

ENTHALPY CHANGES LATTICE ENERGY, ENTROPY CHANGES AND GIBB'S FREE ENERGY

- Standard Conditions -
- ① Temp: $25^{\circ}\text{C} / 298\text{K}$
 - ② Pressure: $1\text{atm} / 10^5\text{Pa}$
 - ③ All reactants should be in their standard physical state

Endothermic Changes

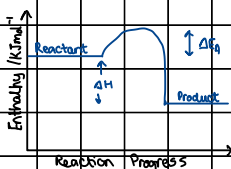
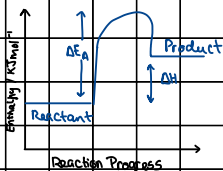
Exothermic Changes

- Heat absorbed
 - Breaking Bonds
 - $\Delta H = +ve$
 - Eg. ① Thermal Decomposition
 - ② Photosynthesis
- $$6\text{CO}_2 + 6\text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2$$

- Heat Produced
 - Making of Bonds
 - $\Delta H = -ve$
 - Eg. ① Combustion
 - ② Respiration
 - ③ Neutralisation
- $$\text{C}_2\text{H}_4 + 3\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$$
- $$\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \rightarrow 6\text{CO}_2 + 6\text{H}_2\text{O}$$
- $$\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$$

→ Standard Enthalpy Change ΔH^{\ominus}

- ① Standard Enthalpy Change of Reaction ΔH_r^{\ominus}
Enthalpy change when the amounts of reactants shown in the equation react to form products under standard conditions.
- ② Standard Enthalpy Change of Combustion ΔH_c^{\ominus}
Enthalpy change when 1 mole of compound burns in excess of oxygen under standard conditions.
- ③ Standard Enthalpy Change of Neutralisation ΔH_n^{\ominus}
Enthalpy change when 1 mole of water is formed by reaction of an acid with an alkali under standard conditions.
- ④ Standard Enthalpy Change of Formation ΔH_f^{\ominus}
Enthalpy change when 1 mole of a compound is formed from its elements under standard conditions.
- ⑤ Standard Enthalpy Change of Solution ΔH_{sol}^{\ominus}
Enthalpy change when 1 mole of solute is dissolved in a solvent to form an infinitely dilute solution under standard conditions.



Activation Energy (E_A): minimum energy required for a reaction to take place

① Enthalpy Change of Bond

Enthalpy change when one mole of bonds are broken in a substance under standard conditions.

② Lattice Formation Enthalpy ($\Delta H_{lattice}^{\ominus}$)

The enthalpy change when one mole of an ionic compound is formed from its isolated gaseous ions under standard conditions.

③ Lattice Dissociation Enthalpy

The enthalpy change needed to convert 1 mole of solid crystals into scattered gaseous ions.

- ⑥ Standard Enthalpy Change of Atomisation ΔH_{at}^{\ominus}
Enthalpy change when 1 mole of gaseous atoms are formed from its elements under standard conditions.
- ⑦ Standard Enthalpy Change of Hydration of Anhydrous Salt ΔH_{hyd}^{\ominus}
Enthalpy change when 1 mole of hydrated salt is formed from 1 mole of anhydrous salt.
- ⑧ Standard Enthalpy of Ionisation: ΔH_i^{\ominus}
Enthalpy change needed to remove 1 electron from each atom of 1 mole of gaseous atoms to form one mole of gaseous $+1$ ions.

⑨ Standard Enthalpy Change of Electron Affinity

The enthalpy change when one mole of gaseous atoms acquires one mole of electrons (from infinity) to form one mole of gaseous -1 ions under standard conditions.

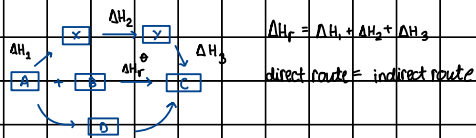
⑩ Enthalpy change of Fusion/Vaporisation

The amount of energy required to change one mole of liquid to one mole of gas.

Notes By
Jay Shah

HESS' LAW

The total enthalpy change in a reaction is independent of the route by which a chemical reaction takes place as long as the initial and final conditions are the same.



