

CHEMISTRY 111 LECTURE  
**Unit 2b Solids and Bonding**

Part 1 PERIODIC TABLES

**A. Trends**

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. 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.

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

a. Cations

b. Anions

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

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

## Part 2 CHEMICAL BONDS

→ 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)

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

(Rem: # valence e<sup>-</sup> = the group number for the "A" subgroup elements)

ex.

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

Atoms lose or/ gain electrons to obtain an octet.

#### IV. Covalent Bonds

A. Bond Energy - The average energy required for the dissociation of a bond

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

#### C. Drawing electron dot structures

##### HOW TO:

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<sup>-</sup> by 2: This will give you the number of e<sup>-</sup> pairs available for bonding.
3. Determine which is the central atom
  - a. The least represented atom that is **not H**
  - b. Usually, the **first** atom in the chemical formula that is **not H**.
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.  
Warning: Do not use a double or triple bond unless you have to!

HONC, a general rule(a help)

Examples.

## B. Specific Electron Dot Cases:

### 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:  $\text{BCl}_3$

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<sup>rd</sup>, 4<sup>th</sup>, 5<sup>th</sup>, 6<sup>th</sup>, or 7<sup>th</sup> period.  
Example:  $\text{SF}_6$

3. Molecules with an odd number of electrons: There are an odd number of valence electrons in the molecule

Example:  $\text{NO}_2$

Practice:

$\text{SO}_2$

$\text{IF}_5$

$\text{NO}_3^-$

$\text{HBrO}$

$\text{CH}_3\text{COCH}_3$

$\text{PF}_5$

## V. Intra and Intermolecular (particle) forces

A.

B. Intramolecular (particle) forces

C. Intermolecular (particle) forces

The attractive forces between particles.

## VI. Electronegativity and bonding

A. Electronegativity - The measure of the attractive force that an atom has 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  $> 1.7$

## Types

### 1. Dipole-Dipole interaction:

Dipole - dipole interactions are electrostatic attractions between polar molecules

### 2. Hydrogen bonds:

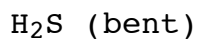
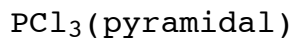
A hydrogen bond is a relatively strong dipole-dipole attractive force between a hydrogen atom and a pair of nonbonding electrons on a F, O, or N atom

### 3. London forces

The attraction between atoms and nonpolar molecules. London forces are very weak electrostatic forces of attraction between molecules with "temporary" dipoles.

## Exercises

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



CO

CO<sub>2</sub> (linear)

CCl<sub>4</sub> (tetrahedral)

CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>

CH<sub>3</sub>OH (tetrahedral)

CH<sub>2</sub>O (Trigonal Planar)

CH<sub>4</sub> (Tetrahedral)

2. Which has the strongest intermolecular forces?

I<sub>2</sub>      or      Br<sub>2</sub>      or      Cl<sub>2</sub>

CH<sub>3</sub>CH<sub>3</sub>      or      CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>      or

CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>

## Part 3 SOLIDS

### A. Types

1. Crystalline Solid

Crystalline solids have a highly ordered arrangement of particles (ions, atoms, and molecules)

2. Amorphous Solid

Amorphous solids have considerable disorder in their structure.

### B. Crystalline Solids

1. Crystalline lattice

A three dimensional array of lattice points in a pattern that defines a crystal.

2. Unit Cell

The Unit cell is the basic repeating unit of the lattice.

