EXAM II Material

<u>Part I Thermochemistry</u>

Chapter 6

Thermodynamics is the study of heat and its relationship to other kinds of energy (chemical or electrical). Thermochemistry is the study of heat released or absorbed during chemical reactions.

<u>I. Energy</u>

$$\text{Internal Energy} = \otimes E = E_{final} - E_{initial}$$

<u>II. Heat and Work</u>

Heat, q, is the heat transferred to or from a system during a reaction. It is the energy that flows to or from a system due to the difference of °T

Work,w, is the energy exchange when a force ,F, moves an object a certain distance.

$$\text{Internal Energy} = \otimes E = q + w$$

<u>III. Units of Energy</u>

Joule,J

Calorie,Cal

IV. State Functions

State Functions are properties that on dependant upon its present state and not dependant upon the pathway to the present state.

V. First Law of Thermodynamics

Energy can neither be created or destroyed

VI. Enthalpy: The Heat Evolved in a Chemical Reaction at Constant Pressure

Enthalpy, H (Heat content of a substance)

Change of Enthalpy,$\otimes$H, is the heat given off or absorbed by a system at constant pressure. For reactions, the change of enthalpy is the
Heat of Reaction:

$$\text{Heat of Reaction} = \otimes H_{rxn} = H_{final} - H_{initial}$$

Mechanics of reactions:

VII. Calorimetry

The Heat Capacity of a substance is the amount of heat required to change its temperature 1 °

The Specific Heat of a substance is the amount of heat required to change 1 gram of the substance its temperature 1 K

Problem: Calculate the amount of heat required to heat 35.0 g of Al from 55.0°C to 75.0°C.
Specific Heat of Al = 0.908

The Heat Capacity of a substance is the amount of heat required to change its temperature 1 °
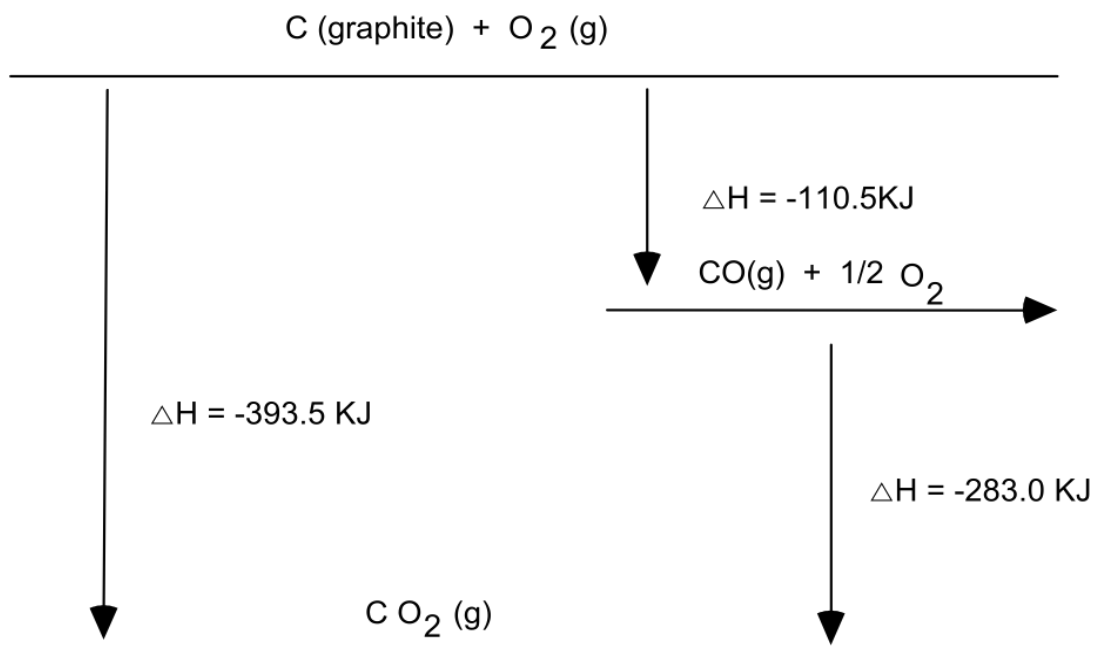
VII. Law of Hess-Law of constant heat summation

A. Enthalphy, $\triangle H$ $\triangle H_{rxn} = \triangle H_{products} - \triangle H_{reactants}$

_____ REACTANTS

_____ PROCUCTS

PRODUCTS

_____ REACTANTS

B. Energy diagram

C (graphite) + O_2 (g)

$\triangle H$ = -110.5KJ

CO(g) + 1/2 O_2

$\triangle H$ = -393.5 KJ

$\triangle H$ = -283.0 KJ

C O_2 (g)

C. Energy Equations:

1. Additon of equations

C (graphite) + O_2(g) $\rightarrow$ CO(g) + 1/2 O_2 $\triangle H$ = -110.5 KJ

CO (g) + 1/2 O_2 (g) $\rightarrow$ CO_2 $\triangle H$ = -283.0 KJ

2. Multiplying:

   HI(g) $\rightarrow$ 1/2 H_2(g) + 1/2 I_2(s) $\triangle H$ = -25.9 KJ

3. Reversing:

   1/2 H_2(g) + 1/2 I_2(s) $\rightarrow$ HI(g) $\triangle H$ = +25.9 KJ

4. Problem:

   Find $\triangle H$ for 2 NH_3 (g) + 3 N_2O(g) $\leftrightarrows$ 4N_2(g) + 3 H_2O (l)
   Given:

   4 NH_3 (g) + 3 O_2(g) $\rightarrow$ 2 N_2(g) + 6 H_2O (l) $\triangle H$ = -1531 KJ

   N_2O(g) + H_2(g) $\rightarrow$ N_2(g) + H_2O (l) $\triangle H$ = -367.4 KJ

   H_2O (l) $\rightarrow$ H_2(g) + 1/2 O_2(g) $\triangle H$ = +285.9 KJ

5
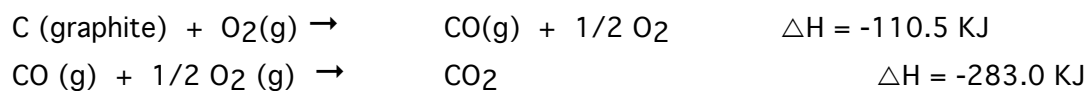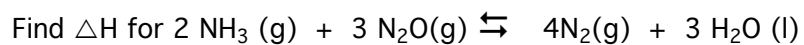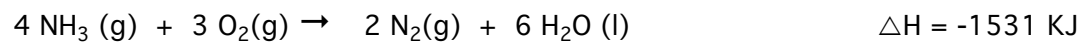
VIII. Standard Heats of Reactions

Calculate the the ΔH for the following reactions :

1. $C_2H_4 + H_2 \leftrightharpoons C_2H_6$

2. $2\ CH_3OH + 3\ O_2 \leftrightharpoons 4\ H_2O + 2\ CO_2$
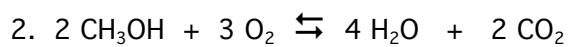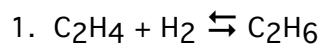
Chapter 8

A. <u>Electron Configuration (review)</u>

B. <u>Sublevel Energy Splitting in Multielectron Atoms</u>
   <u>->Shielding</u>

C. <u>Electron Configurations, Valence electrons, and the Periodic Table (review)</u>

D.   Periodic Trends in the Size of Atoms and Effective Nuclear Charge

   1.   Atomic Radius [Atom Size]
        a. As the number of shells increases, the radius size increases

        b. As you go left to right across a period, the radius size decreases

2 Ion Size - is the measure of the electron cloud around the nucleus.
           a. Cations

           b. Anions

3. Ionization Energy
    The energy required to remove an electron from a neutral atom (in gas phase).

        a. As you go left to right across a period, the ionization energy increases.

        b. As you go down a group (top to bottom), the ionization energy decreases.

4. 1st , 2nd, and 3rd, Ionization Energies

5. Electron Affinity The amount of energy released or absorbed when an electron is added to an atom to form a (-) ion [anion], in gas phase.

        a. As you go left to right across a period, the electron affinity increases.

        b. As you go down a group (top to bottom), the electron affinity decreases.

5. Metalic Character
      a. As you go left to right across a period, metallic decreases.

      b. As you go down a group (top to bottom), the ionization energy increases.

B. Isoelectronic particles - species with the same number of electrons

Problem: Arrange the ions Se^{2-}, Br^-, Rb^+, and Sr^{+2} in decreasing size

Chapter 9

→ The attractive interaction between two atoms or ions

I. Types: -

1. Ionic Bond- Cations (+ charged) and Anions (- charged) are held together by the attractive force of their (+) and (-) charges ⋯→ Electrostatic force.

2. Metallic Bonds

3. Macro molecular crystals

4. Covalent Bonds- Results from the sharing of a pair of electrons between two atoms.

II. Valence electrons (High energy electrons)-Review

The electrons in the outermost shell (energy level). Valence electrons are involved in reactions.

(Rem: # valence e^- = the group number for the "A" subgroup elements)

ex.

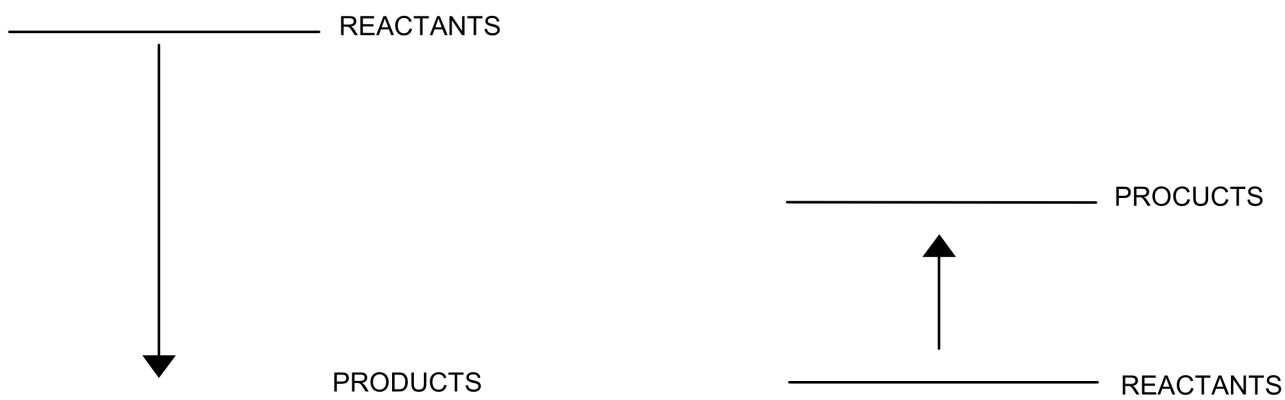III. Ionic Bonds- The attractive force between a cation (+ ion) and anion (- ion).-Review

