8) Rate constant for $A \to P$

i) at $[A] = 4.37 \times 10^{-4}$ mol dm^{-3} is 3.4×10^{-3} s^{-1}

ii) at $[A] = 1 \times 10^{-5}$ mol dm^{-3} is 4.4×10^{-4} s^{-1}

Sol) Mechanism (Lindeman - Hinshelwood)

Excitation due to collision

i) $A + A \longrightarrow A^* + A \qquad = k_a [A]^2$

ii) $A^* + A \longrightarrow A + A \qquad = k_a' [A][A^*]$

Losing energy due to collision

Forming products

$A^* \longrightarrow P \qquad [A] = k_b [A^*]$
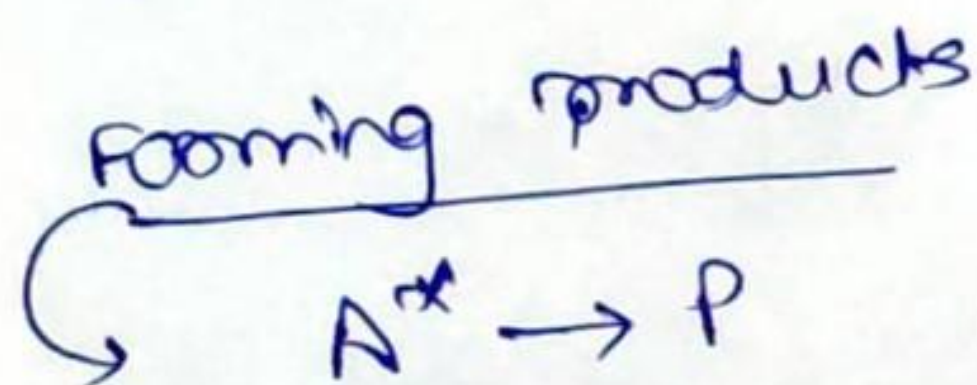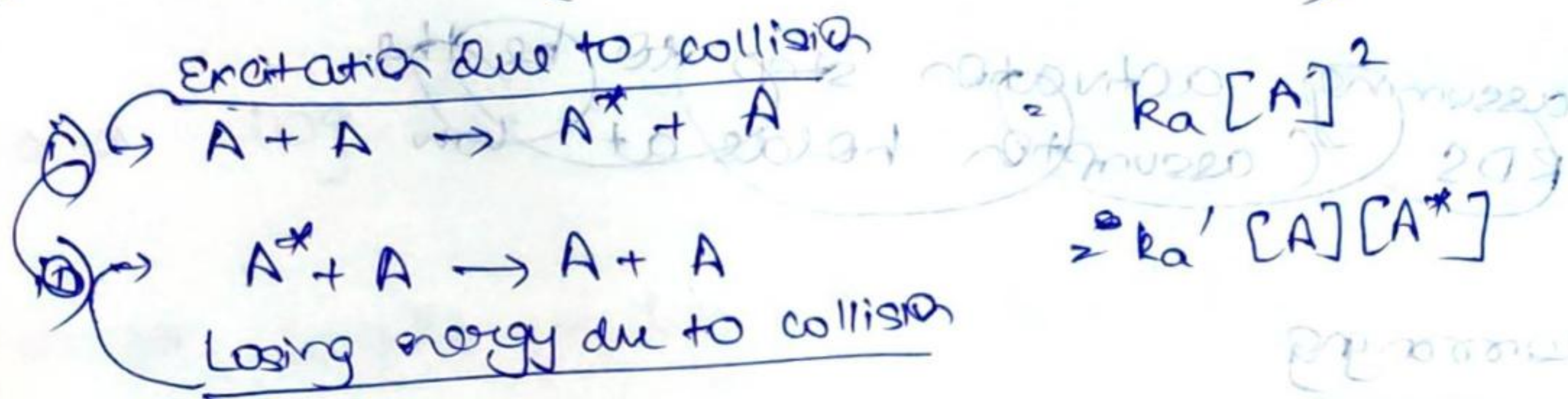
$\therefore \dfrac{d[A^*]}{dt} = k_a [A]^2 - \left[k_a'[A][A^*] + k_b [A^*] \right]$

using SSA $\dfrac{d[A^*]}{dt} = 0$.

