Chemistry 202

مقرر ك 202

4ساعات معتمدة : ٣ ساعات نــــظري

١ ساعة عمــــلي

المراجع

Chang 10th. edition

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THERMOCHEMISTRY

Thermochemistry

الكيمياء الحرارية

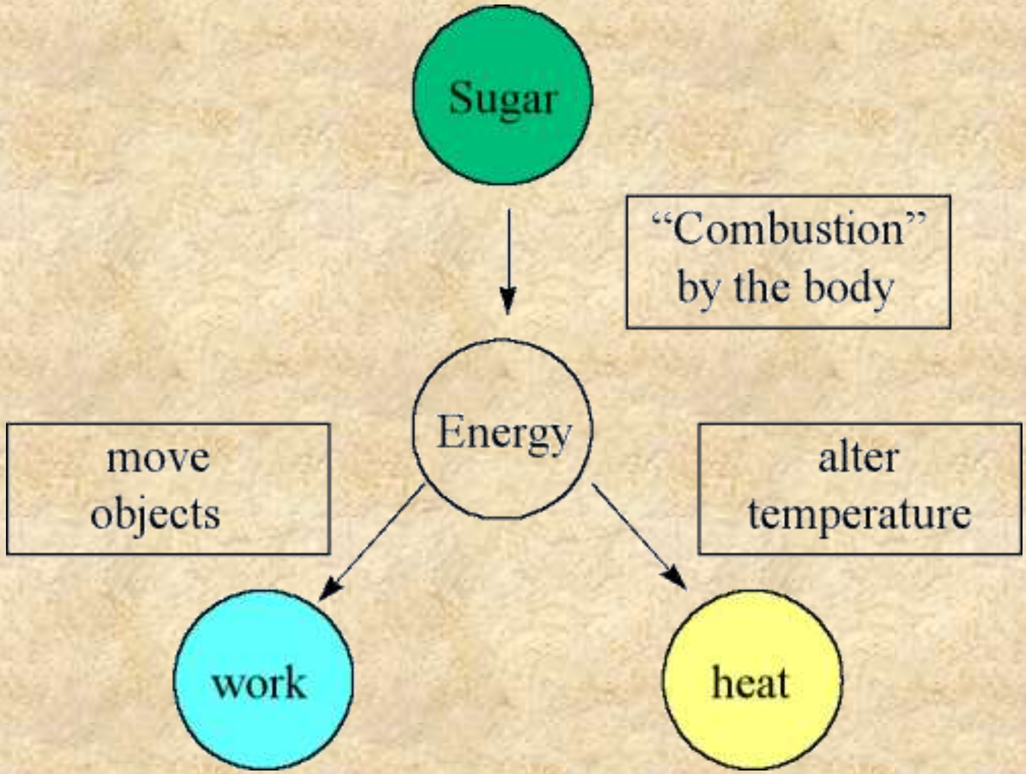
It is the study of heat released or absorbed by chemical or physical changes

هي الفرع من الكيمياء التى تهتم بدراسة الطاقة المصاحبه للتفاعل الكيمائى أو التغير الفيزيائي .

The Nature of Energy

طبيعة الطاقة

Sugar You eat is combusted by your body to produce co_2 and H_2o . During this process energy is released chemical reactions involve change in energy



- Some reactions produce energy
- Some reactions require energy

The study of energy and its transformations is known as Thermochemistry.

Energy measurement

قياس الطاقة

Force , F, is kind of push or pull on object

Gravity , a, is a force which keeps us stuck on the earth

Work , w, is the force on object to move it, $W = f \times d$

Energy : is the form of work , that mean to move an object.

