

Solids

ENTROPY

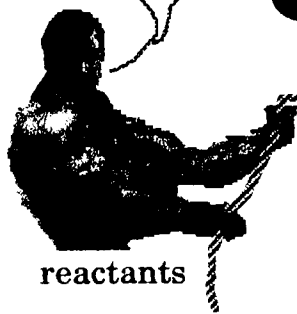
ENTHALPY

Liquids

&

**Phase
changes**

I'll be back!



reactants

*Entropy has a way of
catching up with you!*

Look Ma, an equilibrium!

Unit 10

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*Old chemists never die, they
just reach equilibrium!*



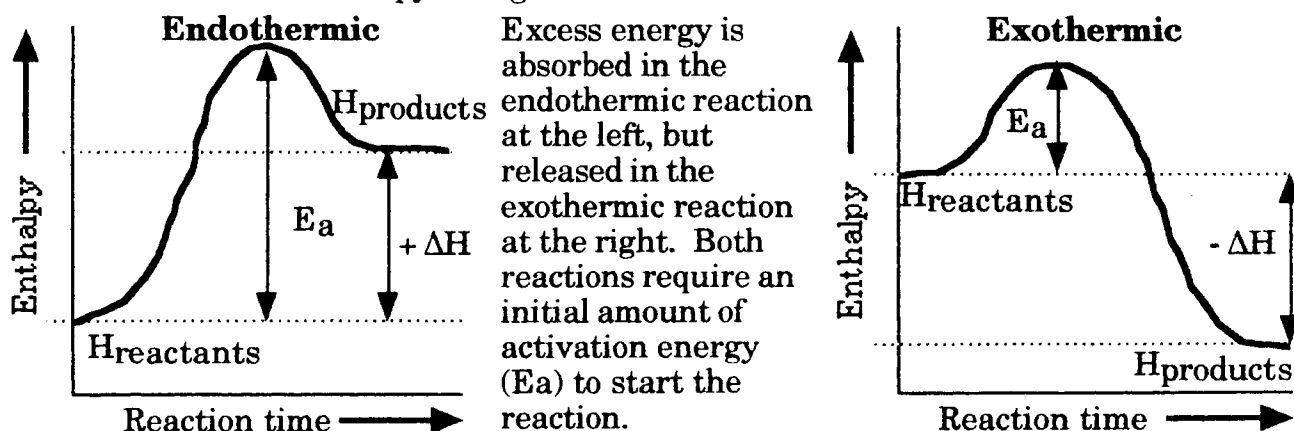
products

*Some like it with a high
negative enthalpy change!*

Unit 10: Solids, Liquids & Phase Changes

I. Enthalpy vs. Entropy.....The Driving Forces

In nature, physical and chemical changes tend to occur spontaneously in order to obtain either a lower energy level or a greater amount of disorder. For example, the batteries in your Walkman™ lose their energy all too quickly and go "dead", and it's almost impossible for your Mom to keep your bedroom neat and organized. The change in energy of a system is determined by its change in **enthalpy**, ΔH . This is a measure of the difference between the heat energy of the reactants and products in a system that undergoes a chemical or physical change at constant pressure. The value of ΔH is positive for endothermic reactions and negative for exothermic reactions. The graphs below illustrate the enthalpy changes that can occur:



Since exothermic reactions result in the formation of products with lower energy levels, they are usually spontaneous changes. Endothermic reactions require a continuous input of energy to proceed, but some may occur spontaneously because of a large increase in the disorder, or randomness, of the system. The change in the amount of disorder of a system is called the **entropy**, symbolized by ΔS . Molecules in the gaseous state have the greatest amount of entropy, due to their random, zig-zag motion. In the solid state, the molecules are held in fixed positions, with a definite pattern of arrangement, and have the least amount of entropy of the three states of matter. An estimate of the ΔS of a system can be made based on the change in the number of moles of gaseous reactants compared to the gaseous products. The greater the number of moles of gas, the greater the entropy. An example of a spontaneous endothermic reaction is the sublimation of solid carbon dioxide, dry ice. The large increase in the entropy of $\text{CO}_2(\text{g})$ causes the spontaneous reaction to occur, even though the enthalpy(heat energy) of the system increases.

Chemists use a relationship, called **Gibbs free energy**, to predict whether or not a reaction will be spontaneous. The change in Gibbs free energy, ΔG , is equal to the change in enthalpy for the reaction minus the change in entropy multiplied by the Kelvin temperature. The equation is written as: $\Delta G = \Delta H - T\Delta S$.

