Lecture: P1_Wk1_L2

Electric Dipoles

Ron Reifenberger

Birck Nanotechnology Center

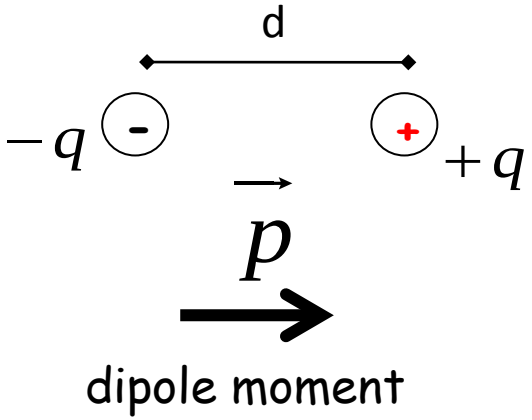
Purdue University

2012

PURDUE UNIVERSITY

In the last lecture, we saw that some molecules, even though electrically neutral, can develop dipole moments.

Two Point Charges of Equal Magnitude, Opposite Polarity
- a permanent electric dipole -



$$\vec{p} = q\vec{d}$$

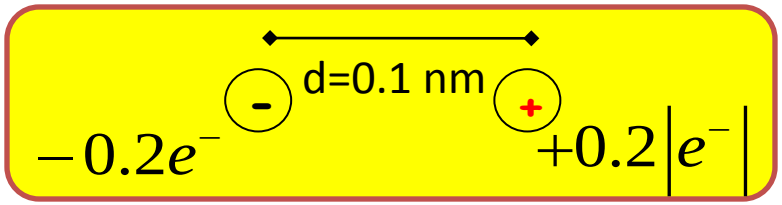
$$\left|\vec{p}\right| = qd$$

Historically the standard unit of a dipole moment was defined by two charges of opposite polarity but with equal magnitude of 10^{-10} statCoulomb (also called an e.s.u. of charge - the electrostatic unit, in older literature), separated by 1 Angstrom = 1.0×10^{-8} cm.

This gives the following unit for molecular dipole moments:

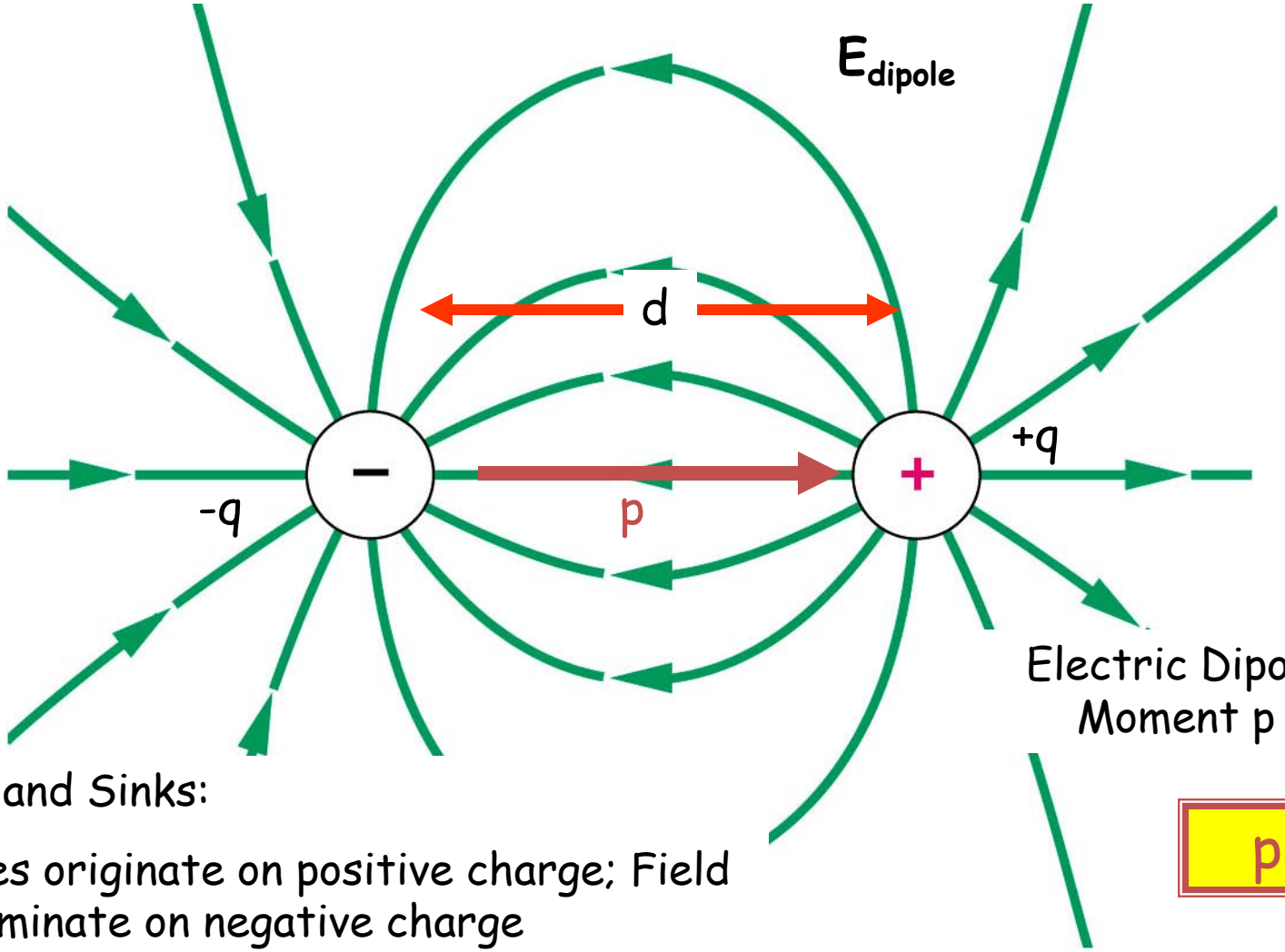
1 Debye $\equiv q\cdot d = (1\times10^{-10}\ \text{statC})(1\times10^{-8}\ \text{cm})(3.33564\times10^{-10}\ \text{C/statC})$

