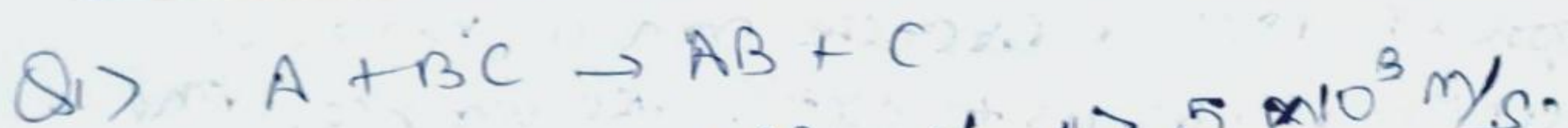


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$$\sigma^2 = \begin{cases} 100 \text{ Å}^2 & \text{if } v > 5 \times 10^3 \text{ m/s} \\ 0 & \text{if } v < 5 \times 10^3 \text{ m/s} \end{cases}$$

if  $\mu$  is 1 amu what is the rate at 300K.  
How long to form 1 mole of C?

sol) Assumptions:

i) all started with equal conc.

i.e.  $[A] = [B] = [C] = x$

ii)  $k = P(\sigma_{NA} \sqrt{\frac{8kT}{\pi\mu}}) e^{-E_a/RT}$

$$E_a/RT = \frac{1}{2} \frac{mv^2}{RT} = \frac{1}{2} \times \frac{(5000)^2}{8.314 \times 300}$$

$$= 5.01$$

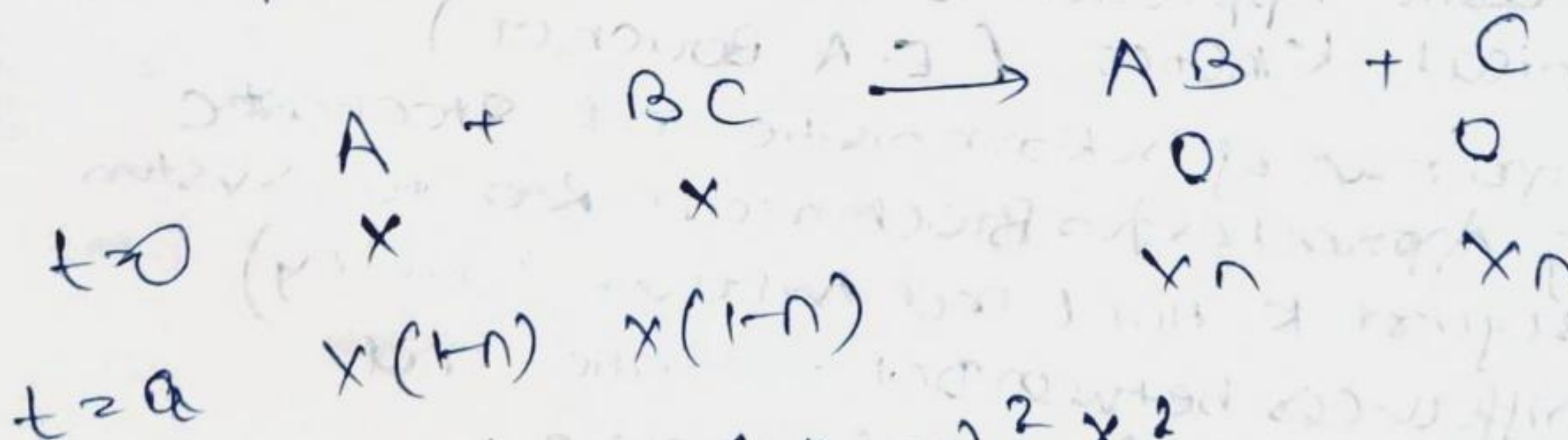
$$k = NA \sigma \sqrt{\frac{8kT}{\pi\mu}} \times e^{-5.01}$$

