

## Lecture 27

We will continue to learn about “Chemical Kinetics”

Suggested book: Physical Chemistry by Ira Levine

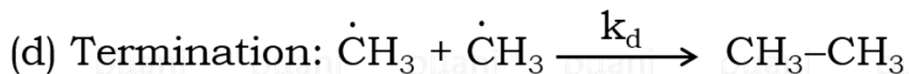
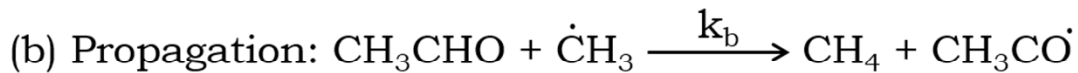
### Chain reactions:

In a chain reaction, an intermediate produced in one step generates an intermediate in a subsequent step, then that intermediate generates another intermediate, and so on....

Let us consider a chain reaction: Pyrolysis (thermal degradation) of  $\text{CH}_3\text{CHO}$  to  $\text{CH}_4$ ,  $\text{CH}_3\text{-CH}_3$ ,  $\text{CO}$  etc.

$$\text{And } \frac{d[\text{CH}_3\text{CHO}]}{dt} = k \times [\text{CH}_3\text{CHO}]^{\frac{3}{2}} \quad \text{CH}_3\text{CHO (g)} \rightarrow \text{CH}_4 \text{ (g)} + \text{CO (g)}$$

The mechanism provided by Rice-Herzfeld is as follows:



Applying steady-state approximation on  $\dot{\text{C}}\text{H}_3$  and  $\dot{\text{C}}\text{H}_3\text{CO}$

$$\frac{d[\dot{\text{C}}\text{H}_3]}{dt} = k_a \times [\text{CH}_3\text{CHO}] - k_b \times [\dot{\text{C}}\text{H}_3] \times [\text{CH}_3\text{CHO}] + k_c \times [\text{CH}_3\dot{\text{C}}\text{O}] - 2k_d \times [\dot{\text{C}}\text{H}_3]^2 = 0$$

$$\frac{d[\text{CH}_3\dot{\text{C}}\text{O}]}{dt} = k_b \times [\text{CH}_3\text{CHO}] \times [\dot{\text{C}}\text{H}_3] - k_c \times [\text{CH}_3\dot{\text{C}}\text{O}] = 0$$

Sum of the above two equations is:  $k_a \times [\text{CH}_3\text{CHO}] - 2 k_d \times [\dot{\text{C}}\text{H}_3]^2 = 0$

$$\Rightarrow [\dot{\text{C}}\text{H}_3] = \left( \frac{k_a}{2 k_d} \times [\text{CH}_3\text{CHO}] \right)^{\frac{1}{2}}$$

The rate of formation of  $\text{CH}_4$  is given by

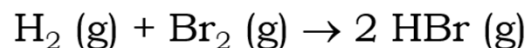
$$\frac{d[\text{CH}_4]}{dt} = k_b \times [\dot{\text{C}}\text{H}_3] \times [\text{CH}_3\text{CHO}]$$

$$\Rightarrow \frac{d[\text{CH}_4]}{dt} = k_b \times \left( \frac{k_a}{2 k_d} \right)^{\frac{1}{2}} \times [\text{CH}_3\text{CHO}]^{\frac{3}{2}}$$

This is in agreement with the three-halves order observed experimentally.

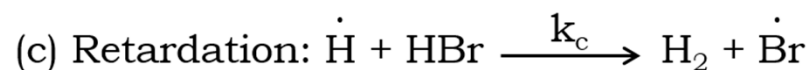
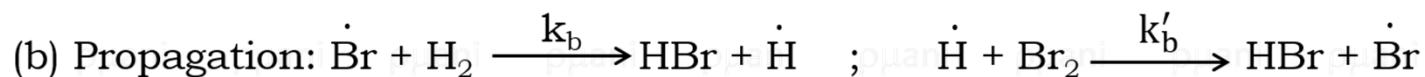
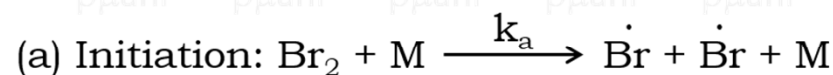
However, true mechanism could be much more complicated.

Let us consider a much more complicated chain reaction



$$\frac{d [\text{HBr}]}{dt} = \frac{k \times [\text{H}_2] \times [\text{Br}_2]^{\frac{3}{2}}}{[\text{Br}_2] + k' \times [\text{HBr}]}$$

The following mechanism has been proposed:



[M is a third body that removes the energy of recombination].

