CHAPTER 13
RATES OF REACTION

WE STUDY RATES OF REACTION SO REACTIONS CAN BE MANIPULATED AND CONTROLLED. THERE IS MUCH USEFUL INFORMATION ON MOLECULAR BEHAVIOR ALSO OBTAINED.

DEFINE: KINETICS IS THE STUDY OF RATES OF REACTION

RATES OF REACTION DEPEND ON:

1) CONCENTRATION OF REACTANTS

   MORE REACTANT GENERALLY MEANS FASTER REACTION

2) CONCENTRATION OF CATALYST

   A CATALYST IS A SUBSTANCE THAT INCREASES THE RATE OF REACTION WITHOUT BEING CONSUMED IN THE OVERALL REACTION

3) TEMPERATURE

   USUALLY, HIGHER TEMPERATURE MEANS FASTER REACTION

4) SURFACE AREA FOR SOLID REACTANTS

KEEP STOCHIOMETRY IN MIND:

FOR THE REACTION

$$2X \longrightarrow Y$$

$$\text{RATE} = \frac{\Delta[Y]}{\Delta t} = -\frac{1}{2}\left(\frac{\Delta[X]}{\Delta t}\right)$$

DIVIDE BY COEFFICIENTS

DEFINE: A RATE LAW IS AN EQUATION THAT RELATES THE RATE OF A REACTION TO THE CONCENTRATION OF REACTANTS RAISED TO CERTAIN EXPONENTIAL POWERS

FOR THE REACTION:

$$2\,NO_2\,(g) + F_2\,(g) \longrightarrow 2\,NO_2F\,(g)$$

$$\text{RATE} = K\,[NO_2][F_2]$$

K IS THE RATE CONSTANT

IT EXPRESSES THE PROPORTIONALITY THE RATE AND [ ]

K VARIES WITH TEMPERATURE

UNITS OF K: $K = \frac{\text{RATE}}{[\ ][\ ]} = \frac{\text{MOLES}/(\text{L}\cdot\text{SEC})}{(\text{M}/\text{L})^2}$

$K = \text{L}/(\text{MOLES}\cdot\text{SEC})$

OR $k = \frac{\text{rate}}{[\ ]} = \frac{\text{moles}/\text{l}\cdot\text{sec}}{\text{moles}/\text{l}} = \frac{1}{\text{sec}}$ or per second /s

IN GENERAL:

$$aA + bB \xrightarrow{C} dD + eE$$

$$\text{rate} = k[A]^m[B]^n[C]^p$$

m, n and p MUST BE DETERMINED <u>EXPERIMENTALLY</u> AND BEAR <u>NO</u> <u>RELATIONSHIP</u> TO STOICHIOMETRY

REACTION ORDER

EXPERIMENTALLY DETERMINED EXPONENTS FOR [ ]

THE OVERALL ORDER IS THE SUM OF THE ORDERS FOR EACH REACTANT

EXAMPLE: $2NO_2(g) + 2H_2(g) \longrightarrow N_2(g) + 2H_2O$

THE EXPERIMENTALLY DETERMINED RATE LAW IS

$$RATE = k[NO_2]^2[H_2]$$

THE REACTION IS SECOND ORDER IN NO_2, FIRST ORDER IN H_2 AND THIRD ORDER OVERALL

DETERMINING THE RATE LAW

THE INITIAL RATE METHOD

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

	INITIAL $[N_2O_5]$	INITIAL RATE
①	1×10^{-2} M	4.8×10^{-6} mol/(L·s)
②	2×10^{-2} M	9.6×10^{-6} mol/(L·s)

$$RATE^{①} = k[N_2O_5]^m$$
$$RATE^{②} = k([N_2O_5](2))^m \text{ or } 2^m[N_2O_5]^m$$

ON DOUBLING $[N_2O_5]$, RATE BECOMES 2^m FASTER

m	RATE IS MULTIPLIED BY
-1	1/2
0	1
1	2
2	4

DETERMINE M FROM THE DATA

DEFINE: RATE OF REACTION IS THE AMOUNT OF PRODUC[T] FORMED OR REACTANT CONSUMED PER UNIT TIM[E]

IN ORDER TO BE INDEPENDENT OF THE TOTAL AMOUNT OF REACTING MATERIAL, DEFINE RATE OF REACTION TO BE;

THE INCREASE IN MOLAR CONCENTRATION OF PRODUCT PER UNIT TIME, OR THE DECREASE OF MOLAR CONCENTRATION OF REACTANT PER UNIT TIM[E]

UNITS MOLES PER LITER PER SECOND $m/(L \cdot sec)$

CONSIDER THIS REACTION

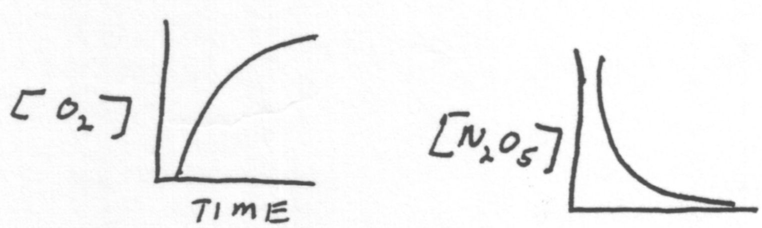
$$2\ N_2O_5\ (g) \longrightarrow 4\ NO_2\ (g) + O_2\ (g)$$

