Lecture 14

Chemical Reaction Engineering (CRE) is the field that studies the rates and mechanisms of chemical reactions and the design of the reactors in which they take place.

Lecture 14 – Thursday

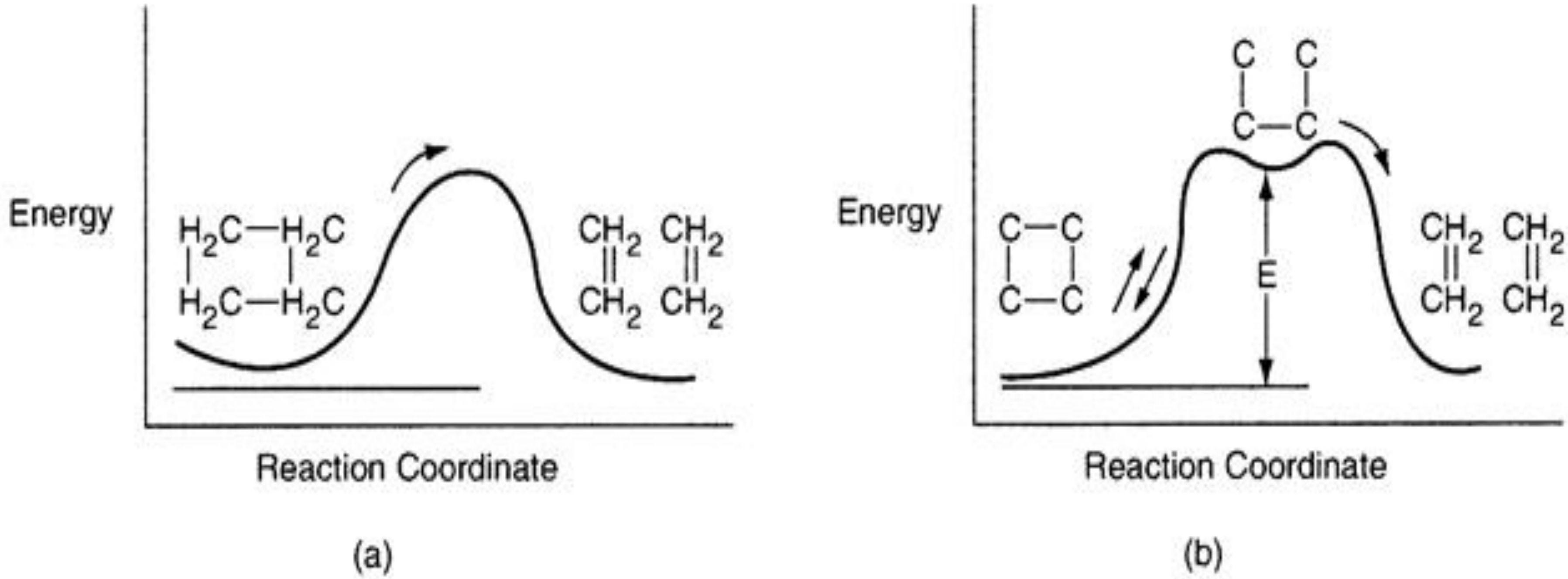
- Pseudo Steady State Hypothesis (PSSH)
  - Net rate of reaction of active intermediates is zero
  - Hall of Fame Reaction: $2NO + O_2 \rightarrow 2NO_2$
  - Introduction to Enzyme Kinetics
  - Begin non-Isothermal reactor design

Active Intermediates and PSSH

An active intermediate is a molecule that is in a highly energetic and reactive state It is short lived as it disappears virtually as fast as it is formed. That is, the net rate of reaction of an active intermediate, A*, is zero.

The assumption that the net rate of reaction is zero is called the Pseudo Steady State Hypothesis (PSSH)

Active Intermediates and PSSH



Reaction coordinate. Courtesy *Science News, 156*, 247 (1999).

