

LECTURE 30/36

NOV-18-02

CHEMICAL KINETICS

RATE OF A RXN

RATE LAW

RATE CONSTANT

B2-RXN

READ TODAY'S LEE CTC p 445-468

NEXT LEE CTC p 469-492

PS #7

GRAY CH3

p 5, 6, 7, 8, 9, 10, 11, 16

DUE

MONDAY

Nov-25

## CHEMICAL KINETICS

IS THE STUDY OF THE TIME EVOLUTION OF A REACTING SYSTEM. IT CONSIDERS THE RATES AND MECHANISMS ASSOCIATED TO A CHEMICAL REACTION.

REACTIONS ARE SEPARATED INTO HOMOGENEOUS AND HETEROGENEOUS REACTIONS.

IN HOMOGENEOUS RXN. ALL OF THE REAGENTS ARE IN THE SAME PHASE. IN CONTRAST, IN HETEROGENEOUS RXN. WE FIND TWO OR MORE PHASES.

THERMODYNAMICS TELLS US WHICH PROCESSES ARE SPONTANEOUS, BUT TELLS US NOTHING ABOUT THE RATE OF THE PROCESS. SINCE THE RATE DEPENDS ON THE MICROSCOPIC MECHANISM, IT DEPENDS ON THE EXISTENCE OF MOLECULES.

IN ORDER TO UNDERSTAND THE MICROSCOPIC MECHANISM, WE HAVE TO MEASURE HOW FAST REACTIONS PROCEED. NAMELY, WE NEED TO MEASURE THE RATE OF THE REACTION.

MEASURING RATES IMPLIES DIFFERENT TIME SCALES

CONSIDER THE FOLLOWING GENERAL REACTION



THE RATE AT WHICH ANY REACTANT IS CONSUMED IS PROPORTIONAL TO ITS STOICHIOMETRIC COEFFICIENT

$$\frac{\frac{dN_A}{dt}}{\frac{dN_B}{dt}} = \frac{a}{b}$$

OR

$$-\frac{1}{a} \frac{dN_A}{dt} = -\frac{1}{b} \frac{dN_B}{dt} \equiv J$$

$J$  IS THE RATE OF CONVERSION (EXTENSIVE)

$$J = +\frac{1}{c} \frac{dN_E}{dt} = +\frac{1}{f} \frac{dN_F}{dt}$$

$$r \equiv \frac{J}{V} \quad \text{RATE OF REACTION (INTENSIVE)}$$

IN MOST CASES  $V = \text{CONST.}$  OR

$$\frac{dV}{dt} = 0.$$

THEREFORE

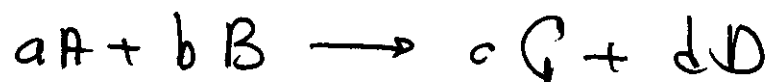
$$-\frac{1}{a} \frac{d[A]}{dt} = r = +\frac{1}{c} \frac{d[E]}{dt}$$

IN GENERAL WE HAVE TO MEASURE THE RATE OF CONSUMPTION OF A REACTANT OR THE RATE OF FORMATION OF A PRODUCT, WHICH DEPEND ON T AND P.

FOR A FIXED T AND P, THE EXPRESSION OF THE RATE AS A FUNCTION OF CONCENTRATIONS IS CALLED THE RATE LAW.

RATE LAWS ARE DETERMINED FROM MEASUREMENTS OF REACTION RATES AND CANNOT BE DETERMINED FROM THE OVERALL REACTION.

IF WE CONSIDER THE FOLLOWING REACTION



THE RATE IS GIVEN BY

$$r = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = +\frac{1}{c} \frac{d[C]}{dt} = +\frac{1}{d} \frac{d[D]}{dt}$$

$r$  IS THE NUMBER OF REACTIVE EVENTS PER UNIT TIME.

THE RATE <sup>LAW</sup> CAN BE WRITTEN AS

$$r = k[A]^x[B]^y[C]^z[D]^w,$$

WHERE  $k$  IS THE RATE CONSTANT OR RATE COEFFICIENT.

NOW WE CAN DEFINE THE ORDER OF THE REACTION

$x + y + z + w = \text{ORDER OF THE REACTION}$

X ORDER WITH RESPECT TO [A]

Y ORDER WITH RESPECT TO [B]

Z ORDER WITH RESPECT TO [C]

W ORDER WITH RESPECT TO [D]

