

Intermolecular Forces and Liquids and Solids

Chapter 11 Based on ppt from Mr. Rapp's AP chemistry website and modified for our needs

http://www.chemistrygeek.com/c hem2.htm

States of Matter

The fundamental difference between states of matter is the distance between particles.



close together

The States of Matter

Because in the solid and liquid states particles are closer together, we refer to them as condensed phases.



The States of Matter



Gas	Assumes both the volume and shape of its container
	Is compressible
	Flows readily
	Diffusion within a gas occurs rapidly
Liquid	Assumes the shape of the portion of the container it occupi
	Does not expand to fill container
	Is virtually incompressible
	Flows readily
	Diffusion within a liquid occurs slowly
Solid	Retains its own shape and volume
	Is virtually incompressible
	Does not flow
	Diffusion within a solid occurs extremely slowly

- The state a substance is in at a particular temperature and pressure depends on two antagonistic entities
 - The kinetic energy of the particles
 - The strength of the attractions between the particles

A **phase** is a

homogeneous part of the system in contact with other parts of the system but separated from them by a welldefined boundary.

Resources and Activities

- Textbook chapter 11 & ppt file
- Online practice quiz from Pearson
 chapter 11
- Lab activities
 - Molar mass of a volatile liquid
- POGIL activities:
 - Phase changes
 - Intermolecular Interactions
 - Vapor Pressure Curves
- Comprehensive tutorial and animations on Intermolecular forces:

http://www.chem.purdue.edu/gchelp/liquids /imf2.html Intermolecular Forces, Liquids and Solids (Chapter 11)

> Chemtour videos from W.W. Norton chapter 10 : intermolecular forces; phase diagrams; (capillary action)

http://www.wwnorton.com/college/ chemistry/gilbert2/contents/ch 10/studyplan.asp

Chapter 11 Animations from glencoe website for Chang's book:

http://glencoe.mcgrawhill.com/sites/0023654666/student _view0/chapter11/animations_cent er.html

Activities and Problem set for chapter 11 (due date)

TextBook ch. 11 - required for regents (in part), SAT II and AP exams

Lab activities: (determining molar mass of volatile liquids)

POGILS (3)

- Phase changes
- Intermolecular Interactions
- Vapor Pressure Curves

Online practice quiz ch 11 due by____

- Do chapter 11 GIST (p. 445, 446, 447, 448, 452, 454, 456, 461, 463) and
 Visualizing concepts problems 11.1-11.6 (6 total) write out questions and answers & show work. (NB Photocopy of questions is also acceptable)
- Do End of chapter exercises:11.9, .11,
 .13, .15, .17, .19, .21, .23, .25, .27, .29,
 .33, .35, .37, .39, .41, .43, .45, .47, .49,
 .51, .53, .55, .71, .73, .75, .85, .100

Animation on intermolecular forces, liquids, and solids to view in class and at home: http://www.wwnorton.com/college/chemistry/gilbert2/contents/ch10/studyplan.asp (Intermolecular forces)

Animations on vapor pressure and unit cells to view in class and at home:

In class preview and then Independent work - students to view animations & interactive activities (4 in total – 1 from Norton and 3 from the Glencoe site for Chang's book) and write summary notes on each. These summaries are to be included in your portfolio

http://glencoe.mcgrawhill.com/sites/0023654666/student_view0/chapter11/animations_center.html

Intermolecular Forces

Intermolecular forces are attractive forces **between** molecules. *Intramolecular forces* hold atoms together in a molecule.

Intermolecular vs Intramolecular

- 41 kJ to vaporize 1 mole of water (inter)
- 930 kJ to break all O-H bonds in 1 mole of water (intra)

Generally, **inter**molecular forces are much weaker than **intra**molecular forces. <u>"Measure" of intermolecular force</u> boiling point melting point ΔH_{vap} ΔH_{fus} ΔH_{sub} 11.2

