"A" students work (without solutions manual)
~ 10 problems/night.

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Office Hours W – F 2-3 pm

Module #12
Intermediate Forces

FITCH Rules

General

- G1: Suzuki is Success
- G2. Slow me down
- G3. Scientific Knowledge is Referential
- G4. Watch out for Red Herrings
- G5. Chemists are Lazy

Chemistry

- C1. It's all about charge
- C2. Everybody wants to "be like Mike"
- C3. Size Matters
- C4. Still Waters Run Deep
- C5. Alpha Dogs eat first

$$E_{el} = k\left(\frac{q_1 q_2}{r_1 + r_2}\right)$$

Properties and Measurements

Property	Unit	Reference State
Size	m	size of earth
Volume	cm^3	m
Weight	gram	mass of 1 cm^3 water at specified Temp (and Pressure)
Temperature	°C, K	boiling, freezing of water (specified Pressure)
$1.66053873 \times 10^{-24}$g	amu	(mass of 1C-12 atom)/12
quantity	mole	atomic mass of an element in grams
Pressure	atm, mm Hg	earth's atmosphere at sea level
Energy, General		
Animal	hp	horse on tread mill
heat	BTU	1 lb water 1 °F
	calorie	1 g water 1 °C
Kinetic	J	m, kg, s
Electrostatic		1 electrical charge against 1 V
electronic states in atom		Energy of electron in vacuum
Electronegativity	F	
Heat flow measurements		constant pressure, define system vs surroundings per mole basis (intensive)

Intermolecular Forces

1. **Evidence for Intermolecular Forces**
2. Phase Diagrams (briefly)
3. Liquid-Vapor Equilibrium
   1. Kinetic theory
   2. Gas escape as a way to measure liquid intermolecular forces
4. Boiling points related liquid Intermolecular Forces
   1. Dipole-dipole
   2. Dispersion
   3. H-bonding
   4. example application – heat capacity of lakes
5. Solid Intermolecular Forces
   1. Molecular Solids (Dispersion/ H-bonding)
   2. Network Covalent (Covalent) – example glass
   3. Ionic solids (Ion/ion)
   4. Metallic solids (metal bonding)
6. Structures of Crystals
   1. Unit Cells
   2. Common Metal Unit cells
      1. Calculate density of lead
   3. Common Ionic Solid Unit cells
      1. Calculate density of ionic solid

We learned about

"Ideal" behavior of gases - do not notice each other

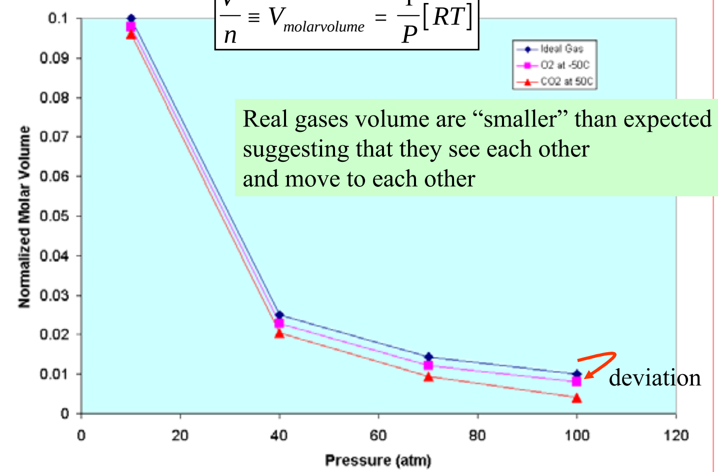
Violate Rules #C1 (charge) & C3 (size)

But - we have accumulated evidence that molecules

a) Real gases "notice" each other
b) Condensed phase (liquids, solids) notice each other

What evidence have we accumulated?

$$\frac{V}{n} \equiv V_{molarvolume} = \frac{1}{P}[RT]$$



Robert Boyle, 1660; Boyle's Law

Specific heats

Material	Specific Heats c, (J/g-°C)
Pb(s)	0.12803
Pb(l)	0.16317
Cu(s)	0.382
Fe(s)	0.446
Cl_2(g)	0.478
C(s)	0.71
CO_2(g)	0.843
NaCl(s)	0.866
Al(s)	0.89
C_6H_6(l)	1.72
H_2O(g)	1.87
C_2H_5OH(l)	2.43
H_2O(l)	4.18

Specific heat of Water increases to A dramatically large Value from gas To liquid (more Condensed – see each Other more) phase

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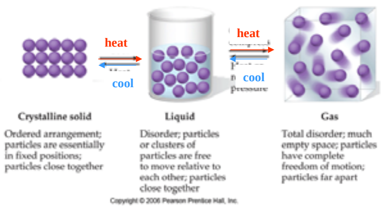
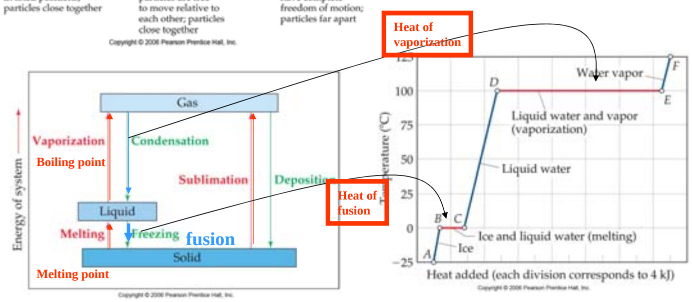
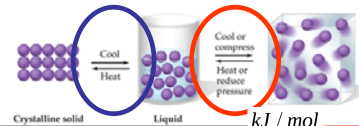
PHASE CHANGES – related to Intermolecular Forces



Some NEWvocabulary
fusion
Vaporization
Condensation
Sublimation





Substance		mp(°C)	ΔH_{fusion} (kJ / mol)	bp(°C)	$\Delta H_{vaporization}$ (kJ / mol)
Bromine	Br_2	-7	10.8	59	29.6
Benzene	C_6H_6	5	9.84	80	30.8
Water	H_2O	0	6.00	100	40.7
Naphthalene	$C_{10}H_8$	80	19.3	218	43.3
Mercury	Hg	-39	2.33	357	59.4

What do you see?

Substance		mp(°C)	ΔH_{fusion}	bp(°C	$\Delta H_{vaporization}$
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Benzene	C_6H_6	5	9.84	80	30.8
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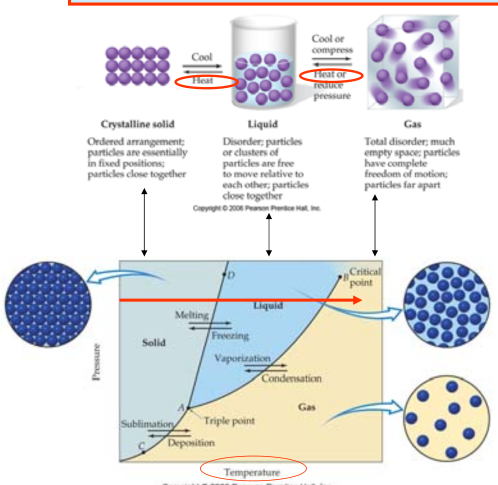
What do you see?

What do you see?

$\Delta H_{vaporization} > \Delta H_{fusion}$

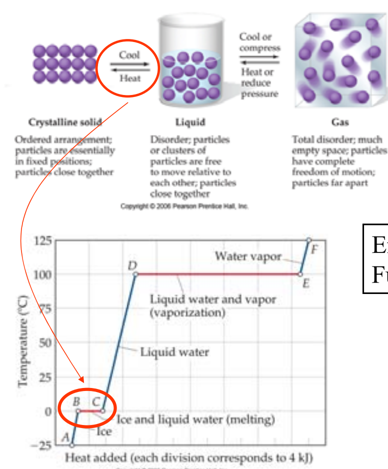
The heats of fusion and vaporization are a way of describing the energy required to break intermolecular forces sufficient to melt or vaporize the material; trends differ because solid, liquid structures of same substance can be very different

PHASE CHANGES – related to Intermolecular Forces



One form
Of A Phase
Diagram

PHASE CHANGES – related to Intermolecular Forces



Energy required to move molecules
Further apart (solid to liquid)

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$$E_{el} = k\left(\frac{q_1 q_2}{r_1 + r_2}\right)$$

Coulomb's law

$$E = \frac{k(Q_1)(Q_2)}{d}$$

$$d = r_{cation} + r_{anion}$$

E = electrical energy of interaction
K = constant, 8.99×10^{-9}J-m/C^2
Q= charge on ion, 1.602×10^{-19}C
r = ionic radius

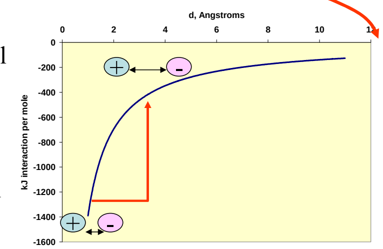
Reference state is some very far distance
Where they don't see each other, 0 E of interaction

-400kJ/mol final

- -1400kJ/mol

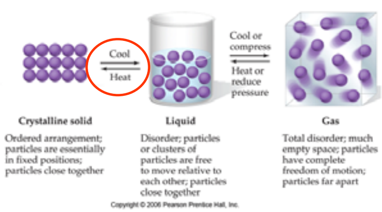
+1000kJ/mol

initial



Costs energy to move apart

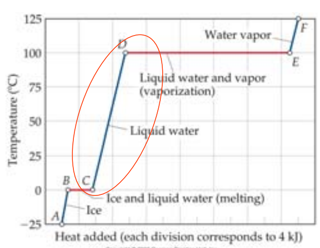
PHASE CHANGES – related to Intermolecular Forces

