# UNIT A

# CHEMICAL ENERGY

## Enthalpy Change

- The basis of all change is due to energy transformations
- Photosynthesis takes solar energy from the sun and transforms it to chemical energy of glucose which in turn is transformed by living things to thermal energy and mechanical energy of movement.
- Fossil fuels are a stored form of chemical energy in which its origin can be traced back to the solar energy of the sun.

Solar energy $\xrightarrow{\text{photosynthesis}}$ glucose (chemical energy) $\xrightarrow{\text{cellular respiration}}$ thermal energy and mechanical energy of movement

Plant matter& dead animals $\xrightarrow{\text{time, pressure, heat, hydrocarbons}}$ (fossil fuels, stored potential energy)

| | | |
|---|---|---|
| **Cellular respiration** (occurs in the body) | Exothermic change | $C_6H_{12}O_6(s) + 6\ O_{2(g)} \rightarrow 6\ CO_2(g) + 6\ H_2O(l) + 2802.7$ kJ<br>(glucose) |
| **Photosynthesis** (occurs in plants) | Endothermic change | $6\ CO_2(g) + 6\ H_2O(l) + 2802.7$ kJ $\rightarrow C_6H_{12}O_6(s) + 6\ O_2(g)$<br>(glucose) |

**Exothermic changes:**

- a change in which energy is produced or given off **by the reactants**
- releases heat (energy) to the surroundings
- causes the surroundings to warm up
- involves an increase in the temperature of the surroundings

example: combustion, hot packs, and cellular respiration

Reactants → Products + energy

***energy becomes a term in the equation on the right hand side of the arrow.***

**Endothermic changes:**

- a change in which energy is required, gained, needed, or accepted **by the reactants** in order for the reaction to occur
- absorbs energy from the surroundings
- causes a decrease in the temperature of the surrounding

examples: cold pack, **photosynthesis**, evaporation, and perspiration

Reactants + energy → Products

***energy becomes a term in the equation on the left hand side of the arrow***

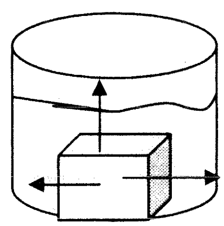
**Fossil fuels**

- major source of stored energy
- nonrenewable resource
- accounts for 20% of Alberta jobs
- found as natural gas, coal, crude oil, oil sands, coal bed methane
- Productions of energy from fossil fuels have become increasingly more efficient.
- The consumption of fossil fuels by cars, furnaces and industry has also been force to become more efficient.
- The four major demands for fossil fuels are for:
    - Heating, Transportation, Industry, & Commercial and institutional

## Calorimetry

1. **First Law:** **Law of Conservation of Energy**
    - Energy cannot be created or destroyed
    - Energy can be changed or converted from one form to another

2. **Second Law:** **Law of Heat Exchange or Transfer**
    - Heat energy flows (moves) from a hot to a cold object until **thermal equilibrium** is reached (i.e. *both are at the same final temperature*).



3. **Total heat lost = Total heat gained**

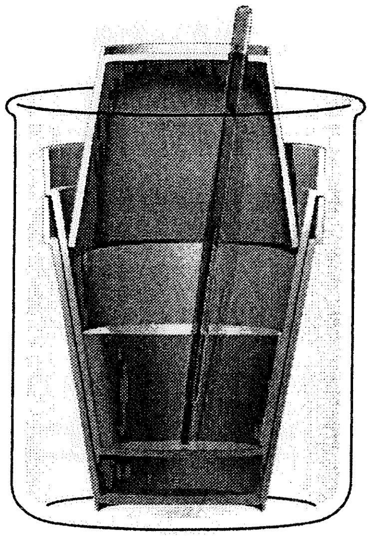
Combination of the above two laws
As a thermal equilibrium is reached, energy lost by the hot object is equal to the energy gained by the cold object.

**Thermochemistry** - study of energy changes (absorbed or produced) during a chemical reaction.

- study of energy changes requires working in an **isolated system**

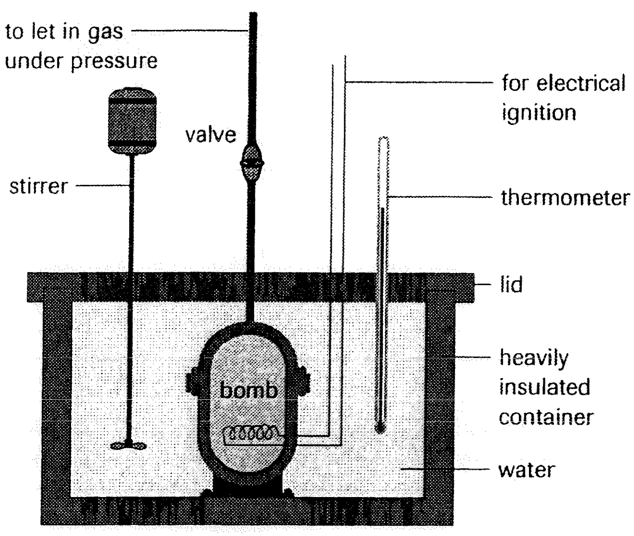
- requires accurate measurements using an isolated system called a **calorimeter.** Process is called **calorimetry**.

## Calorimeters



- A simple laboratory calorimeter consists of an insulated container made of three nested polystyrene cups, a measured quantity of water, and a thermometer.
- The chemical system is placed in or dissolved in the water of the calorimeter.
- Energy (as heat) transfers between the chemical system and the surrounding water are monitored by measuring changes in the water temperature.
- **The energy gained by the chemical system is equal to the energy lost by the calorimeter and its contents, as long as both the calorimeter and its contents (the surroundings) are part of an isolated system.**
- The main assumption is that no heat is transferred to the outside of the calorimeter

## Bomb Calorimeter



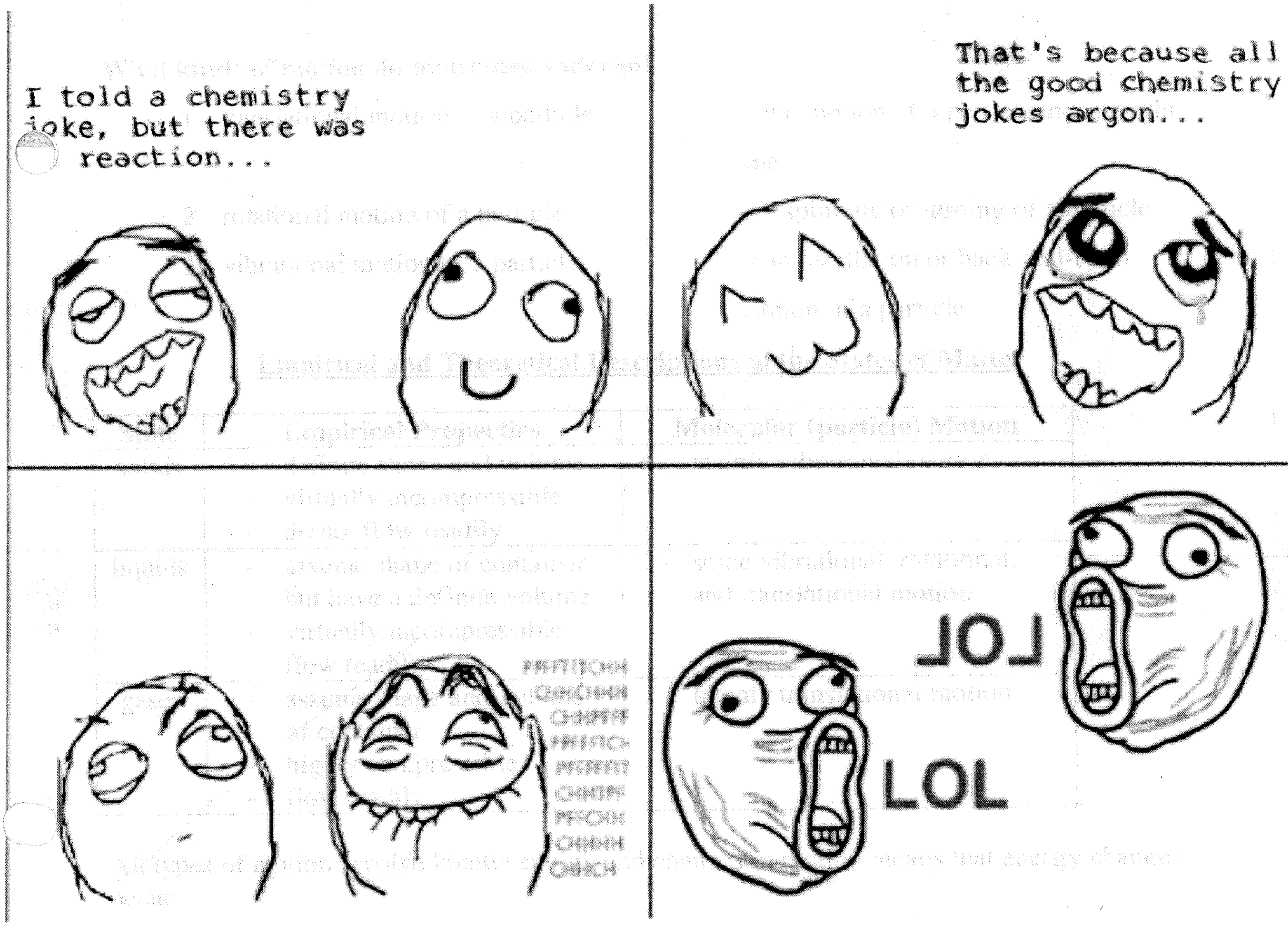

- The reactants are placed inside the calorimeter's bomb, which is surrounded by the calorimeter water.
- Once the calorimeter is sealed and the initial temperature measured, the combustion reaction is initiated by an electric heater or spark.
- Stirring is essential in order to obtain a uniform final temperature for the water.

