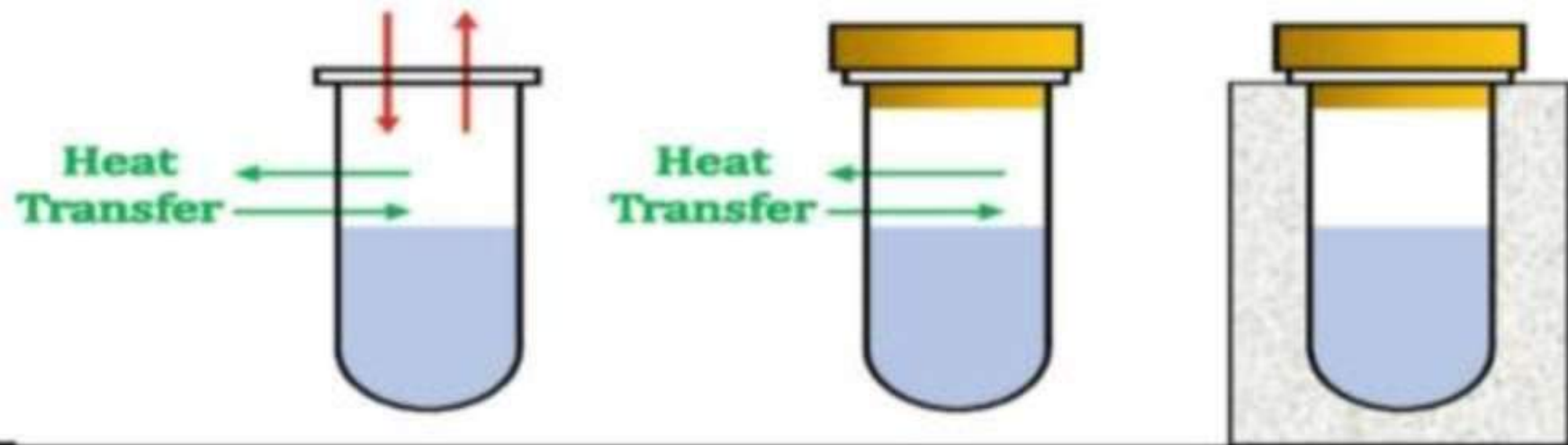


PHYSICAL CHEMISTRY CRASH COURSE

THERMOCHEMISTRY ***IN 1 SHOT***



JEE Main & Advanced

MANZIL SPRINT

JEE CRASH COURSE



IIT/NIT



By Pankaj Sir



Heat of reaction ($\Delta_r H$)

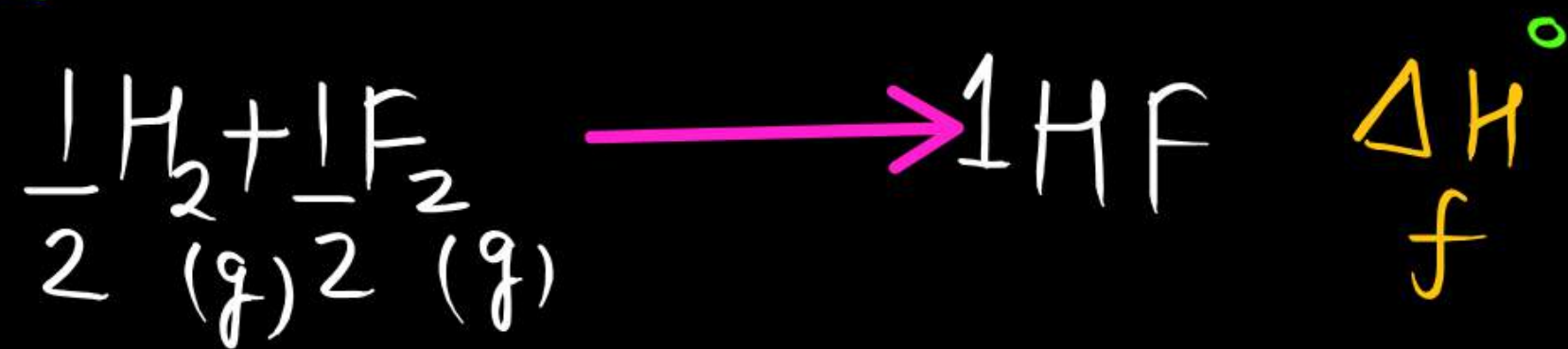


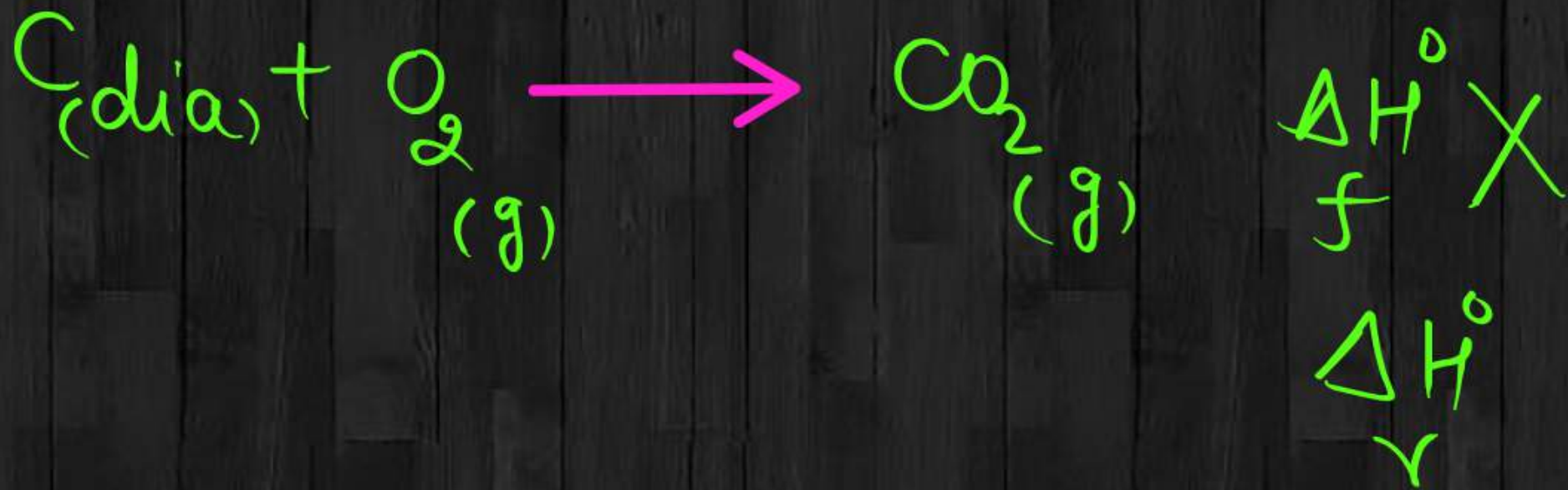
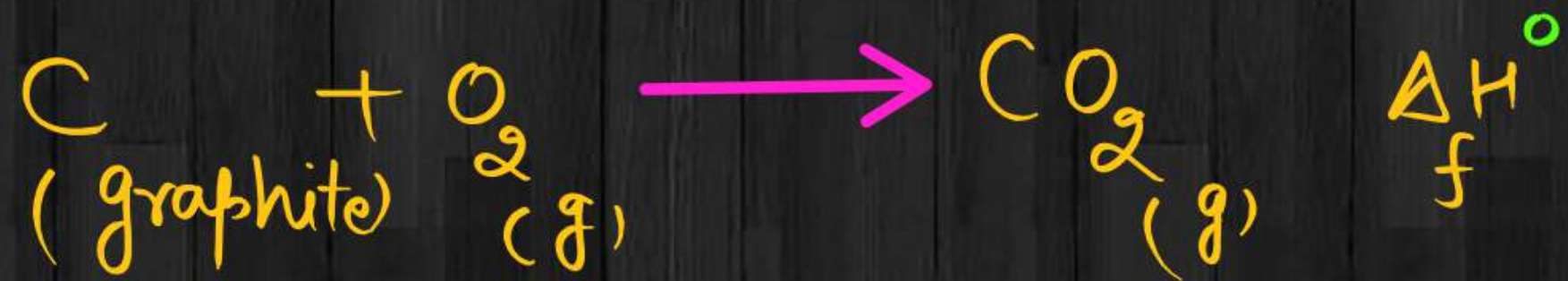
Diff Type of Heat of Rxn



1. Heat of formation ($\Delta_f H^\circ$)

The amount of heat involve in the formation of 1 mol of a compound by its constituent atoms or molecules.