$$= 10^{-18} \times 6.022 \times 10^{23} \sqrt{\frac{8 \times 1.38 \times 300}{3.14 \times 10^{-3}}} \times e^{-5.01}$$

$$= 1.5 \times 10^9 \times e^{-5.01}$$

$$= 6.6 \times 10^{-3} \times 1.5 \times 10^9$$

$$k = 10^7 \text{ mol}^{-1} \text{ s}^{-1}$$



$$\frac{dn}{dt} = k(1-n)^2 \times 2$$



$$\int \frac{dn}{1-n^2} = X_0^2 \int k dt$$

$$t = \frac{1}{(1-n) \times k}$$

for  $C = 1 \text{ mol}$   
 taking  $[C] = 0.001 \text{ (vol } 1 \text{ m}^3)$

also  $n = \frac{1}{1000} \times$

$$\therefore t = \frac{1}{\left(1 - \frac{1}{1000 \times}\right) \times k}$$

$$t = \frac{1000 \times}{(1000 \times - 1) \times 10^7 \times 10^4}$$

$$\times = \frac{0.5}{22.4} = 0.022$$

~~$t = 10^4$~~

$$\therefore t = \frac{(10^{-4} \times)}{(22-1)}$$

$$t = \frac{10^{-4}}{21}$$

$$t = 4.6 \times 10^{-6} \text{ s}$$



Q2) Differences b/w Stochastic & Deterministic approach to kinetics

Q1) In the mathematical modelling of reactions, ODEs have been used traditionally but this deterministic solution is made possible after several simplifications. In contrast, stochasticity of reactions is captured by discrete chemical master equation (CME). Therefore, the CME is frequently applied to mesoscopic systems where random fluctuations are significant.

In the thermodynamic limit, deterministic stable fixed points correspond well in large systems. But this is disrupted in small systems. The discrepancies are characterised and systematically traced back to the magnitude of stoichiometric coefficients and to the presence of non linear reactions. Therefore the deterministic model is the thermodynamic limit of the stochastic one, ~~but~~ in cases where the ODEs admit more than one stable solution, the two formalism give starkly different results for simple small models.

The size of the system is an important parameter. For small systems, the stochastic model produces a bimodal stationary distribution with peaks near the ODE solutions.



the deterministic approach gives only a continuous function of  $t$ , whereas the stochastic approach uses a discrete random variable which allows us to capture the variance. The stochastic approach is capable of dealing with changes in energy levels and is readily applicable to several aspects of physico-chemical nature associated with adsorption at surfaces (interfaces) and to the behaviour of colloidal particles (i.e., dispersed particles in the range  $10^{-1000} \text{ \AA}$ ). It is very useful for problems related to polymers (synthetic & biological, including enzymatic reactions) and to colloids and surfaces.

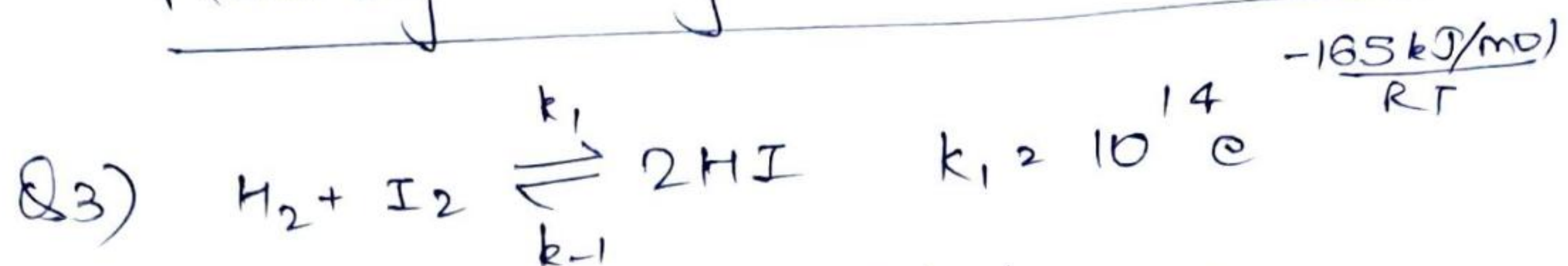
All advocates of deterministic model from the stochastic one can be seen as the inadequacy of the ODE formalism. Gillespie states: "the stochastic approach is always valid whereas the deterministic approach is valid and is sometimes valid even when the deterministic one is not". But one must note that ODE too is based on some simplifying assumptions: random, homogeneous distribution of positions and velocities of reactants.

