Tiny Reservoirs of Energy

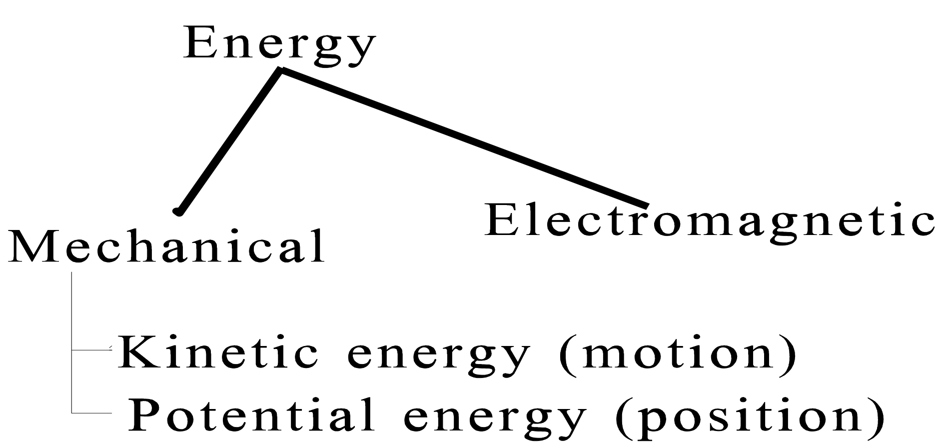
When we fill the gas tank of a car with gasoline, we provide the energy necessary to make the car run. In buying gasoline, we are in fact buying energy. The energy is released when the gas molecules burn. During the combustion process, the break up of the molecules releases energy. The released energy moves the pistons of the motor providing the necessary energy to operate the car.

When we buy groceries, we are also buying energy. In this case, we are buying chemical energy stored in food. During the process of digestion, a kind of slow combustion (burning), the food molecules break and release energy. The released energy is used by the body for all tasks such as running, singing, thinking, breathing, etc.

Molecules have potential energy. A portion of this energy is released during a chemical reaction. When energy is required, we use molecules having a high content of potential energy. From experience, you know that the energy content of chocolate, for example, is much higher than the energy content of celery. In a very real sense, therefore, molecules are tiny reservoirs of energy.

In this chapter, we study the potential energy associated with chemical reactions. Starting with a simple demonstration experiment, we will discover that potential energy (or Ep) is energy of position. In other words, we'll learn that "Ep" is stored energy.

Reminder: There are two types of energy, mechanical and electromagnetic. Mechanical energy is-further divided into two: kinetic energy (E_K), which is energy of motion; and potential energy (Ep), which is energy of position (stored energy). The energy associated with molecules is



mechanical in nature.

Gasoline molecules are similar to stretched rubber bands. Both possess potential energy ready to be released when needed. To release the energy stored in gasoline, all we need is a spark. Indeed, since it is so easy to ignite gasoline and thereby release huge amounts of energy, it is illegal to smoke in the vicinity of gasoline.

Here is the chemical equation representing the combustion of gasoline:

$$C_8H_{18(g)} + 25/2\ O_{2(g)} \longrightarrow 8\ CO_{2(g)} + 9\ H_2O_{(g)}$$

Note that while the gasoline in the tank of a car is in the liquid state, the internal heat of the motor converts the gasoline into the gaseous state. This is the reason why we include the "(g)" in the formula for gasoline, C_8H_{18}(g).

1) Complete the following equation by filling-in the term "+ energy" as necessary:

$C_8H_{18(g)}$ + 25/2 $O_{2(g)}$ ________________ $\longrightarrow$ 8 $CO_{2(g)}$ + 9 $H_2O_{(g)}$ ________________

2) Is the equation above exothermic or endothermic? Explain:

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3) Define "potential energy":

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Note that all molecules possess potential energy. The total potential energy of a substance is known as **enthalpy, H,** and depends upon a number of factors including:

- **Type of chemical bonds**
- **The number of chemical bonds**
- **The temperature**
- **The state of the substance**
- **Etc.**

Note: Due to the many factors involved in the formation of a substance, it is impossible to determine the enthalpy (total energy content) of a substance. The only thing we can determine is the change in enthalpy (increase or decrease) designated as ΔH (usually by heat flow).

4) Study the structural formula for the two molecules given below. Which molecule possesses the greater enthalpy? Explain:

$CH_{4(g)}$ **$C_2H_{6(g)}$**

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5) Which state of water (gas, liquid, or solid) possesses the most enthalpy? Explain why:

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6) An ice cube has a temperature of -10°C. Another cube of ice has a temperature of -30°C. Which of these two cubes possesses more enthalpy? Explain your answer.

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The Steps of a Reaction

Question: Why must we supply energy to a candle in order to light it and thus obtain energy from it? Indeed, once the reaction is initiated, it easily continues by itself. Of course, the candle cannot light itself spontaneously. Why?

Fortunately, paraffin (wax) is a stable substance. This means the candle will not light by itself. However, paraffin is not so stable that it is difficult to burn. If it were, we would have difficulty lighting the candle.

The flame of a burning match plays an important role in lighting a candle:

- First, it melts the wax (solid $\rightarrow$ liquid), an endothermic reaction.
- It then vaporizes the wax (liquid $\rightarrow$ gas), an endothermic reaction
- Lastly, it raises the temperature of gaseous wax and oxygen to a temperature high enough to break the molecular bonds of the wax and oxygen gas, an exothermic reaction.

