

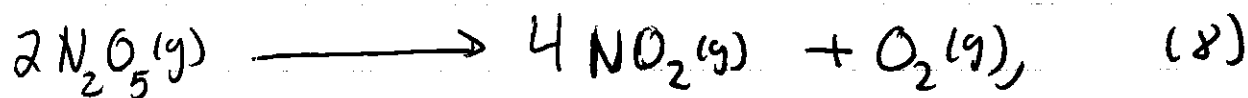
LECTURE 33/36

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) THE MECHANISM.

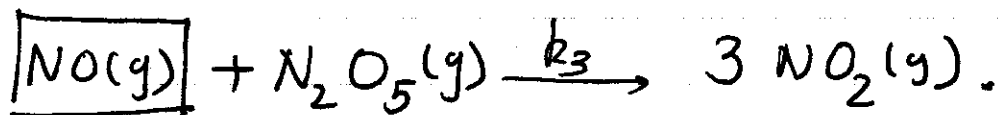
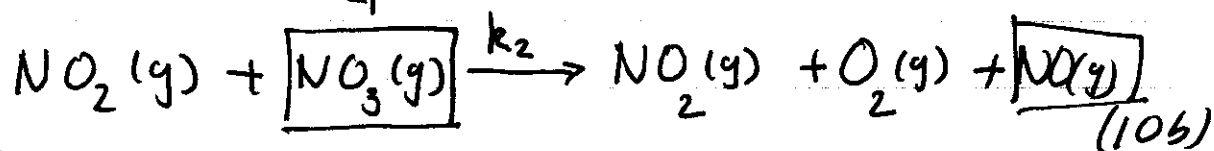
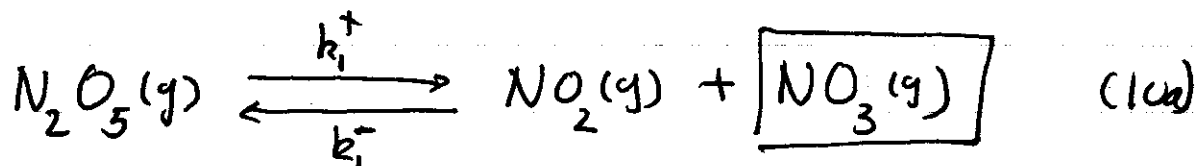
I. — AS AN EXAMPLE, WE CONSIDER THE DECOMPOSITION OF DINITROGEN PENTAOXIDE. THE OVERALL CHEMICAL RXN,



HAS A FIRST ORDER EXPERIMENTAL RATE LAW,

$$r = k^{\text{obs}} [\text{N}_2\text{O}_5]. \quad (2)$$

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



THIS MODEL IS VALID FOR HIGH  $\text{N}_2\text{O}_5$  PRESSURES.

FOR THIS SYSTEM THE CONCENTRATIONS OF  $[\text{NO}]$  AND  $[\text{NO}_3]$  ARE MUCH LESS THAN THE CONCENTRATIONS OF REACTANT AND PRODUCTS.

ALSO THE RATE OF CHANGE ARE MUCH SMALLER SUCH THAT 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:

$$\frac{d[\text{NO}]}{dt} = k_2 [\text{NO}_2] [\text{NO}_3] - k_3 [\text{NO}] [\text{N}_2\text{O}_5]$$

$$\frac{d[\text{NO}_3]}{dt} = k_1^+ [\text{N}_2\text{O}_5] - k_1^- [\text{NO}_2] [\text{NO}_3] - k_2 [\text{NO}_2] [\text{NO}_3]$$

NOW WE APPROXIMATE THE INTERMEDIATE RATES

EQUAL TO ZERO,

$$k_2 [\text{NO}_2] [\text{NO}_3]_{ss} - k_3 [\text{N}_2\text{O}_5] [\text{NO}]_{ss} = 0$$

$$k_1^+ [\text{N}_2\text{O}_5] - k_1^- [\text{NO}_2] [\text{NO}_3]_{ss} - k_2 [\text{NO}_2] [\text{NO}_3]_{ss} = 0.$$