### References

- 1) Stochastic Approach to Reaction and Physico-chemical Kinetics (E. A. Boucher)
- 2) A Comparison of Deterministic and Stochastic Modelling Approaches for Biochemical Reaction Systems (Seyoum K. Hahl and Andreas Kienling)
- 3) On Differences between Deterministic and Stochastic Models of Chemical Reactions: (Michail Vlysidis and Y. N. Kaznessis)



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$k_{-1} = 10^{13} e^{\frac{-185 \text{ kJ/mol}}{RT}} \text{ cm}^3/\text{mol s.}$

find  $K$  for a mixture of  $H_2$ ,  $I_2$  &  $HI$   
and  $T = 300 \text{ K}$  &  $2000 \text{ K}$ .

~~Q3) 300K~~

sol)  $K = k_1 / k_{-1}$

$\therefore K = \frac{10^{14} e^{-165 \text{ kJ}/RT}}{10^{13} e^{-185 \text{ kJ}/RT}}$

$K = 10 e^{\frac{20 \text{ kJ/mol}}{RT}}$

(without any unit  
as it is a ratio  
of 2 similar)

i) for  $T = 300 \text{ K}$

$K = 10 e^{\frac{20 \times 1000}{8.314 \times 300}}$

$= 30,369.32258$

$K = 3.03693 \times 10^4$

