

Chapter 10 LIQUIDS AND SOLIDS

Kevin Kolack, Ph.D. The Cooper Union HW problems: 2, 11, 13, 17, 21, 25, 31, 43, 51, 58, 63, 65, 69





PHASES OF MATTER



- Don't forget KMT
- A *phase* is a mechanically separate, homogeneous part of a heterogeneous system. (dictionary.com)



CH. 10 OUTLINE

- 10.1 Intermolecular Forces
- 10.2 Properties of Liquids
- 10.3 Phase Transitions
- 10.4 Phase Diagrams
- 10.5 The Solid Phase of Matter
- 10.6 Lattice Structures in Crystalline Solids



INTER VS INTRAMOLECULAR FORCES



- Intermolecular forces are attractive forces between molecules.
- Intramolecular forces hold atoms together in a molecule. (ie- bonds)
- Generally, intermolecular forces are much weaker than intramolecular forces.
 - 41 kJ to vaporize 1 mole of water (inter)
 - 930 kJ to break all O-H bonds in 1 mole of water (intra)
- Measures of intermolecular forces
 - boiling point (DHvap)
 - melting point (DHfus)
 - also DHsub



TYPES OF INTERMOLECULAR FORCES

- In order of decreasing strength:
- Ion-dipole (chapter 11)
- Dipole-dipole
 - Hydrogen bonding
- London/Dispersion

- van der Waals forces are a group of intermolecular forces
 - Sadly, the group varies from text to text

ION-DIPOLE FORCES (CHAPTER 11.2)



 Attractive forces between an ion and a polar molecule



WATER-ION INTERACTIONS - SOLVATION



DIPOLE-DIPOLE FORCES



Attractive forces between polar molecules

Orientation of polar molecules in a solid



DIPOLE-DIPOLE (CONT'D) FIG 10.9





- This image shows two arrangements of polar molecules, such as HCI, that allow an attraction between the partial negative end of one molecule and the partial positive end of another.
- Compare HCI (MW= 36.46g/mol; BP=188K) to F₂ (MW=38g/mol; BP=85K)

HYDROGEN BONDING



 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 the lone pair of electrons on a small, electronegative (O, N, or F) atom.



May be intra- or intermolecular.



WATER



Unique in that its solid is less dense than its liquid.











Valley techie who indued butter with coffee and created a diri

yes, it's called FATwater - is hetter than regular water. Valley has been about disruptive technology," says Dove Aspeny, creator of BATwater and a

DNA - FIGURE 10.13





- Two separate DNA molecules form a double-stranded helix in which each base pair is held together by hydrogen bonding.
- A and T share two hydrogen bonds, C and G share three. (credit: modification of work by Jerome Walker, Dennis Myts)

H-BONDING EFFECT ON BP (~FIG 10.12)



 Typically, BP increases with molecular weight due to increased dispersion forces....except...



QUESTION 11.2



- Which of the following can form hydrogen bonds with water? With itself?
- CH₃OCH₃
- CH₄
- F₂
- HCOOH
- Na+

ANSWER 11.2

- **Strategy** A species can form hydrogen bonds with water if it contains one of the three small, electronegative elements (F, O, or N) and/or it has a H atom bonded to one of these three elements.
- **Solution** There are no electronegative elements (F, O, or N) in either CH₄ or Na⁺. Therefore, only CH₃OCH₃, F₂, and HCOOH can form hydrogen bonds with water. Formic acid can do it 2 ways.



(LONDON) DISPERSION FORCES

Cation

Dipole

 Attractive forces that arise as a result of temporary dipoles (induced or instantaneous) in atoms or molecules

Induced dipole

Induced dipole

ion-induced dipole interaction

dipole-induced dipole interaction

DISPERSION FORCES (CONT'D)

 Larger and heavier atoms and molecules are more polarizable and exhibit stronger dispersion forces than do smaller and lighter atoms and molecules.