Heat is an energy

Energy Units

W = F x d = mass x a x d

= kg x m /s^2 x m

= kg m^2 s^{-2} = Joule

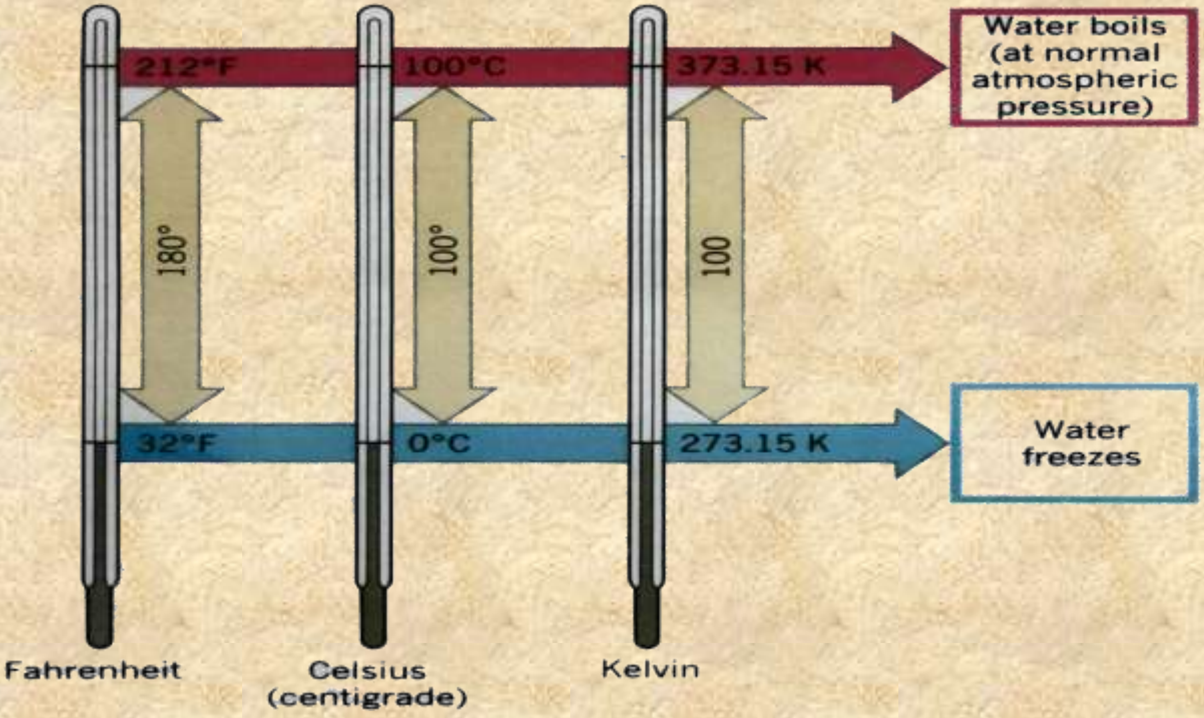
Traditionally , energy changes accompanying chemical reactions have been expressed in calorie

1 calorie = 4.184 J

Temperature and heat

درجة الحرارة والحرارة

- Celsius temperature scale : centigrade scale
- Fahrenheit temperature scale
- Kelvin (k) temperature scale



$$tc = 5^{o}C/9\ ^{o}F\ (T_f - 32\ ^{o}F)$$

Specific heat (sp . Heat)

الحرارة النوعية

It is the a mount of heat required to raise temperature of 1 gm of substance by 1°c

Heat capacity (C)