Kinetic Molecular Theory:
The smallest particles of any substance are in continuous motion. These particles may be:

- atoms,
- molecules, or
- ions.

As these particles move about, they collide with each other and with objects in their path. Energy is released when collisions occur.

If enough energy is produced upon collision a reaction or change will take place.
The energy of motion is given the name **kinetic energy**.




**Temperature:**

The temperature of an object is a measure of how hot or cold the object is.
In terms of the kinetic molecular theory, the **temperature of a substance is a measure of the average kinetic energy** of the particles of the substance.

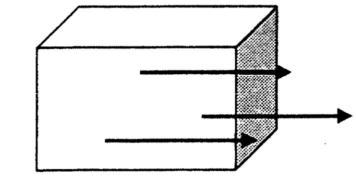
All substances at the same temperature – whether they are solids, liquids, or gases – are believed to have particles with the same average kinetic energy.

temp.$\uparrow$ $\rightarrow$ $\uparrow$ molecular motion $\rightarrow$ $\uparrow E_k$

temp.$\downarrow$ $\rightarrow$ $\downarrow$ molecular motion $\rightarrow$ $\downarrow E_k$

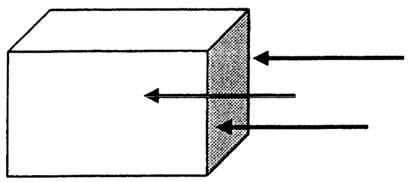
As long as there are no phase or physical changes, the transfer or exchange of heat to a substance (solid, liquid, or gas) increases the temperature of the substance by causing faster molecular motion, that is, an increase in the kinetic energy of the particles of the substance.

A change in temperature, $\Delta t$, of a substance, as measured with a thermometer, is explained theoretically as a change in the average kinetic energy $\Delta E_k$ of the particles in the substance.



**object loses heat to the surroundings**

Temperature of surroundings ↑    Temperature of object ↓



**object gains heat from the surroundings**

temperature of surroundings ↓    temperature of object ↑

An increase in heat results in an increase in:
- $E_k$
- average $E_k$
- temperature

<u>Calculation of Energy Changes</u>

**The quantity of heat, Q, that flows varies directly with the quantity of substance (mass, m), the specific heat capacity, c, and the temperature change, Δt.**

***specific heat capacity, <u>c</u>***

- quantity of heat required (to raise the temperature of) or released (to lower the temperature of) when a unit mass (i.e. one gram) of a substance changes by one degree Celsius

example: c of $H_2O(l)$ = 4.19 J/g°C

1 gram of $H_2O(l)$ by 1 °C involves    4.19 Joules of heat energy

1 °C ↑    4.19 Joules of heat absorbed from the surroundings

1 °C ↓    4.19 Joules of heat released to the surroundings

**Note: Specific heat of substances other than water will be provided in the question or can be found in the data book.** **(page 6)**

| | |
|---|---|
| **$Q = m c \Delta t$** | **Q = quantity of heat**<br>**m = mass of the substance**<br>**c = specific heat capacity**<br>**$\Delta t$ = change in temperature**<br>(higher – lower)<br>**$t_f$ = final temperature**<br>**$t_i$ = initial temperature** |

| | |
|---|---|
| 1 g = 1 mL | 1 kg = 1000 g |
| 1 kg = 1 L | 1 L = 1000 mL |

| |
|---|
| 1 kJ = 1000 J |
| 1 MJ = 1000 kJ |

| | |
|---|---|
| 4.19 J/g°C | 4.19 kJ/kg°C |

## Calorimeter Enthalpy Problems

Many hot water heaters use the combustion of natural gas to heat the water in the tank. When 150 kg of water at 10 °C is heated to 65 °C, how much energy flows into **the water?** **(ans: 35 MJ)**

**$Q = m c \Delta t$**
= ______ g x 4.19 J/g°C x 55°C

**$Q = m c \Delta t$**
= ______ kg x 4.19 kJ/kg°C x 55°C

## Heat Calculation Examples

1. Calculate the quantity of heat that flows into 1.50 L of water at 18.0 °C that is heated in an electric kettle to 98.7 °C. (ans: 507 kJ)

2. Determine the specific heat capacity of rock if 0.72 MJ of heat is released by a 2.5 kg rock when cooled from 350 °C to 15 °C? (ans: 0.86 J/g°C )

3. Determine the amount of heat energy required to warm 200 grams of aluminum from –20.0°C to 35.0° C. (ans: 9.87 kJ)

4. If 25000 J of energy is put into 175 grams of water at 25°C, what will the final temperature be? (ans: 59 °C)

**Energy Problems – Show all Work and Steps**

1. Calculate the heat produced by a chemical reaction, which causes 750 grams of water to undergo a temperature change from 17.4 °C to 63.2 °C. (ans: 144 kJ)

2. Determine the mass of water present if 22.8 kJ of heat is absorbed by the water at 18.0 °C causing the temperature to increase to 35.0 °C. (ans: 0.320 kg)

3. 2500 grams of 1-propanol solution was used in a calorimeter as the heat absorbing substance. 143.75 kJ of heat caused the 1-propanol to undergo a temperature change from 10.0 °C to 35.0 °C. Calculate the specific heat capacity constant for the 1-propanol. (ans: - 2.3 kJ/kg°C)

4. Determine the initial temperature of the water in a calorimeter if 54.0 kJ of energy is used to heat up 0.500 kg of water to 84.0°C. (ans: 58.2 °C)

5. Determine the final temperature of the water in a calorimeter if 65 kJ of heat is used to heat up 0.50 L of water at 24.0 °C. (ans: 55 °C)

6. Experiments have shown that a thermal energy change is affected by mass, specific heat capacity, and change in temperature. What happens to the thermal energy if
   a. the mass is doubled?

   b. the specific heat capacity is divided by two?

   c. the change in temperature has tripled?

   d. all three variables are doubled?

7. If the same quality of energy were added to individual 100 grams samples of water, aluminum, and copper, which substance would undergo the greatest temperature change? Explain.

## Heat Transfer and Enthalpy Change

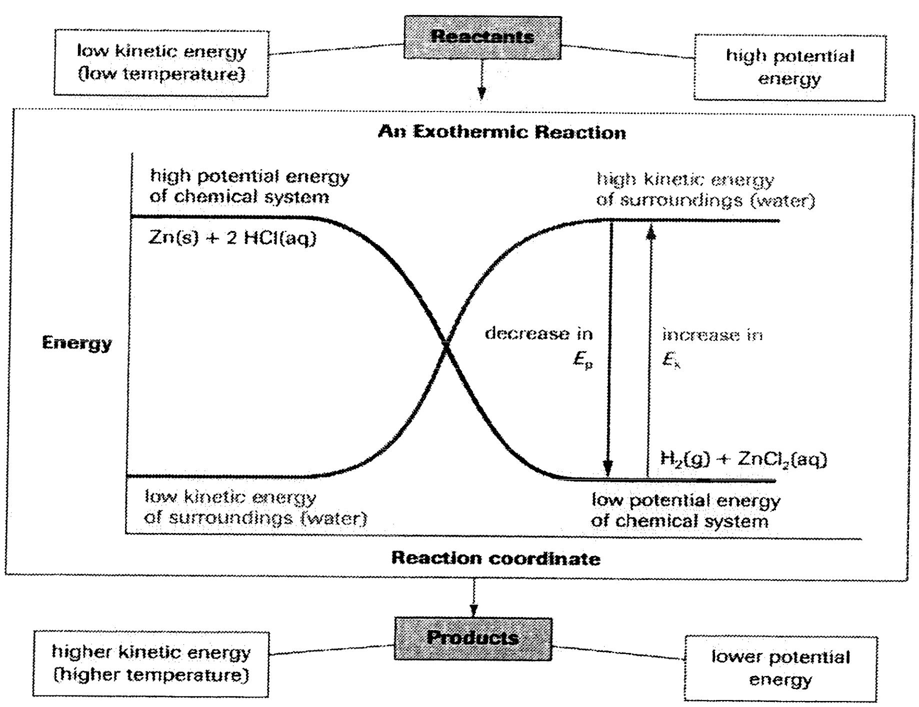
The total of the kinetic and potential energy within a chemical system is called **enthalpy.**

| Chemical Energy of a System | |
|---|---|
| **Kinetic Energy**(energy of motion) | **Potential energy** (stored energy) |
| Moving electron within atoms | Covalent and /or ionic bonds between atoms (**Intramolecular forces**) |
| The vibration of atoms connected by chemical bonds | **Intermolecular** forces between entities (LDF, DDF and HB) |
| Rotational and translational motion of molecules that are made up of all these atoms | |

- If the temperature of the reactants and products are the same then there is no change in kinetic energy of the system.
- Therefore if temperature is kept constant, then the only change of enthalpy is the result of a change in potential energy
- When there is a difference between the enthalpy (assume change in $E_p$) of the products and the enthalpy of the reactants, it is referred to as an enthalpy change, $\Delta H$.
- $\Delta H = H_{products} - H_{reactants}$
- Energy lost by a system will be equal to energy gained by the surrounding (calorimeter)
  - $\Delta H_{(system)} = Q_{(calorimeter)}$
    - $\Delta E_p = \Delta H$ (system) and $\Delta E_k = Q$ (calorimeter)

## Energy Transfer Concept Diagram

**Consider the following reaction:** $Zn(s) + 2\ HCl(aq) \rightarrow H_2(g) + ZnCl_2(aq)$




During an exothermic chemical reaction, some of the potential energy is converted to kinetic energy, which then gets transferred to the surroundings.

