



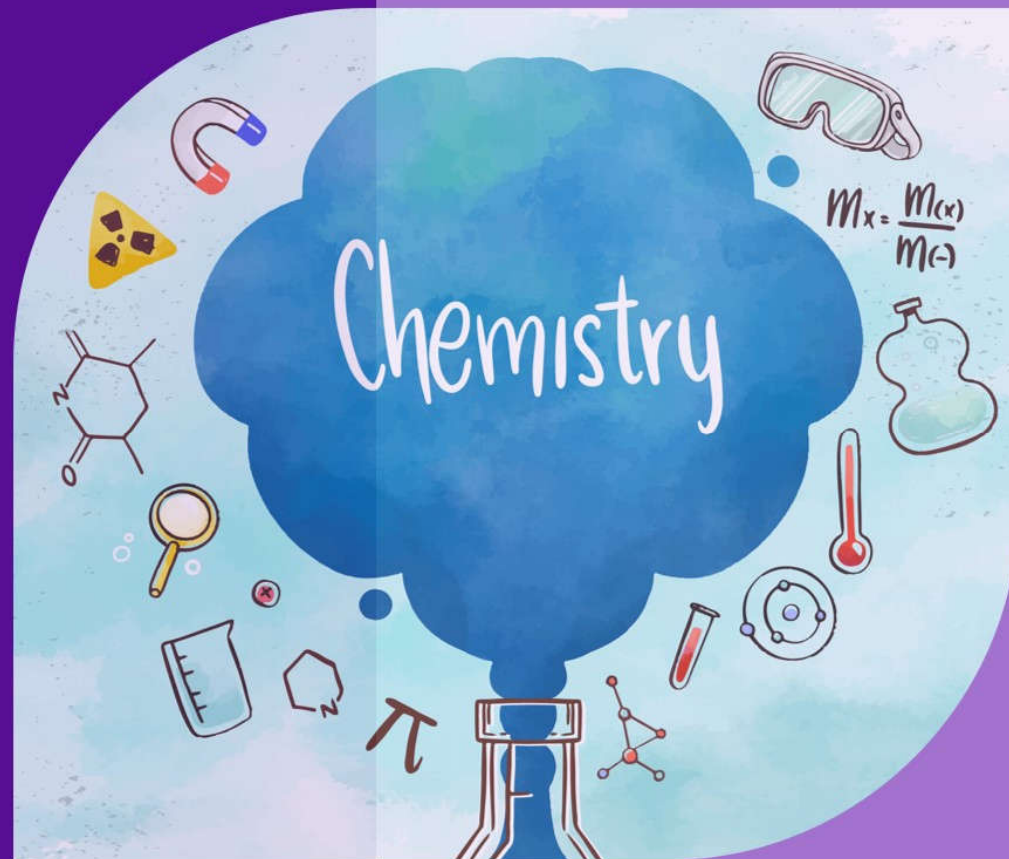
✓✓ VARSITY 'Ka' ADMISSION PROGRAM 2020

CHEMISTRY

LECTURE : C-04

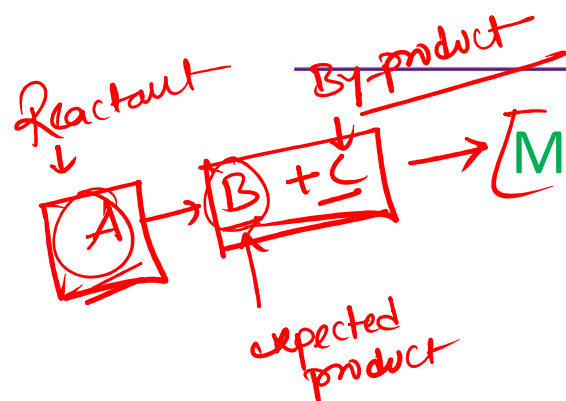
CHAPTER 04 : CHEMICAL EQUILIBRIUM

- ✓ - Chemical kinetics
- ✓ - Thermochemistry



Green chemistry

→ Industry level



Maximum production Minimum pollution

cost ↓ → production ↑
pollutants ↓
↓
env. (greenen)

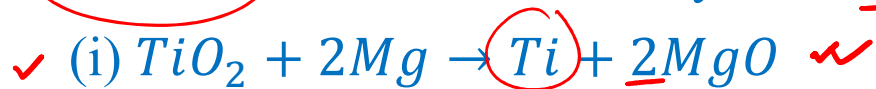
Atom Economy (AE)

A.E. = $\frac{M_B}{M_B + M_C}$ ✓
= $\frac{M_B}{M_A}$
preferable

✓ AE = $\frac{\text{Expected product mass}}{\text{Total product mass}} \times 100$

Math Problem

^{50%}
Titanium can be extracted by two methods :



greener

Which one is greener?

↳ expe. product ↑ ; pollutants ↓ ; ^{healthier} environment ↑ ; greener ↑

(i) A.E. = $\frac{48}{48 + (24+16) \times 2} = \frac{48}{48+80} = \frac{48}{128}$ ✓ ↓

(ii) A.E. = $\frac{48}{48 + 32} = \frac{48}{80}$ ✓ ↑ →

Hydrocarbon
 ↓
 H is replaced by F, Cl
 ↳ CFC

CFC



Chloro Fluoro (Carbon)

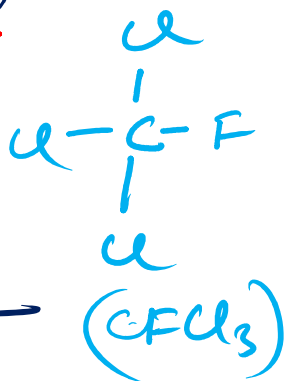
Cl

F

C

(+ H)

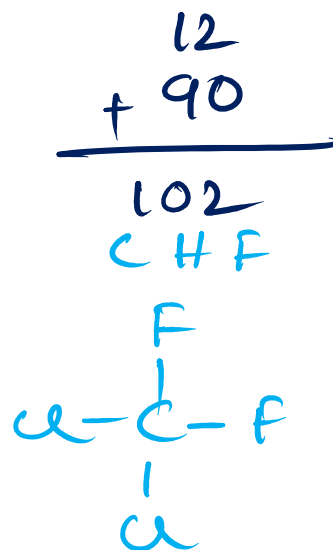
CFC-11



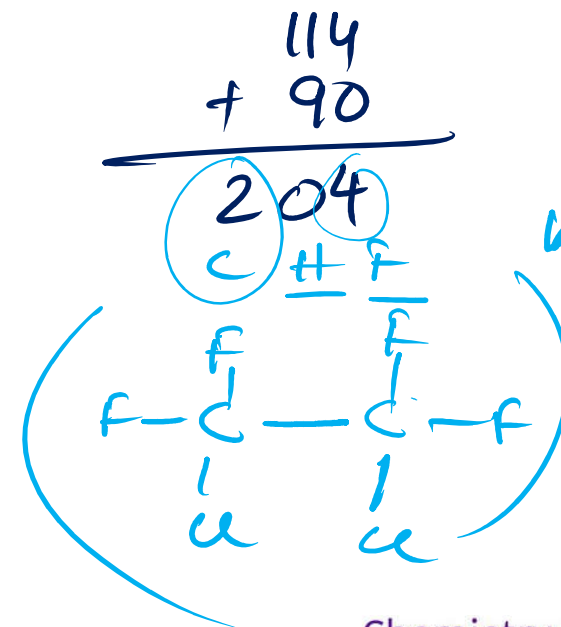
Formula:

$$\begin{array}{r} + 90 \\ \hline 101 \\ \begin{array}{ccc} \swarrow & \uparrow & \swarrow \\ \text{C} & \text{H} & \text{F} \end{array} \end{array}$$