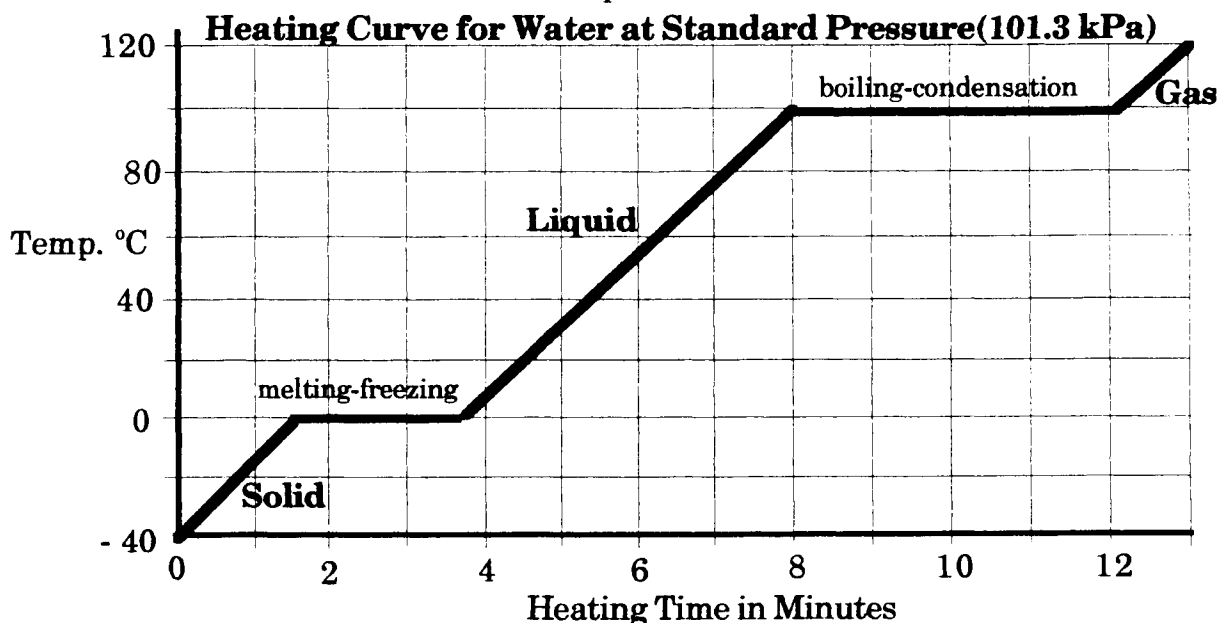
A reaction will be spontaneous **only if** the value of ΔG is negative. If ΔG is positive, then a constant input of energy is required to make the reaction occur.

Problem:

Describe the changes in the enthalpy, entropy and Gibbs free energy that occur during the combustion of charcoal to cook hamburgers on a barbecue grill.

II. Energy and Phase Changes

The temperature remains constant during the melting of a solid or the boiling of a liquid, because the energy that is added is being absorbed to separate the particles and overcome attractive forces (kinetic energy is being converted into potential energy). The same amounts of energy are released when a liquid freezes and a gas condenses, as the attractive forces begin to become effective. This is shown graphically in the heating curve below for distilled water at standard pressure conditions.



The normal melting point of ice is the same as the freezing point of water, 0°C. Water will boil at 100°C (when under standard atmospheric pressure), which is the same temperature at which water vapor will condense. A specific amount of heat energy is required to cause each change in temperature or each phase change. For the portions of the curve where the temperature is rising, the energy needed is determined by using the equation with the specific heat values. Specific heat is the amount of energy required to raise the temperature of 1 g of a particular substance by 1°C.

Heat energy(q) = mass of substance \times change in temperature \times specific heat

Sample Problem 1:

How much heat energy is required to warm 18.0 g of ice from -40.0°C to the melting point of 0.0°C? For ice, the specific heat, C_p , is 2.06 J/g·°C.

ANS: Heat energy = (18.0 g ice) (0.0°C - (-40.0°C)) (2.06 J/g·°C) = 1480J

Sample Problem 2:

How much heat energy is required to warm the 18.0 g of water from the melting point of 0.0°C to the boiling point of 100.0°C? For water, there is a different specific heat, where C_p = 4.18 J/g·°C*. *Notice that the water and ice have their own specific heat values.