## Molar Enthalpies and Calorimetry

### Molar enthalpy of reaction

- is the enthalpy change when one mole of a specified chemical undergoing a change in the system at constant pressure.
- IUPAC symbol is $\Delta_r H_m$
- Units are (kJ/mol)
- If the mass or number of moles of the substance undergoing the change is known, then the energy change of reaction can be found using the following equation:

$\Delta_r H = n\, \Delta_r H_m$ Where - $\Delta_r H$ -change of reaction (kJ)
- $n$ -chemical amount (mol)
- $\Delta_r H_m$ - molar enthalpy of reaction (kJ/mol)

If the reaction was combustion use $\Delta_c H = n\, \Delta_c H_m$

| |
|---|
| $Q = mc\Delta T$ change in $E_k$ |
| $\Delta_r H = n\Delta_r H_m$ change in $E_p$ |

**e.g.#1** Predict the enthalpy change for the combustion of every 100g of methane in a natural gas water heater. ($\Delta_c H_m$ ($CH_4$) = -802.5 kJ/mol (to produce water vapour))

## Molar Heat Problems

***Solve the following problems, including all formulae, substitution with units and an answer with the proper units.***

1. 1.75 grams of ammonia undergoes a reaction. If the molar heat of ammonia for this reaction is -131 kJ/mol, determine the amount of energy produced. (ans: -13.5 kJ)

2. 0.320 grams of methane undergoes combustion producing 17 500 J of heat energy. Calculate the molar heat of combustion of methane (ans: - 878 kJ/mol)

3. Paradichlorobenzene ($C_6H_4Cl_2$) undergoes solidification ( a phase change) and 9 600 J of heat energy is produced. Determine the mass of paradichlorobenzene used if $\Delta_m H_s$ = -320 kJ/mol ($C_6H_4Cl_2$) (ans: 4.41 g)

**<u>Molar Enthalpy of reaction can be calculated using the Law of Conservation of Energy</u>**

change in enthalpy of a chemical system($\Delta H$) = thermal energy change in a calorimeter (Q)

$$\mathbf{\Delta H = Q}$$
$$\mathbf{n\Delta_c H_m = mc\Delta t}$$

| | |
|---|---|
| n = | moles of fuel |
| $\Delta_c H_m$ = | molar enthalpy of combustion of fuel |
| m = | mass of water |
| c = | specific heat capacity of water |
| $\Delta t$ = | temperature change of water |

**e.g.#2** Methanol is one type of fuel that is used in fondue heaters. In an experiment using a simple tin can calorimeter, 2.98 g of methanol was burned to raise the temperature of 650 g of water by 20.0°C. Using this evidence, calculate, the molar enthalpy of combustion of methanol (to produce water as a vapour) (ans: kJ/mol)
-586

e.g.#3 2.10 grams of methane is burned ($\Delta_c H_m$ = -802.5 kJ/mol) is burned to heat up 400 grams of water that is initially at 22.0°C. Determine the final temperature of the water. (ans: 84.6°C)

## Calorimetry Problems

1. Determine the molar heat of combustion if 1.2 grams of ethane burned in a calorimeter causes the temperature of 200 grams of water to rise from 11°C to 94°C. (ans: -1.7 MJ/mol)

2. If 8.00 grams of ammonium nitrate is dissolved in one litre of water for use as a plant fertilizer, the water increases in temperature from 21.00°C to 30.39°C. Determine the molar enthalpy ($\Delta_{sol}H$) of solution of the ammonium nitrate. (ans: -394 kJ/mol)

3. How much propane in grams ($\Delta_c H_m$ = -2043.9 kJ/mol) would have to be burner in an open system to raise the temperature of 300 mL of water from 20.00°C to its boiling point? (ans: 2.17 g)

4. In a calorimetry experiment, the burning of 5.08 grams of benzene ($C_6H_6$) released enough enthalpy to raise the temperature of 5.00 kg of water from 10.1°C to 19.6°C. Calculate the molar heat of combustion of benzene. (ans: – 3.06 MJ/mol)

5. Predict the final temperature of a 500 g aluminum ring that is initially at 25.0°C and is heated by combusting 4.95 grams of ethanol, ($\Delta_c H_m$ = -1234.8 kJ/mol) in an open system. (ans: 321°C)

## Bomb Calorimetry (Extension)

Bomb calorimeters are used in research to measure enthalpy changes of combustion of fuels, foodstuffs, crops, and explosives. It is a useful technology, but calorimeters that are larger and more sophisticated than polystyrene cups usually have a noticeable heat transfer to or from the calorimeter materials. The total energy change of the calorimeter is the sum of the energy changes of all of the components.

| $Q$ | $=$ | $m_w c_w \Delta t$ | $+$ | $m_1 c_1 \Delta t$ | $+$ | $m_2 c_2 \Delta t$ | $+$ | $m_3 c_3 \Delta t$ |
|---|---|---|---|---|---|---|---|---|
| calorimeter | | water | | containers | | stirrer | | thermometer |

leads to $Q = (m_w c_w + m_1 c_1 + m_2 c_2 + m_3 c_3)\,\Delta t$

$Q = C\Delta t$

The **heat capacity** of a calorimeter is the total energy absorbed or released per degree Celsius for the calorimeter and its contents. Its units are J/°C or kJ/°C.

$$Q = C\Delta t \qquad\qquad n\Delta_c H_m = C\Delta t$$

1. An oxygen bomb calorimeter has a heat capacity of 6.49 kJ/°C. The complete combustion of 1.12 g of ethyne, $C_2H_2(g)$, produces a temperature change from 18.60 °C to 27.15 °C. Calculate the molar enthalpy of combustion, $\Delta_c H_m$, for ethyne. (ans: - 1.29 MJ/mol)

2. The molar enthalpy of combustion for gasoline is -1.3 MJ/mol. A particular engine has a heat capacity of 105 kJ/°C. Assuming 100% efficiency, and assuming that gasoline only consists of octane ($C_8H_{18}(l)$), what is the minimum mass of gasoline that must be burned to change the temperature of the engine from 18°C to 120°C? (ans: 0.94 kg)

## Four Methods of Communication Molar Enthalpies

### 1. Molar Enthalpies of Reaction ($\Delta_r H_m$)

- A measure of the amount of heat energy that flows out of or is absorbed by the reaction of one mole of a substance
- Along with the molar enthalpy, the formula of the substance must be included while the reaction **may** be given depending if the reaction is a common one such as combustion, formation or simple decomposition.

- If the reaction is common or well known, it is **not** necessary to include the reaction. For these situations, only the molar enthalpy is given. (I.e. $\Delta_f H_m$ (formation) and $\Delta_c H_m$(combustion))

e.g. $\Delta_f H_m{}^\circ_{CH_4} = -74.5$ kJ/mol assumes $C(s) + 2H_2(g) \text{------------>} CH_4(g)$

or $\Delta_c H_m{}^\circ_{CH_4} = -802.5$ kJ/mol assumes $CH_4(g) + 2O_2(g) \text{--->} CO_2(g) + 2H_2O(g)$

optional to be included for a common reaction ie. Combustion

Standard Molar Enthalpy($\Delta_r H_m{}^\circ$)

- Measure at SATP (both the initial and final conditions)
- Symbol $\Delta_r H_m{}^\circ$
- Most commonly used
- Measure of the total energy absorbed or released as the reactants react at SATP until the products cool down or warm back up to SATP

**Note**: Molar enthalpy must be present along with the chemical equation unless reaction equations are well known.

e.g. $NH_3(g) + HCl(g) \text{--------------->} NH_4Cl(s)$

$\Delta_r H_m{}^\circ_{NH_3} = -176$ kJ/mol

## 2. Enthalpy Changes ($\Delta_r H$)

- Used to calculate enthalpy change, $\Delta_r H^\circ$, of a reaction
- Always includes
  - a balanced chemical reaction
  - a change in enthalpy

$\Delta_r H^\circ = n\Delta_r H_m{}^\circ$ where n = number of moles or amount of substance that is known

i.e. If the $\Delta_r H_m{}^\circ$ for the reaction of sulfur dioxide with oxygen is known to be -98.9 kJ/mol, then the amount of enthalpy for the following reaction

$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ is:

$\Delta_r H^\circ = n\,\Delta_r H_m{}^\circ$
$= 2 \text{ mol} \times -98.9 \text{ kJ/mol}$
$= -197.8$ kJ

therefore ⟶ $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ $\Delta_r H^\circ = -197.8$ kJ

while ⟶ $SO_2(g) + \frac{1}{2}O_2(g) \rightarrow SO_3(g)$ $\Delta_r H^\circ = -98.9$ kJ

**Note:** - a negative enthalpy change represents an exothermic reaction
- a positive enthalpy change represents an endothermic reaction

## 3. Energy Written as Part of the Balanced Equation

- *endothermic* reaction - energy is written as a reactant (LHS of the balanced equation)

e.g. *Decomposition of liquid water*

$H_2O(l)$ + 285.8 kJ → $H_2(g)$ + ½ $O_2(g)$

*decomposition of butane*

$C_4H_{10}(g)$ + 125.7 kJ → 4C(s) + $5H_2(g)$

- *exothermic* reaction - energy is written as a product (RHS of the balanced equation)

*formation of magnesium oxide*

- e.g. Mg(s) + 1/2 $O_2(g)$ → MgO(l) + 601.6kJ

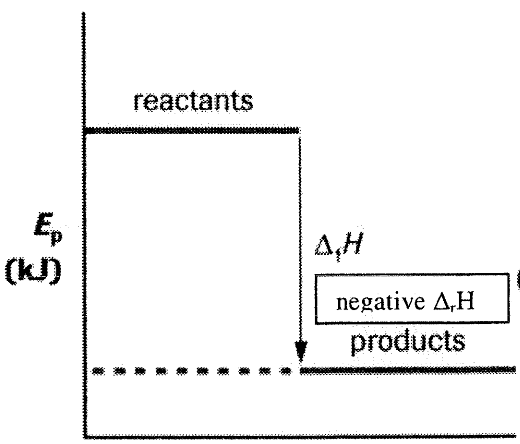
*Combustion of methane*

$CH_4(g)$ + 2 $O_2(g)$ → $CO_2(g)$ + 2 $H_2O(g)$ + 802.5 kJ

## 4. Potential Energy Diagrams

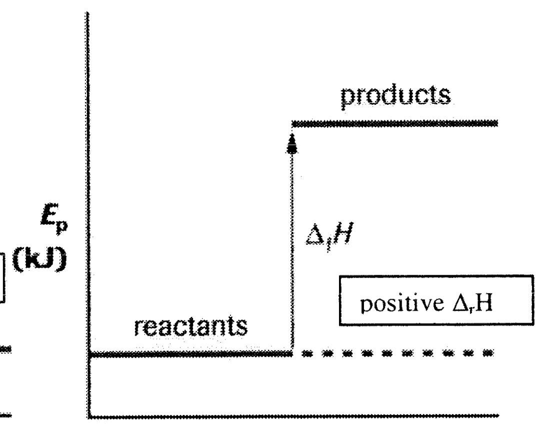
- shows change in $E_p$ during a chemical reaction
- as a reaction occurs, positions of atoms are changed, existing bonds are broken and new bonds are formed with new strengths and new potential energies.
- This change in $E_p$ can be represented by an $E_p$ diagram
- An $E_p$ diagram shows the $E_p$ of the reactants and products. The difference between them represents the enthalpy change.