Example

The rate law for the reaction

$$\mathrm{A} \rightarrow \mathrm{B} + \mathrm{C}$$

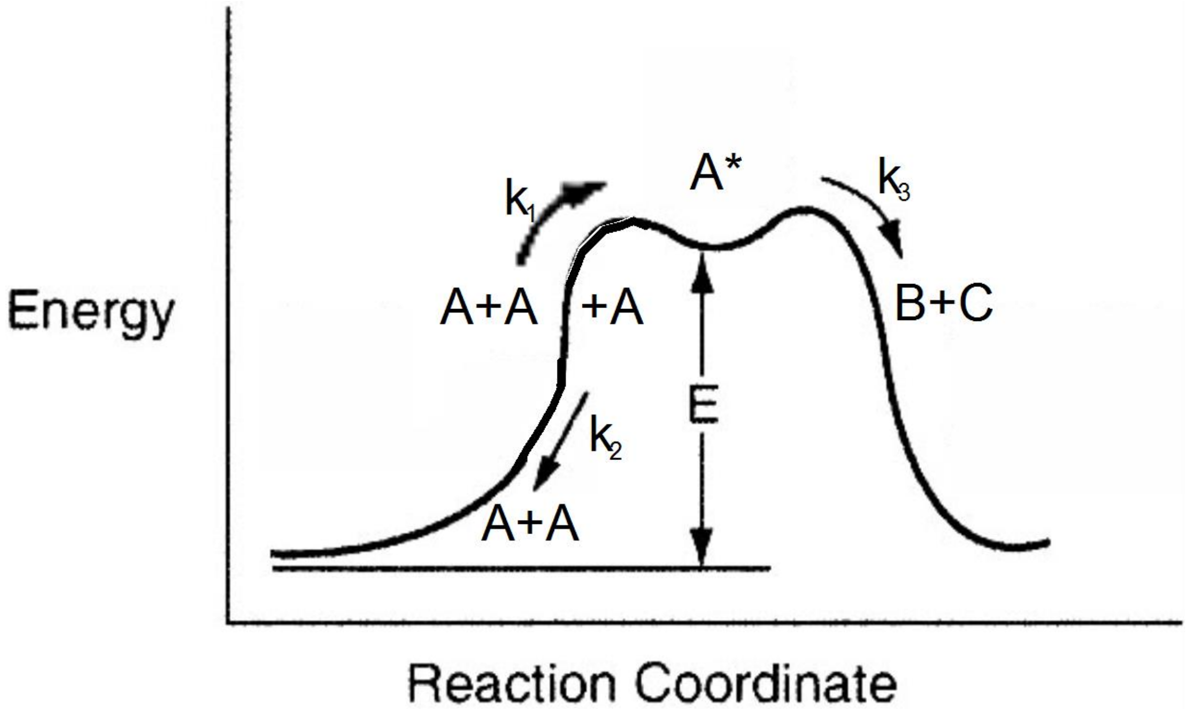
is found from experiment to be

$$-r_A = \frac{kC_A^2}{1 + k'C_A}$$

How did this rate law come about? Suggest a mechanism consistent with the rate law.

Example

For reactions with active intermediates, the reaction coordinated now has trough in it and the active intermediate, A*, sits in this trough



Example - Solution

$$(1)\quad \mathrm{A}+\mathrm{A}\xrightarrow{\mathrm{k}_1}\mathrm{A}^*+\mathrm{A}\qquad r_{1A^*}=k_1C_A^2$$

$$(2)\quad \mathrm{A}^*+\mathrm{A}\xrightarrow{\mathrm{k}_2}\mathrm{A}+\mathrm{A}\qquad r_{2A^*}=-k_2C_{A^*}C_A$$

$$(3)\quad \mathrm{A}^*\xrightarrow{\mathrm{k}_3}\mathrm{B}+\mathrm{C}\qquad r_{3A^*}=-k_3C_{A^*}$$

Rate Laws:

k_3 is defined w.r.t. A*

Reaction (1) $r_{1A*} = k_1 C_A^2$ (1)