CFC-12



CFC-114



Poll question: 01

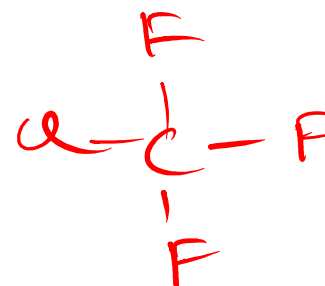
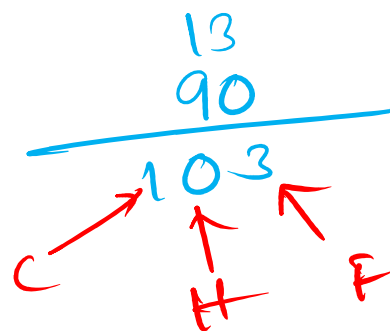
Chemical formula of CFC-13 is ?

(a) CF_2Cl_2

(b) CFCl_3

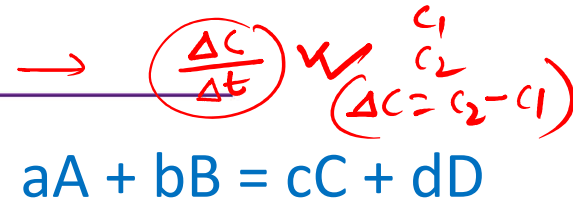
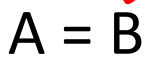
(c) CCl_4

(d) CF_3Cl



Reaction rate

Reactant → Products

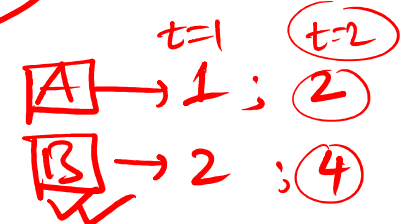


rate ← always (+)
 with respect to Reactant ↓
 Product ↓
 $\frac{\Delta B}{\Delta t}$

$r = -\frac{d[A]}{dt} = -\frac{d[B]}{dt}$

$= \frac{dC}{dt} = \frac{dD}{dt}$

$r = -\frac{dA}{dt} = \frac{1}{2} \cdot \frac{dB}{dt}$



$r = -\frac{1}{a} \cdot \frac{dA}{dt} = -\frac{1}{b} \cdot \frac{dB}{dt}$
 $= \frac{1}{c} \cdot \frac{dC}{dt}$
 $= \frac{1}{d} \cdot \frac{dD}{dt}$

$r = -\frac{dA}{dt} = -\frac{1}{2} \cdot \frac{dB}{dt} = \frac{dC}{dt} = \frac{dD}{dt}$

$r = -\frac{d[A]}{dt} = +\frac{d[B]}{dt}$

Formula

Math Problem



a. Write the rate equation.

b. Calculate the rate of water production.

Given,

$$-\frac{d[\text{NH}_3]}{dt} = 0.24$$

a. rate = $-\frac{1}{4} \frac{d[\text{NH}_3]}{dt}$ (rate of NH_3 dissociation) = $-\frac{1}{5} \frac{d[\text{O}_2]}{dt} = \frac{1}{4} \frac{d[\text{NO}]}{dt} = \frac{1}{6} \frac{d[\text{H}_2\text{O}]}{dt}$ (rate of water production)

rate of reaction → $-\frac{1}{4} \frac{d[\text{NH}_3]}{dt}$

rate of reaction → $\frac{1}{6} \frac{d[\text{H}_2\text{O}]}{dt}$

b. $\frac{d[\text{H}_2\text{O}]}{dt} = ?$

$$\Rightarrow -\frac{1}{4} \frac{d[\text{NH}_3]}{dt} = \frac{1}{6} \frac{d[\text{H}_2\text{O}]}{dt}$$

$$\Rightarrow \frac{1}{4} \times 0.24 = \frac{1}{6} \times 4$$

$$\Rightarrow \frac{d[\text{H}_2\text{O}]}{dt} = \frac{6}{4} \times 0.24 = 0.36 \text{ mol L}^{-1} \text{ s}^{-1}$$

any reaction rate
↓
unit
↓
 $\frac{\text{mol L}^{-1}}{\text{s}}$

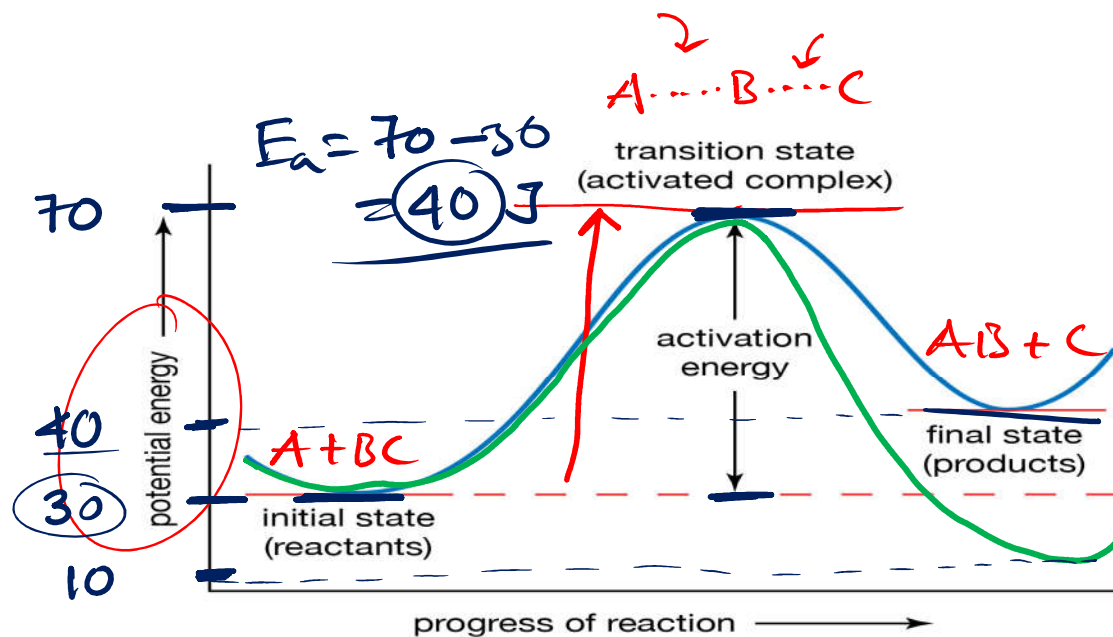
Reaction theory



Collision theory

Transition state theory

- ✓ The reactants must collide
- ✓ Collision must occur with a minimum energy (Activation energy: E_A) → Kinetic energy
- ✓ Collision must occur with proper orientation →



endothermic →

(Blue)

$$\Delta H = E_2 - E_1 = 40 - 30 = (+)10$$

(Green)

$$\Delta H = E_2 - E_1 = 10 - 30 = -20$$

exothermic

Chemistry 1st Paper

Chapter 04 : Chemical Equilibrium

Rate determining factors

1. Surface area of reactant : area ↑ ; r ↑
2. Temperature : T ↑ ; r ↑
3. Concentration : (C ↑ ; r ↑)
4. Catalyst : positive catalyst → r ↑
5. Pressure : (only for gas) P ↑ ; motion ↑ ; r ↑
6. Nature of reactant :

NaCl(s)	→	T ↑
NaCl(aq.)	→	T ↓

↙ Na⁺Cl⁻

NaCl(s) → r ↓

NaCl(aq) → r ↑
7. Presence of light :

eye ; photosynthesis

Poll question: 02

Which one isn't a factor of reaction rate?