**Exothermic Reaction**




**Reaction coordinate**

**Endothermic Reaction**




**Reaction coordinate**

## Thermochemical Equations

A. Rewrite the following equations by expressing the balanced equation for **one** mole of the substance underlined and using the $\Delta_r$H notation.

1. 2 $PF_3$ + <u>3 $PbCl_2$</u> → 2 $PCl_3$ + 3 $PbF_2$ + 356 kJ

2. 3 $NaNH_2$ + 1 $NaNO_3$ + 280 kJ → 1 $NaN_3$ + 3 NaOH + 1 $NH_3$

3. 4 $NH_3$ + 5 $O_2$ → 4 NO + 6 $H_2O$ + 279.4 kJ

4. 1 CuS + 2 $Cu_2O$ + 456.8 kJ → 1 $SO_2$ + 5 Cu

B. Rewrite the following equations by expressing the energy change as a **term in the equation.** Write the equation using the **simplest** whole numbers.

1. 1 $NH_3$ + ¾ $O_2$ → ½ $N_2$ + 3/2 $H_2O$ $\Delta_rH°$ = + 91.4 kJ

2. 1 $Al_2O_3$ → 2 Al + 3/2 $O_2$ $\Delta_{sd}H°$ = - 1680 kJ

3. ½ $N_2$ + ½ $O_2$ → 1 NO $\Delta_fH°$ = - 21.6 kJ

**Communicating Enthalpy in Four Methods**

Enthalpy change may be communicated by any one of the following four methods:

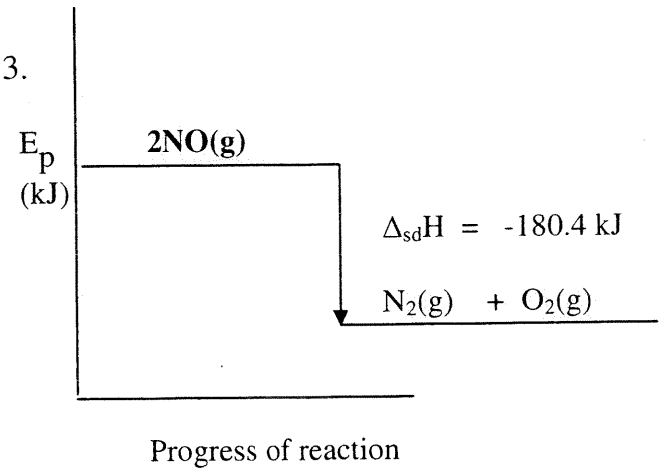
- Molar enthalpy method ($\Delta_rH_m$)
- Enthalpy as part of the equation
- $\Delta_rH°$
- $E_p$ diagram

In each of the following questions molar enthalpy is communicated using one of the above methods. In the space provided, show how communication would occur for the **bold-faced** substance using the other 3 methods.

1. 2 NO(g) + $O_2$(g) -----------------> **2$NO_2$(g)** + 114.0 kJ

2. $\Delta_c H_m^\circ$ = -1428.5 kJ/mol for $C_2H_6(g)$

3.




4. For each of the following balanced chemical equations and enthalpy changes, calculate the molar enthalpy of combustion and give the answer using the appropriate molar enthalpy communication for the substance that reacts with oxygen.
   a. $2\ H_2(g) + O_2(g) \rightarrow 2H_2O(g)$ $\Delta_c H^\circ = -483.6$ kJ

   b. $4NH_3(g) + 7\ O_2(g) \rightarrow 4\ NO_2(g) + 6\ H_2O(g) + 1272.1$ kJ

5. Translate the empirical molar enthalpies given below into a balance chemical equation, including the enthalpy change ($\Delta_r H$)
   e.g. $CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(g)$ $\Delta_c H = -\ 802.5$ kJ

   a. The standard molar enthalpy of combustion for methanol to produce water vapour is – 725 kJ/mol.

   b. The standard molar enthalpy of simple decomposition $\Delta_{sd}H_m^\circ$, for iron(III)oxide is 824.2 kJ/mol.

6. Iron(II) sulfide ore is roasted according to the following chemical equation.
   $4\ FeS(s) + 7\ O_2(g) \rightarrow 2\ Fe_2O_3(s) + 4\ SO_2(g)$   $\Delta_c H = -2456$ kJ

   (a) Rewrite this chemical equation including the energy as a term in the balanced equation.

   (b) What is the molar enthalpy for iron(II) sulfide in this reaction? (ans: -614 kJ/mol)

## HESS' LAW - Principle of Additivity of Reaction Enthalpies

The enthalpy absorbed or evolved in a given chemical reaction is independent of whether the reaction occurs in one step or in several steps. If the reaction occurs in several steps, the over-all heat of reaction will be the algebraic sum of the heats of the various steps. Furthermore, this heat of reaction will be numerically the same as that obtained if the reacting were carried out in one step. Thus heats of reaction may be calculated for reactions which do not lend themselves to direct experimental techniques.

Example 1   Determine the heat of reaction for the following reaction at SATP.

$$C_{(s)} + 2H_2(g) \text{ ------------> } CH_4(g) \qquad \Delta_f H = ???$$

Given the following equations:

1. $H_2(g) + \frac{1}{2}\ O_2(g) \text{ ----------> } H_2O(l)$   $\Delta_f H° = -286.0$ kJ
2. $C(s) + O_2(g) \text{ ----------> } CO_2(g)$   $\Delta_f H° = -393.5$ kJ
3. $CH_4(g) + 2\ O_2(g) \text{ -------> } CO_2(g) + 2\ H_2O(l)$   $\Delta_f H° = -890.8$ kJ

Rearrange the equations to give the desired reactants and products, altering ΔH° accordingly.

**Leave equation 2 unchanged:**

$C(s) + O_2(g) \text{ ----------> } CO_2(g)$   $\Delta_f H° = -393.5$ kJ

**Double equation 1:**

$2\ H_2(g) + O_2(g) \text{ ----------> } 2\ H_2O(l)$   $\Delta_f H° = -572.0$ kJ

**Reverse equation 3:**

$CO_2(g) + 2\ H_2O(l) \text{ ------> } 2O_2(g) + CH_4(g)$   $\Delta_r H° = +890.8$ kJ

---

**Add:**

$C(s) + 2\ H_2(g) \text{ ----------> } CH_4(g)$   $\Delta_f H° = -74.7$ kJ

> **Hess's Law**
> **The amount of energy involved in a chemical reaction is the same whether the reaction occurs in one single step or in a series of smaller steps.**

$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$ $\Delta_c H° = ???$

1. $3C_{(s)} + 4H_{2(g)} \rightarrow C_3H_{8(g)}$ $\Delta_f H° = {}^{-}103.8\text{kJ}$
2. $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta_f H° = {}^{-}393.5\text{kJ}$
3. $H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(g)}$ $\Delta_f H° = {}^{-}241.8\text{kJ}$

Rewrite

eg. #3 a. Determine the $\Delta_f H_m°$ for $C_3H_7OH_{(l)}$ formation

b. Predict the enthalpy change for the ~~combustion~~ formation of 4.50g of propanol.(ans: -11.1kJ/mol)

using:

1. $C(s) + O_2(g) \rightarrow CO_2(g) + 393.5\text{ kJ}$
2. $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(g) + 241.8\text{ kJ}$
3. $C_3H_7OH(l) + 9/2\ O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O(g) + 2000\text{kJ}$

Rewrite

**Solve the following problems using Hess's Law. Show all work.**

1. Determine the change of enthalpy of reaction for the following reaction at SATP.

$C(s) + H_2O(g)$ -----> $CO(g) + H_2(g)$

Given:

$C(s) + O_2(g)$ -----> $CO_2(g)$ $\Delta_f H° = -393.5$ kJ

$CO(g) + 1/2\ O_2(g)$ -----> $CO_2(g)$ $\Delta_f H° = -283.0$ kJ

$H_2(g) + 1/2\ O_2(g)$ -----> $H_2O(g)$ $\Delta_f H° = -242.0$ kJ

2. Determine the change in enthalpy of reaction for the following reaction at SATP

$2\ C(s) + 2\ H_2(g) + O_2(g) \text{ -----> } CH_3COOH(l)$

Given:

| | |
|---|---|
| $H_2(g) + 1/2\ O_2(g) \text{ -----> } H_2O(l)$ | $\Delta_f H° = -286.0$ kJ |
| $C(s) + O_2(g) \text{ -----> } CO_2(g)$ | $\Delta_f H° = -393.5$ kJ |
| $CH_3COOH(l) + 2\ O_2(g) \text{ -----> } 2\ CO_2(g) + 2\ H_2O(l)$ | $\Delta_c H° = -871.5$ kJ |

3. Given:

$N_2(g) + 5/2\ O_2(g) + 15\text{ kJ} \text{ -----> } N_2O_5(g)$

$H_2(g) + 1/2\ O_2(g) \text{ -----> } H_2O(l) + 286\text{ kJ}$

$1/2\ H_2(g) + 1/2\ N_2(g) + 3/2\ O_2(g) \text{ -----> } HNO_3(l) + 173\text{ kJ}$

The change of heat of reaction for:

$N_2O_5(g) + H_2O(l) \text{ -----> } 2\ HNO_3(l)$ is:

4 a. Calculate the molar enthalpy of formation of iron (III) oxide from iron and oxygen from the following data: Hint: Write a formation reaction for iron(III)oxide.

b. Determine the amount of heat energy produced during the formation of 20.0 grams of iron(III)oxide.