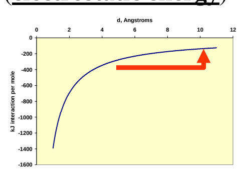


Represents increase
In **kinetic energy** of
Molecules moving

$$E_k = \tfrac{1}{2}mv^2$$

And increasing distance
(**electrostatic energy**)





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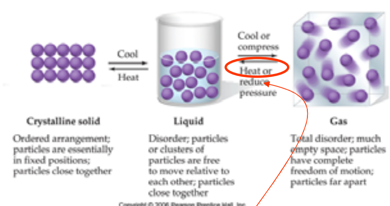
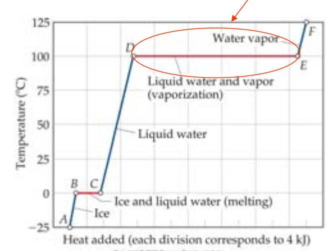
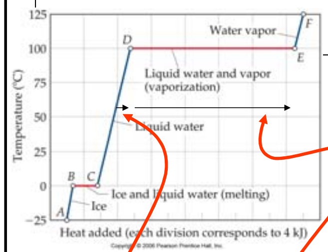




Represents **kinetic energy** needed
To escape solution

Example Problem: What energy is required to take 100.0 g Of water at 57 ^oC into the gas phase? The heat of vaporization of water at 100^oC is 40.67 kJ/mol, c water is 4.184 J/g-K



$$\left[\frac{40.67kJ}{mol_{H_2O\,at\,100^\circ C}}\right]\left[100gH_2O\right]_{100^\circ C}\left[\frac{mol}{18g}\right] = 225.94kJ$$

$q = cm\Delta T$

$$q = \left(\frac{4.184J}{g-K}\right)(100.0g)[(100+273)K-(57+273)K]$$

$q = 17{,}991J$

$Total = q + \Delta H_{vap}$

$225.94kJ + 17.9kJ = 243.8444 = 244.8kJ$

What was the most "costly" part of the process?

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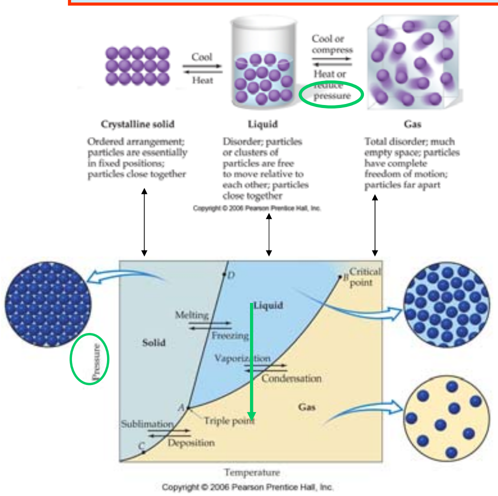
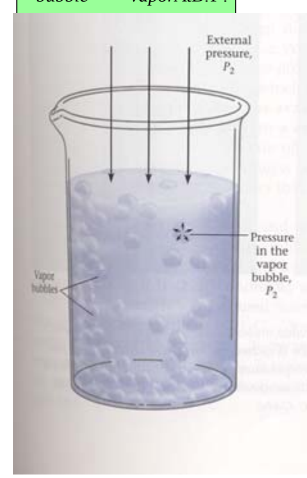
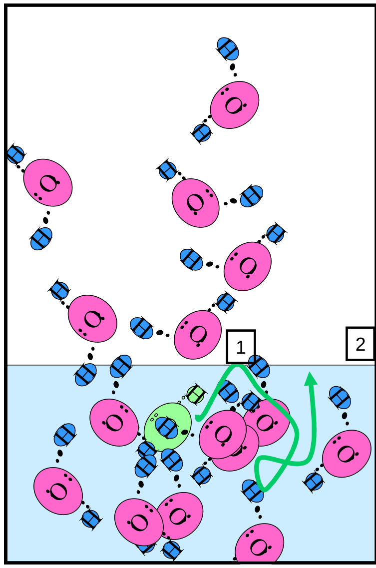
PHASE CHANGES – related to Intermolecular Forces



How does Pressure affect What is Going on?

For a bubble to break $P_{bubble} \geq P_{vaporAtB.P.}$





How do we get the heat of vaporization
And
What is it related to (what "picture" should we have)?

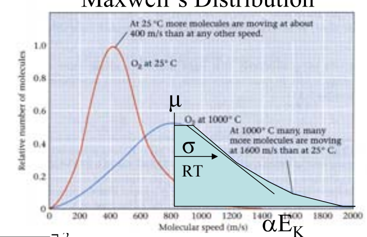
Only 1 of 2 times water "hits" the Surface does it actually have Enough energy to leave.

From earlier chapter we learned of kinetic energy:

$$E_k = \frac{1}{2}mv^2$$

$$u_{rms} = \sqrt{\frac{3kT}{g_{molecule}}}$$

Maxwell's Distribution



$$E_k = \frac{1}{2}m_{ass\ of\ molecule}\left[\sqrt{\frac{3kT}{mass\ of\ molecule}}\right]^2$$

$$E_k = \left(\frac{1}{2}m_{ass\ of\ molecule}\right)\left(\frac{3kT}{mass\ of\ molecule}\right)$$

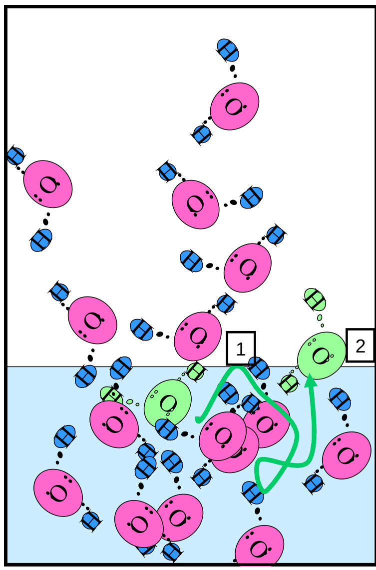
$$E_k = \left(\frac{3kT}{2}\right)$$

However, only a **fraction** of molecules at a given emperature that average speed, and therefore, Average energy

If you assume a normal distribution for the "bell curve" you can calculate the fraction of molecules with an energy above the average value

$$f(x) = e^{-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2}$$

$$f(x) = e^{-\frac{E_{molecule}}{kT}} = e^{-\frac{E_{mole}}{RT}}$$



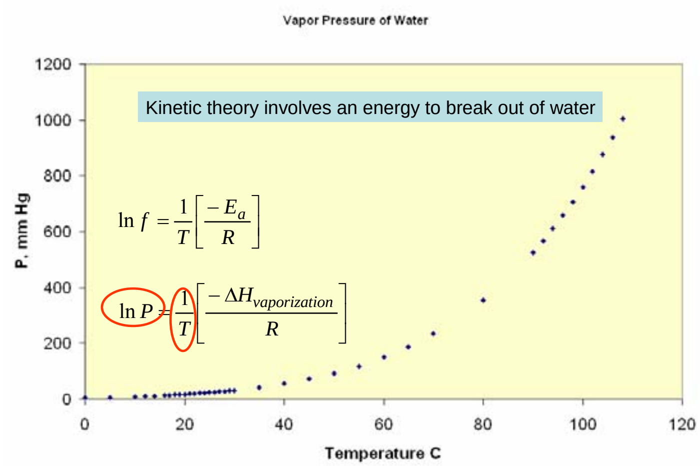
Fraction of collisions in which the energy is sufficient to allow water to leave the liquid state

$$fraction = f$$

$$f = e^{-\frac{E_a}{RT}}$$

$$\ln f = \frac{1}{T}\left[\frac{-E_a}{R}\right]$$

Only 1 of 2 times water "hits" the Surface does it actually have Enough energy to leave.



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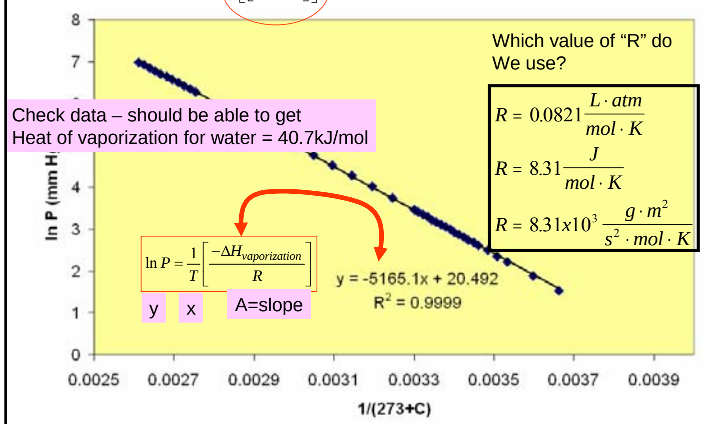
$$E_{el} = k\left(\frac{q_1 q_2}{r_1 + r_2}\right)$$

$$\ln P = \frac{1}{T}\left[\frac{-\Delta H_{vaporization}}{R}\right] = \left[\frac{1}{K}\right]\left[\frac{\left[\frac{J}{mol}\right]}{\left[\frac{J}{mol \cdot K}\right]}\right]$$

Rule G5: Chemists are Lazy:



Which value of "R" do We use?