- (a) Temperature
- (b) Pressure
- (c) Product
- (d) Concentration

T, C, Catalyst

Temperature

(small) $k \rightarrow$ (reaction) rate constant
 $A \rightarrow$ Arrh. constant
 $T \rightarrow$ Temp. $E_a \rightarrow$ Activation E.
 $R \rightarrow 8.314 \text{ J mol}^{-1} \text{ K}^{-1} (\text{SE})$ \leftarrow +ve

Arrhenius Equation: $k = Ae^{-\frac{E_a}{RT}}$

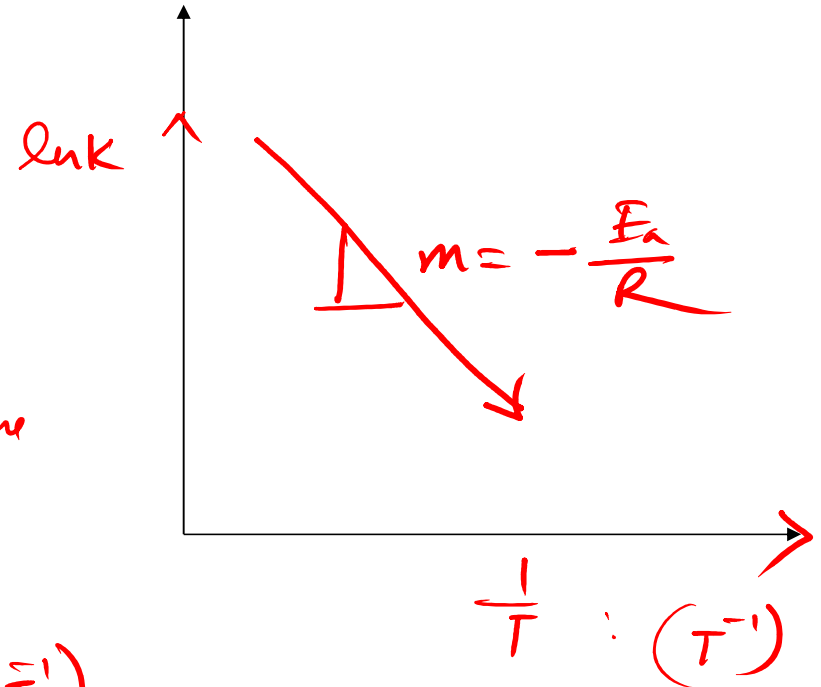
$$\begin{aligned} \ln k &= \ln \left(A \cdot e^{-\frac{E_a}{RT}} \right) \\ &= \ln A + \ln e^{-\frac{E_a}{RT}} \\ &= \ln A - \frac{E_a}{RT} \end{aligned}$$

$$\ln k = -\frac{E_a}{R} \cdot \frac{1}{T} + \ln A$$

y m x C \rightarrow eq. of a straightline

$$\log k = -\frac{E_a}{2.303R} \cdot \frac{1}{T} + \log A$$

$m = -\frac{E_a}{2.303R}$ (log k vs T^{-1})



Math Problem

~~**~~ If slope of $\ln k$ vs T^{-1} is -100K , calculate the activation energy?

$$m = -100 \text{ [K]}$$

$$-\frac{E_a}{R} = -100$$

$$E_a = 100R = (100 \times 8.314) \frac{\text{K} \cdot \text{Jmol}^{-1}\text{K}^{-1}}{\text{K}}$$
$$= \underline{831.4 \text{ Jmol}^{-1}}$$

Rate constant at two different Temp.

Definite reaction

K

Let's assume!

(ii) - (i):

$$\ln k_2 - \ln k_1 = -\frac{E_a}{R} \cdot \frac{1}{T_2} + \frac{E_a}{R} \cdot \frac{1}{T_1}$$

$$\therefore \ln \left(\frac{k_2}{k_1} \right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

8.314

$$\log \left(\frac{k_2}{k_1} \right) = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$T_1 \rightarrow k_1$
 $T_2 \rightarrow k_2$

$$\ln k_1 = -\frac{E_a}{R} \cdot \frac{1}{T_1} + \ln A \quad \text{(i)}$$

$$\ln k_2 = -\frac{E_a}{R} \cdot \frac{1}{T_2} + \ln A \quad \text{(ii)}$$

Given,

$E_a, k_1, k_2, T_1 \rightarrow T_2$

$E_a, T_1, T_2, k_1 \rightarrow k_2$

$E_a, T_1, T_2 \rightarrow k_1 \text{ or } k_2$

$T_1, T_2, k_1, k_2 \rightarrow E_a$



একাডেমিক এন্ড এডমিশন কেয়ার

Math Problem

Activation energy of N_2O_5 dissociation is 100 kJ/mol . Calculate the ratio of rate constant at 0°C 25°C temperature.

T_1 T_2

$$\frac{k_1}{k_2} = ?$$

HJC + V.V.I. for DU

$$\begin{aligned} T_1 &= 273\text{K} \\ T_2 &= 298\text{K} \\ E_a &= 100 \times 10^3 \text{ J/mol} \end{aligned}$$

$$\therefore \ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R} \cdot \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$
$$\Rightarrow \frac{k_1}{k_2} = e^{\frac{100 \times 10^3}{8.314} \left(\frac{1}{298} - \frac{1}{273}\right)}$$

shift
↓
ln

= H.w.

Reaction order

☐ This relation with rate and reactant conc. depends on the reaction order ✓

Concentration;
Initial conc.
C-01
← mol L⁻¹

C - rate

0.1	0.01
0.2	0.01
0.3	0.01

exp. data (std. data)

A = B

C - rate

0.1	0.01
0.2	0.02
0.3	0.03

C-03

C - rate

0.1	0.01
0.2	0.04
0.3	0.09

rate $\propto (C)^n$

(Reaction Order)