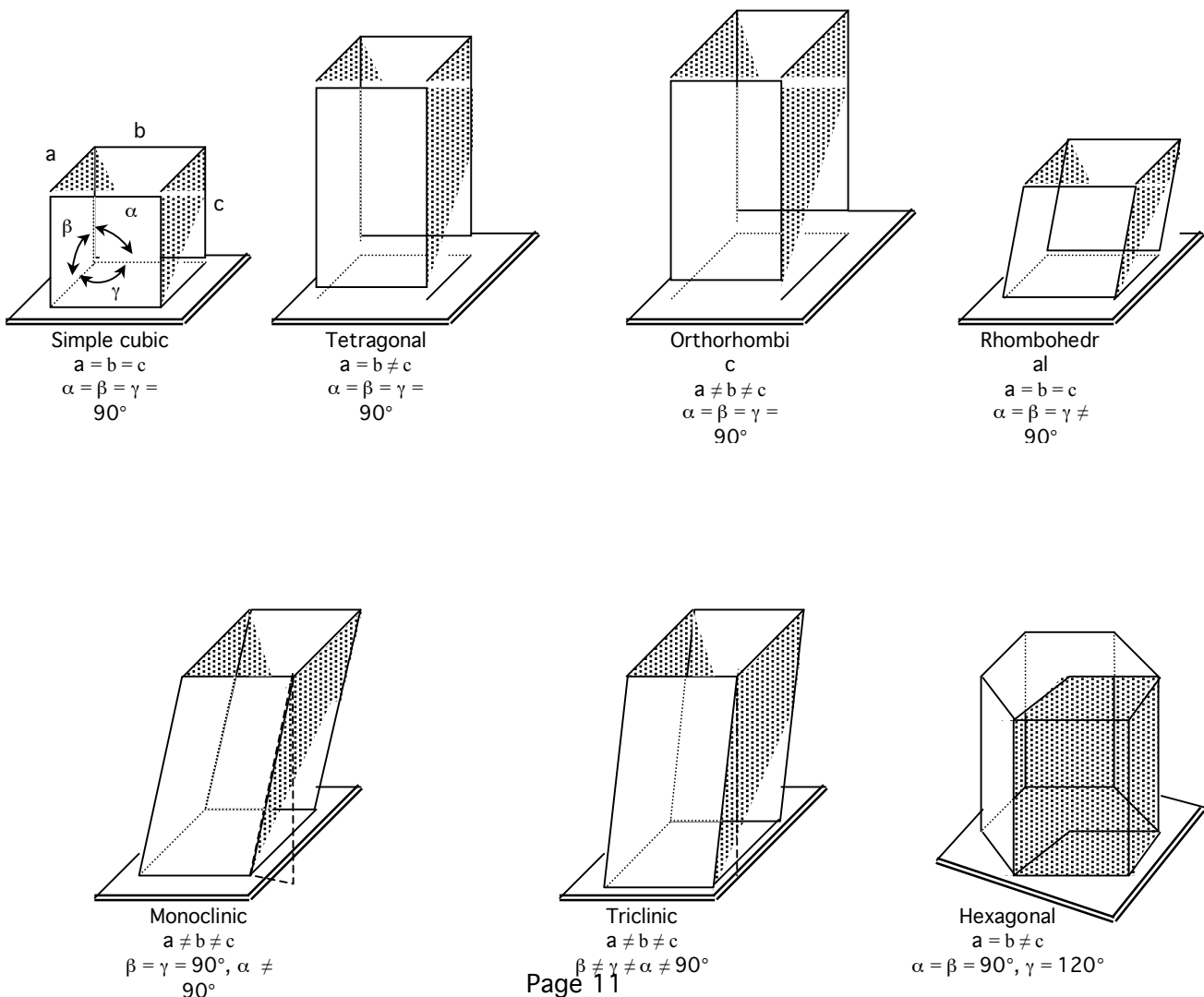
3. Coordination Number

The coordination number of a particle in a crystal is the number of nearest neighbors .

4. Lattice Points

The points in a lattice occupied by atoms, ions or molecules.

