Ex. 26

Mechanism of the reaction $C_2H_6 + H_2 \longrightarrow 2CH_4$ **can be presented as**

$$C_2H_6 \rightleftharpoons 2CH_3\cdot$$

Equilibrium constant K

$$CH_3\cdot + H_2 \xrightarrow{k_1} CH_4 + H\cdot$$

$$C_2H_6 + H\cdot \xrightarrow{k_2} CH_4 + CH_3\cdot$$

$H\cdot$ is at steady state

Try to prove $$\frac{d[CH_4]}{dt} = 2k_1K^{1/2}[C_2H_6]^{1/2}[H_2]$$

Ex. 26

$$C_2H_6 \rightleftharpoons 2CH_3\cdot$$

$$CH_3\cdot + H_2 \xrightarrow{k_1} CH_4 + H\cdot$$

$$C_2H_6 + H\cdot \xrightarrow{k_2} CH_4 + CH_3\cdot$$

$$\frac{d[CH_4]}{dt} = k_1[CH_3\cdot][H_2] + k_2[H\cdot][C_2H_6]$$

$$d[H\cdot]/dt = k_1[CH_3\cdot][H_2] - k_2[H\cdot][C_2H_6] = 0$$ $H\cdot$ is at steady state

$$[CH_3\cdot]^2/[C_2H_6] = K$$ Equilibrium constant K

$$\frac{d[CH_4]}{dt} = k_1[CH_3\cdot][H_2] + k_2[H\cdot][C_2H_6] = 2k_1[CH_3\cdot][H_2]$$

$$= 2k_1K^{1/2}[C_2H_6]^{1/2}[H_2]$$

Ex. 27

Mechanism of the decomposition reaction of N_2O_5 can be presented as

$$N_2O_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2 + NO_3 \cdot \qquad 1$$

$$NO_2 + NO_3 \cdot \xrightarrow{k_2} NO\cdot + O_2 + NO_2 \qquad 2$$

$$NO\cdot + NO_3 \cdot \xrightarrow{k_3} 2\,NO_2 \qquad 3$$

(1) If NO and NO_3 are active intermediates, try to give the production rate of O_2 by **Steady State Approximation**

(2) Suppose the step 2 is the rate-controlled step, try to give the production rate of O_2 under the **Pre-Equilibrium Approximation**

Ex. 28

Mechanism of the reaction $CH_3CHO \longrightarrow CH_4 + CO$ **can be presented as**

$$CH_3CHO \xrightarrow{k_1} CH_3\cdot + CHO\cdot \qquad E_1$$

$$CH_3\cdot + CH_3CHO \xrightarrow{k_2} CH_4 + CH_2CHO\cdot \qquad E_2$$

$$CH_2CHO\cdot \xrightarrow{k_3} CO + CH_3\cdot \qquad E_3$$

$$CH_3\cdot + CH_3\cdot \xrightarrow{k_4} C_2H_6 \qquad E_4$$

Try to give the express of $\mathrm{d}c_{CH_4}/\mathrm{d}t$ and the apparant activation energy of the reaction?

Ex. 29

For reaction $A \rightarrow C$, there are two possible reeaction mechanisms:

(1) the reaction took place directly, and displayed the characterizations of first oeder reaction. the half time at 294K is 1000min, while at T=340K, the time needed to reduce the concentration of A to 1/1024 C_{A0} is 0.1min.

(2) the reaction took place by two steps:

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} A^* \qquad A^* \xrightarrow{k_2} C$$

the activation energies of each step were $E_{a,1}$=125.52kJ/mol, $E_{a,-1}$=120.3kJ/mol and $E_{a,2}$=167.36kJ/mol

Try to determine which one is the most possible mechanism at T=500K?