Once the reaction starts, it is self-sustaining as the gaseous mixture of wax and oxygen react chemically to form carbon dioxide and water. As well, the reaction releases heat and light energy. Obviously, we must supply some energy (lighted match) in order to start a reaction which, once started, releases much more energy than was used to start the reaction.

This is the same with the combustion of gasoline. In this case, a spark plug supplies the initial energy to ignite the gasoline; no spark, no combustion.

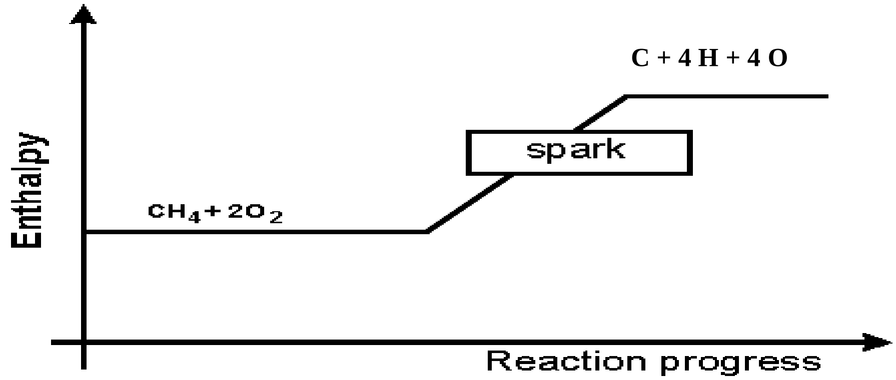
Likewise with food, the body supplies enzymes to digest (burn) the food.

Consider the combustion of natural gas, CH_4:

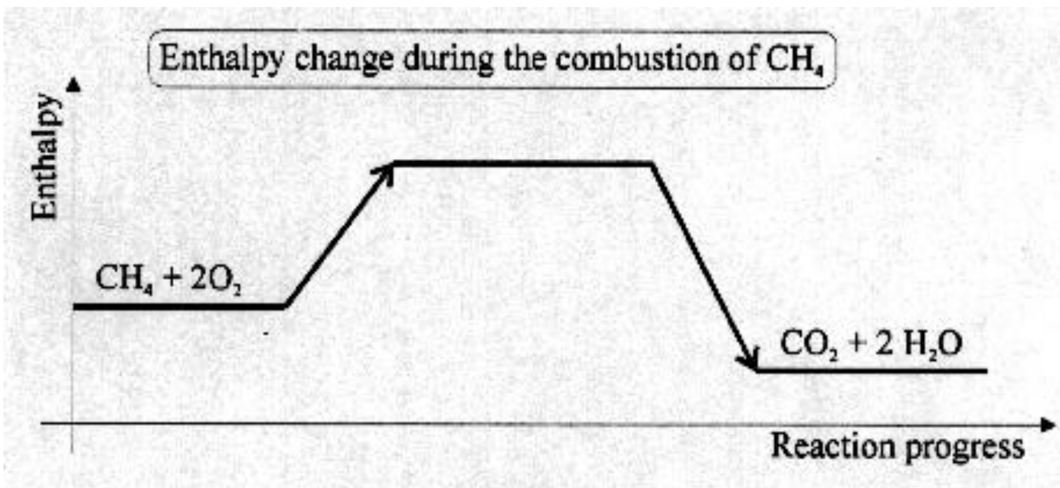
$$\mathbf{CH_{4(g)} + 2\ O_{2(g)} \rightarrow CO_{2(g)} + 2\ H_2O_{(g)}}$$

To start the reaction, we need some initial energy such as a spark. In effect, the spark breaks the molecular bonds. The energy of the spark used to start the reaction is called the "**activation energy**". The activation energy is only needed to start the reaction. Once the reaction starts, the energy released during the formation of new bonds will provide the activation energy required to sustain reaction.

Enthalpy change during the combustion of CH_4.



Remember: Bond breaking requires energy and bond forming release energy.



7) Study the graph above. Is the first part of the reaction endothermic or exothermic? Justify your answer:

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8) From the above graph, is the second part of the reaction endothermic or exothermic? Justify your answer:

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9) Is the overall reaction endothermic or exothermic? Explain:

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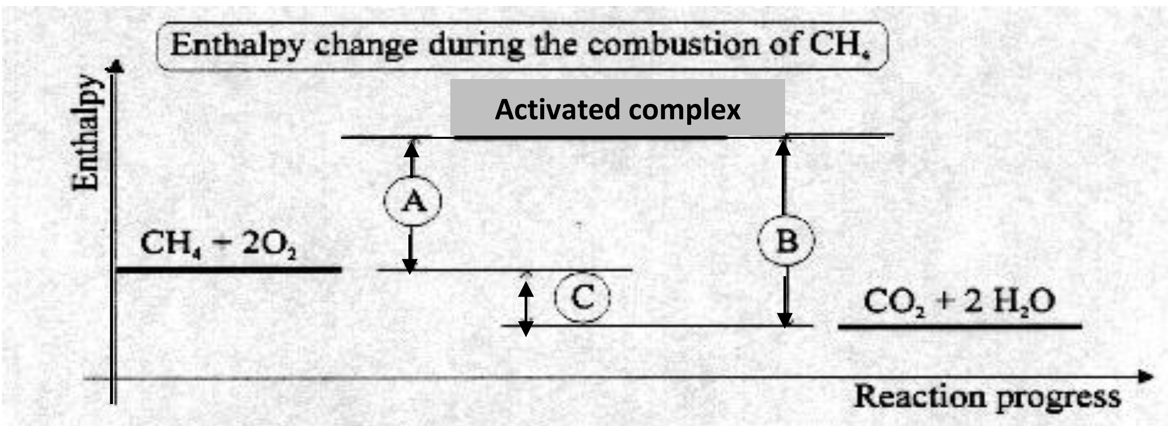

10) In the potential energy graph above, we note three enthalpy changes indicated by the arrows; A, B, and C. Which arrow represents the enthalpy change for the overall reaction given by the following equation? Explain:

$$CH_{4(g)} + 2\ O_{2(g)} \longrightarrow CO_{2(g)} + 2\ H_2O_{(g)}$$

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Note: As the graph above indicates, the potential energy of the reactants (left) is **higher** than the potential energy of the products (right). This means the reactants lost energy, **Δ**H is negative, and the reaction is exothermic.

