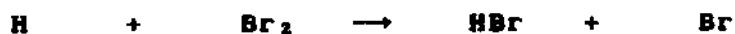


A single reactive collision between reactant molecule is called an elementary process or reaction step. The theories of how such processes occur, and what determines their rates are the subjects of next term's course. However, most reactions do not take place at a single reactive encounter. Instead, they involve many elementary steps. Such 'complex' reactions are the subject of this lecture course.

From the chemists' viewpoint, one of the most interesting aspects of the study of rates is the insight afforded into the mechanism of reaction. We shall be concerned with the interpretation of the kinetics of complex reactions in terms of the elementary steps of which they are made up. We shall also explore what information can be obtained from the overall kinetics of complex reaction systems. We shall be dealing with several processes that are of practical importance such as atmospheric chemistry, combustion, and explosions.

Dependence of rate of reaction on concentrations, temperature, etc., is more involved than for elementary reactions. For example,



has a rate proportional to [H] and to [Br<sub>2</sub>].

$$\text{rate} \propto [\text{H}][\text{Br}_2]$$

The reaction is second order and bimolecular. On the other hand,

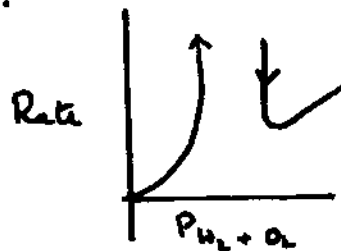


has rate proportional to  $[H_2][Br_2]^{1/2}$ , and the rate decreases as  $[HBr]$  builds up during the reaction.

$$\text{rate} = \frac{a[H_2][Br_2]^{1/2}}{1 + b[HBr]/[Br_2]}$$

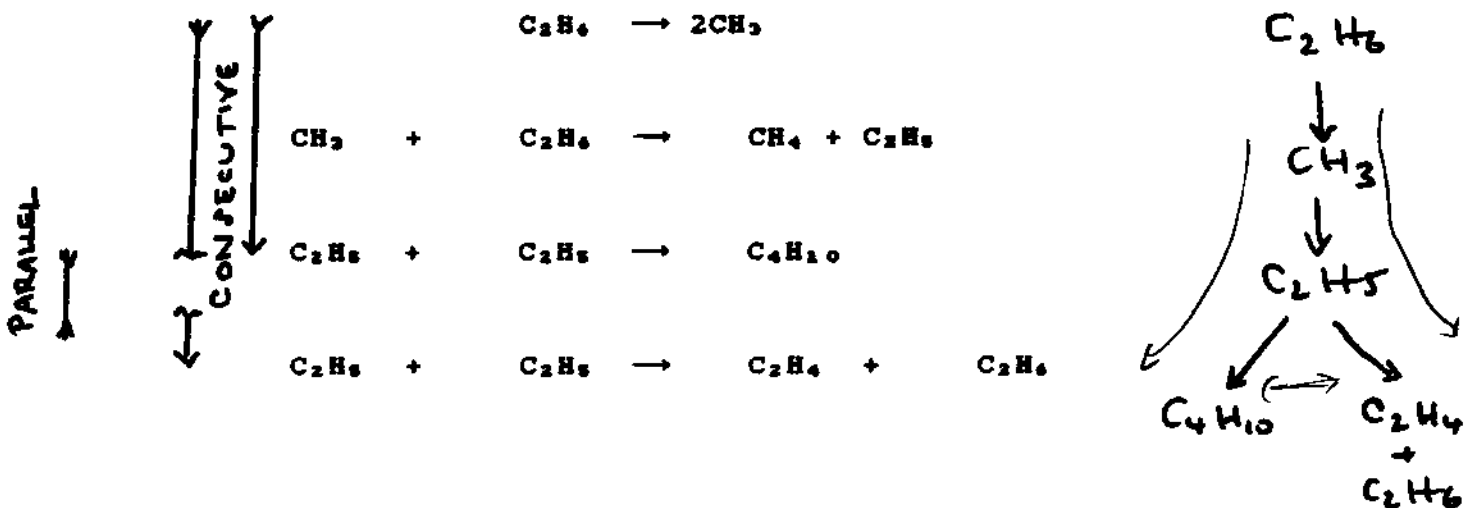
This result is NOT consistent with a simple bimolecular reaction. In general, the order and molecularity differ, and the order may be a function of concentration, in complex reactions.

Sometimes the function may be a very funny one indeed, as is observed in the  $H_2/O_2$  reaction:



09.08

Multistep processes involving reactive intermediates are characterized by two types of process involving the intermediate : parallel (side) and series (consecutive). Illustrate by simplified version of ethane pyrolysis:



Reactive intermediates here are the two free radicals  $\text{CH}_3$  and  $\text{C}_2\text{H}_5$ .

Types of intermediates: atoms, radicals, ions, energy-rich species. Highly reactive, so cannot keep in bottles or cylinders, but not necessarily unstable: note importance of collisions.

( Compare  $\text{CH}_4$ ,  $\text{CH}_3$ ,  $\text{CH}_4^+$ ,  $\text{CH}_4^*$  (from  $\text{H} + \text{CH}_3$ )

[nb stabilization of  $\text{CH}_4^*$  by M to obtain product]

or  $\text{Ar}$ ,  $\text{Ar}_2^+$ ,  $\text{Ar}_2$

Point is binding energy cf. internal (perhaps thermal) energy.

)  
0913

Low concentrations of intermediates in general because of high reactivity. Techniques for study of intermediates include mass spectrometry, ESR, and optical spectroscopy (especially, because of specificity). Some methods will be touched on as we discuss specific examples.

Appropriate to devote rest of this lecture to a discussion of the elementary reactions of reactive intermediates that make up the multi-step mechanisms that are the underlying theme of the lecture course.

Modern chemical kinetics emphasizes study of these individual elementary steps: requires methods for a) generation of intermediate directly, b) measurement of its concentration, and c) achievement of a) and b) on a short (and measured) time scale.

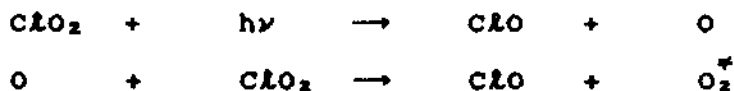
Two very important techniques to provide these facilities

- flash photolysis
- flow systems (often with electric discharges)

Propose to show some demonstrations concerning the flow methods today. Flash demonstrations fall more naturally into next week's lecture, so first explain principles of flash photolysis briefly.

Flash photolysis of ClO<sub>2</sub>:

0915



SLIDE F1 slides: apparatus

SLIDE F2 spectra

TV Flow technique: distance  $\longleftrightarrow$  time

0920

TV Addition of reactants at jets, follow concentration of reactants as a function of time.

Make reaction intermediates such as atoms by passing electric discharge through parent molecular gas

e.g.: O, H, N

TV OFF

Other intermediates by chemical reaction

e.g. OH from H+NO<sub>2</sub>; ClO from Cl+O<sub>3</sub>; NO<sub>2</sub> from F + HNO<sub>2</sub>

First method of detection to demonstrate: chemiluminescence (because you can see it!)

FLUORESCENCE

DEMONSTRATIONS But what is this about chemiluminescence? First fluorescence!

UV OFF

Now chemiluminescence: "firefly"

CHEMILUMINESCENCE DEMONSTRATIONS

Concentrations of atoms by chemiluminescence

BOARD UV ON

(a) 0 (i) relative, NO

FLOW DEMONSTRATIONS

[note NO regeneration]

inc. Decay with xs NO  
Decay with just O<sub>2</sub>  
Flow velocity  
(b) H

[decay with xs. NO; just with O<sub>2</sub>]

(ii) absolute, NO<sub>2</sub> — titration

(c) N

inc. yellow titration 2-3 colour

Another important technique for

0940

TV ON

detection: resonance absorption and fluorescence

VAC PUMP OFF

BRING IN Na LAMP

Basis: resonant energy levels

Specificity: only atom of right kind

TV 'H-atom lamp'

Source: discharge lamp

RES. ABS. EXPTS

Demonstration of absorption: Na and Li

TV cross S1 cross

Even greater sensitivity: observe fluorescence

S2 Ly- $\alpha$  spectrum

Vacuum ultraviolet for O, H, etc. → detectors such as channeltron

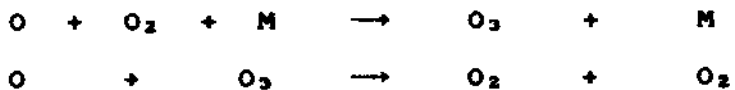
TV channeltron ('volunteer')

what are the measurements for?

One area: atmospheric chemistry

0948

Just one example: reactions such as



make and destroy ozone (explain importance). Can thus measure rates in lab.

Also use the resonance fluorescence method to measure [O] in situ.

SL 956  
951  
952  
953  
962

Balloons!