Ex. 27

$$N_2O_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2 + NO_3\cdot$$

$$NO_2 + NO_3\cdot \xrightarrow{k_2} NO\cdot + O_2 + NO_2$$

$$NO\cdot + NO_3\cdot \xrightarrow{k_3} 2NO_2$$

(1) $$\frac{d[O_2]}{dt} = k_2[NO_2][NO_3]$$

$$\begin{cases} \dfrac{d[NO]}{dt} = k_2[NO_2][NO_3] - k_3[NO][NO_3] = 0 \\ \dfrac{d[NO_3]}{dt} = k_1[N_2O_5] - k_{-1}[NO_2][NO_3] - k_2[NO_2][NO_3] - k_3[NO][NO_3] = 0 \end{cases}$$

$$[NO_3] = \frac{k_1[N_2O_5]}{(k_{-1}+2k_2)[NO_2]} \qquad \frac{d[O_2]}{dt} = \frac{k_1k_2}{k_{-1}+2k_2}[N_2O_5]$$

(2) $$K = \frac{[NO_2][NO_3]}{[N_2O_5]} = \frac{k_1}{k_{-1}} \qquad \frac{d[O_2]}{dt} = k_2[NO_2][NO_3] = \frac{k_1k_2}{k_{-1}}[N_2O_5]$$

Ex. 28

（1） $$\mathrm{d}c_{\mathrm{CH_4}}/\mathrm{d}t = k_2[\mathrm{CH_3}\cdot][\mathrm{CH_3CHO}]$$

$$\mathrm{d}[\mathrm{CH_3}\cdot]/\mathrm{d}t = k_1[\mathrm{CH_3CHO}] - k_2[\mathrm{CH_3}\cdot][\mathrm{CH_3CHO}]$$
$$+ k_3[\mathrm{CH_2CHO}\cdot] - 2k_4[\mathrm{CH_3}\cdot]^2 = 0$$

$$\mathrm{d}[\mathrm{CH_2CHO}\cdot]/\mathrm{d}t = k_2[\mathrm{CH_3}\cdot][\mathrm{CH_3CHO}] - k_3[\mathrm{CH_2CHO}\cdot] = 0$$

$$[\mathrm{CH_3}\cdot] = \sqrt{\frac{k_1[\mathrm{CH_3CHO}]}{2k_4}}$$

$$\therefore \mathrm{d}[\mathrm{CH_4}]/\mathrm{d}t = k_2[\mathrm{CH_3CHO}]\sqrt{k_1[\mathrm{CH_3CHO}]/2k_4}$$
$$= k_2(k_1/2k_4)^{1/2}[\mathrm{CH_3CHO}]^{3/2}$$

（2） $$E_a = \frac{1}{2}E_1 + E_2 - \frac{1}{2}E_4$$

Ex. 29

(1)

$$k(294\ \text{K}) = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{1000\ \text{min}} = 6.93\times10^{-4}\ \text{min}^{-1}$$

$$k(340\ \text{K}) = \frac{1}{t}\ln\frac{1}{1-y} = \frac{1}{0.10\ \text{min}}\ln\frac{1}{1-\frac{1023}{1024}} = 69.31\ \text{min}^{-1}$$

$$\ln\frac{k(T_2)}{k(T_1)} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\frac{69.31}{6.93\times10^{-4}} = \frac{E_a}{R}\left(\frac{1}{294\ \text{K}} - \frac{1}{340\ \text{K}}\right)$$

$$E_a(1) = 208.0\ \text{kJ}\cdot\text{mol}^{-1}$$

(2)

$$r_2 = k_2[\text{A}^*] = \frac{k_1k_2}{k_{-1}}[\text{A}] = k[\text{A}]$$

$$k = \frac{k_1k_2}{k_{-1}}$$

$$k_1[\text{A}] = k_{-1}[\text{A}^*]\ ,\quad [\text{A}^*] = \frac{k_1}{k_{-1}}[\text{A}]\ ,$$

$$E_a(2) = E_{a,1} + E_{a,2} - E_{a,-1} = (125.52 + 167.36 - 120.30)\ \text{kJ}\cdot\text{mol}^{-1} = 172.58\ \text{kJ}\cdot\text{mol}^{-1}$$