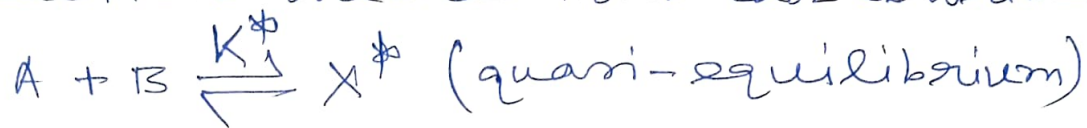


①
* Let us consider a bimolecular reaction where A and B are the reactants, X^\ddagger is the activated complex.

* The reaction mechanism can be written as



The quasi-equilibrium constant K^\ddagger is

$$K^\ddagger = \frac{a_{X^\ddagger}}{a_A a_B}, \quad \text{--- (1)}$$

where a_{X^\ddagger} , a_A and a_B are the activity of the activated complex X^\ddagger , reactants A and B, respectively.

We know activity a is related to concentration (c) as

$$a = c\gamma \quad \text{--- (2)}$$

γ is the activity coefficient.

From equations (1) & (2), we get

$$K^\ddagger = \frac{[X^\ddagger] \gamma_{X^\ddagger}}{[A] \gamma_A [B] \gamma_B} = \frac{[X^\ddagger]}{[A][B]} \frac{\gamma_{X^\ddagger}}{\gamma_A \gamma_B}$$

$$[X^\ddagger] = K^\ddagger [A][B] \frac{\gamma_A \gamma_B}{\gamma_{X^\ddagger}} \quad \text{--- (3)}$$

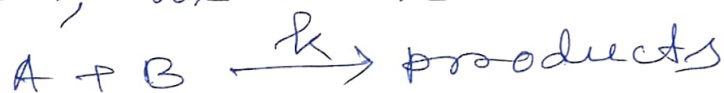
② The rate of the reaction

$$v \propto [X^\ddagger] \quad \left(\begin{array}{l} \text{According to the} \\ \text{Transition state} \end{array} \right) \text{ theory}$$

Inserting the expression of $[X^\ddagger]$ into the equation ④, we obtain

$$v \propto K^\ddagger [A][B] \frac{\gamma_A \gamma_B}{\gamma_{X^\ddagger}} \quad \text{--- ⑤}$$

* Now, if k is the rate for above reaction, we have



Experimentally

$$\text{Rate of reaction } v = k[A][B]$$

Comparing equations ⑤ & ⑥, we get

$$k \propto K^\ddagger \frac{\gamma_A \gamma_B}{\gamma_{X^\ddagger}} \quad \text{--- ⑦}$$

For an ideal gaseous system or an ideal solution,

$$\gamma_i = 1, \quad \text{--- ⑧}$$

Therefore, for the rate constant for gaseous reaction k_g is

$$k_g \propto K^\ddagger \quad \text{--- ⑨}$$

③ Putting Eq. (9) into the Eq. (2), we get

$$k = k_g \frac{\gamma_A \gamma_B}{\gamma_{X^\ddagger}} \quad \text{--- ①}$$

~~The~~ \downarrow
rate constant
in solution
phase reaction

\searrow rate constant in
gas phase reaction.

* The above equation relates the rate constant in solution to the rate constant in the gas phase reaction.

The rates in solution and gas phase reactions must be equal if

$$\left(\frac{\gamma_A \gamma_B}{\gamma_{X^\ddagger}} = 1 \right) \quad \left| \quad k = k_g \cdot 1 \Rightarrow k = k_g \right.$$

* This may arise easily for unimolecular reaction for which appropriate factor is $\frac{\gamma_A}{\gamma_{X^\ddagger}}$.

* If reactant and activated complex have similar state then γ_A and γ_{X^\ddagger} will not differ much and rate in solution is similar to that in gas phase.

Abnormally slow rate of decomposition of N_2O_5 in HNO_3 and correspondingly high activation energy may be due to formation of a complex between reactant and solvent (HNO_3).

Such complex formation decreases γ_A , ~~and consequently rate of reaction~~

Therefore reaction rate decreases according to

$$k = k_g \frac{\gamma_A \gamma_B}{\gamma_{X^\ddagger}}$$