Types of Bonding in Crystalline Solids

Force	Model	Basis of Attraction	Energy (kJ/mol)	Example
Bonding				
Ionic		Cation-anion	400-4000	NaCl
Covalent	•:•	Nuclei-shared e ⁻ pair	150-1100	н—н
Metallic		Cations-delocalized electrons	75-1000	Fe
Nonbonding (Inte	ermolecular)			.Н
Ion-dipole	•••••	Ion charge- dipole charge	40-600	Na+····O
H bond -	δ ⁻ δ ⁺ δ ⁻ -A—H	Polar bond to H- dipole charge (high EN of N, O, H	10-40 F)	:Ö— H·····Ю— н н н
Dipole-dipole	_	Dipole charges	5-25	I-CICI
Ion-induced dipole	J	Ion charge– polarizable e ⁻ cloud	3-15	$Fe^{2+\cdots}O_2$
Dipole-induced dipole	9	Dipole charge- polarizable e ⁻ cloud	2-10	H—CI····CI—CI
Dispersion (London)	<u></u>	Polarizable e ⁻	0.05 - 40	F-FFF

Molecular Interaction Flowchart



1. Hydrogen Bond (strongest)

The *hydrogen bond* is a special dipole-dipole interaction between the hydrogen atom in a polar N-H, O-H, or F-H bond and an electronegative O, N, or F atom. IT IS NOT A BOND.



A & B are N, O, or F











2. Ion-Dipole Forces

Attractive forces between an **ion** and a **polar molecule**. The magnitude of the attraction increases as either the charge of the ion or the magnitude of the dipole increases.

Ion-Dipole Interaction



3. Dipole-Dipole Forces

Attractive forces between **polar molecules**

Orientation of Polar Molecules in a Solid



4. Dispersion Forces – van der Walls forces/London forces (weakest)

Attractive forces that arise as a result of **temporary dipoles induced** in atoms or molecules





ion-induced dipole interaction



dipole-induced dipole interaction

Intermolecular Forces

4. Dispersion Forces Continued (see Animation)

Polarizability is the ease with which the electron distribution in the atom or molecule can be distorted.

Polarizability increases with:

- greater number of electrons
- more diffuse electron cloud



Dispersion forces usually increase with molar mass.

Melting Points of Similar Nonpolar Compounds		
Melting Point Compound (°C)		
CH₄	-182.5	
CF ₄	-150.0 -23.0	
CBr ₄ CI ₄	9 <mark>0.0</mark> 171.0	

н



What type(s) of intermolecular forces exist between each of the following molecules?

HBr

HBr is a polar molecule: dipole-dipole forces. There are also dispersion forces between HBr molecules.

CH₄

 CH_4 is nonpolar: dispersion forces.



 SO_2 is a polar molecule: dipole-dipole forces. There are also dispersion forces between SO_2 molecules.

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Intermolecular Forces Affect Many Physical Properties



The strength of the attractions between particles can greatly affect the properties of a substance or solution.

Viscosity

- Resistance of a liquid to flow is called viscosity.
- It is related to the ease with which molecules can move past each other.
- Viscosity:
 - Increases with stronger intermolecular forces
 - Increases with the size of the molecules
 - Decreases with increasing temperature.



Two methods of measuring viscosity:

- Timing the flow of a liquid through an opening.
- 2. A disk or drum type viscometer

Properties of Liquids

Cohesion is the intermolecular attraction between like molecules

Adhesion is an attraction between unlike molecules



Properties of Liquids

Surface tension is the amount of energy required to stretch or increase the surface of a liquid by a unit area. It results from the net inward force experienced by the molecules on the surface of a liquid.



Strong intermolecular forces

> High surface tension





- Vapor pressure increases with temperature.
- When the vapor pressure of a liquid equals the atmospheric pressure, the liquid boils.
- The normal boiling point of a liquid is the temperature at which its vapor pressure is 760 torr.



Due to both temperature effects and energy transfers from collisions, molecules on the surface of a liquid are able to gain sufficient kinetic energy to escape into the atmosphere



- At any temperature, some molecules in a liquid have enough energy to escape.
- As the temperature rises, the fraction of molecules that have enough energy to escape increases.



Kinetic energy

If the container is open to the atmosphere, the molecules simply escape. This process is called evaporation.

As molecules escape from the surface, they take energy with them resulting in a cooling effect on the liquid.



If the container is closed to the atmosphere, as more molecules escape the liquid, the pressure they exert increases.





Which Will Evaporate First?

What factors affect evaporation?



Which Will Evaporate First?

What factors affect evaporation?