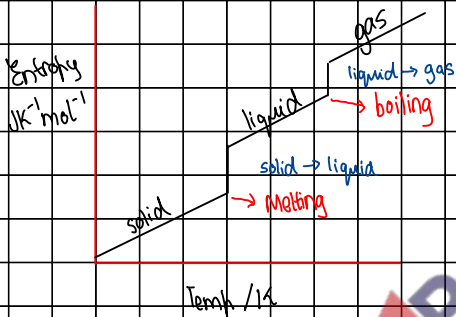
CALORIMETRY

- Used to measure enthalpy change of neutralisation: ΔH_n^\ominus
- Polystyrene Cup
- $\Delta H = -mc\Delta T$ used to find enthalpy change of x moles.
- When enthalpy change is calculated for 1 mol in kJ mol^{-1}

Entropy: Measure of dispersal of energy at a specific temperature.

or measure of randomness or disorder of a system.

Standard Molar Entropy: Entropy of 1 mole of a substance under standard conditions.



If increasing the temperature involves a change of state in the material, its entropy increases significantly.

- When an ionic solid dissolves in water.

The ionic solid is highly ordered, and has relatively low entropy. When the solid dissolves in water, the whole system becomes highly disordered as the crystal breaks up and the ions find their way between water molecules. So Entropy increases.

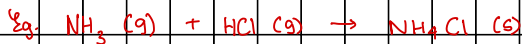
- Simpler substances with fewer atoms have lower entropy values than more complex substances with a greater number of atoms.



- For similar substances, harder substances have a lower entropy value. For example, diamond has a lower entropy value than graphite & calcium has a lower entropy value than lead.

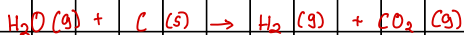
If entropy increases i.e

if Entropy Product > Entropy Reactant, then Entropy change "+", Spontaneous feasible
if Entropy Product < Entropy Reactant, then Entropy change "-", less likely to occur



Reactant Entropy > product entropy

$$\therefore \Delta S = -\text{ve}$$



Reactant Entropy < Product Entropy

$$\therefore \Delta S = +\text{ve}$$

Formulas

Calculating Entropy change of a reaction, ΔS° system

$$\Delta S^\circ \text{ system} = \sum S^\circ \text{ products} - \sum S^\circ \text{ reactants}$$

Calculating Entropy change of surrounding, ΔS° surr

$$\Delta S^\circ \text{ surrounding} = -\frac{\Delta H^\circ \text{ reaction}}{T_{\text{emh}}}$$

increase in temp, increases entropy of surrounding
(Temp $\propto 1/T$) becomes less negative or more positive

Calculating the total Entropy change, ΔS° total

$$\Delta S^\circ \text{ total} = \Delta S^\circ \text{ system} + \Delta S^\circ \text{ surrounding}$$

- At equilibrium entropy of forward reaction = entropy of backward reaction, therefore overall entropy change is 0.

Gibbs Free Energy

$$\Delta S^\circ \text{ total} = \Delta S^\circ \text{ system} + \Delta S^\circ \text{ surrounding}$$

$$\Delta S^\circ \text{ total} = \Delta S^\circ \text{ system} - \frac{\Delta H^\circ \text{ reaction}}{T}$$

Multiplying by -T

$$-T\Delta S^\circ \text{ total} = -T\Delta S^\circ \text{ system} + \Delta H^\circ$$
$$= \Delta G^\circ$$

$$\therefore \Delta G^\circ = -T\Delta S^\circ \text{ total}$$
$$= -T\Delta S^\circ \text{ system} + \Delta H^\circ$$

$$\therefore \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \text{ system}$$

$$\Delta H^\ominus = T\Delta S_{\text{system}} + \Delta G \rightarrow \text{Gibbs "free energy"}$$