$= 3.33\times10^{-28}\ \text{C}\cdot\text{cm} = 3.33\times10^{-30}\ \text{C}\cdot\text{m}$ (about $0.2e^-$ displaced by 0.1 nm)



$$\left|\vec{p}\right| \simeq 1.0\ D$$

Electric Field Lines Produced by Two Point Charges of Equal Magnitude but Opposite Polarity

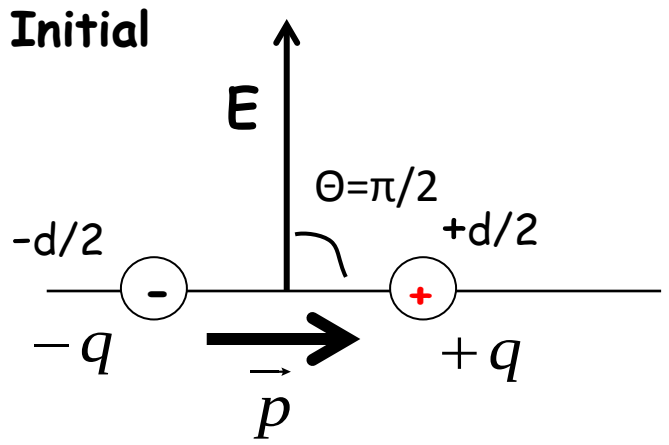


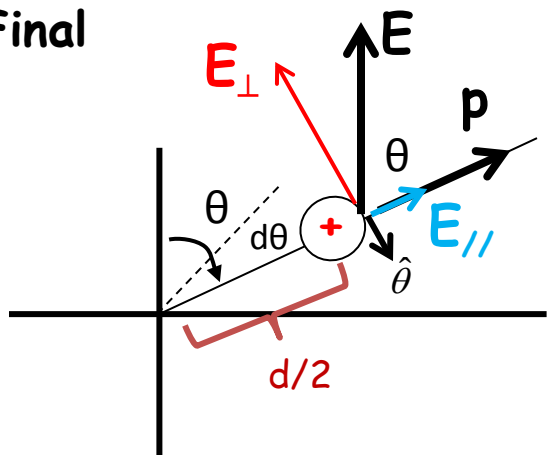
Sources and Sinks:

Field lines originate on positive charge; Field lines terminate on negative charge

$p=qd$

The electrostatic potential energy of a permanent electric dipole in an external electric field





Work to rotate dipole to angle Θ:

$$dW_+ = \vec{F}\cdot d\vec{\ell} = (-qE_\perp)\left(\frac{d}{2}d\theta\right); \quad E_\perp = E\sin\theta$$

$$= -(qE\sin\theta)\frac{d}{2}d\theta$$

$$W_+ = -\frac{1}{2}qdE\int_{\pi/2}^{\theta}\sin\theta\,d\theta = \frac{1}{2}qdE\left[\cos\theta\right]\Big|_{\pi/2}^{\theta}$$

$$= \frac{1}{2}pE\cos\theta$$

Similarly, for the negative charge:

$$W_- = \frac{1}{2}pE\cos\theta$$

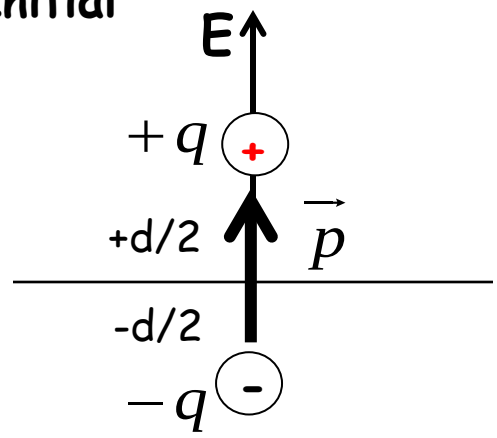
Finally,

$$W_{total} = pE\cos\theta$$

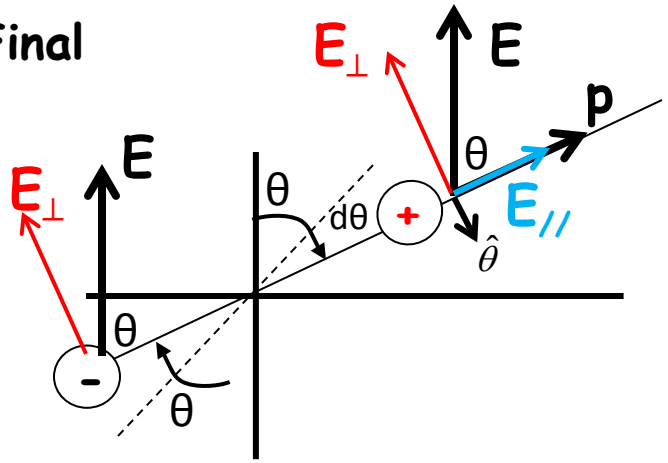
$$U(\theta) \equiv -W_{total} = -pE\cos\theta = -\vec{p}\cdot\vec{E}$$

Beware: the formula derived depends on initial orientation of dipole and the definition of the angle. Consider

Initial



Final



Work to rotate dipole to angle θ:

$$dW_+ = \vec{F}\cdot d\vec{\ell} = (-qE_\perp)\left(\frac{d}{2}d\theta\right); \quad E_\perp = E\sin\theta$$

$$= -(qE\sin\theta)\frac{d}{2}d\theta$$

$$W_+(\theta) = -\frac{1}{2}qdE\int_0^\theta \sin\theta\, d\theta = \frac{1}{2}qdE\left[\cos\theta\right]\Big|_0^\theta$$

$$= \frac{1}{2}qdE\left[\cos\theta - 1\right]$$

$$dW_- = \vec{F}\cdot d\vec{\ell} = (-qE_\perp)\left(\frac{d}{2}d\theta\right); \quad E_\perp = E\sin\theta$$

$$W_- = -\frac{1}{2}qdE\int_0^\theta \sin\theta\, d\theta = \frac{1}{2}qdE\left[\cos\theta\right]\Big|_0^\theta$$

$$= \frac{1}{2}qdE\left[\cos\theta - 1\right]$$

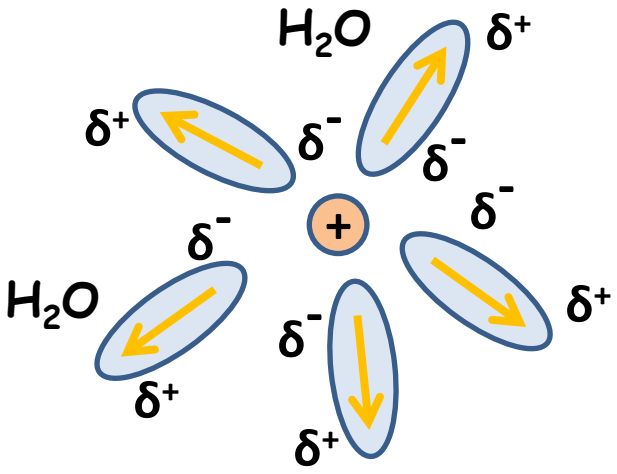
$$W_{total} = qdE\left[\cos\theta - 1\right]$$

$$U(\theta) = -W_{total} = -qdE\left[\cos\theta - 1\right]$$

$$= constant - \vec{p}\cdot\vec{E}$$

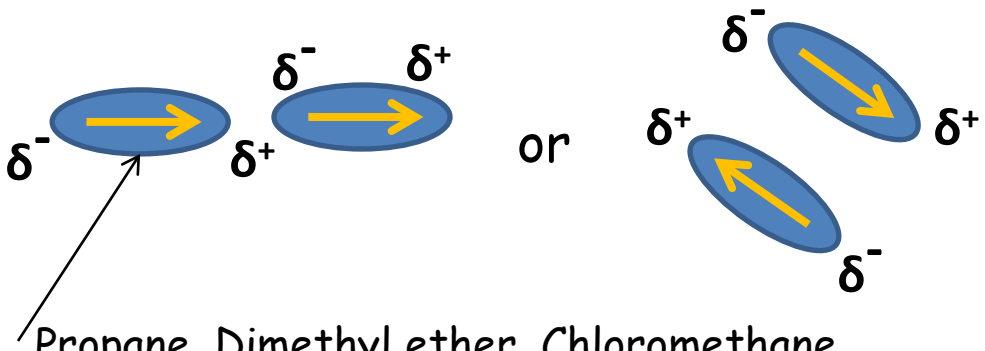
Physical Effects Produced by Interactions Mediated by (di)Polar Molecules

ion-dipole interaction:

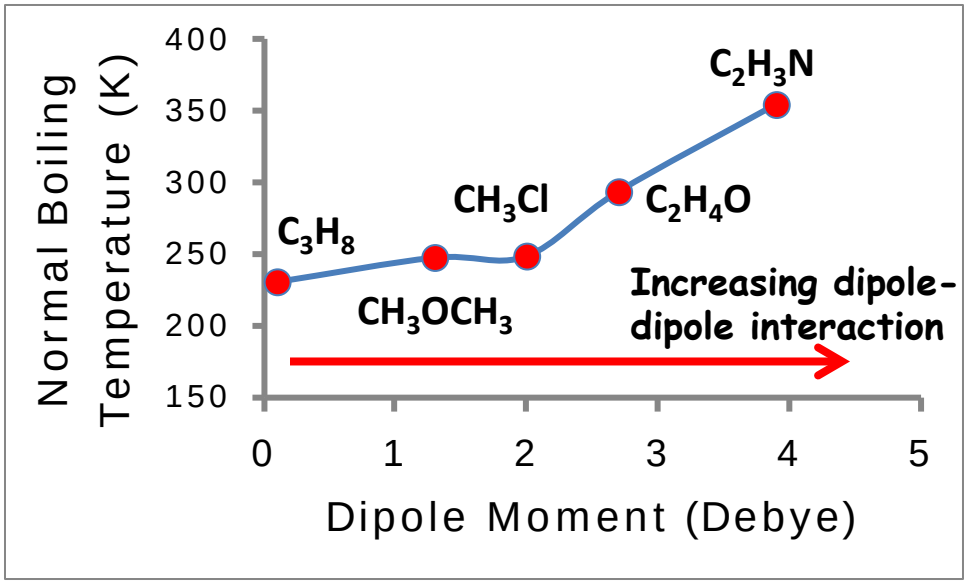


NaCl melts at 1074 K (800°C), yet NaCl readily dissolves at room temperature in a polar solvent like H_2O.

dipole-dipole interaction:



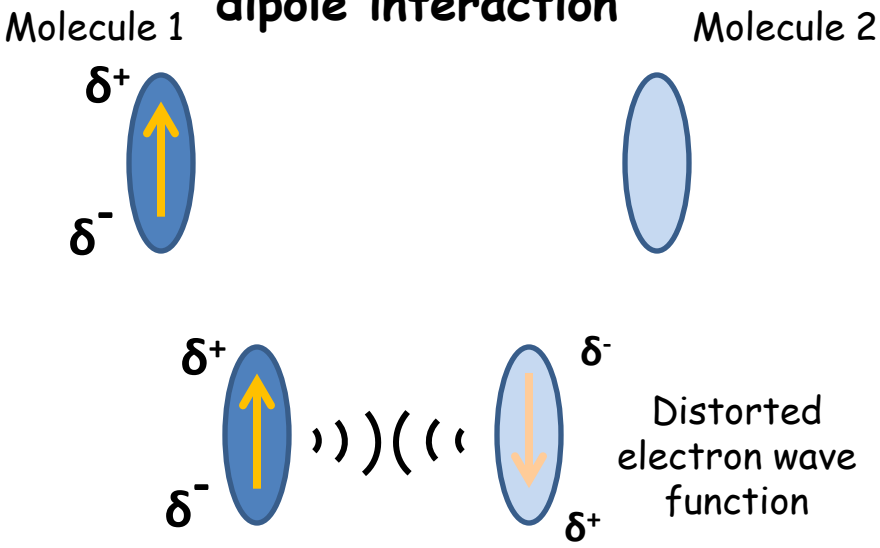
Propane, Dimethyl ether, Chloromethane, Actealdehyde, Acetonitrile