$$R = 0.0821\frac{L \cdot atm}{mol \cdot K}$$

$$R = 8.31\frac{J}{mol \cdot K}$$

$$R = 8.31x10^3\frac{g \cdot m^2}{s^2 \cdot mol \cdot K}$$

Check data – should be able to get Heat of vaporization for water = 40.7kJ/mol

$$\ln P = \frac{1}{T}\left[\frac{-\Delta H_{vaporization}}{R}\right]$$

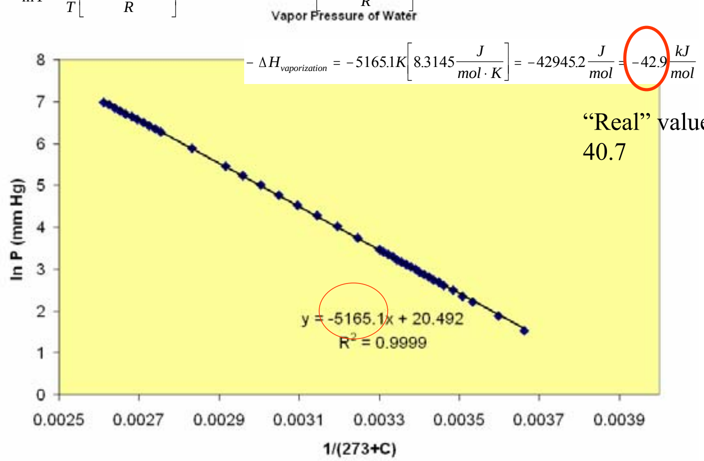
y x A=slope

$$\ln P = \frac{1}{T}\left[\frac{-\Delta H_{vaporization}}{R}\right]$$

$$slope = \left[\frac{-\Delta H_{vaporization}}{R}\right] = -5165.1K$$

$$-\Delta H_{vaporization} = -5165.1K\left[8.3145\frac{J}{mol \cdot K}\right] = -42945.2\frac{J}{mol} = -42.9\frac{kJ}{mol}$$

"Real" value 40.7



$$\ln P_1 - \frac{1}{T_1}\left[\frac{-\Delta H_{vaporization}}{R}\right] = b$$

$$\ln P_2 - \frac{1}{T_2}\left[\frac{-\Delta H_{vaporization}}{R}\right] = b$$

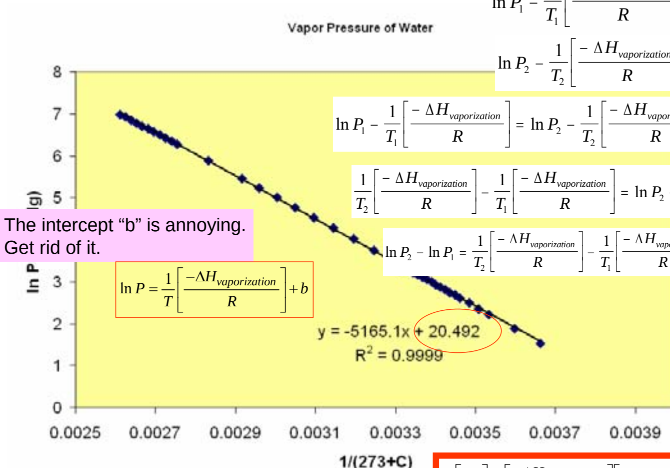
$$\ln P_1 - \frac{1}{T_1}\left[\frac{-\Delta H_{vaporization}}{R}\right] = \ln P_2 - \frac{1}{T_2}\left[\frac{-\Delta H_{vaporization}}{R}\right]$$

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

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

The intercept "b" is annoying. Get rid of it.

$$\ln P = \frac{1}{T}\left[\frac{-\Delta H_{vaporization}}{R}\right] + b$$

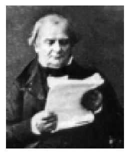


$$\boxed{\ln\left[\frac{P_2}{P_1}\right] = \left[\frac{-\Delta H_{vaporization}}{R}\right]\left[\frac{1}{T_2} - \frac{1}{T_1}\right]}$$

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

Clausius-Clapeyron equation 1834

Rudolph Clausius
Polish born German
1822-1888
Mathematical Physics



Benoit Paul Emile Clapeyron
1799-1864, French Engineer
Mathematical physicist (developed concept of entropy)

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

Example, Calculate the heat of vaporization for lead knowing that the vapor pressure
Of elemental lead is 1 mm Hg at 987 ºC and 10 mm Hg at 1167º C.

$$\ln\left[\frac{1mm}{10mm}\right] = \left[\frac{-\Delta H_{vaporization}}{8.31\left[\frac{J}{mol\cdot K}\right]}\right]\left[\frac{1}{(273+987)K} - \frac{1}{(273+1167)K}\right]$$

$$-2.302 = \left[\frac{-\Delta H_{vaporization}}{8.31\left[\frac{J}{mol\cdot K}\right]}\right]\left[\frac{1}{(1260)K} - \frac{1}{(1440)K}\right]$$

$$-2.302 = \left[\frac{-\Delta H_{vaporization}}{8.31\left[\frac{J}{mol\cdot K}\right]}\right]\left[7.9365x10^{-4}\frac{1}{K} - 6.9444x10^{-4}\frac{1}{K}\right]$$

$$-2.302 = \left[\frac{-\Delta H_{vaporization}}{8.31\left[\frac{J}{mol\cdot K}\right]}\right]\left[9.9205x10^{-5}\frac{1}{K}\right]$$

$$\frac{[-2.302]8.31\left[\frac{J}{mol\cdot K}\right]}{9.92063x10^{-5}\frac{1}{K}} = -\Delta H_{vaporization}$$

$$\boxed{\begin{array}{l} -192875.5798\left[\frac{J}{mol}\right] = -\Delta H_{vaporization} \\ \Delta H_{vaporization} = 192.9\frac{kJ}{mol}\end{array}}$$

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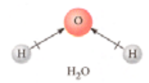
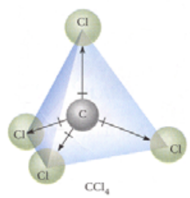
Molecular Substances, Liquids: Intermolecular Forces

1. Uncharged = non conductors of electricity when pure (I_2)
2. Uncharged = nonsoluble in water
   soluble in nonpolar solvents such as CCl_4
3. Uncharged = low interactions holding them in liquid = low boiling points
4. Uncharged = low interactions holding them in solid = low melting points





$:\ddot{\underset{..}{I}}-\ddot{\underset{..}{I}}:$

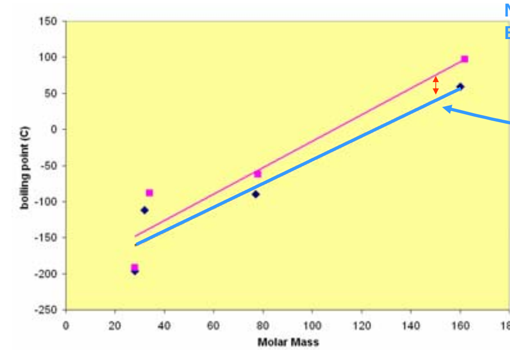
Both have same electro-
Negativity so equally
Share electrons in the bonds
= non polar

Holding mass approximately constant:

Non-polar formula	g/mol	bp (oC)	polar formula	g/mol	bp (ºC)
N_2	28	-196	CO	28	-192
SiH_4	32	-112	PH_3	34	-88
GeH_4	77	-90	AsH_3	78	-62
Br_2	160	59	ICl	162	97

Look at one polar molecule

Non polar molecules
Boil at lower temperature

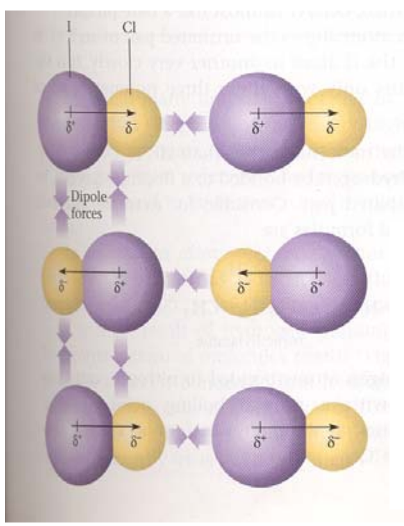


Total valence electrons:		14
skeleton bond		-2
remaining electrons		12
required for octets		12

$:\ddot{\underset{..}{I}}-\ddot{\underset{..}{Cl}}:$

Who pulls electrons Best?

Permanent
Dipole moments
affect
boiling point



Holding mass approximately constant:

formula	g/mol	bp (oC)	formula	g/mol	bp (ºC)
N2	28	-196	CO	28	-192
SiH4	32	-112	PH3	34	-88
GeH4	77	-90	AsH3	78	-62
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Non polar molecules
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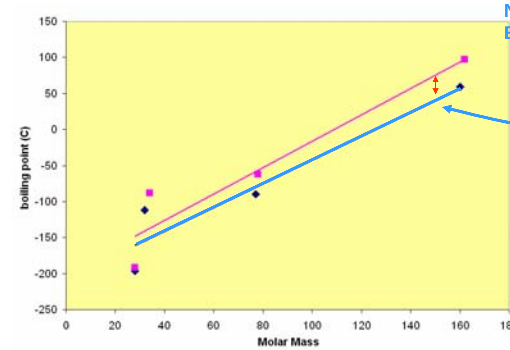
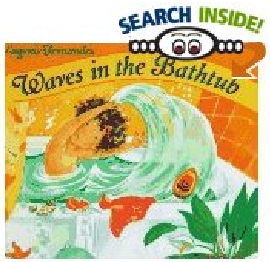


Boiling point can
Increase if the
Molar mass goes up

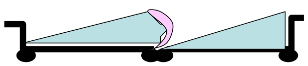
Why?

