

LECTURE 31136

NOV-20-02

— INTEGRATED RATE LAWS

EXAMPLES

— RATE LAWS

— MECHANISMS

READ: TODAY'S LEC ETC 458-468

NEXT LEC EPL NOTES

PS #8 CTC $\frac{1}{2}$ CH 12

PROBLEMS: 9, 10, 11, 13, 17, 18, 22, 23

25, 28, 29, 30, 33, 44, 48

54, 58, 59, 60, 61

DUE: FRIDAY
DEC-6-02

SUMMARY

OVERALL RXNS

ZERO ORDER



$$r = k$$

$$[A] = [A]_0 - kt$$

$[A]$ vs t

$$\text{SLOPE} = -k$$

$$t_{\frac{1}{2}} = \frac{[A]_0}{2k}$$

FIRST ORDER



$$r = k[A]$$

$$[A] = [A]_0 e^{-kt}$$

$$\ln\left(\frac{[A]}{M}\right) = \ln\left(\frac{[A]_0}{M}\right) - kt$$

$\ln\left(\frac{[A]}{M}\right)$ vs t

$$\text{SLOPE} = -k'$$

$$t_{\frac{1}{2}} = \frac{\ln 2}{k}$$

SECOND ORDER



$$r = k[A]^2$$

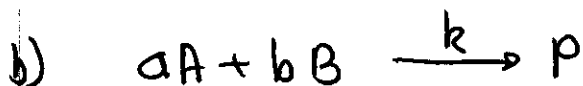
$$[A] = \frac{[A]_0}{1 + k'[A]_0 t}$$

$$\frac{1}{[A]} = \frac{1}{[A]_0} + k' t$$

$\frac{1}{[A]}$ vs t

SLOPE = k'

$$t_{1/2} = \frac{1}{k'[A]_0}$$



$$r = k[A][B]$$

$$S = b[A] - a[B] = \text{CONSTANT}$$

i) $S = 0$ BACK TO a)

ii) $S \neq 0$

$$[A] = \frac{\delta [A]_0}{\delta + a[B]_0 (1 - e^{-\delta k t})}$$

$\ln [A]$ vs t IS NOT LINEAR

BUT INITIAL SLOPE = $\frac{a[B]_0 k}{[A]_0}$

RATES AND RATE LAWS

THE RATE MEASURES HOW FAST A

QUANTITY CHANGES WITH RESPECT TO TIME.

FOR EXAMPLE, CONSIDER THE RXN



THE RATE IS GIVEN BY THE RATIO OF THE CHANGE IN CONCENTRATION AND THE TIME

ELAPSED

$$\text{rate} = \frac{[P]_2 - [P]_1}{t_2 - t_1} = \frac{\Delta[P]}{\Delta t} > 0 \quad (2)$$

THE UNITS OF THE RATE ARE ALWAYS $M s^{-1}$

FOR THE REACTANTS WE HAVE

$$\text{rate} = - \frac{\Delta[A]}{\Delta t} > 0 \quad (3)$$

THUS THE RATE OF A RXN IS ALWAYS

POSITIVE. PHYSICALLY, IT IS THE NUMBER

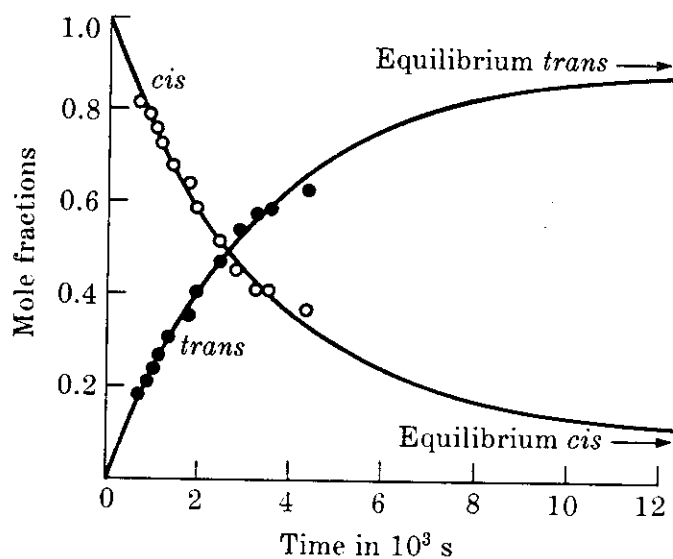
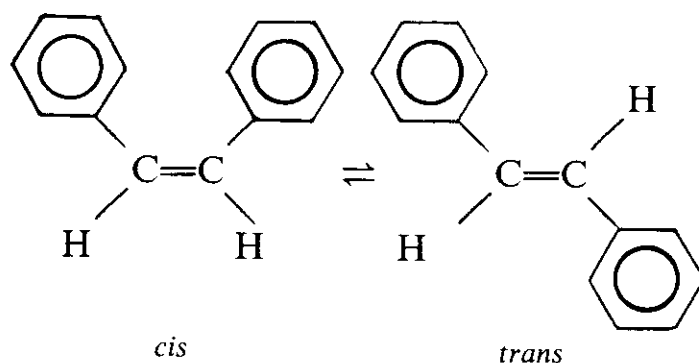