\downarrow total energy change
 \downarrow energy not available, (involved in disorder of system)

energy available to do work

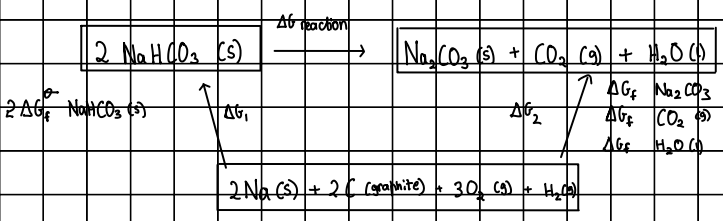
• Reaction Spontaneous if

$$\Delta S_{\text{total}} = +$$

$$\Delta G = -T\Delta S$$

∴ Spontaneous if $\Delta G = -ve$

Gibbs Free Energy Cycle



↳ Elemental State

$$\Delta G_{\text{reaction}} = \Delta G_2 - \Delta G_1$$

• Reaction Not Spontaneous if

$$\Delta S_{\text{total}} = -$$

$$\Delta G = -T\Delta S$$

∴ Not spontaneous if $\Delta G = +ve$

Note:
When $\Delta G = 0$,
the point of feasibility has
reached.

Temperature Change & Reaction Spontaneity

$$\Delta G = \Delta H_{\text{reaction}} - T\Delta S_{\text{system}}$$

• For Exothermic Reaction

First term negative (ΔH),

hence if ΔS_{system} is positive, then ΔG negative so reaction spontaneous

if ΔS_{system} is negative, then if temperature is lower then ΔG is negative hence spontaneous

if temperature is higher then ΔG is +ve hence not spontaneous

∴ Exothermic Reaction's forward reaction favours a lower temperature

• For Endothermic Reaction

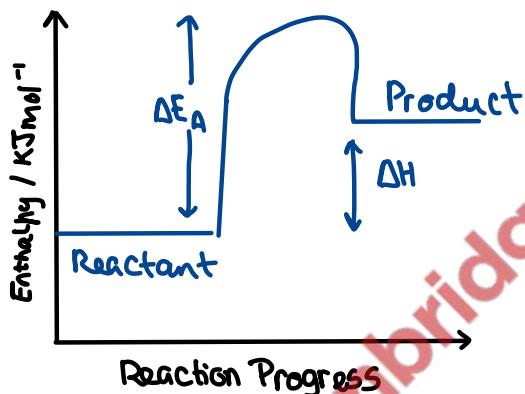
First term positive (ΔH)

hence if ΔS_{system} is positive, and temperature high, second term negative value $>$ positive value then ΔG is negative so reaction spontaneous

if ΔS_{system} negative then ΔG positive hence not spontaneous

∴ Endothermic Reaction's forward reaction favours a higher temperature.

Describe endothermic changes



QUESTION

Heat absorbed,
Bonds broken
Energy change positive

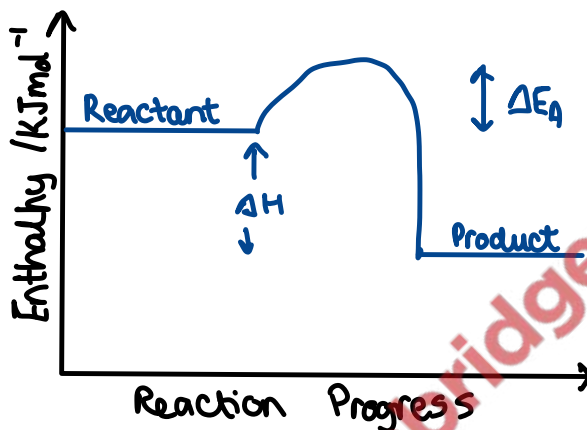
Example: (anything that absorbs energy to carry out reaction)

- 1) thermal decomposition
- 2) photosynthesis



ANSWER

Describe exothermic changes

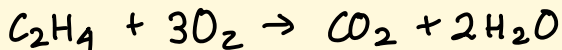


QUESTION

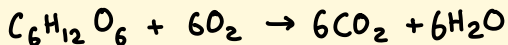
Heat produced,
making of bonds,
Energy change is negative

Example: reaction that removes energy

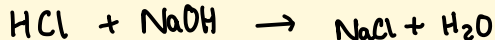
1) Combustion



2) Respiration



3) Neutralisation



ANSWER

Describe Activation Energy. ΔH_{EA}

QUESTION

The minimum amount of energy required for a reaction to take place

ANSWER

Standard Conditions

QUESTION

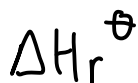
298k

1 atm ($1 \times 10^5 \text{ Pa}$)

all reactants in their standard physical state

ANSWER

Standard Enthalpy Change of Reaction



QUESTION

Enthalpy change when the amount of reactants shown in the equation react to form products under standard conditions.