NEXT WE SOLVE FOR  $[\text{NO}]_{ss}$  AND  $[\text{NO}_3]_{ss}$

AND GET

$$[\text{NO}_3]_{ss} = \frac{k_1^+ [\text{N}_2\text{O}_5]}{(k_2 + k_1^-) [\text{NO}_2]}$$

$$[\text{NO}]_{ss} = \frac{k_2 [\text{NO}_2] [\text{NO}_3]_{ss}}{k_3 [\text{N}_2\text{O}_5]} = \frac{k_1^+ k_2}{k_3 (k_2 + k_1^-)}$$

FROM EQ (8)

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

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

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

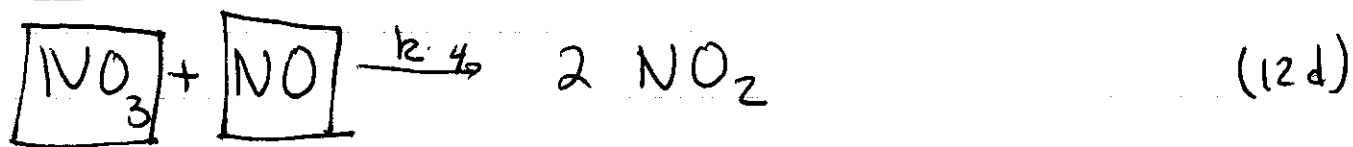
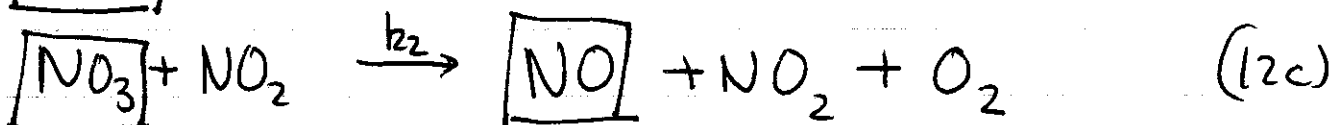
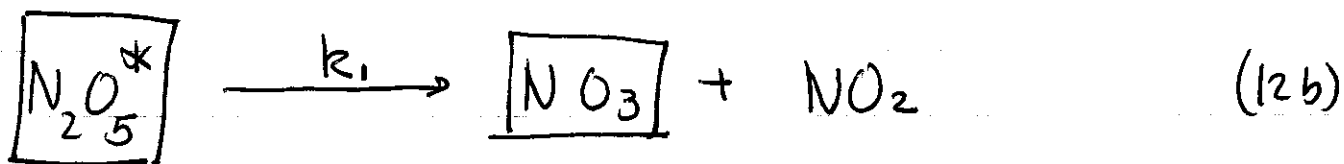
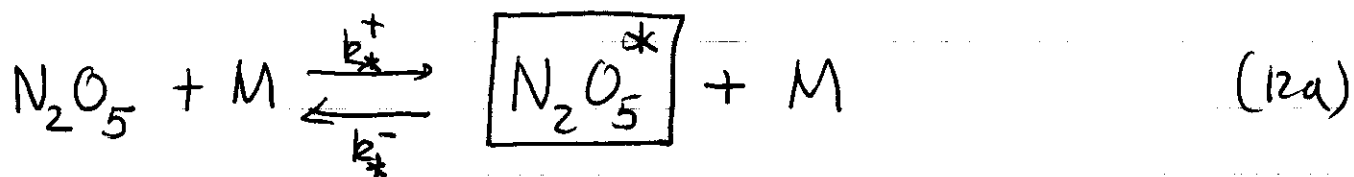
CONSEQUENTLY

$$r^{OAS} = \frac{k_2 k_1^+}{k_2 + k_1^-}$$

AND WE PREDICT A FIRST ORDER RATE LAW.

II.-

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



(a) IN THIS CASE WE HAVE THREE INTERMEDIATES

$\text{N}_2\text{O}_5^*$ ,  $\text{NO}$ , AND  $\text{NO}_3$ .

(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. (ii)

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

FROM i)

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

FROM ii)

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

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

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

c) RATE

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

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

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