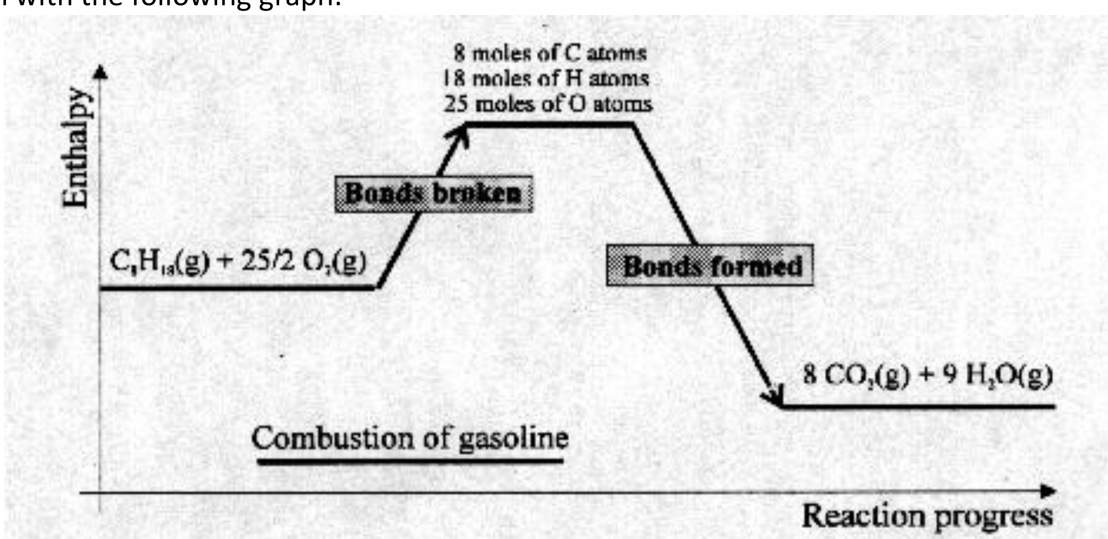
As we saw, gasoline has a high potential energy content. When gasoline burns, the following exothermic reaction releases energy used to run a car:

$$C_8H_{18(g)} + 25/2\ O_{2(g)} \longrightarrow 8\ CO_{2(g)} + 9\ H_2O_{(g)} + \text{energy}$$

Let's analyze further the action of gasoline burning in the combustion chamber of a gasoline motor. First, gasoline is injected into the chamber in the presence of oxygen. A spark provides the starting energy which ignites (oxidizes) the gasoline. The burning process causes the molecules of the gasoline and the oxygen (the reactants) to break their bonds thus releasing energy, which sustains the reaction. The atoms, which are liberated, rearrange themselves to form new bonds and thus form new molecules (products).

$C_8H_{18(g)} + 25/2\ O_{2(g)}$ → [8 moles of C atoms
18 moles of H atoms
25 moles of O atoms] → $8\ CO_{2(g)} + 9\ H_2O_{(g)}$

The activated complex corresponds to a very high level of energy. With bonds broken, the freed atoms are very energetic and very unstable. In forming new bonds, they form new substances (the products) which have less energy but are much more stable. We may summarize this action with the following graph:



10) In the above graph, why are the reactants on a higher enthalpy level than the products?

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11) Why are the reactants drawn on the left and the products on the right?

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12) Which have a higher enthalpy content, the reactants or the products?

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13) During the ***bond breaking*** process for the combustion of gasoline, is this process exothermic or endothermic? Explain:

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14) During the ***bond forming*** process for the combustion of gasoline, is this process exothermic or endothermic? Explain:

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15) Explain the overall effect of the reaction when an exothermic process follows an endothermic process:

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16) From the graph above representing the combustion of gasoline, do the reactants have a positive or a negative energy flow? Explain:

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17) Does the reaction for the combustion of gasoline have a positive or a negative **Δ**H value?