rate $\propto C^0$

$\therefore \text{rate} = k \cdot C^0$

$\gamma = k$

rate constant

rate $\propto C^1$

$\therefore \text{rate} = k \cdot C^1$

$\gamma = k \cdot C$

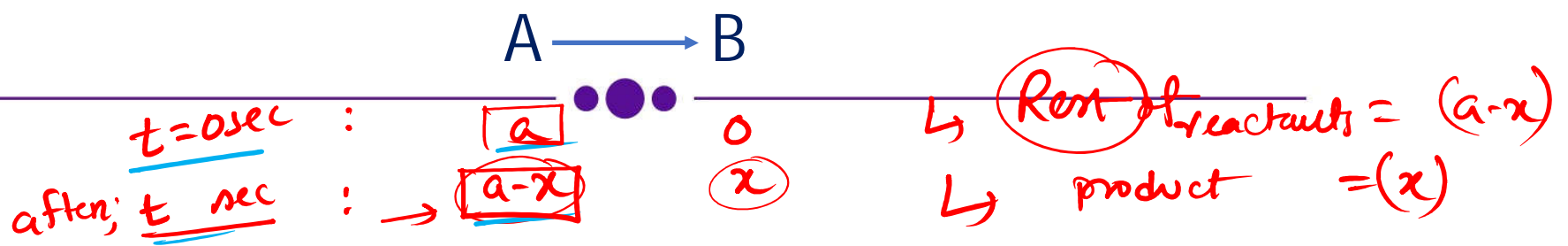
rate $\propto C^2$

$\therefore \text{rate} = k \cdot C^2$

*** (experimental value)



with respect to reactant



0th

$r = k$

$\Rightarrow -\frac{dc}{dt} = k$

$\Rightarrow \int_a^{a-x} dc = -k \cdot \int_0^t dt$

$k = \frac{x}{t}$

1st

$r = k \cdot c$

$\Rightarrow -\frac{dc}{dt} = kc$

$\int_a^{a-x} \frac{dc}{c} = -k \int_0^t dt$

$k = \frac{1}{t} \cdot \ln \frac{a}{a-x}$

2nd

$r = k \cdot c^2$

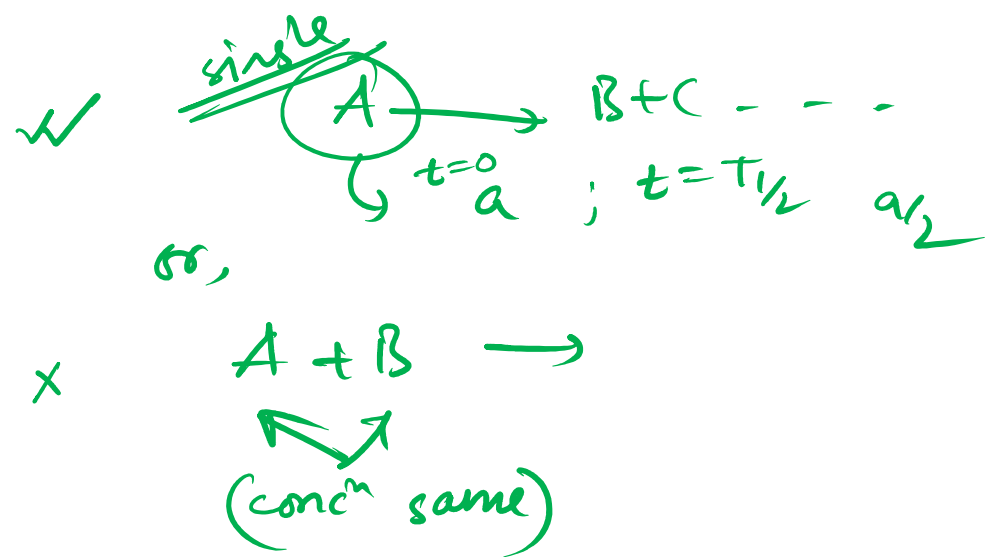
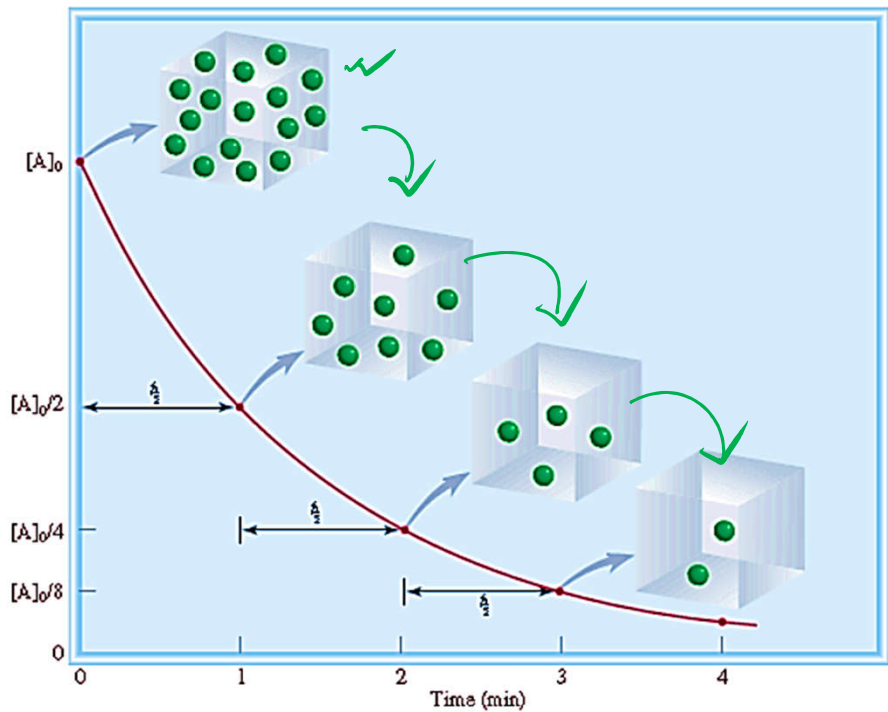
$\Rightarrow -\frac{dc}{dt} = kc^2$

$\int_a^{a-x} \frac{dc}{c^2} = -k \cdot \int_0^t dt$

$k = \frac{1}{t} \cdot \frac{x}{a(a-x)}$

Half life, $T_{1/2}$

Time required for a single reactant reaction to completely converts its 50% reactant into product(s).



0th

$$k = \frac{x}{t}$$

$$t = T_{1/2}$$
$$x = a/2$$

$$t = T_{1/2}$$
$$x = a/2$$

$$T_{1/2} = \frac{a}{2k}$$

$$T_{1/2} \propto a$$

↑
reactant's
concⁿ

1st

$$k = \frac{1}{t} \cdot \ln \frac{a}{a-x}$$

$$T_{1/2} = \frac{\ln 2}{k}$$

$T_{1/2} = \text{constant}$

$$\# \text{ rate} = k \cdot c^n$$

$$\therefore k = \frac{\text{rate}}{c^n} = \frac{\text{mol L}^{-1} \text{s}^{-1}}{(\text{mol L}^{-1})^n}$$

2nd

$$k = \frac{1}{t} \cdot \frac{x}{a(a-x)}$$

$$T_{1/2} = \frac{1}{a \cdot k}$$

$$T_{1/2} \propto \frac{1}{a}$$

unit Δ (cancel)

$$= (\text{mol L}^{-1})^{1-n} \cdot \text{s}^{-1}$$

All in ONE

10 → 5 → 0

Order	Equation	Rate constant	Half life, $t_{1/2}$	Half life, $t_{1/2}$	Unit of k	Completion
0 th	$-\frac{dc}{dt} = kc^0$	$k = \frac{x}{t}$	$t_{1/2} = \frac{a}{2k}$	$t_{1/2} \propto a$	$\text{molL}^{-1}\text{s}^{-1}$	Will be completed
1 st	$-\frac{dc}{dt} = kc^1$	$k = \frac{1}{t} \ln \frac{a}{a-x}$	$t_{1/2} = \frac{\ln 2}{k}$	constant	s^{-1}	Will not be completed
2 nd	$-\frac{dc}{dt} = kc^2$	$k = \frac{1}{t} \frac{x}{a(a-x)}$	$t_{1/2} = \frac{1}{ak}$	$t_{1/2} \propto \frac{1}{a}$	$\text{L mol}^{-1}\text{s}^{-1}$	Will not be completed

10 days (10 days)
10 → 5 → 2.5 →

Poll question: 03

Rate constant of a reaction is $6.3 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$.