Winch

0955

\*\*\*\*\*  
LECTURE SYNOPSIS  
\*\*\*\*\*

1. General

2 x red boxes from stores for moving stuff  
glassblowing torch, knife, oxygen  
screwdrivers, pliers, black tape, tissue, handouts

Fluorescence

blackboard strip lamp + mounting  
2 x 125 watt or 80 watt 'Blacklamp' UVs with shields  
fluorescent chalks  
fluorescent cloths and clothes - concealed on RPW

Chemiluminescence

Cyalume light sticks  
Knife or scalpel  
'Firefly'

4. Flow

flow apparatus  
flow pump  
microwave supply  
    Tesla or starter  
    cavity  
    air tube for cooling  
cylinders: WITH KEYS  
    oxygen  
    nitrogen ('white spot': NOT refilled)  
    black cloth to cover discharge

5. Televisions

camera  
4 x monitors wired (not too tight)  
suitable plug board for all to be controlled from one switch

6. Resonance Fluorescence

Na lamp + control gear  
Bunsen burner  
NaCl, LiCl, spatulae, glass rods  
channeltron  
"observation region" ("cross")  
gas resonance lamp

7. Slides

2 x Flash photolysis: F1, F2  
2 x Resonance fluorescence: S1, S2  
4 x Balloons: G56, G51, G52, G53  
1 x Winch G62 [-RG52]

UV ON - WARM UP

SLIDE F1 Flash photolysis: apparatus  
SLIDE F2 : ClO results

TV Flow tube apparatus Scan Left to Right (pump end)  
Close-up of jets

TVs OFF ('chemiluminescence')  
Fluorescence: chalks  
: cloths/underwear

UV OFF  
Chemiluminescence: lightsticks into 'firefly'

UV ON (Board) for next part of lecture  
Gas Phase chemiluminescence: atoms

For oxygen atom experiments, use N<sub>2</sub> carrier and titrate out yellow N<sub>2</sub> afterglow with O<sub>2</sub> through discharge: allows higher pressures (and better flow velocities) without excessive decay of O. Can use NO<sub>2</sub> in first injector even for 'NO' experiments: saves changing over.

(i) O + NO  
include decay with excess NO  
note decay just with O<sub>2</sub>  
flow velocity demonstration

(ii) O + NO<sub>2</sub>  
titration

(iii) N + N  
include yellow  
titration with NO  
2 & 3 colour  
'triple colour flow speed'

TVs ON ('Resonance absorption and fluorescence')  
PUMPS OFF  
Na lamp (warmed up) from side room

Resonance absorption experiments: Na and Li

TV Cell ('Cross')  
SLIDE S1 ('Cross')

TV Lamp  
SLIDE S2 Spectrum Lyman- $\alpha$

TV Channeltron (held by 'volunteer')

('Atmospheric studies')

SLIDE G56 Balloon tethered  
SLIDE G51 Balloon rising  
SLIDE G52 Payload cable  
SLIDE G53 Balloon against sunset  
SLIDE G62 Winch [Slide is also RG52]



KINETICS OF MULTISTEP REACTIONS - II

0905

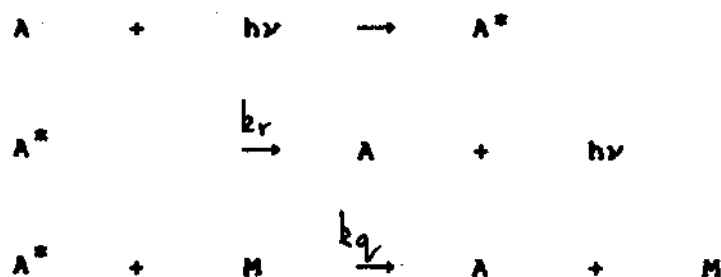
Last week we examined methods for studying elementary reaction steps. Now we wish to consider the kinetics of systems in which many consecutive and parallel reactions are occurring.

Must first find out how to analyse the kinetics of multistep reactions. Let us illustrate the procedure by discussing the quenching of fluorescence.

The chemical equations involved in the process are

Equation for using fluorescence quenching

Two processes essential  
↓  
hv, in addition  
↓  
quenching



Rate =  $I_{abs}$

DEMOS : QUININE/SALT EXPTS

and the appropriate (differential) rate equations are :

0910

Rate equations

(write out)

(both for  $A^*$  and for  $A$ )

The difficulty lies in the simultaneous differential equations: often they won't integrate analytically; these days we can use computers to integrate numerically, but we may lose chemical insight.

The alternative procedure is to assume that because of their high reactivity, the concentrations of intermediates are constant (or, at least change slowly) during the reaction.

That is, we assume that the intermediates are in a 'steady' or 'stationary' state - they are being created and destroyed at the same rate.

\* Point about high reactivity is that destruction can keep up with formation : bath analogy :: leads to conclusion that as concentrations are low.

[Essential that loss rate increases with intermediate

0915

\* For a reaction carried out under constant conditions (eg. a photochemical process with steady illumination)

NOT an equilibrium

concentration of course, otherwise steady state cannot be attained]. We shall return to the 'criteria' <sup>later</sup> in ~~next~~ lecture - first we see here how the hypothesis is applied in practice : in form  $d[X]/dt = 0$  for intermediate X.

A 'definition' of SS is in front of H/O

$$I_{fl} = k_r [A^*] = \frac{k_r I_{abs}}{k_r + k_q [M]}$$

(Derive for Fluorescence Quenching scheme).

(Stern-Volmer Plot)

$$\frac{1}{I_{fl}} = \frac{1}{I_{abs}} \left( 1 + \frac{k_q [M]}{k_r} \right) \longrightarrow \frac{\text{slope}}{\text{intercept}} = \frac{k_q}{k_r}$$

Before going any further, we must examine the type of information that can be obtained from stationary and non-stationary systems :: 'Suspect' we will obtain ratios of rate constants, as we did here, because it is competition that establishes ss.

The only way to obtain the individual rate constants is to perform experiments under non-stationary conditions. Illustrate this very important point with reference again to the fluorescence quenching system. As it happens, the equations we have written can be solved analytically. What happens after the exciting radiation is shut off?

0920

of 'Pam Photolysis'

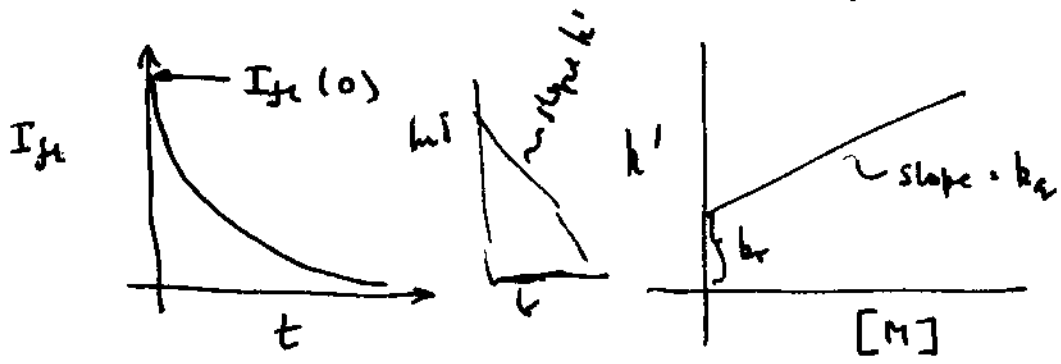
### DEMOS WITH FLASH LAMP (Experiment)

The  $I_{abs}$  term in the differential equation is zero, and the mathematical solution trivial

(Derive on Board)

(Plots of  $I_{fl}$  vs.  $t$  and  $k'$  vs  $[M]$ )

$$I_{fl}(t) = I_{fl}(0) \exp(-[k_r + k_q [M]]t) = I_{fl}(0) \exp(-k't)$$

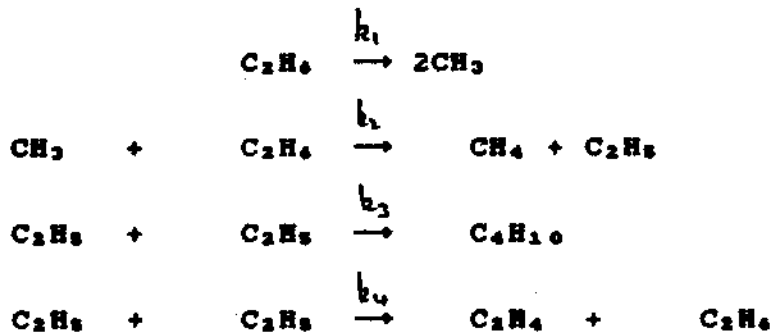


0930

Hence obtain  $k_r$  and  $k_q$  separately

OMIT 1998

Let us examine application of the SS treatment to another reaction system: the ethane pyrolysis that we started with last week



The differential kinetic equations for the intermediates  $\text{CH}_3$  and  $\text{C}_2\text{H}_5$  are

$$\frac{d[\text{CH}_3]}{dt} = 2k_1[\text{C}_2\text{H}_6] - k_2[\text{CH}_3][\text{C}_2\text{H}_6]$$

and

$$\frac{d[\text{C}_2\text{H}_5]}{dt} = k_2[\text{CH}_3][\text{C}_2\text{H}_6] - k_3[\text{C}_2\text{H}_5]^2 - k_4[\text{C}_2\text{H}_5]^2$$

Set these equations to zero in the steady state treatment

$$\begin{aligned}
 [\text{CH}_3] &= \frac{2k_1}{k_2} ; & [\text{C}_2\text{H}_5] &= \left( \frac{k_2[\text{CH}_3][\text{C}_2\text{H}_6]}{k_3 + k_4} \right)^{\frac{1}{2}} \\
 & & &= \left( \frac{2k_1[\text{C}_2\text{H}_6]}{k_3 + k_4} \right)^{\frac{1}{2}}
 \end{aligned}$$

so that, for example

$$\frac{d[\text{C}_4\text{H}_{10}]}{dt} = k_3[\text{C}_2\text{H}_5]^2 = \frac{2k_1k_3[\text{C}_2\text{H}_6]}{k_3 + k_4}$$

Reaction is first order, but certainly not unimolecular.