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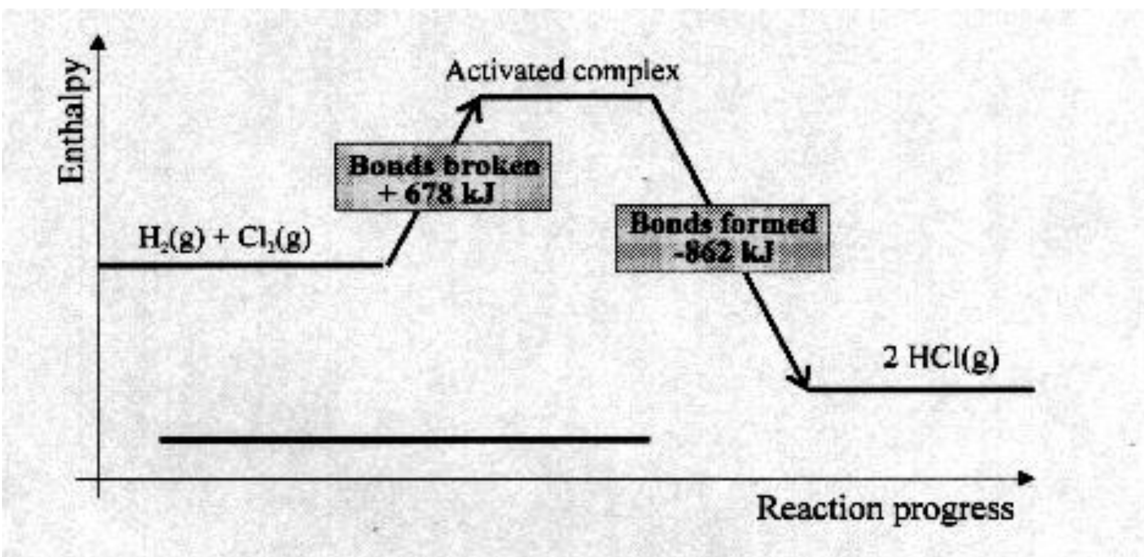
Let us now study the synthesis (formation) of hydrogen chloride. Historically, this reaction is achieved by mixing hydrogen gas, $H_{2(g)}$ with chlorine gas, $Cl_{2(g)}$.

The reaction occurs by the breaking of chemical bonds thereby releasing atoms, followed by the making of new bonds (rearrangement of atoms).

In their free state, the hydrogen and chlorine atoms are very energetic and thus very unstable. Upon colliding with each other, the hydrogen and chlorine atoms merge and form new bonds thus forming hydrogen chloride gas. Since the process is exothermic, energy is released to the environment. Thus, the enthalpy (total energy content) of the product, HCl, is less than the enthalpy of the reactants, H_2 and Cl_2 (**ΔH** is negative).

Recall that energy is required to break bonds (or anything else). Therefore, as indicated below, the reaction takes place in two steps:



Step- 1: Bond breaking $H_{2(g)} + Cl_{2(g)} \longrightarrow$ [activated complex] **Δ**H = +678 kJ
Step- 2: Bond forming [activated complex] $\longrightarrow$ 2 $HCl_{(g)}$ **Δ**H = -862 kJ

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17) Write the overall equation for the formation of hydrogen chloride gas (including **Δ**H):

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TERMINOLOGY

Chemists use specific terms for the different potential energies involved in chemical reactions. Be sure you know what these terms represent:

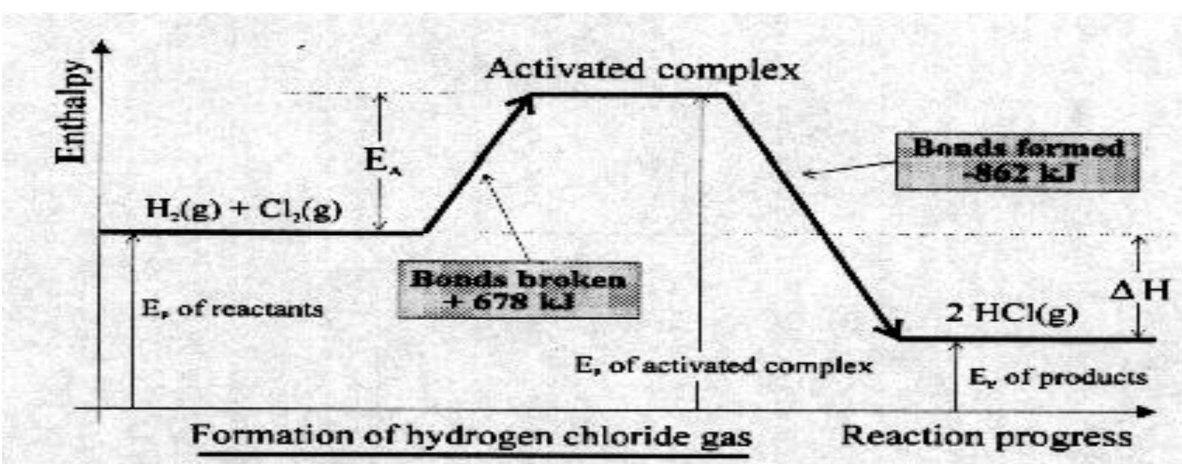
Ep OF REACTANTS: The Ep of the reactants is the potential energy of the reactants at the start of a chemical reaction as illustrated in the graph below.

ACTIVATION ENERGY: This is the energy required to start (or trigger) a reaction.
On the Ep graph below, the activation energy (E_A) is the difference between the highest peak (Ep of activated complex) minus the Ep of the reactants.

Ep OF ACTIVATED COMPLEX: When molecules break, they release atoms. The atoms form temporary molecules known as an activated complex. These activated complex molecules are very unstable existing only for a very short period of time till they break and form the products. Remember, as illustrated below, the Ep of an activated complex is the **highest** point on the graph.

Ep OF PRODUCTS: The Ep of the products is the energy of the products when the reaction has finished. Note that if the reaction is **endothermic**, then the line representing the Ep of the products is **higher** than the line representing the Ep of the reactants. Conversely, if the reaction is **exothermic**, the line representing the Ep of the products is lower than the line representing the Ep of the reactants. Thus, the graph illustrated below represents an **exothermic** reaction.

