Intermolecular Forces and Phase Equilibria

Chemistry 36

Spring 2002

Intermolecular Forces

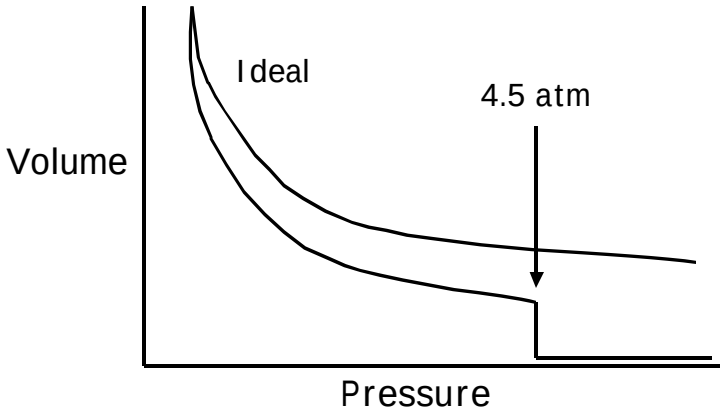
- What happens to gas phase molecules when subjected to *increased pressure?*
  - Volume occupied by gas *decreases (IGL)*
  - At higher pressures: get *negative deviations from IGL*
    - due to intermolecular attraction (*Van deWaals Equation*)
  - At a high enough pressure:

ABRUPT decrease (100x or more) in volume

Phase Transition: *Gas* ® **Liquid**

-due to *intermolecular attractive forces*

Example: 1 mol SO_2 @ 30°C



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Intermolecular Forces

- All based on *electrostatic* attraction, but not strong enough to be considered a **chemical bond**
- Recall: **Ionic Bonds**

  -electrostatic attraction between two ions:

  Na^+ Cl^-

  Bond strength varies with: -charge on ions
  -distance (r) separating ions

  -force varies with $1/r^2$

  -bond *energy* (force acting over a distance r) then varies with ***1/r***

  -ionic bond energies: very large (300 - 600 kJ/mol)

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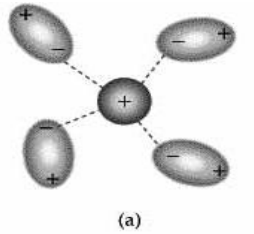
Ion-Dipole Interactions

- Ions can have electrostatic interactions with *polar molecules:*

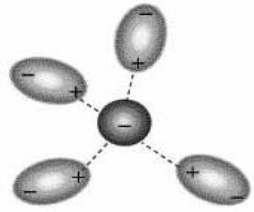
-both *attractive* and **repulsive** forces

-**lower energy interaction**
(10 - 20 kJ/mol)

-energy drops off as ***1/r²***



(a)



(b)

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Dipole-Dipole Interactions

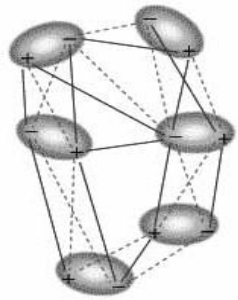
- Polar molecules can have *electrostatic interactions* with <u>*other*</u> polar molecules:

-both *attractive* and **repulsive** forces

-even **lower energy interaction**
(1 - 5 kJ/mol)

-energy drops off as ***1/r³***

(a)



Attraction ——
Repulsion - - - - - -

(b)

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Hydrogen Bonding

- **<u>Hydrogen is unusual</u>: its *only* electron is its *valence electron***

  -if bound to a *very electronegative* element, the unshielded hydrogen nucleus has a significant positive charge

  -the hydrogen is, thus, attracted to the *lone pair electrons* on the *very electronegative* atom <u>of an adjacent molecule</u>

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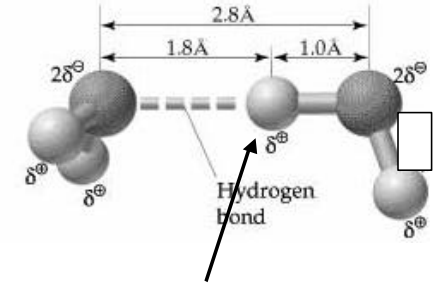
H-bonding in Water

- Hydrogen bonding in water is very significant
- Without H-bonding, we would expect water to have a B.P. of about -123 ^{o}C



Hydrogen acts as a *bridge* to facilitate electron-sharing between the oxygen atoms on adjacent molecules

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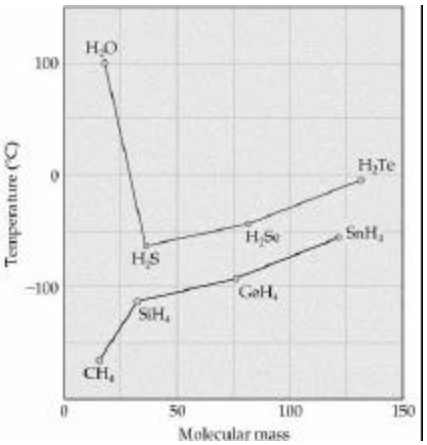
Hydride Boiling Points

- **Hydrogen bonding results in anomolous behavior:**

  -unusually high B.P. for water

  -same effect observed with other 2nd Period hydrides:

