# Intermolecular Forces

Chemistry 35

Fall 2000

## 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*

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# Electrostatic Attraction

- 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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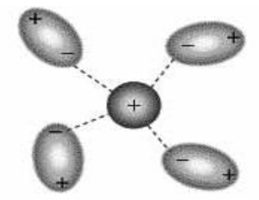
# Ion-Dipole Interactions

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

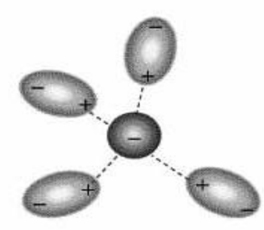


(a)

Both *attractive* and **repulsive** forces are operative here

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

-energy drops off as ***1/r²***



(b)

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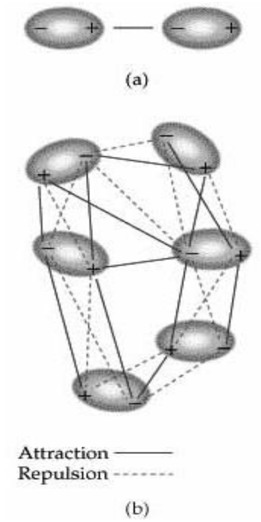
# Dipole-Dipole Interactions

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

Again, both *attractive* and **repulsive** forces are operative here

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

-energy drops off as $\boldsymbol{1/r^3}$

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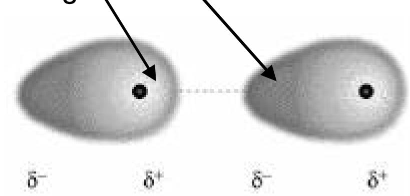
# London Dispersion Force

- How, then, 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 of as ***$1/r^6$***
- 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 $\Delta H^o_{vap}$ is reflected in the *boiling point temperature* ($T_b$) for a compound
- For *polar* molecules:

| Substance | Molecular Weight (amu) | Dipole Moment, M (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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# Hydride Boiling Points

- Something strange in the B.P. of some hydrides:

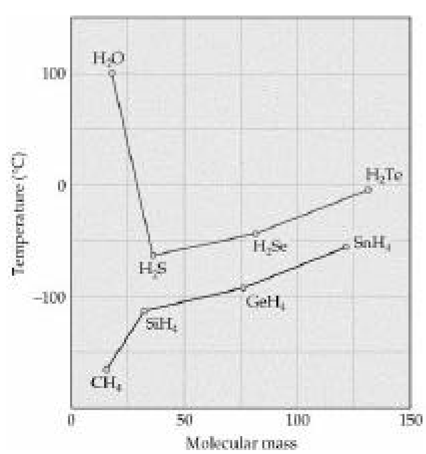
  -unusually high B.P. for water

  -same effect observed with other 2nd Period hydrides:

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

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

**What's going on here?**

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## Hydrogen Bonding

- Why is there an unusually strong intermolecular attraction between 2nd Period hydrides?
  - Hydrogen is unusual: its *only* electron is its *valence electron*

    -so, 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 of an adjacent molecule

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## More Hydrogen Bonding

- Why only with Group 5, 6 and 7 hydrides?

  -the most significant dipole will occur 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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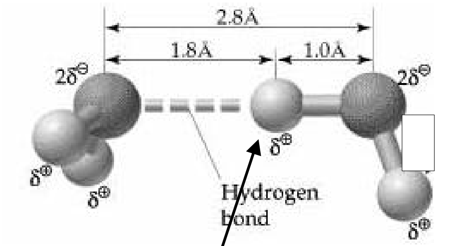
# H-bonding in Water

- 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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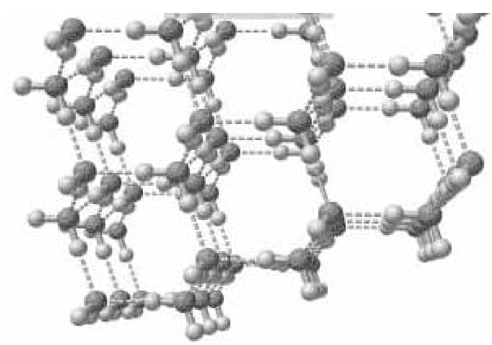
# Structure of Water

- Each oxygen can accommodate interactions with *four* hydrogen atoms (2 bonding, 2 H-bonding)

  -gives a *hexagonal structure* in solid phase

  -more open space than liquid phase, so solid water is *less dense* than liquid water



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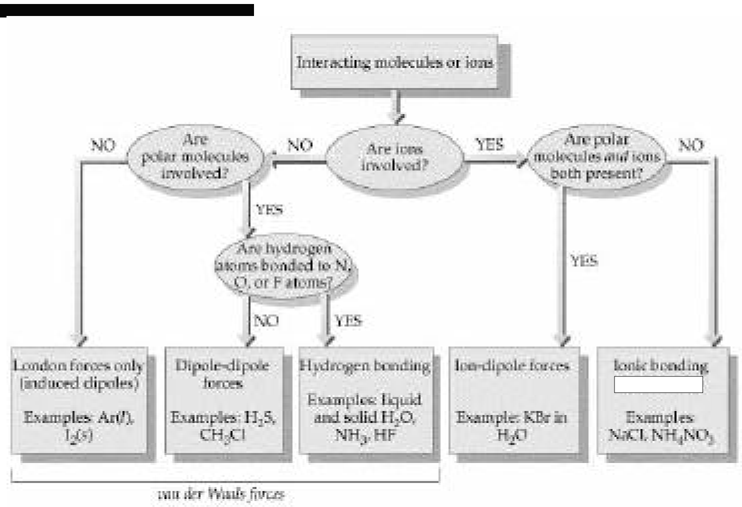
# Overview of IM-Forces

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# Some Properties of Liquids

- **Viscosity**

  -characterizes a liquid's *resistance to flow*

  -varies with the degree of intermolecular attraction

- **Surface Tension**

  -molecules on the surface of a bulk liquid experience intermolecular attraction *only* from molecules in the *bulk solution* below the surface

  -so, *surface molecules* are more **tightly packed** than molecules in the bulk solution

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# Adhesive and Cohesive Forces

- Attraction of molecules to a *surface* is due to *adhesive forces*
- Attraction of molecules to *each other* is due to *cohesive forces*
- **Examples:**

-*Meniscus:* adhesive > cohesive (water)
cohesive > adhesive (mercury)

-*Capillary Action:* In a small-diameter tube, the *adhesive force* is sufficient to *increase the surface area of the liquid,* drawing the bulk liquid up into the tube.

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