$\therefore [A^*] = \dfrac{k_a [A]^2}{k_a'[A] + k_b}$

② product formation rate $V = k_b [A^*]$

$V = \dfrac{k_b \cancel{k_a} k_b k_a [A]^2}{k_a'[A] + k_b}$

expected rate: $V = k_a [A]^2$

$\therefore k = \dfrac{k_b k_a [A]}{k_a'[A] + k_b}$

Rearranging

$$\frac{1}{k} = \frac{ka'}{ka \, kb} + \frac{1}{ka \, [A]}$$

i) $\frac{1}{3.4 \times 10^{-3} \, s^{-1}} = \frac{ka'}{ka \, kb} + \frac{1}{ka \, (4.37 \times 10^{-4} \, mol \, dm^{-3})}$

ii) $\frac{1}{4.4 \times 10^{-4} \, s^{-1}} = \frac{ka'}{ka \, kb} + \frac{1}{ka \, (10^{-5} \, mol \, dm^{-3})}$

i) − ii)

$= \left(\frac{10^{3} \, s}{3.4} - \frac{10^{4} \, s}{4.4} \right) = \frac{1}{ka} \left[\frac{10^{4}}{4.37} - \frac{10^{3}}{1} \right] mol^{-1} dm^{3}$

$= 294.1176 - 2272.7272 = \frac{1}{ka} \left[2288.3295 - 100000 \right]$

$\therefore \quad ka = \frac{97711.67}{1978.62}$

$$\boxed{ka = 49.383 \ mol^{-1} dm^{3} s^{-1}}$$

↳ Rate constant for activaton step

Q2) Pre exponential factor

$$A = e^{-(\Delta n^{\ddagger} - 1)} \frac{k_B T}{h} e^{\frac{\Delta S^{\ddagger}}{R}}$$

Q1) we assume a quasi equilibrium

$$K^{\ddagger} = \frac{[AB]^{\ddagger}}{[A][B]}$$

and $v = ($ rate of product formation $)$

$$= k^{\ddagger} [AB]^{\ddagger}$$

$$= k^{\ddagger} \left(K^{\ddagger} [A][B] \right)$$

$$v = k^{\ddagger} K^{\ddagger} [A][B]$$

exported $v = k [A] B$

$$\therefore k = k^{\ddagger} K^{\ddagger}$$

now not all vibrations lead to product

hence we introduce a transmission factor

$$k^{\neq} = \overset{\frown}{K}v$$

transmission coefficient

also taking out $\dfrac{k_B T}{hv}$ mode from $k^{\neq}$

we get $\quad K^{\neq} = \dfrac{k_B T}{hv}\left(K^{\neq'}\right)$

we know $\quad \ln K^{\neq'} = -\dfrac{\Delta G^{\neq}}{RT}$

$\therefore \quad K^{\neq'} = e^{-\frac{\Delta G^{\neq}}{RT}}$

$\therefore \quad k = (Kv)\left(\dfrac{k_B T}{hv}\right)\left(e^{-\frac{\Delta G^{\neq}}{RT}}\right)$

so now frequency terms cancel and

using $\quad \Delta G = \Delta H - T\Delta S$.

we get $\quad k = (K)\left(\dfrac{k_B T}{h}\right)\left(e^{-\frac{\Delta H^{\neq}}{RT} + \frac{\Delta S^{\neq}}{R}}\right)$