Let us apply steady state approximation on two intermediate, i.e.  $\dot{\text{H}}$  and  $\dot{\text{Br}}$

$$\frac{d [\dot{\text{H}}]}{dt} = k_b \times [\dot{\text{Br}}] \times [\text{H}_2] - k'_b \times [\dot{\text{H}}] \times [\text{Br}_2] - k_c \times [\dot{\text{H}}] \times [\text{HBr}] = 0$$

$$\frac{d [\dot{\text{Br}}]}{dt} = 2 k_a \times [\text{Br}_2] \times [\text{M}] - k_b \times [\dot{\text{Br}}] \times [\text{H}_2] + k'_b \times [\dot{\text{H}}] \times [\text{Br}_2] + k_c \times [\dot{\text{H}}] \times [\text{HBr}] - 2 k_d \times [\dot{\text{Br}}]^2 \times [\text{M}] = 0$$

From these two equations we get,

$$[\dot{\text{Br}}] = \left(\frac{k_a}{k_d}\right)^{\frac{1}{2}} \times [\text{Br}_2]^{\frac{1}{2}}$$

$$[\dot{\text{H}}] = \frac{k_b \times \left(\frac{k_a}{k_d}\right)^{\frac{1}{2}} \times [\text{H}_2] \times [\text{Br}_2]^{\frac{1}{2}}}{k'_b \times [\text{Br}_2] + k_c \times [\text{HBr}]}$$

(To note, [M] has cancelled)

$$\text{Thus, } \frac{d[\text{HBr}]}{dt} = \frac{2 k_b \times \left(\frac{k_a}{k_d}\right)^{\frac{1}{2}} \times [\text{H}_2] \times [\text{Br}_2]^{\frac{3}{2}}}{[\text{Br}_2] + \left(\frac{k_c}{k'_b}\right) \times [\text{HBr}]}$$

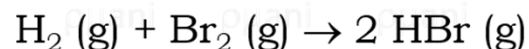
This equation is similar to the empirical rate law

$$\frac{d[\text{HBr}]}{dt} = \frac{k \times [\text{H}_2] \times [\text{Br}_2]^{\frac{3}{2}}}{[\text{Br}_2] + k' \times [\text{HBr}]}$$

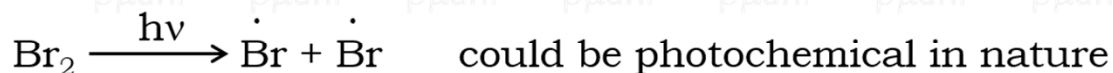
$$\text{where } k = 2 k_b \times \left(\frac{k_a}{k_d}\right)^{\frac{1}{2}} \quad \text{and} \quad k' = \left(\frac{k_c}{k'_b}\right)$$

(Presence of [HBr] in the denominator is a sign that it acts as an inhibitor and reducing the rate of the reaction)

Photochemical rate laws:



Instead of thermal reactions,



i.e. rate =  $I_{\text{abs}}$ , where,  $I_{\text{abs}}$  is the rate at which photons of appropriate frequency (or wavelength) are absorbed divided by the volume in which absorption occurs.

The rate of photochemical formation of HBr can be shown to be

$$\frac{d[\text{HBr}]}{dt} = \frac{2 k_b \times \left(\frac{1}{k_d \times [\text{M}]}\right)^{\frac{1}{2}} \times [\text{H}_2] \times [\text{Br}_2] \times (I_{\text{abs}})^{\frac{1}{2}}}{[\text{Br}_2] + \left(\frac{k_c}{k_b}\right) \times [\text{HBr}]}$$

$I_{\text{abs}} = k_a \times [\text{Br}_2] \times [\text{M}]$  in the thermal reaction scheme.

### Quenching:

Some photochemical reactions can be slowed down by the addition of a species that removes energy from the excited species, and its effect may be studied by monitoring fluorescence photons from the excited state.

For example,



S is the absorbing species (molecule/ion etc.)

$S^*$  → excited singlet state

Q → quenching agent

$h\nu_i$  and  $h\nu_f$  represent incident and fluorescent photons respectively.