Interactions Involving Nonpolar Molecules

- inductive forces -

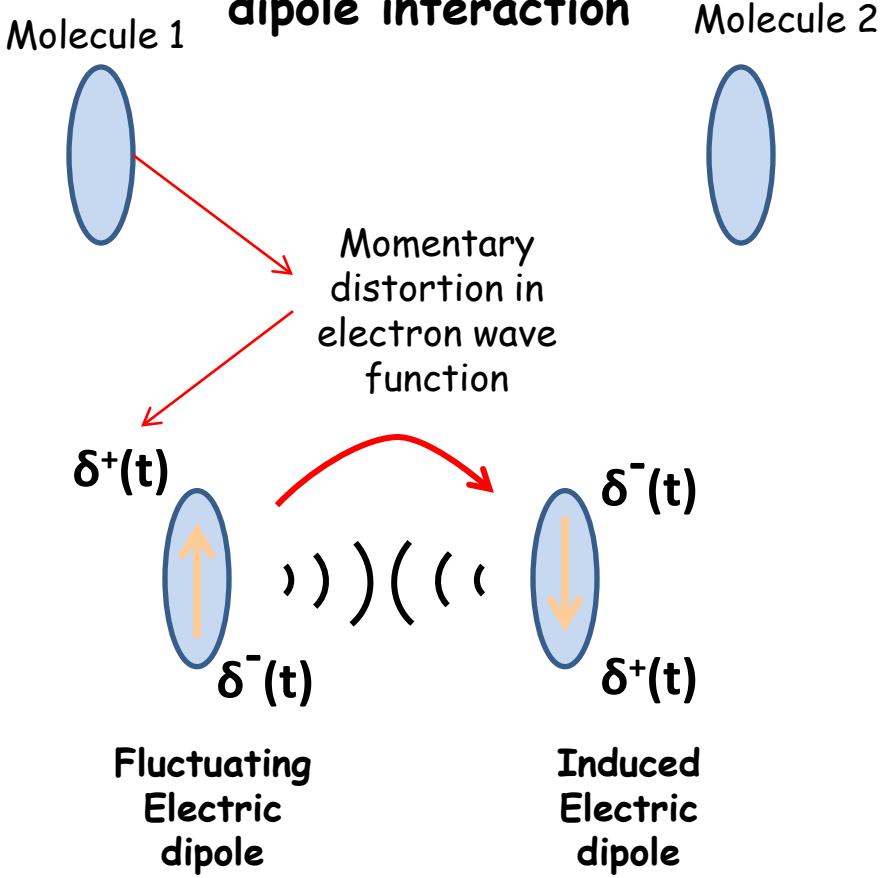
dipole/induced dipole interaction



Polarization

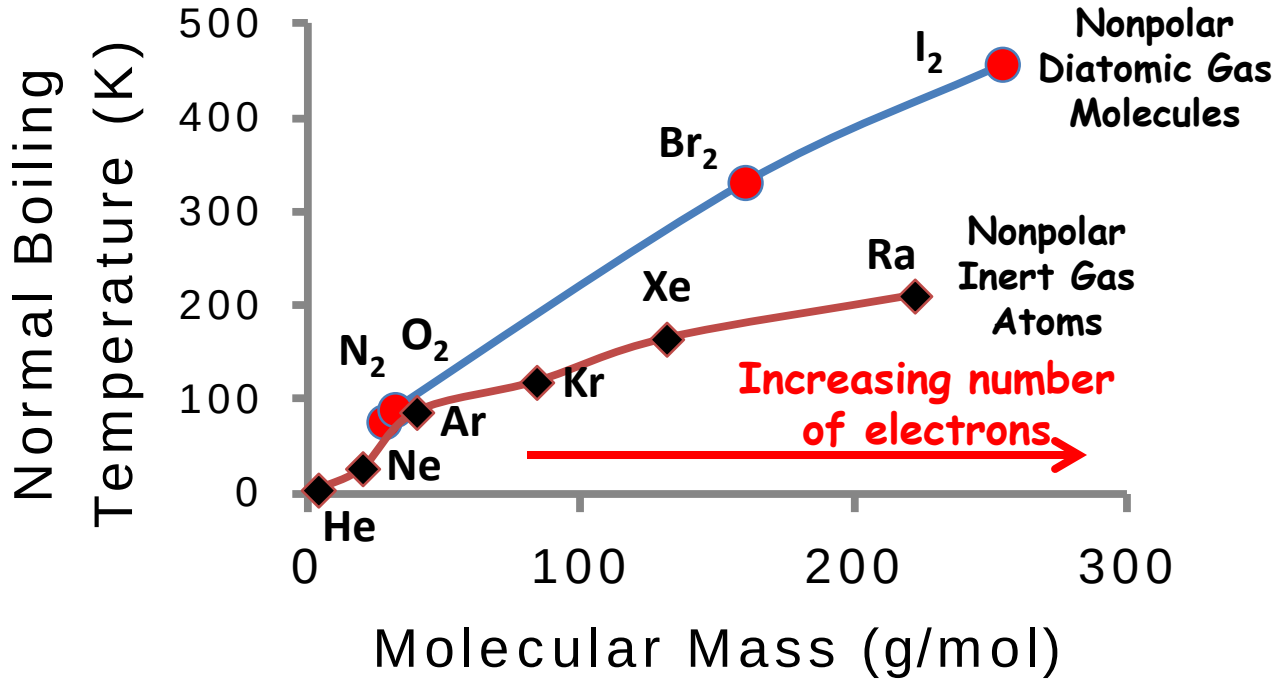
The polarizability of a nonpolar molecule scales roughly with the number of electrons in the molecule.

induced dipole/induced dipole interaction



A correlation between electron motion in each molecule leads to a lower energy state which is weakly bonded. Known as the London dispersion force.