Standard state

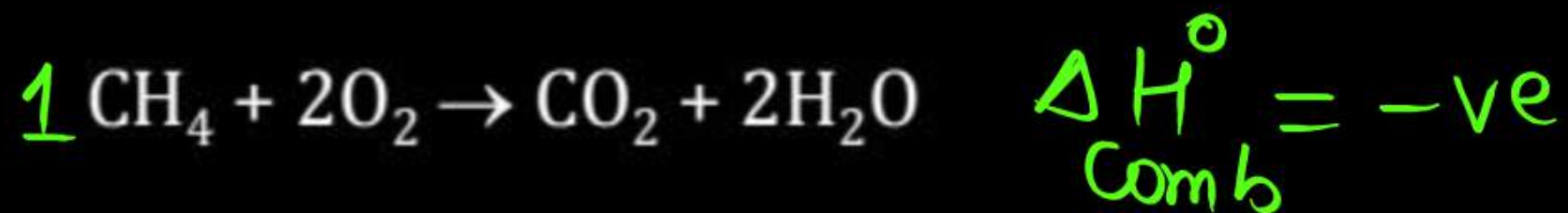
$$\Delta H_f^\circ = 0$$





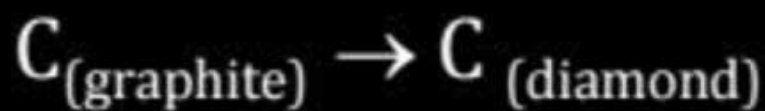
2. Heat of combustion $\Delta^\circ H_{\text{comb}}$

The heat released when 1 mol of a substance is combined with O_2 to form products.



3. Heat of transition $\Delta^\circ H_{\text{trans}}$

The heat absorbed or released during conversion of one allotropic form to another form.

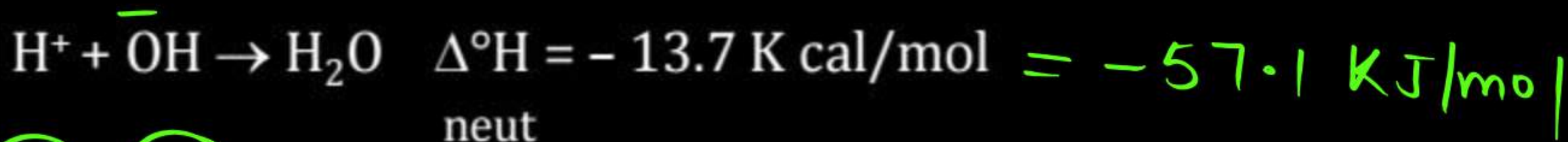


ΔH_{trans}



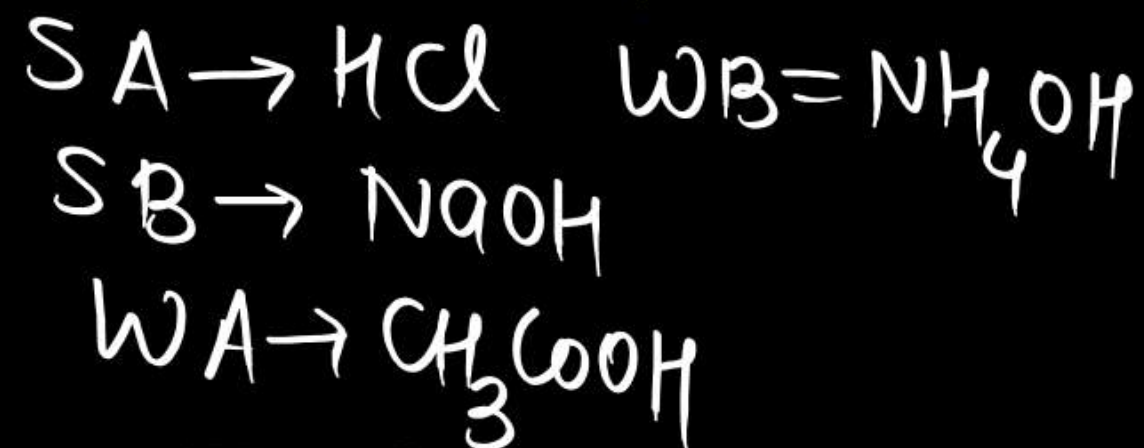
4. Heat of neutralization $\Delta^\circ H_{\text{neut}}$ $\Delta H^\circ_{\text{neut}} = -ve$

It is the heat released when 1 gm equi of acid is neutralized by 1 gm equi of base



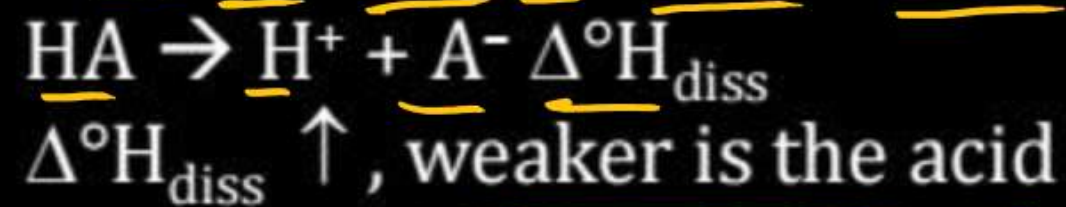
SA SB

$$\Delta^\circ H_{\text{neut}} (\text{SA} + \text{SB}) > (\text{WA} + \text{SB}) > (\text{WA} + \text{WB})$$



5. Heat of Ionisation (or dissociation) ($\Delta^\circ H_{\text{diss}}$ or $\Delta^\circ H_{\text{ion}}$)

It is the heat required for the diss of 1 mol of acid (or base)



$$\Delta H^\circ_{\text{diss}} = +ve$$



Q. ^{SA} 200 mL of 0.1 M H_2SO_4 is mixed with ^{SB} 150 mL of 0.2 M KOH find the value of heat evolved (in KJ)

$$\begin{aligned}\text{mili eqvi of } \text{H}_2\text{SO}_4 &= M \times n_f \times V_{(\text{mL})} \\ &= 0.1 \times 2 \times 200 \\ &= 40\end{aligned}$$

$$\text{gm eqvi} = 40 \times 10^{-3}$$

$$1 \text{ gm eq} \longrightarrow -57.1$$

$$30 \times 10^{-3} \text{ gm eq} \longrightarrow -57.1 \times 30 \times 10^{-3}$$

$$\begin{aligned}\text{mili eqvi of base} &= M \times n_f \times V_{(\text{mL})} \\ &= 0.2 \times 1 \times 150 \\ &= 30 \\ \text{gm eqvi} &= 30 \times 10^{-3}\end{aligned}$$



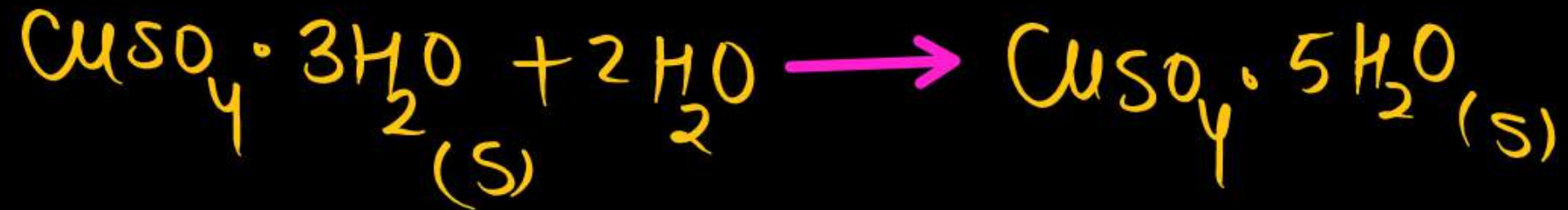
6. Enthalpy of Hydration ($\Delta^\circ H_{\text{hyd}}$)