Applying steady state approximation on  $S^*$ ,

$$\frac{d[S^*]}{dt} = I - \{(k_f + k_Q \times [Q]) \times [S^*]\} = 0$$

$$\Rightarrow [S^*] = \frac{I}{k_f + k_Q \times [Q]}$$

Fluorescence intensity is proportional to  $k_f \times [S^*]$ , so,

$$I_f = \frac{k_f \times I}{k_f + k_Q \times [Q]}$$

If we denote fluorescence intensity in absence of Q as  $I_f^0$ , then,

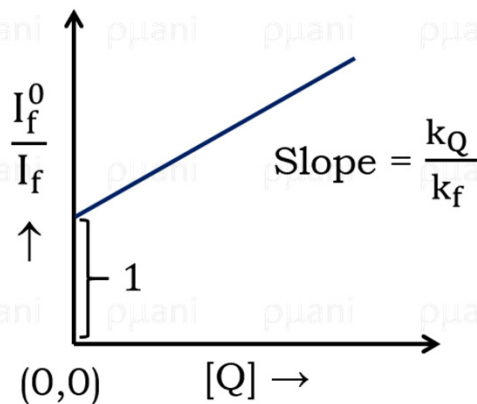
$$I_f^0 = \frac{k_f \times I}{k_f} = I$$

$$\frac{I_f^0}{I_f} = \frac{I}{k_f \times I} \times (k_f + k_Q \times [Q]) = \frac{k_f + k_Q \times [Q]}{k_f} = 1 + \frac{k_Q}{k_f} \times [Q]$$

$$\frac{I_f^0}{I_f} = 1 + \frac{k_Q}{k_f} \times [Q]$$

Therefore, a plot of  $\frac{I_f^0}{I_f}$  against  $[Q]$  should be a straight line with slope =  $\frac{k_Q}{k_f}$  and intercept = 1.

Such a plot is known as Stern-Volmer (quenching) plot.



Alternatively,

When no quencher is present:

$$\frac{d[S^*]}{dt} = I - k_f \times [S^*] = 0$$

$$\Rightarrow [S^*] = \frac{I}{k_f}$$

$$I_f^0 = k_f \times [S^*] = k_f \times \frac{I}{k_f} = I$$

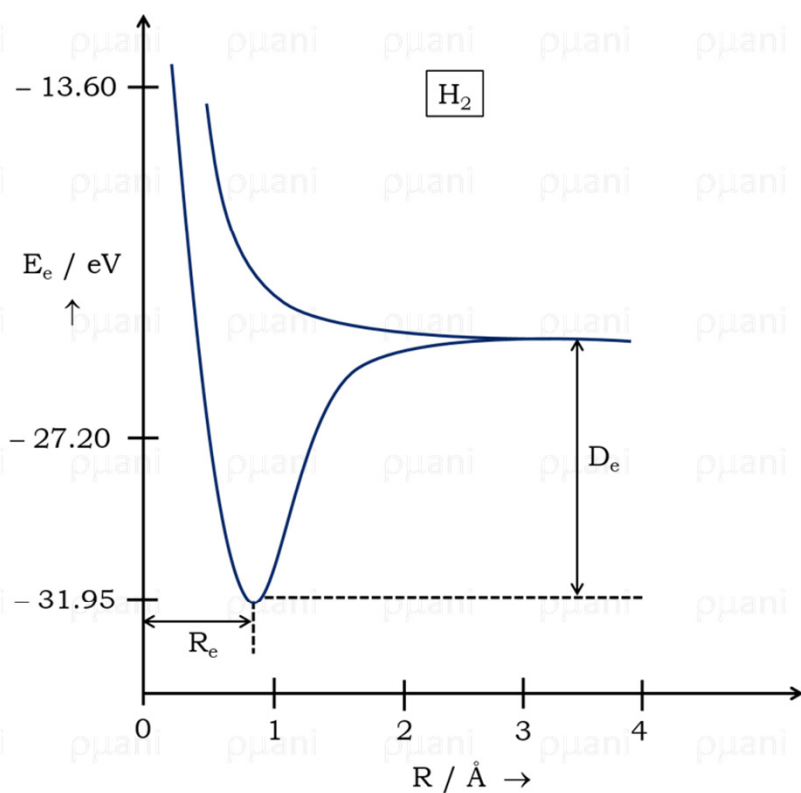


## Introduction to collision theory, potential energy surfaces and transition state theory

If the number of collisions is in the range of billions ( per atmosphere, per number of molecules), then why a chemicals reaction takes so long to complete?