ANSWER

Standard Enthalpy
Change of combustion ΔH_c^\ominus

QUESTION

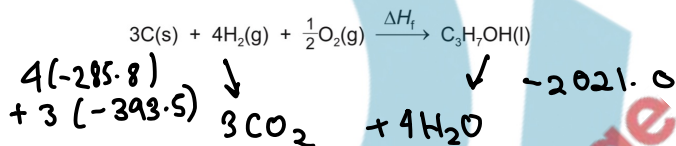
Enthalpy change when 1 mole of compound burns in excess of oxygen under standard conditions

ANSWER

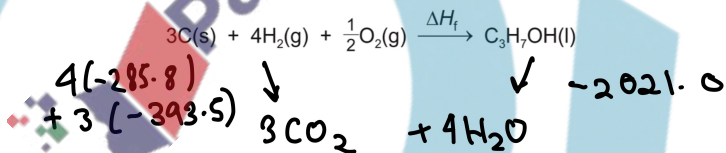
(c) The table gives some enthalpy change of combustion values.

substance	enthalpy change of combustion / kJ mol ⁻¹
C(s)	-393.5
H ₂ (g)	-285.8
C ₃ H ₇ OH(l)	-2021.0

(i) Construct a labelled energy cycle to show how these values could be used to calculate the enthalpy change of formation of C₃H₇OH(l), ΔH_f^\ominus .



QUESTION

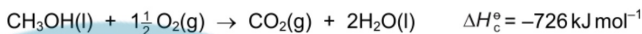
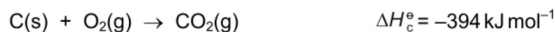


$$\Delta H_f - 2021.0 = 4(-285.8) + 3(-393.5)$$

$$\Delta H_f^\ominus = -302.7$$

ANSWER

The standard enthalpy changes of combustion of carbon, hydrogen and methanol are shown.



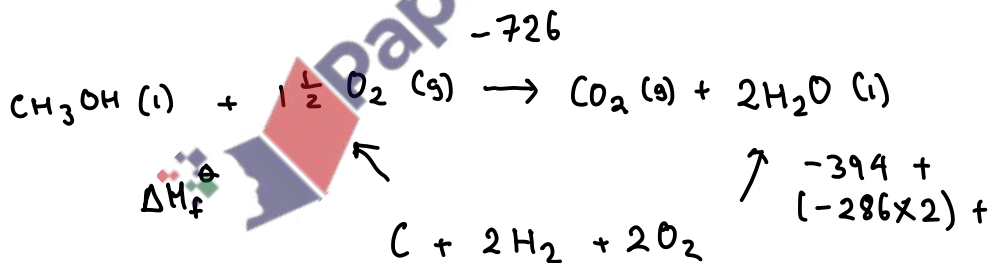
Which expression gives the standard enthalpy change of formation of methanol in kJ mol^{-1} ?

- A $-394 + (-286) - (-726)$
- B $-394 + (-286 \times 2) - 726$
- C $-394 + (-286 \times 2) - (-726)$
- D $-726 - (-394) - (-286 \times 2)$

(Question 8 of Paper 1, Variant 2, March, 2019)

Show Answer

Q1



$$\Delta H_f^\ominus - 726 = -394 + (-286 \times 2)$$

$$\Delta H_f^\ominus = -394 + (-286 \times 2) - (-726)$$

$$\Delta H_f^\ominus = -240 \text{ kJ mol}^{-1}$$

ANSWER

Ans. C

Enthalpy change
of Neutralisation ΔH_n^\ominus

QUESTION

Enthalpy change when 1 mole of water is formed by reaction of alkali and acid under standard conditions.

ANSWER

Standard Enthalpy Change of Formation

QUESTION

Enthalpy change when 1 mole of a compound is formed from its elements under standard conditions.

ANSWER

Standard Enthalpy
Change of solution ΔH_{sol}^{\ominus}

QUESTION

Enthalpy change when 1 mole of solute is dissolved in a solvent to form an infinity dilute solution under standard conditions.