5. Kinds of Lattice



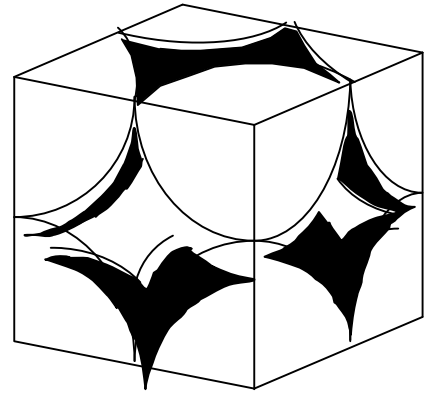
5. Geometry

6. Simple Cubic

a. Calculate the volume of the unit cell

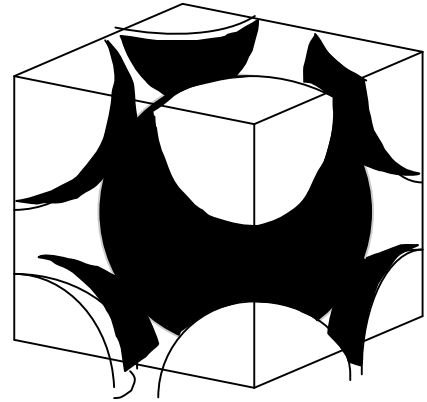
b. Calculate the volume of the spheres

c. Calculate the percent occupied (packing efficiency)



6. Body Centered Cubic

a. Calculate the volume of the unit cell

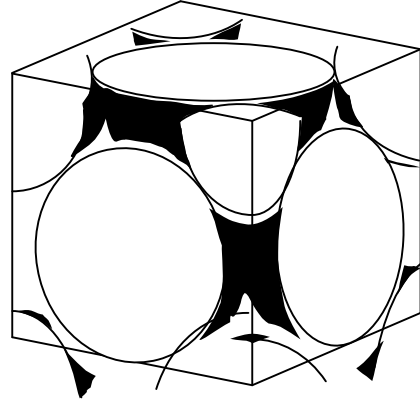


b. Calculate the volume of the spheres

c. Calculate the percent occupied (packing efficiency)

7. Face Centered Cubic

a. Calculate the volume of the unit cell



b. Calculate the volume of the spheres

c. Calculate the percent occupied (packing efficiency)

**Problems:**

1. Molybdenum has an atomic radius of 136 pm and crystallizes in a body centered cubic system.
  - a. What is the length of the edge of a unit cell.
  - b. Calculate the density of molybdenum

Problems continued,

2. Aluminum crystallizes in the face-centered cubic system, and the edge of a unit cell is 287.5 pm. Calculate the atomic radius of Al.

## 8. Packing Efficiency

a. Closest cubic packing

b. Hexagonal

### C. Types of Solids

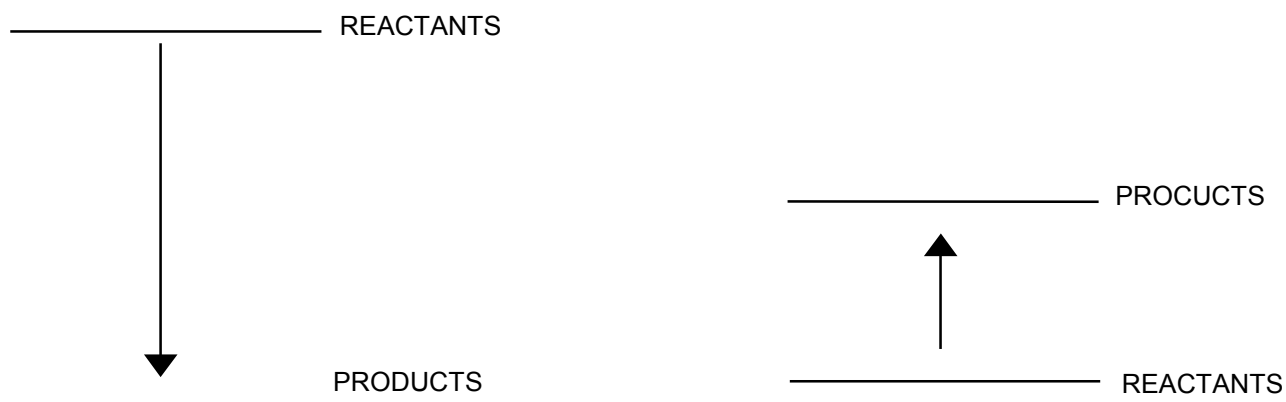
	<u>IONIC</u>	<u>MOLECULAR</u>	<u>NETWORK COVALENT</u>	<u>METALLIC</u>
PARTICLES AT LATTICE POINTS	cations and anions [positive and negative ions]	polar or nonpolar covalent molecules	atoms	metallic cations [positive metallic ions]
BONDING BETWEEN PARTICLES (attractive forces)	electrostatic attractions [ionic bond]	<u>intermolecular forces</u> dipole-dipole, hydrogen bond, london forces	covalent bonds	metallic bonds between positive metal ions and mobile electrons
PROPERTIES	high M.P. high B.P. nonconductors brittle hard/brittle	moderate to low M.P. moderate to low B.P. nonconductors or semi conductors soft	high M.P. high B.P. nonconductors brittle hard	variable M.P. variable B.P. malleable and ductile
EXAMPLES	NaCl KBr LiNO <sub>3</sub>	H <sub>2</sub> O SO <sub>2</sub> NH <sub>3</sub> C <sub>2</sub> H <sub>5</sub> OH	C (diamond) SiC SiO <sub>2</sub>	Au Cu Fe Na Hg