ANS: Heat energy = (18.0 g water) (100.0°C - 0.0°C) (4.18 J/g·°C) = 7520J

Problem 1:

How much heat energy is required to warm 18.0 g of the steam from the boiling point of 100.0°C to the final temperature of 120.0°C? For steam, the specific heat(C_p) is 2.02 J/g·°C.

ANS: 727 J

During the actual phase changes, the temperature(average KE) remains constant, but the potential energy of the molecules increases. As the attractive forces between the molecules are broken, they gain a greater freedom of movement. The energy required to melt one gram of a specific substance at its melting point is called the **heat(enthalpy) of fusion**. For ice this value is 334 J/g.

The equation to calculate the heat required to break the intermolecular attractions and melt a known mass of ice is: **$q = \text{mass of ice} \times \text{heat of fusion}$**

The energy required to vaporize(boil) one gram of a specific substance at its boiling point is called the **heat(enthalpy) of vaporization**. For water this value is 2260 J/g.

The equation to calculate the heat required to boil a known mass of water is:

$$q = \text{mass of water} \times \text{heat of vaporization}$$

Problem 2:

How much more heat energy is required to boil the 18.0 g of water as compared to the heat energy needed to melt the 18.0 g of the ice?

ANS: 34700 J more energy

Problem 3:

How much heat energy will be released when 75.0 g of water at a room temperature of 25.0°C is cooled down to 0°C and completely frozen?

ANS: 32900 J

III. Hess's Law

It is possible to predict the overall enthalpy change for a reaction, called the *heat of reaction* (ΔH_{rxn}), without having to actually perform the experiment. **Hess's Law** states that the net enthalpy change for a reaction is the same whether the reaction takes place in one step or in a sequence of several steps. The ΔH_{rxn} will be the sum of the enthalpy changes of each individual step.

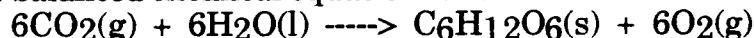
In order to create a reference point for enthalpy values, chemists have agreed to assign a zero energy value to all elements in their normal state at standard pressure. The energy change that occurs when a compound is formed from a mixture of its elements can then be determined. Some standard enthalpies(heats) of formation, ΔH_f , for common compounds are shown in the chart below:

Compound	Chemical Formula	ΔH_f , at 25°C (kJ/mole)
water	H ₂ O(l)	- 286
water	H ₂ O(g)	- 242
carbon monoxide	CO(g)	- 110
carbon dioxide	CO ₂ (g)	- 394
glucose	C ₆ H ₁₂ O ₆ (s)	- 1268
methane	CH ₄ (g)	- 75
ethyne(acetylene)	C ₂ H ₂ (g)	+ 227
ammonia	NH ₃ (g)	- 46

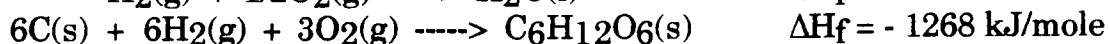
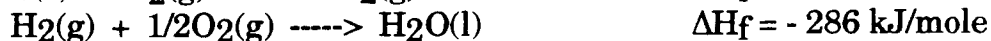
Sample Problem:

What is the heat of reaction for the production of glucose and oxygen from liquid water and carbon dioxide gas during photosynthesis?

Step 1: Write the balanced chemical equation for the desired overall reaction.



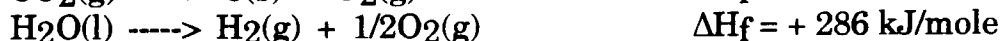
Step 2: Write the balanced enthalpy of formation equation for each compound found in the reactants and products and include the ΔH_f values.



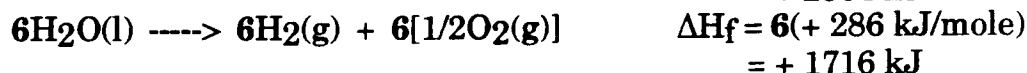
Note that the $\text{O}_2(\text{g})$ formed is an element, and as such, has a $\Delta H_f = 0 \text{ kJ/mole}$

Step 3: Re-arrange the enthalpy of formation equations so that they add up to equal the balanced overall reaction. If a desired reactant or product is on the wrong side of the reaction, reverse the equation and change the sign of the ΔH_f value. Also multiply the enthalpy of formation equations by the appropriate coefficients so that the reactants and products have the same coefficients as they have in the balanced overall reaction.

Since both the $\text{CO}_2(\text{g})$ and the $\text{H}_2\text{O}(\text{l})$ are reactants, these equations must be reversed and the ΔH_f values are changed to + signs.