ANSWER

Standard Enthalpy
Change of Atomisation ΔH_{at}^\ominus

QUESTION

Enthalpy change when 1 mole of gaseous atoms are formed from its elements under standard conditions.

ANSWER

Standard Enthalpy Change of
Hydration of Anhydrous salt. ΔH_{hyd}

QUESTION

Enthalpy change when 1 mole of hydrated salt
is formed from 1 mole of anhydrous salt.

ANSWER

Standard Enthalpy of Ionisation ΔH_i^\ominus

QUESTION

Enthalpy change needed to remove 1 electron from each atom of 1 mole of gaseous atoms to form one mole of gaseous + 1 ions.

ANSWER

Standard Enthalpy change of
Electron Affinity. ΔH_{ea}^{\ominus}

QUESTION

The enthalpy change when one mole of gaseous atoms acquires one mole of electrons from infinity to form one mole of gaseous 1- ions under standard conditions.

ANSWER

Enthalpy change of fusion/vaporisation

QUESTION

The amount of energy required to change one mole of liquid to one mole of gas.

ANSWER

Bond Energy

QUESTION

Energy required to break 1 mole of bonds in the gas phase.

ANSWER

Lattice Formation Enthalpy (ΔH_{latt}°)

QUESTION

The enthalpy change when one mole of an ionic compound is formed from its isolated gaseous ions under standard conditions.

ANSWER

Lattice Dissociation Enthalpy

QUESTION

The enthalpy change needed to convert 1 mole of solid crystals into scattered gaseous ions.

ANSWER

11 The diagram shows the skeletal formula of cyclopropane.



The enthalpy change of formation of cyclopropane is $+53.3 \text{ kJ mol}^{-1}$ and the enthalpy change of atomisation of graphite is $+717 \text{ kJ mol}^{-1}$.

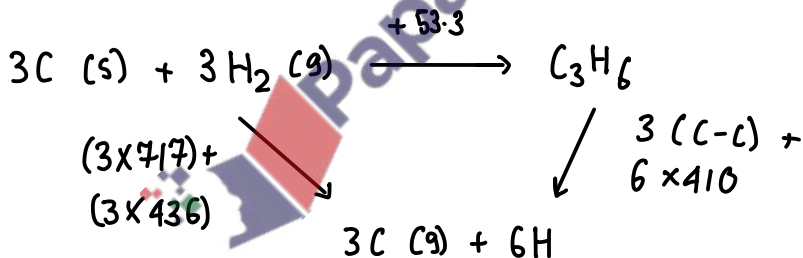
The bond enthalpy of H-H is 436 kJ mol^{-1} and of C-H is 410 kJ mol^{-1} .

What value for the average bond enthalpy of the C-C bond in cyclopropane can be calculated from this data?

- A 187 kJ mol^{-1} B 315 kJ mol^{-1} C 351 kJ mol^{-1} D 946 kJ mol^{-1}

12 When barium is burnt in oxygen, what colour is the flame?

QUESTION



$$53.3 + 3(\text{C-C}) + (6 \times 410) = (3 \times 717) + (3 \times 436)$$

$$\text{C-C} = 315.23 \text{ kJ mol}^{-1}$$

$$\approx 315 \text{ kJ mol}^{-1}$$

ANSWER

Gaseous phosphorus pentachloride can be decomposed into gaseous phosphorus trichloride and chlorine by heating. The table below gives the bond energies.

bond	bond energy / kJ mol^{-1}
P-Cl (in both chlorides)	330
Cl-Cl	240

What is the enthalpy change in the decomposition of PCl_5 to PCl_3 and Cl_2 ?

- A -420 kJ mol^{-1} B -90 kJ mol^{-1} C $+90 \text{ kJ mol}^{-1}$ D $+420 \text{ kJ mol}^{-1}$

(Question 7 of Paper 1, Summer, 2003)

Show Answer

QUESTION



$$\Delta H = \text{Reactants} - \text{Products}$$

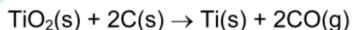
$$= (330 \times 5) - (330 \times 3 + 240)$$

$$= +420$$

Ans. D

ANSWER

Titanium occurs naturally as the mineral rutile, TiO_2 . One possible method of extraction of titanium is to reduce the rutile by heating with carbon.