## D. Born-Haber Cycle

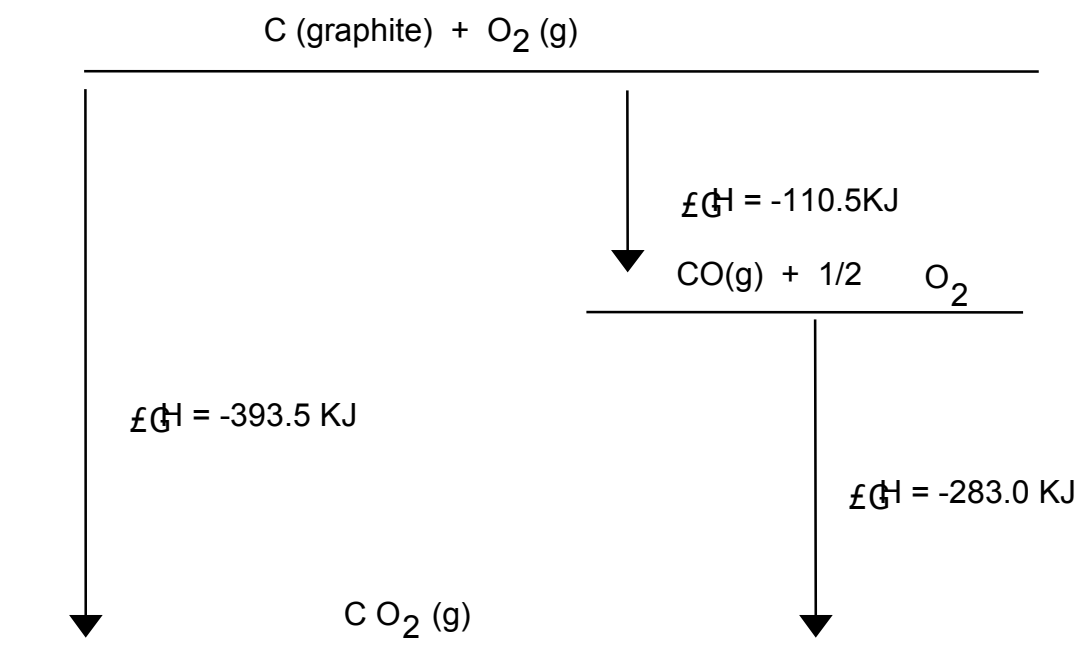
BACKGROUND:

I. Law of Hess-Law of constant heat summation

A. Enthalpy,  $\Delta H$        $\Delta H_{\text{rxn}} = \Delta H_{\text{products}} - \Delta H_{\text{reactants}}$

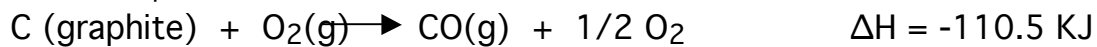


B. Energy diagram

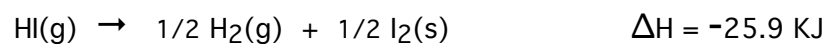


C. Energy Equations:

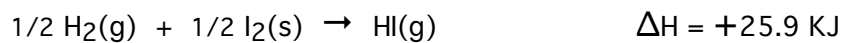
1. Addition of equations



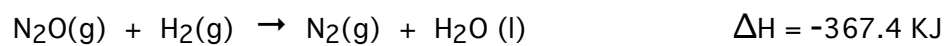
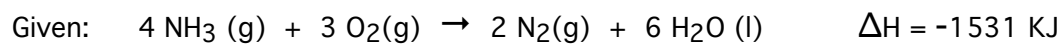
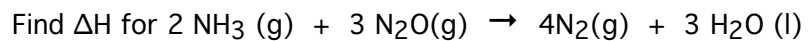
2. Multiplying:



3. Reversing:

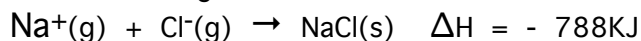


4. Problem:



## II BORN-HABER CYCLE

The Born- Haber cycle uses the law of Hess to determine the Lattice Energy. The lattice energy is the enthalpy change,  $\Delta H$ , associated when gaseous cations and anions form a crystal:



Since heat is always evolved in these processes, all lattice energies have a negative sign (Energy is lost). Lattice energies 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:

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

- 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

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

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

- C. Gaseous  $\text{Cl}_2$  molecules are dissociated. (Bonds are broken). This is the enthalpy change when 1 mole of  $\text{Cl}_2$  molecules are dissociated.

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

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

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

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

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

$$\Delta H_{\text{lattice energy}} = -788 \text{ KJ}$$

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



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

Problem: Calculate the Lattice energy for:



Given:

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

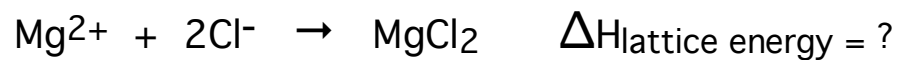
$$\Delta H_{\text{ionization}} = +520. \text{ KJ}$$

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

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

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

Problem: Calculate the Lattice energy for:



Given:

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

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

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

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

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

### B. 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.

$$\text{Specific heat}_{\text{ether}} = \frac{0.529 \text{ cal}}{\text{g } ^\circ\text{C}}$$

### B. 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

Gas  $\longrightarrow$  Solid

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

$$\text{Ex. } \Delta H_{\text{vap}} = \frac{2.26 \text{ KJ}}{\text{g}}$$

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

$$\text{Ex. } \Delta H_{\text{fus}} = \frac{3.35\text{J}}{\text{g}}$$

**Problem.** How much energy [Heat in kilojoules] is needed to convert 500.0 g of ice at  $-15.0^{\circ}\text{C}$  to steam at  $105.0^{\circ}\text{C}$ ?