Fig. 9.1 Experimental results for $cis \rightleftharpoons trans$ isomerization of the stilbenes. The points are for various total pressures and surface areas for the gas-phase reaction at 301°C . The curves are calculated assuming no side reactions. (Data from G. B. Kistiakowsky and W. R. Smith, Kinetics of thermal cis - $trans$ isomerism. III, *Journal of the American Chemical Society*, **56**, 638, 1934.)

with the fit to these data that we obtained from an integrated rate law. The points were measured for a particularly simple reaction, the **isomerization** of two structurally related compounds. Their older names are stilbene and isostilbene, but their systematic names are *trans*-1,2-diphenylethene and *cis*-1,2-diphenylethene, *trans* and *cis* $\text{C}_6\text{H}_5\text{CH}=\text{CHC}_6\text{H}_5$. The reaction is



where the reaction involves a rotation of two groups around a double bond that accomplishes the isomerization. At room temperature this reaction is so slow that both the *cis* and *trans* isomers can be prepared and stored free of each other. For the data shown in Fig. 9.1 obtained by G. B. Kistiakowsky and W. R. Smith, a sample of the *cis* isomer was quickly vaporized into a bulb at 301°C and held at that temperature. Then the gas sample was cooled back to room temperature. Conversion to the *trans* isomer was ascertained by determining the melting point of the product. This is a very simple experiment typical of many reaction-rate measurements.

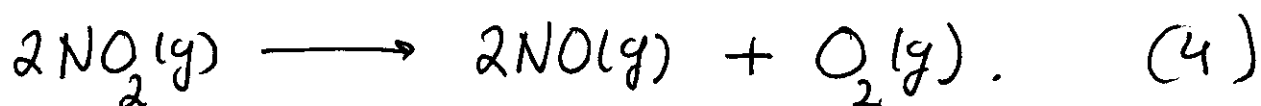
Table 13-1 Concentration of $\text{N}_2\text{O}_5(\text{g})$, $\text{NO}_2(\text{g})$, and $\text{O}_2(\text{g})$ as a function of time at 45°C for an initial concentration of $[\text{N}_2\text{O}_5]_0 = 1.24 \times 10^{-2} \text{ M}$ in the reaction $\text{N}_2\text{O}_5(\text{g}) \rightarrow 2\text{NO}_2(\text{g}) + 1/2\text{O}_2(\text{g})$

t/min	$[\text{N}_2\text{O}_5]/\text{M}$	$[\text{NO}_2]/\text{M}$	$[\text{O}_2]/\text{M}$
0	1.24×10^{-2}	0	0
10	0.92×10^{-2}	0.64×10^{-2}	0.16×10^{-2}
20	0.68×10^{-2}	1.12×10^{-2}	0.28×10^{-2}
30	0.50×10^{-2}	1.48×10^{-2}	0.37×10^{-2}
40	0.37×10^{-2}	1.74×10^{-2}	0.44×10^{-2}
50	0.28×10^{-2}	1.92×10^{-2}	0.48×10^{-2}
60	0.20×10^{-2}	2.08×10^{-2}	0.52×10^{-2}
70	0.15×10^{-2}	2.18×10^{-2}	0.55×10^{-2}
80	0.11×10^{-2}	2.26×10^{-2}	0.57×10^{-2}
90	0.08×10^{-2}	2.32×10^{-2}	0.58×10^{-2}
100	0.06×10^{-2}	2.36×10^{-2}	0.59×10^{-2}

The rate of this reaction can be determined by measuring the increase in the intensity of the brown color of NO_2 in the reaction mixture as a function of time. The concentration of NO_2 is directly proportional to the intensity of the brown color.