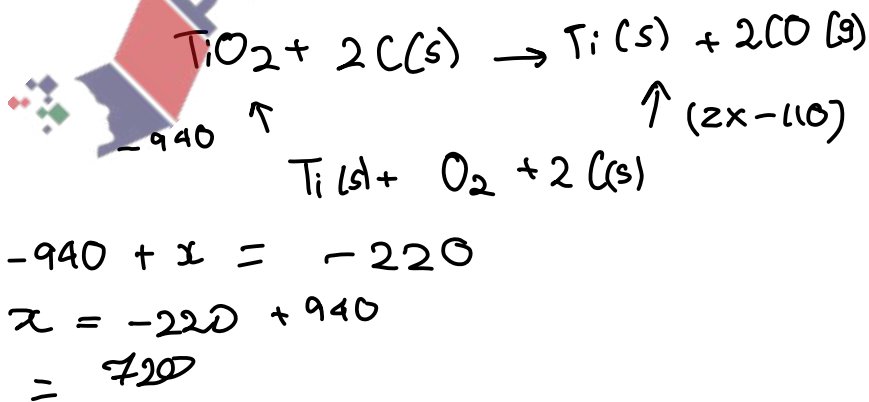
The standard enthalpy changes of formation of $\text{TiO}_2(\text{s})$ and $\text{CO}(\text{g})$ are -940 kJ mol^{-1} and -110 kJ mol^{-1} respectively.

What is the standard enthalpy change of this reaction?

- A -830 kJ mol^{-1}
- B -720 kJ mol^{-1}
- C $+720 \text{ kJ mol}^{-1}$
- D $+830 \text{ kJ mol}^{-1}$

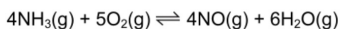
(Question 9 of Paper 1, Summer, 2008)

QUESTION



ANSWER

The first stage in the industrial production of nitric acid from ammonia can be represented by the following equation.



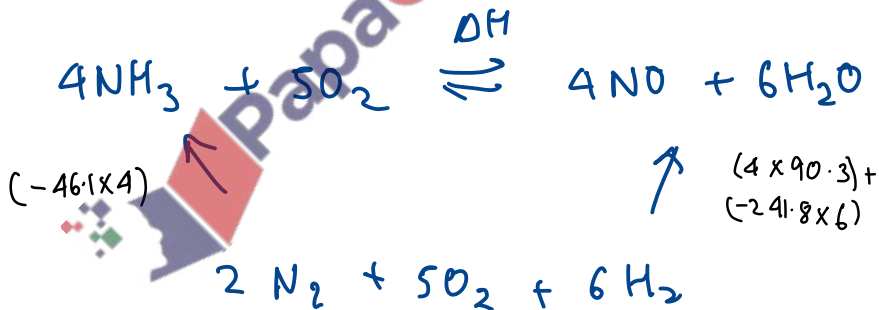
Using the following standard enthalpy change of formation data, what is the value of the standard enthalpy change, ΔH^\ominus , for this reaction?

compound	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$
$\text{NH}_3(\text{g})$	-46.1
$\text{NO}(\text{g})$	+90.3
$\text{H}_2\text{O}(\text{g})$	-241.8

- A +905.2 kJ mol⁻¹
- B -105.4 kJ mol⁻¹
- C -905.2 kJ mol⁻¹
- D -1274.0 kJ mol⁻¹

(Question 6 of Paper 1, Variant 1, Winter, 2009)

QUESTION



$$(-46.1 \times 4) + \Delta H = (4 \times 90.3) + (-241.8 \times 6)$$

$$\Delta H = -905.2 \text{ kJ mol}^{-1}$$

ANSWER

- (b) Describe and explain what is observed when a red-hot wire is plunged into separate samples of the gaseous hydrogen halides HCl and HI .
How are bond energy values useful in interpreting these observations?

- (c) The following reaction occurs in the gas phase.



Use these and other data from the *Data Booklet* to calculate the average bond energy of the Cl-F bond in ClF_3 .