Dispersion (London) Forces



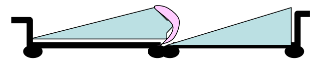
Largest possible wave crests at each end of bathtub

Place two bathtubs end to end with a rubber divider:

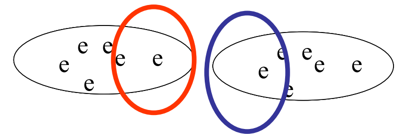


As one wave piles up the water in the Bathtub responds creating a sympathetic Wave

---



Two bath tubs with sloshing Water separated by rubber



Temporary Negative charge

temporary Positive charge

$$E = \frac{k(Q_1)(Q_2)}{d}$$

$$d = r_{cation} + r_{anion}$$

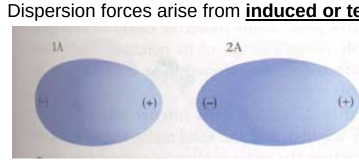
Oscillations of electrons Set up temporary and Oppositely charged Dipoles which attract Each other

London dispersion Also referred to as Van der Waals forces

Schroedinger Fritz London
1928

Fritz London
1900-1954
Born Breslau, Germany
Duke University physical chemist

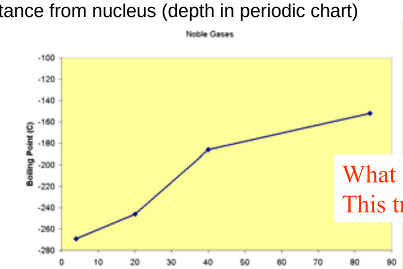
Dispersion forces arise from **induced or temporary dipoles**



Effect depends upon

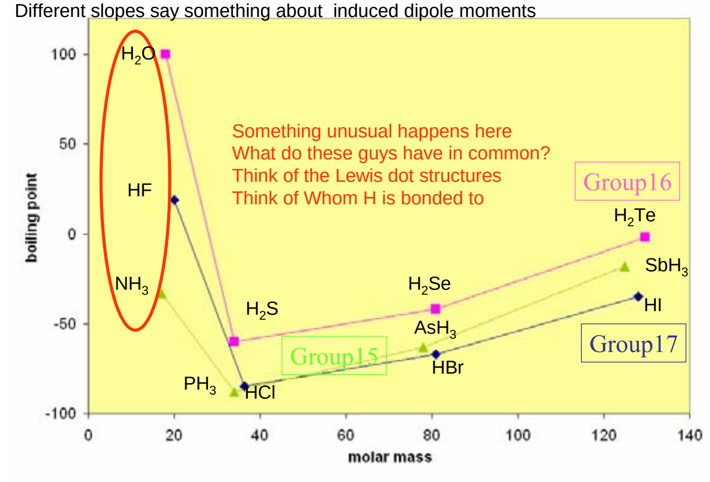
1. number of electrons in the molecule
2. ease of creating a bathtub wave
   (less rigidity or spatial fixedness of electron)
3. distance from nucleus (depth in periodic chart)

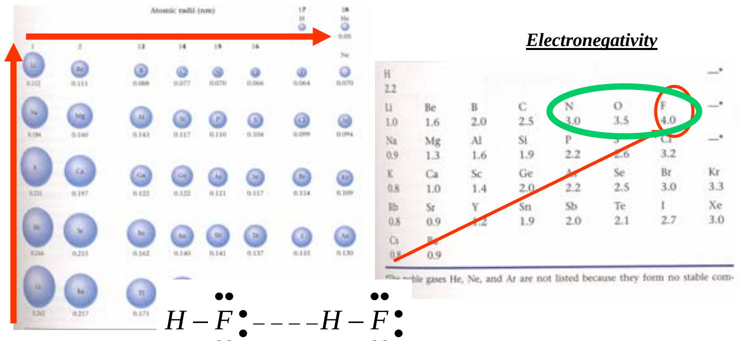
	g/mol	bp (C)
He	4	-269
Ne	20	-246
Ar	40	-186
Kr	84	-152



What explains This trend?

As the molar mass goes up
boiling point goes up due to dispersion forces
Different slopes say something about induced dipole moments

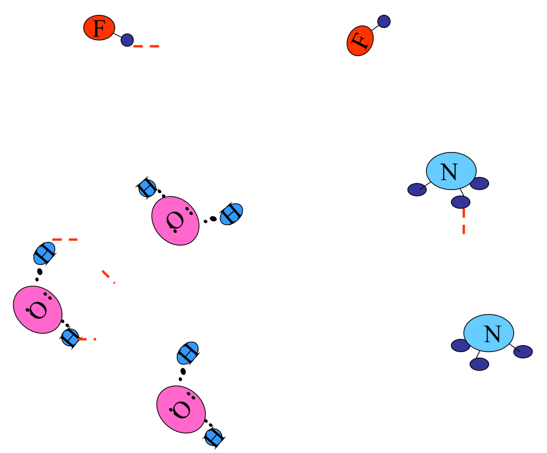




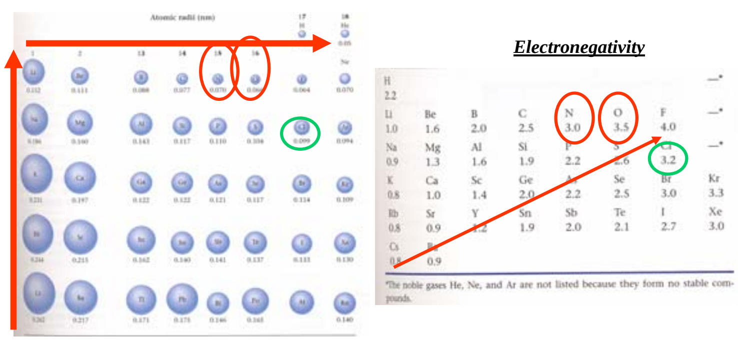
$$H-\ddot{\underset{\cdot\cdot}{F}}: - - - - H-\ddot{\underset{\cdot\cdot}{F}}:$$

Hydrogen is bonded with three highly electronegative species
Also having unpaired electrons N, O, F

Hydrogen loses control of most of its shared electron and is an
Unhappy camper – needs more electrons



Hydrogen bonds are formed in each case



Why not HCl also, similar in electronegativity to oxygen and nitrogen?.

$$E = \frac{k(Q_1)(Q_2)}{d}$$

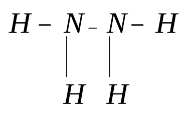
Do you see anything here?

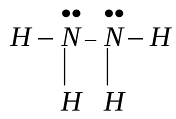
$$d = r_{cation} + r_{anion}$$

Need to be able to get close to the other
molecule, - small size matters

Example: Would you expect to find hydrogen bonds in hydrazine? (Rocket fuel), N_2H_4

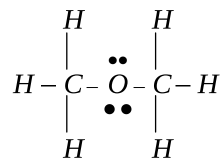
Valence shell electrons:	2(N)	2(5)	10
	4(H)	4(1)	4
Total			14
Skeleton structure $H_2N\text{-}NH_2$			
Single bonds	5(2)		-10
Remaining electrons			4



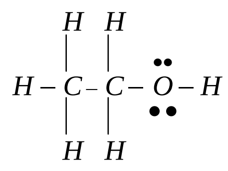


Example: Would you expect to find hydrogen bonds in Dimethyl ether Vs ethyl alcohol?

Both have lone pair (unbonded) electrons on one of the three elements we Are interested in (N, O, F).

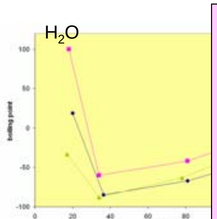


But hydrogen is not bonded to the atom in dimethyl ether – expect no hydrogen bonding

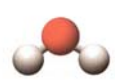


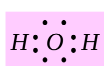
In Ethyl alcohol hydrogen is bonded to oxygen. Expect hydrogen bonding

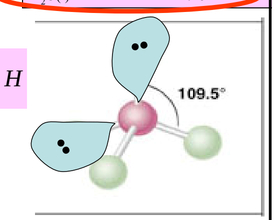
Hydrogen Bonding explains much of what we have Learned about water.



Material	Specific Heats c, (J/g-°C)
$Pb(s)$	0.12803
$Pb(l)$	0.16317
$Cu(s)$	0.382
$Fe(s)$	0.446
$Cl_2(g)$	0.478
$C(s)$	0.71
$CO_2(g)$	0.843
$NaCl(s)$	0.866
$Al(s)$	0.89
$C_6H_6(l)$	1.72
$H_2O(g)$	1.87
$C_2H_5OH(l)$	2.43
$H_2O(l)$	4.18



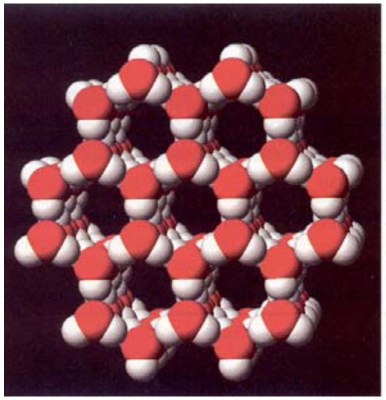




Hydrogen bonding gives a low density structure in ice

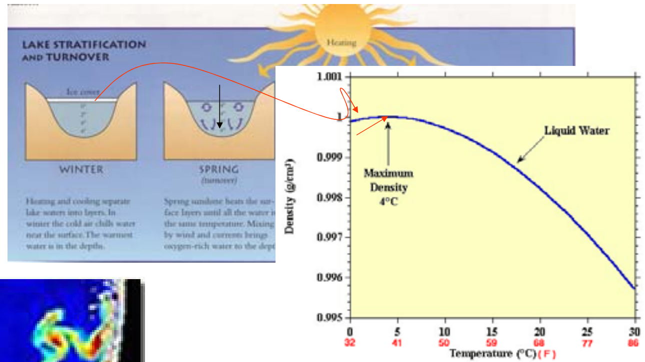
$$d_{liquid H_2O} = 1.000 \frac{g}{cm^3}\Big|_{0^o C}$$

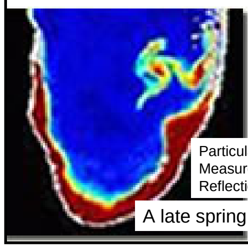
$$d_{solid H_2O} = 0.917 \frac{g}{cm^3}\Big|_{0^o C}$$



Hydrogen bonded ice structure

Nutrient Cycling in Lake Michigan





Particulate matter as
Measured by satellite
Reflection measurements

A late spring phenomena

Surface temperature rises, Ice melts,
becomes more dense,
falls to bottom
pushing up nutrient
Rich particulate matter which feeds
The spring algae

"A" students work
(without solutions manual)
~ 10 problems/night.