| Halogen | Molar Mass | Atomic Radius | Melting Point | Boiling Point |
|---------------------------|------------|---------------|---------------|---------------|
| fluorine, F ₂ | 38 g/mol | 72 pm | 53 K | 85 K |
| chlorine, Cl ₂ | 71 g/mol | 99 pm | 172 K | 238 K |
| bromine, Br ₂ | 160 g/mol | 114 pm | 266 K | 332 K |
| iodine, I ₂ | 254 g/mol | 133 pm | 387 K | 457 K |
| astatine, At ₂ | 420 g/mol | 150 pm | 575 K | 610 K |

Melting and Boiling Points of the Halogens

Table 10.1





DISPERSION FORCES (CONT'D)



- 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



Small contact area weakest attraction







neopentane boiling point: 9.5 °C





isopentane boiling point: 27 °C







n-pentane boiling point: 36 °C

QUESTION



• Which has the higher BP, N₂ or CO?

QUESTION



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

(a) HBr and H_2O

(b)Cl₂ and CBr₄

(c) I_2 and NO_3^-

(d) NH_3 and C_6H_6

ANSWER



 Strategy Classify the species into three categories: ionic, polar (possessing a dipole moment), and nonpolar. Keep in mind that dispersion forces exist between all species.

Solution

- (a)Both HBr and H_2O are polar molecules. Therefore, the intermolecular forces present are dipole-dipole forces, as well as dispersion forces.
- (b)Both Cl₂ and CBr₄ are nonpolar, so there are only dispersion forces between these molecules.
- (c) I₂ is a homonuclear diatomic molecule and therefore nonpolar, so the forces between it and the ion are ion-induced dipole forces and dispersion forces.
- (d) NH_3 is polar, and C_6H_6 is nonpolar. The forces are dipole-induced dipole forces and dispersion forces.

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VISCOSITY



- Viscosity is a measure of a fluid's resistance to flow.
- Strong intermolecular forces = high viscosity
- Lower T = higher viscosity



Viscosities of Common Substances at 25 °C

| Substance | Formula | Viscosity (mPa·s) |
|-----------------|--|-------------------|
| water | H ₂ O | 0.890 |
| mercury | Hg | 1.526 |
| ethanol | C₂H₅OH | 1.074 |
| octane | C ₈ H ₁₈ | 0.508 |
| ethylene glycol | CH ₂ (OH)CH ₂ (OH) | 16.1 |
| honey | variable | ~2,000–10,000 |
| motor oil | variable | ~50–500 |

Table 10.2

ADHESION AND COHESION



- Cohesion is the intermolecular attraction between like molecules
 - Responsible for round water droplets
- Adhesion is an attraction between unlike molecules
 - Responsible for capillary action ~Fig. 10.18





Attractive forces result in a spherical water drop that minimizes surface area; cohesive forces hold the sphere together; adhesive forces keep the drop attached to the web. (credit photo: modification of work by "OliBac"/Flickr)

SURFACE TENSION



- Surface tension is the amount of energy required to stretch or increase the surface of a liquid by a unit area.
- Strong intermolecular forces = High surface tension



CAPILLARY ACTION (FIGURE 10.20) open**stax**** Capillary tubes Capillary repulsion Capillary attraction

water

mercury

- Depending upon the relative strengths of adhesive and cohesive forces, a liquid may rise (such as water) or fall (such as mercury) in a glass capillary tube. The extent of the rise (or fall) is directly proportional to the surface tension of the liquid and inversely proportional to the density of the liquid and the radius of the tube.
- We will not do the math on page 535

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EFFECT OF T ON KE



• Remember, hotter is faster



 Temperature affects the distribution of kinetic energies for the molecules in a liquid. At the higher temperature, more molecules have the necessary kinetic energy, KE, to escape from the liquid into the gas phase.

DYNAMIC EQUILIBRIUM & VAPOR PRESSURE



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





 In a closed container, dynamic equilibrium is reached when the rate of molecules escaping from the liquid to become the gas eventually equals the rate of gas molecules entering the liquid. When this equilibrium is reached, the vapor pressure of the gas is constant, although the vaporization and condensation processes continue.

BOILING POINT



- 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.