Atoms lose or/ gain electrons to obtain an octet.
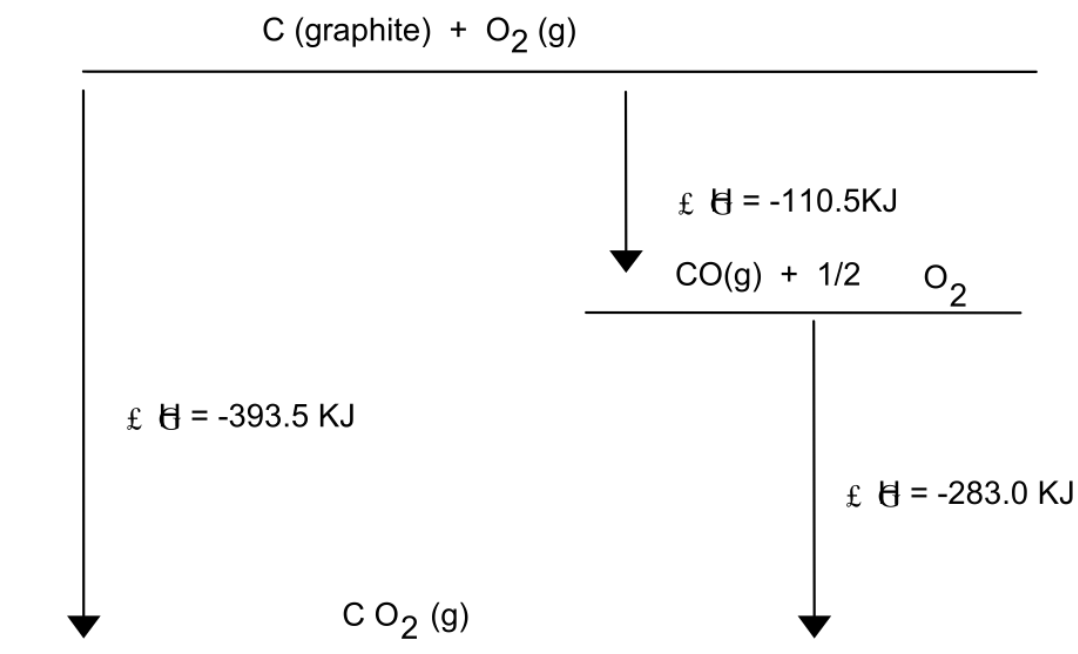
IV BORN-HARBER CYCLE

BACKGROUND:

I. Law of Hess-Law of constant heat summation (again!)

A. Enthalphy, ΔH $\Delta H_{rxn} = \Delta H_{products} - \Delta H_{reactants}$

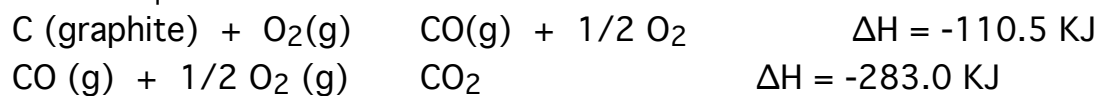——————————— REACTANTS

——————————— PRODUCTS

——————————— PROCUCTS

——————————— REACTANTS

B. Energy diagram

C (graphite) + O_2 (g)
—————————————————————

£ Ħ = -110.5KJ

CO(g) + 1/2 O_2
——————————

£ Ħ = -393.5 KJ

£ Ħ = -283.0 KJ

C O_2 (g)
—————————————————————

C. Energy Equations:

1. Additon of equations

C (graphite) + O_2(g)   CO(g) + 1/2 O_2 ΔH = -110.5 KJ
CO (g) + 1/2 O_2 (g) CO_2 ΔH = -283.0 KJ

_____

2. Multiplying:

HI(g) → 1/2 H_2(g) + 1/2 I_2(s) ΔH = -25.9 KJ

3. Reversing:

1/2 H_2(g) + 1/2 I_2(s) → HI(g) ΔH = +25.9 KJ
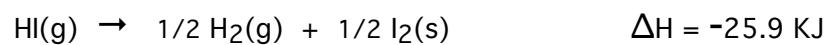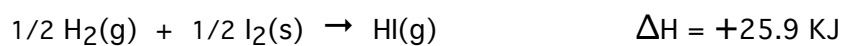
V BORN-HABER CYCLE

The Born- Haber cycle uses the law of Hess to determine the <u>Lattice Energy.</u> The lattice energy is the enthalphy change, ΔH, associated when gaseous cations and anions from a crystal:

$$Na^+(g) + Cl^-(g) \rightarrow NaCl(s) \quad \Delta H = -788KJ$$
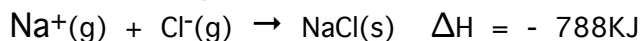
Since heat is always evolved in these processes, all lattice energies have a negative sign (Energy is lost). Lattice enrgies cannot be determined directly; therefore, the law of Hess is applied to indirectly determine the lattice energy:

To prepare 1 mole of NaCl, for example, the following steps must be taken:

A. Crystalline Na metal is sublimed into gaseous Na:

$\Delta H_{sublimation} = +108$ KJ

B. Gaseous sodium atoms are ionized into gaseous sodium ions. The amount of energy required for 1 mole of Na is the first ionization energy of sodium

$\Delta H_{ionization} = +496$ KJ

*Note some cations will require the second ionization energy step:

C. Gaseous Cl_2 molecules are dissociated. (Bonds are broken). This the enthalpy change when 1 mole of Cl_2 molecules are dissociated.