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Module #12
Intermolecular Forces

Summary of Intermolecular Forces in Liquids

Dipole/dipole Dispersion (bathtubs) Hydrogen bonding	Effect Observed as: boiling points melting points heat capacity vapor pressure of liquid Heat of fusion Heat of vaporization

Water and it's density!

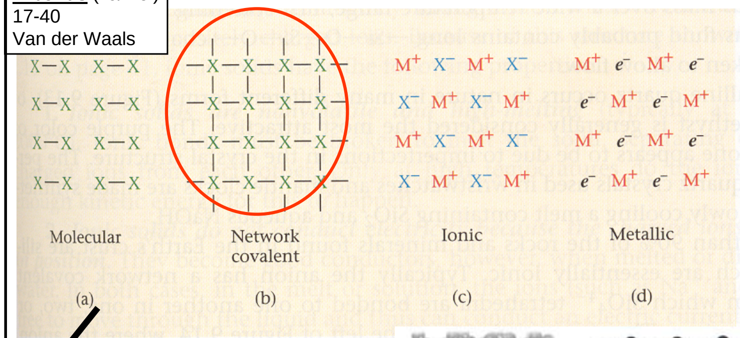
Effects also observed for molecular **solids**

Intermolecular Forces

1. Evidence for Intermolecular Forces
2. Phase Diagrams (briefly)
3. Liquid-Vapor Equilibrium
    1. Kinetic theory
    2. Gas escape as a way to measure liquid intermolecular forces
4. Boiling points related liquid Intermolecular Forces
    1. Dipole-dipole
    2. Dispersion
    3. H-bonding
    4. example application – heat capacity of lakes
5. **Solid Intermolecular Forces**
    1. Molecular Solids (Dispersion/ H-bonding)
    2. Network Covalent (Covalent) – example glass
    3. Ionic solids (Ion/ion)
    4. Metallic solids (metal bonding)
6. Structures of Crystals
    1. Unit Cells
    2. Common Metal Unit cells
        1. Calculate density of lead
    3. Common Ionic Solid Unit cells
        1. Calculate density of ionic solid

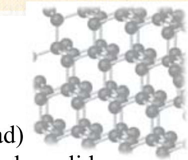
H bonds (kJ/mol)
17-40
Van der Waals

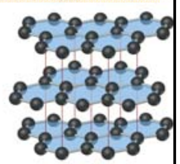
Network Covalent, Ionic, and Metallic Solids



Forces between molecules
dispersion
dipole/dipole
H-bonding
Tendency towards
softness, low mp

Graphite
(pencil lead)
Is a molecular solid

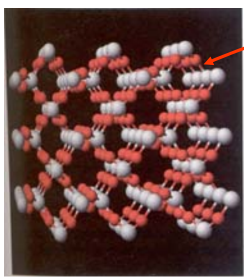


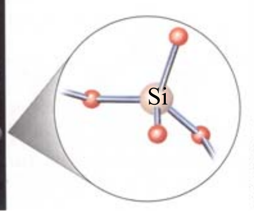


Covalent Bond Energies for bonds **inside** a molecule that we have already examined

Bond	Bond Length pm	Enthalpy Single Bond kJ/mol (Average)
C--C	154	348
C--N	147	308
C--O	143	360
C--S	182	272
C--F	135	488
C--Cl	177	330
C--Br	194	288
C--I	214	216

Covalent bonds in solids





These are all Covalent bonds!

Si-O-Si-…..

Crystal structure of quartz

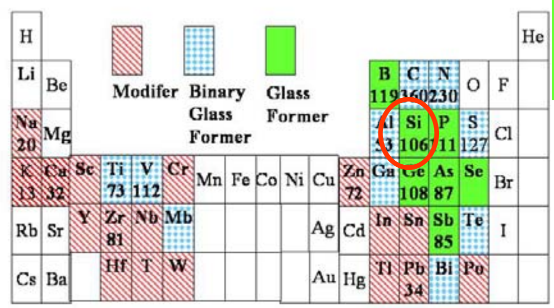
Covalent bonds in the network imply
1. high melting points (~1000ºC)
2. insoluble in all common solvents (solvents can't break the bonds)
3. poor electrical conductors (like molecular solids)

Glass making from 2000 B.C. Egypt
how did they do it?

Could not get temperatures > 1000ºC

Single Bond Energies in kcal/mol (to O)

What do you observe?

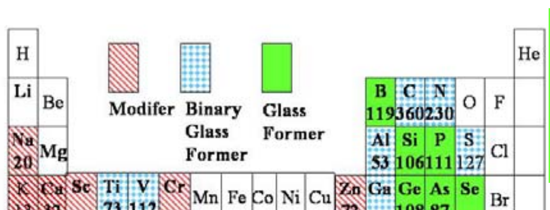


Glass formers have intermediate bond energies with Oxygen

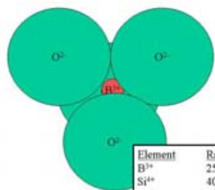
$$\left[\frac{4.184kJ}{1kcal}\right]\left(\frac{106kcal}{mol}\right) = \frac{443.504kJ}{mol}$$

Maximum value of glass formers is: 498 kJ/mol for Boron

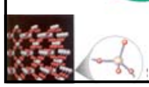
Single Bond Energies in kcal/mol



Glass formers have intermediate bond energies with Oxygen, also have the ability to create three or more bonds



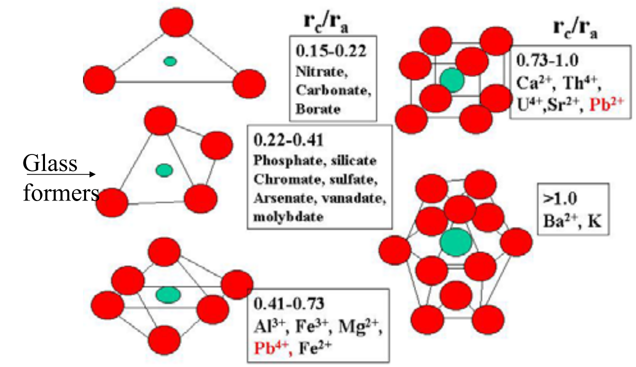
Element	Radius (pm)	Ratio
B^{3+}	25	0.206
Si^{4+}	40	0.330
Ge^{4+}	53	0.438
P^{5+}	31	0.256
Se^{6+}	42	0.347
O^{2-}	121	1



Rule: Size Matters!

Also have a particular **small** Radius with respect to oxygen.

Need to form tetrahedra



How did the Egyptians do it? – a topic to explore

$$B.E._{SiO_2} = \frac{443.504kJ}{mol}$$

Why is mp so high when enthalpy of fusion is not?

Hint: naphthalne a large (multimolar) solid?

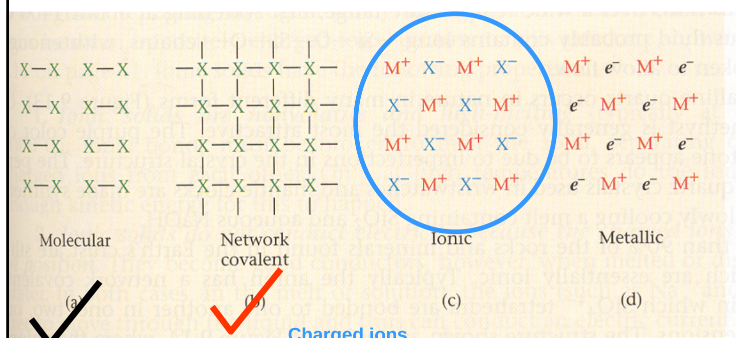
$$\Delta H_{f(SiO_2)} = \frac{14.22kJ}{mol}$$

Substance		mp(°C)	ΔH_{fusion}	bp(°C	$\Delta H_{vaporization}$
Mercury	Hg	-39	2.33	357	59.4
Bromine	Br_2	-7	10.8	59	29.6
Water	H_2O	0	6.00	100	40.7
Benzene	C_6H_6	5	9.84	80	30.8
Naphthalene	$C_{10}H_8$	80	19.3	218	43.3
Quartz	SiO_2	1470	14.22		

Typical fire temp 500-600°C

Typical chimney fire temp 1000°C

Network Covalent, Ionic, and Metallic Solids



Charged ions

1. strong electrostatic interaction
   = high melting point (600-2000°C)

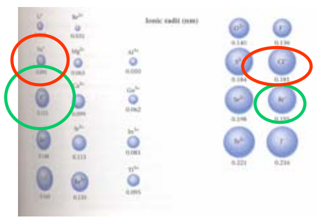
What Rule(s) Do We Invoke Here?

$$E = \frac{k(Q_1)(Q_2)}{d}$$ Coulomb's law

$$d = r_{cation} + r_{anion}$$

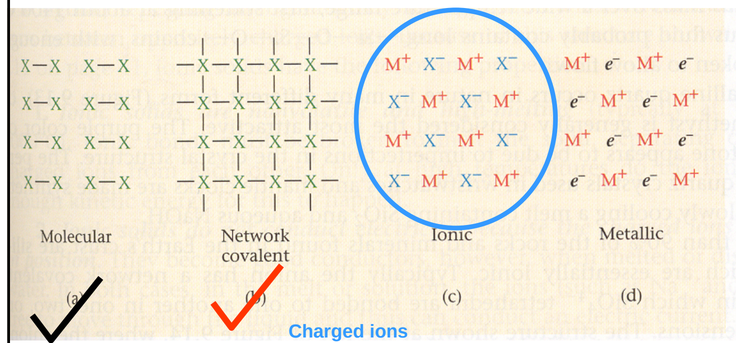
E = electrical energy of interaction
K = constant
Q= charge on ion
r = ionic radius

Explain this difference in melting points?



	mp °C
NaCl	801
KBr	734

Network Covalent, Ionic, and Metallic Solids



What Rule(s) Do We Invoke Here?