 The boiling points of liquids are the temperatures at which their equilibrium vapor pressures equal the pressure of the surrounding atmosphere. Normal boiling points are those corresponding to a pressure of 1 atm (101.3 kPa.)





What happens to the BP of a liquid at lower external pressure?



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SOLID-LIQUID EQUILIBRIA

 The melting point of a solid or the *freezing point* of a liquid is the temperature at which the solid and liquid phases coexist in equilibrium.

$H_2O(s) \rightleftharpoons H_2O(l)$



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ENTHALPY OF PHASE CHANGES

- Just as it takes (or releases) energy to heat (or cool) a liquid, it takes/releases energy to change a phase.
- Yes, we skipped the thermo chapter...



RELATING VP AND AH

Molar heat of vaporization (
 \(\Delta H_{vap}\)) is the energy required to vaporize 1
 mole of a liquid at its boiling point.







QUESTION



 Diethyl ether is a volatile, highly flammable organic liquid that is used mainly as a solvent.

 The vapor pressure of diethyl ether is 401 mmHg at 18°C. Calculate its vapor pressure at 32°C.

ANSWER



- **Strategy** We are given the vapor pressure of diethyl ether at one temperature and asked to find the pressure at another temperature. Therefore, we need Equation (11.5).
- **Solution** Table 11.6 tells us that $\Delta H_{vap} = 26.0$ kJ/mol. The data are

$$P_1 = 401 \text{ mmHg}$$
 $P_2 = ?$ $T_1 = 18^{\circ}\text{C} = 291 \text{ K}$ $T_2 = 32^{\circ}\text{C} = 305 \text{ K}$

• From Equation (11.5) we have

$$\ln \frac{401}{P_2} = \frac{26,000 \text{ J/mol}}{8.314 \text{ J/K} \cdot \text{mol}} \left[\frac{291 \text{ K} - 305 \text{ K}}{(291 \text{ K})(305 \text{ K})} \right]$$
$$= -0.493$$

ANSWER (CONT'D)



Taking the antilog of both sides (see Appendix 4), we obtain



Hence

 Check We expect the vapor pressure to be greater at the higher temperature. Therefore, the answer is reasonable.



HEATING CURVE



 A typical heating curve for a substance depicts changes in temperature that result as the substance absorbs increasing amounts of heat. Plateaus in the curve (regions of constant temperature) are exhibited when the substance undergoes phase transitions.

QUESTION



 Calculate the amount of energy (in kilojoules) needed to heat 346 g of liquid water from 0°C to 182°C.

Assume that the specific heat of water is 4.184
 J/g•°C over the entire liquid range and that the specific heat of steam is 1.99 J/g•°C.

ANSWER



- Strategy The heat change (q) at each stage is given by q = mc∆t (see p. 546), where m is the mass of water, c is the specific heat, and ∆t is the temperature change.
- If there is a phase change, such as vaporization, then q is given by $n\Delta H_{\rm vap}$, where n is the number of moles of water.
- Solution
- Step 1: Heating water from 0°C to 100°C

$$q_1 = ms\Delta t$$

= (346 g)(4.184 J/g · °C)(100°C - 0°C)
= 1.45 × 10⁵ J
= 145 kJ

ANSWER (CONT'D)



• Step 2: Evaporating 346 g of water at 100°C (a phase change) On p. 541 we see $\Delta H_{vap} = 40.79$ kJ/mol for water, so

$$q_2 = 346 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} \times \frac{40.79 \text{ kJ}}{1 \text{ mol H}_2\text{O}}$$
$$= 783 \text{ kJ}$$

• Step 3: Heating steam from 100°C to 182°C

$$q_{3} = ms\Delta t$$

= (346 g) (1.99 J/g · °C) (182°C - 100°C)
= 5.65 × 10⁴ J
= 56.5 kJ

ANSWER (CONT'D)



• The overall energy required is given by

$$q_{\text{overall}} = q_1 + q_2 + q_3$$

= 145 kJ + 783 kJ + 56.5 kJ
= 985 kJ

 Check All the qs have a positive sign, which is consistent with the fact that heat is absorbed to raise the temperature from 0°C to 182°C. Also, as expected, much more heat is absorbed during the phase transition.