السعة الحرارية

It is the amount of heat to raise its temperature by 1°C

$C = \text{mass} \times \text{sp.heat}$

$q = C (t_2 - t_1)$

- Temperature is the degree of hotness
- Heat is a form of energy

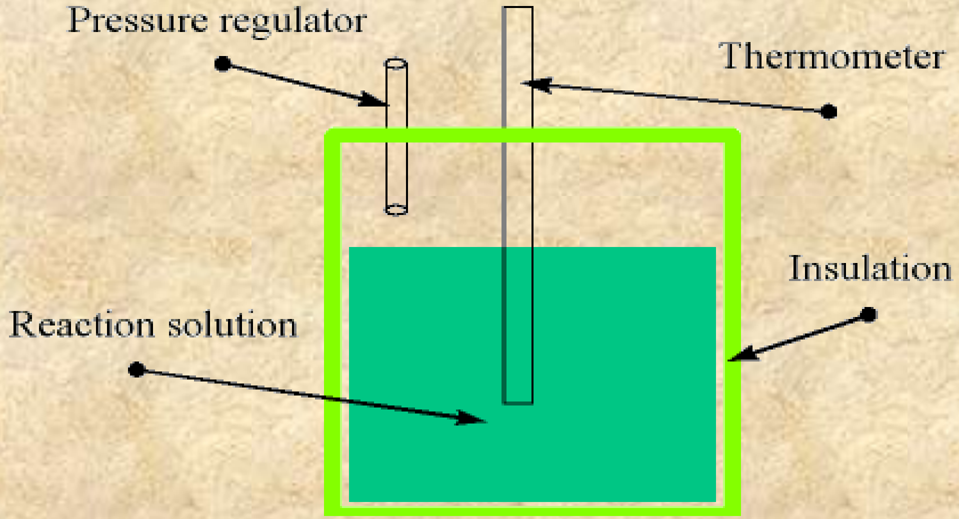
Calorimeter

المسعر الحراري

Calorimeter is a device to measure the heat changes that accompany chemical reactions .

Constant – pressure Calorimeter

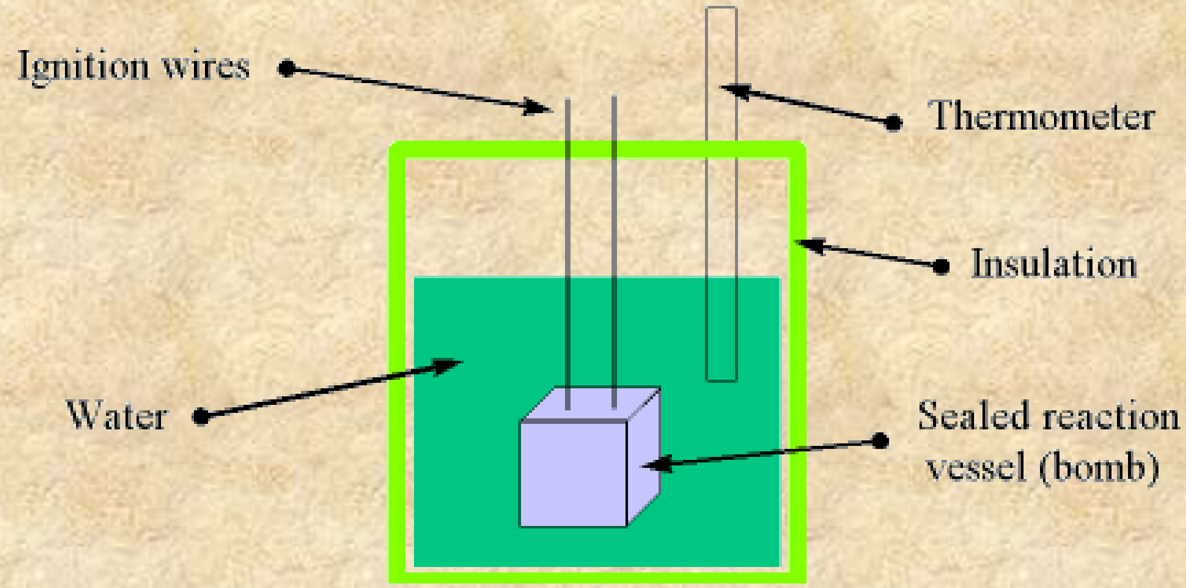
This Calorimeter is measure the heat change (q) at constant pressure (q_p)



The heat absorbed by an aqueous solvent is equal to the heat given off by the reaction of the solute

q reaction = q absorbed by solvent

Bomb calorimeter (constant – volume calorimeter)



This calorimeter is measure the heat change (q) at constant volume q_v .

In this case the calorimeter is sealed in insulated with no pressure regulation

Example

A bomb type calorimeter used to measure the heat evolved by the combustion of glucose $C_6H_{12}O_6$

$C_6H_{12}O_6$ (s) + $6O_2$(g) → $6CO_2$(g) +6 H_2O (l)

A 3.0 g sample of glucose is placed in bombs which is then filled with oxygen gas under pressure . The bomb is placed in wall insulated colorimeter vessel that is filled with 1.20 kg of water the initial temperature of the assembly is 19.00°C . The reaction mixture is ignited by the electrical heating of a wire within the bomb . The reaction causes the temperature of the calorimeter and its contents to increase to 25.50°C . The heat capacity of the calorimeter is 2.21 kJ / °C .How much heat is evolved by the combustion of 1 mol of glucose ?