Case (1) for Salt

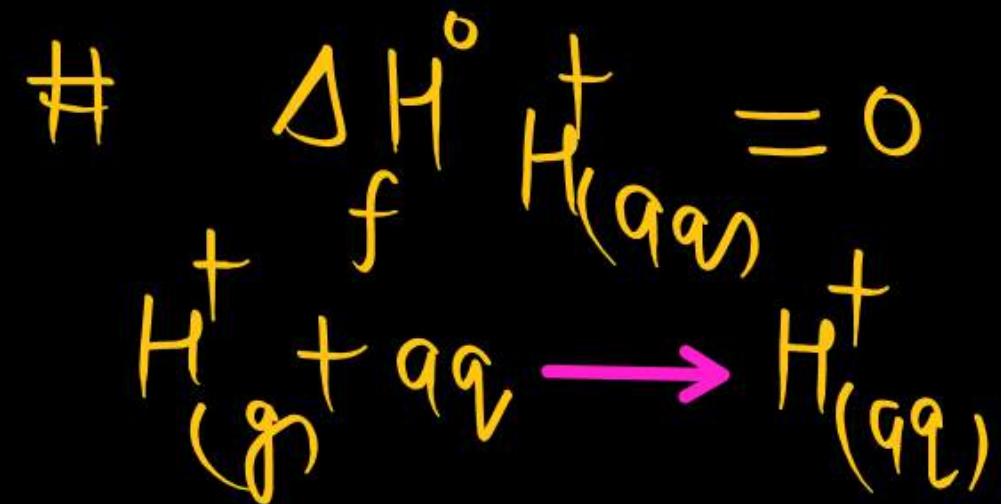
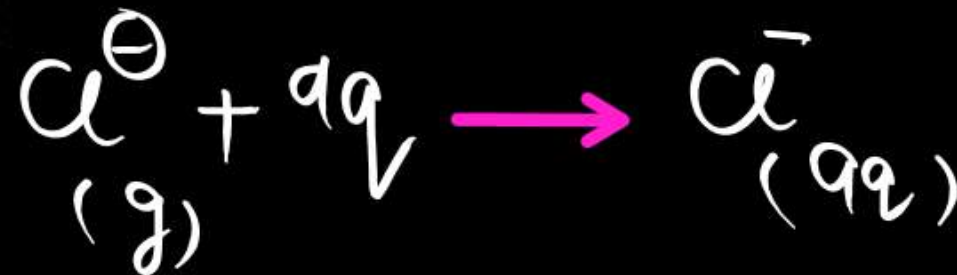
1. Anhydrous salt



2. Partially hydrated



Case (2) for ion

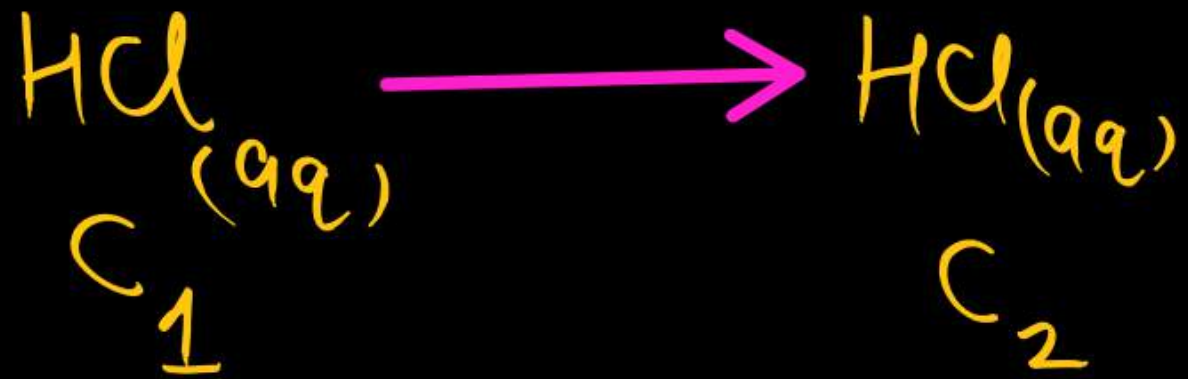




7. Enthalpy of Solution ($\Delta^\circ H_{\text{sol}}$)



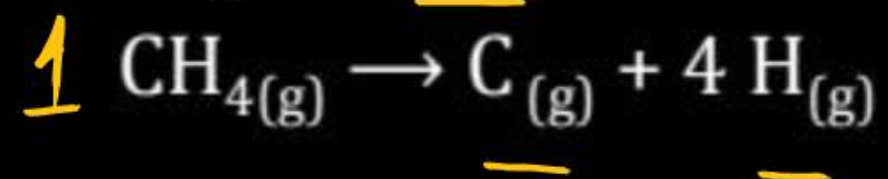
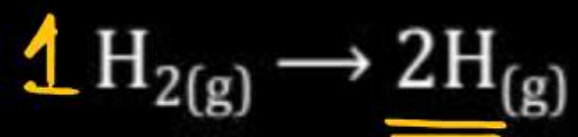
8. Enthalpy of dilution ($\Delta^\circ H_{\text{dil}}$)





9. Heat of atomisation ($\Delta_a H^\circ$)

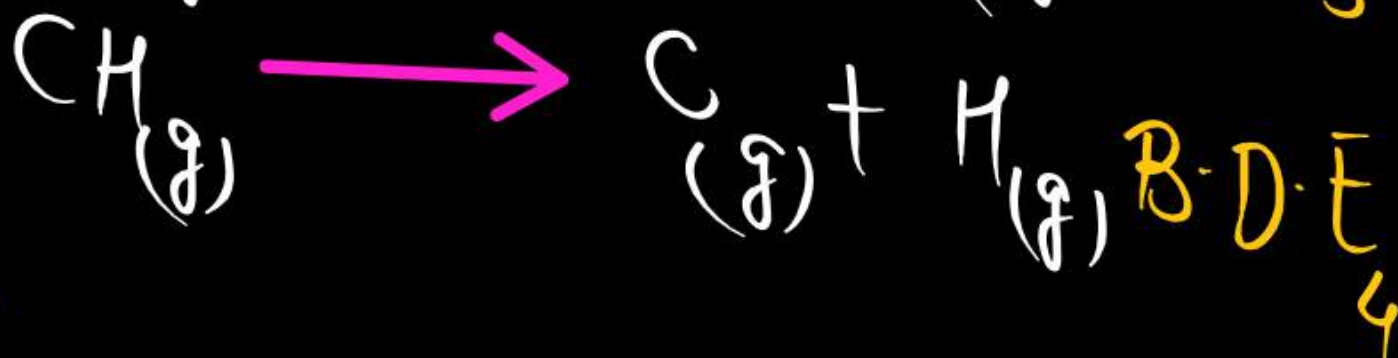
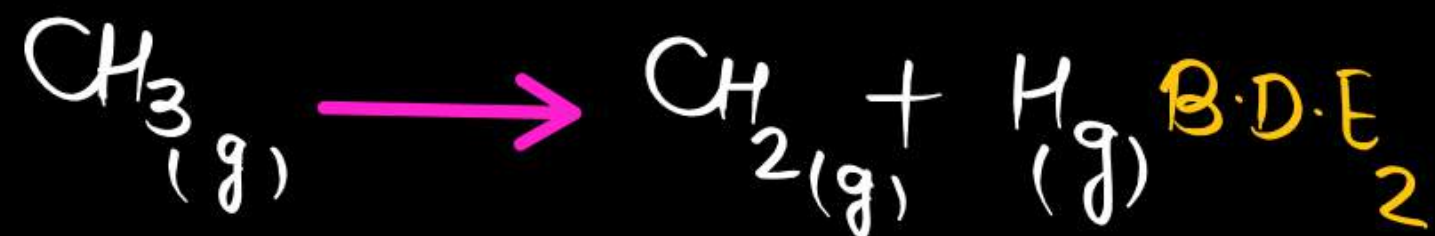
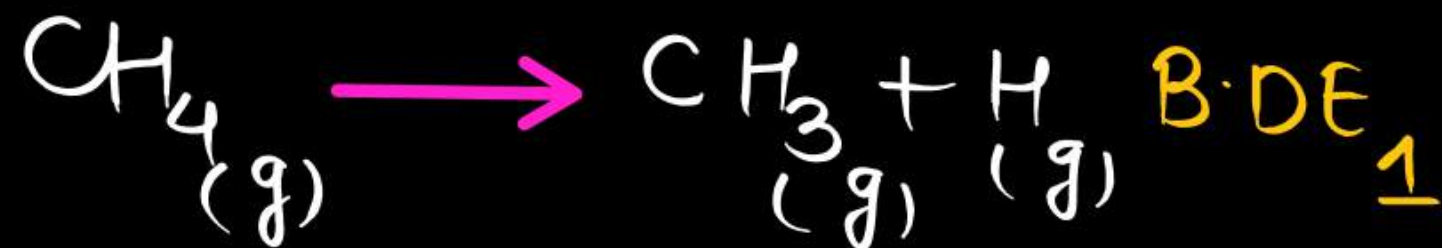
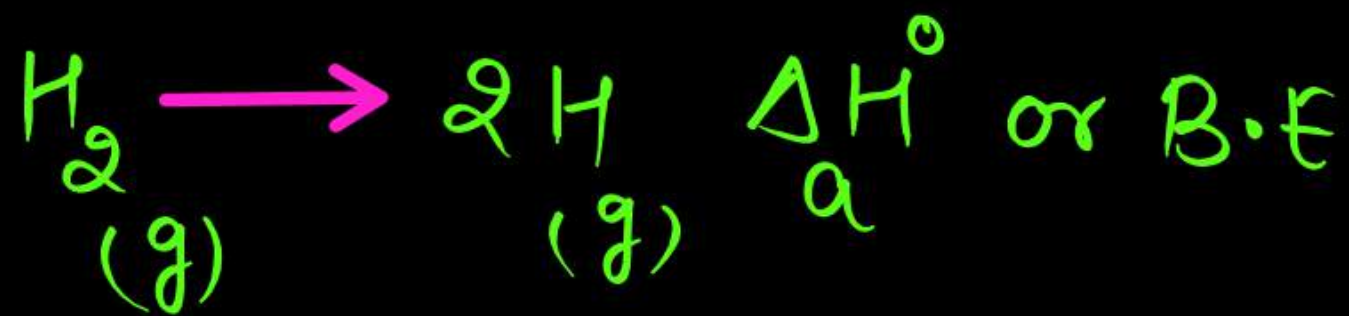
It is the enthalpy change when 1 mol of gas molecule is broken
free atoms in gas phase