$\Delta H_{dissociation} = +243$ KJ

D. Electrons are added to the gaseous chlorine atoms.   The enthalpy change per mole of Cl(g) is the first electron affinity of chlorine

$\Delta H_{electron\ affinity} = -349$ KJ

*Note some anions will require the second electron affinity energy step:

E. In this step, gaseous Na^+ and Cl^- condense into one mole of crystalline sodium chloride. The lattice energy is the amount of energy released per mole of NaCl.
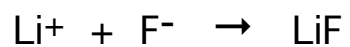
$\Delta H_{lattice\ energy} = -788$ KJ

F. Once steps A-E are added, the sum will give you the $\Delta H_{formation}$:

$$Na(s) + 1/2\ Cl_2\ (g) \rightarrow NaCl(s)\Delta H_{formation} = -411\ KJ$$

Comparison between Lattice energy and $\Delta H_{formation}$:

    Problem: Calculate the Lattice energy for:

$$Li^+ \; + \; F^- \; \rightarrow \; LiF \qquad \Delta H_{lattice\ energy} = \;?$$

    Given:

$\Delta H_{sublimation} = +155.2$ KJ

$\Delta H_{ionization} = +520.$ KJ

$\Delta H_{dissociation} = +150.6$ KJ (Bond energy)

$\Delta H_{electron\ affinity} = -333$ KJ

$\Delta H_{formation} = -594.1$ KJ

Problem: Calculate the Lattice energy for:

$$Mg^{2+} + 2Cl^- \rightarrow MgCl_2 \qquad \Delta H_{lattice\ energy} = ?$$
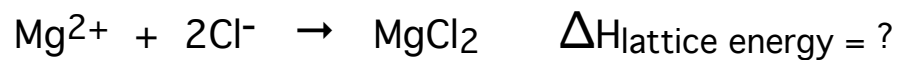
Given:

$\Delta H_{sublimation}$ = +120. KJ

$\Delta H_{ionization}$: the first and second ionization energy of Mg is: 756 KJ/mole and 1490. KJ/mole, respectively.

$\Delta H_{dissociation}$ = +248 KJ (Bond energy)

$\Delta H_{electron\ affinity}$ = -368 KJ

$\Delta H_{formation}$ = -698 KJ

$\longrightarrow$

$\longrightarrow$

16

VI. Electronegativity and Bond Polarity

A. Electronegativity - The measure of the attractive force that an atom for its shared electrons. In general, electronegativity increases left to right and bottom to top on the periodic table.

B. Electronegativities and bond polarity

1. Covalent Bonds

a. Non polar covalent bonds - differences in the electronegativities is $\leq$ 0.4

b. Polar covalent bonds - differences in the electronegativities is between 0.5 -1.7

2. Ionic bonds

Differences in electronegativities is $>$ 1.7

Examples:

1.

2.

3.

4.

5.

VII. Covalent Bonds

A. <u>Bond Energy</u> - The average energy required for the dissociation of a bond

B. <u>Bond Length</u> - The average distance between the two nuclei of covalently bonded atoms.

C. <u>Drawing LEWIS STRUCTURES</u> - Electron dot structures-Review

<u>HOW TO:</u>

1.   Write e- dot structure for the individual atoms.

2.   a) Add together the number of valence electrons for all the atoms
(If it is an ion, you must add or subtract electrons accordingly)

b) Divide the total number of e$^-$ by 2: This will give you the number of e$^-$ pairs available for bonding.

3.   Determine which is the central atom   a. The least represented atom that is <u>not H</u>

b. Usually, the <u>first</u> atom in the chemical

formula that is <u>not H</u>.

4.   Arrange atoms symmetrically around the central atom.

5.   Draw a single line (or 2 dots) between the central and outer atoms.

6.   From the total number of valence electrons subtract 2 electron for each bond made.

7.   Attempt to place the remaining electron pairs around the outer atoms to make an octet

or duet (for H)

8.   Additional electrons are placed on the central atom

9.   If the central atom still has less than an octet ; then, a double or triple bond must be formed.
<u>Warning:</u> Do not use a double or triple bond unless you have to!

<u>HONC</u>, a general rule(a help)

Examples.