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11.9 PHASE DIAGRAM



 A phase diagram summarizes the conditions at which a substance exists as a solid, liquid, or gas.









 Freeze-dried foods, like this ice cream, are dehydrated by sublimation at pressures below the triple point for water. (credit: "lwao"/Flickr)

REGELATION OF ICE/WATER





ice cube

copper wire

CHILL OUT WITH THE PERFECT ICE SPHERE.

The solid aluminum Spherical Ice Maker marries science and design to perfectly chill your beverage of choice. The process is easy! Simply use the included ice mold to make a small ice slab in your freezer. Then place the slab into the Spherical Ice Maker. The weight of the machine at room temperature compresses the ice into a 2.6" sphere in less than a minute. The sphere has less surface area than a cube — so it melts more slowly and evenly to chill drinks without watering them down. Includes drip pan, tongs and 4 ice molds.

Spherical Ice Maker 202668 \$399.99









 The immense pressures beneath glaciers result in partial melting to produce a layer of water that provides lubrication to assist glacial movement. This satellite photograph shows the advancing edge of the Perito Moreno glacier in Argentina. (credit: NASA)

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• At 1 atm $CO_2(s) \rightarrow CO_2(g)$





P VS BP AND MP



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CRITICAL T AND P



- The *critical temperature* (T_c) is the temperature above which the gas cannot be made to liquefy, no matter how great the applied pressure.
- The critical pressure (P_c) is the minimum pressure that must be applied to bring about liquefaction at the critical temperature.

| Substance | <i>T</i> _c (°C) | P _c (atm) |
|--|----------------------------|----------------------|
| Ammonia (NH ₃) | 132.4 | 111.5 |
| Argon (Ar) | -186 | 6.3 |
| Benzene (C ₆ H ₆) | 288.9 | 47.9 |
| Carbon dioxide (CO ₂) | 31.0 | 73.0 |
| Diethyl ether (C2H5OC2H5) | 192.6 | 35.6 |
| Ethanol (C ₂ H ₅ OH) | 243 | 63.0 |
| Mercury (Hg) | 1462 | 1036 |
| Methane (CH ₄) | -83.0 | 45.6 |
| Molecular hydrogen (H2) | -239.9 | 12.8 |
| Molecular nitrogen (N2) | -147.1 | 33.5 |
| Molecular oxygen (O ₂) | -118.8 | 49.7 |
| Sulfur hexafluoride (SF ₆) | 45.5 | 37.6 |
| Water (H ₂ O) | 374.4 | 219.5 |





Soaked beans

Water





(b) The schematic shows a typical decaffeination process involving supercritical carbon dioxide.

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solvents of varying polarities.

FIGURE 10.35





(a) A sealed container of liquid carbon dioxide slightly below its critical point is heated, resulting in
 (b) the formation of the supercritical fluid phase. Cooling the supercritical fluid lowers its temperature and pressure below the critical point, resulting in the reestablishment of separate liquid and gaseous phases (c and d). Colored floats illustrate differences in density between the liquid, gaseous, and supercritical fluid states. (credit: modification of work by "mrmrobin"/YouTube)

CRITICAL PHENOMENON OF SF₆











 $T < T_c$

 $T > T_c$

 $T \sim T_c$

 $T < T_c$

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SOLIDS



- 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.



SEVEN BASIC TYPES OF UNIT CELLS



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http://www.compoundchem.com/2014/12/10/snowflakes/



SIMPLE CUBIC UNIT CELLS

x

(a)



(c)

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(b)

BODY-CENTERED CUBIC (BCC) UNIT CELLS

(a)



(c)

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(b)

65

ATOMIC POSITIONS IN CELLS

open**stax**" COLLEGE

Corner, edge-centered and face-centered atoms

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CHEMISTRY 151 - KOLACK

Chapter 11

Sections 11.5 - 11.7

Intermolecular Forces – Liquids and Solids








TYPES OF CRYSTALS – IONIC

- Lattice points occupied by cations and anions
- Held together by electrostatic attraction
- Hard, brittle, high melting point

CsCl

Poor conductor of heat and electricity







QUESTION



How many Na⁺ and Cl⁻ ions are in each NaCl

unit cell?