Which order is it belong to?

- (a) 0th
- (b) 1st
- (c) 2nd
- (d) 3rd

$$\begin{aligned} r &= k \cdot c \\ \text{or, } k &= \frac{r}{c^2} \\ &= \frac{(\text{mol l}^{-1} \text{ s}^{-1})}{(\text{mol l}^{-1})^2} \\ &= \text{L mol}^{-1} \text{ s}^{-1} \end{aligned}$$

Rate constant of a 1st order reaction is $6.3 \times 10^{-3} \text{ s}^{-1}$ and the initial conc. is 0.8M

$$k = 6.3 \times 10^{-3} \text{ s}^{-1}; a = 0.8 \text{ M}$$

a. Rate at beginning?

$$\hookrightarrow r = k \cdot c = k \cdot a = 6.3 \times 10^{-3} \times 0.8 = \square \text{ mol l}^{-1} \text{ s}^{-1}$$

b. Conc of reactant after 5s?

$$\hookrightarrow t = 5; k = \frac{1}{t} \ln \frac{a}{a-x} \quad \text{or, } \ln \left(\frac{a}{a-x} \right) = kt$$

$$a-x = \frac{a}{e^{kt}} = \frac{0.8}{6.3 \times 10^{-3} \times 5} = \square \text{ mol l}^{-1}$$

c. Rate at 5s?

$$\hookrightarrow r = k \cdot c = k \cdot (a-x) = 6.3 \times 10^{-3} \times (a-x)$$

d. When will reactant conc. become 0.2M?

$$a = 0.8 \quad t = ? \quad k = \frac{1}{t} \ln \frac{a}{a-x} \Rightarrow t = \frac{1}{6.3 \times 10^{-3}} \ln \left(\frac{0.8}{0.2} \right) = \square \text{ sec}$$

e. When will reactant conc. become 0.4M?

$$\hookrightarrow t = \frac{1}{6.3 \times 10^{-3}} \ln \left(\frac{0.8}{0.4} \right) = \square \text{ sec.}$$

f. When all amount of reactant will be converted to product?

\hookrightarrow reaction will not be completed.

Box $\square \rightarrow$ H.W.

Poll question: 04

✓ Time required for 40% completion of a 1st order reaction is 10 min. Time required for 100% completion is ?

- (a) 30 min
- (b) 25 min
- ✓ (c) Doesn't complete
- (d) 40 min

Half life of a 1st order reaction is 400s

$$k = \frac{1}{t} \cdot \ln\left(\frac{a}{a-x}\right)$$

a. When $\frac{1}{8}$ of reactant will be remaining?

$$\hookrightarrow t = 1200s$$

b. When 12.5% of reactant will be remaining?

$$\hookrightarrow t = 1200sec$$

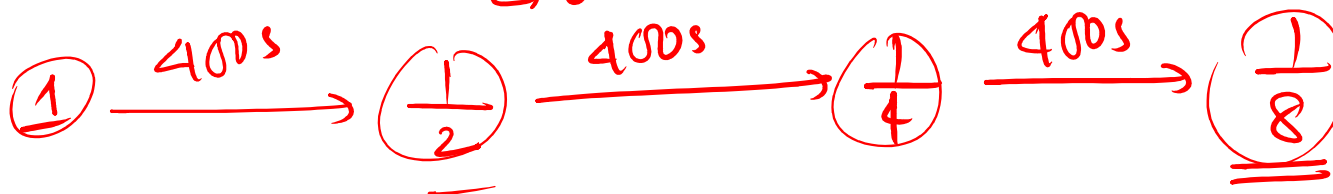
c. Time required for $\frac{7}{8}$ of reactant converted to product?

$$\hookrightarrow t = 1200s$$

d. Time required for 87.5% of reactant converted to product?

$$\hookrightarrow t = 1200s$$

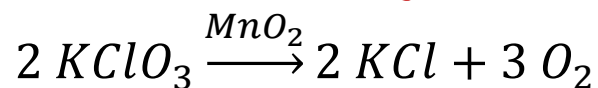
$$1 - \frac{1}{8} = \frac{7}{8}$$



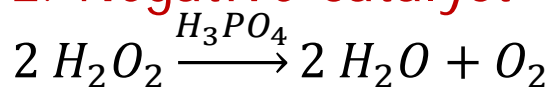
Catalyst

T, C
□ Speed up or Slow down a reaction. Will remain unchanged after reaction

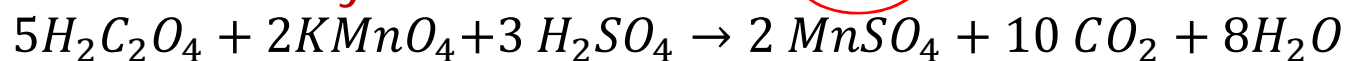
1. Positive catalyst



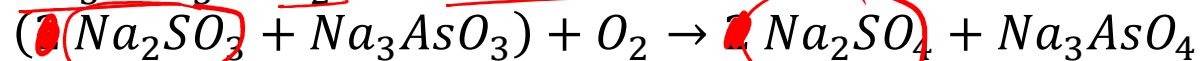
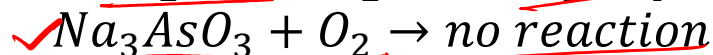
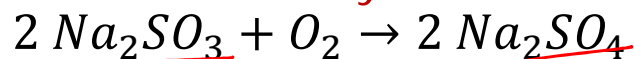
2. Negative catalyst



✓ 3. Auto catalyst



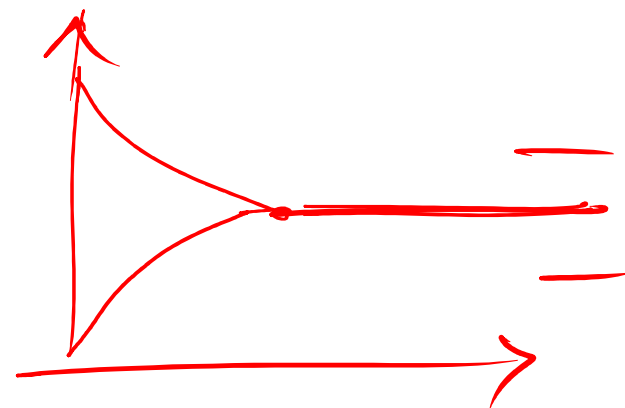
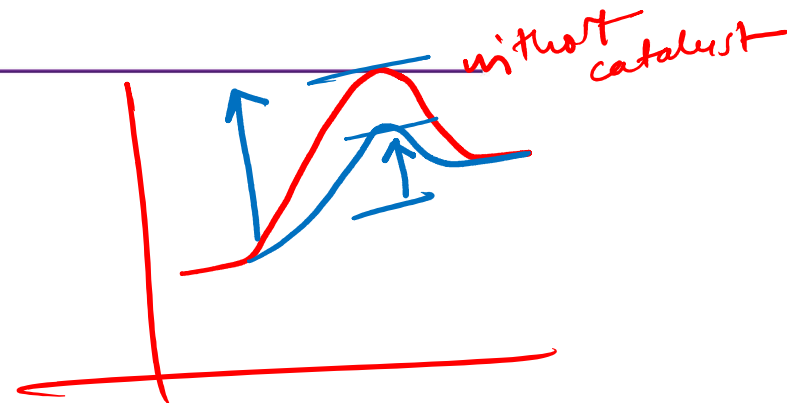
** ✓ 4. Induced catalyst



Poll question: 05

Which one a (positive catalyst) doesn't ?