B. Specific Electron Dot Cases-Review:

1. Ions:

2. Oxy Acids

3. Carbon chains

D. Exceptions to the Octet Rule
   1. Electron deficient molecules: Molecules where the central atom does not have an octet. Usually a group IIIA atom
      Example: BCl_3

   2. Expanded valence shell: Molecules where the central atom has more than 8 valence around the central atom. The central atom would belong to the $3^{rd,}$ 4th,5th,6th,or 7^{th}period.
      Example: SF_6

3. <u>Molecules with an odd number of electrons</u>: There are an odd number of valece electrons in the molecule
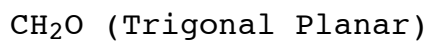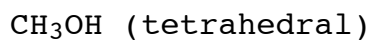
   Example: NO_2
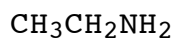
<u>Practice:</u>
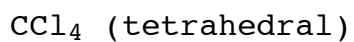 SO_2

  IF_5

  NO_3^-

  $HBrO$

  CH_3COCH_3

  PF_5

Excersizes

1. What is the major type of intermolecular forces for the following

   I_2

   PCl_3(pyrimidal)

   H_2S (bent)

   CO

   CO_2 (linear)

   CCl_4 (tetrahedral)

   $CH_3CH_2NH_2$

   CH_3OH (tetrahedral)

   CH_2O (Trigonal Planar)

   CH_4(Tetrahedral)
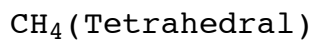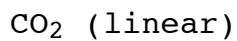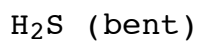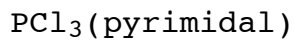
Chapter 11

I. Solids, Liquids, and Gases: A Molecular Comparison

PROPERITIES OF GASES
    A. Gas particles are far apart from each other - there is no attraction between particles

    B. Gases have an indefinite shape.

    C. Gases have a low density

    D. Gases are very compressible

    E. Gases exert pressure equally in all directions on the walls of a container.

    F   Gases have a high flow rate. Gases mix spontaneously and completely with one or more other gases.

PROPERITIES OF SOLIDS
    A. A Solid contain particles which are <u>very</u> close to each other-there are very large attractive forces between particles

    B. Solids have a definite shape. Solids maintain its shape regardless of the container they are in.

    C. Solids in general have a high density

    D. Solids are not compressible (or negligibility)

    E. Solids do not flow

PROPERITIES OF LIQUIDS
    A. Liquids contain particles which are (somewhat) close to each other - there are attractive forces between particles

    B. Liquids have a definite shape. Liquids maintain the shape of the bottom of the container.

    C. Liquids in general have a medium density

    D. Liquids are not compressible (or negligibility)

    E.Liquids have a medium flow rate

II. Intra and Intermolecular (particle) forces-Review

<u>A.</u>

<u>B. Intramolecular (particle) forces</u>

<u>C. Intermolecular (particle) forces</u>
The attractive forces between particles.

Types

1. <u>Dispersion Forces (London forces)</u>The attraction between atoms and nonpolar molecules. London forces are very weak electrostatic forces of attraction between molecules with "temporary" dipoles.

2. <u>Dipole-Dipole interaction</u>:
   Dipole - dipole interactions are electrostatic attractions between polar molecules

3. <u>Hydrogen bonds:</u>
   A hydrogen bond is a relatively strong dipole-dipole attractive force between a hydrogen atom and a pair of nonbonding electrons on a F,O, or N atom

3. <u>Ion-Dipole bonds:</u>
   A Ion-Dipole bonds occur when an ionic compound is mixed with a polar compound. – such as : aqueous solution!!

III Intermolecular Forces in ActionSurface Tension, Viscosity, and Capillary Action

A. SURFACE TENSION

B. VISCOSITY

B. EVAPORATION OF LIQUIDS
Evaporation is the change from the liquid state to the gaseous or vapor state .

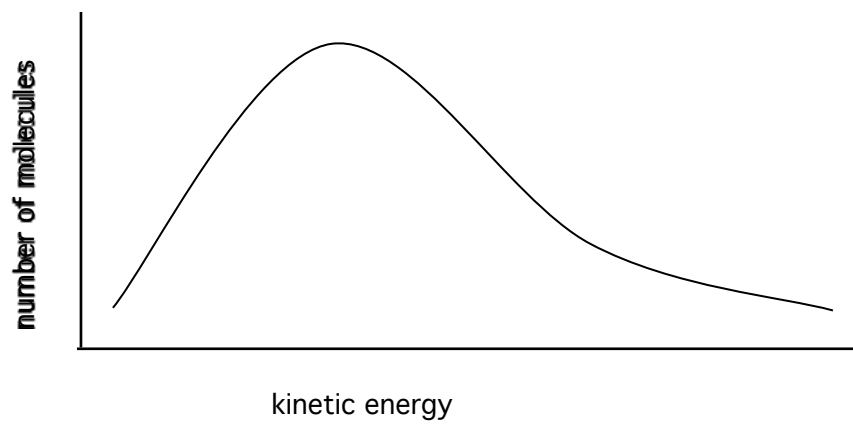$$Liquid + \ heat \ \rightleftharpoons Vapor$$

1. Effect of intermolecular forces on evaporation

2. Effect of temperature on evaporation

3. Effect of surface area on surface area

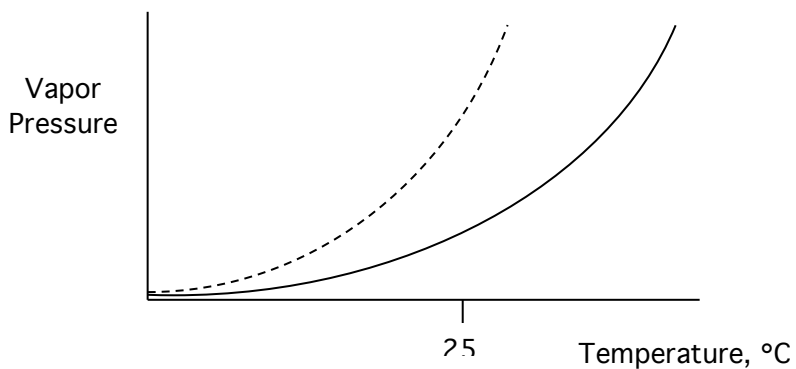4. Effect of evaporation on the average kinetic energy

kinetic energy

C. VAPOR PRESSURE OF LIQUIDS

The vapor pressure of a liquid is the pressure exerted by the vapor above a liquid.