OF REACTIVE EVENTS PER UNIT OF TIME.

FOR EXAMPLE, LET US CONSIDER THE DECOMPOSITION OF DINITROGEN PENTOXIDE, WHICH HAS FOLLOWING OVERALL CHEMICAL REACTION



FOR THIS CASE

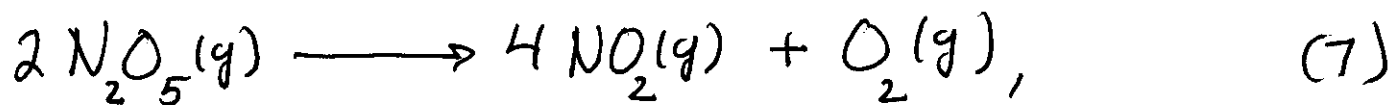
$$\frac{\Delta[\text{NO}]}{\Delta t} = -\frac{\Delta[\text{NO}_2]}{\Delta t} = \frac{2\Delta[\text{O}_2]}{\Delta t} \quad (5)$$

THUS

$$\text{rate} = \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{NO}]}{\Delta t} = -\frac{1}{2} \frac{\Delta[\text{NO}_2]}{\Delta t}. \quad (6)$$

NOTICE THE PRESENCE OF THE STOICHIOMETRIC COEFFICIENTS.

FOR THE OVERALL RXN



THE RATE CAN BE FOLLOWED BY MONITORING THE INCREASE IN THE TOTAL PRESSURE AS A FUNCTION OF TIME. FROM THE FIGURE, WE NOTICE THAT RATE OF THE REACTION IS

$$\text{rate} = -\frac{1}{2} \lim_{\Delta t \rightarrow 0} \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = -\frac{1}{2} \frac{d}{dt}[\text{N}_2\text{O}_5] \quad (8)$$

IN GENERAL, THE RATE OF A REACTION DEPENDS ON THE CONCENTRATIONS OF THE REACTANTS AND PRODUCTS. IN OTHER WORDS, WE CAN EXPRESS THE RATE AS

$$r = k [\text{N}_2\text{O}_5]^x [\text{NO}_2]^y [\text{O}_2]^z \quad (9)$$

WHERE k IS THE RATE CONSTANT OR RATE COEFFICIENT. THE VALUES OF x , y AND z MUST BE DETERMINED EXPERIMENTALLY. WE CAN NOT DEDUCE THEIR VALUES FROM THE OVER ALL CHEMICAL EQUATION

EXPERIMENTALLY
STUDYING THE INITIAL RATES, r_0 , AS A FUNCTION OF INITIAL CONCENTRATIONS, $[\dots]_0$, WE FIND THE FOLLOWING

RELATION

$$r = k [N_2O_5] \quad (10)$$

THE EQUATION THAT GIVES THE DEPENDENCE OF THE RATE OF A REACTION ON THE CONCENTRATIONS OF THE REAGENTS INVOLVED IS CALLED THE RATE LAW OF THE REACTION.

IN THE PREVIOUS CASE

$$x = 1$$

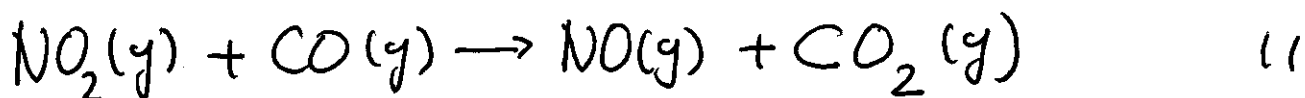
$$y = 0$$

$$z = 0$$

AND

$$k = 1.8 \text{ h}^{-1}.$$

IN THE CASE OF

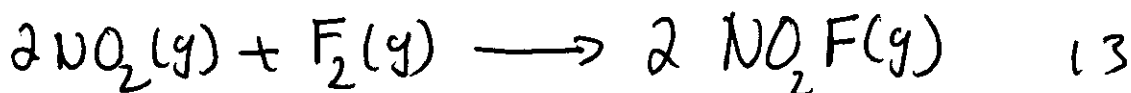


THE RATE LAW IS GIVEN BY

$$r = k[\text{NO}_2]^2 \quad (2)$$

WHICH IS CASE OF A SECOND-ORDER RATE LAW AND k HAS UNITS OF $\text{M}^{-1}\text{S}^{-1}$.