Reaction (2) $r_{2A*} = -k_2 C_A C_{A*}$ (2)

Reaction (3) $r_{3A*} = -k_3 C_{A*}$ (3)

But C^*_A cannot be measured since it is so small

Relative Rates: $r_{1A} = -r_{1A*}$, $r_{3B} = -r_{3A*}$

Net Rates: Rate of Formation of Product

$$r_B = r_{3B} = -r_{3A*} = k_3 C_{A*} \tag{4}$$

Pseudo Steady State Hypothesis $r^*_A = 0$

$$r_{A*} = \sum r_{A*} = r_{1A*} + r_{2A*} \neq r_{3A*} \tag{5}$$

$$= k_1 C_A^2 - k_2 C_A C_{A*} - k_3 C_{A*} = 0 \tag{6}$$

Solving for C_{A*}

$$C_{A*} = \frac{k_1 C_A^2}{k_3 + k_2 C_A}$$

Substituting for $\mathrm{C}_{\mathrm{A}*}$ in Equation (4) the rate of formation of B is

$$r_B = \frac{k_1 k_3 C_A^2}{k_3 + k_2 C_A} \qquad (8)$$

Relative rates overall

$$\mathrm{A} \rightarrow \mathrm{B} + \mathrm{C}$$

$$\frac{r_A}{-1} = \frac{r_B}{1}$$

$$r_A = -r_B = -\frac{k_1 k_3 C_A^2}{k_3 + k_2 C_A} \qquad (9)$$

For high concentrations of A, we can neglect k_3 in the denominator with respect to $k_2 C_A$

$$k_2 C_A >> k_3$$

and the rate law becomes

$$r_A = -\frac{k_1 k_3}{k_2} C_A = -k C_A \qquad (10)$$

(apparent first order)

For low concentrations of A, we can neglect $k_2 C_A$ in the denominator with respect to k_3.

$$k_3 >> k_2 C_A$$

and the rate law becomes

$$r_A = -\frac{k_3 k_1}{k_3} C_A^2 = -k_1 C_A^2 \qquad (11)$$

(apparent second order)

Dividing by k_3 and letting $k' = k_2/k_3$ and $k = k_1$ we have the rate law we were asked to derive

$$\boxed{-r_A = -\frac{kC_A^2}{1 + k'C_A}} \qquad (12)$$

Active Intermediates

Why do so many reactions follow elementary rate laws?

What about $-r_A = kC_A$

$$-r_A = \frac{kC_A}{1 + k'C_I} \qquad (I = Inert)$$

$$(1) \quad A + I \xrightarrow{k_1} A^* + I$$

$$(2) \quad A^* + I \xrightarrow{k_2} A + I$$

$$(3) \quad A \xrightarrow{k_3} B + C$$

$$-\mathrm{r_A} = \frac{k_1 k_3 C_A}{k_2 + k_2 C_I}$$

Active Intermediates/Free Radicals and PSSH

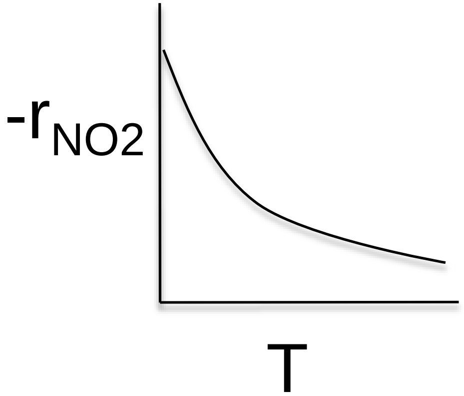
Hall of Fame Reaction

The reaction: $2NO + O_2 \rightarrow 2NO_2$

has an elementary rate law

$$r_{NO_2} = kC_{NO}^2 C_{O_2}$$

However… Look what happens to the rate as the temperature increases:



Why does the rate law decrease with increasing temperature?