Dynamic equilibrium: rate of evaporation = rate of condensation

1. Effect of intermolecular forces on vapor pressure

2. Effect of temperature on vapor pressure

*Note: The vapor pressure of a liquid is independent of the volume of the container, provided that there is some liquid present so that equilibrium is established

D. BOILING POINT

The boiling point of a liquid is the temperature at which a liquid is changed to a gas *within* the liquid (bubbles formed underneath the surface). The **boiling point** is the temperature at which the vapor pressure equals the atmospheric pressure (external pressure).

    1. The **normal boiling point** is the temperature at which the vapor pressure equals the atmospheric pressure of 1 atm.

    2. Effect of intermolecular forces on the boiling point

IV Changes of State-Review

A. HEAT CAPACITY [Specific heat]

The amount of heat required to raise the temperature of 1 g of a substance exactly 1°C.

Example: How many degrees Celsius will the temperature rise if 25 g ether absorbs 160. cal of energy.

Specific heat $_{ether}$ = $\dfrac{0.529 \text{ cal}}{\text{g °C}}$

B. SUBLIMATION AND FUSION - ENERGY AND CHANGE OF STATE

Energy (as heat) is either lost or absorbed when a substance changes its state

Solid $\longrightarrow$ Liquid

Liquid $\longrightarrow$ Gas

Solid $\longrightarrow$ Gas

C. HEAT OF VAPORIZATION- The quantity of heat needed to convert a liquid at its boiling point to the gaseous state.

Ex. ΔH_{vap} = $\dfrac{2.26 \text{ KJ}}{\text{g}}$

D. HEAT OF FUSION - The quantity of heat needed to convert a solid at its melting point to the liquid state.

Ex. ΔH_{fus} = $\dfrac{3.35 \text{J}}{\text{g}}$

IV HEATING CURVE FOR WATER

<u>Problem.</u> How much energy [Heat in kilojoules] is needed to convert 500.0 g of ice at -15.0°C to steam at 105.0 °C?
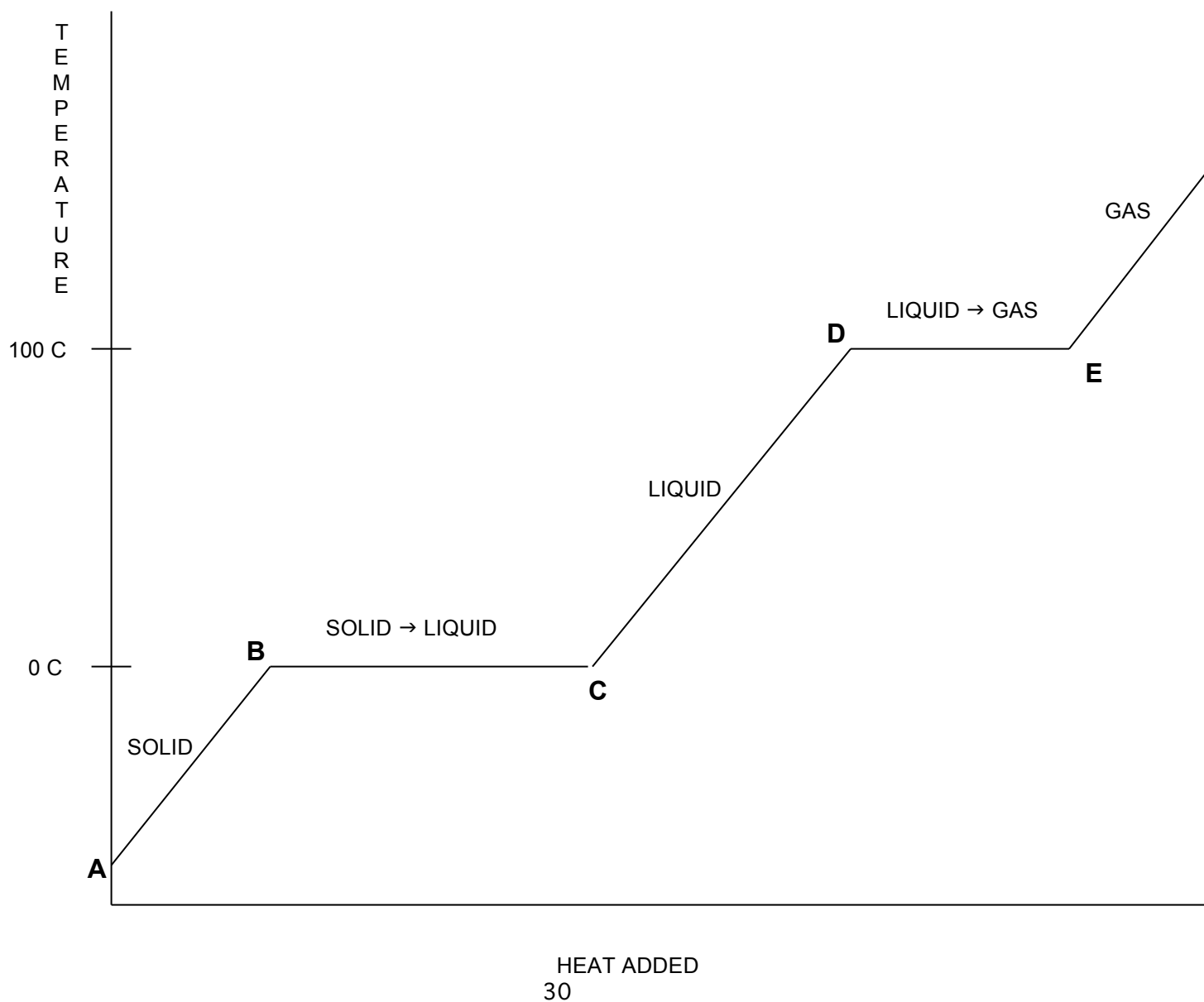
$$H_{fusion} = \frac{335 \text{ J}}{g} \quad\quad H_{vap} = \frac{2.26 \text{ kJ}}{g}$$