Charged ions

1. strong electrostatic interaction
   = high melting point (600-2000°C)
2. Strong electrostatic interaction
   = fixed positions = no electrical conduction
3. Most (not all) soluble in water (polar water organizes around the ions and satisfies their charges)

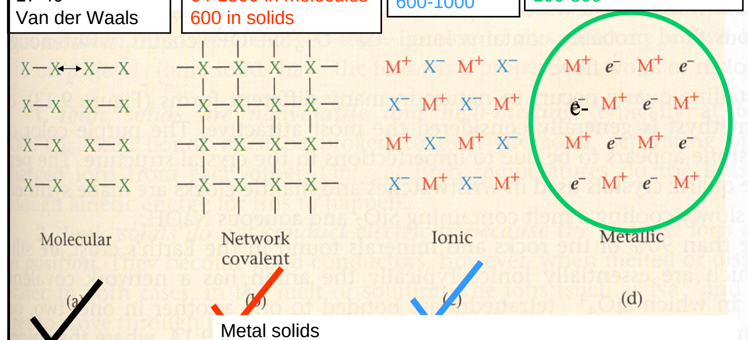
No Clean Socks	Oh Card me PleaSe
$CuSO_{4(s)} \rightarrow Cu^{2+}_{(aq)} + SO^{2-}_{4(aq)}$ $\Delta H^O = -66.15kJ$	$CuS_{(s)} \rightarrow Cu^{2+}_{(aq)} + S^{2-}_{(aq)}$ $\Delta H^O = -14.5kJ$
$H_2SO_{4(l)} \rightarrow H^{+}_{(aq)} + HSO^{-}_{4(aq)}$ $\Delta H^O = -73.3kJ$	$H_3PO_{4(l)} \rightarrow H^{+}_{(aq)} + H_2PO^{-}_{3(aq)}$ $\Delta H^O = -20.1kJ$

What do you observe?

How do you explain it?

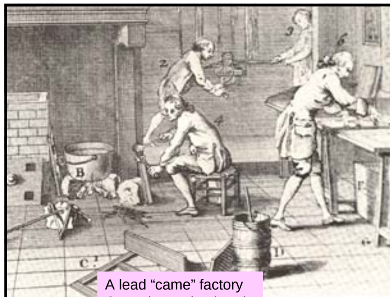
Network Covalent, Ionic, and Metallic Solids

H bonds (kJ/mol)	Covalent (kJ/mol)	Ionic (kJ/mol)	Metallic bonds (kJ/mol)
17-40 Van der Waals	64-1500 in molecules 600 in solids	600-1000	100-800



Metal solids

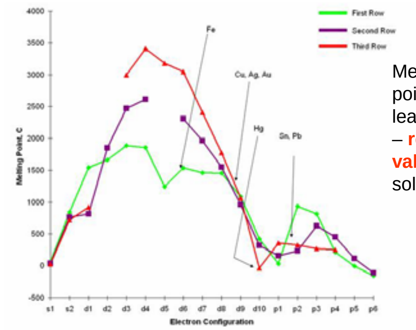
1. No covalent bonding
2. But strong attraction holds atoms in fixed lattice points
3. Attraction is greater than H bonds or van der Waals forces
4. Metallic bonds can be as strong as ionic bonds
5. Sea of fluid electrons flows around the fixed metal ions
   Determines properties



A lead "came" factory
Came is used to bend
Around pieces of cut
Glass for stained glass
windows

Fluid electron sea explains

1. high electrical conductivity
2. high thermal conductivity: heat is carried by electron collisions
3. Ductile, malleable, electrons are a flexible glue
4. Luster, electrons not restricted to specific bonds
5. Insoluble – electrons are not soluble

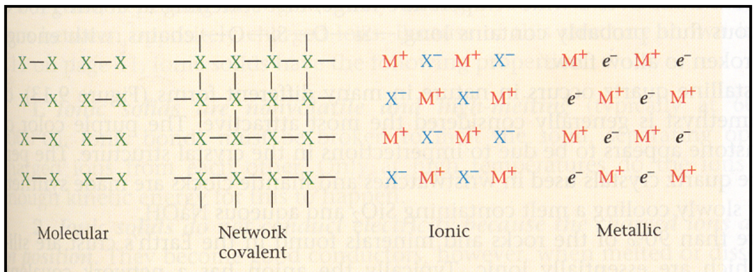


Melting point: Lowest melting point occurs when electrons are least "fixed" around metal cations – **related to filling of the valence shell electrons**, and solid structure structure

The seven metals earliest
Discovered have low
Melting points

Fluid electron sea explains

1. high electrical conductivity
2. high thermal conductivity: heat is carried by electron collisions
3. Ductile, malleable, electrons are a flexible glue
4. Luster, electrons not restricted to specific bonds
5. Insoluble – electrons are not soluble
6. Can have relatively low melting points



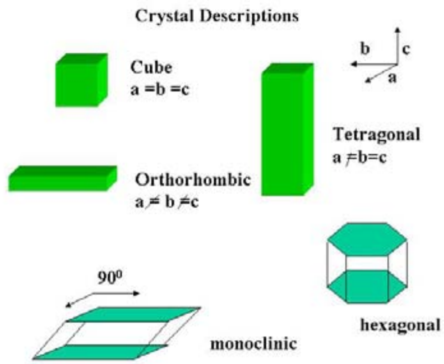
Low Melting Point	High Melting point (~1000 °C)	High Melting Point (600-2000 °C)	Variable Melting Point
Nonconducting of electricity	Nonconducting of electricity	Nonconducting of electricity	Conductor of Electricity
Insoluble in Water	Insoluble in all common solvents	Most are soluble in water	Insoluble
Low Boiling Point			
			High Thermal Conductivity
			Ductile/Malleable
			Luster

Intermolecular Forces

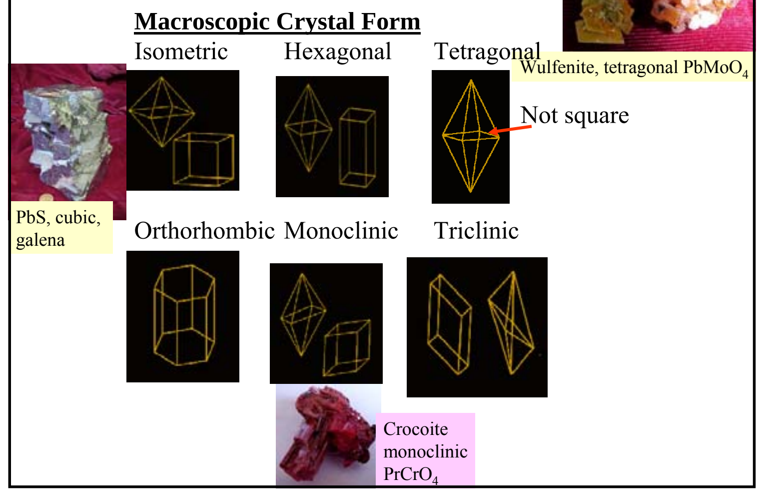
1. Evidence for Intermolecular Forces
2. Phase Diagrams (briefly)
3. Liquid-Vapor Equilibrium
   1. Kinetic theory
   2. Gas escape as a way to measure liquid intermolecular forces
4. Boiling points related liquid Intermolecular Forces
   1. Dipole-dipole
   2. Dispersion
   3. H-bonding
   4. example application – heat capacity of lakes
5. Solid Intermolecular Forces
   1. Molecular Solids (Dispersion/ H-bonding)
   2. Network Covalent (Covalent) – example glass
   3. Ionic solids (Ion/ion)
   4. Metallic solids (metal bonding)
6. **Structures of Crystals**
   1. Unit Cells
   2. Common Metal Unit cells
      1. Calculate density of lead
   3. Common Ionic Solid Unit cells
      1. Calculate density of ionic solid

CRYSTAL STRUCTURES

Macroscopic Minerals

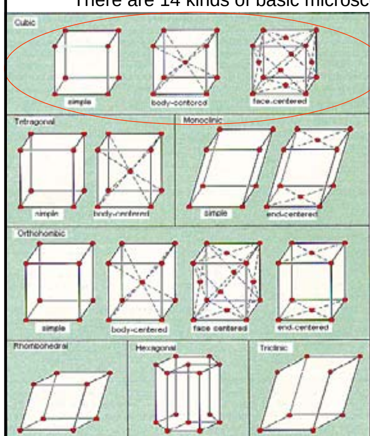


Macroscopic Structures of Minerals



Macroscopic Structures are often driven by
Three dimensional **microscopic** organization of atoms or ions

There are 14 kinds of basic microscopic organizational structures (**unit cells**).