Now we must examine the circumstances under which the SS is valid. We use an extremely simple two step example

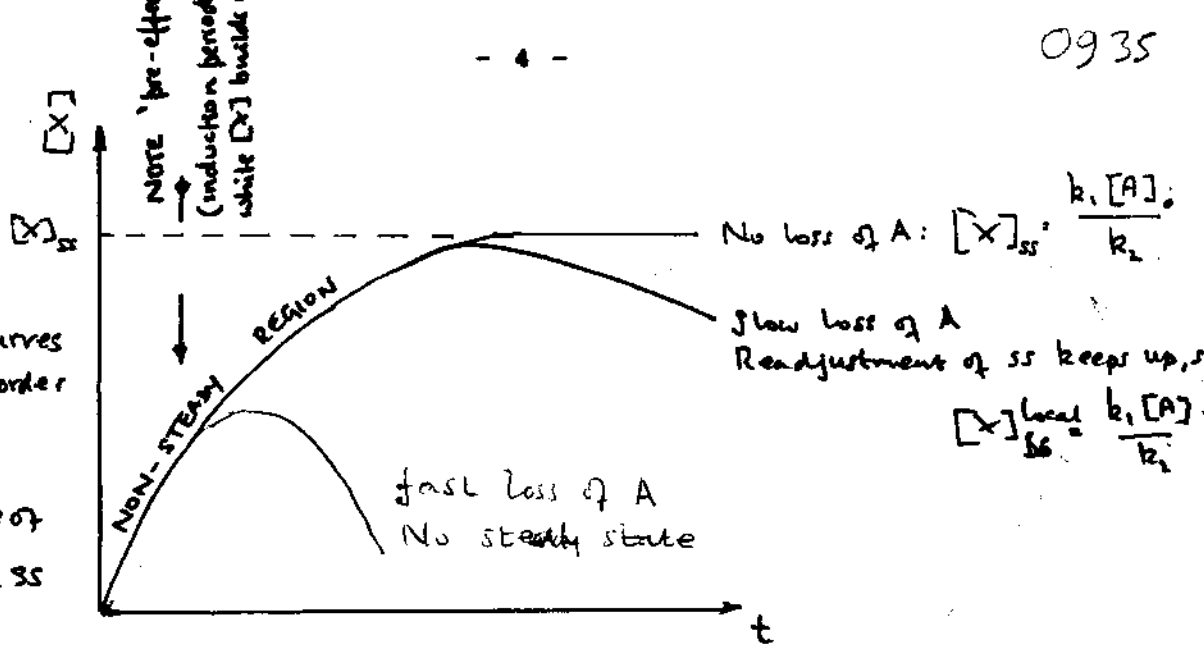


COMPUTER DEMONSTRATIONS HERE : EXPLAIN COMPUTER INTEGRATION

write out first in this form, then put zeros in a different column.

n.b. Handout deals with same problem, and has a 'definition' of the SS

0930



- Draw these three curves as separate items in order
- ① - : SS depends on whether  $k_2 \gg k_1$
  - ② - : Local SS if rate of loss of A < rate of establishment of SS
  - ③ - : No SS

Exact differential equations

①  $-\frac{d[A]}{dt} = k_1[A]$

Steady state  
slow loss of A No rapid loss of A Slow

$[A] = [A]_0$

②  $\frac{d[X]}{dt} = k_1[A] - k_2[X]$

$[X]_{ss} = \frac{k_1[A]_0}{k_2}$

$[X]_{ss}^{local} = \frac{k_1[A]}{k_2}$

For the non-steady solution solve the differential equations

①  $\rightarrow [A] = [A]_0 e^{-k_1 t}$

②  $\rightarrow \frac{d[X]}{dt} = k_1 [A]_0 e^{-k_1 t} - k_2 [X]$

$\rightarrow [X] = \frac{k_1 [A]_0}{k_2 - k_1} \left\{ e^{-k_1 t} - e^{-k_2 t} \right\}$

↑ represents loss of A      ↑ represents time to reach ss

If  $k_2 t \gg 1$  and  $k_1 t \ll 1$ , then  
first exponential  $\rightarrow 1$   
second  $\rightarrow 0$

(implies  $k_2 \gg k_1$ )

and

$[X] \rightarrow [X]_{ss}$

If  $k_2 t \gg 1$  and  $k_1 \gg k_2$  only

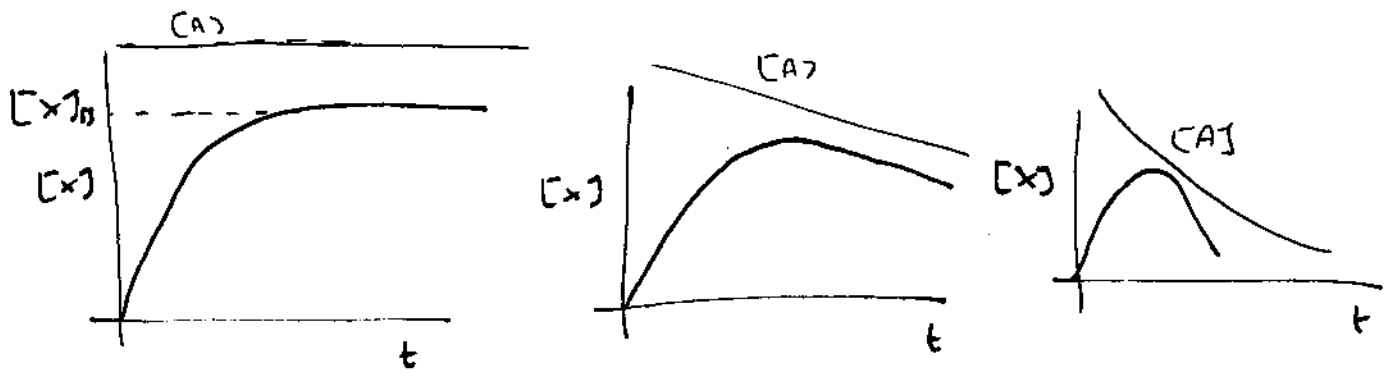
$[X] \rightarrow [X]_{ss}^{local}$

Thus steady state requires  $k_2$  to be very large: i.e. highly reactive X

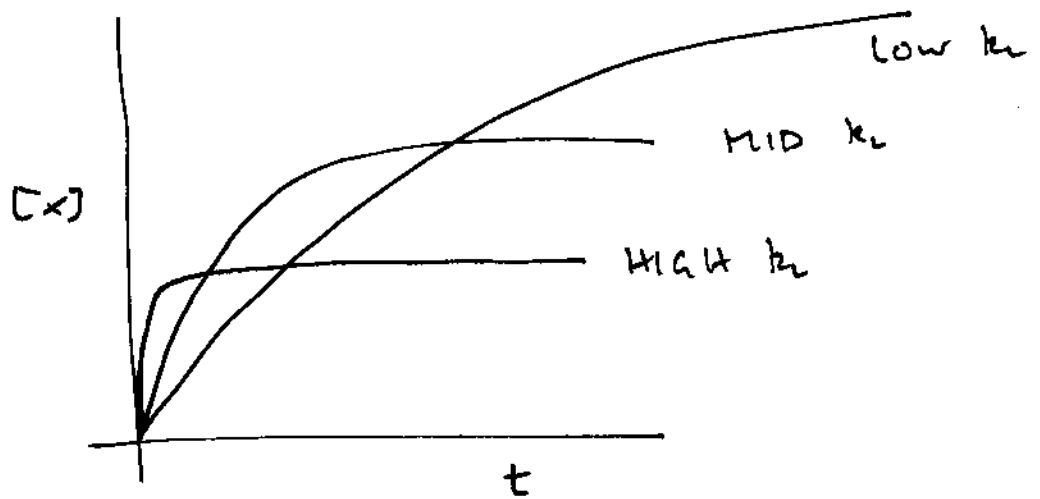
SHOULD TEST FOR STEADY STATE: SIMPLIFIED SCHEME  
COMPUTER SIMULATIONS

(VALUE OF OBTAINING AN ANALYTICAL SOLUTION)

(A) The three fixations



(B) Effect of altering  $k_2$



0945

Chain reactions

Now introduce idea of chain reactions that we shall be discussing in next two lectures.