now for $\boxed{A + B \rightleftharpoons P}$

$$E_a = \Delta H^{\neq} + 2RT \quad (\text{in gas phase})$$
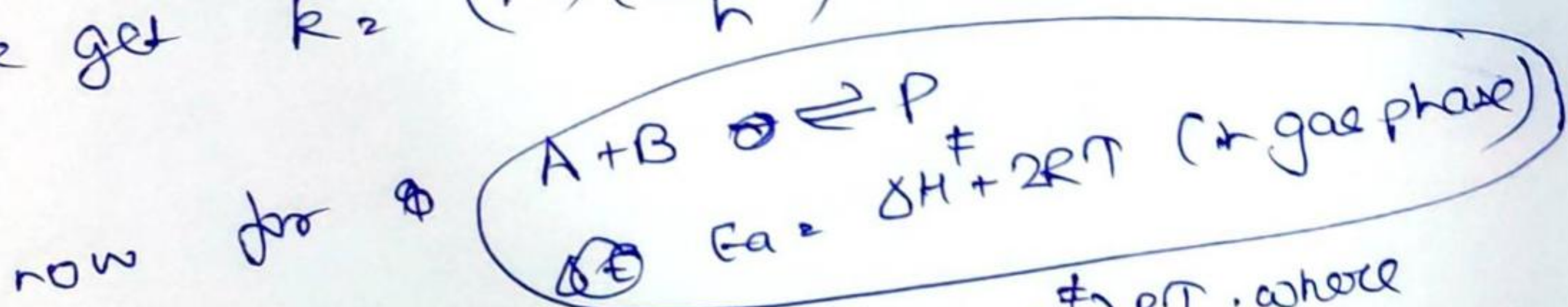
or in general $\quad E_a = \Delta H^{\neq} + (1 - \Delta n^{\neq})RT$. where

$\Delta n^{\neq} = $ change in number of moles in activation

$k = (K)\left(\dfrac{k_B T}{h}\right)\left(e^{\frac{\Delta S^{\neq}}{R}}\right)\left(e^{-\frac{E_a}{RT}}\right)\left(e^{\frac{(1-\Delta n^{\neq})RT}{RT}}\right)$
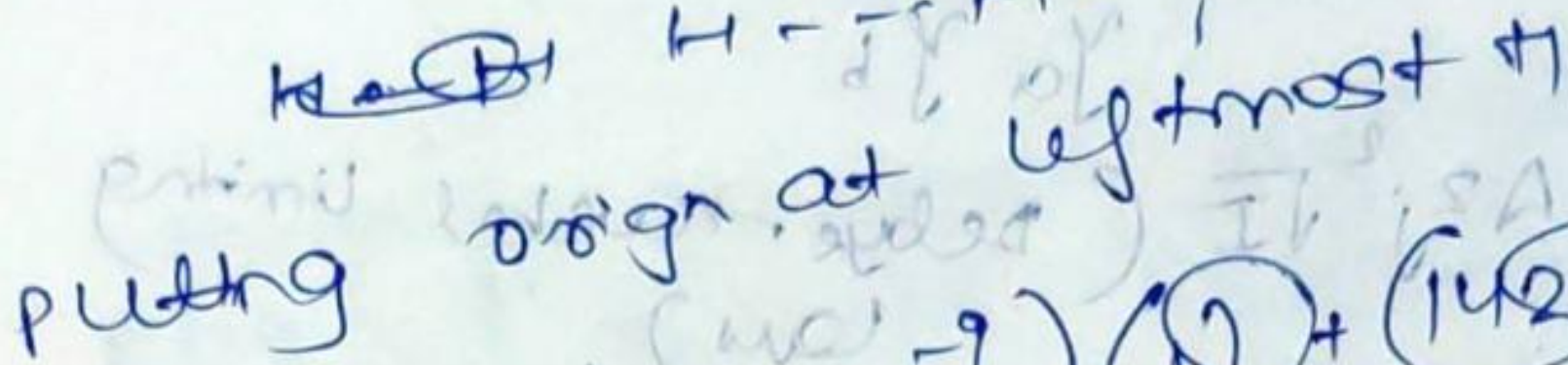
$\therefore \quad k = A e^{-E_a/RT} \quad (\text{with } K)$

