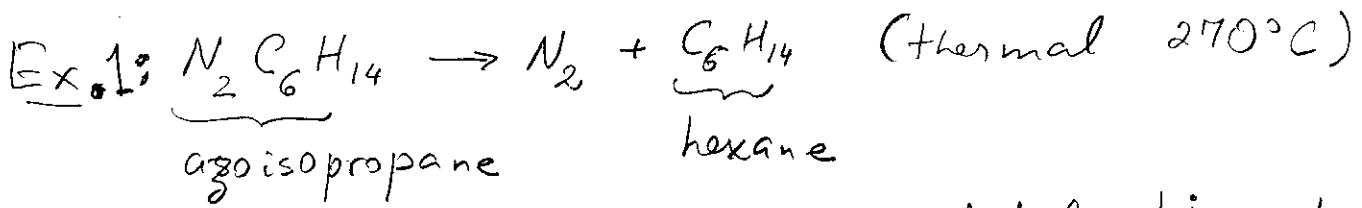


Chemical kinetics (reactions).

I. First order: $A \xrightarrow{k_1} \text{products}$



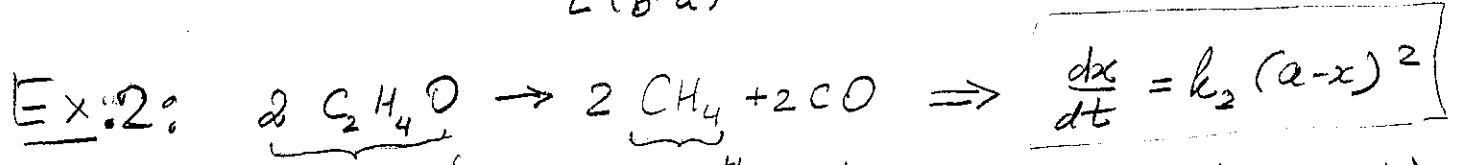
$x(t)$ - amount/concentration reacted by time t
 a - initial amount

$\Rightarrow \boxed{\frac{dx}{dt} = k_1 (a-x)}$ $\Rightarrow \begin{cases} \text{sol: } x = a(1 - e^{-k_1 t}) \\ \text{rate: } k_1 = \frac{\ln(1-x/a)}{t} \end{cases}$

II. Second order: $A + B \xrightarrow{k_2} \text{products}$
 $(a-x)(b-x); x(t) = \# \text{ reacted}$

$\boxed{\frac{dx}{dt} = k_2 (a-x)(b-x)}$ $\Rightarrow \text{sol. } x(t) = \dots$

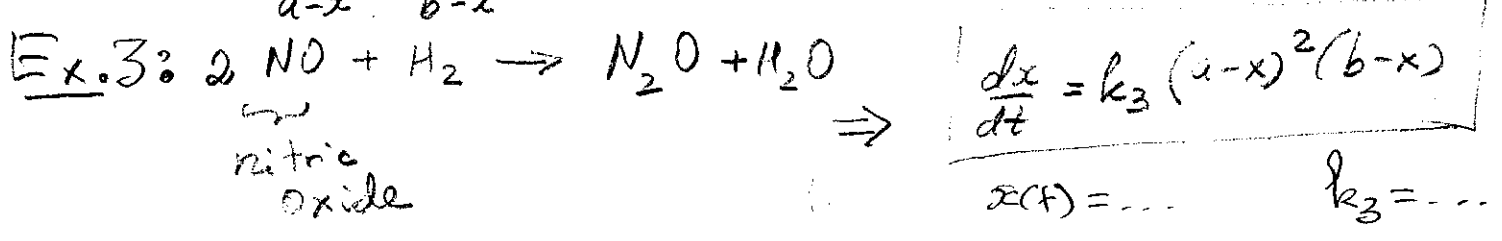
$\Rightarrow \text{rate } k_2 = \frac{1}{t(b-a)} \ln\left(\frac{a-x}{b-x}\right)$



sol: $x(t) = \dots$ Rate: $k_2 = \frac{1}{t} \left(\frac{1}{a-x} - \frac{1}{a} \right)$

III. Third: $A + B + C \rightarrow \text{products}$
 $a-x \quad b-x \quad c-x$

$\Rightarrow \boxed{\frac{dx}{dt} = k_3 (a-x)(b-x)(c-x)}$ $\Rightarrow \dots$



From this equation we find $x = P - P_i$, and on substitution of this value for x into $P_A = P_i - x$, we get

$$\begin{aligned} P_A &= P_i - x \\ &= P_i - (P - P_i) \\ &= 2P_i - P \end{aligned}$$

Since a in Eq. (6) is proportional to P_i , and $(a - x)$ to P_A , the expression for k_1 is

$$\begin{aligned} k_1 &= \frac{2.303}{t} \log_{10} \frac{P_i}{P_A} \\ &= \frac{2.303}{t} \log_{10} \frac{P_i}{2P_i - P} \end{aligned}$$

The constants thus calculated from experimental data for a typical run at 270°C are shown in Table 16-2. Column 1 gives the time in seconds, column 2 the total pressure P , and column 3 the values of k_1 . P_i is the pressure of the system at $t = 0$, which for the experiment in question was 35.15 mm Hg. Since k_1 exhibits satisfactory constancy, the decomposition of azoisopropane must be a first order reaction.