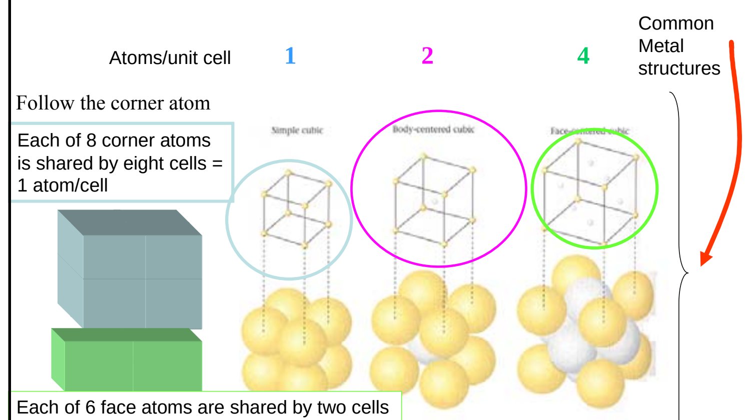


Simplest unit cell
Is cubic

7 groups of unit cells

METAL CRYSTAL STRUCTURES

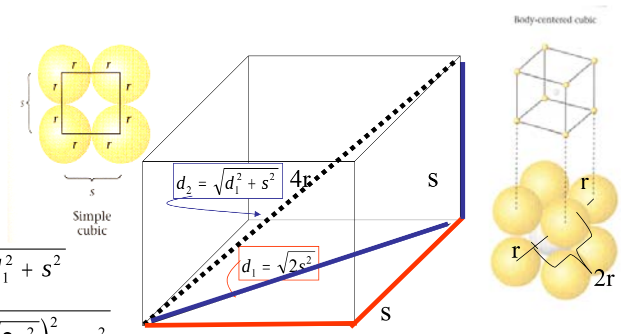
Macroscopic Structures are often driven by
Three dimensional microscopic organization of atoms or ions



Total atoms = 6face/2 +8corner/8=4

Total atoms = 1body +8corner/8=2

	Simple cubic	bcc	fcc
Atoms/unit cell	1	2	4
Geometry	$2r = s$	$4r = s\sqrt{3}$	

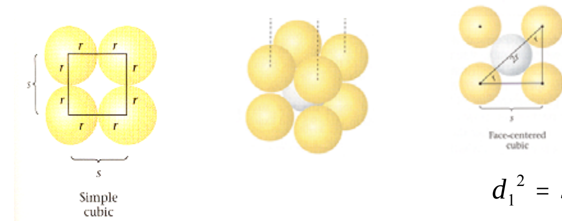


$d_2 = \sqrt{d_1^2 + s^2}$

$d_2 = \sqrt{\left(\sqrt{2s^2}\right)^2 + s^2}$

$d_2 = \sqrt{2s^2 + s^2}$ $\quad d_2 = \sqrt{3s^2}$ $\quad d_2 = s\sqrt{3}$ $\quad 4r = s\sqrt{3}$

	Simple cubic	bcc	fcc
Atoms/unit cell	1	2	4
Geometry	$2r = s$	$4r = s\sqrt{3}$	$4r = s\sqrt{2}$



$d_1 = 4r$

$d_1^2 = s^2 + s^2$

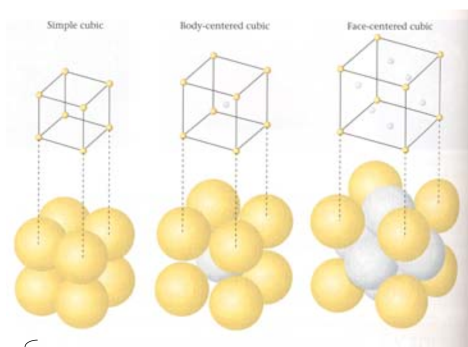
$d_1 = \sqrt{2s^2}$

$d_1 = s\sqrt{2}$

$4r = s\sqrt{2}$

	Simple cubic	bcc	fcc
Atoms/unit cell	1	2	4
Geometry	$2r = s$	$4r = s\sqrt{3}$	$4r = s\sqrt{2}$
%empty space	47.6	32.0	26.0

Empty space related to organization of atoms



Number of metals having this unit cell shape	Unstable	20 metals	40 metals Pb

Example: Calculate the density of lead from its molar mass and the fact that it Has a face centered cubic structure and bond length for elemental lead (center of one atom to another) 349.9 pm for elemental lead.

Complicated example from some textbook.

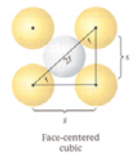
What do we know?

What do we need to know?

Example: Calculate the density of lead from its molar mass and the fact that it Has a face centered cubic structure and bond length for elemental lead (center of one atom to another) 349.9 pm for elemental lead.

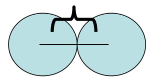
$$d_{ensity} = \frac{g}{cm^3}$$

1. Need volume
   a) fcc determines
   b) side, s, of cube
   c) s^3 is volume
2. Need radius
   a) fcc determines bond length
   b) bond length represents sum of 2 radii
3. Need mass
   a) fcc determines → 4 atoms/volume
   b) number of atoms
   c) convert atoms to moles to grams



$$\rightarrow 4r = s\sqrt{2}$$

Bond length = 2r



Want in cm^3

Example: Calculate the density of lead from its molar mass and the fact that it Has a face centered cubic structure and the bond distance of 349.9 pm for elemental lead.

$$2r = 349.9\,pm$$

$$r = \left[\frac{349.9\,pm}{2}\right]\left[\frac{1m}{10^{12}\,pm}\right]\left[\frac{100cm}{m}\right] = 174.95x10^{-10}\,cm$$

$$4r = s\sqrt{2} \quad \text{fcc}$$

$$\left[\frac{4atoms}{1.21x10^{-22}cm^3}\right]\left[\frac{mol}{6.02x10^{23}atoms}\right]\left[\frac{207.2g}{mol}\right] = 11.37\frac{g}{cm^3}$$

$$\frac{4(174.95x10^{-10}\,cm)}{\sqrt{2}} = s$$

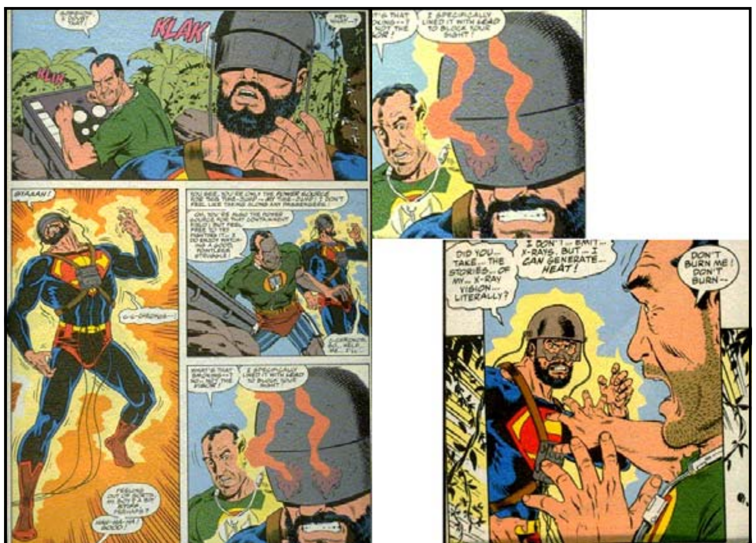
$$s = 494.8x10^{-10}\,cm$$

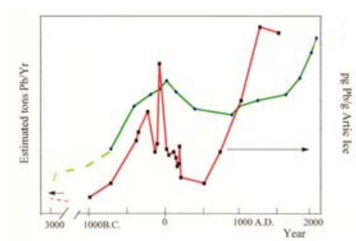
This calculated value is consistent with the reported value of 11.34 g/cm³

$$s^3 = V = \left[494.8x10^{-10}\,cm\right]^3 = 1.21x10^{-22}\,cm^3$$

Atoms in a face centered cubic cell: 8corners/8 + 6faces/2=4

We now know atoms/cm³; what next?





~4,000 deaths of mute swans in England/year from fishing sinkers
O'Halloran , 1988

Use "Go Back" on your Browser to return to previous page

Photograph / Copyright - Milton Friend.
Bright green staining of the vent area is often indicative of lead poisoning.

Use "Go Back" on your Browser to return to previous page

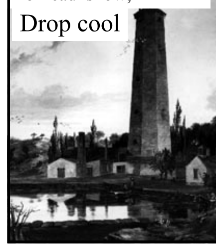
Photograph / Copyright - Milton Friend.
Wing droop in a tundra swan in advanced stages of lead intoxication.