also $\therefore \quad A = \dfrac{k_B T}{h}\left(e^{\frac{\Delta S^{\neq}}{R}}\right)\left(e^{(1-\Delta n^{\neq})}\right) \quad$ proved
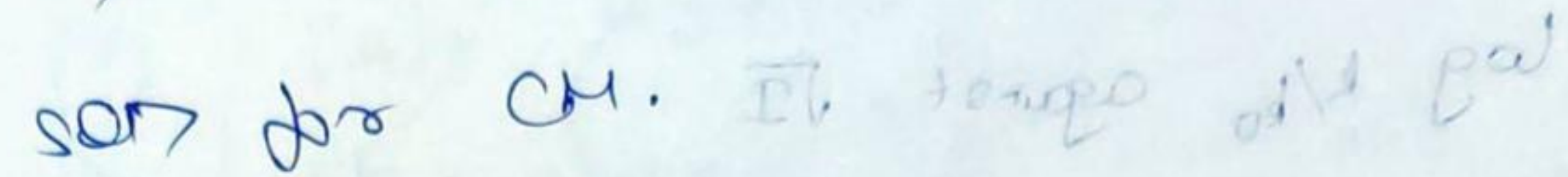
———— b ————

Q3) $H + HBr \rightarrow H_2 + Br$

Sol⟩ for C.M. ⊥ $torque$ oil pal

$$\sum_i m_i \, r_i = 0.$$

activated complex X

$$H - \overset{150pm}{H_2} \overset{142pm}{-} Br$$

H_2Br

putting origin at leftmost H

$$O(1) + (150 \times 10^{-9})(1) + (142 \times 10^{-9}(80))$$

$(H)(R)$

and let CM be as at X_o

then

$$(-x)(1) + (150pm - x)(1)$$
$$+ (292\,pm - x)(80) = 0$$

$$-x + 150pm - x + 292pm \times 80 - 80x = 0.$$

$$82x = (150 + (292 \times 80))\,pm$$

$$x = \frac{(150 + (292 \times 80))}{82}\,pm$$

$$\boxed{x = 286.70\,pm}$$

6) $I = \sum_i m_i r_i^2$

$$= (1)(286.70)^2 + (1)(136.70)^2$$
$$+ (80)(5.30)^2$$

$$I = 82196.89 + 18686.89 + 2,247.2$$

$$\boxed{I = 103129.2 \times 10^{-18} \; amu}$$

Q4> $\log k/k_0$ against $\sqrt{I}$

using $\log k_2 = k_2^\circ / K_y$

where $K_y = \dfrac{y_{c^{\ddagger}}}{y_a\, y_b}$

and $\log y_j = -Az_j^2 \sqrt{I}$ (Debye-Huckel limiting law).

we get $\log k_2 = \log k_2^\circ - \log(K_y)$

$= \log k_2^\circ - A\langle 2_A^2 + 2_B^2 - (2_A + 2_B)^2\rangle \sqrt{I}$

$\log k_2 = \log k_2^\circ + 2A\sqrt{I}\, z_A z_B$. $A = 0.509$ in aq.