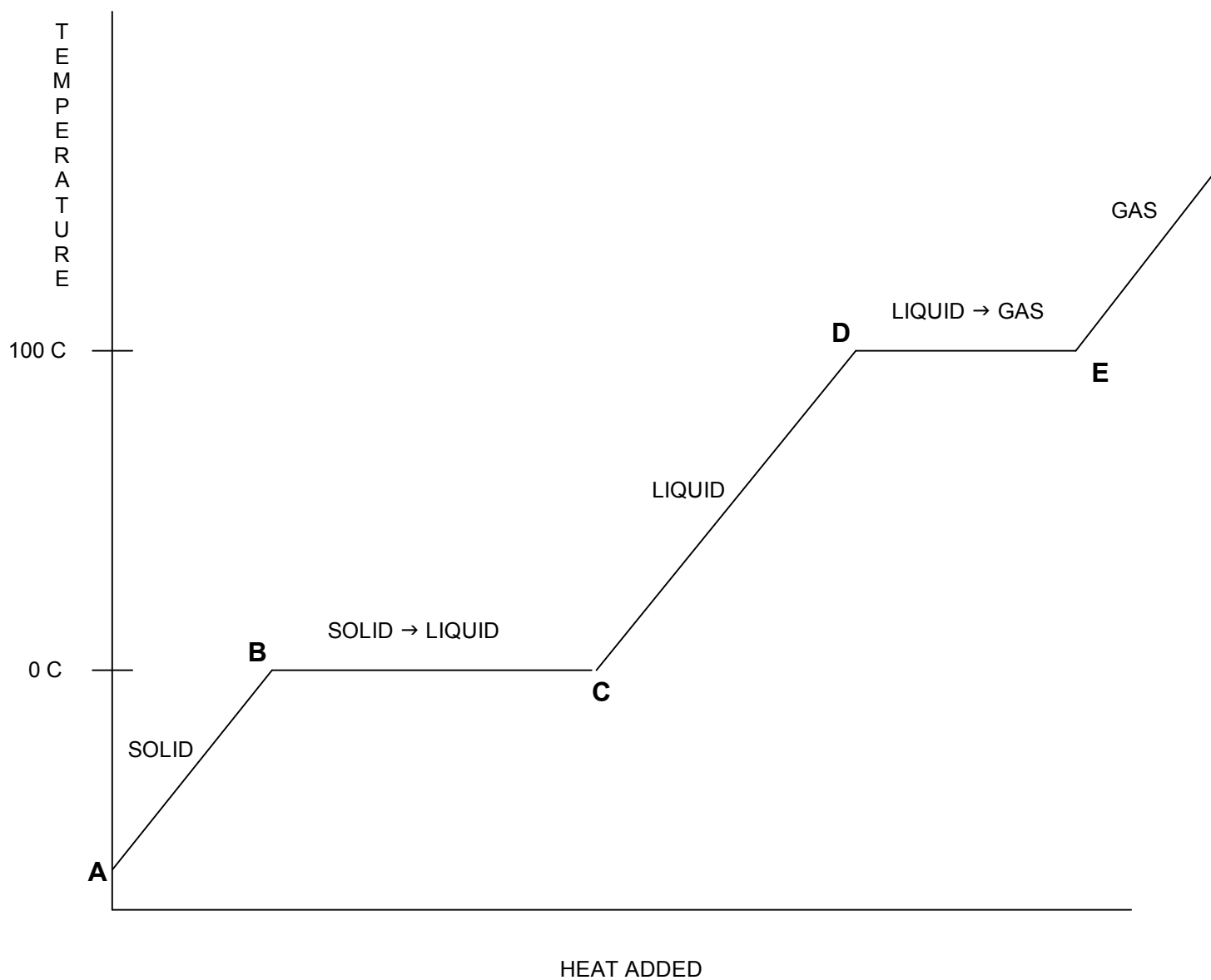
$$H_{\text{fusion}} = \frac{335 \text{ J}}{\text{g}} \quad H_{\text{vap}} = \frac{2,26 \text{ KJ}}{\text{g}}$$

$$\text{Specific heat of ice} = \frac{2.10 \text{ J}}{\text{g } ^{\circ}\text{C}}$$

$$\text{Specific heat of water} = \frac{4.18 \text{ J}}{\text{g } ^{\circ}\text{C}}$$

$$\text{Specific heat of steam} = \frac{2.0 \text{ J}}{\text{g } ^{\circ}\text{C}}$$

GRAPH:



Calculations:

A→B      HEATING A SOLID

B→C      SOLID → LIQUID

C→D      HEATING A LIQUID

D→E      LIQUID → GAS

E→F      HEATING A GAS

TOTAL HEAT ADDED