HEAT OF REACTION: This is the difference between the Ep of products minus the Ep of reactants and is labeled as **ΔH**. If the reaction is exothermic, then **Δ**H has a negative value (Ep of reactants is greater than Ep of products). If the reaction is endothermic, then **Δ**H is positive (Ep of reactants is less than Ep of products).



18) Using the above graph, determine:

a) The activation energy, E_A: ______________________________________

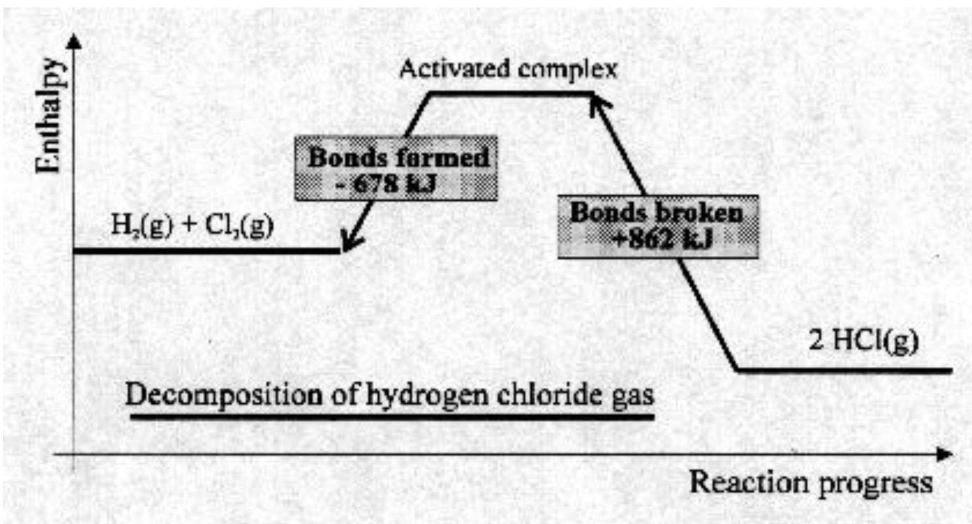
b) The heat of reaction, **Δ**H: _______________________________________

REVERSE REACTIONS

In the lab, it is possible to reverse the reaction for the formation of hydrogen chloride gas into its constituents hydrogen and chlorine gas. Thus, all we need to do is read the reaction from right-to-left:

$$H_{2(g)} + Cl_{2(g)} \longrightarrow 2\ HCl_{(g)}$$

Since this reaction is the reverse of the previous one, the graph is the same except that it proceeds in the reverse direction as illustrated below:



19) Determine the **Δ**H value for the above reverse reaction?

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20) What is the activation energy for the above reaction?

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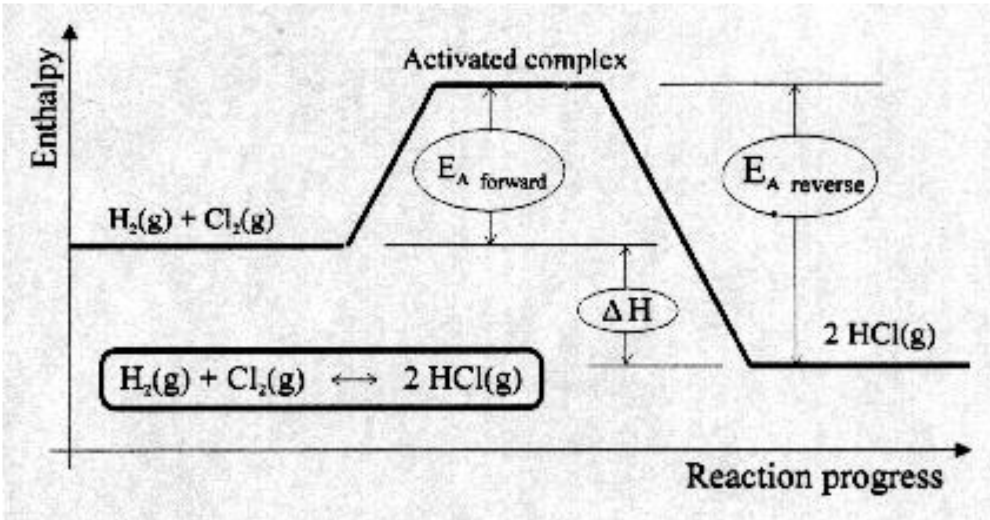
The following graph summarizes the enthalpy of the forward and reverse reactions for the formation and decomposition of hydrogen chloride gas:



FORWARD REACTION $H_{2(g)} + Cl_{2(g)} \longrightarrow 2\,HCl_{(g)}$

From the above graph, the ***forward*** reaction (formation of hydrogen chloride gas) is from left-to-right. Thus, for the forward reaction:

E_A forward = activation energy for the ***forward*** reaction
ΔH = the heat of reaction (change in enthalpy)

REVERSE REACTION. $H_{2(g)} + Cl_{2(g)} \longleftarrow 2\,HCl_{(g)}$

Again from the above graph, the ***reverse*** reaction (decomposition of hydrogen chloride gas) is from right-to-left. Thus, for the reverse reaction:

E_A reverse = activation energy for the ***reverse*** reaction
ΔH = the heat of reaction (change in enthalpy)

Note: As you can see, both for the forward and reverse reaction, **Δ**H has the same magnitude (**but not the same sign**). In the example above, **Δ**H is **negative** for the **forward** reaction but **positive** for the **reverse** reaction.