- ✓ ~~(a)~~ Lowering activation energy
 - ~~(b)~~ Speeding up reaction
 - ~~(c)~~ Accelerating the equilibrium arisen
 - ✓ ~~(d)~~ Change the equilibrium
- bypass*



Type 01 (Bond energy)

Reaction enthalpy

$$\Delta H = \text{Bond breakdown} - \text{Bond formation}$$

energy input

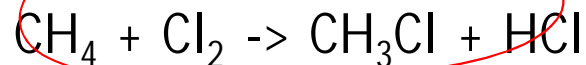
energy output

$$\Delta H = \text{input} - \text{output}$$

$$\left. \begin{array}{l} \Delta H = (-)ve \longrightarrow \text{Exothermic} \\ \Delta H = (+)ve \longrightarrow \text{Endothermic} \end{array} \right\}$$

Math Problem

Calculate heat of the following reaction using the bond dissociation energy data given-

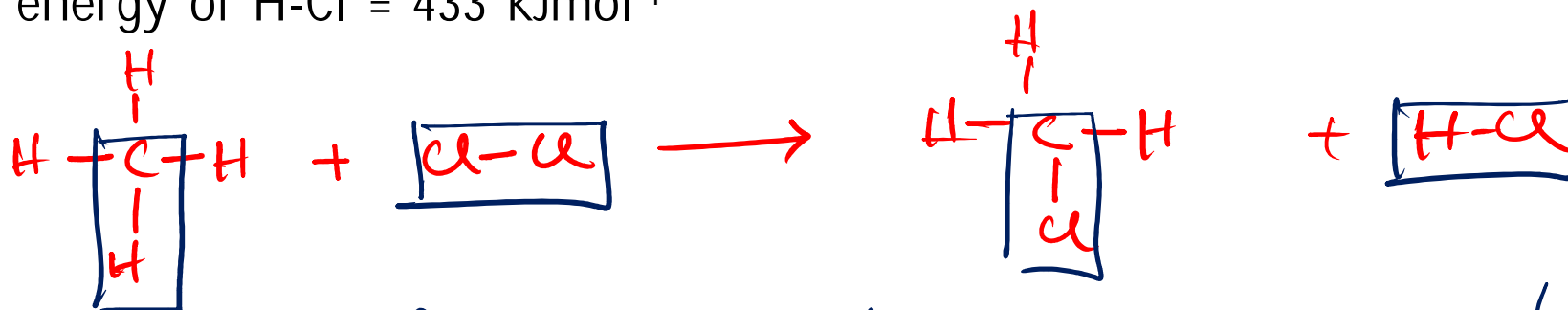


Bond energy of C-H = $430.532 \text{ kJmol}^{-1}$

Bond energy of Cl-Cl = $242.90 \text{ kJmol}^{-1}$

Bond energy of C-Cl = 328 kJmol^{-1}

Bond energy of H-Cl = 433 kJmol^{-1}



$$\Delta H = \{ (\text{C-H}) + (\text{Cl-Cl}) \} - \{ (\text{C-Cl}) + (\text{H-Cl}) \}$$

$$= 430.532 + 242.90 - 328 - 433$$

$$= \boxed{} \text{ kJ/mol unit}$$

Type 02 Heat of neutralization (ΔH_n)

1 mol H_2O production
 ΔH

Neutralization reacⁿ

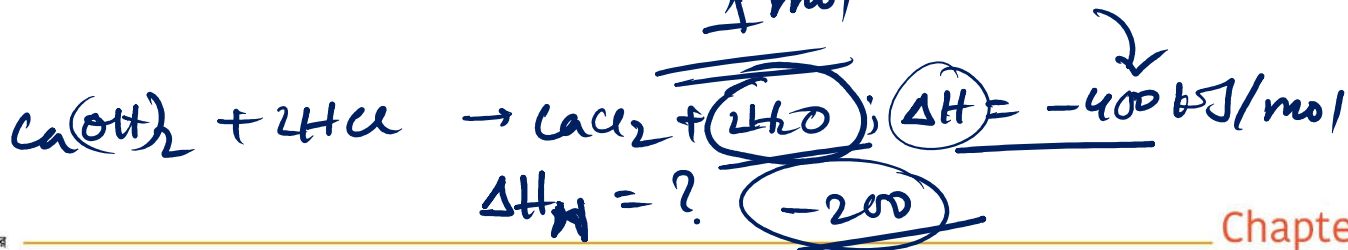
aq. solⁿ statⁿ



n mol of water
 $\Delta H = n \times \Delta H_n$



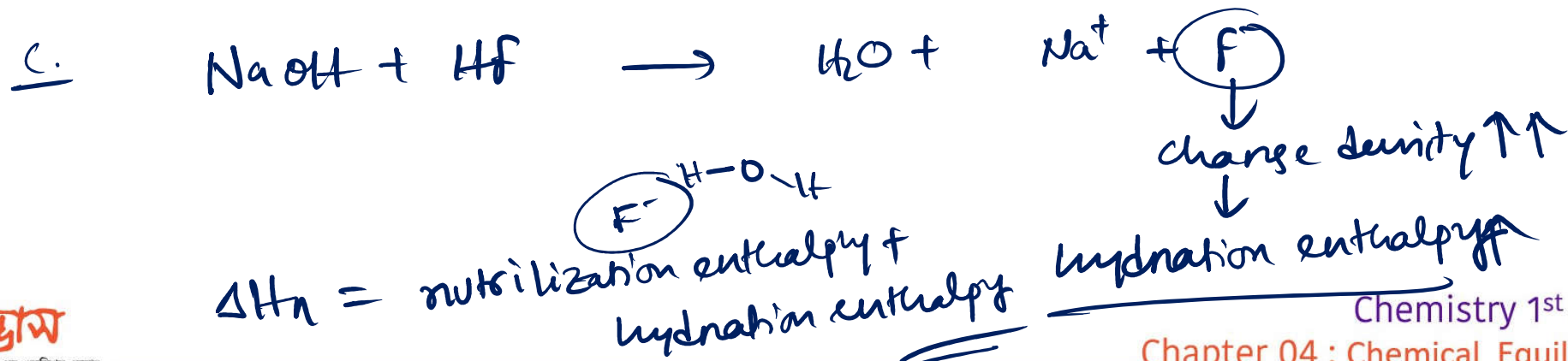
1 mol



Math Problem

- a. Why ΔH_n of strong acid and strong base is constant? ✓ \rightarrow $(H^+ + OH^- \rightarrow H_2O)$
- b. If one or both of them is weak, what will happen?
- c. Though HF is a weak acid, why ΔH_n of HF & NaOH is greater than the constant value? $[-68.6 \text{ kJ mole}^{-1}]$

$\Delta H_n \downarrow$; production of H^+ & OH^- will be reduced
 production of H_2O will also " " .

