LECTURE 33/36 NOV-25-02

- Steady State Approximation

A SIMPLE RATE LAW DOES NOT NECESSARY IMPLY A SIMPLE MECHANISM. A MECHANISM CONSISTS OF SEVERAL ELEMENTARY REACTIONS OR STEPS. FROM THESE STEPS SHOULD BE ONE ABLE TO DETERMINE THE RATE LAW ASSOCIATED (WITH to) THE MECHANISM.

I.– AS AN EXAMPLE, WE CONSIDER THE DECOMPOSITION OF DINITROGEN PENTAOXIDE. THE OVERALL CHEMICAL RXN,

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g), \qquad (8)$$

HAS A FIRST ORDER EXPERIMENTAL RATE LAW,

$$r = k^{obs}[N_2O_5]. \qquad (4)$$

A PROPOSE MECHANISM IS GIVEN BY THE FOLLOWING SET OF ELEMENTARY REACTIONS:

$$N_2O_5(g) \underset{k_1^-}{\overset{k_1^+}{\rightleftharpoons}} NO_2(g) + \boxed{NO_3(g)} \qquad (1a)$$

$$NO_2(g) + \boxed{NO_3(g)} \xrightarrow{k_2} NO_2(g) + O_2(g) + \boxed{NO(g)} \qquad (1b)$$

$$\boxed{NO(g)} + N_2O_5(g) \xrightarrow{k_3} 3\,NO_2(g).$$

THIS MODEL IS VALID FOR HIGH N_2O_5 PRESSURES.

FOR THIS SYSTEM THE CONCENTRATIONS OF [NO] AND [NO_3] ARE MUCH LESS THAN THE CONCENTRATIONS OF REACTANT AND PRODUCTS.

ALSO THE RATE OF CHANGE ARE MUCH SMALLER SUCH THAN WE CAN NEGLECT THE INTERMEDIATE RATE OF CHANGE.

WE CAN EITHER ASSUME THE STEADY-STATE CONDITIONS OR EXPERIMENTALLY CHECK THEM.

FOR THE INTERMEDIATES, THE RATE OF CHANGE EQS. ARE GIVEN BY:

$$\frac{d[NO]}{dt} = k_2[NO_2][NO_3] - k_3[NO][N_2O_5]$$

$$\frac{d[NO_3]}{dt} = k_1^+[N_2O_5] - k_1^-[NO_2][NO_3] - k_2[NO_2][NO_3]$$

NOW WE APPROXIMATE THE INTERMEDIATE RATES EQUAL TO ZERO,

$$k_2[NO_2][NO_3]_{ss} - k_3[N_2O_5][NO]_{ss} = 0$$

$$k_1^+[N_2O_5] - k_1^-[NO_2][NO_3]_{ss} - k_2[NO_2][NO_3]_{ss} = 0.$$

NEXT WE SOLVE FOR $[NO]_{ss}$ AND $[NO_3]_{ss}$ AND GET

$$[NO_3]_{ss} = \frac{k_1^+[N_2O_5]}{(k_2+k_1^-)[NO_2]}$$

$$[NO]_{ss} = \frac{k_2[NO_2]}{k_3[N_2O_5]}[NO_3]_{ss} = \frac{k_1^+ k_2}{k_3(k_2+k_1^-)}$$

FROM EQ (8)

$$r = -\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{4}\frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt}$$

$$\frac{d[O_2]}{dt} = k_2 [NO_2][NO_3]_{ss}$$

$$r = \frac{k_2 k_1^+}{k_2 + k_1^-}[N_2O_5]$$

CONSEQUENTLY

$$k^{obs} = \frac{k_2 k_1^+}{k_2 + k_1^-}.$$

AND WE PREDICT A FIRST ORDER RATE LAW.

II.-

ANOTHE MODEL OF THE DECOMPOSITION OF DINITROGEN PENTAOXIDE ASSUMES THE PRESENCE OF A HOST INERT GAS LIKE ARGON. IN THIS CASE THE MECHNISM IS GIVEN BY:

$$N_2O_5 + M \underset{k_*^-}{\overset{k_*^+}{\rightleftharpoons}} \boxed{N_2O_5^*} + M \qquad (12a)$$

$$\boxed{N_2O_5^*} \xrightarrow{k_1} \boxed{NO_3} + NO_2 \qquad (12b)$$

$$\boxed{NO_3} + NO_2 \xrightarrow{k_2} \boxed{NO} + NO_2 + O_2 \qquad (12c)$$

$$\boxed{NO_3} + \boxed{NO} \xrightarrow{k_4} 2\,NO_2 \qquad (12d)$$

(a) IN THIS CASE WE HAVE THREE INTERMEDIATES $N_2O_5^*$, NO, AND NO_3.

(b) RATE OF CHANGE FOR INTERMEDIATES

$$\frac{d}{dt}[N_2O_5^*] = k_*^+ M [N_2O_5] - k_*^- M [N_2O_5^*] - k_1 [N_2O_5^*]$$

$$\frac{d}{dt}[NO_3] = k_1 [N_2O_5^*] - k_2 [NO_2][NO_3] - k_4 [NO][NO_3]$$

$$\frac{d}{dt}[NO] = k_2 [NO_2][NO_3] - k_4 [NO][NO_3]$$

(c) SET THE RATES OF THE INTERMEDIATES EQUAL TO ZERO

(d) SOLVE FOR THE INTERMEDIATES

i) $k_*^+ M [N_2O_5] - k_*^- M [N_2O_5^*]_{ss} - k_1 [N_2O_5^*]_{ss} = 0$

ii) $k_1 [N_2O_5^*]_{ss} - k_2 [NO_2][NO_3]_{ss} - k_4 [NO]_{ss} [NO_3]_{ss} = 0$

iii) $k_2 [NO_2][NO_3]_{ss} - k_4 [NO]_{ss} [NO_3]_{ss} = 0$

FROM EQ. (iii)

$$[NO]_{ss} = \frac{k_2}{k_4} [NO_2]$$

FROM i)

$$[N_2O_5^*]_{ss} = \frac{k_*^+ M [N_2O_5]}{k_1 + k_*^- M}$$

FROM ii)

$$k_1 [N_2O_5^*]_{ss} = \{ k_2 [NO_2] + k_4 [NO]_{ss} \} [NO_3]_{ss}$$

$$= 2 k_2 [NO_2] [NO_3]_{ss}$$

$$[NO_3]_{ss} = \frac{k_*^+ M [N_2O_5]}{2 k_2 (k_1 + k_*^- M) [NO_2]}$$

a) RATE

$$r = -\frac{1}{2} \frac{d[N_2O_5]}{dt} = \frac{1}{4} \frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt}$$

$$r = \frac{d[O_2]}{dt} = k_2 [NO_2] [NO_3]_{ss}$$

$$= \frac{k_*^+ M}{2(k_1 + k_*^- M)} [N_2O_5]$$