Mechanism:

$$NO + O_2 \xrightarrow{k_1} NO_3^* \qquad (1)$$

$$NO_3^* \xrightarrow{k_2} NO + O_2 \qquad (2)$$

$$NO_3^* + NO \xrightarrow{k_3} 2NO_2 \qquad (3)$$

Write rate of formation of product r_{NO2}

Note: k_3 is defined w.r.t. NO_3*

Define k with respect to NO_3^*

Assume that all reactions are elementary reactions, such that:

$$r_{1NO_3} = k_1 C_{NO} C_{O_2} = k_1 \left[NO\right]\left[O_2\right]$$

$$r_{2NO_3^*} = -k_2 C_{NO_3^*} = k_2 \left[NO_3^*\right]$$

$$r_{3NO_3^*} = -k_3 C_{NO_3^*} C_{NO} = k_3 \left[NO_3^*\right]\left[NO\right]$$

$$r_{NO_2} = 2\left[-r_{3NO_3^*}\right]$$

The net reaction rate for NO$_3$* is the sum of the individual reaction rates for NO$_3$*:

$$r_{1NO_3^*} = r_1 \Rightarrow r_{1NO_3^*} = k_1[NO][O_2]$$

$$-r_{2NO_3^*} = r_2 \Rightarrow r_{2NO_3^*} = -k_2\left[NO_3^*\right]$$

$$-r_{3NO_3^*} = r_3 \Rightarrow r_{3NO_3^*} = -k_3\left[NO_3^*\right][NO]$$

$$r_{NO_3^*} = r_{1NO_3^*} + r_{2NO_3^*} + r_{3NO_3^*}$$

$$r_{NO_3^*} = k_1[NO][O_2] - k_2\left[NO_3^*\right] - k_3\left[NO_3^*\right][NO]$$

Pseudo Steady State Hypothesis (PSSH)

The PSSH assumes that the **net rate** of species A* (in this case NO_3^*) is zero.

$$r_{NO_3^*} \cong 0$$

$$0 = k_1\left[NO\right]\left[O_2\right] - k_2\left[NO_3^*\right] - k_3\left[NO_3^*\right]\left[NO\right]$$

$$0 = k_1[NO]\left[O_2\right] - \left[NO_3^*\right]\left(k_2 + [NO]\right)$$

$$\left[NO_3^*\right] = \frac{k_1[NO][O_2]}{k_2 + k_3[NO]}$$

Pseudo Steady State Hypothesis (PSSH)

$$[NO_3^*] = \frac{k_1[NO][O_2]}{k_2 + k_3[NO]}$$

$$r_{NO_2} = -2r_{3NO_3^*} = 2\left[NO_3^*\right][NO]$$

$$r_{NO_2} = 2\,\frac{\mathrm{k_1 k_3 [NO]^2 [O_2]}}{\mathrm{k_2 + k_3 [NO]}}$$

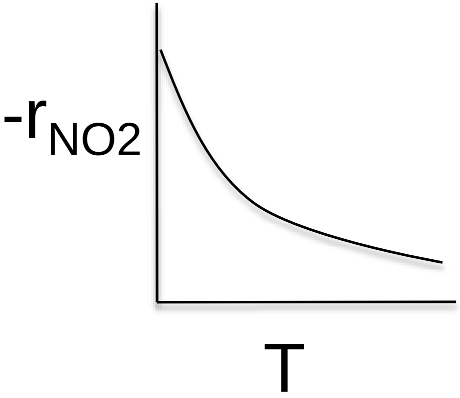
Pseudo Steady State Hypothesis (PSSH)

$$k_2 >> k_3[NO]$$

$$r_{NO_2} = 2\frac{k_1 k_3}{k_2}[NO]^2[O_2] = 2\frac{A_1 A_3}{A_2} e^{\frac{E_2 - (E_1 + E_3)}{RT}}[NO]^2[O_2]$$

$$E_2 > (E_1 + E_3)$$

This result shows why the rate decreases as temperature increases.



End Lecture 14