FINALLY FOR THE REACTION

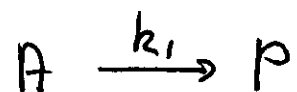


WE FIND

$$r = (1.0 \times 10^{-4} \text{ M}^{-1}\text{S}^{-1}) [\text{NO}_2][\text{F}_2], \quad (4)$$

ELEMENTARY PROCESS

a) ELEM. FIRST ORDER PROCESS



$$r_1 = k_1 [A]$$

b) ELEMENTARY SECOND ORDER PROCESS



$$r_2 = k_2 [A][B]$$

c) ELEMENTARY THIRD ORDER PROCESS



$$r_3 = k_3 [A][B][C]$$

MECHANISMS

A REACTION THAT TAKES PLACE IN A SINGLE MOLECULAR EVENT,

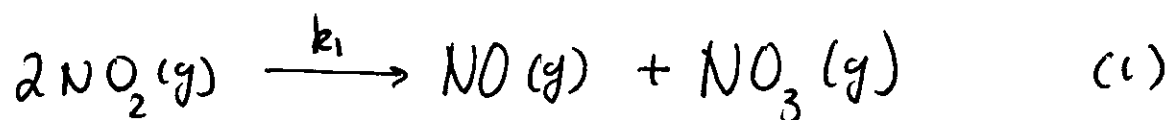
STEP, IS CALLED AN ELEMENTARY

PROCESS, REACTION OR STEP. FOR

EXAMPLE THE FOLLOWING CHEMICAL REACTIONS

(AS FAR AS WE KNOW,

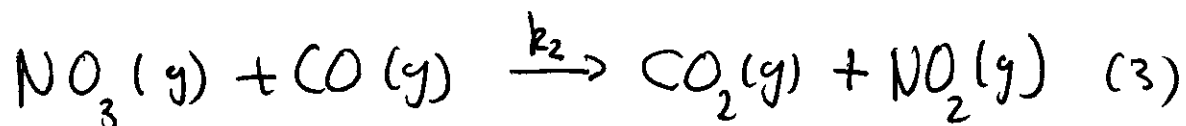
OCCUR \wedge IN ONE STEP



with

$$r = k_1 [\text{NO}_2]^2 \quad (2)$$

also



with

$$r = k_2 [\text{NO}_3][\text{CO}]. \quad (4)$$

THE RATE LAW ASSOCIATED TO AN

ELEMENTARY STEP CAN BE WRITTEN

DIRECTLY FROM THE CHEMICAL EQUATION

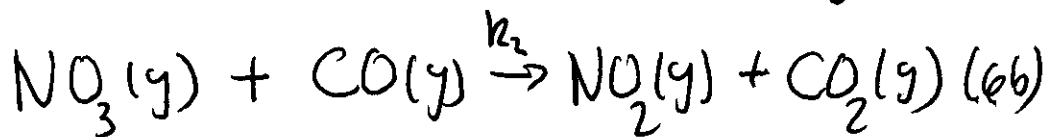
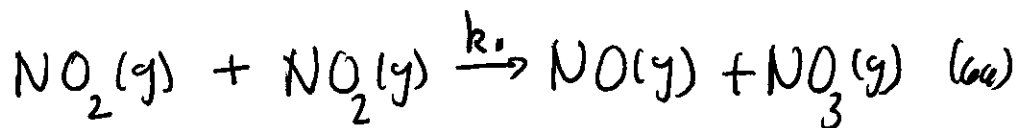
RECALL THAT MOST OF THE CHEMICAL EQUATIONS REPRESENTING CHEMICAL REACTIONS ARE NOT ELEMENTARY (MACROSCOPIC) REACTIONS BUT OVERALL CHEMICAL REACTIONS. MOST OF THE CHEMICAL REACTIONS OCCUR AS A SERIES OF ELEMENTARY PROCESSES (MICROSCOPIC).