Water methanol ethanol 2-propanol

Effect of molecular weight:

 $H_2O = 18$ $CH_3OH = 32$ $C_2H_5OH = 46$ $C_3H_8OH = 60$

Effect of polarity

- Vapor pressure increases with temperature.
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Vapor pressure of water versus temperature

Atmospheric pressure at various altitudes

Atmospheric pressure at various altitudes

	Feet	Meters	Atm	Mm Hg
Sea level 🗲	0	0	1.00	760
	328	100	0.99	752
	500	150	0.98	747
	656	200	0.97	743
	1000	300	0.96	734
	1312	400	0.95	725
	1500	450	0.94	719
	2000	600	0.93	706
Tucson 🗲	2500	750	0.91	694
	3000	900	0.89	681
	3500	1070	0.88	668
	4000	1220	0.86	655
	4500	1370	0.85	645
Denver 🗲	5000	1520	0.83	633
	5500	1680	0.81	620
	6000	1830	0.80	610
	6500	1980	0.78	597
	7000	2130	0.77	587
	7500	2290	0.76	577
	8000	2440	0.74	564
	8500	2590	0.73	554

Vapor pressure of water at various temperatures

Temp. °C.	0.0°	0.2°	0.40	0.6°	0.8°
	mm of Hg				
80	355,40	358.28	361.19	364.11	367.06
81	370.03	373.01	376.02	379.05	382.09
82	385.16	388.25	391.36	394.49	397.64
83	400.81	404.00	407.22	410.45	413.71
84	416.99	420.29	423.61	426.95	430.32
85	433.71	437.12	440,55	444.01	447.49
86	450,99	454.51	458.06	461.63	465.22
87	468.84	472.48	476.14	479.83	483.54
88	487.28	491.04	494.82	498.63	502.46
89	506.32	510.20	514.11	518.04	521.99
90	525.97	529.98	534.01	538.07	542.15
91	546.26	550,40	554.56	558.75	562.96
92	567.20	571.47	575.76	580.08	584.43
93	588.80	593.20	597.63	602.09	606.57
94	611.08	615.62	620.19	624.79	629.41
95	634.06	638.74	643.45	648.19	652.96
96	657.75	662.58	667.43	672.32	677.23
97	682.18	687.15	692.15	697.19	702.25
98	707.35	712.47	717.63	722.81	728.03
99	733.28	738.56	743.87	749.22	754.59
100	760.00	765.44	770.91	776.42	781.95

Phase Changes



Heating Curve



Energy Changes Associated with Changes of State



 Heat of Fusion: Energy required to change a solid at its melting point to a liquid.

Phase Changes

 $H_2O(s) \implies H_2O(g)$

Molar heat of sublimation (ΔH_{sub}) is the energy required to sublime 1 mole of a solid.

$$\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$$

(Hess's Law)


Molar heat of fusion (ΔH_{fus}) is the energy required to melt 1 mole of a solid substance.

<u>ب</u>					
	Molar Heats of Fusion for Selected Substances				
Ľ	Substance	Melting Point* (°C)	∆H _{fus} (kJ/mol)		
E A	Argon (Ar)	-190	1.3		
-	Benzene (C_6H_6)	5.5	10.9		
	Ethanol (C ₂ H ₅ OH)	-117.3	7.61		
	Diethyl ether $(C_2H_5OC_2H_5)$	-116.2	6.90		
	Mercury (Hg)	-39	23.4		
	Methane (CH ₄)	-183	0.84		
	Water (H ₂ O)	0	6.01		

* Measured at 1 atm.

The *boiling point* is the temperature at which the (equilibrium) vapor pressure of a liquid is equal to the external pressure.

The *normal boiling point* is the temperature at which a liquid boils when the external pressure is 1 atm.

11	Molar Heats of Vaporization for Selected Liquids				
LE	Substance	Boiling Point* (°C)	∆ <i>H</i> _{vap} (kJ/mol)		
AB	Argon (Ar)	-186	6.3		
F	Benzene (C_6H_6)	80.1	31.0		
	Ethanol (C ₂ H ₅ OH)	78.3	39.3		
	Diethyl ether $(C_2H_5OC_2H_5)$	34.6	26.0		
	Mercury (Hg)	357	59.0		
	Methane (CH ₄)	-164	9.2		
	Water (H ₂ O)	100	40.79		

* Measured at 1 atm.

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Energy Changes Associated with Changes of State



- Temperature remains constant at the melting and boiling points
 - Energy needed to break the intermolecular forces between the molecules.
 - Added kinetic energy for liquid or gaseous states.