Solution

To solve this problem we have to calculate

- The heat capacity of water , specific heat of water is 4.18 J / g.°C

- The heat evolved from the combustion of 3.0g of glucose

- Then the heat capacity evolved by 1 mol of glucose

C_{H2O} = (mass of H_2O) sp.heat of H_2O

= (1200 g) (4.18 J / g °C)

= 5016 J / °C

= 5.016 KJ / °C

The heat capacity of calorimeter = C_{cal} = 2.2 KJ / °C

C_{Total} = C_{H2O} + C_{cal} = 5.016 + 2.21

= 7.226 KJ / °C

$q_1 = C_{Total} \times (t_2 - t_1)$

= 7.226 kg/°C (25.50°C – 19.00 °C)

= 47.0 KJ

$$q_2 = \frac{q_1 \times 180\ g}{3\ g}$$

$$= \frac{47KJ \times 180\ g}{3\ g}$$

=2.82 x 10^3 KJ for one mol $C_6H_{12}O_6$

Thermochimical equation

المعادلة الكيمياء الحرارية

We have two kind of reactions

- reactions done in closed calorimeter
- reactions done at open calorimeter (open to atmosphere)

For the second reaction , the pressure is constant

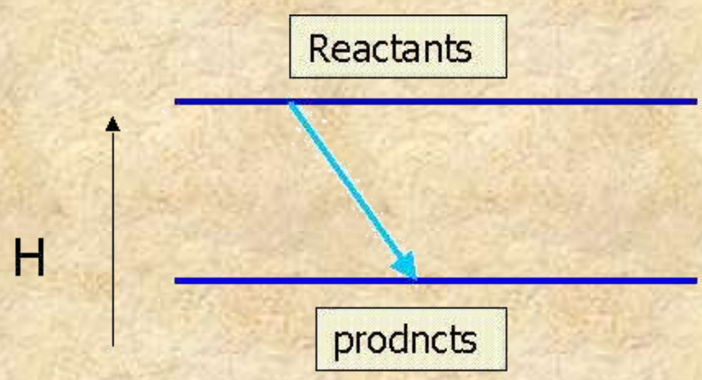
For a reaction done at consent pressure the heat evolved or liberated are called enthalpy and given symbol H .

Any pure substance has an enthalpy

For a reaction, reactants → products, the reactants has a definite H_R and the products has a definite H_p

The heat of reaction is given by

$$\Delta H = H_p - H_R$$



From this equation it is clear that ΔH may negative value or positive value

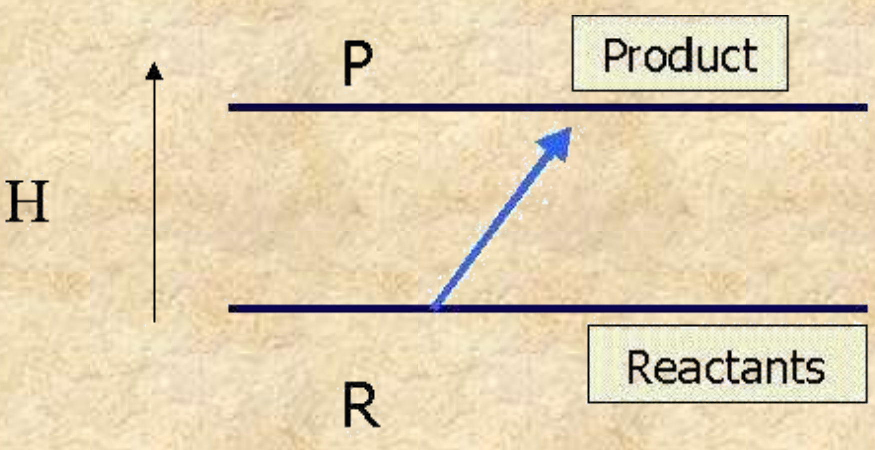
For-ve value of ΔH

$$H_p < H_R$$

The reaction liberate energy , that means gives heat so it called EXOTHERMIC Reaction

For the value of ΔH

$H_p > H_R$



The reactants needs energy to converted to products

This type of reaction is a absorbed energy so it called ENDOTHERMIC Reaction

The enthalpies of chemical substance depend on temperature and Pressure

If reaction done at 25°C and 1atm. ΔH is given ΔH° Known as standard Enthalpy

Thermochemical equation may be give by writing a chemical equation for a reaction and listing beside it ΔH value for the reaction

ΔH depends on the molar quantity (Extensive variable)

depends on the state of each substance , gas (g), liquid (l) , solid (s) and aqueous (aq) .