Writing the forward and reverse reactions including the activation energies, we have:

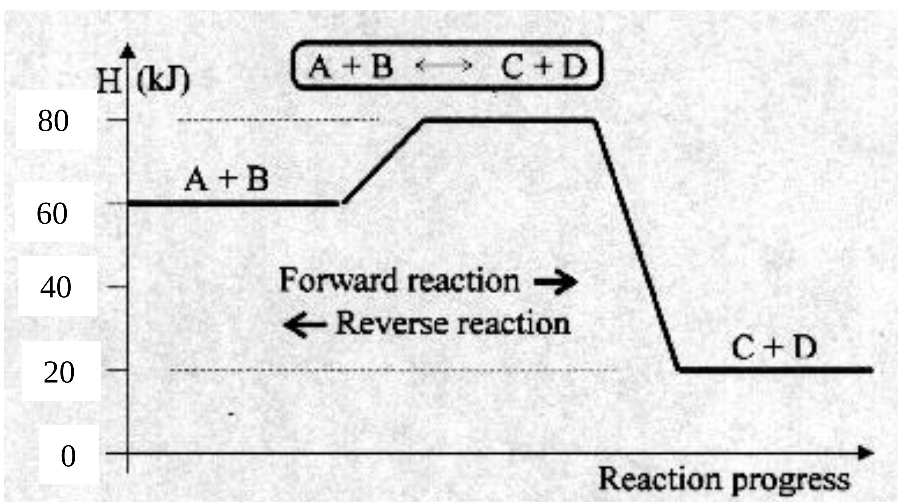
Forward:	$H_{2(g)} + Cl_{2(g)}$	$\longrightarrow$	$2\ HCl_{(g)}$	$E_{A\ forward}$ = +678 kJ
Reverse:	$H_{2(g)} + Cl_{2(g)}$	$\longleftarrow$	$2\ HCl_{(g)}$	$E_{A\ reverse}$ = +862 kJ

Note that the activation energy for the reverse reaction is higher (862 kJ) than the activation energy for the forward reaction (678 kJ). And, the change in enthalpy (ΔH) for the reaction (which is the heat of reaction) is calculated as follows:

$$\Delta H = E_{p\ PRODUCTS} - E_{p\ REACTANTS}$$

EXAMPLE

Consider the following enthalpy graph. Note the information the graph provides:



FOR THE FORWARD REACTION (A + B ⟶ C + D)

E_P REACTANTS = 60 kJ

E_P ACTIVATED COMPLEX = 80 kJ

E_P PRODUCTS = 20 kJ

Activation energy = 20 kJ

ΔH = - 40 kJ

FOR THE REVERSE REACTION (C + D → A + B)

E_P REACTANTS = 20 kJ

E_A ACTIVATED COMPLEX = 80 kJ

E_P PRODUCTS = 60 kJ

Activation energy = 60 kJ

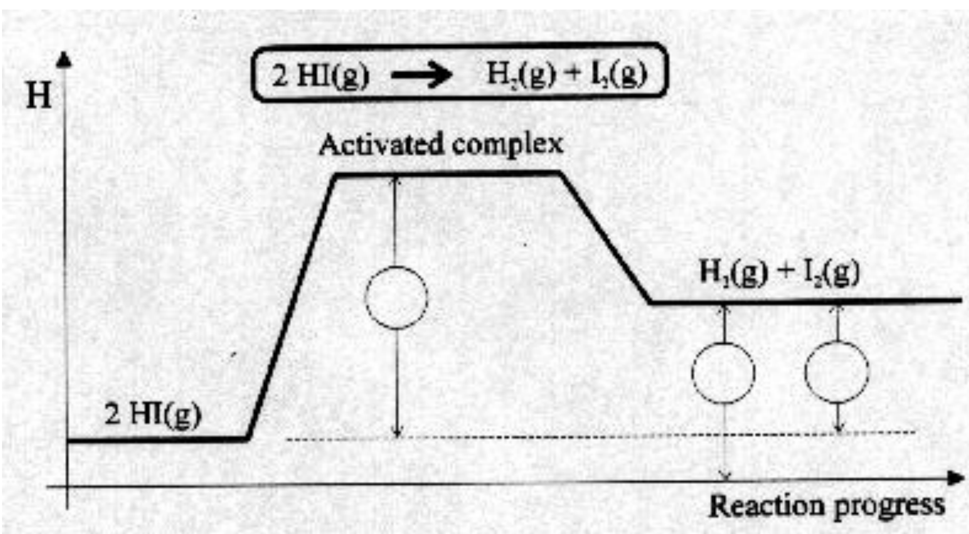
ΔH = + 40 kJ

21) The energy diagram below represents the potential energy for the decomposition of hydrogen iodide gas (HI) into its constituent elements $I_{2(g)}$ and $H_{2(g)}$.

In this reaction, chemists believe that the activated complex consists of large, unstable H_2I_2 molecules, resulting from the union of two reacting molecules.

In the "circles" provided in the graph below, fill-in the energy corresponding to:

A = Heat of reaction (**Δ**H)
B= Activation energy
C= Potential energy of products



22) Is the reaction above exothermic or endothermic? Explain:

The molecules having the highest energy are very unstable and form the activated complex. Indeed, the molecules of the activated complex are so unstable that they quickly transform themselves either back to reactant molecules or to the product molecules. In either case, these temporary molecules lose some of their energy.

23) In the graph above, depicting the energy involved in the decomposition of hydrogen iodide, identify the activated complex molecules.