10. Bond energy (B.E or ϵ)

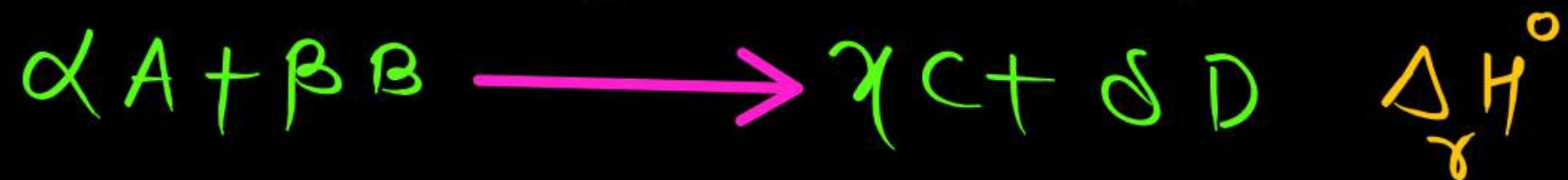


It is the avg of enthalpies when 1 mol of comp is converted into atoms.



$$\begin{aligned} &\text{B.E of C-H} \\ &= \text{B.D.E}_1 + \text{B.D.E}_2 + \text{B.D.E}_3 \\ &\quad + \text{B.D.E}_4 \\ &\hline &4 \end{aligned}$$

Calculation of $\Delta_r H^\circ$ when $\Delta_f H^\circ$ given

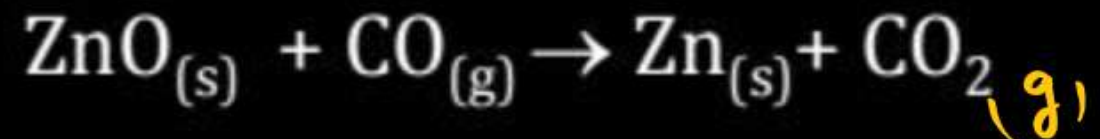


$$\Delta_r H^\circ = \left[\gamma \Delta_f H^\circ(C) + \delta \Delta_f H^\circ(D) \right] - \left[\alpha \Delta_f H^\circ(A) + \beta \Delta_f H^\circ(B) \right]$$

$$\Delta_r H^\circ = (\Delta_f H^\circ)_P - (\Delta_f H^\circ)_R$$



Q. Find $\Delta_r H^\circ$ for the Rxn



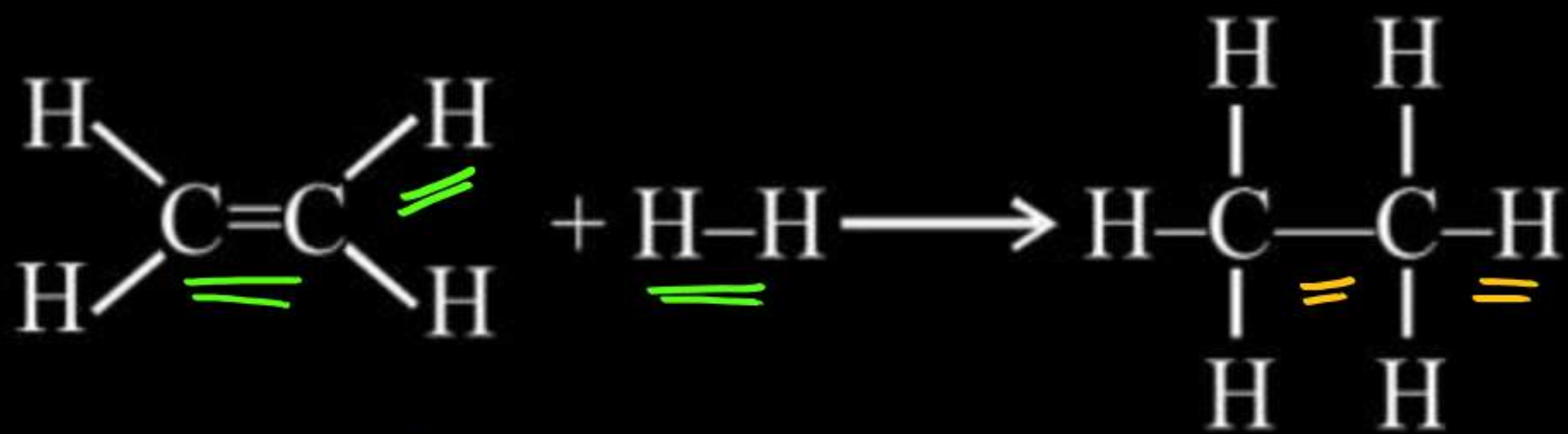
Given,	Comp	$\Delta_f H^\circ (\text{KJmol}^{-1})$
	$\text{ZnO}_{(s)}$	-250
	$\text{CO}_{2(g)}$	-390
	$\text{CO}_{(g)}$	-110

$$\Delta_r H^\circ = \left[\cancel{\Delta_f H^\circ(\text{Zn})} + \Delta_f H^\circ(\text{CO}_2) \right]$$

$$\left[\Delta_f H^\circ(\text{ZnO}) + \Delta_f H^\circ(\text{CO}) \right]$$

$$= (0 - 390) - (-250 - 110)$$

Calculation of $\Delta_r H^\circ$ when B.E is given

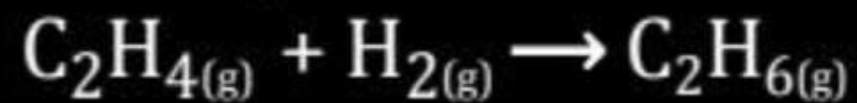


$$\Delta_r H^\circ = (B.E)_R - (B.E)_P$$

$$= [BE_{C=C} + 4BE_{C-H} + BE_{H-H}] - [BE_{C-C} + 6BE_{C-H}]$$



Q. Find $\Delta_r H^\circ$ for the Rxn



Given bonds BE(KJ/mol)