Consider the sequence of reactions



(A, C and E are displayed in the computer simulation)

CH. "NORM" -1  
MECH M1

This is a simple sequence of consecutive reactions. The computer demonstration shows what happens if we make the second two steps fast (so that the first reaction is rate-determining).

Now consider what happens if the third reaction, instead of forming a new product, F, regenerates one of the earlier intermediates, B



MECH M2

Once the process has been started by the decomposition of one A molecule, many molecules of C and E can be consumed, as illustrated in the next computer demonstration. We have, in fact, a chain reaction, with the intermediates B and D being the chain carriers.

An example with "real" A, B, C, D etc is the H<sub>2</sub>-Cl<sub>2</sub> reaction: write out steps on board. Another important example: polymerization.

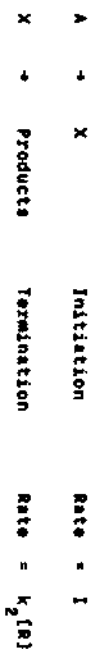
The example chosen shows two of the essential processes in a chain reaction: initiation, and propagation. These steps alone would give a chain that never ended: infinitely long (and polymers of infinite MW). In the real world, terminating steps compete to limit the length of the chain, and are the third essential component of any chain reaction.

0955

## Stationary State Method

A complete kinetic description of a many-stage reaction requires solution of the rate equations for not only reactants, but also the reaction intermediates. A number of simultaneous differential equations may therefore be involved. Fortunately, it is often possible to assume that the concentration of highly reactive intermediates (such as free radicals) is constant during the major period of reaction. The assumption is the "Stationary State Hypothesis", and is usually applied by writing the differential equation governing the rate of increase of intermediate concentration, and setting it equal to zero. The purpose of this handout is to examine the conditions under which the assumption is likely to be valid by obtaining a general solution of the rate equation in a simple case.

Let us consider the simplest chain reaction, which has only initiating and termination steps, and let X be an intermediate in the reaction:



The equations define the rate constant  $k_2$ .

The Stationary State Hypothesis is usually applied in the form

$$\frac{d[X]}{dt} = I - k_2[X]^2 = 0 \quad (1)$$

where  $[X]_g$  is the steady state concentration of X. Thus

$$I = k_2[X]_g^2 \quad \text{or} \quad [X]_g = (I/k_2)^{1/2}$$

However, if a steady state may not exist for X, we must write the general equation

$$\frac{d[X]}{dt} = I - k_2[X]^2 \quad (2)$$

and obtain a value for  $[X]$  at any time  $t$ . It is apparent that

$$(1) \quad d[X]/dt = 0 \quad \text{at } t = 0,$$

$$(2) \quad I = k_2[X]^2 \quad \text{only at } t = \infty.$$

This result suggests that in the non-stationary state,  $d[X]/dt$  is of the same order of magnitude as  $I$ , while in the stationary state  $d[X]/dt \ll I$ . Thus a

useful definition of the stationary state is:

That phase of reaction in which the net rate of change of concentration of intermediates is very much less than their rates of production and then their rates of destruction.

Consider first the case where  $I$  is effectively constant throughout the reaction. Equation (2) then integrates to give the result

$$[X] = \frac{I}{k_2} \{1 - e^{-k_2 t}\} \quad (3)$$

Thus for  $[X]$  to approach  $[X]_g$  within one percent (i.e.  $[X]/[X]_g > 0.99$ ),  $k_2 t > 4.6$ . In general, then, for the steady state to apply

$$k_2 t \gg 1 \quad (4)$$

Whether or not the Stationary State Hypothesis can be applied to a particular reaction therefore depends on whether the magnitude of  $t$  required to give the above inequality is considerably less than the reaction time.

A further complication arises if  $I$  is not constant, a situation bound to exist if the reactant A is consumed. For the initiation reaction as written

$$I = \frac{-d[A]}{dt} = k_1[A] \quad (5)$$

so that

$$[A] = [A]_0 e^{-k_1 t} \quad (6)$$

where  $[A]_0$  is the initial concentration of A.

Equation (1) thus becomes

$$\frac{d[X]}{dt} = k_1[A]_0 e^{-k_1 t} - k_2[X]^2 \quad (7)$$

which integrates to

$$[X] = \frac{k_1[A]_0}{k_2 - k_1} \{e^{-k_1 t} - e^{-k_2 t}\} \quad (8)$$

This result implies that, for the steady state treatment to be valid, not only must inequality (4) be achieved, but also  $k_2 \gg k_1$ . If, in addition,  $k_1 t \ll 1$ , then  $[A] \approx [A]_0$  and little loss of reactant has occurred over the time  $t$ .

## Multistep Kinetics II - Requirements

\*\*\*\*\*  
Handout: Steady state Kinetics  
\*\*\*\*\*

### 1. Stationary and non-stationary fluorescence

UV lamp: board

UV lamp: 2 x 125 watt table — ON

'Tonic water' (requires quinine sulphate in distilled H<sub>2</sub>O + few drops ca. 2M H<sub>2</sub>SO<sub>4</sub>)

salt (+ salt cellar)

beakers

card with phosphor

flash lamp (ex. photoflash with UV filter fixed in front)

### 2. Computer integration of differential equations

BBC-B computer wired to Monitors

Disk with 'Auto-1', 'NORM-1', 'MCODE' programs and 'DEMDATA', M1, M2 mechanisms.



## Multistep Kinetics II - Demonstrations

### Steady state and non-stationary experiments

Quinine-salt experiments: steady state  
(remind about fluorescence with chalks)

'Tonic water': in two beakers  
Add salt to one to quench

Photographic flash on phosphorescent screen:  
non-stationary experiment.

### Computer demonstrations

Mode 1 colours programs "Auto-1" and "Norm-1" (Mode 0 programs are "Auto-0" and "Black" and "Blue": set the colour by the VDU19 statement in line 320)

In these programs, "MCODE" should load automatically if needed, and \*RAMON should be ignored by a machine with a second processor

### Approach to steady state

Mechanism for steady states is "DEMDATA"

The error limits and scale factors are set within the program for each of the rate constants used. The error limit is made smaller as the integration proceeds

Initial parameters:

A=1 B=0 C=0 [Err Lim=1E-8] Init Step=4.52E-3 t=3E-2

RUN	1	2	3	4	5
k <sub>1</sub>	1E-1	1E0	1E1	1E2	1E0
k <sub>2</sub>	1E3	1E3	1E3	1E3	1E2
A scale	5E2	5E2	5E2	5E2	5E2
B scale	4E6	4E5	4E4	4E3	4E4
C scale	1E5	1E4	1E3	1E2	3E4
[EPS	1E-5	1E-4	1E-3	1E-2	1E-4]

re run 2 before 5

observations:

1-4 Steady State, with increasingly large decays  
5 No Steady State

### Chain reactions

Use program "NORM-1" with mechanisms M1 (consecutive reactions) or M2 (chain).

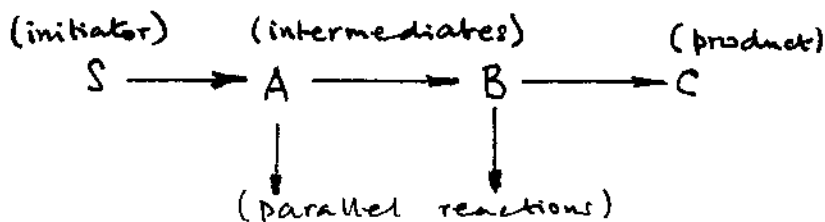
A→B; B+C→D; D+E→F (or B)

k<sub>1</sub>=10<sup>1</sup>; k<sub>2</sub>=10<sup>5</sup>; k<sub>3</sub>=10<sup>5</sup>

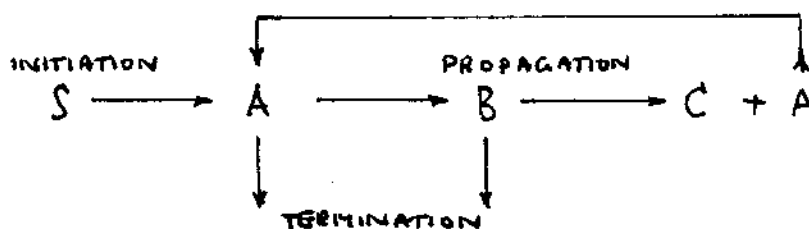
A<sub>0</sub>=0.1; B<sub>0</sub>=0; C<sub>0</sub>=0.095; D<sub>0</sub>=0; E<sub>0</sub>=0.090; F<sub>0</sub>=0

Chain reactions

Multistep reactions considered so far are of type



If one or more of the intermediates is regenerated, then we can have a chain reaction



