$

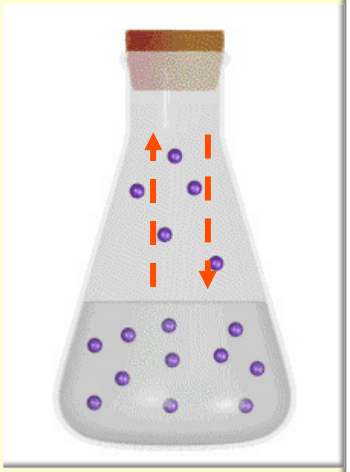
Liquid + energy = Vapor

Notice how the types of forces greatly affects the ΔH_{vap} and boiling point.

Compound	IMF	$\Delta_{vap}H$ (kJ/mol)	BP
H_2O	H-bonds	40.7	100 °C
SO_2	Dipole	26.8	– 47 °C
Xe	London	12.6	– 107 °C

Liquids: Enthalpy of Vaporization

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



The ***EQUILIBRIUM VAPOR PRESSURE*** is the pressure exerted by a vapor over a liquid in a closed container.

At equilibrium,

rate of evaporation = the rate of condensation.

Vapor Pressure

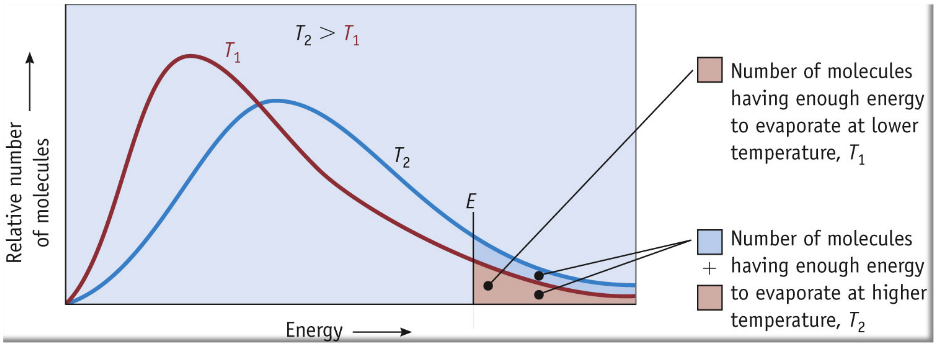
When molecules of liquid are in the vapor state, they exert a VAPOR PRESSURE

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.

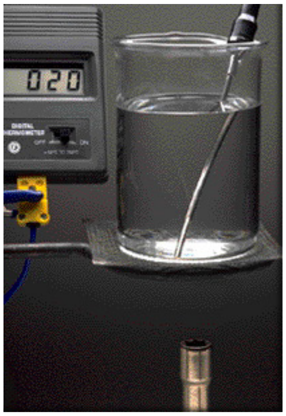
Vapor Pressure

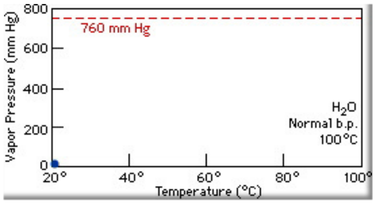
Recall from kinetic molecular theory…

As Temp increases, so does the average KE of the particles. This means that there are more particles that can escape into the gas phase!



Boiling Point





Liquid boil when $P_{vap} = P_{atm}$
(Vapor pressure equals
atmospheric pressure.

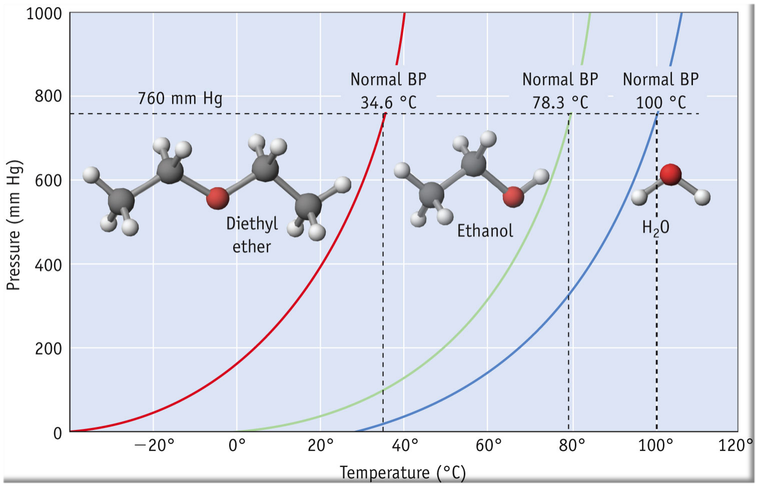
Boiling Point at Reduced Pressure

As the external pressure is lowered, the vapor pressure equals the external pressure at a lower temperature. Boiling therefore occurs at a reduced temperature.