C-H 414

C-C 347

C=C 615

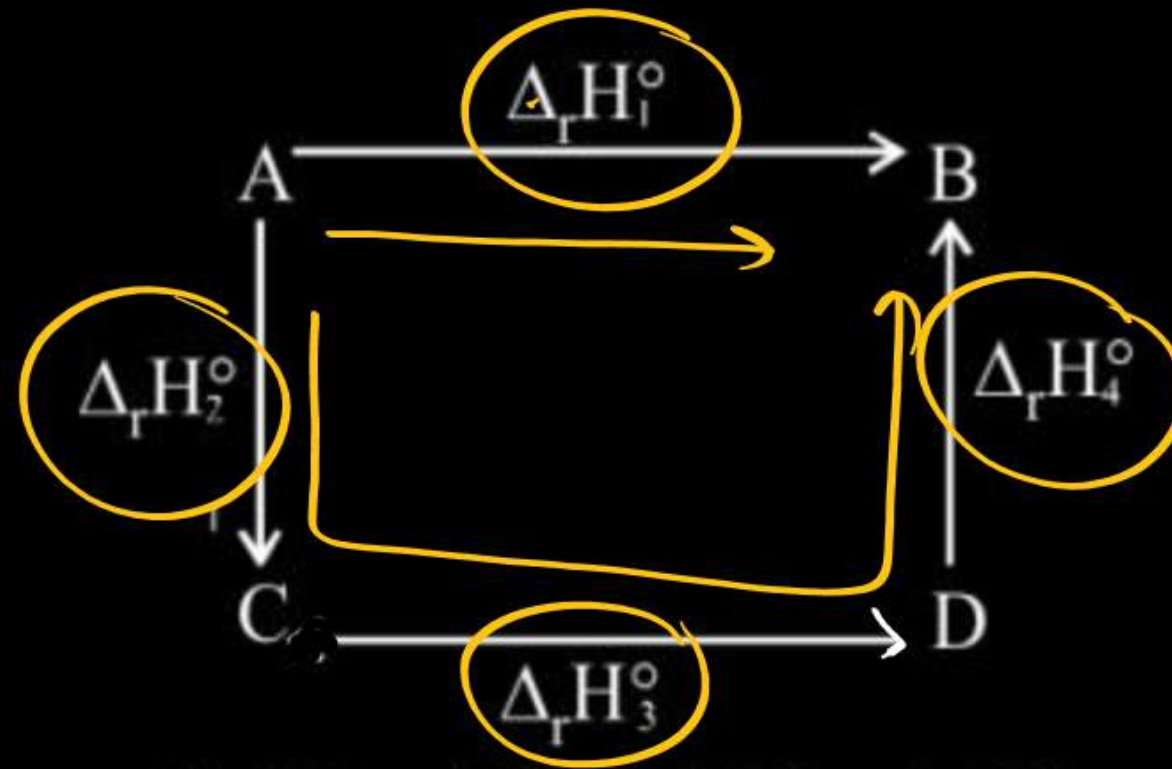
H-H 435

Solution:

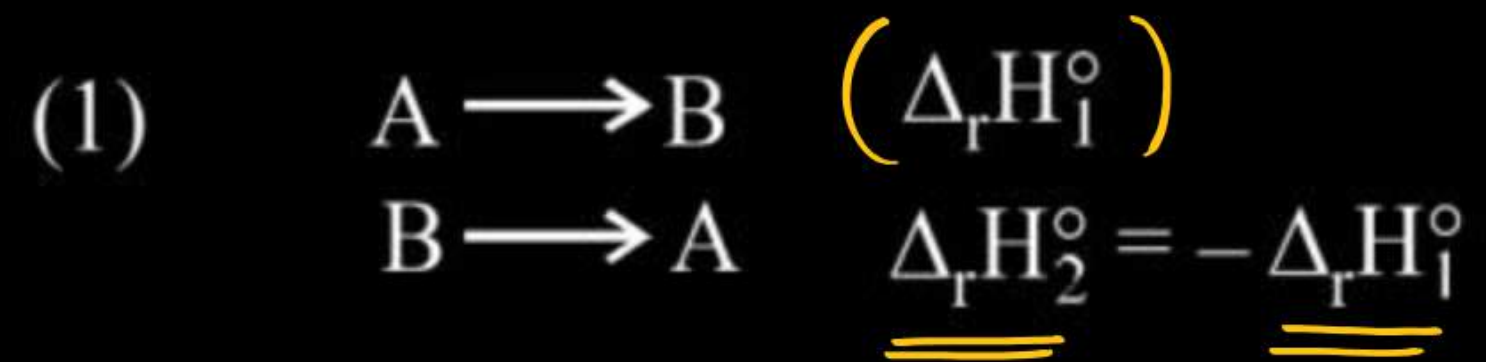
$$\Delta_r H^\circ = [615 + 4 \times 414 + 435] \\ - [347 + 6 \times 414]$$

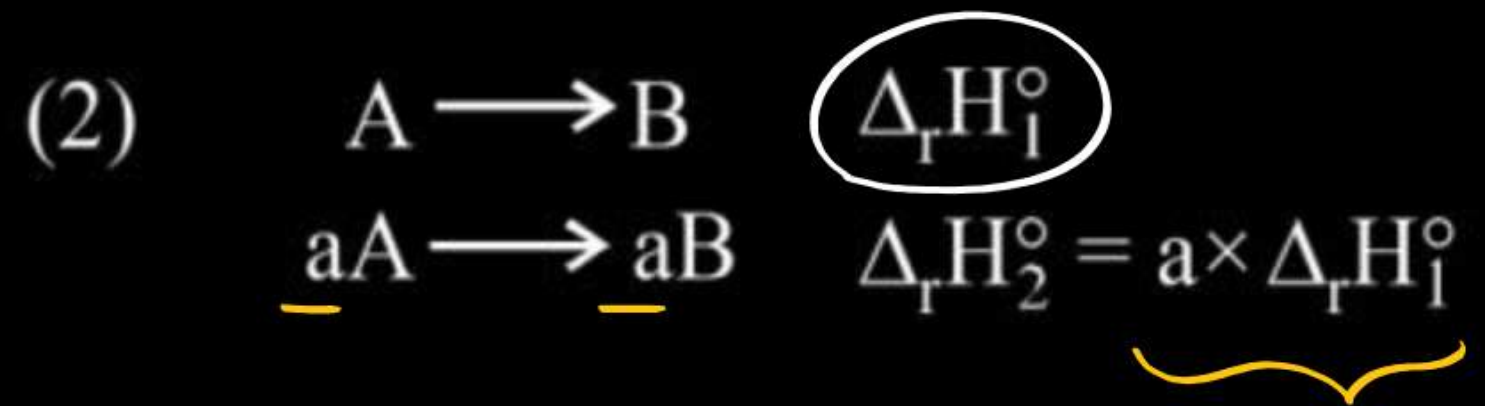
Hess's Law

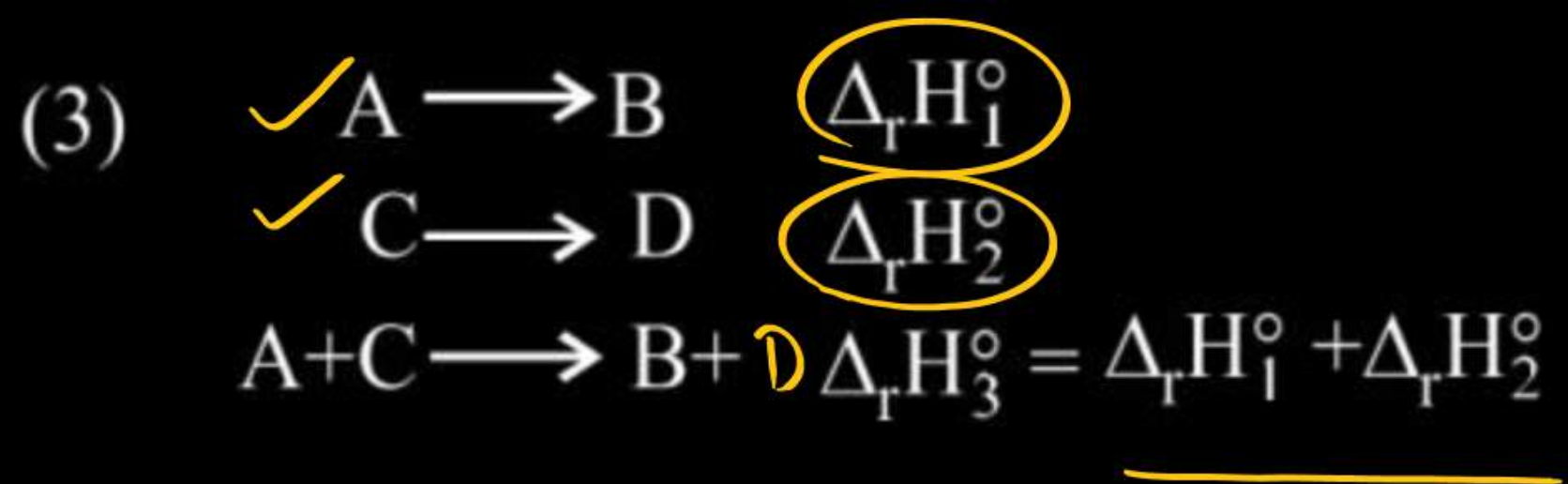
The total heat content of a Rxn is same whether the rxn is carried out by direct path or indirect path



$$[\Delta_r H_1^\circ = \Delta_r H_2^\circ + \Delta_r H_3^\circ + \Delta_r H_4^\circ]$$