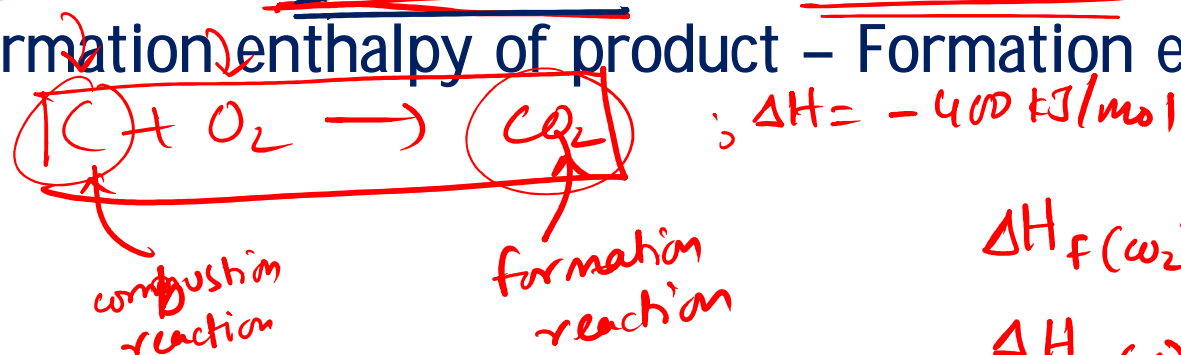


Type 03: Formation enthalpy (ΔH_f) Heat of combustion (ΔH_c)

Conditions (ΔH_f) : 1 mol product & direct reaction between ^{primary} elements

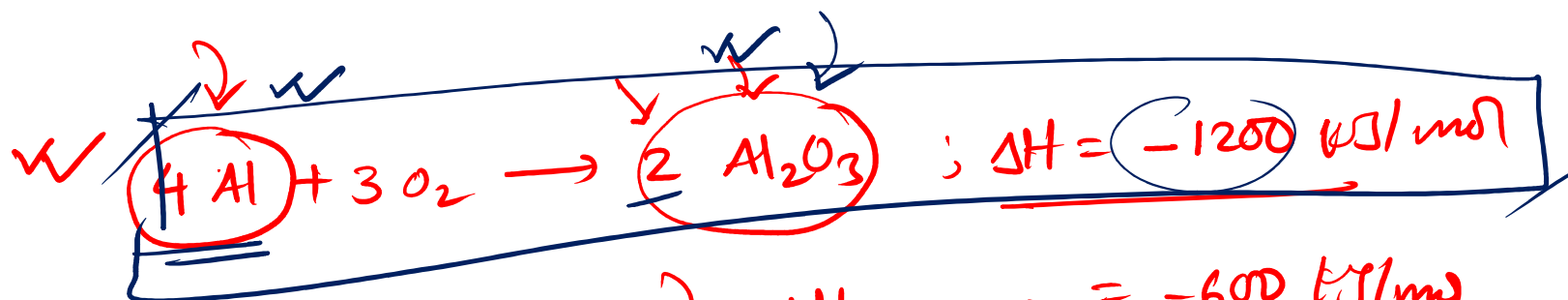
Conditions (ΔH_c) : 1 mol reactant & enough oxygen

$\Delta H =$ Formation enthalpy of product - Formation enthalpy of reactant



$$\Delta H_f(\text{CO}_2) = -400$$

$$\Delta H_c(\text{C}) = -400$$



$$\Delta H_f(\text{Al}_2\text{O}_3) = -600 \text{ kJ/mol}$$

$$\Delta H_c(\text{Al}) = -300 \text{ kJ/mol}$$

Math Problem



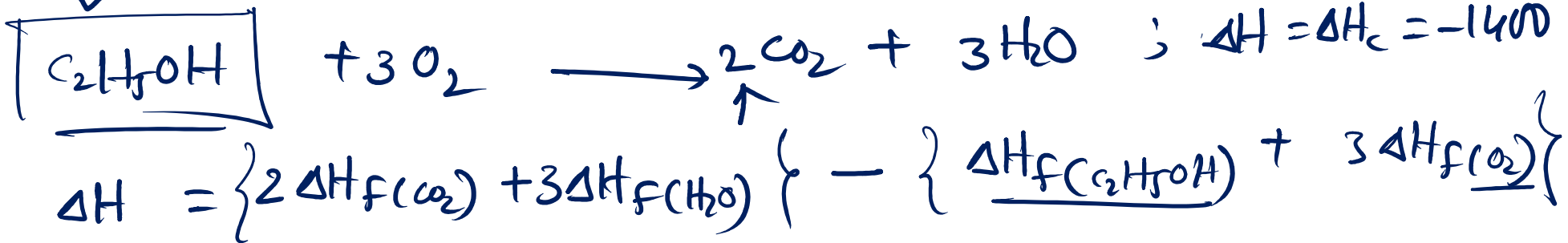
At std. condition, formation enthalpy of $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ are -400 kJ and -300 kJ .

If heat of combustion of ethanol is -1400 kJ then calculate the formation enthalpy of ethanol.

Given, $\Delta H_f(\text{CO}_2) = -400$; $\Delta H_f(\text{H}_2\text{O}) = -300$

$\Delta H_c(\text{C}_2\text{H}_5\text{OH}) = -1400$; $\Delta H_f(\text{C}_2\text{H}_5\text{OH}) = ?$