Given:

$3\ C(s) + 2\ Fe_2O_3(s) + 481.0\text{ kJ} \text{ -----> } 4\ Fe(s) + 3\ CO_2(g)$

$C(s) + O_2(g) \text{ -----> } CO_2(g) + 393.5\text{ kJ}$

5. Ethyne gas may react with hydrogen gas to form ethane gas in the following reaction:

$C_2H_2(g) + 2\ H_2(g) \rightarrow C_2H_6(g)$

Predict the enthalpy change for the reaction of 200 grams of ethyne, using the following information. (ans: -2.39 MJ)

| | | |
|---|---|---|
| (1) | $C_2H_2(g) + 5/2\ O_2(g) \rightarrow 2\ CO_2(g) + H_2O(l)$ | $\Delta_cH = -1299 kJ$ |
| (2) | $H_2(g) + ½\ O_2(g) \rightarrow H_2O(l)$ | $\Delta_cH = -286\ kJ$ |
| (3) | $C_2H_6(g) + 7/2\ O_2(g) \rightarrow 2\ CO_2(g) + 3\ H_2O(l)$ | $\Delta_cH = -1560\ kJ$ |

**Answers**

1. $\Delta_rH° = +131\ 5\ kJ$
2. $\Delta_rH° = -487.5\ kJ$
3. $\Delta_rH° = -75\ kJ$
4. $\Delta_fH_m° = -830.8\ kJ$, 104 kJ
5. $\Delta_rH° = -2.39\ MJ$

## Molar Enthalpies of Formation

**Molar Heat of Formation (Data Table page 4/5)**

- **Is the amount of enthalpy released or absorbed when one mole of a compound is formed from its elements.**
  e.g. $2Al(s) + 3/2\ O_2(g) \longrightarrow Al_2O_3(s)$

  $$\mathbf{\Delta_fH_m° = {}^-1675.7\ kJ/mol}$$

To calculate the enthalpy change during any type of change (i.e. chemical change) use:

$$\mathbf{\Delta H_f° = n\Delta_fH_m°}$$

Calculate the enthalpy change for the formation of:

a) 2 moles of $Al_2O_3$

$\Delta_fH° = n\Delta_fH_m°$

$= 2\ mol \times {}^-1675.7\ kJ/mol$

$= {}^-3351.4\ kJ$

b) 39.4 grams of $Al_2O_3$

c) 21.4 grams of sulfur dioxide

**Molar Heat of Decomposition** **(Reverse reading of $\Delta_f H_m$ Data Table page 4/5)**

- Is the amount of enthalpy released or absorbed when one mole of a compound decomposes to its elements.
  e.g. Simple decomposition of 1 mole of nitric acid.

Reversed of formation $HNO_3(g) \rightarrow 1/2H_2(g) + 1/2N_2(s) + 3/2\ O_2(g)$

**Energy is the opposite of formation** $\Delta_{sd}H_m = {}^{+}174.1$ kJ/mol

Note: sign is opposite to that of formation (page 4/5 –data book)

e.g. Calculate the energy required for the simple decomposition of 6.41mol of $HNO_3$.

$\Delta H_{sd}° = nH_{sd}°$

$= 6.41\text{mol} \times {}^{+}174.1$ kJ/mol

$= {}^{+}1116$ kJ

Calculate the energy involved to decompose 23.0 grams of methane gas into its elements

**Predicting $\Delta_r H°$ can be done in one of three methods**

- Calorimetry
- Hess's Law
- Using formation rxns

The enthalpy produced in a reaction can be calculated by adding up the enthalpies of formation of all products and subtracting the enthalpies of formation of all the reactants.

$$\Delta_r H = \Sigma n\Delta_{fP}H_m - \Sigma n\Delta_{fR}H_m$$

- **elements** serve as the reference energy point and are set with an energy level equal to zero
- The formation of compounds can be found in the data book.

e.g. $Pb_{(s)} + Br_{2(l)} \longrightarrow PbBr_{2(s)}$

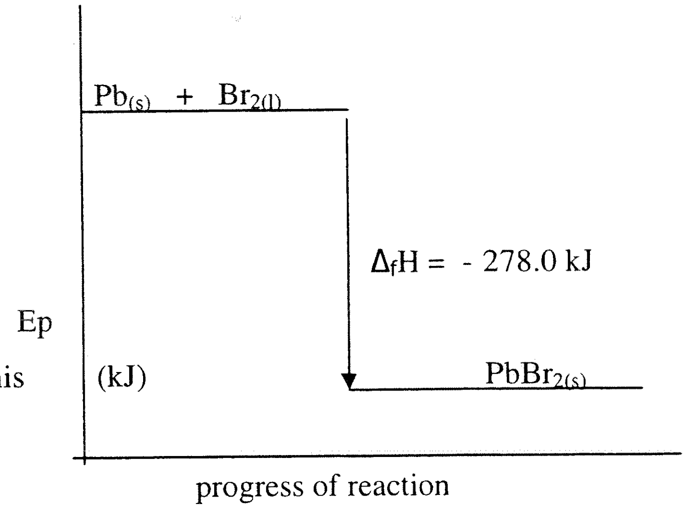
$\quad 0 \qquad 0 \qquad (^{-}278.7\ kJ/mol)$

$\Delta_r H = \Sigma n \Delta_{fP} H_m - \Sigma n \Delta_{fR} H_m$

$= (^{-}278.7kJ) - (0) \quad = {}^{-}278.7kJ$

If this value is very large it means it has a high $\triangle_{sd}H° = {}^{+}278.7kJ$ and has a high thermal stability this compound will not decompose unless 278.7kJ of energy has been added.

Therefore the <u>higher negative</u> $\Delta_f H_m°$ a compound has, the <u>greater</u> that <u>compounds thermal stability</u>. This means these compounds need a lot of energy to break the chemical bonds of the compound to form its elements.




e.g. $Al_2O_3$ is more stable than $PbBr_2$

i.e. $^{-}1675.7$kJ/mol is a higher negative value than $^{-}278.7$kJ/mol

e.g. Rank the following compound from the most to the least thermally stable.

1. $AgI(s)$
2. $AgCl(s)$
3. $HNO_3(l)$
4. $C_3H_8(l)$ ____ ____ ____ ____

Calculate the $\Delta_r H_m°$ of $H_2SO_4$ in the following reaction

1. $H_2SO_4(aq) + Mg(OH)_2(s) \longrightarrow 2HOH(l) + MgSO_4(s)$

a. $\Delta_r H = \Sigma n \Delta_{fP} H_m - \Sigma n \Delta_{fR} H_m$

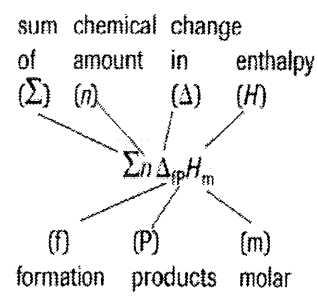
b. Draw a potential energy diagram for the above reaction

c. How much energy would be produce after 8.50 grams of $H_2SO_4(aq)$ has been consumed?

2. Determine the enthalpy of combustion for one mole of ethanol

$$\Delta_c H = \Sigma n \Delta_{fP} H_m - \Sigma n \Delta_{fR} H_m$$

The symbols for this method of calculating the enthalpy of reaction are meant to help but, initially, can be confusing.




3. What is the molar heat of combustion of acetylene (ethyne) if the products are carbon dioxide and liquid water? (ans: -1300.2 kJ/mol)

4. a. Carbohydrates, such as sugars and starches, are oxidized in the body to provide needed energy. The oxidation of carbohydrates is the reverse of photosynthesis and therefore the energy released in respiration must ultimately have come from the sun (solar energy). Calculate the molar heat of combustion for glucose assuming the products are carbon dioxide and liquid water. (ans: -2802.5 kJ/mol)

b. How much energy would be produced during cellular respiration if 50.0 g of glucose was consumed? (ans: -778 kJ)

5 a. Calculate the molar heat of reaction for the incomplete combustion of acetic acid according to the following equation. (ans: -692.0 kJ/mol)

$$6\ CH_3COOH(l) + 11\ O_2(g) \rightarrow 10\ CO_2(g) + 2\ CO(g) + 12\ H_2O(g)$$

b. How much energy would be produce if 10.0 grams of acetic acid burned? (ans: -115 kJ)

c. What is the molar enthalpy of reaction for carbon dioxide in the above reaction? (ans: -415.2 kJ/mol)

**Determining an unknown heat of formation**

1. The reaction for the combustion of octene is

   $C_8H_{16}(l) + 12\ O_2(g) \rightarrow 8\ CO_2(g) + 8\ H_2O(g)$ $\Delta H = -4902.4$ kJ

   The heat of formation of $C_8H_{16}(l)$ is? (ans: -180 kJ/mol)

## Multi-Step Energy Calculations

1. For the following combustion, what mass of carbon dioxide is produced when 1500 kJ of energy is released? (ans: 105 g)

   $2\ C_2H_6(g) + 7\ O_2(g) \rightarrow 4\ CO_2(g) + 6\ H_2O(g) + 2502$ kJ

2. How much energy is released when 1.00 t of sulfur trioxide is produced by the following reaction? (ans: 1.20 GJ)

   $2\ SO_2(g) + O_2(g) \rightarrow 2\ SO_3(g)$ $\Delta_r H = -192.6$ kJ

3. A waste heat exchanger is used to absorb the energy from the complete combustion of hydrogen sulfide gas. What volume of water undergoing a temperature change of 64 °C is required to absorb all of the energy from the burning of 15 kg of hydrogen sulfide? (ans: $8.3 \times 10^2$ L)

## Activation Energy

### Reactions Progress

- Some exothermic reaction do not occur spontaneously at room temperature
    - They need an external source of energy like a spark to get them started. Why?
    - Amount of energy required to initiate a reaction is dependant on the reactants.
    - Reaction of similar materials may occur at different rates.
    - Reaction rates may be affected by the amount of available surface area of the reactants

### Activation Energy

- Since exothermic reactions are energetically (thermodynamically) favoured, a careless thinker might conclude that all such reactions will proceed spontaneously to their products.