Example :

$H_2 (g) + ½ O_2 (g) \longrightarrow H_2O (l) ,\ \Delta H = -286\ KJ$

$H_2 (g) + ½ O_2 (g) \longrightarrow H_2O (g) ,\ \Delta H =-242\ KJ$

When a reaction is Exothermic ΔH is - ve

If a reaction reverse, it becomes Endothermic ΔH is +ve

Example :

$1/2\ H_2 (g) + 1/2\ I_2 (s) \longrightarrow HI (g),\quad \Delta H =25.9\ KJ$

$HI(g) \longrightarrow 1/2\ H_2 (g) +1/2\ I_2 (s) ,\quad \Delta H = -25.9KJ$

Example :

The thermic reaction below is highly exothermic

$2Al\ (s) + Fe_2\ O_3\ (s) \longrightarrow 2Fe\ (s) + Al_2\ O_3\ (s)\ ,\ \Delta H = -848\ KJ$

How much heat is liberated when 36.0 g of Al,reacts with excess $Fe_2\ O_3$?

Solution :

From the equation we have 2 mol of Al Liberated 848 kJ, since atomic mass of Al is 27 g / mol

The heat liberated when 36.0 g Al reacted is q

$$q = \frac{36 \times (-848)}{2 \times 27}$$

= - 565 KJ

The law of Hess

قانون هس

Is known as the law of constant heat summation

This law states , the change in enthalpy for any chemical reaction is constant , whether the reaction occurs in one step or in several steps

Consider the reaction :

$$C\ (graphite) + O_2\ (g) \rightarrow CO_2\ (g) \quad , \qquad \Delta H = -393.5 KJ$$

This reaction can occurs by tow steps:

$C(graphite) + \frac{1}{2} O_2 (g) \rightarrow \cancel{CO}(g) \qquad \Delta H_1 = -110.5 \text{ KJ}$

$\cancel{CO}(g) + \frac{1}{2} O_2 (g) \rightarrow CO_2(g) \qquad \Delta H_2 = -283.0 \text{ KJ}$

$C(graphite) + O_2 (g) \rightarrow CO_2(g) \qquad \Delta H = \Delta H_1 + \Delta H_2 = -393.5 \text{ KJ}$

Ways to calculate ΔH Of reaction

i. From the law of Hess

Since thermochemical data can be treated algebraically and by using Hess law we can calculate ΔH for a reaction from other reactions with know ΔH

Example :

Given the following thermochemical equations

- ❖ $4NH_3\ (g) + 3O_2\ (g) \rightarrow 2N_2\ (g) + 6H_2O\ (l)$, $\Delta H = -\ 1531\ kJ$ (1)
- ❖ $N_2O(g) + H_2\ (g) \rightarrow N_2(g) + H_2O\ (l)$, $\Delta H = -\ 367.4 kJ$ (2)
- ❖ $H_2(g) + ½\ O_2\ (g) \rightarrow H_2O(g)$, $\Delta H = -\ 285.9\ kJ$ (3)

Find the value of ΔH for the reaction

$2NH_3\ (g) + 3N_2O\ (g) \rightarrow 4N_2\ (g) + 3H_2O\ (l)$

Solution

Since we need $2NH_3$ (g) on the left of the equation, equation (1) divided by (2)

$2NH_3$ (g) + 3/2 O_2 (g) → N_2 (g) + $3H_2O$ (l) , ΔH = - 1531 KJ/ 2, (4)

Since we need in the equation $3N_2O$ on the left of the equation, equation (2) multiplied by (3)