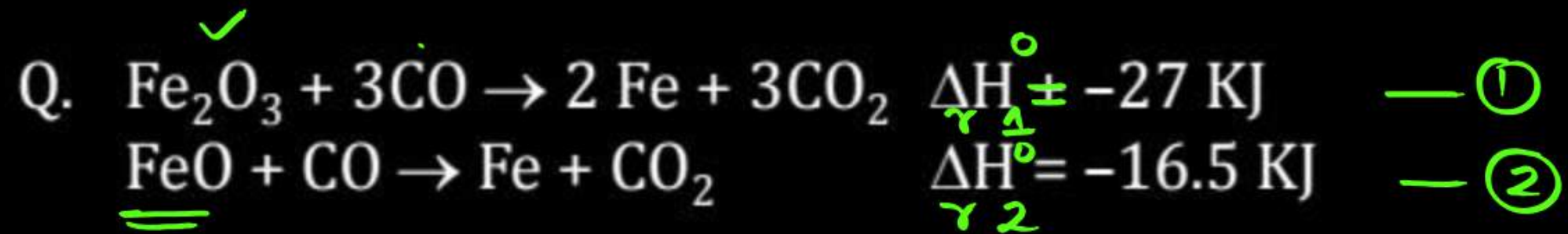
Q.	Rxn	$\Delta_r H$ (KJ/mol)
----	-----	-----------------------



Find ΔH for



$$\Delta_r H_4^0 = 150 \times 2 - 125 - 350$$



Find ΔH° for $\text{Fe}_2\text{O}_3 + \text{CO} \rightarrow 2\text{FeO} + \text{CO}_2$

$$\Delta H^\circ_3 = \Delta H^\circ_1 + (-2 \Delta H^\circ_2)$$

$$= -27 \text{ KJ} - 2 \times (-16.5)$$

Entropy of Chemical Rxn



$$\Delta_r S^\circ = [\gamma S^\circ_{(C)} + \delta S^\circ_{(D)}] - [\alpha S^\circ_{(A)} + \beta S^\circ_{(B)}]$$

Q. Find $\Delta_r S^\circ$ $\frac{1}{2}X_2 + \frac{3}{2}Y_2 \rightarrow XY_3$

Comp	S_m° (JK ⁻¹ mol ⁻¹)
X ₂	60
Y ₂	40
XY ₃	50

$$\Delta_r S^\circ = S_m^\circ(XY_3) - \frac{1}{2} S_m^\circ(X_2) - \frac{3}{2} S_m^\circ(Y_2)$$

$$= 50 - \frac{1}{2} \times 60 - \frac{3}{2} \times 40$$

Gibbs free energy of a Rxn



$$\Delta G_r^\circ = \left[\gamma \Delta G_{f(C)}^\circ + \delta \Delta G_{f(D)}^\circ \right] - \left[\alpha \Delta G_{f(A)}^\circ + \beta \Delta G_{f(B)}^\circ \right]$$



Kirchoff's Equation

At Cont press

$$\underbrace{(\Delta H)_{T_2} - (\Delta H)_{T_1}} = \underbrace{\Delta C_p}_{\text{At Const volume}} (T_2 - T_1)$$

At Const volume

$$\begin{aligned} (\Delta U)_{T_2} - (\Delta U)_{T_1} &= \Delta C_v (T_2 - T_1) \\ \underline{\quad} &= \underline{\quad} = \end{aligned}$$

$$\Delta C_p = (C_p)_P - (C_p)_R$$

$$\Delta C_v = (C_v)_P - (C_v)_R$$



Q. Find ΔH at 400 K for



Given	Gas	C_p ($\text{JK}^{-1} \text{mol}^{-1}$)
	NO_2	35
	N_2	30
	O_2	30

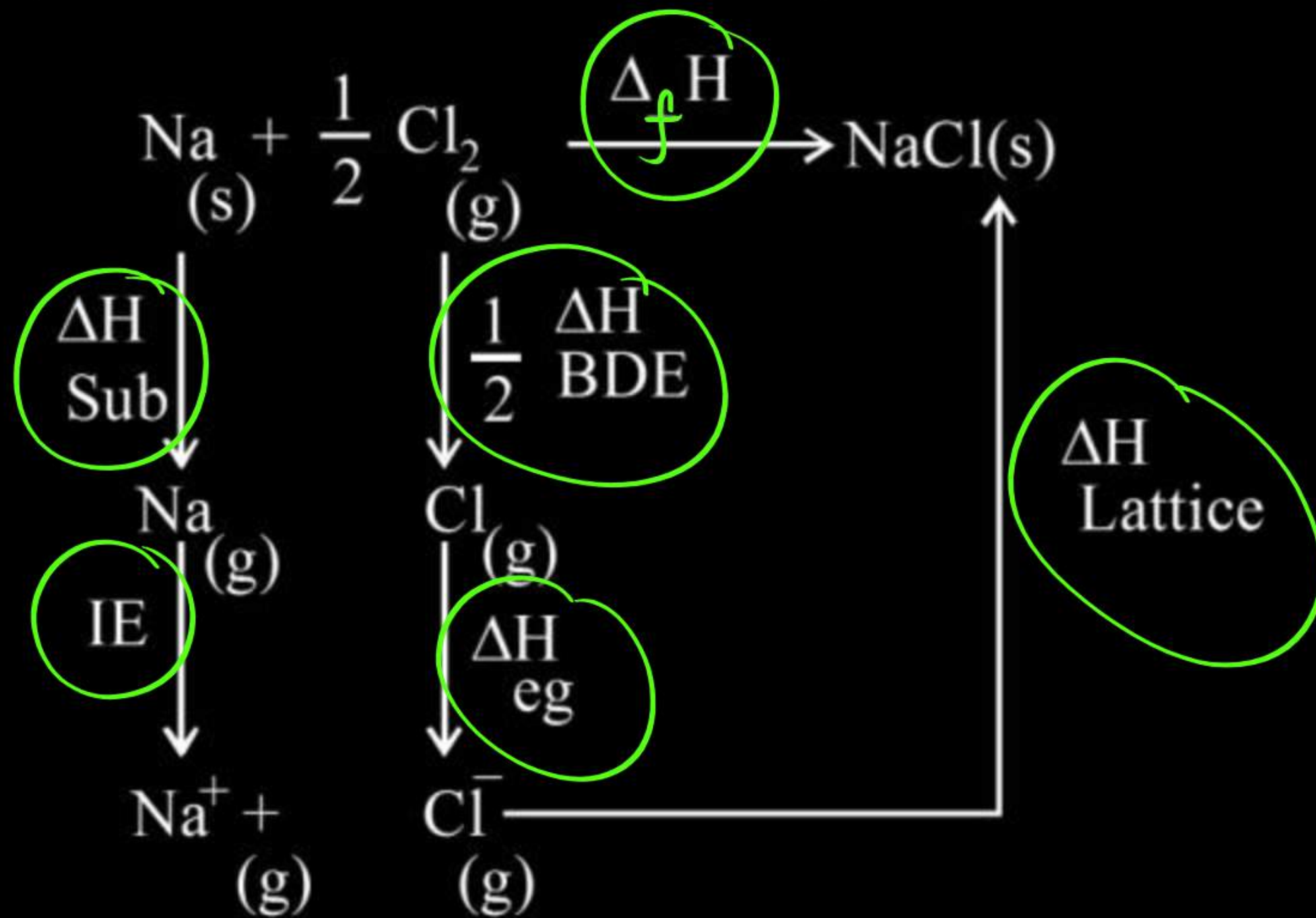
$$\begin{aligned}\Delta C_p &= 35 - \frac{1}{2} \times 30 - 30 \\ &= 35 - 15 - 30 \\ &= -10\end{aligned}$$

$$(\Delta H)_{400} - (\Delta H)_{300} = \Delta C_p (400 - 300)$$

$$(\Delta H)_{400} - (-35 \times 10^3) = -10 \times 100$$

Born Haber's cycle

L.E of Ionic Comp



Born Haber's cycle



$$\Delta H_f = \Delta H_{\text{sub}} + \text{IE} + \frac{1}{2} \Delta H_{\text{BDE}} + \Delta H_{\text{eg}} + \Delta H_{\text{Lattice}}$$

$$\Delta H_{\text{Lattice}} = \Delta H_f - \left(\Delta H_{\text{sub}} + \text{IE} + \frac{1}{2} \Delta H_{\text{BDE}} + \Delta H_{\text{eg}} \right)$$