- Were this true, no life would exist on Earth, because the numerous carbon compounds that are present in and essential to all living organisms would spontaneously combust in the presence of oxygen to give carbon dioxide-a more stable carbon compound.

- The combustion of methane, for example, does not occur spontaneously, but requires an initiating energy in the form of a spark or flame.

- It seems that reactants must reach a certain minimum energy (**Activation Energy**) before they can react.

- This activation energy may be in any form of energy such as light, electricity or heat as when a match needs to be put to a combustible reactant to initiate a reaction.

- Once a reaction begins the energy given off by that reaction is passes on to neighboring molecules supplying them with *activation energy,* sustaining the reacti

## Activation Energy and Potential Energy

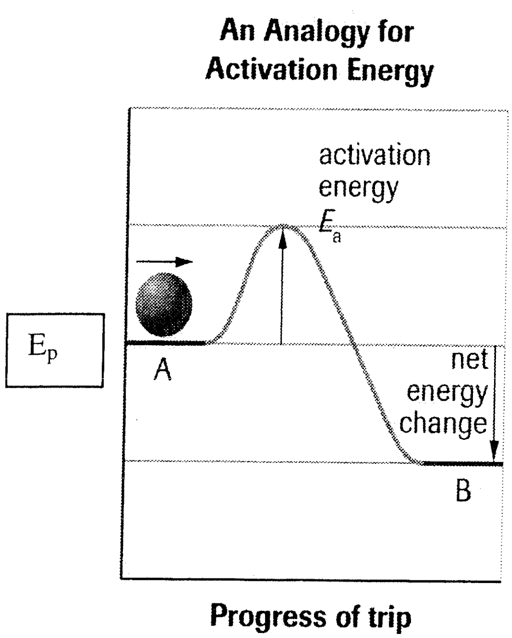
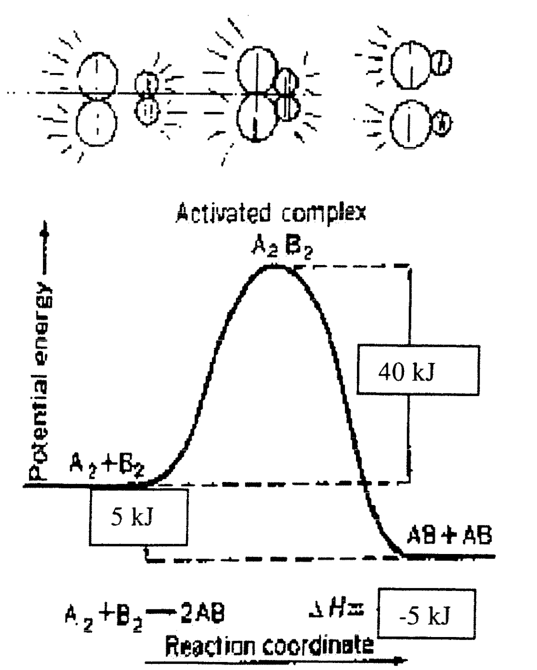



**Figure 3 (rolling billiard ball)**

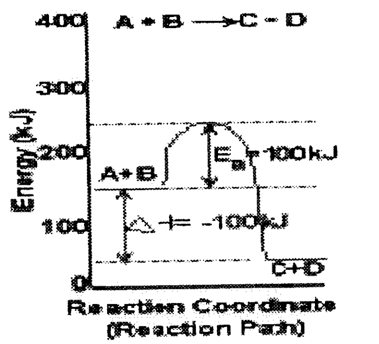
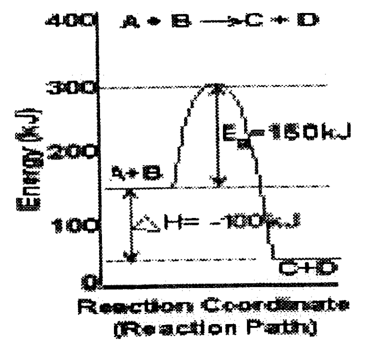
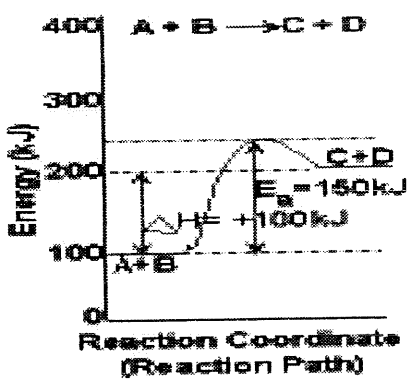
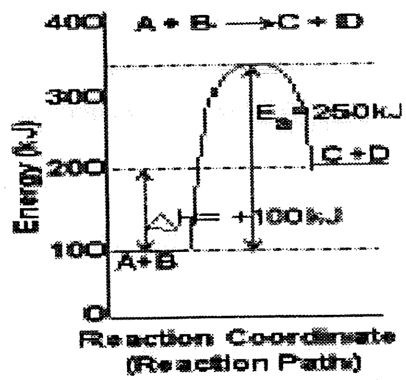
- On a trip from A to B, there is a net decrease in potential energy, but there must be an initial increase in potential energy (activation energy) for the trip to be possible.
- The ball will not complete the trip unless it has a minimum $E_k$ to get to the top of the slope.
- This is the same for an exothermic chemical reaction, if the reactants do not have a minimum energy, a reaction will not occur and the reactant will remain unreacted with the same initial $E_p$ as it had before.




**Consider the exothermic reaction to the left**

$A_2 + B_2 \rightarrow 2\,AB \qquad \Delta_rH = -5\ \text{kJ}$

- The energy pathway is the relative $E_p$ as the reaction move from reactants to activated complex to products.
- **Activated complex** – chemical entity momentarily created by the combination of the reactants.
- For a reaction to occur $A_2$ and $B_2$ must collide with enough kinetic energy to exceed the level of the activation energy.
- This will allow them to overcome the repulsive forces between the reactants in order to get close enough to form the **activated complex.**
- Once the activated complex forms, the bonds will rearrange to form AB + AB

| Type of Reaction | Faster Reaction<br>Lower activation energy | Slower Reaction<br>Higher activation energy |
|---|---|---|
| Exothermic |  |  |
| Endothermic |  |  |

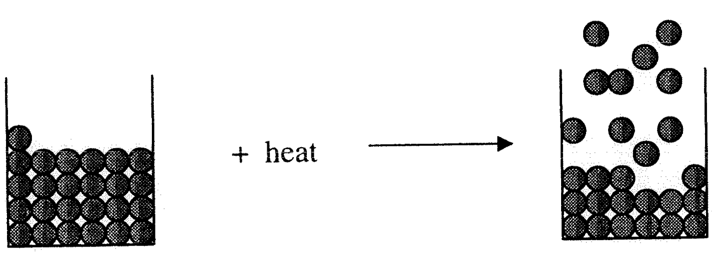


## Bond Energy and Reactions

BOND ENERGIES

- Bond energy is the energy required to break a bond or the energy released when a bond is formed
- When bonds form, energy is released and when bonds are broken energy is required.

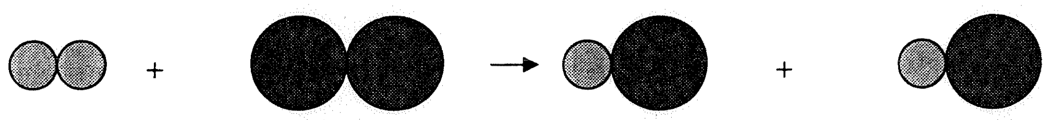
In **phase** changes, **INTERMOLECULAR BONDS** (the bonds holding one molecule to another molecule ie LDF, H-bonding & dipole-dipole) are broken and formed.




When a liquid is changed to a gas, the bonds holding these molecules together must be broken. Energy is **required** to break these **intermolecular forces.**

The opposite occurs when a gas changes to a liquid, the molecules come together and bonds are formed. Energy is **released** in this process.

In a **chemical** reaction, **INTRAMOLECULAR FORCES** (the bonds between one atom and another atom within a given molecule) are broken and formed.