$3N_2O$ (g) + $3H_2$ (g) → $3N_2$ (g) + $3H_2O$ (l) ΔH = 3 (-367.4 KJ), (5) To eliminate $3H_2$ (g) from left we have to reverse eq(3) and multiplied by 3

$3H_2O(l) \rightarrow 3H_2\,(g) + 3/2\ O_2\,(g)$, $\Delta H = 3\,(+285.9\ KJ)$, (6)

By summation of equations , (4), (5) and (6) we get

$2NH_3\,(g) + 3N_2\,(g) \rightarrow 4N_2\,(g) + 3H_2\,O\,(l)$ $\Delta H = -1010\ KJ$

ii. ΔH from the Enthalpy of formations

Standard state of substance is the state in which the substance is stable at 1atm pressure and 25 °C

Standard Enthalpies

It Is the enthalpies change of a reaction involving the materials at their standard states, ΔH°

The enthalpy of formation : $\Delta H°_f$

The enthalpy of formation of substance is the enthalpy for the formation of 1 mol of substance at its standard state from its elements at their standard stats

$H_2 (g) + ½ O_2 (g) \rightarrow H_2O (l) , \Delta H = -286$ KJ

$H_2 (g) + ½ O_2 (g) \rightarrow H_2O (g) , \Delta H=-242$ KJ

What is the deferent between the two equations ?

Table 3.1 Enthalpies of formation at 25°C and 1 atm

Compound	**ΔH°_f (KJ/mol)**	**compound**	**ΔH°_f (KJ/mol)**
$H_2O(g)$	-241.8	$COCl_2(g)$	-223
$H_2O(g)$	-285.9	$SO_2(g)$	-296.9
$HF(g)$	-269	$CO(g)$	-110.5
$HCl(g)$	-92.30	$CO_2(g)$	- 393.5
$HBr(g)$	-36.2	$NO(g)$	+ 90.37
$HI(g)$	+25.9	$NO_2(g)$	+33.8
$H_2S(g)$	-20.2	$HNO_3(l)$	-173.2
$HCN(g)$	+130.5	$NH_4NO_3(s)$	-365.1
$NH_3(g)$	-46.19	$NaCl(s)$	-411.0
$PH_3(g)$	+9.25	$MgO(s)$	-601.83
$CH_4(g)$	-74.85	$CaO(s)$	-635.5
$C_2H_6(g)$	-84.68	$Ca(OH)_2(s)$	-986.59
$C_2H_4(g)$	+52.30	$CaCO_3(s)$	-1206.9

Compound	ΔH°_f (KJ/mol)	compound	ΔH°_f (KJ/mol)
$C_2H_2(g)$	+226.7	$Ca_3P_2(s)$	-504.17
$C_6H_6(l)$	+49.04	$BaO(s)$	-588.1
$CH_3OH(g)$	-201.2	$BaCO_3(s)$	-1218
$CH_3OH(l)$	-238.5	$Al_2O_3(s)$	-1669.8
$CH_3NH_2(g)$	-28	$Fe_2O_3(s)$	-822.2
$NF_3(g)$	-113	$AgC(s)$	-127.0
$CF_4(g)$	-913.4	$HgBr_2(s)$	-169
$CHCl_3(l)$	-132	$ZnO(s)$	-348.0

Standard enthalpy for any reaction can be calculated from the enthalpy of formation of products and reactants

$$\Delta H^o = \Sigma\, \Delta H^o_f\, P - \Sigma\, \Delta H^o_f\, R$$

Note: the enthalpy of formation of any element is zero at its standard state

Example

Use enthalpies of formation to calculate ΔH^o for the reaction .

$Fe_2O_2(s) + 3CO\ (g) \rightarrow 2Fe(s) + 3CO_2\ (g)$

Solution

From the table of ΔH°_f we get ΔH°_f For the products and the reactants , then we apply equation(2)

$$\Delta H^\circ = 3\Delta H^\circ_f\ CO_2\ (g)\ - [\Delta H^\circ_f\ Fe_2\ O_3(s)\ + 3\ \Delta H^\circ_f\ CO(g)\ ]$$

$$= 3\ (\ -393.5\ KJ\ ) - [\ -(822.2\ KJ\ ) + 3\ (\ -110.5\ KJ)]$$

$$= -\ 1180.5\ KJ + 1153.7\ KJ$$

$$= -\ 26.8\ KJ$$

iii. ΔH from Bond energies

Atoms are held together in molecules by chemical bonds. The energy required to break the bond that holds two atoms together in a diatomic molecules is called bond dissociation energy.