RATE = MOLAR INCREASE IN O_2 PER SECOND

$$= \frac{\Delta [O_2]}{\Delta t}$$

THIS IS THE AVERAGE RATE OVER THE INTERVAL Δ[t]

MAKE A PLOT OF CONCENTRATION VS TIME



NOTICE THAT RATES ARE NEGATIVE FOR REACTANTS

FOR THE REACTION $X \longrightarrow Y$

RATE OF DISAPPEARANCE OF X = $\frac{-\Delta [X]}{\Delta t}$

RATE OF APPEARANCE OF Y = $\frac{\Delta [Y]}{\Delta t}$

IN THIS EXAMPLE, DOUBLING THE CONCENTRATION DOUBLES THE RATE, SO $m = 1$ AND $RATE = k[N_2O_5]$

k CAN BE CALCULATED BY SUBSTITUTING VALUES FOR THE RATE AND $[N_2O_5]$

$$RATE = k[N_2O_5]$$

$$k = \frac{RATE}{[N_2O_5]}$$

$$k = \frac{9.6 \times 10^{-6} \frac{MOL}{L \cdot SEC}}{2.0 \times 10^{-2} \frac{MOL}{L}} = 4.8 \times 10^{-4} \, s^{-1}$$

CONCENTRATION AND REACTION TIME

RATE LAWS ARE DIFFERENTIAL EQUATIONS

INTEGRATED RATE LAWS SHOW THE RELATIONSHIP BETWEEN CONCENTRATION OF REACTANTS OR PRODUCTS AND REACTION TIME

FIRST ORDER REACTIONS $X \rightarrow$ PRODUCT

RATE LAW

$$\text{RATE} = -\frac{\Delta[X]}{\Delta t}$$

RATE LAW

$$\text{RATE} = k[X]$$

FROM THESE EXPRESSIONS (DERIVATION ON PG 476) COMES THE INTEGRATED RATE LAW

$$\ln \frac{[X]_t}{[X]_0} = -kT$$

$[X]_t$ MEANS $[X]$ AT ANY CHOSEN TIME

$[X]_0 = [X]$ AT ANY INITIAL TIME

THIS ALLOWS CALCULATION OF CONCENTRATIONS AT ANY TIME

HALF-LIFE - VERY USEFUL IDEA!

$t_{1/2}$ = TIME FOR 50% REACTION → SO $\frac{[X]_t}{[X]_0} = \frac{1}{2}$

$$\ln \tfrac{1}{2} = 0.693 = -kT$$

SO, $t_{1/2} = \frac{0.693}{k}$ FOR FIRST ORDER REACTIONS

USE THE HALF-LIFE TO ESTIMATE ANSWERS TO CONC/TIME PROBLEMS

CALCULATE $t_{1/2}$

FOR A REACTION WITH RATE CONSTANT $5.36 \times 10^{-4}\ s^{-1}$ AT 700°C

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{5.36 \times 10^{-4}\ s^{-1}} = 1.29 \times 10^{3}\ \text{SEC}$$

EXAMPLE 5

N_2O_5 DECOMPOSES WITH A FIRST ORDER RATE CONSTANT OF 4.81×10^{-4}/SEC

IF THE INITIAL CONCENTRATION IS 1.65×10^{-2} M

1) WHAT IS THE CONCENTRATION AFTER 825 SEC?

2) HOW LONG WOULD IT TAKE FOR $[N_2O_5]$ TO REACH 1.00×10^{-2} M

GET THE HALF LIFE (STRONGLY SUGGESTED)

$$t_{1/2} = \frac{0.693}{4.81 \times 10^{-4}/\text{SEC}} = 1440 \text{ SEC}$$

1) $[N_2O_5]$ AFTER 825 SEC

825 SEC IS LESS THAN 1 HALF LIFE, SO LESS THAN HALF OF N_2O_5 HAS REACTED

$$\ln \frac{[N_2O_5]}{1.65 \times 10^{-2} M} = -4.81 \times 10^{-4} \text{ SEC}^{-1} \times 825 \text{ SEC}$$

$$\ln \frac{[N_2O_5]}{1.65 \times 10^{-2} M} = -0.397$$

NOW TAKE ANTI LOG OF BOTH SIDES

$$\frac{[N_2O_5]}{1.65 \times 10^{-2} M} = 0.673$$

$$[N_2O_5] = 1.65 \times 10^{-2} M \times 0.673 = 1.11 \times 10^{-2} M$$

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2) TO REACH 1.00×10^{-2} M MUST BE LESS THAN 1 HALFLIFE

$$\ln \frac{[N_2O_5]_t}{[N_2O_5]_0} = -kt \quad \text{so} \quad \ln \frac{1.00 \times 10^{-2} M}{1.65 \times 10^{-2} M} = -4.81 \times 10^{-4} s^{-1} \times t$$

$$t = \frac{0.501}{4.81 \times 10^{-4} s^{-1}} = 1040 \text{ s}$$