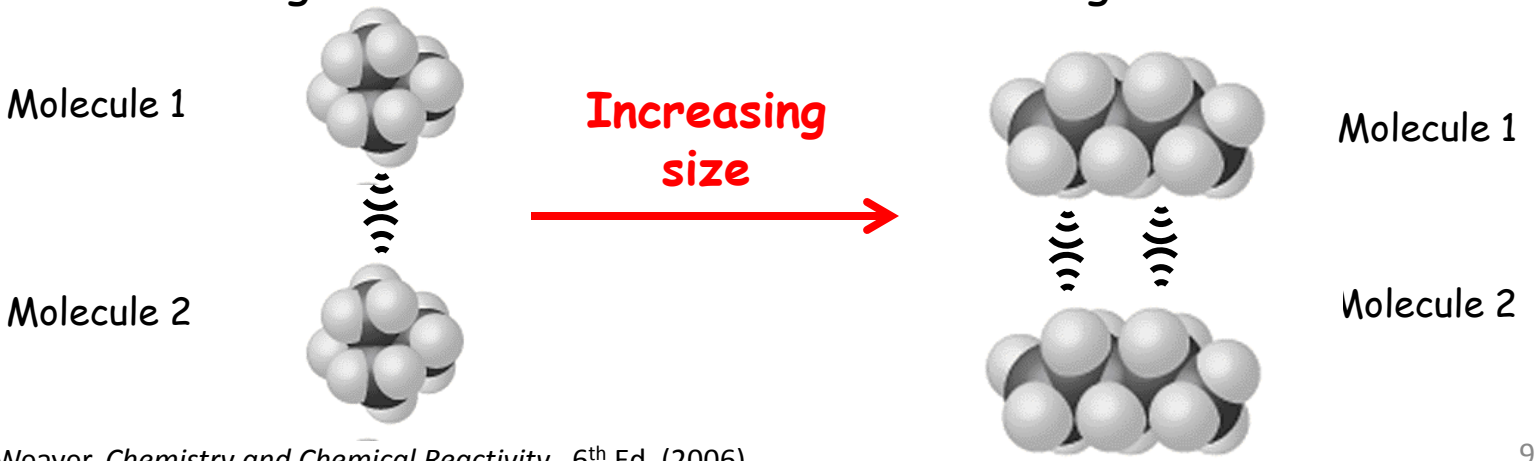
Ex. 1:



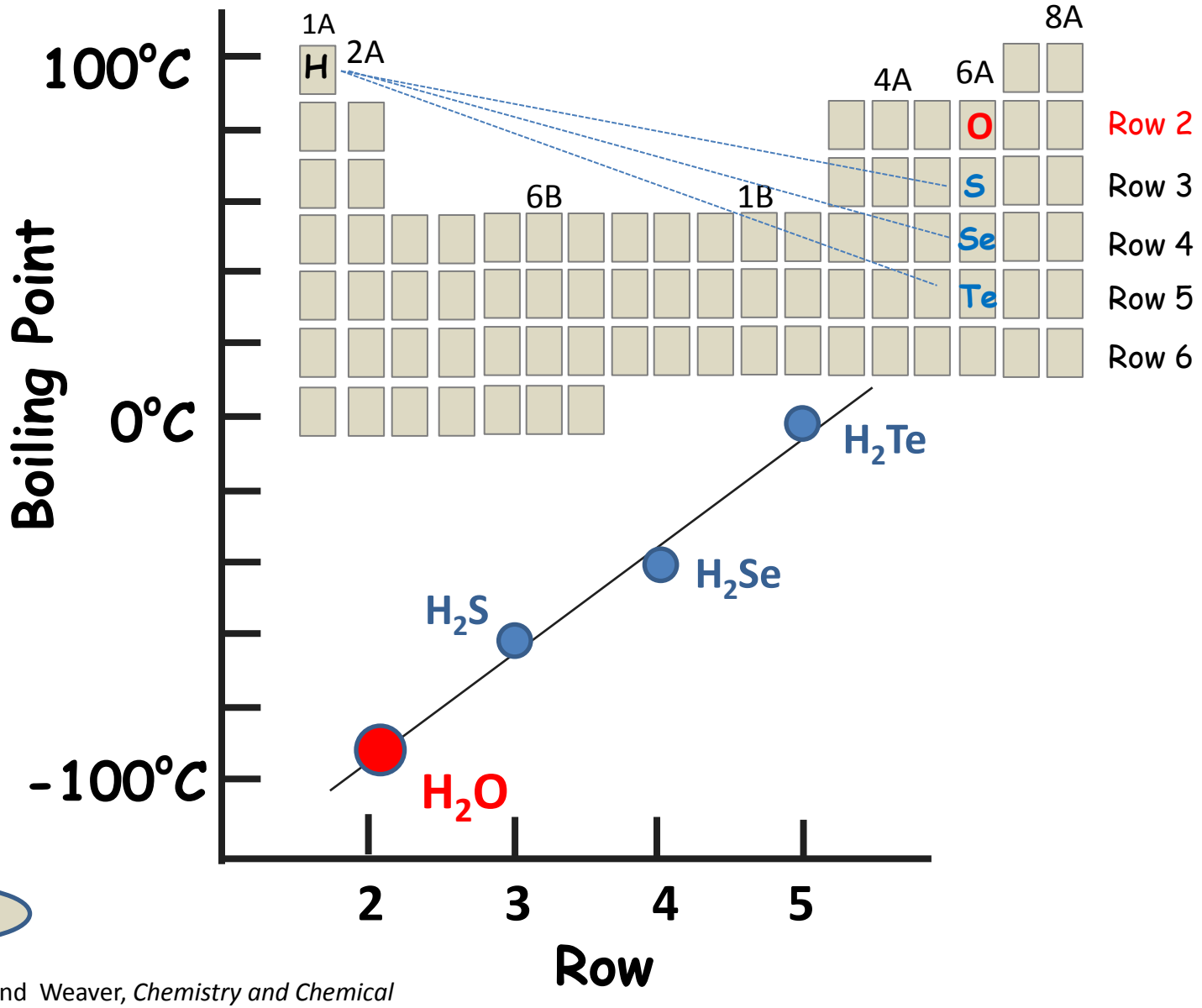
Ex. 2:

neopentane: C_5H_{12}
Boiling Point: **283 K**

N-pentane: C_5H_{12}
Boiling Point: **309 K**



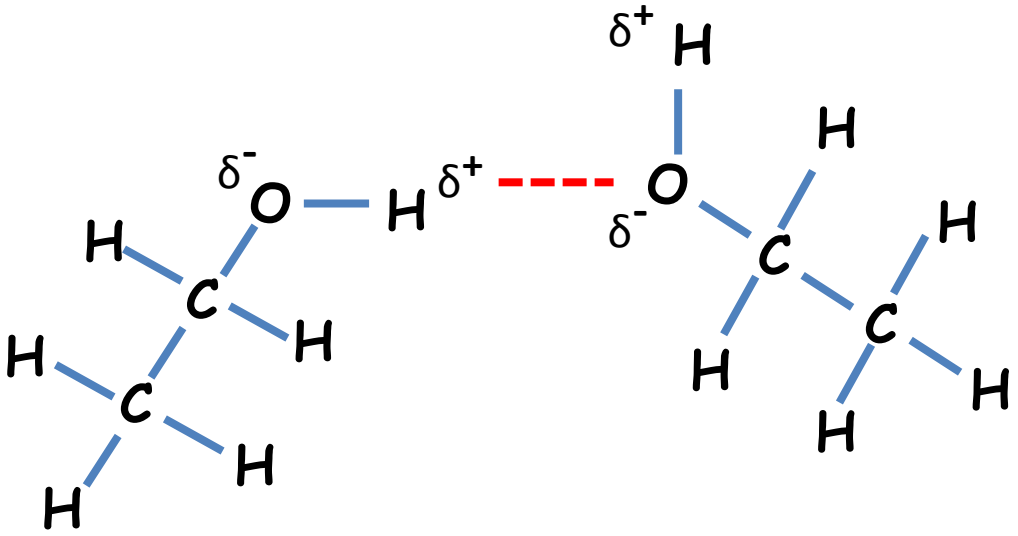
H bonded to O: An Anomaly



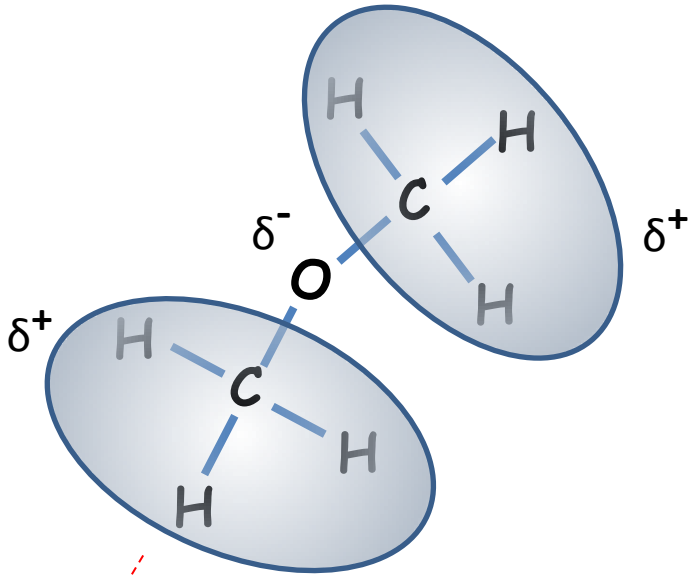
one click

Kotz, Treichel and Weaver, *Chemistry and Chemical Reactivity*, 6th Ed. (2006).

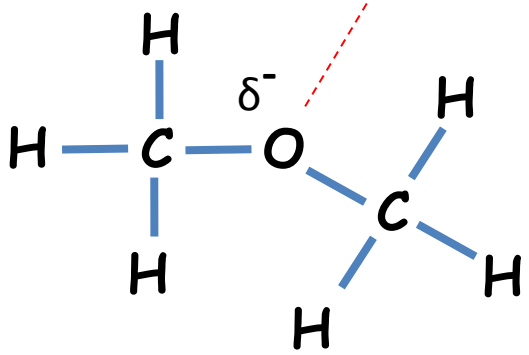
Ethanol C_2H_6O
Boiling Point: 78.3°C



"Hydrogen Bonding"