Table 16-2
DECOMPOSITION OF AZOISOPROPANE AT 270°C

t (sec)	P (mm Hg)	k_1 (sec ⁻¹)
0	35.15	—
180	46.30	2.12×10^{-3}
360	53.90	2.11
540	58.85	2.07
720	62.20	2.03
1020	65.55	1.96
		Average = 2.06×10^{-3}

An example of a first order reaction in solution is the decomposition of benzene diazonium chloride, $C_6H_5N=NCl$, in water. This compound, known only in solution, dissociates readily on heating to liberate nitrogen. As the nitrogen all comes from the compound, the volume of it liberated may be used as a measure of the decrease in concentration of the diazo salt. Cain and Nicoll utilized this fact in their kinetic study of this reaction. A

Again, when the pressure of acetaldehyde drops by x , the pressures of methane and carbon monoxide must each increase by x . We obtain thus for the total pressure of the system, P ,

$$\begin{aligned} P &= P_{\text{CH}_3\text{CHO}} + P_{\text{CH}_4} + P_{\text{CO}} \\ &= (P_i - x) + x + x \\ &= P_i + x \end{aligned}$$

from which x follows as $x = P - P_i$. Further, since $P_i - x$ is proportional to $(a - x)$ and P_i to a , substitution of these into Eq. (16) yields for k_2

$$\begin{aligned} k_2 &= \frac{1}{at} \left(\frac{x}{a - x} \right) \\ &= \frac{1}{P_i t} \left(\frac{x}{P_i - x} \right) \end{aligned}$$

In Table 16-3 are given data obtained by Hinshelwood and Hutchison for this reaction during an experiment at 518°C with an initial pressure of acetaldehyde equal to 363 mm Hg. The good constancy of k_2 confirms both the reaction order and the correctness of the formulation.

Among the many reactions in solution which are of second order may be mentioned the saponifications of various esters by bases, the conversion



Table 16-3
THERMAL DECOMPOSITION OF ACETALDEHYDE AT 518°C
($P_i = 363$ mm Hg)

t (sec)	$x = P - P_i$ (mm Hg)	$k_2 = \frac{1}{P_i t} \left(\frac{x}{P_i - x} \right)$
42	34	6.79×10^{-6}
73	54	6.59
105	74	6.71
190	114	6.64
242	134	6.66
310	154	6.55
384	174	6.61
480	194	6.59
665	124	6.68
840	244	6.72
1070	264	6.86
1440	284	6.88
Average = $6.69 \times 10^{-6} \text{ mm}^{-1} \text{ sec}^{-1}$		

and on integration

$$k_3 = \frac{1}{2t} \left[\frac{1}{(a-x)^2} - \frac{1}{a^2} \right] \quad (29)$$

$$= \frac{1}{2ta^2} \left[\frac{x(2a-x)}{(a-x)^2} \right] \quad (30)$$

From (30) the period of half-life of a third order reaction follows as

$$t_{1/2} = \frac{3}{2k_3a^2} \quad (31)$$

and hence for such a reaction $t_{1/2}$ is inversely proportional to a^2 .

Only five homogeneous gas reactions are definitely known to be third order, and every one of these involves the interaction of nitric oxide with either chlorine, bromine, oxygen, hydrogen, or heavy hydrogen. As an example of one of these may be taken the work of Hinshelwood and Green on the reaction



For hydrogen present in excess, k_3 for this reaction should be given by Eq. (26). Now, at a time t' when the nitric oxide is half consumed $2x = a/2$, and this equation becomes

$$k_3 = \frac{1}{t'(2b-a)^2} \left[\frac{2b-a}{a} + \ln \frac{2b}{4b-a} \right] \quad (32)$$

This is the relation Hinshelwood and Green used to evaluate k_3 from various initial pressures of nitric oxide ($a = P_{\text{NO}}$) and hydrogen ($b = P_{\text{H}_2}$), and the observed times, t' , of half decomposition of nitric oxide. Their results, given in Table 16-5, yield fairly satisfactory constants, and indicate that the reduction of nitric oxide by hydrogen is a third order reaction.

Table 16-5
KINETICS OF THE REACTION $2\text{NO} + \text{H}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$ AT 826°C

P_{NO} (mm Hg)	P_{H_2} (mm Hg)	t' (sec)	$k_3 \times 10^7$
110	316	270	1.19
152	404	204	0.91
359	400	89	1.12
144	323.5	227	1.10
181	209.5	264	1.39
370	376	92	1.17
300	404	100	1.09
232	313	152	1.19