  - $T_b(HF) > T_b(HCl)$
  - $T_b(NH_3) > T_b(PH_3)$



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More Hydrogen Bonding

- **Only occurs with Group 5, 6 and 7 hydrides**

  -get biggest dipole if the atom is both *very electronegative* as well as ***small***

  -so, **N and O and F** hydrides experience this unusually strong *dipole-dipole* interaction

- **Hydrogen "bonds" are the *strongest* intermolecular interaction**

  - typically: 20 - 40 kJ/mol

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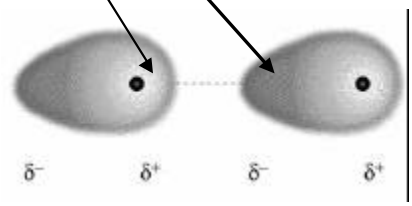
The London Dispersion Force

- How, can there be *intermolecular attraction* between **nonpolar molecules?**
  - nonpolar species (including ALL atoms) can have an *instantaneous* or *momentary* dipole
  - This can then *induce* a dipole on an adjacent species, resulting in an *electrostatic interaction:*



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London Dispersion Forces

- These are usually very weak interactions
  (0.05 - 2 kJ/mol)
- Energy drops off as ***1/r⁶***
- ALL atoms and molecules will experience *London Dispersion Forces*
- **Magnitude** of force will depend upon how easy it is to distort the electron cloud (*polarize):*

  - favors atoms and molecules that are **LARGE** and have the **greatest surface area**

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Boiling Point Trends

- The enthalpy change associated with vaporization is due to the ***disruption*** of these intermolecular forces
- The magnitude of ΔH^{o}_{vap} is reflected in the *boiling point temperature* (T_b) for a compound
- For *polar* molecules:

Substance	Molecular Weight (amu)	Dipole Moment, μ (D)	Boiling Point (K)
Propane, $CH_3CH_2CH_3$	44	0.1	231
Dimethyl ether, CH_3OCH_3	46	1.3	248
Methyl chloride, CH_3Cl	50	1.9	249
Acetaldehyde, CH_3CHO	44	2.7	294
Acetonitrile, CH_3CN	41	3.9	355

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More BP Trends

- For **NONPOLAR** species:

Halogen	Molecular Weight (amu)	Boiling Point (K)	Noble Gas	Molecular Weight (amu)	Boiling Point (K)
F_2	38.0	85.1	He	4.0	4.6
Cl_2	71.0	238.6	Ne	20.2	27.3
Br_2	159.8	332.0	Ar	39.9	87.5
I_2	253.8	457.6	Kr	83.8	120.9
			Xe	131.3	166.1

increased molar mass = *greater polarizability*

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Vapor Pressure

- If we put a liquid in a container (and $V_{container} > V_{liquid}$ and $T < T_b$): ***some of the liquid will vaporize***

Why?

- If molecules on the *surface* have sufficient Kinetic Energy, they can overcome intermolecular attraction and escape to the gas phase
- The **reverse** process can happen too!
- Process reaches a *steady state condition* (equilibrium):

$$X(l) \quad X(g)$$

amt in gas phase = ***vapor pressure***

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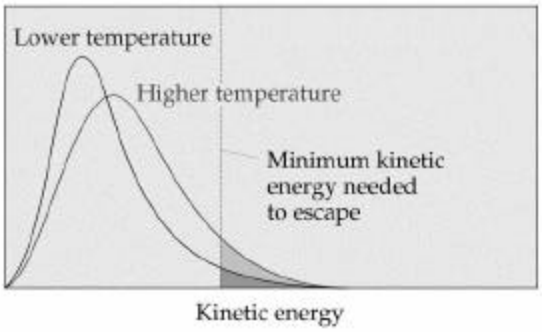
Vapor Pressure is Temperature Dependent

- Fraction of molecules with sufficient K.E. to escape surface *increases with temperature:*



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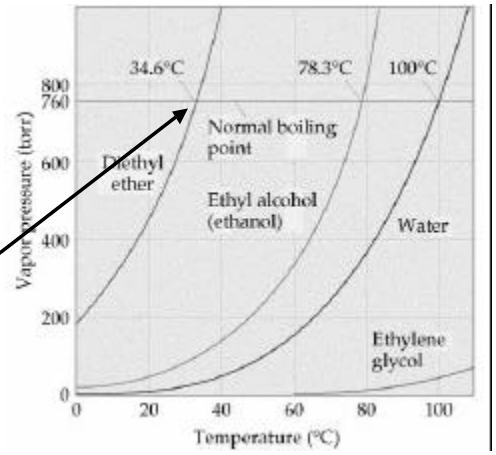
Temp Dependence of VP

- We define the ***boiling point*** as the *temperature at which:*

$$VP = P_{ext}$$

- At P_{ext} = 1 atm, this is called the ***Normal BP***



Clausius-Clapeyron Equation

- The relationship between VP and temperature can be quantified by the equation:

$$\ln P = (-\Delta H_{vap}/RT) + C$$

- Thus, a plot of *Ln P versus 1/T* will be a straight line with a <u>slope = $-\Delta H_{vap}/R$</u>

  -convenient way to: determine value of ΔH_{vap}
  determine VP at any temp T