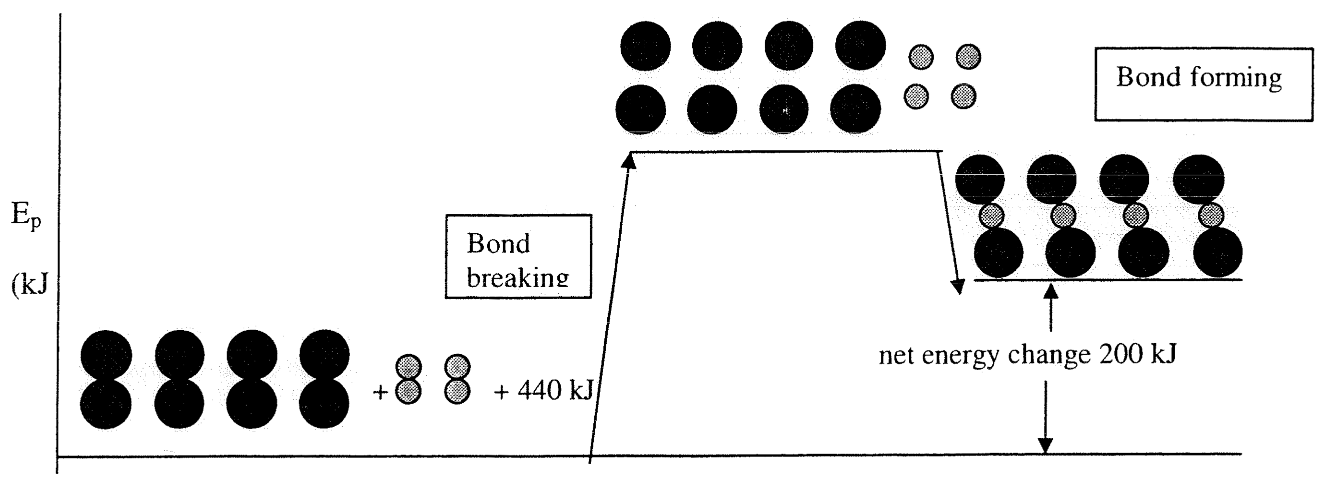


H-H + Cl-Cl → H-Cl + H-Cl

| H-H | + Cl-Cl | → H-Cl | + H-Cl |
|---|---|---|---|
| Energy required to break bond | Energy required to break bond | Energy released when bonds form | Energy released when bonds form |

- In an **exothermic** reaction, **more energy** is **released** when new bonds are formed than the energy required to break the bonds.
- In an **endothermic** reaction, **more energy** is **required** to break bonds than is released when new bonds are formed.

**An endothermic reaction can be represented by the following graph**




Since energy cannot be created or destroyed, the total energy of the right hand side of the equation must equal the total energy of the left hand side of the equation.

For an endothermic reaction $E_p$ of the reactants + energy → $E_p$ of the products

For an exothermic reaction $E_p$ of the reactants → $E_p$ of the products + energy

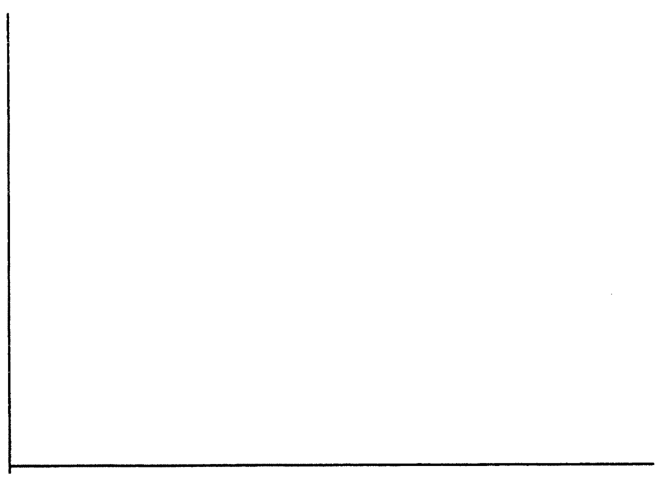
## Summary: Bond Energy and Enthalpy Changes

- Bond energy is the energy required to break a chemical bond; it is also the energy released when a bond is formed.
- The change in enthalpy represents the net effect from breaking and making bonds.
  $\Delta_r H$ = (energy released from bond making) − (energy required for bond breaking)
  Exothermic reaction: making > breaking ($\Delta_r H$ is negative.)
  Endothermic reaction: breaking > making ($\Delta_r H$ is positive.)

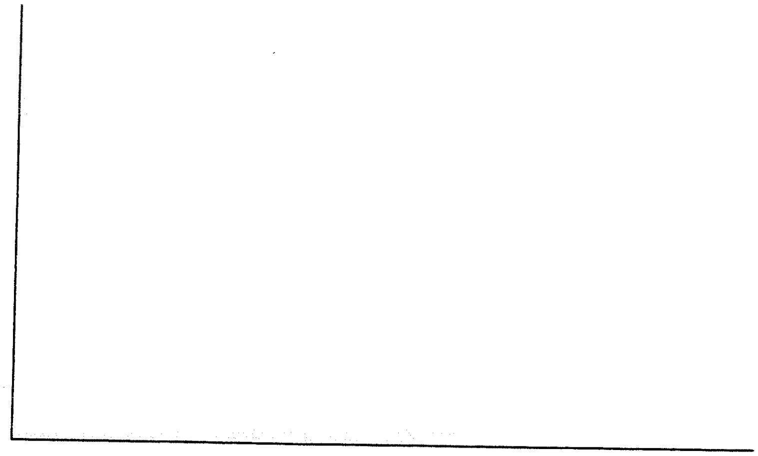
Questions

1. Bonded particles + ________________ → separated particles
2. Separated particles → bonded particles + ________________
3. In a chemical reaction, when the energy required to separate the reactants is greater than the energy released when new bonds form, the reaction is ____________________
4. Do the reactants or the products contain more energy in an **exothermic** chemical reaction? ____________________ .
5. For each of the following reactions, determine whether the reaction is endothermic or exothermic. Then sketch a labeled graph showing potential energy as the reaction progresses.

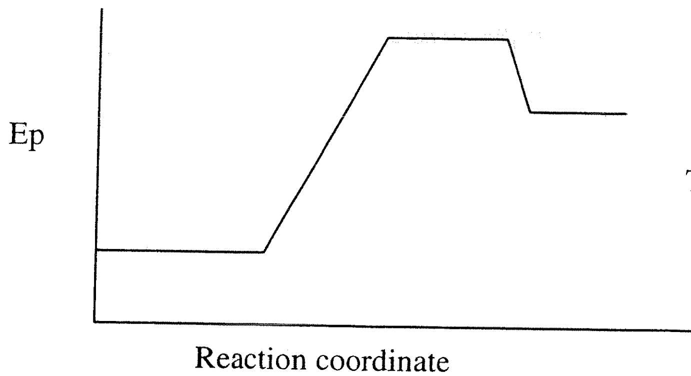
   a. $C_3H_{8(g)} + 5\ O_{2(g)} \longrightarrow 3\ CO_{2(g)} + 4\ H_2O_{(g)} + 2043.9\text{kJ}$



b. A + B + 200 kJ ⟶ C + D + 350kJ



c.




This represents a ________ reaction

## Catalysis and Reaction Rates

### Catalysts

- Is not consumed in the reaction
- Does not affect the equilibrium position of the reaction
- Does not affect the enthalpy change ($\Delta_rH$) of a reaction
- Reduces the amount of energy needed for a reaction to begin (Activation energy)
    - Increases the rate of reaction

- Part of a variety of reactions, from enzymes (*compounds that act as catalysts in living systems*) in the stomach to help digest food to catalytic converters in a car exhaust system which speeds up the combustion process to reduce pollutants.
- Results in many reactions made economical due to an increase in the efficiency of the reaction

### Inhibitors

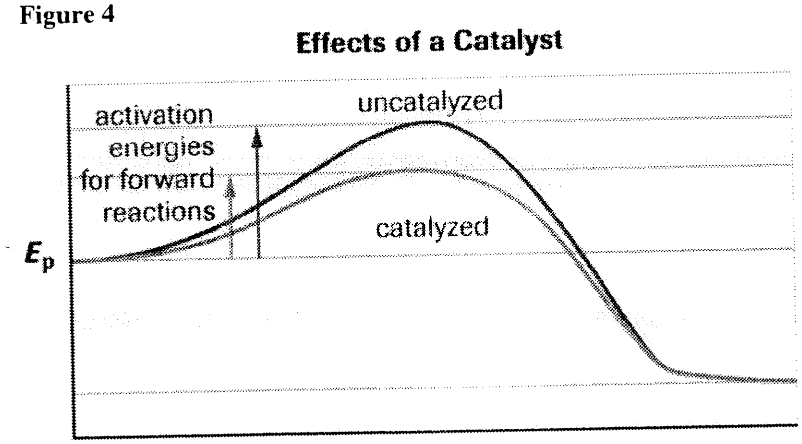
- Substances used to slow or stop reactions
- Act completely different that catalysts
- Food preservatives are examples of inhibitors to slow down deterioration.

## How do Catalysts Work?

- Provide an alternate pathway that has a lower *activation energy*
- Produces a different *activated complex* that uncatalyzed reactions
- As a result more molecules have sufficient energy to react resulting in a faster reaction rate for both forward and reverse reactions

### A Theoretical Explanation of Catalysis

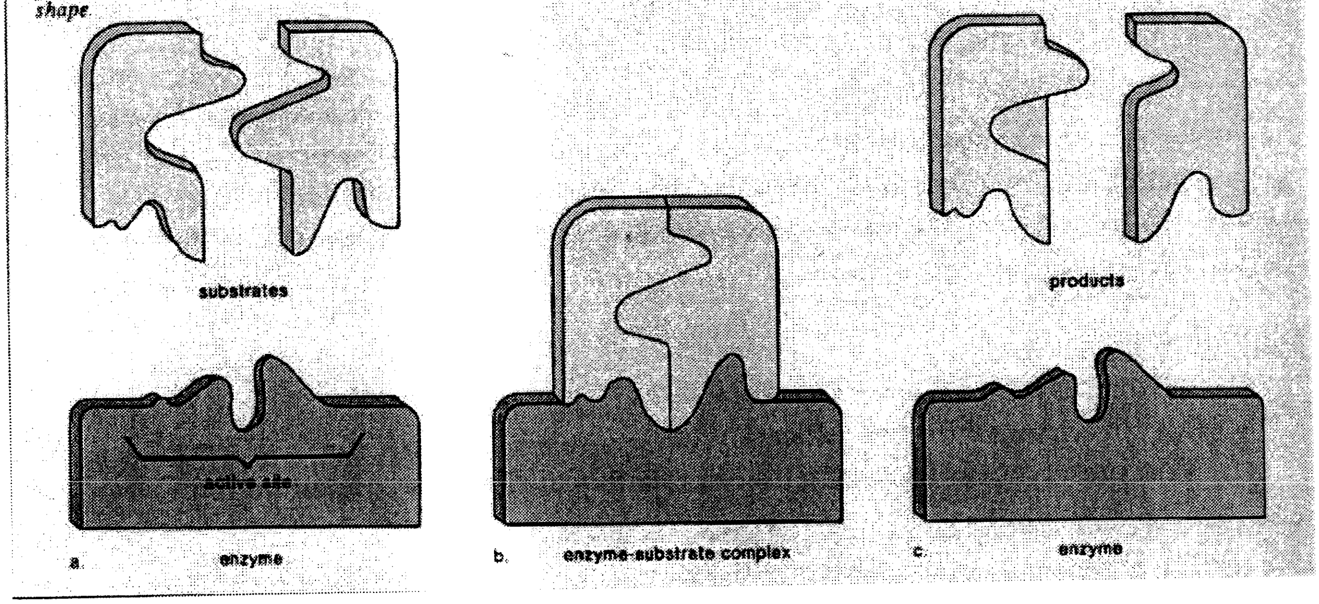
**Figure 4**




The catalyzed pathway has a lower activation energy, so more collisions lead to a successful reaction.