The *equilibrium vapor pressure* is the vapor pressure measured when a dynamic equilibrium exists between condensation and evaporation



Molar heat of vaporization (ΔH_{vap}) is the energy required to vaporize 1 mole of a liquid.

Clausius-Clapeyron Equation

$$\ln P = - \frac{\Delta H_{\text{vap}}}{RT} + C$$

Is this equation on your AP reference tables?

C = constant (depends on P & T)

- P = (equilibrium) vapor pressure
- T =temperature (K)
- $R = \text{gas constant} (8.314 \text{ J/K} \cdot \text{mol})$





Vapor Pressure vs. Temperature

Phase diagrams display the state of a substance at various pressures and temperatures and the places where equilibria exist between phases.

Each substance has its own unique phase diagram.



Temperature



Where's Waldo?



Carbon Dioxide

Can you find... The Triple Point? **Critical pressure?** Critical temperature? Where fusion occurs? Where vaporization occurs? Melting point (at 1 atm)? Boiling point (at 6 atm)?

- The AB line is the liquid-vapor interface.
- It starts at the triple point (A), the point at which all three states are in equilibrium.



Temperature

The critical point (B) is the highest temperature and pressure where the liquid form of the substance can exist.

Above the critical temperature and critical pressure the liquid and vapor are indistinguishable from each other.



Temperature

- The AD line is the interface between liquid and solid.
- · The melting point at each pressure can be found along this line.
- The substance represented in this phase diagram tends to decrease in volume on freezing, the melting point line slants to the right.



- Below A the substance cannot exist in the liquid state.
- Along the AC line the solid and gas phases are in equilibrium.
- · This is called the sublimation curve.



Temperature

Phase Diagram of Water



- Note the high critical temperature and critical pressure:
 - These are due to the strong polar bonding between water molecules.
- Water expands on freezing, so the melting point line slants to the left.

Phase Diagram of Water



- The slope of the solid– liquid line is negative.
 - This means that as the pressure is increased at a temperature just below the melting point, water goes from a solid to a liquid.
 - This is why an ice skater can skate on ice.

Phase Diagram of Carbon Dioxide

Carbon dioxide cannot exist in the liquid state at pressures below 5.11 atm CO_2 sublimes at normal pressures.



Temperature (°C)

Phase Diagram of Carbon Dioxide

The low critical temperature and critical pressure for CO_2 make supercritical CO_2 a good solvent for extracting nonpolar substances (such as caffeine).

Supercritical CO_2 is being used for dry cleaning of clothing,



Temperature (°C)



Although these structures appear to be planar in the drawing, they are actually in a tetrahedral arrangement.

Solids



Amorphous—no particular order in the arrangement of particles.

Amorphous SiO₂

An *amorphous solid* does not possess a well-defined arrangement and long-range molecular order.

A *glass* is an optically transparent fusion product of inorganic materials that has cooled to a rigid state **without crystallizing**



Crystalline quartz (SiO₂) Non-crystalline quartz glass A crystalline solid possesses rigid and long-range order. In a crystalline solid, atoms, molecules or ions occupy specific (predictable) positions.

An *amorphous solid* does not possess a well-defined arrangement and long-range molecular order.

A *unit cell* is the basic repeating structural unit of a crystalline solid.



Crystalline Solids



Because of the order in a crystal, we can focus on the repeating pattern of arrangement called the unit cell.

Some variations of a cubic unit cell are diagrammed below.



Primitive cubic



Body-centered cubic



Face-centered cubic

Go to Glencoe animations chapter 11 part I and II packing spheres (units cells)

http://glencoe.mcgrawhill.com/sites/0023654666/student_view0/chapter11/ animations_center.html

The Cubic Unit Cell



Lattice points in a unit cell are considered to be at the nuclei of the atoms making up the unit cell. A simple (or primitive) unit cell contains one atom. Body-centered and face-centered unit cells contain two or more atoms enclosed in the unit cell.