Note the recycling: many reaction steps for each chain started

→ INFINITELY long chain without loss of X or Y

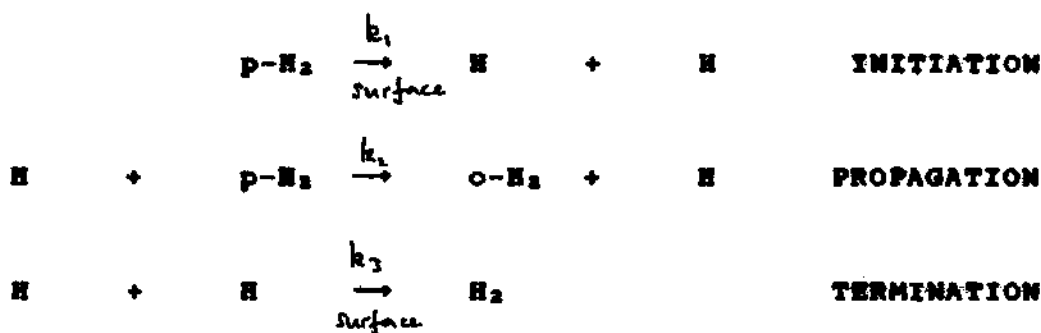
The parallel (non-regenerating) steps limit the length of the chain and are "Terminating"

Thus the essential components of a chain reaction are:

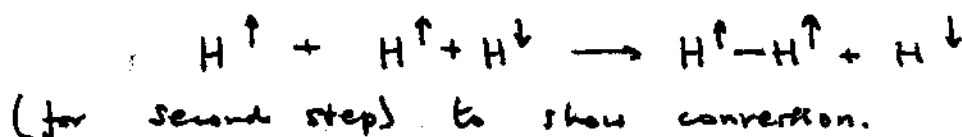
(MARK IN RED PARTS ON DIAGRAM ABOVE)

*repeat diagram*

Simple example: conversion of para to ortho H<sub>2</sub>



\* Explain o- and p-H<sub>2</sub> : draw as H<sup>↑</sup>-H<sup>↓</sup>, then write



$$\frac{d[H]}{dt} = 2k_1[p-H_2] - k_3[H]^2$$

Steady state  $\rightarrow$

$$[H] = \left( \frac{2k_1}{k_3} \right)^{\frac{1}{2}} [p-H_2]^{\frac{1}{2}}$$

Thus

$$\frac{d[o-H_2]}{dt} = k_2[H][p-H_2] - k_3[H]^2$$

*highlighted term represents production of o-[H<sub>2</sub>] in termination step Occurs relatively rarely.*

$$= k_2 \left( \frac{2k_1}{k_3} \right)^{\frac{1}{2}} [p-H_2]^{\frac{3}{2}} - k_3 \left( \frac{2k_1}{k_3} \right) [p-H_2]$$

Experimentally, find that order is 3/2, so that the  $k_3[H]^2$  is negligible. That is, the chains are long.

Introduce concept of kinetic chain length,  $\nu$

- $\nu$  = Number of links in chain
- = Number of propagation steps per chain started
- =  $\frac{\text{Rate of propagation}}{\text{Rate of initiation}}$

In our example of p- to o- H<sub>2</sub> conversion,

$$\nu = k_2 \left( \frac{1}{2k_1k_3} \right)^{\frac{1}{2}} [p-H_2]^{\frac{1}{2}}$$

*(rate from simplified, single term form)*

From rate constants, can show that for T = 1000K and P = 10 mmHg

$$\nu \rightarrow 10^7$$

so that chain really is long, and termination as a source of o-H<sub>2</sub> can be neglected. Note that steady state [H] = 10<sup>-7</sup> mmHg, or about 1 part in 10<sup>8</sup>.

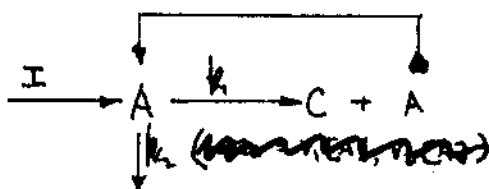
## Mean kinetic chain length

The definitions for the chain length give a single value.

However, in reality not all chains will have the same length, and it is necessary to calculate a mean kinetic chain length,  $\bar{\nu}$ . However, we shall prove that  $\nu$  obtained from the simple definition is, in fact, equal to  $\bar{\nu}$ .

First demonstrate that  $\nu = \alpha/(1-\alpha)$

Handout  
p1



$\alpha = \text{probability of propagation}$   
 $= k_1/(k_1+k_2)$

$$\text{Rate} = d[C]/dt = k_1[A]$$

$$\frac{d[A]}{dt} = I - k_2[A] \implies [A] = \frac{I}{k_2} \quad (55)$$

$$\therefore \nu = \frac{\text{Rate}}{I} = \frac{k_1[A]}{I} = \frac{1}{I} \left( k_1 \cdot \frac{I}{k_2} \right) = \frac{k_1}{k_2} = \frac{\alpha}{1-\alpha}$$

Now calculate  $\bar{\nu}$ : first we need the probability distribution P

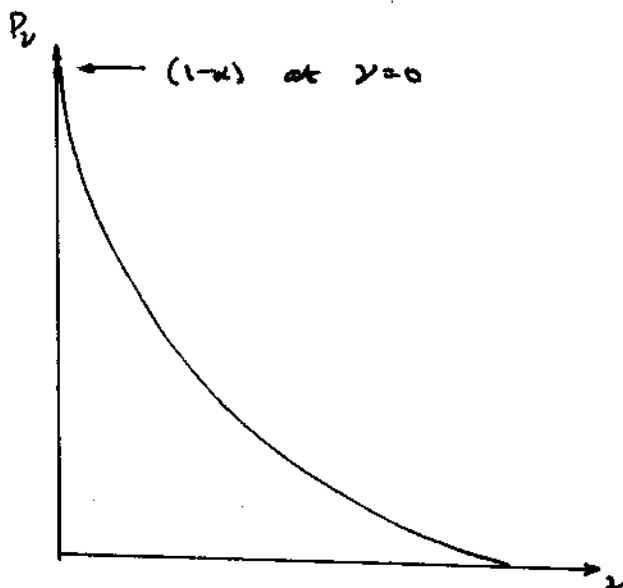
$$P_\nu = \alpha^\nu (1-\alpha)$$

$$\bar{\nu} = \frac{\sum_0^{\infty} \nu P_\nu}{\sum_0^{\infty} P_\nu} \quad \begin{aligned} &\rightarrow (1-\alpha) \cdot (0 + \alpha + 2\alpha^2 + 3\alpha^3 + \dots) = 1-\alpha \cdot \alpha(1+2\alpha+3\alpha^2+\dots) \\ &= \frac{1-\alpha}{(1-\alpha)^2} \cdot \alpha = \frac{\alpha}{1-\alpha} \end{aligned}$$

$$\therefore \bar{\nu} = \nu$$

$$(check) \rightarrow (1-\alpha)(1 + \alpha + \alpha^2 + \alpha^3 + \dots) = \frac{1-\alpha}{1-\alpha} = 1 \quad (\text{as it should be})$$

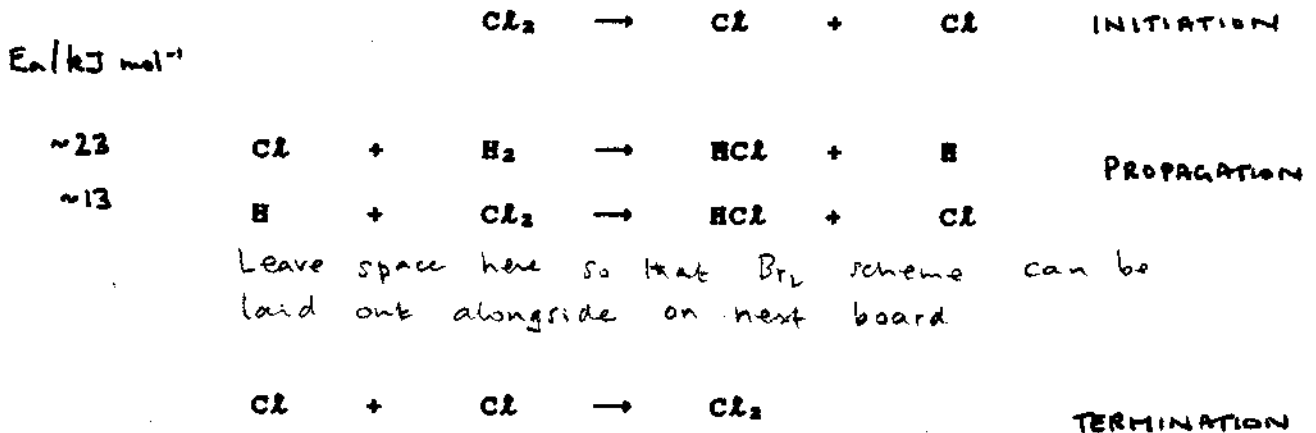
Note that the expression for P indicates that most chains will be short.



Importance in relation to polymer chemistry

Hydrogen-halogen reactions

(a) Hydrogen-chlorine

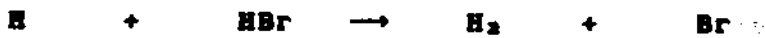


$\gamma \rightarrow 10^6$  : thermal explosion  
(cf.  $E_a$  values on left)

(b) Hydrogen-bromine

More controlled, slower

Additional reaction: "inhibition"



doesn't break chains, but does undo effect of second propagation step.