- For catalyst (enzymes) for biological reaction substrates (reactants fit into the enzyme like a "lock and key" as shown in the diagram below. They link on to the enzyme and then detach as the new product molecule.

*Enzymatic action. a. An enzyme has an active site, where (b) the substrates and enzyme fit together in such a way that the substrates are oriented to react. c. Following the reaction, the products are released and the enzyme assumes its original shape.*



<u>**Use for Catalysts**</u>

Oil Industry

- Reforming and cracking of crude oil and bitumen to produce gasoline and other products that are more marketable.
- Use of catalyst have allow ½ of a barrel of oil now to be converted to gasoline. In the 1920's only ¼ of a barrel of oil could be converted.
- Catalyst used include zeolite (silicates), Pt(s), $H_2SO_4$(aq), Pd(s) etc.

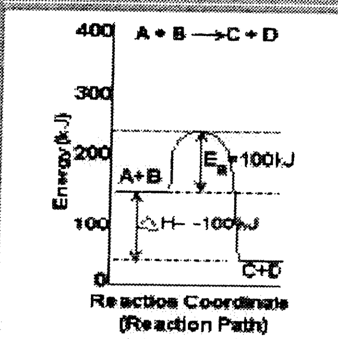
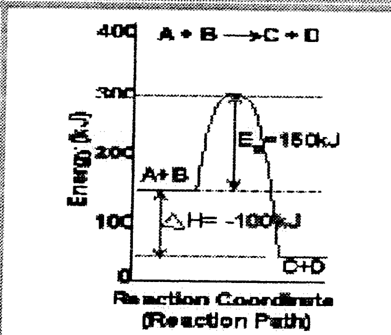
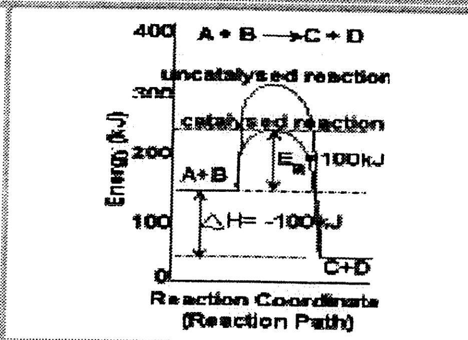
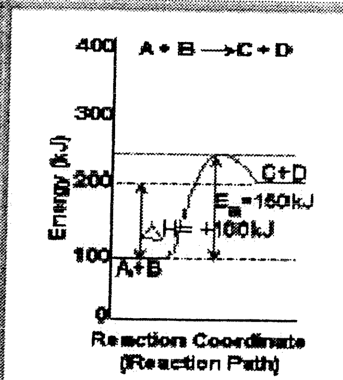
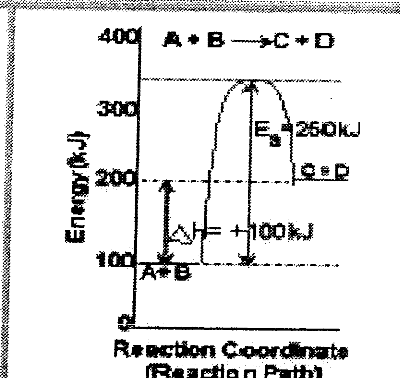
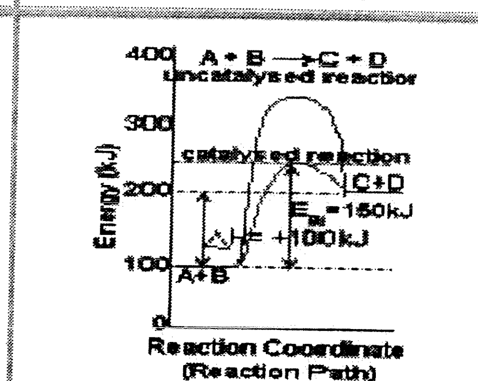
Emissions Control

- Breakdown and capture of emissions from power plants and from gas plants
- Include nitrogen oxides, sulfur compounds that contribute to pollution

Enzymes

- Used as catalysts for production of chemicals not found in nature for pharmaceuticals and agriculture

**Examples**

| Type of Reaction | Faster Reaction<br>Lower activation energy | Slower Reaction<br>Higher activation energy | Catalysed Reaction<br>A catalyst lowers the activation energy |
|---|---|---|---|
| Exothermic |  |  |  |
| Endothermic |  |  |  |

## Questions

1. Compare two reactions with the same reactants. One reaction involves a catalyst: the other does not.
   a. What is the same for both reactions?

   b. What is different for both reactions?

2. Consider the following reaction mechanism, in which A, B, and E may be elements or compounds, and C, D and F are compounds:

   (1) 2A + B ---> C

   (2) C --> D

   (3) D + E --> F

   a. Which entities are intermediates?

   b. Which entities are reactants?

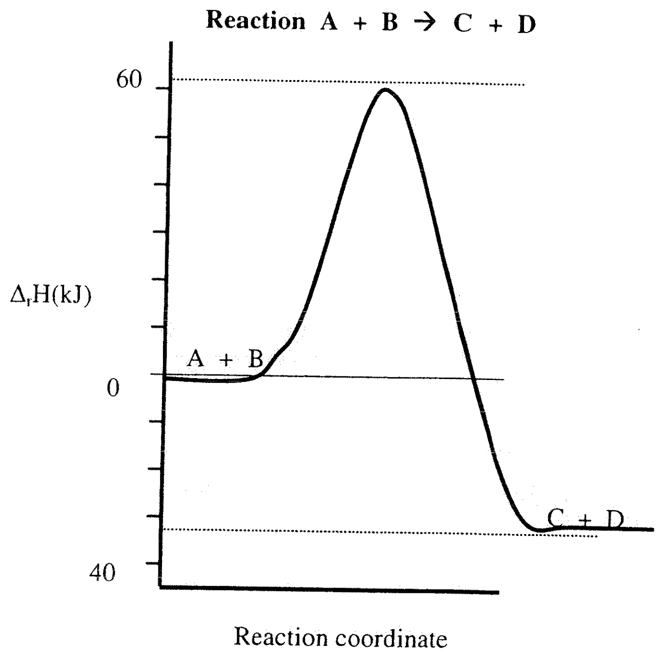
   c. Which entities are products?

   d. What is the overall reaction equation?

**Use this information to answer questions 3 to 4.**
Consider the energy pathway diagram for the hypothetical reaction in the diagram below. This reaction is reversible because under certain conditions, products will re-form the reactants.

3. a. What is the activation energy for the following net reaction.

   A + B --> C + D




b. What is the activation energy for the following net reverse reaction?

   C + D --> A + B

c. What is the change in enthalpy (net energy change) for the net forward reaction?

d. What is the change in enthalpy (net energy change) for the net reverse reaction?

e. Which reaction (forward or reverse) is exothermic?

4. Explain what you would expect to occur if the original collision of particles in the forward reaction has a total available kinetic energy equivalent to 55 kJ.

## Old Diploma Written Response Questions

1. The combustion of sugar in a bomb calorimeter is similar to the oxidation of sugar in the body. A student ate three sugar cubes, with masses of 6.84 g, 6.75 g, and 6.79 g.

   a. Calculate the overall molar enthalpy of oxidation of sugar, $C_{12}H_{22}O_{11}(s)$, in the body.
   (ans: -5639.7 kJ/mol)

   b. Using these sugar cubes as representative of regular sized cubes, determine the amount of energy released by an average-sized cube. (ans: 111.9 kJ)

   c. Draw and label a potential energy diagram representing the molar enthalpy of oxidation of sugar in the body.

2. *Use the following information to answer the next question*

The Uranium-235 isotope is used as a fuel in some nuclear power plant. This isotope is used to enrich natural uranium ore. Prior to the enrichment process. The uranium ore, $UO_2(s)$ is converted to $UF_6(s)$. The conversion is represented by the following sequential equations.

**Equation I** $UO_2(s) + 4\,HF(g) \rightarrow UF_4(s) + 2\,H_2O(l)$

**Equation II** $UF_4(s) + F_2(g) \rightarrow UF_6(s)$

a. Use molar heats of formation to calculate the amount of heat energy involved in producing 2.00 Mg of $UF_6(s)$ from natural uranium ore, $UO_2(s)$. (ans: 2.17 GJ)

**Molar Heats of Formation**

| **Substance** | $\Delta_f H_m$ |
|---|---|
| $UO_2(s)$ | -1129.7 |
| $UF_4(s)$ | -1914.0 |
| $UF_6(s)$ | -2112.9 |

b. Evaluate the use of nuclear energy for the generation of electricity. Include two reasons for and two reasons against the use of nuclear power.