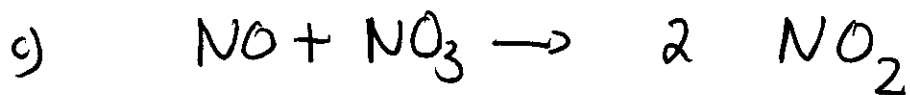
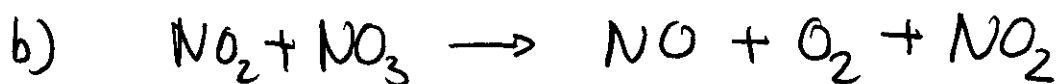
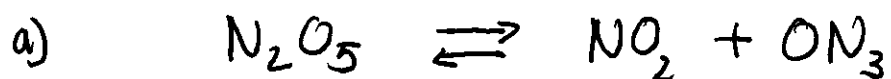
REMEMBER THAT THERE IS NO NECESSARY CONNECTION BETWEEN THE ORDER OF A REACTANT IN THE RATE LAW AND THE STOICHIOMETRIC COEFFICIENT IN THE OVERALL BALANCED CHEMICAL EQUATION

FOR EXAMPLE



$$r = k[\text{N}_2\text{O}_5]$$

THE OVERALL STOICHIOMETRY OF THE REACTION  
DOES NOT TELL US THE MECHANISM



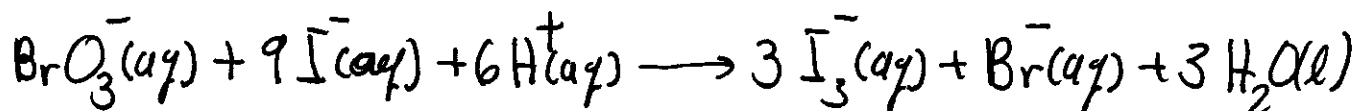


## INITIAL RATES METHOD

THE EXPERIMENTAL METHOD OF INITIAL RATES GIVES THE ORDER OF A REACTION

$$V_0 = k [A]_0^x [B]_0^y [C]_0^z [D]_0^w$$

ONE VARIES THE INITIAL CONCENTRATIONS SYSTEMATICALLY. FOR EXAMPLE, IF DOUBLING  $[A]_0$  DOUBLES THE RATE, THE RATE LAW IS FIRST-ORDER WITH RESPECT TO A. IF DOUBLING  $[A]_0$  QUADROPLES THE RATE, THE ORDER WITH RESPECT TO A IS TWO



	$[\text{I}^-]/\text{M}$	$[\text{BrO}_3^-]/\text{M}$	$[\text{H}^+]_0/\text{M}$	Rate / $\text{M s}^{-1}$
a)	0.1	0.1	0.1	X
b)	0.2	0.2	0.1	4X
c)	0.1	0.2	0.1	2X
d)	0.2	0.2	0.2	4X

FROM a) AND b) FIRST ORDER WITH RESPECT  $\text{BrO}_3^-$

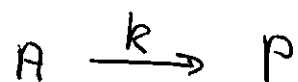
c) AND b) FIRST ORDER WITH RESPECT  $\text{I}^-$

b) AND d) ZEROth ORDER WITH RESPECT  $\text{H}^+$

$$r = k [\text{BrO}_3^-] [\text{I}^-]$$

## UNIMOLECULAR REACTIONS

OR FIRST ORDER REACTIONS.



$$r = k[A]$$

BUT

$$r = - \frac{d[A]}{dt} = \frac{d[P]}{dt}$$

THUS

$$\frac{d[A]}{dt} = -k[A]$$

AFTER INTEGRATION

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

FOR THE PRODUCT

$$\frac{d[P]}{dt} = -k[A] = -k[A]_0 e^{-kt}$$

$$[P] - [P]_0 = [A]_0 [1 - e^{-kt}]$$

$$[P] - [P]_0 = [A]_0 - [A]$$

OR

$$[A]_0 + [P]_0 = [A] + [P]$$

IF WE CONSIDER A

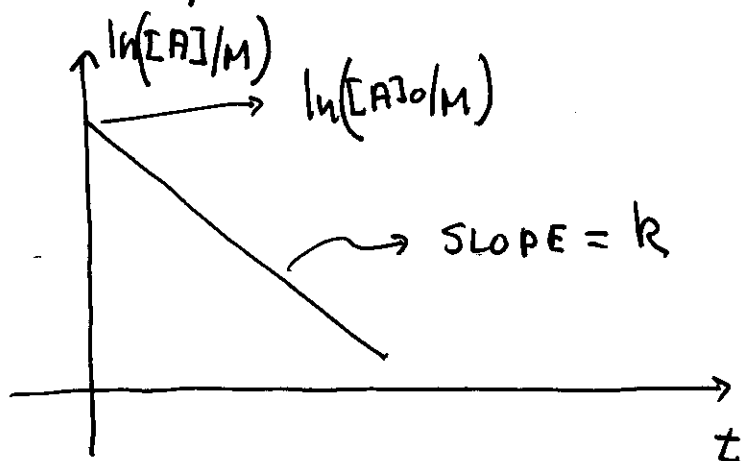
$$[A] = [A]_0 e^{-kt}$$

OR

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

IN A PLOT  $\ln\left(\frac{[A]}{M}\right)$  VS  $t$ , A FIRST ORDER

RXN YIELDS A STRAIGHT LINE



ANOTHER WAY TO CHARACTERIZE A REACTION IS BY CONSIDERING THE TIME AT WHICH THE RXN HAS GONE A "FRACTION  $f$ " TO COMPLETION