[Total: 7]



QUESTION

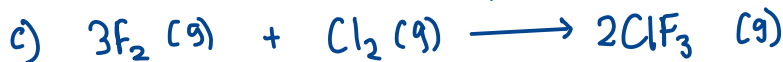
b) $\text{HCl} \rightarrow$ nothing happens

$\text{HI} \rightarrow$ purple fumes are seen, which is the iodine formed

This is because the HCl bond is stronger than the HI bond, hence requires more energy to break.

The H-X bond becomes weaker down the group.

$$\Delta H_r^\ominus = -328 \text{ kJ mol}^{-1}$$



$$\Delta H_r^\ominus = \text{Reactants} - \text{Products}$$

$$-328 = [242 + 158 \times 3] - 2(3(\text{Cl-F}))$$

$$-328 = 716 - 6(\text{Cl-F})$$

$$1044 = 6(\text{Cl-F})$$

ANSWER

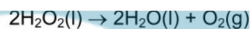
\therefore Bond Cl-F
is 174 kJ mol^{-1}

Hydrogen peroxide slowly decomposes into water and oxygen. The enthalpy change of reaction can be calculated using standard enthalpies of formation.

$$\Delta H_f^\ominus(\text{hydrogen peroxide(l)}) = -187.8 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\ominus(\text{water(l)}) = -285.8 \text{ kJ mol}^{-1}$$

Using a Hess cycle, what is the enthalpy change of reaction for this decomposition?

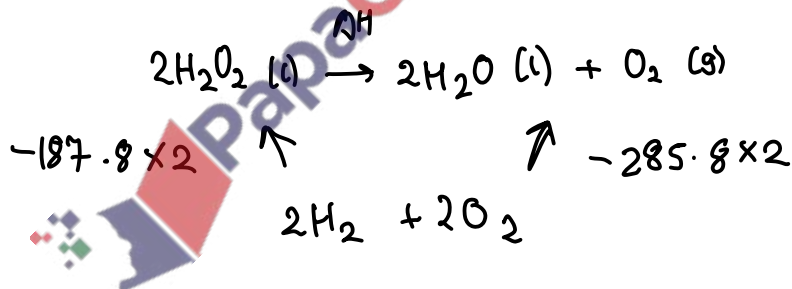


- A +98 kJ mol⁻¹
- B -98 kJ mol⁻¹
- C -196 kJ mol⁻¹
- D -947.2 kJ mol⁻¹

(Question 8 of Paper 1, Summer, 2009)

Show Answer

QUESTION



$$\Delta H + (-187.8 \times 2) = (-285.8 \times 2)$$

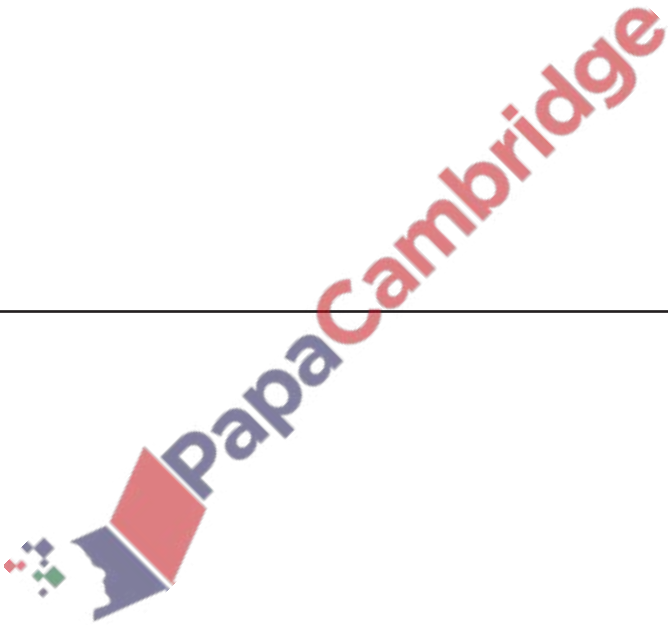
$$\Delta H = (-285.8 \times 2) - (-187.8 \times 2)$$

$$\Delta H = -196 \text{ kJ mol}^{-1}$$

Ans. C

ANSWER

QUESTION



ANSWER