1 mol \rightarrow

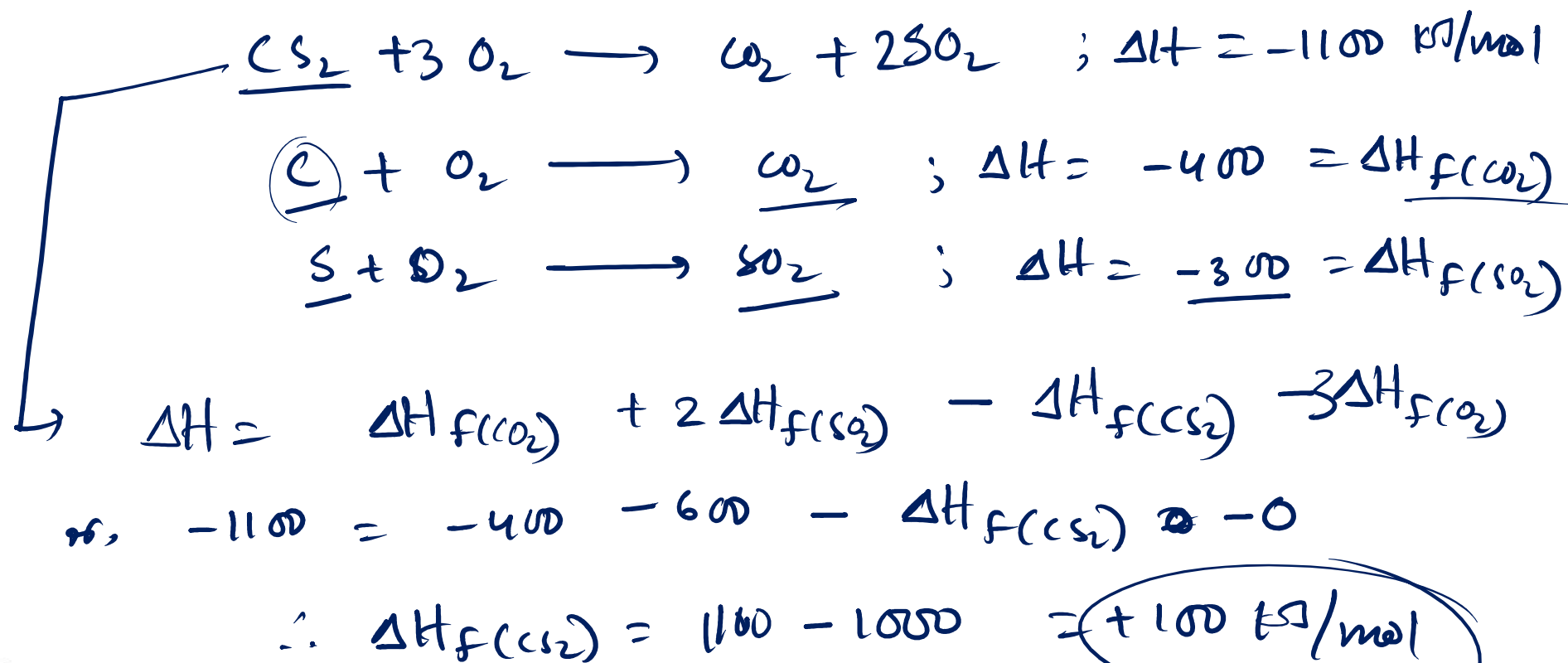


$$\text{or, } -1400 = -800 - 900 - x - 0$$

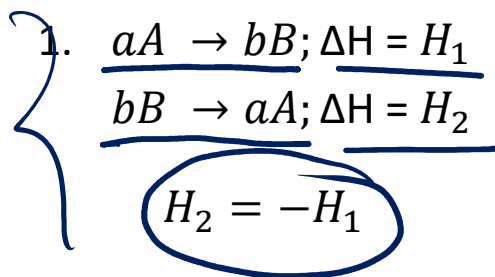
$$\therefore x = 1400 - 1700 = -300 \text{ kJ/mol}$$

Math Problem

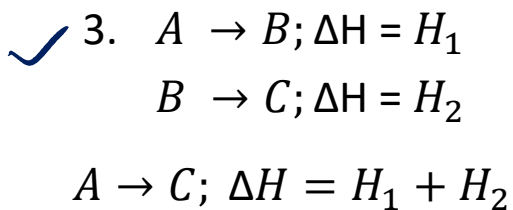
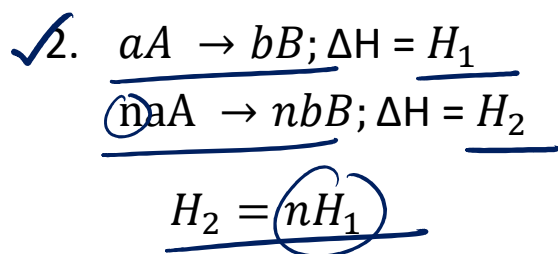
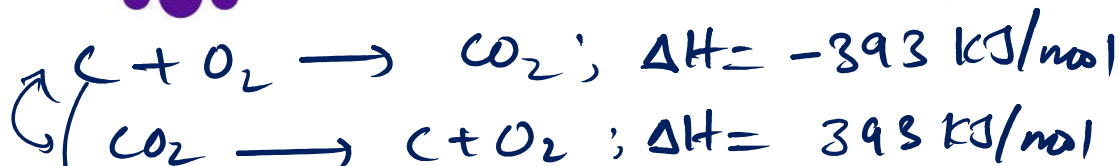
Heat of combustion of CS_2 , C and S is $-1100 \text{ kJ mol}^{-1}$, -400 kJ mol^{-1} and -300 kJ mol^{-1} respectively. Calculate the formation enthalpy of CS_2



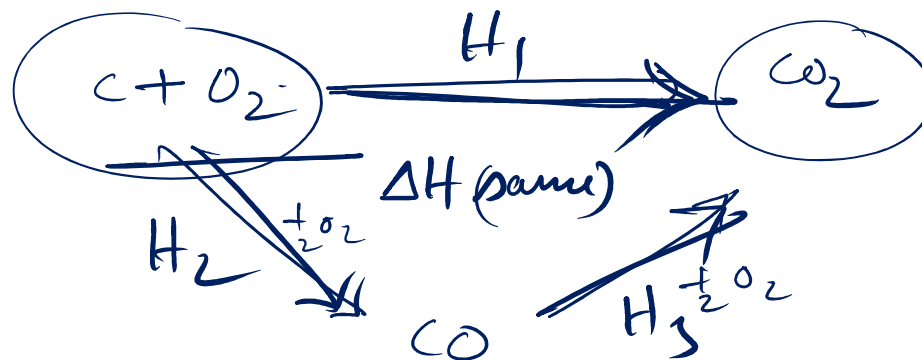
Type 04 : Equation Based



Lavoisier-Laplace law



Hess's law

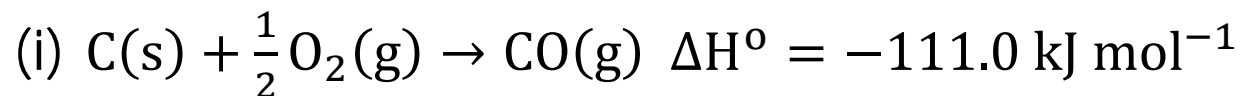
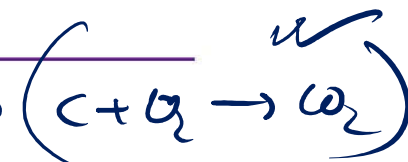


$(\Delta H = H_1 = H_2 + H_3)$

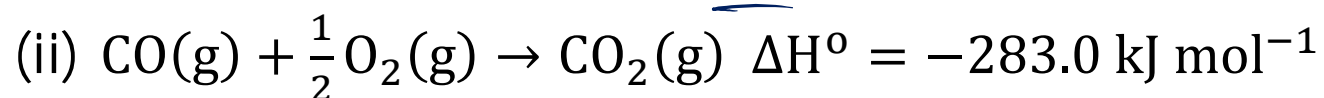
Math Problem

Calculate the heat of combustion of carbon

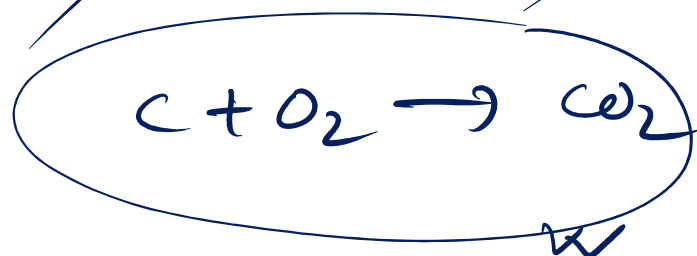
$$\Delta H_c(\text{C}) = ?$$



[DU'15-16]



(+)



$$\Delta H = -111 - 283$$

$$= -394 \text{ kJ/mol}$$

$\Delta H_c(\text{carbon})$

Some Important Formulas

Thermodynamics

$$\underline{\Delta H = \Delta U + \Delta W}$$

$$\Delta H = \Delta U + P \cdot \Delta V$$

$$\Delta H = \Delta U + \Delta nRT$$

$$\underline{Q_p = Q_v + \Delta nRT}$$

Gibbs Free energy

$$\underline{\Delta G = \Delta H - T\Delta S}$$

change in entropy

$$\underline{\Delta G < 0; \text{Spontaneous}}$$

$$\underline{\Delta G > 0; \text{Nonspontaneous}}$$

$$\underline{\Delta G = 0; \text{Equilibrium}}$$

লেগে থাকো সৎ ভাবে,
স্বপ্ন জয় তোমারই হবে।