Overall kinetic scheme and Bodenstein results.

(c) Hydrogen-iodine

No chains

Handout  
p2 (LHS)  
(V21)

(d) Differences in behaviour

Largely accounted for in terms of activation energies

for reaction

H/O p3 #1 : net  $X_2$  dissociation energies

H/O p3 #2

Show net

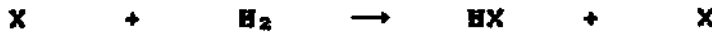
H +  $X_2$  rxn

net

A factor

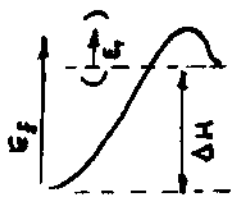
for  $X + H_2$  rxn

that are responsible



X =	$\Delta H / \text{kJ mole}^{-1}$	$E_a / \text{kJ mole}^{-1}$	$T_{1/2}$
Cl	4	23	$3.5 \times 10^{-4} \text{ s}$
Br	70	82	16 hr
I	137	142	55000 yr

Explain the  $\Delta H$  and  $E_a$  relation



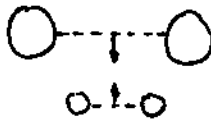
for  $[H_2] = 1 \text{ mol kg}^{-1}$   
 $\approx 5 \times 10^{-2} \text{ M}$

(e) Hydrogen-iodine again

V22, V23

Reaction long thought to be a prime example for TST

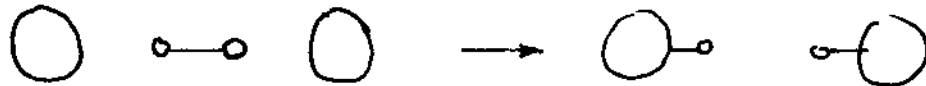
Show overheads of pages from Laidler (brief start!); but



puts no energy into the reaction coordinate.

H/O Alternative suggestion

p 4-5



Observed rate: (1)

Two expressions: (3) or (b)  $\rightarrow$  (7)

[n.b.  $[I] = K[I_2]$ ]

Photochemical results give  $[I]$ , and hence  $k_2$  directly ○

Thermal results give  $k_2$  via  $k_{eq}$  and  $K$  ●

Figure compares over temperature range:

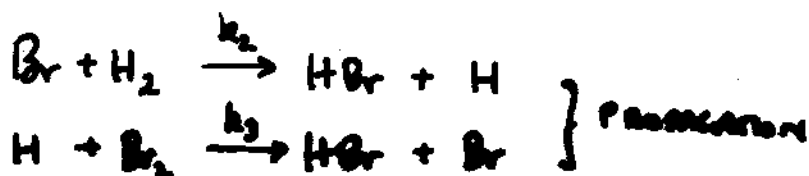
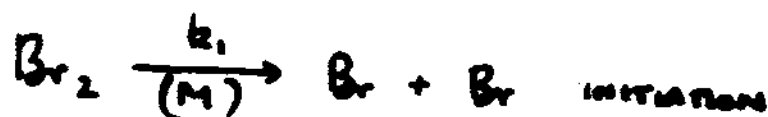
Continuity of graph confirms same mechanism.

## HYDROGEN - BROMINE REACTION

Bodenstein's experimental result:

$$\frac{d[\text{HBr}]}{dt} = \frac{a[\text{H}_2][\text{Br}_2]^{\frac{1}{2}}}{1 + \frac{b[\text{HBr}]}{c[\text{Br}_2]}}$$

SCHEME:



Steady state analysis  $\rightarrow$

$$\frac{d[\text{HBr}]}{dt} = \frac{2k_2 \left( \frac{2k_1}{k_5} \right)^{\frac{1}{2}} [\text{H}_2][\text{Br}_2]^{\frac{1}{2}}}{1 + \frac{k_4[\text{HBr}]}{k_3[\text{Br}_2]}}$$

## Comparison of Hydrogen-Halogen Reactions

### 1. Dissociation energies for X<sub>2</sub>

X <sub>2</sub>	Dissociation Energy kJ mol <sup>-1</sup>
H <sub>2</sub>	436
Cl <sub>2</sub>	242
Br <sub>2</sub>	193
I <sub>2</sub>	151

### 2. Rate Parameters for Propagation Steps

Reaction	$\Delta H$ kJ mol <sup>-1</sup>	$E_a$ kJ mol <sup>-1</sup>	A dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	k(400 K)
Cl+H <sub>2</sub>	4.4	23	$0.4 \times 10^{11}$	$4 \times 10^7$
Br+H <sub>2</sub>	69.6	82	$1.4 \times 10^{11}$	$4 \times 10^{-1}$
I+H <sub>2</sub>	137.7	142	$2.4 \times 10^{11}$	$8 \times 10^{-9}$
H+Cl <sub>2</sub>	-189.0	13	$3.0 \times 10^{11}$	$6 \times 10^9$
H+Br <sub>2</sub>	-173.3	4	$1.5 \times 10^{11}$	$5 \times 10^{10}$
H+I <sub>2</sub>	-147.2	0	$1.5 \times 10^{10}$	$1.5 \times 10^{10}$



negative iodine atoms. This was the first case in which the rate of reaction was independent of the concentration of the reactants. More recently, Benson and Schirra<sup>1</sup> noted that there is a different temperature dependence of the activation energies for the reaction between hydrogen and iodine, and for the reverse decomposition of hydrogen iodide. They concluded from this that the reactions are not simple elementary but occur in part by ionic reactions. In the case of the reaction between hydrogen and iodine the spin density is not constant and is dependent on the concentration of the reactants.



This chain component of the iodine mechanism clearly parallels the reactions occurring in the catalytic hydrogen-iodine and hydrogen-iodine reactions.

The whole question has been examined by Sullivan,<sup>2</sup> who carried out a careful experimental study of the reaction with the object of estimating the temperature of the chain process under various conditions. From the temperature dependence of the activation energy he concluded that when the iodine pressure is  $\frac{1}{2}$  atm, the atomic mechanism accounts for about 10 percent of the overall reaction at 625°K, and 27 percent at 725°K. On the basis of his analysis, Sullivan was able to arrive at rate constants and activation energies for some of the elementary steps. Since these are of aid in connection with a comparison of the various hydrogen-halogen reactions, they will be considered in a later chapter (Chap. 5).

Application of the collision theory to the results was made by Lewis, using the equations given on page 64. The experimental value of  $k$  is 40 kcal per mole, and with  $d$  as equal to  $3 \times 10^{-8}$  cm, the calculated value of  $h$  at 700°K is

$$h = 14 \times 10^{-1} \text{ liter mole}^{-1} \text{ sec}^{-1}$$

This is in satisfactory agreement with the observed value of  $6.48 \times 10^{-1}$  at this temperature. The frequency factor is about  $3 \times 10^{11}$  liter mole<sup>-1</sup> sec<sup>-1</sup>, or  $3 \times 10^{14}$  cm<sup>3</sup> mole<sup>-1</sup> sec<sup>-1</sup>.

The reaction has also been treated in terms of the theory of absolute reaction rates, by Wheeler, Topley, and Eyring.<sup>3</sup> This work included quantum-mechanical calculations of the energy of activation of the reaction, using methods outlined in Chap. 3. The result obtained was 60 kcal, a good deal higher than the experimental value of 40 kcal; how-

<sup>1</sup> B. W. Benson and R. Schirra, *ibid.*, **28**, 300 (1955).  
<sup>2</sup> J. H. Sullivan, *ibid.*, **29**, 1522, 1577 (1955); **29**, 1525 (1955).  
<sup>3</sup> A. Wheeler, R. Topley, and H. Eyring, *ibid.*, **4**, 175 (1936).

V 22

ever, as has been seen, the calculations cannot be expected to yield more than a very rough approximation to the true value. The most important outcome of these calculations has in the fact that they show why the reaction between hydrogen and iodine is so slow, the corresponding reactions of chlorine and bromine being much faster. The calculated energy of activation for the reaction of hydrogen and iodine is 60 kcal, which is a very good agreement with the experimental value of 40 kcal.