FOR EXAMPLE, THE OVERALL REACTION



OCCURS IN TWO STEPS. THESE

STEPS CONSTITUTE THE MECHANISM



THE EXPERIMENTAL DETERMINED RATE LAW IS AN EXAMPLE OF A SECOND ORDER RATE

$$r = k_3 [\text{NO}_2]^2 \quad (7)$$

NOTICE THAT $\text{NO}_3(\text{g})$ IS AN INTERMEDIATE SPECIE AND DOES NOT APPEAR IN THE OVERALL REACTION, EQ(5),

IN GENERAL, IN ANY MECHANISM, THE SLOWEST STEP CONTROLS THE RATE AND IS CALLED THE RATE-DETERMINING STEP. FOR EQ(6), WE FIND THAT THE FIRST STEP IS MUCH SLOWER THAN THE SECOND STEP. THEREFORE THE RATE IS CONTROLLED BY THE FIRST STEP AND

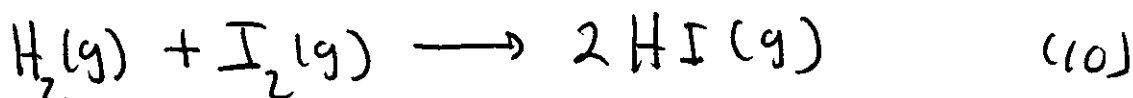
GIVEN BY:

$$r = k_1 [\text{NO}_2]^2 \quad (8)$$

AND

$$k_3 = k_1 \quad (9)$$

THE SIMPLE REACTION

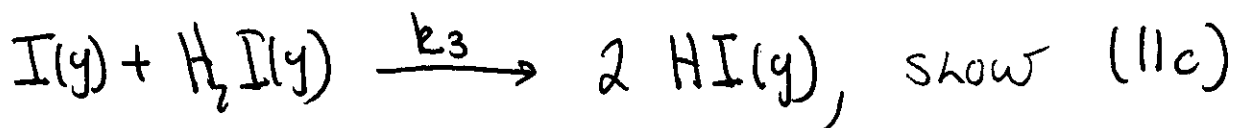
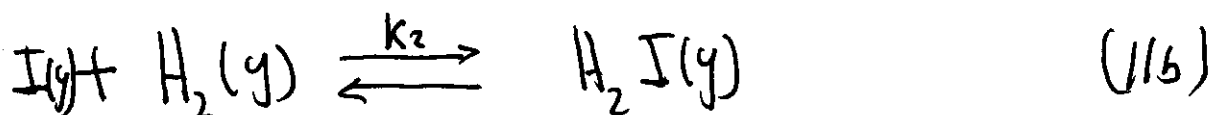
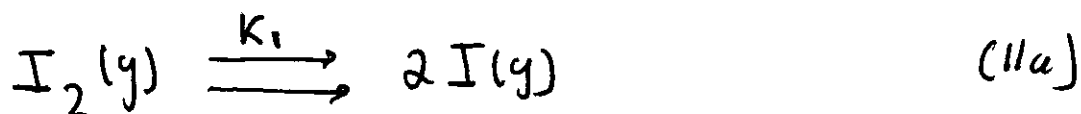


UNTIL RECENTLY, AS
WAS CONSIDERED, AS AN ELEMENTARY

REACTION. PRESENTLY WE KNOW THAT

REACTION DEPICTED BY EQ. (10) FOLLOWS

AS A THREE STEP MECHANISM



WHERE THE THIRD STEP, EQ. (11c), IS
VERY SLOW COMPARED WITH ^{THE FIRST TWO} STEPS.

THUS STEP THREE CONTROLS THE RATE, AND

WE CAN WRITE THE RATE AS

$$r = k_3 [I] [H_2I]. \quad (12)$$

BUT EQ (12) EXPRESSES THE RATE AS A

FUNCTION OF INTERMEDIATES, WHICH

CANNOT BE MEASURED. REMEMBER THAT

THE EXPERIMENTAL RATE LAW RELATES

THE MEASURED RATE OF THE REACTION

WITH THE CONCENTRATIONS OF

REACTANTS AND PRODUCTS BUT NOT

THE INTERMEDIATES.