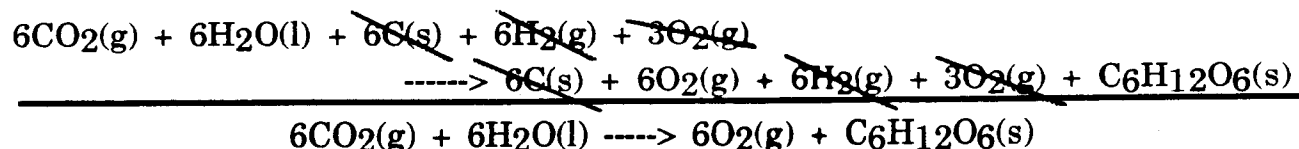


In the overall reaction, 6 moles of both $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ are needed to form the glucose, so each of these equations must be multiplied by 6.



No change for glucose: $6\text{C}(\text{s}) + 6\text{H}_2(\text{g}) + 3\text{O}_2(\text{g}) \rightarrow \text{C}_6\text{H}_{12}\text{O}_6(\text{s}) \quad \Delta H_f = -1268 \text{ kJ/mole}$

Step 4: Add the enthalpy of formation equations and the ΔH_f values. Simplify by eliminating terms that appear on both sides of the equation.



$$\Delta H_{\text{rxn}} = (+2364 \text{ kJ}) + (+1716 \text{ kJ}) + (-1268 \text{ kJ/mole}) = +2812 \text{ kJ}$$

Photosynthesis is an endothermic reaction that requires a constant input of energy(sunlight) in order to produce the products of glucose and oxygen gas.

Problem:

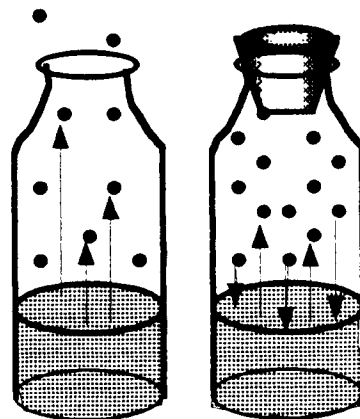
Use Hess's Law to calculate the heat energy that would be produced by burning 1 mole of ethyne in the lab to form $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$.

$$\text{ANS: } \Delta H_{\text{rxn}} = -1257 \text{ kJ/mole}$$

IV. Phase Changes and Equilibrium

At the conditions which cause a change in phase of a substance, there exist two opposing forces. One force results from the addition of energy to break apart the particles and the other force involves the particles being overcome by the attractive forces between them and releasing energy. When the **rates** at which the two opposing forces occur become equal, then a state of **dynamic equilibrium** exists.

In the open bottle on the left, molecules with high kinetic energy can break away from the liquid's attractive forces and "jump" out of the liquid as a gas (evaporation). When a stopper is placed in the bottle on the right, the concentration of gas molecules increases, and the resulting vapor pressure makes it more difficult for other liquid molecules to evaporate. Eventually, the rate of evaporation will become equal to the rate of condensation of the gas molecules, and a state of equilibrium will exist. At this point, the air is said to be **saturated** with the maximum amount of gas possible at the experimental temperature.



The equation to represent this physical equilibrium is: **liquid + energy** \rightleftharpoons **gas**

Le Chatelier's Principle states that if a stress is applied to a system at equilibrium, the system readjusts to form either more products or more reactants so that the stress is reduced and an equilibrium is re-established.

For example, if the closed bottle is heated in a hot water bath, the extra heat energy absorbed will cause more of the liquid to evaporate. As the volume of liquid decreases and more gas is produced, the vapor pressure above the surface will increase. The increased vapor pressure will increase the rate of condensation until it, once again, equals the increased rate of evaporation. At this point, an equilibrium is re-established.