Not all collisions lead to reaction. Reaction occurs only when the relative translational kinetic along the line of the centers of the colliding molecules exceeds a threshold energy. This means angle of collision becomes important since a certain minimum energy is needed to initiate the breaking of the chemical bond(s) to initiate a reaction.

Potential energy diagram:



N atoms

3N nuclear coordinates

3 Translational

2 Rotational

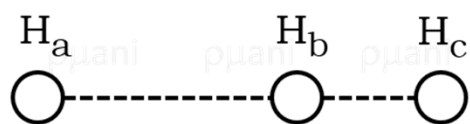
1 Vibrational

➤ Potential energy diagram

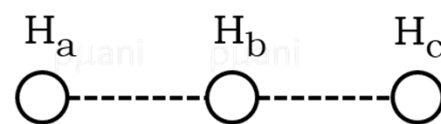
Potential-energy curves for the lowest few electronic states of  $H_2$ .  $R_e$  and  $D_e$  of the ground electronic state are shown.



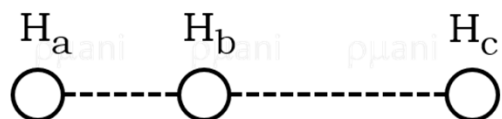
Point p



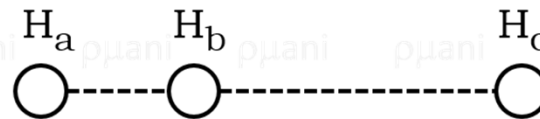
Point q



Point s



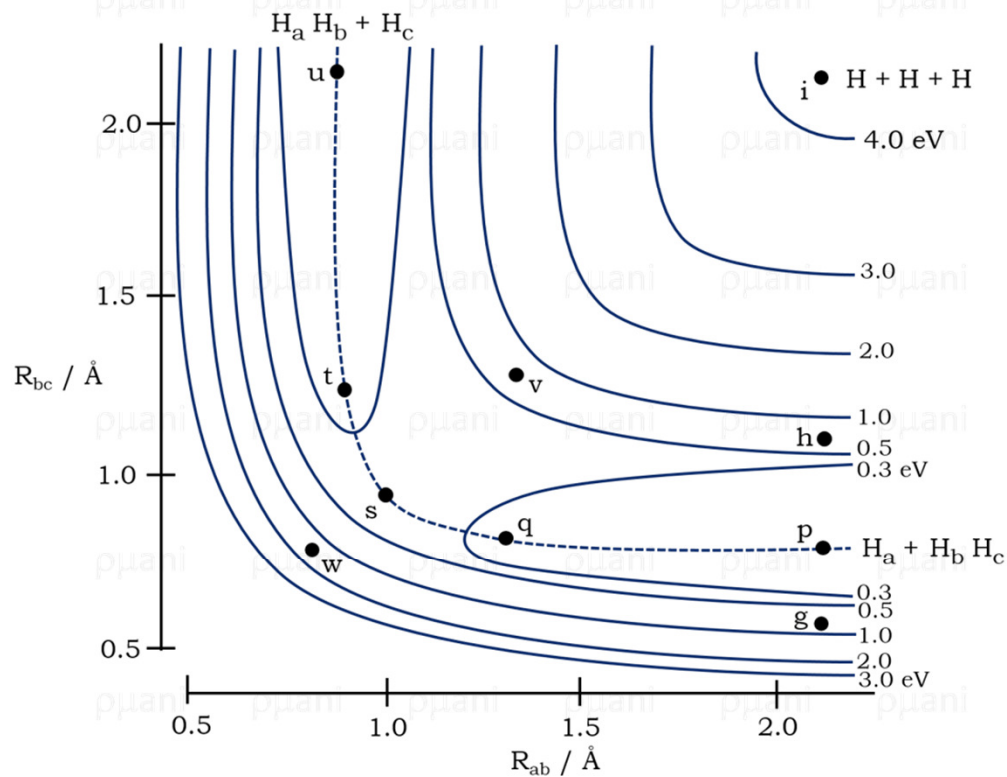
Point t



Point u

Configurations of the  $H_3$  super-molecule for various points on the minimum-energy path.

Potential energy surface:



Contour map of the  $\text{H} + \text{H}_2$  potential-energy surface for  $\theta = 180^\circ$ . Note that this diagram starts at  $R_{ab} = R_{bc} = 0.5 \text{ \AA}$  rather than at zero.

[Data from R. N. Porter and M. Karplus, *J. Chem. Phys.*, **40**, 1105 (1964).]

Saddle point “s” is known as transition state.