$$t \equiv \tau_f$$

SUCH THAT

$$[A(\tau_f)] = f [A]_0.$$

FOR A FIRST ORDER  
RXN

$$[A]_0 e^{-k\tau_f} = f [A]_0$$

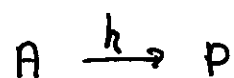
$$-k\tau_f = \ln f$$

$$\tau_f = \frac{\ln(1/f)}{k}$$

$\tau_f$  IS INDEPENDENT OF INITIAL CONCENTRATION  $[A]_0$  FOR FIRST ORDER RXN.

FOR EXAMPLE  $f = 1/2$

ZERO-ORDER

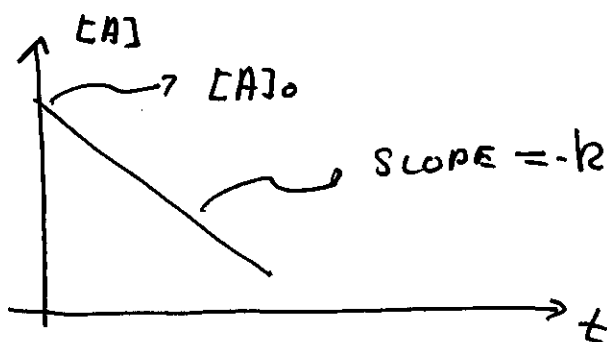


$$r = k$$

$$\frac{d[A]}{dt} = -k$$

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

IN A PLOT  $[A]$  vs  $t$  WE GET A STRAIGHT LINE



$$[A(t_{1/2})] = \frac{1}{2} [A]_0 = [A]_0 - kt_{1/2}$$

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

## BIMOLECULAR REACTIONS

OR SECOND ORDER RATES.



$$r = k[A]^2$$
$$= -\frac{1}{2} \frac{d[A]}{dt}$$

IN THIS CASE WE HAVE THE FOLLOWING DIFFERENTIAL EQUATION

$$\frac{d[A]}{dt} = -2k[A]^2$$

AN EXAMPLE IS THE REACTION



WITH RATE CONSTANT  $k = 0.5 \text{ M}^{-1} \text{ s}^{-1}$

AT  $T = 325^\circ\text{C}$  AND RATE LAW

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

## INTEGRATION OF THE RATE LAW

$$\begin{aligned}\frac{d[A]}{dt} &= -2k[A]^2 \\ &\equiv -k'[A]^2\end{aligned}$$

WHERE WE HAVE DEFINED  $k' = 2k$ .

$$\int \frac{d[A]}{[A]^2} = -\int k' dt$$

$$-\frac{1}{[A]} \Big|_{[A]_0}^{[A]} = -k'(t-t_0)$$

IF WE SET  $t_0 = 0$ , WE GET

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

$$-[A]_0 + [A] = -k'[A]_0 [A] t$$



$$[A] [1 + k' [A]_0 t] = [A]_0$$

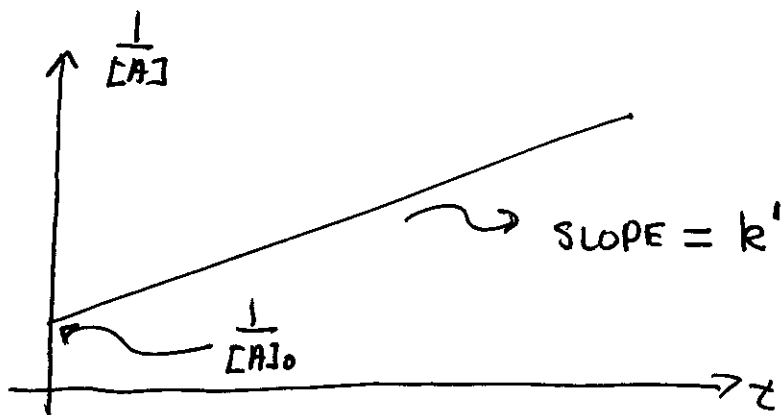
$$[A] = \frac{[A]_0}{1 + k' [A]_0 t}$$

OR

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

A PLOT  $\frac{1}{[A]}$  vs  $t$  YIELDS A STRAIGHT

LINE



## HALF-LIFE

$$\begin{aligned} [A(t_{1/2})] &= \frac{1}{2} [A]_0 \\ &= \frac{[A]_0}{1 + k'[A]_0 t_{1/2}} \end{aligned}$$

OR

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

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

NOTICE

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

$$t_{1/2} = \frac{[A]_0}{\left(-\frac{d[A]}{dt}\right)_{t=0}}$$