Problem:

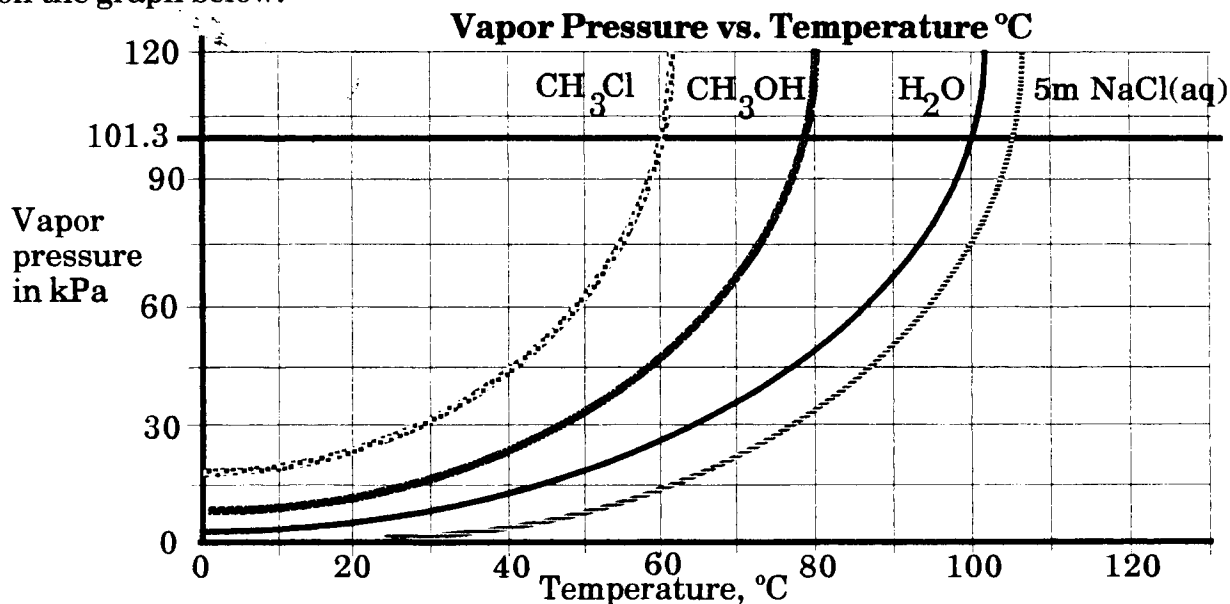
Can an equilibrium condition exist in the open bottle of water? Explain why or why not.

Other phase changes have similar equilibrium expressions to represent them. The normal melting point of a solid is the temperature at which the vapor pressure of the solid and liquid phases are equal. This is written as: **solid + energy** \rightleftharpoons **liquid**

Some solids, such as dry ice and iodine, change directly to a gas when heated by a process called **sublimation**. This is written as: **solid + energy** \rightleftharpoons **gas**

The normal boiling point of a liquid is the temperature at which the vapor pressure of the escaping liquid molecules becomes equal to (or greater than) standard atmospheric pressure of 101.3 kPa. Liquids that have stronger intermolecular attractions must be heated to a higher temperature before boiling will occur. The boiling point of a liquid is lowered when the atmospheric pressure is lowered, such as in the Rocky Mountains. At higher elevations, the atmosphere is thinner and exerts less pressure, so you need to cook food longer in water that boils at a temperature below 100°C. When atmospheric pressure increases, such as in a pressure cooker, the temperature can get well above 100°C without the water reaching its boiling point. Therefore, food cooks faster in a pressure cooker or covered pot. Compare the boiling points of the various liquids shown

on the graph below:



Note: The 5 m NaCl(aq) is a 5 molal solution. **Molality** = # moles solute/kg solvent

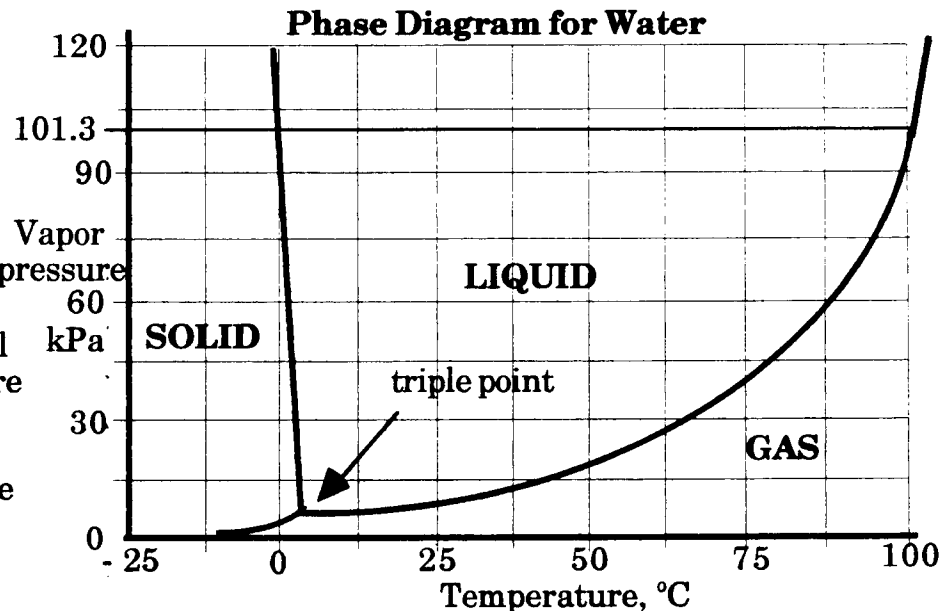
The normal boiling points of the four liquids shown on the vapor pressure curve are:
 CH₃Cl = 60°C; CH₃OH = 78°C; H₂O = 100°C; 5 m NaCl(aq) = 105°C