Specific heat of ice   = $\dfrac{2.10 \text{ J}}{g \ ^oC}$

Specific heat of water = $\dfrac{4.18 \text{ J}}{g \ ^oC}$

Specific heat of steam = $\dfrac{2.0 \text{ J}}{g \ ^oC}$

GRAPH:

Calculations:

A→B   <u>HEATING A SOLID</u>

B→C   <u>SOLID → LIQUID</u>

C→D   <u>HEATING A LIQUID</u>

D→E   <u>LIQUID → GAS</u>

E→F   <u>HEATING A GAS</u>

<u>TOTAL HEAT ADDED</u>

E. <u>CRITICAL TEMPERATURE, CRITICAL PRESSURE, AND CRITICAL POINT</u>

To convert a gas to a liquid, you must:
   a. Lower the temperature
        and/ or
   b. Increase the pressure

1. The **<u>Critical temperature</u>** of a gas is the highest temperature above which a substance can only exist as a gas. <u>Above</u> its critical temperature, no increase in pressure will convert the gas into a liquid.

2.   The **<u>Critical pressure</u>** is the minimum vapor pressure at the critical temperature. It is the minimum pressure required to convert the gas into a liquid it its critical temperature.
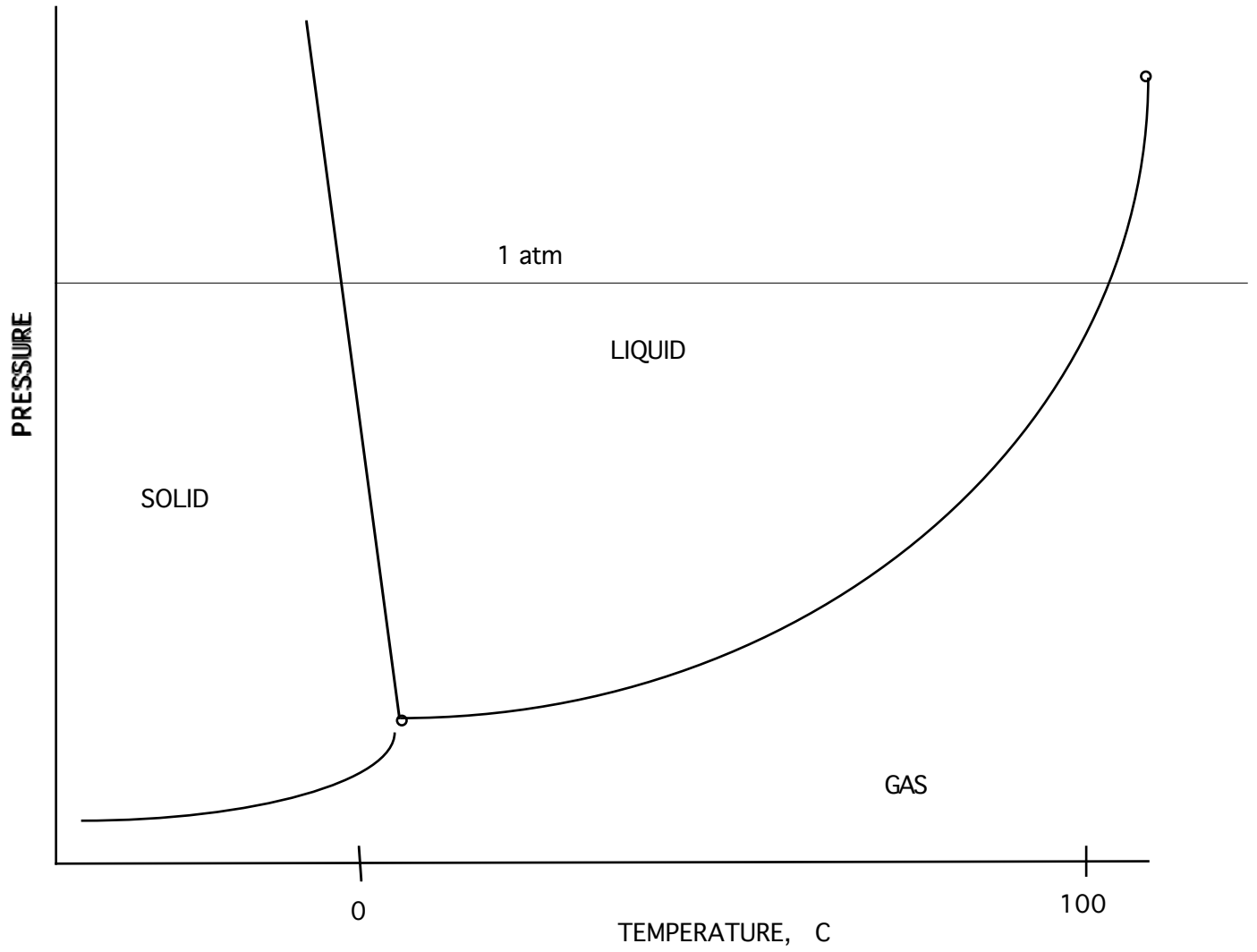
31