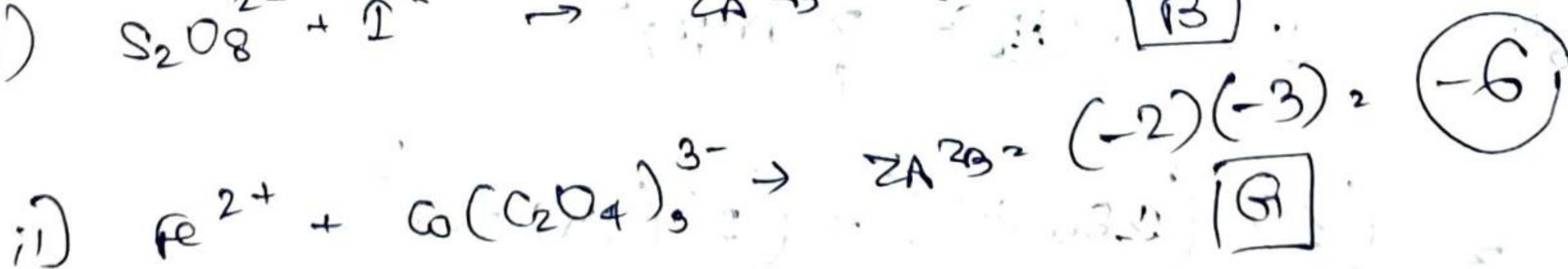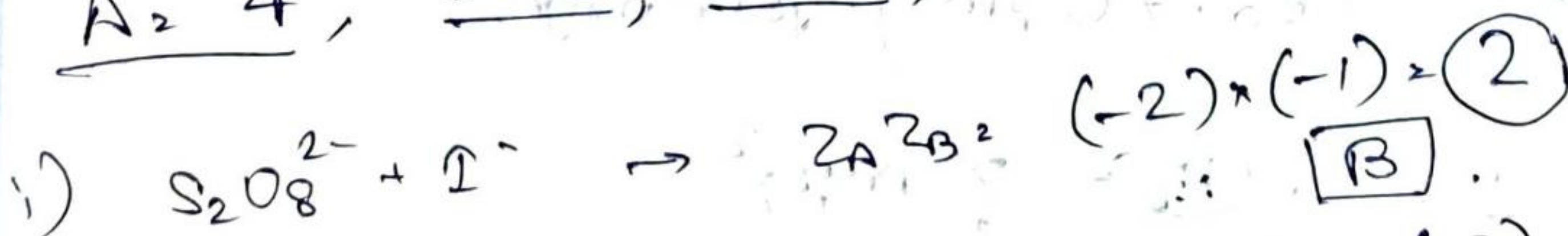$\therefore \log(k_2/k_2^\circ) = 2(0.509)(z_A z_B)\sqrt{I}$.

$\therefore$ for a plot of $\log(k_2/k_2^\circ)$ versus

$\sqrt{I}$, the slope is $= \boxed{2(0.509)(z_A z_B)}$.

Looking at the graph approximately computing

$z_A z_B$ for $A \to G$ -6.

$\underline{A = 4}$, $\underline{B = 2}$, $\underline{C = 1}$, $\underline{D = 0}$, $\underline{E = -1}$, $\underline{f = -2}$, $G = \textcircled{6}$

i) $S_2O_8^{2-} + I^- \longrightarrow z_A z_B = (-2)\times(-1) = \textcircled{2}$

$\therefore \boxed{B}$.

ii) $Fe^{2+} + Co(C_2O_4)_3^{3-} \to z_A z_B = (-2)(-3) = \encircle{-6}$

$\therefore \boxed{G}$.

5) i) atom on a metal surface is hit 100 times/s. If $T(\times 4)$ then how many times will the surface atom be hit

sa) collision flux Z_w

is dependent on P & on $1/\sqrt{T}$.

precisely $Z_{w_1} = \dfrac{P}{\sqrt{2\pi m k T}}$

if $T = 4T$ then (assuming constant pressure)

$$Z_{w_2} = \dfrac{P}{\sqrt{2\pi m k}\sqrt{4T}} = \left(\dfrac{P}{\sqrt{2\pi m k T}}\right) \times \dfrac{1}{2} = \dfrac{Z_{w_i}}{2}$$

∴ If atom was hit 100 times per second

now it will be hit $(100/2) =$ 50 times per second.

---

ii) Do both diffusion controlled & activation controlled reactions have activation energies? $\longrightarrow K_2 = K_d$

sol) <u>Diffusion controlled reaction</u>'s rate depends on the rate at which reactant molecules diffuse through the solvent. It does not ~~depend on activation energies and~~ These reactions have little activation energies and.

eg → atom radical recombination reaction.

Takes place when rate of separation of encounter pair is much slower than product formation. hence molecules linger in the neighbourhood of one another due to ~~steric~~ steric hindrance, by other solvent molecules, thereby called the "cage effect". Such an encounter ends up reacting even if it didn't have enough energy initially.

In an activator controlled reaction, a large enough activation energy is required as the rate of separation is much higher than rate of formation of product ($ka' \gg ka$) hence ka must be dependent on activation energy.

final rate t_2 $\dfrac{ka \, kd}{kd'}$. Therefore reaction proceeds at the rate of accumulation of energy by collisions with solvent in the neighbourhood