Problems:

1. What is the boiling point of water at an atmospheric pressure of 60 kPa?
2. How much vapor pressure does methanol, CH₃OH, exert at a temperature of 25°C?
3. Explain why chloromethane, CH₃Cl, has the lowest normal boiling point.
4. What effect does the addition of salt, NaCl, have on the normal boiling point of water?

V. Phase Diagrams

A phase diagram summarizes the relationships among temperature, pressure and physical state of a particular substance. Each line represents the conditions at which a phase change occurs. There is a point where all three states of matter are in equilibrium with each other. This is called the triple point. Examine the phase diagram for water shown at the right.



By using a phase diagram, it is easy to determine what state a substance will exist as, under given experimental conditions. Water, for example, is a liquid at room

temperature (about 25°C) and standard pressure of 101.3 kPa. As the temperature is increased, boiling begins at 100°C, as you cross the liquid-gas curve. Freezing will occur as the temperature is reduced to below 0°C, and you cross the liquid-solid curve. Water could be changed into all gas vapor at a temperature of 75°C if the atmospheric pressure is reduced to less than 40 kPa. By the same token, water vapor can be condensed into liquid water at temperatures above 100°C by increasing the atmospheric pressure on it. There is a point where a gas cannot be liquefied, no matter how much pressure is exerted on it. This is called the **critical temperature** and for water this has a value of 374°C. At this temperature, it would require 22,100 kPa of pressure (called the **critical pressure**) to compress the steam and allow the attractive forces to take effect. At any temperature above the critical temperature value, the kinetic energy of the molecules is so great and the intermolecular collisions are too forceful to allow the gas to condense.

Problems:

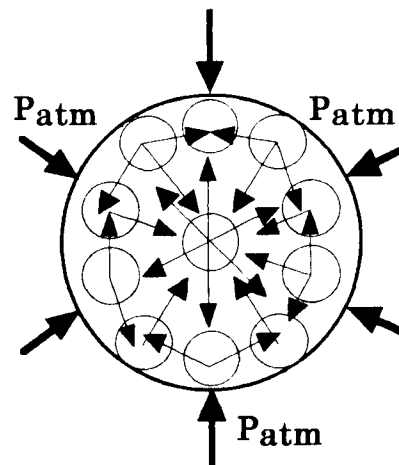
1. What happens to ice at 0°C when the blade from an ice skate increases the pressure exerted on the ice to 450 kPa?
2. Explain what changes occur when an ice cube at - 5°C is placed in a vacuum and the atmospheric pressure is reduced to almost 0 kPa.
3. Carbon (IV) oxide has a triple point that occurs at 518 kPa of pressure and - 56.6°C. What state does this substance exist in at normal laboratory conditions? Explain.
4. Describe what 2 changes you would make in experimental conditions in order to liquefy any gas.

VI. Viscosity and Surface Tension in Liquids

Viscosity is the "friction" or resistance to motion that exists between the molecules of a liquid as they move past each other when being poured. Pancake syrup has a high viscosity because of the large concentration of sugar molecules which have many sites for hydrogen bonding. The strong attractive forces help to keep the syrup on top of your pancakes, rather than running off onto the plate. The syrup can be made to flow more readily by warming it to give the molecules greater kinetic energy to break away from each other. In general, as the temperature increases, the viscosity of a liquid decreases.