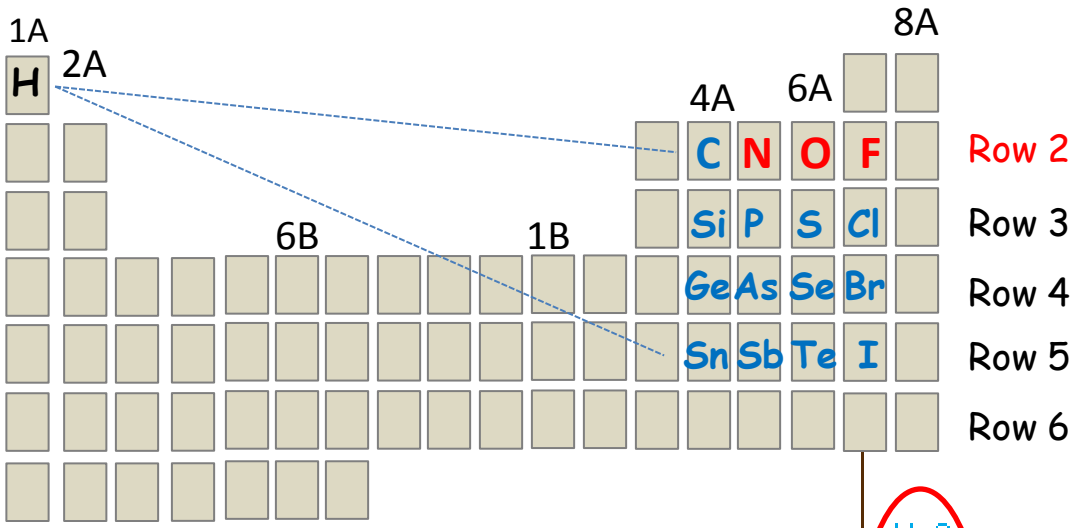


Dimethyl Ether C_2H_6O
Boiling Point: -24.8°C

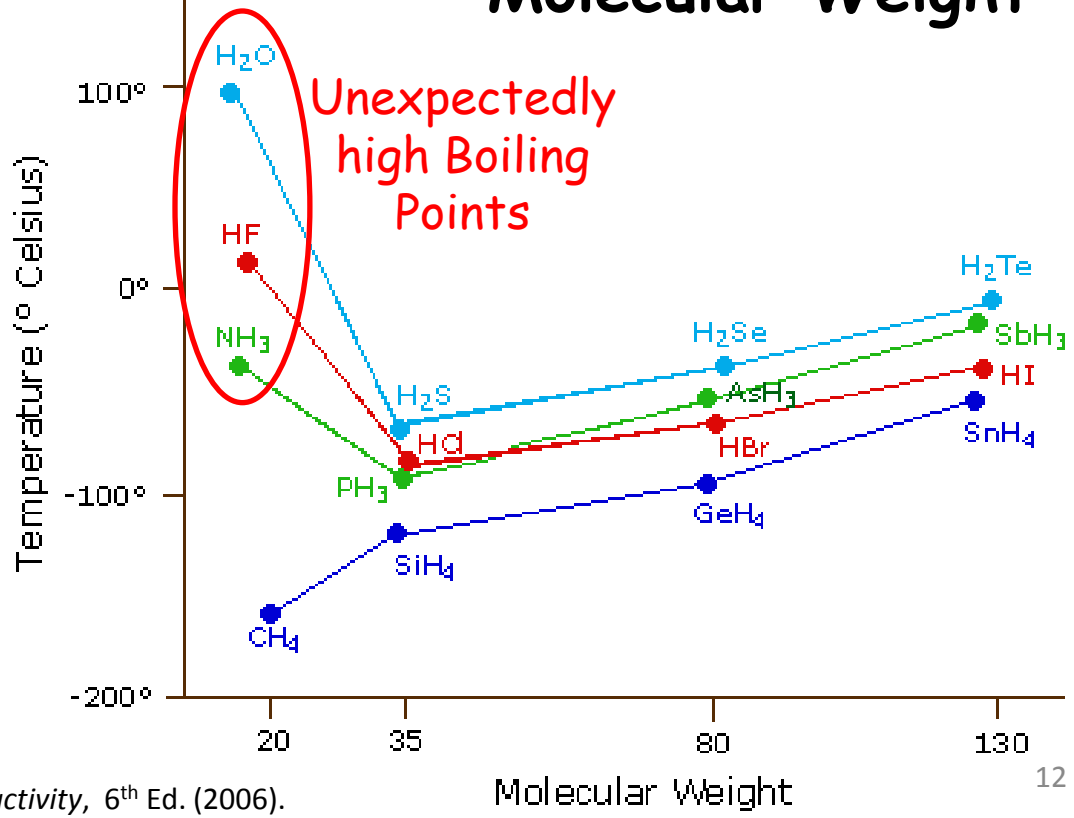


two clicks

H bonds to N, O, F are anomalous



Boiling Point vs. Molecular Weight



Kotz, Treichel and Weaver, *Chemistry and Chemical Reactivity*, 6th Ed. (2006).

Up Next

How to apply this information to tip-substrate interactions?

Develop quantitative models?