ANSWER



- Solution NaCl has a structure based on a face-centered cubic lattice. One whole Na⁺ ion is at the center of the unit cell, and there are twelve Na⁺ ions at the edges. Because each edge Na⁺ ion is shared by four unit cells, the total number of Na⁺ ions is 1 + (12 × ¼) = 4.
- Similarly, there are six Cl⁻ ions at the face centers and eight Cl⁻ ions at the corners. Each face-centered ion is shared by two unit cells, and each corner ion is shared by eight unit cells, so the total number of Cl⁻ ions is (6 × ½) + (8 × 1/8) = 4. Thus, there are four Na⁺ ions and four Cl⁻ ions in each NaCl unit cell.

• Check This result agrees with sodium chloride's empirical formula.





Courtesy of Edmund Catalogs

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Courteey Railway Technical Research Institute, Tokyo, Japan

COVALENT CRYSTALS

- Lattice points occupied by atoms
- Held together by covalent bonds
- Hard, high melting point





MOLECULAR CRYSTALS

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



benzene



METALLIC CRYSTALS

- Lattice points occupied by metal atoms
- Held together by metallic bonds

nucleus &

inner shell *e*⁻

mobile "sea"

of e

- Soft to hard, low to high melting point
- Good conductors of heat and electricity



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CRYSTAL STRUCTURES OF METALS



| 1 1A | | | | Copyr | ight © The | McGraw-I | Hill Compa | anies, Inc. | Permissio | n required | for reproc | uction or o | lisplay | | | | 18 8A |
|---------|---------|---------|---------|------------------|----------------|----------|------------|------------------|----------------------|------------|------------|-------------|----------|----------|----------|----------|----------|
| | 2 2A | | | Hexag close-j | onal packed | | | Body- cubic | centered | | | 13 3A | 14 4A | 15 5A | 16 6A | 17 7A | |
| Li | Be | | | Face-c cubic | entered | | | Other (see ca | structure aption) | s | | | | | | | |
| Na | Mg | 3 3B | 4 4B | 5 5B | 6 6B | 7 7B | 8 | 9 | 10 | 11 1B | 12 2B | Al | | | | | |
| к | Ca | Sc | Ti | v | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | | | | | |
| Rb | Sr | Y | Zr | Nb | Мо | Te | Ru | Rh | Pd | Ag | Cd | In | Sn | | | | |
| Cs | Ba | La | Hf | Та | W | Re | Os | Ir | Pt | Au | Hg | TI | Pb | | | | |
| | | | | | | | | | | | | | | | | | |

CRYSTALS – A SUMMARY



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| Table 11.4 | Types of Crystals and General Properties | | | | | | | | | | |
|--------------------|---|---|---|--|--|--|--|--|--|--|--|
| Type of Crystal | Force(s) Holding the Units Together | General Properties | Examples | | | | | | | | |
| Ionic | Electrostatic attraction | Hard, brittle, high melting point, poor conductor of heat and electricity | NaCl, LiF, MgO, CaCO ₃ | | | | | | | | |
| Covalent | Covalent bond | Hard, high melting point, poor conductor of heat and electricity | C (diamond), [†] SiO ₂ (quartz) | | | | | | | | |
| Molecular* | Dispersion forces, dipole-dipole forces, hydrogen bonds | Soft, low melting point, poor conductor of heat and electricity | Ar, CO ₂ , I ₂ , H ₂ O, C ₁₂ H ₂₂ O ₁₁ (sucrose) | | | | | | | | |
| Metallic | Metallic bond | Soft to hard, low to high melting point, good conductor of heat and electricity | All metallic elements; for example, Na, Mg, Fe, Cu | | | | | | | | |

*Included in this category are crystals made up of individual atoms. [†]Diamond is a good thermal conductor.

AMORPHOUS SOLIDS AND GLASSES



- 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)





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HW problems:

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