"muck" grazing birds, pick Up solid lead as a "pebble" to Grind in their gizards

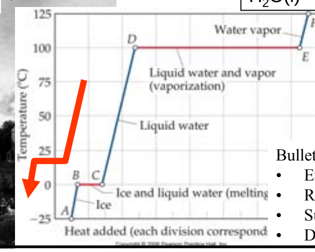
To create spherical Lead shot, Want the material To solidify Before it hits to Ground so it Does not deform

Rate of Cooling Related to Heat capacity; For lead is low;

Drop cool



Material	Specific Heats c, (J/g-°C)
Pb(s)	0.12803
Pb(l)	0.16317
Cu(s)	0.382
Fe(s)	0.446
Cl_2(g)	0.478
C(s)	0.71
CO_2(g)	0.843
NaCl(s)	0.866
Al(s)	0.89
C_6H_6(l)	1.72
H_2O(g)	1.87
C_2H_5OH(l)	2.43
H_2O(l)	4.18



$$\Delta H_{f,Pb} = 5.12\frac{kJ}{mol}$$

$$m.p._{Pb} = 327.3^{o}C$$

$$d_{Pb} = 11.34\frac{g}{cm^3}$$

Bullet technology
- Energy cost to melt (low)
- Rate of cooling (heat capacity) fast
- Surface tension and deformation**
- Density (for final use as a bullet)

2 bullets retained from 2 duels

Costiveness	(colic or constipation)
Fatigue	
Paranoia	
Unable to write	(peripheral nerve loss)

Uses of lead: summary to date:

Lead - useful material for environmental transport studies (isotopes)
Lead - Lead acetate – used to "sweeten" wines; **easily** made from lead and wine
Lead – lead azide (firing ranges)
(Electron transfer reactions; low melting points)
Lead – soldering (radiators, cars, electronics)
(Low vapor pressure)
Lead – malleable metal (roofs, downspots, stained glass)
(Metallic bonding, heat capacity)
Lead - Glasses and glazes (pottery) **Low energy requirements**
(Group 4 covalent network with extra electron pair = "spaghetti"
Lead - Solvent for other metals: purifying silver (Greek/Roman production)
(Group 4 covalent network with extra electron pair = "spaghetti"
Lead - Density of solid = good Xray shield
Lead – low melting point, high density = bullets (**low energy requirements**)

Toxicity of lead: summary to date:
Similar ionic size to Ca^{2+} Covalent and Ionic bonding
Same charge as Ca^{2+}
Electrostatic attraction of lead to calcium binding sites will be similar

Difference: has s^2 electrons – distorts binding in biomolecule

What is the learning point of harping on lead examples?

Ionic crystals

somewhat similar to metallic crystals

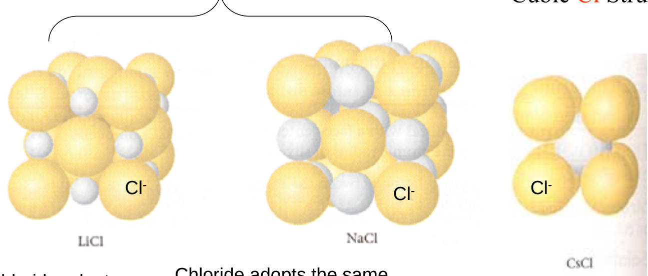
One ion forms, for example, a uniform cell
The second ion fits in between the first ion

Is this lithium or chloride?
How did you know?

What happens when the cation size is increased?

Face Centered Cubic Cl Structure

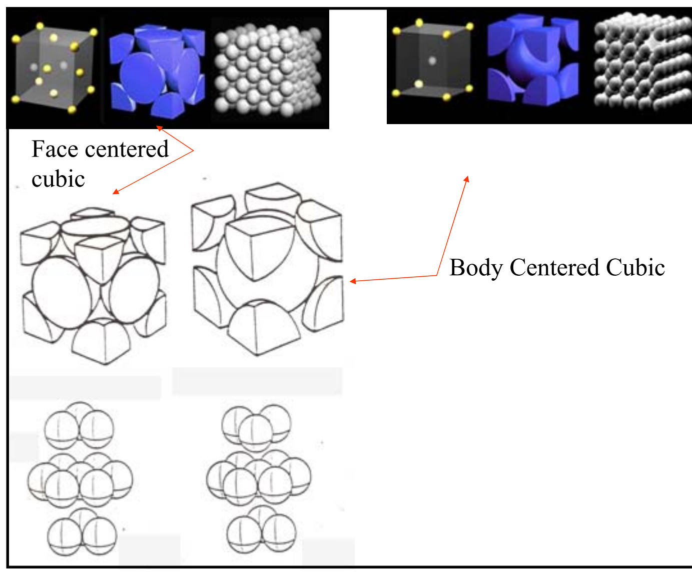
Body Centered Cubic Cl Structure



Chloride adopts a uniform structure and the smaller Li^+ fits in between to satisfy the charge.

Chloride adopts the same structure as for Lithium chloride but the cell is larger because of movement to accommodate the larger Sodium cation.

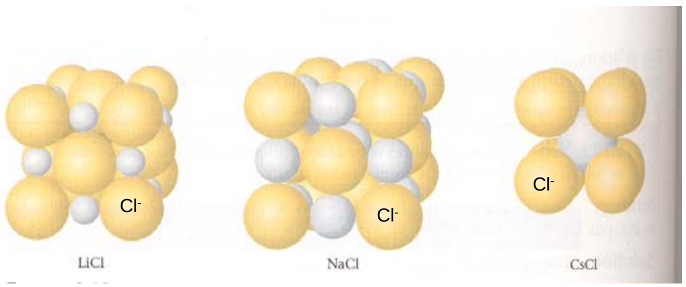
Cesium is so large that the same structure can not be adopted by chloride



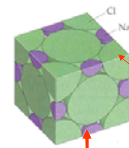
Ionic Bonds: Collection of Interactions (kJ/mol)

LiF – 1017		NaF	910	KF	808		
LiCl – 828		NaCl	788	KCl	701	CsCl	657
LiBr – 787		NaBr	732	KBr	671	CsI	600
LiI -737	NaI	682					
(625 -1550)							

What "rules" apply here?

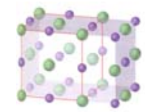


A warning: have to account for all the atoms and their individual Unit cells

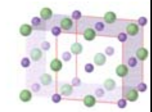


Cl-
Easy to "see" fcc
Fcc = 4 atoms

How about for Na$^+$?

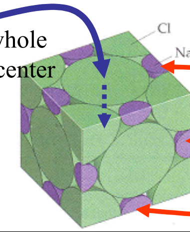


Cl^- fcc



Na^+ fcc

1 whole
In center



4 ¼ atoms at top

4 ¼ atoms at the "waist"

4 ¼ atoms at bottom

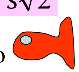
12 ¼ atoms= 3

Total atoms= 4
Fcc

Example: Determine the net number of Li+ and F- ions in the LiF unit cell, given that the structure is fcc (for both ions). Calculate its density given that s is 4.02A on a side.

Fcc = 4 for Li+
Fcc = 4 for F-
Total = 8 ions

$4r = s\sqrt{2}$ Necessary?

No 

$$d = \frac{g}{vol} = \frac{(4 moleculesLiF)\left(\frac{1moleLiF}{6.02x10^{23} atomsLiF}\right)\left(\frac{4(6.94)+4(19.0)}{moleLiF}\right)}{\left[(4.02\,\dot{A})\left(\frac{10^{-8}cm}{\dot{A}}\right)\right]^3}$$

$$d = \frac{g}{vol} = 2.65\frac{g}{cm^3}$$

"A" students work
(without solutions manual)
~ 10 problems/night.

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Office Hours W – F 2-3 pm

Module #12
Intermolecular Forces

Intermolecular Forces

1. Evidence for Intermolecular Forces
2. Phase Diagrams (briefly)
3. Liquid-Vapor Equilibrium
    1. Kinetic theory
    2. Gas escape as a way to measure liquid intermolecular forces
4. Boiling points related liquid Intermolecular Forces
    1. Dipole-dipole
    2. Dispersion
    3. H-bonding
    4. example application – heat capacity of lakes
5. Solid Intermolecular Forces
    1. Molecular Solids (Dispersion/ H-bonding)
    2. Network Covalent (Covalent) – example glass
    3. Ionic solids (Ion/ion)
    4. Metallic solids (metal bonding)
6. Structures of Crystals
    1. Unit Cells
    2. Common Metal Unit cells
        1. Calculate density of lead
    3. Common Ionic Solid Unit cells
        1. Calculate density of ionic solid

7. **Summary slides**

Summary Slide

bond energy (kJ/mol)

Ionic Bonds: Collection of Interactions (kJ/mol)

See also Table 8.2

LiF – 1017	NaF	910	KF	808		
LiCl – 828	NaCl	788	KCl	701	CsCl	657
LiBr – 787	NaBr	732	KBr	671	CsI	600
LiI -737 NaI	682					

(625 -1550)

Environmental/Geology

Covalent Bonds (kJ/mol)
74-1000 Organic Chemistry
See also Table 8.4
Also bio

Metallic bonds (kJ/mol)
100-800 Metallurgy

Other Interactions (kJ/mol)
H bonding: 17 to 40
Dispersion: 0.02 to 40
Dipole-dipole: 0-20
Self Assembled
Biology

Network forming covalent bonds (kJ/mol)

B-O	498
P-O	464
Ge-O	451
Si-O	443

Ceramics
Geology

Summary Slide

Vapor pressure over a solution is related to the energy required to escape the solution: this ideal leads to the following equation

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

Summary Slide

The boiling point
melting point
vapor pressure over a solid
are affected by intermolecular forces acting in liquids

Forces are:
dipole/dipole
dispersion (induced dipole/induced dipole)
hydrogen bonding: hydrogen bonding occurs with H-F; H-O; and H-N where FON have unbonded electrons

Intermolecular forces operating in solids are:
the above
covalent bonding
ionic bonding
metallic bonding

Because the type of bond is different the trends change when a material goes from solid to liquid to gas

Summary Slide

Relative interaction for ionic bonding can be calculated from Coulomb's law

$$E = \frac{k(Q_1)(Q_2)}{d}$$

$$d = r_{cation} + d_{anion}$$

Organization of molecules (or atoms) within a solid follow **14** different structural types

3 are most common for metals: simple cubic, face centered cubic and body-centered cubic

The structure of the cell affects empty volume and therefore, the melting point, density, and stability of the material

Ionic crystal structures are similar except cations occupy the space that was "empty" in metals