When C_p is temperature dependent

$$\Delta H = n \int_{T_1}^{T_2} C_p dT$$





Q.

For silver, $C_p(\text{J K}^{-1}\text{mol}^{-1}) = 23 + 0.01T$. If the temperature (T) of 3 moles of silver is raised from 300 K to 1000 K at 1 atm pressure, the value of ΔH will be close to (2019 Main, 8 April I)

a.

62 kJ

b.

16 kJ

c.

21 kJ

d.

13 kJ

Solution:

$$\Delta H = n \int_{T_1}^{T_2} C_p dT$$
$$\Delta H = 3 \int_{300}^{1000} (23 + 0.01T) dT$$



Q. For $A_{2(g)} \rightarrow 2A_{(g)}$ correct option is

$\Delta n_g > 0$

	ΔH	ΔS
(a)	+	-
<input checked="" type="checkbox"/> (b)	+	+
<input checked="" type="checkbox"/> (c)	-	-
<input checked="" type="checkbox"/> (d)	-	+



Q.

The standard reaction Gibbs energy for a chemical reaction at an absolute temperature T is given by, $\Delta_r G^\circ = A - BT$

Where A and B are non-zero constants.

Which of the following is true about this reaction? (2019 Main, 11 Jan II)

$$\Delta H^\circ - T \Delta S^\circ$$

- ☐ *a.* Endothermic if, $A < 0$ and $B > 0$ ☐ *b.* Exothermic if, $B < 0$
- ☐ *c.* Exothermic if, $A > 0$ and $B < 0$ ☒ *d.* Endothermic if, $A > 0$

Solution:

Q.

For the chemical reaction, $X \rightleftharpoons Y$, the standard reaction

Gibbs energy depends on temperature T (in K) as

$$\Delta_r G^\circ \text{ (in kJ mol}^{-1}\text{)} = 120 - \frac{3}{8}T$$

The major component of the reaction mixture at T is

(2019 Main, 11 Jan II)

~~a.~~

Y if $T = 280$ K

b.

X if $T = 350$ K

c.

X if $T = 315$ K

d.

Y if $T = 300$ K

Solution:

$$\Delta_r G^\circ = 120 - \frac{3}{8} \times 280 > 0 \quad \leftarrow$$

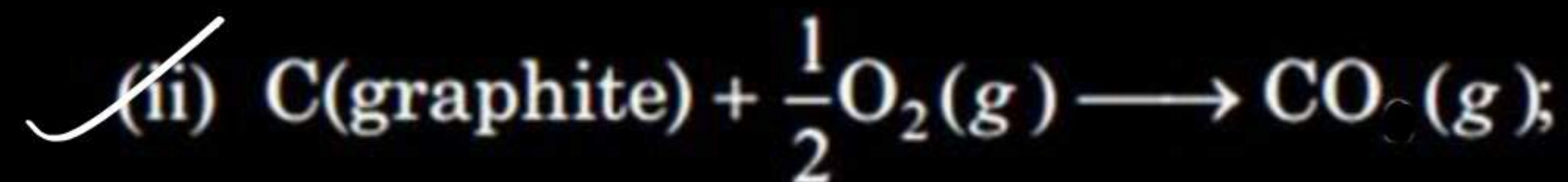
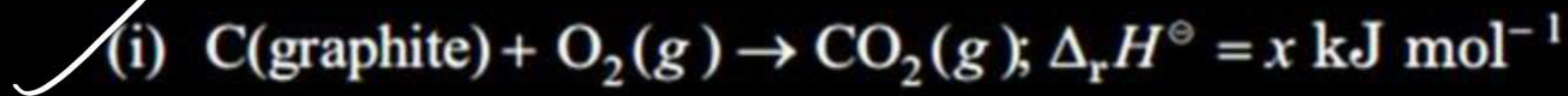
$$120 - \frac{3}{8} \times 315$$

$$\Delta_r G^\circ = > 0$$

$$\begin{array}{l} T \checkmark \quad \Delta_r G^\circ < 0 \rightarrow \\ T \checkmark \quad \Delta_r G^\circ > 0 \leftarrow \end{array}$$

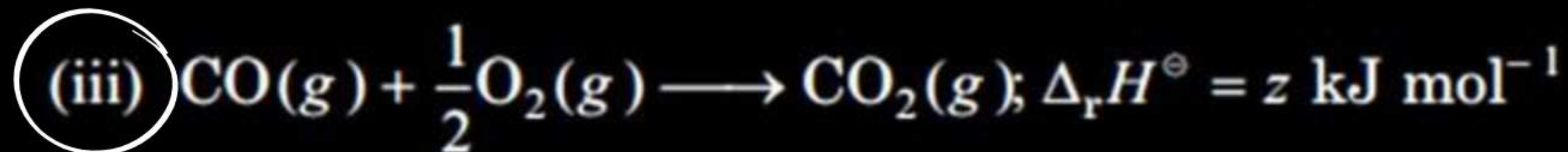


Q. Given :



$$\Delta_r H^\ominus = y \text{ kJ mol}^{-1}$$

$$x - y = z$$



Based on the above thermochemical equations, find out which one of the following algebraic relationships is correct?

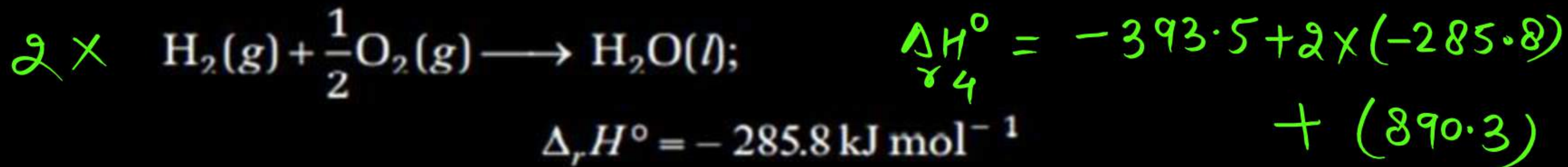
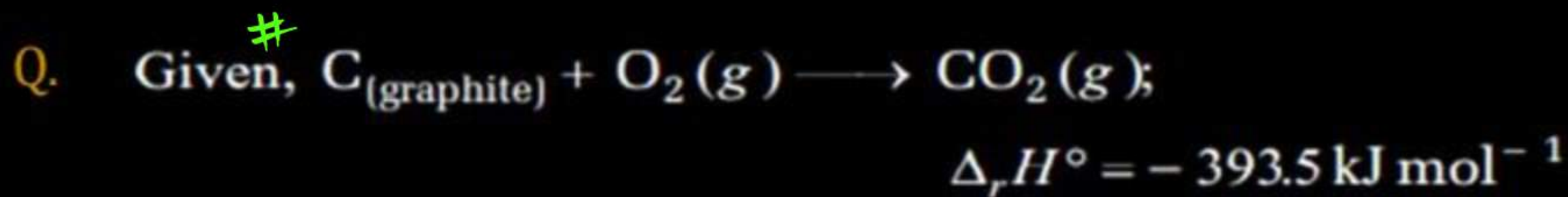
(2019 Main, 12 Jan II)