The energy required to dissociate an iodine atom is 34 kcal per mole, so that the energy required for the reaction would be 68 kcal per mole of  $I_2$ . The energy of activation for the reaction between hydrogen and iodine is 40 kcal, which is 28 kcal less than the energy required to dissociate the iodine molecule. The energy of activation for the reaction between hydrogen and iodine is 40 kcal, which is 28 kcal less than the energy required to dissociate the iodine molecule. This is considerably higher than the energy of activation for the reaction between hydrogen and iodine, which is 40 kcal. This is considerably higher than the energy of activation for the reaction between hydrogen and iodine, which is 40 kcal.



is in equilibrium with the reactants  $H_2$  and  $I_2$ , and the rate of the reaction is controlled by the rate of decomposition of the complex. The equilibrium constant for the process



is given by the expression

$$K_c = \frac{P_{HI}^2}{P_{H_2} P_{I_2}} e^{-2u/RT} \quad (3)$$

where the  $P_i$ 's are the partition functions per unit volume, and  $u$  is the activation energy per mole at the absolute zero. The rate constant of the reaction is then given by [cf. Eq. (20), p. 76]

$$k = \frac{h^{\ddagger}}{h} \frac{P_{HI}^2}{P_{H_2} P_{I_2}} e^{-2u/RT} \quad (4)$$

where the partition function  $P_i$  differs from  $P_i^0$  by the removal of the vibrational factor corresponding to dissociation into 2HI. The partition

functions may now be expressed in terms of the translational, rotational, and vibrational factors. The functions for  $H_2$  and  $I_2$  both contain terms for three degrees of translational freedom, two of rotational (using linear molecules), and one of vibrational, and can be expressed as

$$F_{tr} = \frac{(2\pi mkT)^3}{h^3} \frac{V}{N} \frac{1}{1 - \exp(-h\nu_{vib}/kT)} \quad (6)$$

$$F_r = \frac{(2\pi mkT)^2}{h^2} \frac{V}{N} \frac{1}{1 - \exp(-h\nu_{vib}/kT)} \quad (6)$$

The partition function for the activated complex is given by

$$F_{\ddagger} = \frac{(2\pi mkT)^3}{h^3} \frac{V_{\ddagger}}{N_{\ddagger}} \frac{1}{1 - \exp(-h\nu_{vib}/kT)} \prod_{i=1}^6 \frac{1}{1 - \exp(-h\nu_i/kT)} \quad (7)$$

There are five vibrational degrees of freedom ( $3n - 7$  where  $n = 4$ ). In accordance with the discussion on page 84, symmetry numbers have been omitted. The final rate expression must be multiplied by the statistical factor of two, which is the number of ways an  $H_2$  and an  $I_2$  molecule can come together.

The numerical evaluation of the translational factors presents no problem, as the molecular masses are known with precision. Evaluation of the rotational factors involves the moments of inertia; these are known with accuracy for  $H_2$ ,  $HI$ , and  $I_2$  and are known for the complex on the basis of the quantum-mechanical estimation of its properties. A little more uncertainty enters into the vibrational terms, since the calculations do not allow a very accurate determination of the frequencies in the activated complex; however, the vibrational factors are not highly sensitive to these frequencies. Some adjustment to the values was made so as to give agreement at 700°K.

The partition functions being evaluated in this manner, and using the observed activation energy (this is equivalent to 39.7 kcal at the absolute zero), the rate constants were calculated; they are compared with the experimental results at 578 and 791°K in Table 12. The agree-

Table 12 CALCULATED AND OBSERVED RATES FOR THE HYDROGEN-IODINE REACTION

T, °K	$k$ , cc mole <sup>-1</sup> sec <sup>-1</sup>	
	Calculated	Observed
578	0.153	0.245
781	1.240	900

V 23

ment is seen to be quite satisfactory, although it must be remembered that the standard entropies are available in view of the dependence of the vibrational frequencies. It is to be expected that the agreement is not perfect to the extent that the vibrational frequencies are not perfectly known, but the agreement is within the limits of experimental error.

The rate constants of this reaction can be formulated in an alternative manner, making use of the corresponding potentials. It was seen in the last section that the equilibrium is given in general by

$$K = \frac{F_{\ddagger}}{F_{H_2} F_{I_2}} \exp(-\Delta F^\ddagger/kT) \quad (8)$$

where  $\Delta F^\ddagger$  and  $\Delta G^\ddagger$  are the heat and entropy of activation. The heat of activation is related to the energy of activation  $E_a$ , and if the latter is to be used, the equilibrium becomes

$$K = \frac{F_{\ddagger}}{F_{H_2} F_{I_2}} \exp(-E_a/kT) \quad (9)$$

In the above expression the standard state for the entropy is unit concentration. The separate translational, rotational, and vibrational entropies for  $H_2$ ,  $I_2$ , and the activated complex have been evaluated and are shown in Table 13. The entropies, except for the figure in the last column, all

Table 13 ENTROPIES OF ACTIVATION FOR THE  $H_2$ - $I_2$  REACTION

$T = 300^\circ K$

The standard state for  $\Delta F^\ddagger$  is 1 mole per liter.

Molecule	Entropy			Total	$\Delta F^\ddagger$	$\Delta S^\ddagger$
	Translational	Rotational	Vibrational			
$H_2$	29.1	5.7	0	34.8	-29.3	-12.0
$I_2$	49.5	7.3	0	56.8		
$H_2I_2$	49.5	22.1	1.9	73.5		

refer to a standard state of 1 atm pressure. If the rate constant is written in the form of the collision theory, i.e., as

$$k = Z_p \exp(-E_a/kT) \quad (10)$$

It follows that

$$Z_p = \frac{kT}{h} \exp(\Delta S^\ddagger/kT) \quad (11)$$

# H<sub>2</sub> - I<sub>2</sub> REACTION

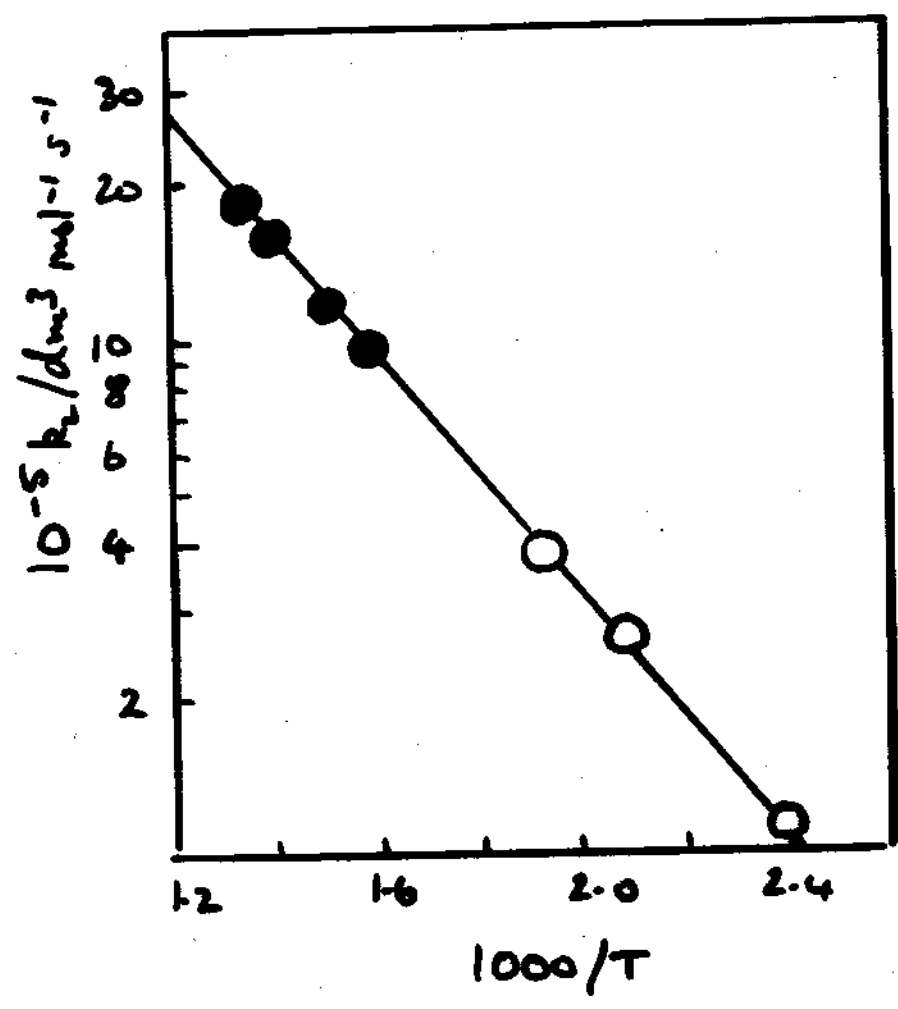
THERMAL



AND

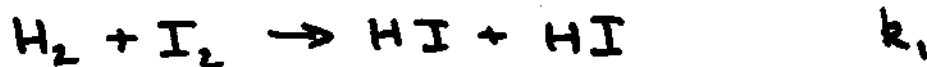
RESULTS

PHOTOCHEMICAL



HIGH-T  
VIA  
EQUILIBRIUM  
CONSTANT  
K

LOW-T  
VIA  
PHOTOLYSIS  
RATE,  $f_{hv}$ ,  
AND  $k_3$

H<sub>2</sub> - I<sub>2</sub> REACTIONOBSERVED : RATE = k<sub>obs</sub> [H<sub>2</sub>] [I<sub>2</sub>]SIMPLE  
BIMOLECULAR :

RATE = k<sub>1</sub> [H<sub>2</sub>] [I<sub>2</sub>]

PRE-EQUILIBRIUM  
AND

TERMOLECULAR :



RATE = k<sub>2</sub> [H<sub>2</sub>] [I]<sup>2</sup>

= k<sub>2</sub> [H<sub>2</sub>] K [I<sub>2</sub>]