Consequences of Vapor Pressure Changes

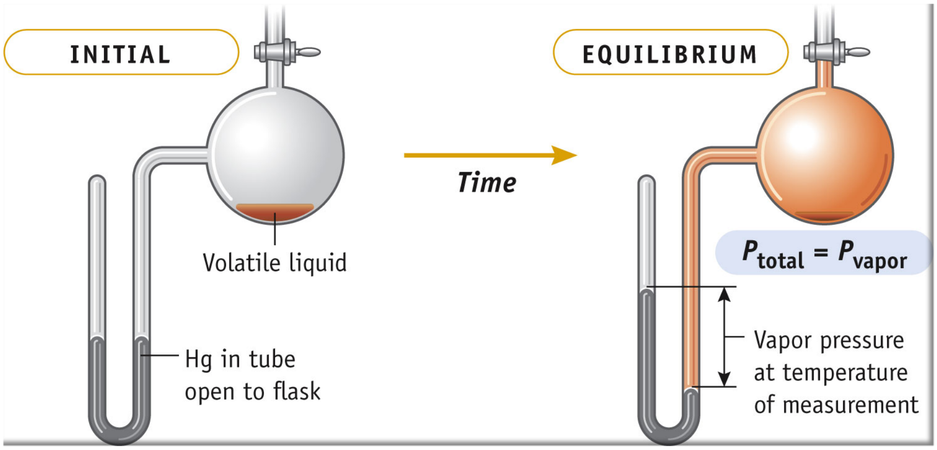
When can cools, vapor pressure of water drops. Pressure inside of the can is less than that of atmosphere, which collapses the can.

Equilibrium Vapor Pressure



The vapor pressure of a liquid is seen to increase exponentially with temperature.

Measuring Equilibrium Vapor Pressure



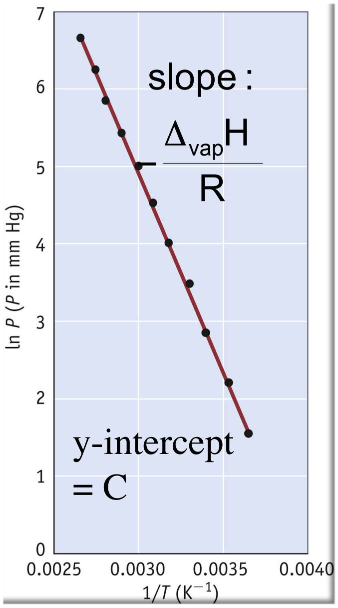
Liquid in flask evaporates and exerts pressure on manometer.

Temperature Dependence of Vapor Pressure

$$\ln P_{vap} = -\frac{\Delta_{vap}H^\circ}{RT} + C$$

A plot of $\ln P_{vap}$ vs. $\frac{1}{T}$ yields a slope of:

$\Delta_{vap}H^\circ$ is related to T and P by the *Clausius-Clapeyron* equation



Rather than plot the data, it is convenient to arrange the equation in terms of two temperatures:

$$\ln P_{vap} = -\frac{\Delta_{vap}H^\circ}{RT} + C$$

$$\underbrace{\ln P(T_2) - \ln P(T_1)}_{} = -\frac{\Delta_{vap}H^\circ}{RT_2} + \cancel{C} - \left[-\frac{\Delta_{vap}H^\circ}{RT_1} + \cancel{C}\right]$$

$$\ln\left(\frac{P(T_2)}{P(T_1)}\right) = -\frac{\Delta_{vap}H^\circ}{RT_2} + \frac{\Delta_{vap}H^\circ}{RT_1}$$

$$\ln\left(\frac{P(T_2)}{P(T_1)}\right) = \frac{\Delta_{vap}H^\circ}{R} \times \left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

Where P = vapor pressure, T = temp (K)

$$R = 8.314 \frac{J}{mol \cdot K}$$

Problem:

Determine the vapor pressure of water at 50.0 °C given that the ΔH_{vap} = 40.7 kJ/mol and the vapor pressure at 20.0 °C is 17.54 torr.

$$\ln\left(\frac{P(T_2)}{P(T_1)}\right) = \frac{\Delta_{vap}H^\circ}{R} \times \left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

solving:

$$\left(\frac{P(T_2)}{P(T_1)}\right) = \exp\left[\frac{\Delta_{vap}H^\circ}{R} \times \left[\frac{1}{T_1} - \frac{1}{T_2}\right]\right]$$

$$P(T_2) = P(T_1) \times \exp\left[\frac{\Delta_{vap}H^\circ}{R} \times \left[\frac{1}{T_1} - \frac{1}{T_2}\right]\right]$$

Problem:

Determine the vapor pressure of water at 50.0 °C given that the ΔH_{vap} = 40.7 kJ/mol and the vapor pressure at 20.0 °C is 17.54 torr.

$$P(T_2) = P(T_1) \times \exp\left(\frac{\Delta_{vap}H^\circ}{R} \times \left[\frac{1}{T_1} - \frac{1}{T_2}\right]\right)$$

$$P(50.0\ ^\circ\mathrm{C}) = 17.54\ \mathrm{torr} \times \exp\left(\frac{40.7\frac{\cancel{\mathrm{kJ}}}{\cancel{\mathrm{mol}}} \times \frac{10^3\cancel{\mathrm{J}}}{\cancel{1\mathrm{kJ}}}}{8.341\frac{\cancel{\mathrm{J}}}{\cancel{\mathrm{mol}}\cdot\cancel{\mathrm{K}}}} \times \left[\frac{1}{293.15\cancel{\mathrm{K}}} - \frac{1}{323.15\cancel{\mathrm{K}}}\right]\right)$$

$$= 82.7\ \mathrm{Torr}$$

Liquids: IMF's Summary

Molecules in the Liquid State	**$\Delta_{vap}H$**	**Volatility**	**Equilibrium Vapor Pressure**	**Boiling Point**
Strong IMF's	**More Endothermic**	**Low**	**Low**	**High**
Weak IMF's	**Less Endothermic**	**High**	**High**	**Low**