Surface tension of a liquid is the apparent elasticity of its surface due to unbalanced forces acting upon it. The diagram below of a drop of liquid shows the forces acting on it:

When a small amount of liquid falls through the air, it forms spherical-shaped drops to minimize the amount of surface area that is exposed to the atmospheric pressure. The molecules in the interior of the drop are equally pulled in all directions. Whereas, a molecule on the surface is only attracted by particles in the interior, so there is a net inward pull. Larger amounts of liquid inside a container create a "skinlike" layer as the surface molecules experience a net downward pulling force. The strength of the surface tension is dependent upon the strength of the intermolecular attractions. A needle will be able to float on the surface of water, but it sinks in vegetable oil, which is primarily nonpolar.



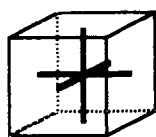
If a thin, glass tube is placed into a liquid, the liquid will move up the tube due to capillary rise caused by the attractions between the liquid molecules and the walls of the tubing. Water will have a high degree of surface tension and capillary rise because of its polar nature and extensive hydrogen bonding. Other liquids, such as nonpolar hexane, will have very little surface tension or capillary rise due to having much weaker intermolecular attractions. Capillary action is partly responsible for the rise of water and sap up the trunk of a tree and into the leaves.

Problem: Take-home Experiment

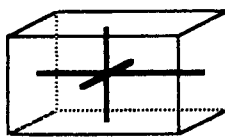
Take a drinking glass out of the kitchen cupboard at home and set it into a small bowl. Fill the glass completely with water to be level with the rim. Carefully push a penny through the surface of the water and drop it into the glass. Continue adding pennies until the water spills over the edge of the glass into the bowl. How many pennies does it take to break the surface tension of the water and make it spill out? Conduct 2 more experiments, by dissolving a heaping tablespoon of table salt in the water for the second trial and then add some dishwashing liquid to a fresh glass of water for the third trial. Make sure the glass is filled to the same level for each trial. Compare the number of pennies added in each trial. Which liquid has the weakest surface tension? Which has the strongest surface tension? Record your results below:

VII. Crystal Structure of Solids

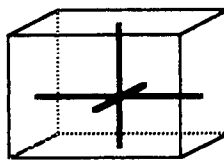
In true solids, the particles are arranged in a definite, rigid geometric pattern forming a **crystal**. The structure of the crystal (or space lattice) can be represented by a unit cell, which is the smallest unit of repetition illustrating the pattern of the entire crystal. Below are diagrams of the unit cell arrangements for the seven basic crystal structures:



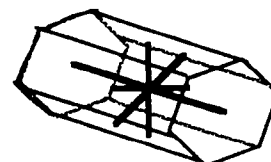
cubic
all equal
dimensions
& 90° angles



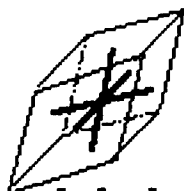
tetragonal
all 90° angles
2 equal, 1 unequal
dimension



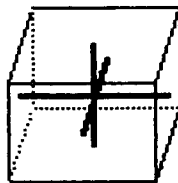
orthorhombic
all 90° angles
all unequal
dimensions



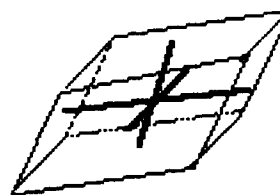
hexagonal
3 equal length axes
at 60° angles, 4th
perpendicular axis



rhombohedral
all dimensions
are equal length
no angles = 90°



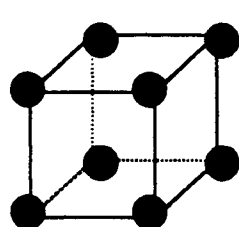
monoclinic
all dimensions
are unequal
2 = 90°, 1 ≠ 90°



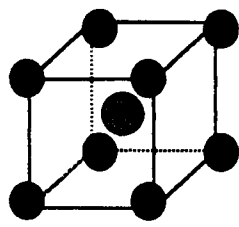
triclinic
all dimensions are
unequal; no 90°

Sometimes it is possible to determine the type of crystal structure of the unit cell by visually examining the appearance of the actual crystals. For example, snowflakes are six-sided, hexagonal crystals and sodium chloride (table salt) has a cubic crystal structure. Chemists normally determine the arrangement of particles in the unit cell by x-ray analysis. The rows and layers of particles in the crystal bend the x-rays the

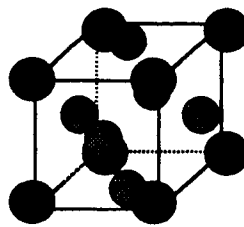
same way that the grooves do in a diffraction grating, creating an interference pattern. There are several different packing arrangements of the particles in the unit cell, depending upon the radii and charges of the ions involved.



