* Hinshelwood Theory :-

The first difficulty with the Lindemann treatment that the 1st order rates are maintained down to lower concentration than the theory appeared to permit. Hinshelwood suggested that the expression $Z_1 \exp(-E_a/RT)$ applied only if the energy is distributed among two degrees of freedom. However for some unimolecular reaction, the no. of degree of freedoms(s) is very large.

Hinshelwood derived the following formula for the fraction of molecules having energy in excess of ε^*.

$$f^* = \frac{1}{(s-1)!}\left(\frac{\varepsilon_0^*}{KT}\right)^{s-1} \exp\left(-\varepsilon_0^*/KT\right) \quad \text{—— (1)}$$

where 's' = no. of degrees of freedom.

The rate constant K_1 is given as;

$$K_1 = Z_1 \frac{1}{(s-1)!}\left(\frac{\varepsilon_0^*}{KT}\right)^{s-1} \exp\left(-\frac{\varepsilon_0^*}{KT}\right) \quad \text{—— (2)}$$

or Simply.

$$K_1 = Z_1 \exp\left(-\frac{\varepsilon_0^*}{KT}\right). \quad \text{—— (3)}$$

The term $\frac{1}{(s-1)!}\left(\frac{\varepsilon_0^*}{KT}\right)^{s-1}$ has appeared and if 's' is sufficiently large, this may be greater than unity by many powers of 10.

Eqs- (1) can give much higher rate of activation and therefore much higher K_1/K_{-1} values than those given by the —

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— Simple Collision theory.

The activation energy per molecule (experimental) E_a is related to ε_0^* as:

$$\varepsilon_0^* = E_a + \left(s - \frac{3}{2}\right) KT \cdot$$

Objections to Hinshelwood theory :-

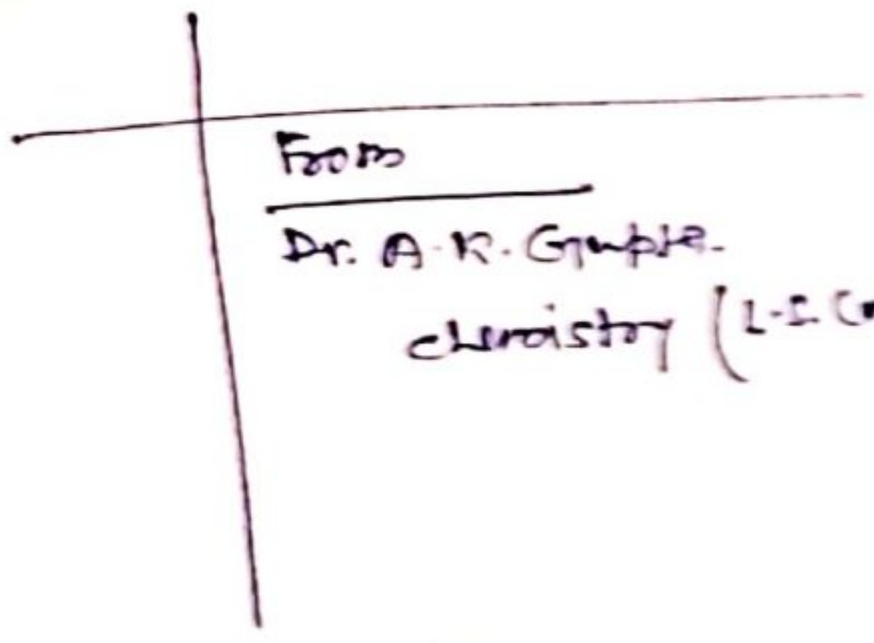
1). The no. of degree of freedom (s) required to give agreement with experiment on the basis of Hinshelwood theory is about one-half of the total no. of vibrational modes.

2). A/c to Hinshelwood Theory :

$$k_\infty^1 = \frac{k_1 k_2}{k_{-1}} = k_2 \frac{1}{(s-1)!} \left[\frac{\varepsilon_0^*}{KT}\right]^{s-1} \exp\left(-\frac{\varepsilon^*}{KT}\right) \quad \text{—— (1)}$$

This expect a strong temperature-dependence of the pre-exponential factor, especially for large values of 's'. No experimental evidence exists for this.

3). The Hinshelwood treatment cannot account for the lack of linearity found experimentally for the plot of $1/k^1$ Vs $1/[A]$.



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