(a) $y = 2z - x$

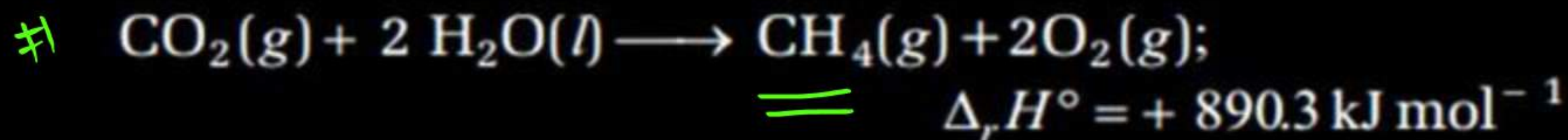
(b) $x = y - z$

(c) $z = x + y$

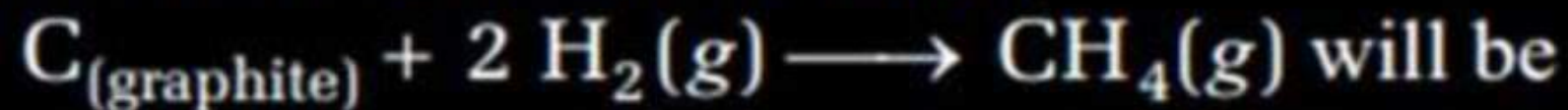
✓ (d) $x = y + z$



$$\Delta H^\circ = -393.5 + 2 \times (-285.8) + (890.3)$$



Based on the above thermochemical equations, the value of $\Delta_r H^\circ$ at 298 K for the reaction, (2017 Main)



(a) $+78.8 \text{ kJ mol}^{-1}$

(b) $+144.0 \text{ kJ mol}^{-1}$

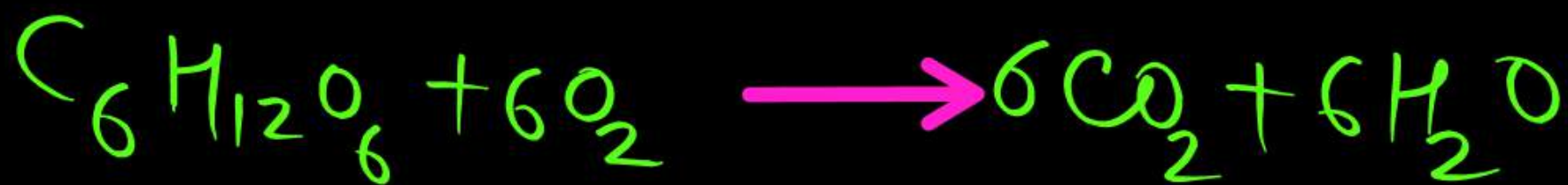
(c) $-74.8 \text{ kJ mol}^{-1}$

(d) $-144.0 \text{ kJ mol}^{-1}$



Q. The standard enthalpies of formation of $\text{CO}_2(g)$, $\text{H}_2\text{O}(l)$ and glucose(s) at 25°C are -400 kJ/mol , -300 kJ/mol and -1300 kJ/mol , respectively. The standard enthalpy of combustion per gram of glucose at 25°C is (2013 Adv.)

- (a) $+2900 \text{ kJ}$ (b) -2900 kJ
(c) -16.11 kJ (d) $+16.11 \text{ kJ}$



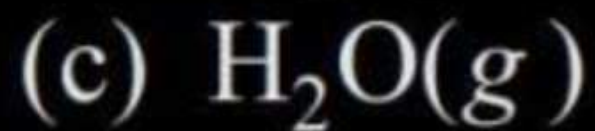
$$\begin{aligned}\Delta H_{\text{comb}}^\circ &= \Delta H^\circ = \left[6 \times \Delta H_f^\circ(\text{CO}_2) + 6 \times \Delta H_f^\circ(\text{H}_2\text{O}) \right] - \left[\Delta H_f^\circ(\text{C}_6\text{H}_{12}\text{O}_6) \right] \\ &= 6 \times (-400) + 6 \times (-300) - (-1300)\end{aligned}$$

for 1mol $\Delta_c H^\circ_{\text{comb}} = -2900$

for 180gm $\Delta_c H^\circ_{\text{comb}} = -2900$

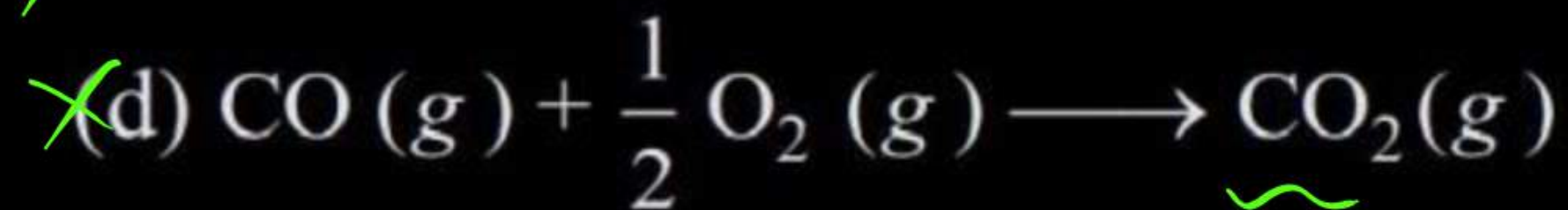
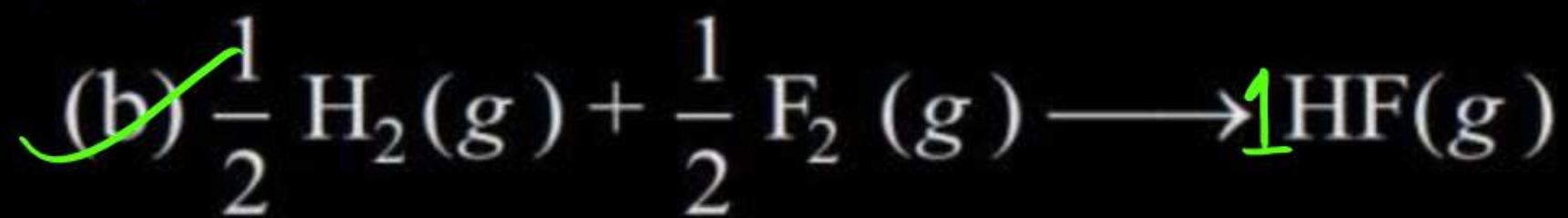
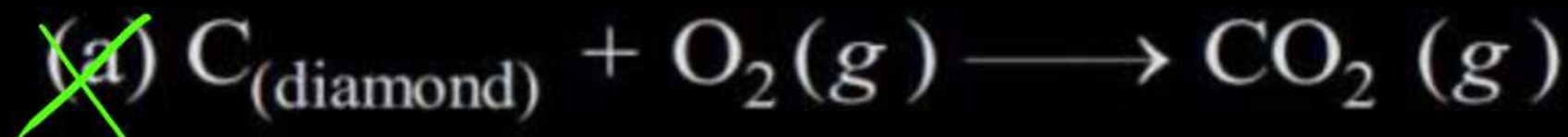
for 1gm $\Delta_c H^\circ_{\text{comb}} = \frac{-2900}{180}$

Q. The species which by definition has zero standard molar enthalpy of formation at 298 K is (2010)



Q. Which of the following reactions defines ΔH_f° ?

(2003, 1M)





Q. The ΔH_f° for $\text{CO}_2(g)$, $\text{CO}(g)$ and $\text{H}_2\text{O}(g)$ are -393.5 , -110.5 and $-241.8 \text{ kJ mol}^{-1}$ respectively. The standard enthalpy change (in kJ mol^{-1}) for the reaction $\text{CO}_2(g) + \text{H}_2(g) \longrightarrow \text{CO}(g) + \text{H}_2\text{O}(g)$ is (2000, 1M)

(a) 524.1

(b) +41.2

(c) -262.5

(d) -41.2

$$\begin{aligned}\Delta_r H^\circ &= [\Delta_f H^\circ(\text{CO}) + \Delta_f H^\circ(\text{H}_2\text{O})] - [\Delta_f H^\circ(\text{CO}_2) + 0] \\ &= [-110.5 - 241.8] - [-393.5]\end{aligned}$$

Thank you!!!