$H - H(g) \rightarrow 2H(g)$, $\Delta H = + 435$ KJ

$Cl - Cl(g) \rightarrow 2Cl(g)$, $\Delta H = + 243$ KJ

$H\text{-}Cl(g) \rightarrow H(g) + Cl(g)$, $\Delta H = + 431$ KJ

- Bond dissociation energy is always +ve value (Endothermic)

- **The reverse of bond dissociation energy is -ve (because it forms bonds)**

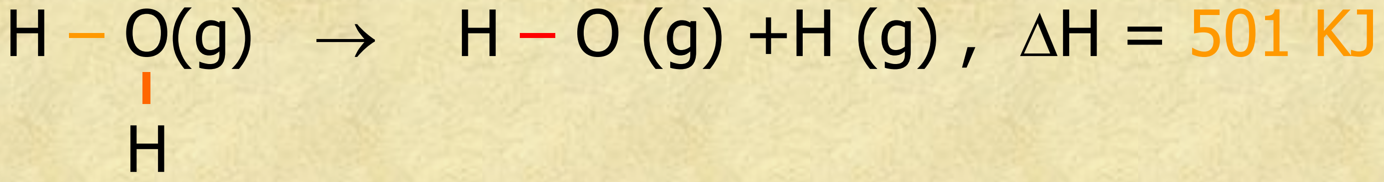
$H(g) + Cl(g) \rightarrow HCl(g)$, $\Delta H = -431\ KJ$

ΔH for any reaction can be calculated from bond energies dissociation of reactant and product

Since the reaction is the breaking of bonds for reactants and forms bonds for products

$\Delta H_{reaction} = \Sigma$ bond energies of reactants $- \Sigma$ bond energies of products

Polyatomic molecules



$$\mathrm{H-\underset{\underset{\displaystyle H}{|}}{O}(g)} \rightarrow \mathrm{H-O\,(g) + H\,(g)}\ ,\ \Delta H = 501\ \mathrm{KJ}$$

$$\mathrm{H-O(g)} \rightarrow \mathrm{H(g) + O}\ ,\ \Delta H = 425\ \mathrm{KJ}$$

H – O = 463 KJ (average bond energy)

Average Bond energies

Bond	Average Bond Energy (KJ/mol)	Bond	Average Bond Energy(KJ/mol)
H-H	**435**	**P-H**	**318**
H-F	**565**	**N-Cl**	**201**
H-Cl	**431**	**P-CL**	**326**
H-Br	**364**	**C-C**	**347**
H-l	**297**	**C=C**	**619**
F-F	**155**	**C≡C**	**812**
Cl-Cl	**243**	**C-H**	**414**
Br-Br	**193**	**C-O**	**335**
l-l	**151**	**C=O**	**707**
O-O	**138**	**C-F**	**485**
O_2^b	**494**	**C-Cl**	**326**
O-H	**463**	**C-N**	**293**
O-F	**183**	**C=N**	**616**
O-Cl	**205**	**C≡N**	**879**
N-N	**159**	**S-H**	**339**
N=N	**418**	**S-S**	**213**
N≡N	**914**	**S-Cl**	**276**
N-H	**389**		

Example

Use the average board energies to calculate the value of for the reaction

$2NH_3\,(g) + 3Cl - Cl\,(g) \rightarrow N \equiv N(g) + 6H - Cl(g)$

Solution

from the Reaction equation : we have

In the reactants

6 bonds of N-H

3 bonds of cl-cl

in Product

One bond of $N \equiv N$

6 bond of H- Cl

$\Delta H = 6 (N-H) + 3 (Cl – Cl) – [N \equiv N +6(H – Cl)]$

$= 6 (389) + 3 (243) – [941 + 6 (431)]$

$= 2334+729 –(3527)$

$= - 464$ KJ