Unit cell structures are determined by x-ray crystallography



Seven Types of Unit Cells



Simple cubic a = b = c $\alpha = \beta = \gamma = 90^{\circ}$



Tetragonal $a = b \neq c$ $\alpha = \beta = \gamma = 90^{\circ}$

Orthorhombic $a \neq b \neq c$ $\alpha = \beta = \gamma = 90^{\circ}$



Rhombohedral a = b = c $\alpha = \beta = \gamma \neq 90^{\circ}$



 $\begin{array}{l} \textbf{Monoclinic} \\ a \neq b \neq c \\ \alpha = \gamma = \textbf{90}^\circ, \, \beta \neq \textbf{90}^\circ \end{array}$



 $\begin{array}{c} \mathbf{Triclinic} \\ a \neq b \neq c \\ \alpha \neq \beta \neq \gamma \neq \mathbf{90}^{\circ} \end{array}$



Hexagonal $a = b \neq c$ $\alpha = \beta = 90^{\circ}, \gamma = 120^{\circ}$

Types of Bonding in Crystalline Solids

Type of Solid	Form of Unit Particles	Forces Between Particles	Properties	Examples
Molecular	Atoms or molecules	London dispersion forces, dipole-dipole forces, hydrogen bonds	Fairly soft, low to moderately high melting point, poor thermal and electrical conduction	Argon, Ar; methane, CH ₄ ; sucrose, C ₁₂ H ₂₂ O ₁₁ ; Dry Ice™, CO ₂
Covalent- network	Atoms connected in a network of covalent bonds	Covalent bonds	Very hard, very high melting point, often poor thermal and electrical conduction	Diamond, C; quartz, SiO ₂
Ionic	Positive and negative ions	Electrostatic attractions	Hard and brittle, high melting point, poor thermal and electrical conduction	Typical salts—for example, NaCl, Ca(NO ₃) ₂
Metallic	Atoms	Metallic bonds	Soft to very hard, low to very high melting point, excellent thermal and electrical conduction, malleable and ductile	All metallic elements—for example, Cu, Fe, Al, Pt

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Metallic		Cations–delocalized electrons	75–1000	Fe
Nonbonding (Inte	ermolecular)			
Ion-dipole		Ion charge– dipole charge	40-600	Na+·····O
H bond -	δ [−] δ ⁺ δ [−] -A−H·····:B−	Polar bond to H– dipole charge (high EN of N, O, H	10-40 ⁷)	:ö—н;ö—н н н
Dipole-dipole	__	Dipole charges	5-25	I−CII−CI
Ion-induced dipole	€	Ion charge– polarizable e [–] cloud	3-15	$\mathrm{Fe}^{2+}\cdots\mathrm{O}_{2}$
Dipoleinduced dipole	9	Dipole charge– polarizable e cloud	2-10	H—CI····CI—CI
Dispersion (London)	<u>)</u>)	Polarizable e ⁻ clouds	0.05-40	F-FFF

Types of Crystals

<u>Ionic Crystals</u> – Ion-Ion interactions are the strongest (including the "intermolecular forces" (H bonding, etc.)

- Lattice points occupied by cations and anions
- Held together by electrostatic attraction
- Hard, brittle, high melting point
- Poor conductor of heat and electricity



Ionic Solids

What are the empirical formulas for these compounds?

- (a) Green: chlorine; Gray: cesium
- (b) Yellow: sulfur; Gray: zinc
- (c) Green: calcium; Gray: fluorine



Types of Crystals

Molecular Crystals

- Lattice points occupied by molecules
- Held together by intermolecular forces
- Soft, low melting point
- Poor conductor of heat and electricity



Types of Crystals

<u>Covalent Crystals</u> – Stronger than IM forces but generally weaker than ion-ion

- Lattice points occupied by atoms
- Held together by covalent bonds
- Hard, high melting point
- Poor conductor of heat and electricity



11.6

Covalent-Network and Molecular Solids



- Graphite is an example of a molecular solid in which atoms are held together with van der Waals forces.
 - They tend to be softer and have lower melting points.

Covalent-Network and Molecular Solids



- Diamonds are an example of a covalentnetwork solid in which atoms are covalently bonded to each other.
 - They tend to be hard and have high melting points.

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Metallic Solids

- Metals are not covalently bonded, but the attractions between atoms are too strong to be van der Waals forces.
- In metals, valence electrons are delocalized throughout the solid.



Types of Crystals

<u>Metallic Crystals</u> – Typically weaker than covalent, but can be in the low end of covalent

- Lattice points occupied by metal atoms
- Held together by metallic bonds
- Soft to hard, low to high melting point
- Good conductors of heat and electricity



Molecular Orbitals in Lithium

The 2s orbitals in lithium atoms combine to form molecular orbitals. In a metallic solid, the orbitals are so close, they merge to form bands of molecular orbitals


Depending on the solid material, the bands can be continuous or separated