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24) Are the molecules of the activated complex you selected above stable? Explain:

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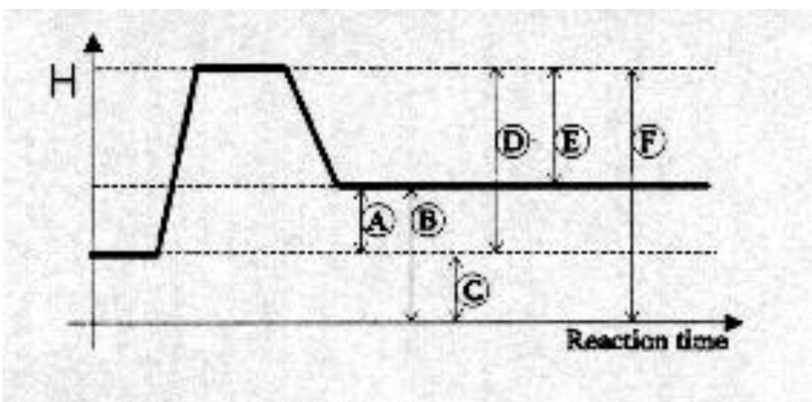
25) The following questions refer to the enthalpy (H) diagram below.
For each case, write the ***letter*** corresponding to the correct **arrow**:



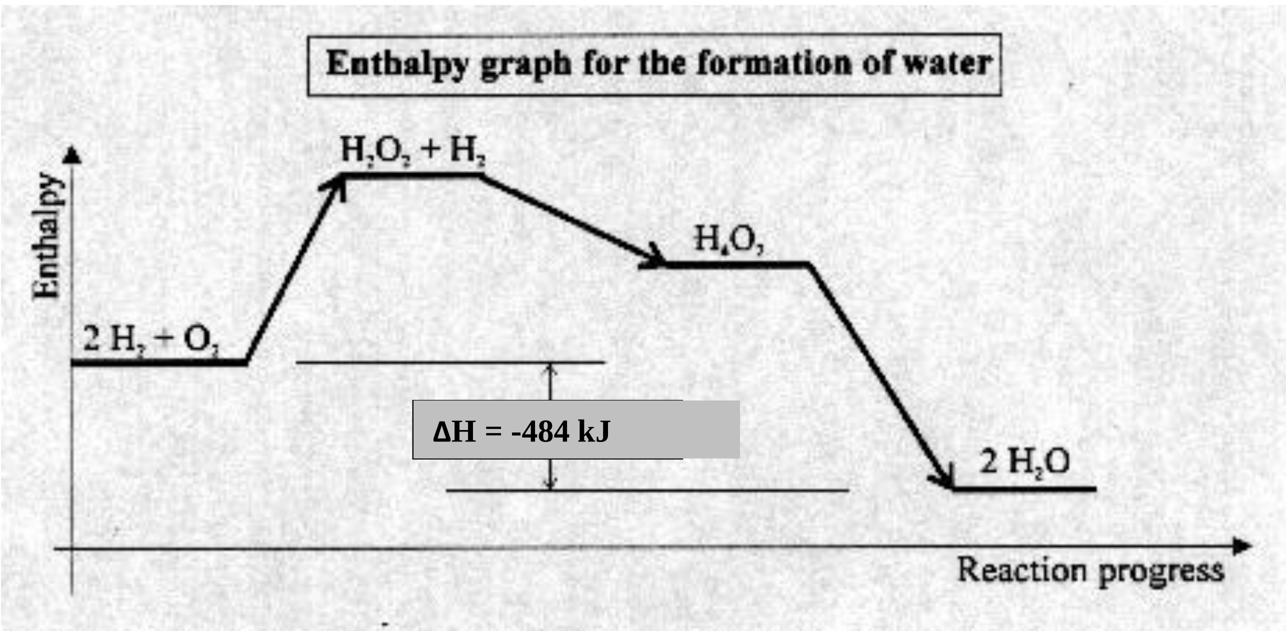
a) _____ Activation energy for the forward reaction.
b) _____ Potential energy of the products for the forward reaction.
c) _____ Activation energy for the reverse reaction.
d) _____ Heat of reaction for the forward reaction.
e) _____ Heat of reaction for the reverse reaction.
f) _____ Potential energy of the reactants for the forward reaction.
g) _____ Potential energy of the products for the reverse reaction.
h) _____ Potential energy of the activated complex.
i) _____ Potential energy of the reactants for the reverse reaction.

ENTHALPY IN REAL LIFE

Let's use the enthalpy graph to explain some daily occurrences.

We have already prepared hydrogen and oxygen gas by the electrolysis of water. We collected hydrogen gas in an open test tube. Oxygen gas present in the atmosphere did not cause the hydrogen to react. A spark or a flame is required in order to start the (explosive) reaction forming water.

How is it possible for hydrogen and oxygen gas to be present in a mixture without transforming themselves into water? Why is it that a spark or a flame is necessary to initiate the reaction? These are some questions we will try to answer.



Enthalpy graph for the formation of water

26) Write the reaction above in terms of energy per mole of product:

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27) Is this reaction endothermic or exothermic? Explain:

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28) In your opinion, why doesn't the mixture of hydrogen and oxygen gas react spontaneously to form water.

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29) What is the role of the flame or spark in this reaction?