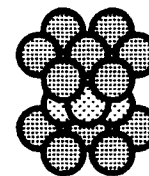
simple cubic



**body-centered
cubic**



**face-centered
cubic**



**hexagonal
closest packing**

The **simple cell** has particles only at the corners of the unit cell. A **body-centered cell** has one additional particle in the center of the unit cell. In the **face-centered cell** there is an additional particle in each one of the faces of the unit cell. The **hexagonal closest packing** unit cell has alternate layers of a face-centered hexagon and a triangular arrangement.

The slower a crystal forms, the more uniform its arrangement will be and the larger the crystal that will form.

Problem: Take-home Experiment

Fill a 1 L glass jar (such as a pickle or spaghetti sauce jar) with water to a depth of about 3 cm. Dissolve a half cup of a common crystalline solid found around the house in the water. You could try MgSO_4 (Epsom salt), CuSO_4 (root killer), NaCl (table salt), sucrose (sugar), etc. Make sure you read the labels first and follow any prescribed methods for safe handling and disposal of the selected solid. If all of the solid dissolves, add some more until the solution becomes saturated. Then heat the water in the microwave on high setting for 30-60 seconds to help dissolve the excess solid. If some solid still remains after heating and stirring, add a little more water. Place the open jar on the windowsill and allow the water to evaporate over the next few days. Draw a diagram below to show the appearance of your crystals and describe the dimensions and angles that are apparent in their structure. What type of shape does your crystal have? Place a few of your best-shaped crystals in a zip-lock baggie and attach it to your study guide.

VIII. Binding Forces in Crystals

The positions in a unit cell can be occupied by either ions, atoms or molecules. The type of particles in the cell determines the strength of the attractive forces that hold the crystal together.

Ionic solids have an arrangement of alternating positive and negative ions at the lattice points in the unit cell. This results in strong, 3-dimensional ionic bonding.

Examples: NaCl , Li_2O , KI

Metallic solids have positive ions at each position in the unit cell that are attracted to a free-floating 'sea' of delocalized electrons. This provides a strong, but flexible bonding structure. Examples: Cu , Fe , Ag

Covalent Network or Macromolecular solids have atoms at the lattice points that are held together by 3-dimensional covalent bonding. The crystal is considered

to be one, giant molecule, which makes them very hard solids with high melting points. Examples: diamonds(C_n), Si

Covalent Molecular solids have molecules at the lattice points that are held together by only van der Waals forces(dispersion interaction and dipole-dipole attractions). These are very weak forces of attraction resulting in soft, low melting temperature solids. Examples: ice(H_2O), graphite(layers of C molecules with 2-dimensional covalent bonding)

Other Crystal Properties

- Different substances may have the same crystal structures and are said to be **isomorphous**. If the same substance forms crystals with 2 or more different structures then it is said to be **polymorphous**.
- A crystal may have defects or abnormalities, such as a dislocation of a layer of atoms or missing particles. Silicon and germanium crystals are deliberately "doped" with arsenic or gallium to produce transistors that will conduct electricity.
- Many ionic solids absorb water molecules when they form crystals and are called **hydrated crystals**. This water can be lost or re-absorbed from the surrounding air.
- Liquid quartz crystals are solids that lose their crystalline order in only one or two dimensions at their melting point. This allows them to block the passage of light through them when melted, making them ideal for displays in electronic devices.
- **Amorphous materials**, such as glass, appear to be solids but do not have a crystalline arrangement of its particles. They do not have definite melting points, but slowly soften and become more viscous(easier flowing) when heated.

Unit 10 Objectives:

After completing the study guide and solving the problems you should be able to:

1. Explain the relationship between Gibbs free energy, enthalpy and entropy.
2. Describe what conditions are necessary for a reaction to occur spontaneously.
3. Calculate the energy required to change a given mass of a substance from a solid to a liquid to a gas.
4. Use Hess's Law to calculate the heat of reaction for a new equation resulting from a series of reactions with known enthalpies of formation.
5. Describe how the concentrations of reactants and products in an equilibrium system will change in order to relieve a stress placed upon the system.
6. Interpret vapor pressure curves and phase diagrams to determine the physical state of a substance at given experimental temperature and pressure conditions.
7. Differentiate between viscosity and surface tension of a liquid.
8. Define "crystal" and explain how the 7 basic crystal structures are identified.
9. Describe what conditions favor the growth of large, more perfect crystals
10. Distinguish between the different packing arrangements within crystals.
11. List the characteristic properties of the various types of crystalline solids.