V. PHASE DIAGRAMS

    A phase diagram is a graph of pressure versus temperature that shows the region of stability for each of the physical states. The three line segments show the combinations of pressure and temperature at which any two phases exist in equilibrium.

TEMPERATURE, CELSIUS
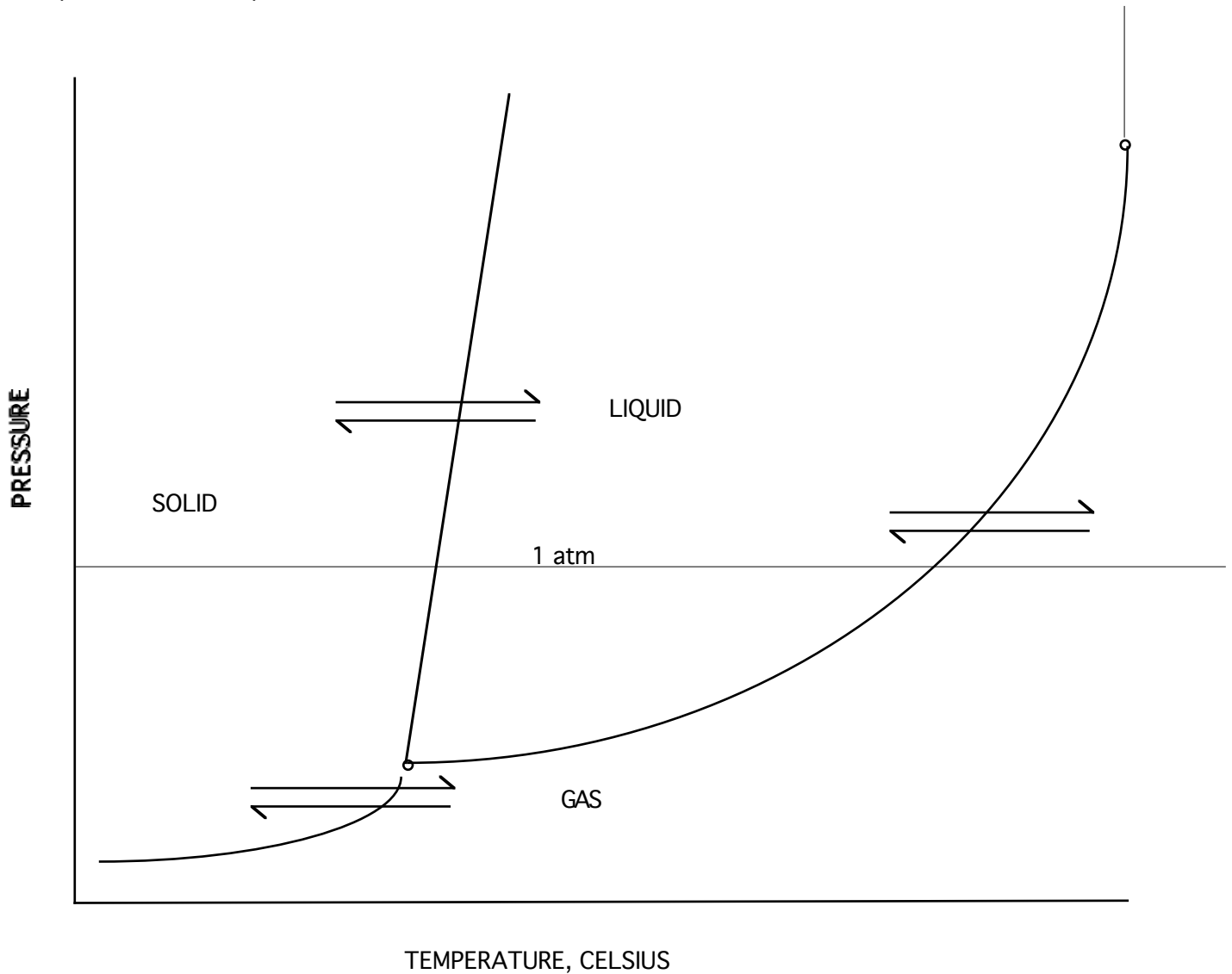
1. The line that separates the gas from the liquid is the vapor pressure curve

2. The **Triple point** is the pressure and temperature at which solid, liquid, and gas all coexist at the same time.

3. The liquid-gas equilibrium line ends at the critical point. Above the critical temperature only a gas exists.

PHASE DIAGRAM FOR H$_2$O

PHASE DIAGRAM FOR CO_2

SOLID

LIQUID

GAS

PRESSURE

10

5

1

TEMPERATURE

-75

-50

-25

0