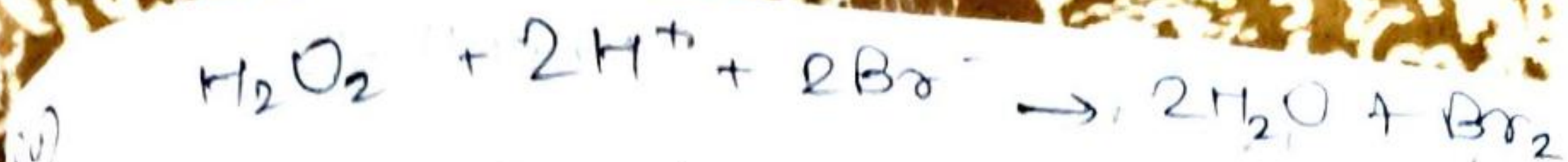
ii) for  $T = 2000 \text{ K}$

$K = 10 e^{\frac{20 \times 1000}{8.314 \times 2000}}$

$= 33.29394$

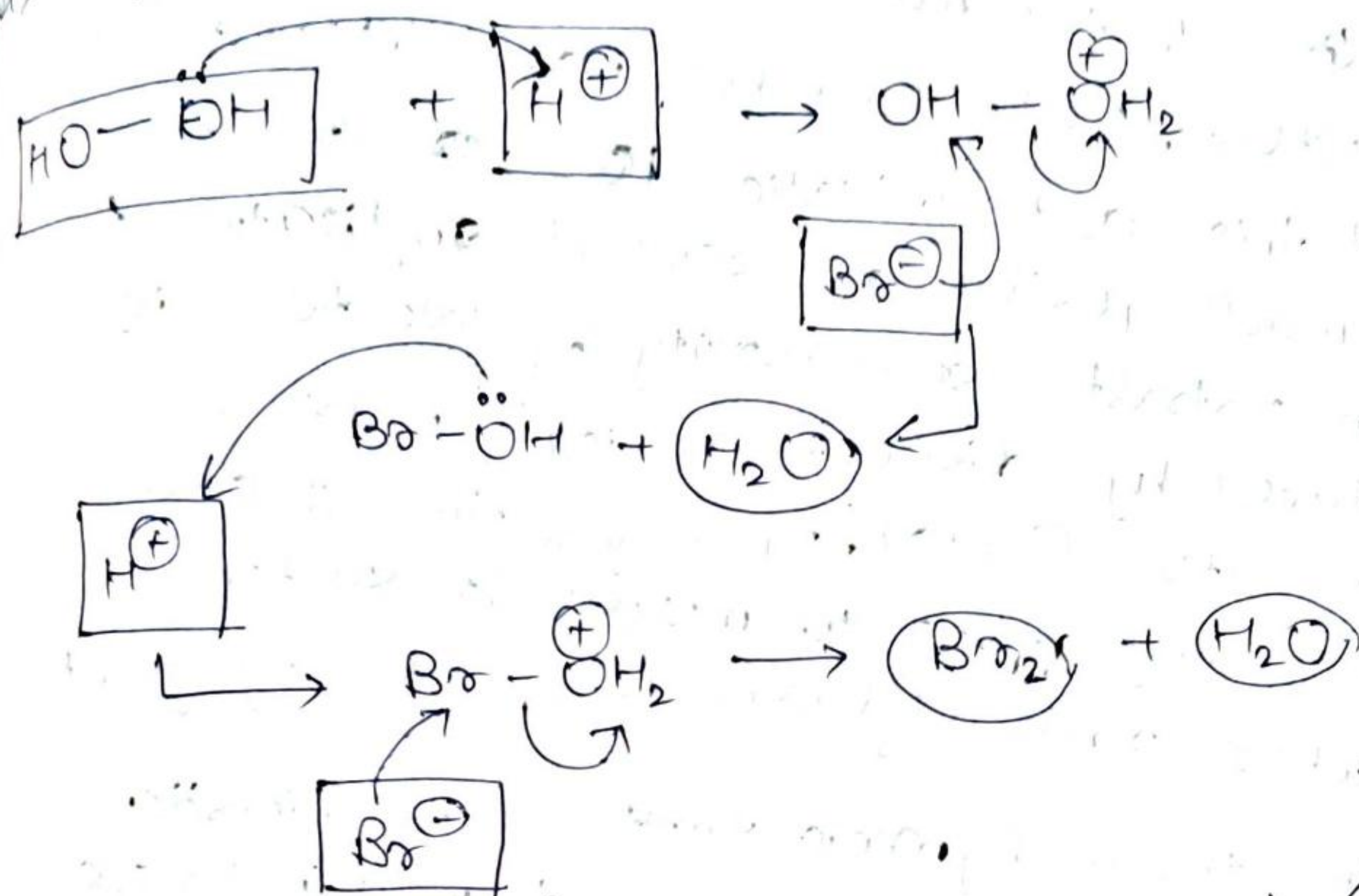
$K = 3.32939 \times 10^1$





How does increasing ionic strength affect the rate?  
What strength will cause a 25% change?

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Reactants are circled in  $\square$  and products in  $\bigcirc$ .

from the reaction mechanism:  $\frac{z_A^2 + 1}{z_B^2 - 1}$

$$\therefore \Rightarrow K = K_0 e^{-2(0.509)\sqrt{I}}$$

now if  $I \uparrow$  then  $\sqrt{I} \uparrow \therefore -2(0.509)\sqrt{I} \downarrow$   
and  $K \downarrow$ .

Increasing ionic strength reduces the rate of the reaction.

for a 25% change (decrease)

$$0.75 \times K_0 = K_0 e^{-2(0.509)\sqrt{I}}$$

$$\ln(3/4) = -2(0.509)\sqrt{I}$$

$$I \text{ or } \sqrt{I} = \left[ \ln(4/3) \times \frac{1}{1.018} \right]^2$$

$$I > 0.07986 \text{ or } 7.986\%$$