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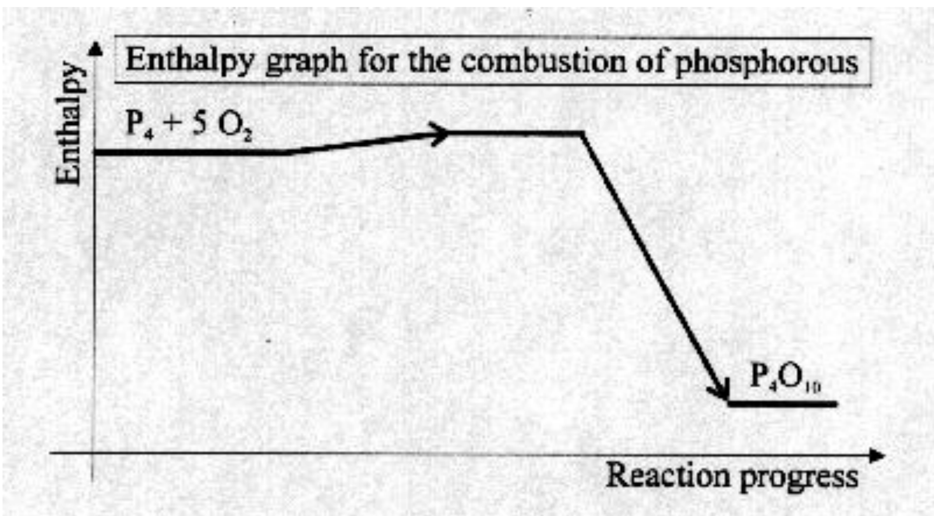
30) Phosphorous is a substance, which burns so spontaneously with oxygen that it must be kept in water to prevent it from reacting with the oxygen in the air. Study the graph below then explain why this reaction is so spontaneous:



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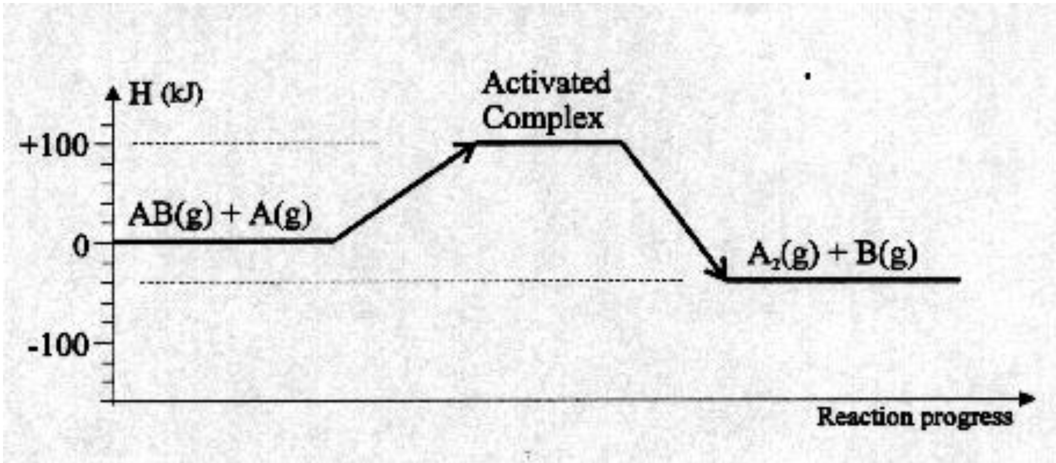
FOR THE PROS

Consider the following hypothetical reaction and enthalpy graph:

$$AB_{(g)} + A_{(g)} \longrightarrow A_{2(g)} + B_{(g)}$$



31) What is the heat of reaction? __________

32) What is the activation energy for the forward reaction?__________

33) What is the activation energy of the reverse reaction? __________

34) Is the reaction exothermic or endothermic? Explain: __________

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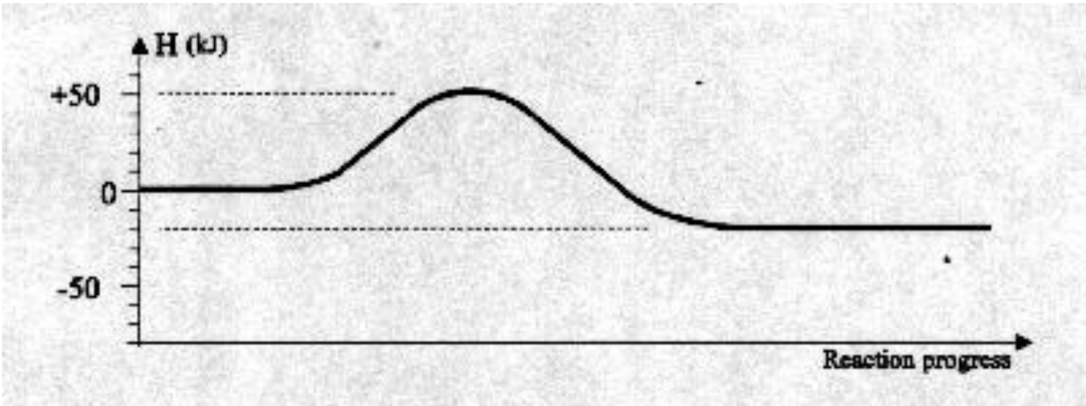
The graph below represents the potential energy of a substance as a function of the progress of the reaction (time).



35) What is the heat of reaction? ________

36) What is the activation energy for the forward reaction?________

37) What is the activation energy of the reverse reaction? ________

38) Is the reaction exothermic or endothermic? Explain:

____

____

39) Consider the following hypothetical reaction:

$A_2(g) + B_2(g) \longrightarrow 2\ AB_{(g)}$ $\Delta H = +40$ kJ

Given that the activation energy for the reverse reaction is +80 kJ, sketch the potential energy graph for this reaction.