∴ k<sub>obs</sub> = k<sub>2</sub> K

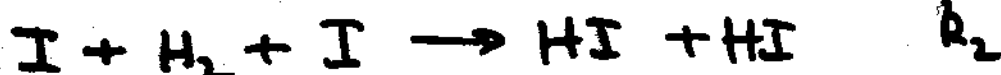
LOW TEMPERATURE

CHECK USING

PHOTOCHEMISTRY



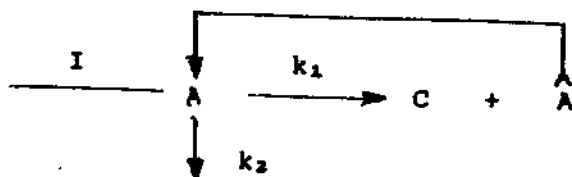
[I] =  $\left(\frac{J_{h\nu}}{k_3}\right)^{\frac{1}{2}}$



RATE = k<sub>2</sub> [H<sub>2</sub>] [I]<sup>2</sup>

## Straight Chain Kinetics

Formal Chains:



Let probability of propagation be

$$\alpha = \frac{k_1}{k_1 + k_2}$$

Rate of reaction,  $\omega$ , given by

$$\begin{aligned} \omega &= d[C]/dt = k_1[A] \\ d[A]/dt &= I - k_2[A] \\ &= I - (1 - \alpha)k_1[A]/\alpha \\ &= I - (1 - \alpha)\omega/\alpha \end{aligned}$$

Thus, when  $d[A]/dt = 0$  (stationary state), chain length,  $\nu$ , is given by

$$\nu = \omega/I = \alpha/(1 - \alpha)$$

To contain  $\nu$  "links" a chain must have propagated (chance  $\alpha$ )  $\nu$  times and not propagated (chance  $1-\alpha$ ) once. Thus probability,  $P_\nu$ , for a chain  $\nu$  links long is

$$P_\nu = \alpha^\nu(1-\alpha)$$

The mean kinetic chain length  $\bar{\nu}$  is defined by

$$\bar{\nu} = \frac{\sum_{\nu=0}^{\infty} \nu P_\nu}{\sum_{\nu=0}^{\infty} P_\nu} = \sum_{\nu=0}^{\infty} \nu P_\nu = (1-\alpha)(\alpha + 2\alpha^2 + 3\alpha^3 \dots) = \alpha/(1-\alpha)$$

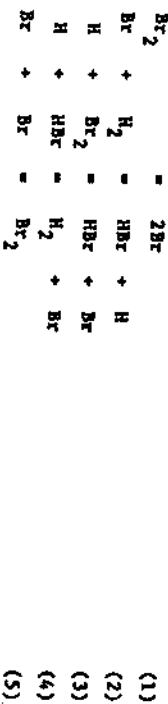
i.e.  $\bar{\nu} = \nu$

### The Hydrogen-Bromine Reaction

The  $H_2/Br_2$  reaction was found experimentally to proceed at a rate described by the equation:

$$\frac{d[HBr]}{dt} = \frac{a[H_2][Br_2]^{\frac{1}{2}}}{1 + \frac{b[HBr]}{[Br_2]}}$$

Christiansen, Herzfeld and Polanyi independently suggested that the reaction proceeded via a chain mechanism involving H and Br atoms. The derivation of the rate equation from the reaction scheme provides a good example of the application of the Stationary State Approximation.



(Note: A third body may be necessary in both steps (1) and (5).)

The rate of formation of HBr is given by

$$d[HBr]/dt = k_2[Br][H_2] + k_3[H][Br_2] - k_4[H][HBr] \quad (A)$$

The Stationary State Approximation may be assumed for H and Br atoms, so

$$0 = d[Br]/dt = 2k_1[Br_2] - k_2[Br][H_2] + k_3[H][Br_2] + k_4[H][HBr] - k_5[Br]^2 \quad (B)$$

$$0 = d[H]/dt = k_2[Br][H_2] - k_3[H][Br_2] - k_4[H][HBr] \quad (C)$$

Adding (B) to (C) and solving for [Br], we get  $[Br] = (2k_1[Br_2]/k_5)^{\frac{1}{2}}$  and substituting this result in (C),

$$[H] = \frac{k_2[H_2](2k_1[Br_2]/k_5)^{\frac{1}{2}}}{k_3[Br_2] + k_4[HBr]}$$

Substitution of (C) from (A) yields  $d[HBr]/dt = 2k_3[H][Br_2]$ , so that substitution of the value for [H] gives

$$\frac{d[HBr]}{dt} = \frac{2k_2k_3[H_2](2k_1[Br_2]/k_5)^{\frac{1}{2}}[Br_2]}{k_3[Br_2] + k_4[HBr]} = \frac{2k_2(2k_1/k_5)^{\frac{1}{2}}[H_2][Br_2]^{\frac{3}{2}}}{1 + \frac{k_4[HBr]}{k_3[Br_2]}}$$

which is of the same form as the experimentally determined expression.

### Comparison of Hydrogen-Halogen Reactions

#### 1. Dissociation energies for X<sub>2</sub>

X <sub>2</sub>	Dissociation Energy kJ mol <sup>-1</sup>
H <sub>2</sub>	436
Cl <sub>2</sub>	242
Br <sub>2</sub>	193
I <sub>2</sub>	151

#### 2. Rate Parameters for Propagation Steps

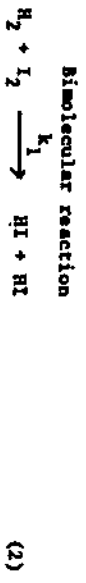
Reaction	ΔH kJ mol <sup>-1</sup>	E <sub>0</sub>	A	k (400 K)
			dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	
Cl+H <sub>2</sub>	4.4	23	0.4 × 10 <sup>11</sup>	4 × 10 <sup>7</sup>
Br+H <sub>2</sub>	69.6	82	1.4 × 10 <sup>11</sup>	4 × 10 <sup>-1</sup>
I+H <sub>2</sub>	137.7	142	2.4 × 10 <sup>11</sup>	8 × 10 <sup>-9</sup>
H+Cl <sub>2</sub>	-169.0	13	3.0 × 10 <sup>11</sup>	6 × 10 <sup>9</sup>
H+Br <sub>2</sub>	-173.3	4	1.5 × 10 <sup>11</sup>	5 × 10 <sup>9</sup>
H+I <sub>2</sub>	-147.2	0	1.5 × 10 <sup>10</sup>	1.5 × 10 <sup>9</sup>

H<sub>2</sub>/I<sub>2</sub> Reaction

Observed

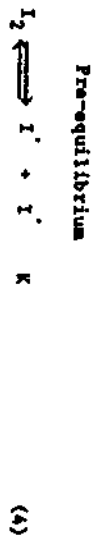
Rate = k<sub>obs</sub> [H<sub>2</sub>][I<sub>2</sub>] (1)

Simple Explanation



k<sub>obs</sub> = k<sub>1</sub> (3)

Complicated Explanation



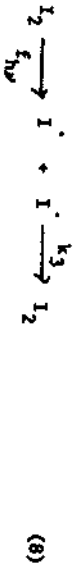
Ter-molecular step



rate = k<sub>2</sub> [H<sub>2</sub>][I·]<sup>2</sup> = k<sub>2</sub> [H<sub>2</sub>]K[I<sub>2</sub>] (6)

k<sub>obs</sub> = k<sub>2</sub> K (7)

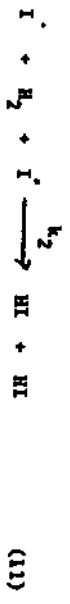
Photochemical System



$\frac{d[I \cdot]}{dt} = f_{hv} - k_3 [I \cdot]^2 = 0$  (9)

$[I \cdot] = \sqrt{f_{hv}/k_3}$  (10)

*Point is that  
 10<sup>10</sup> times  
 [I·]*



rate = k<sub>2</sub> [H<sub>2</sub>][I·]<sup>2</sup> (12)

Sullivan's & Bodenstein's Results.

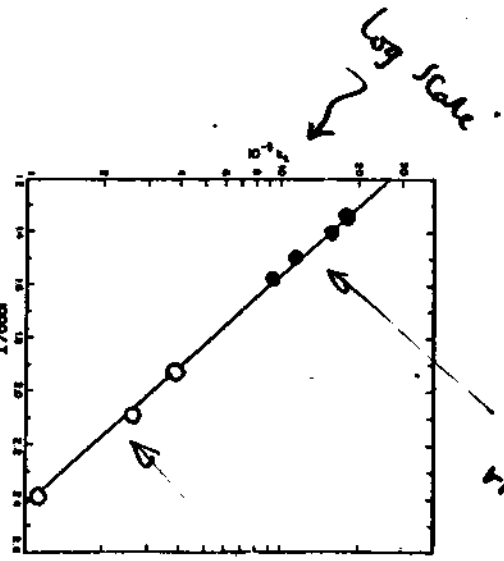
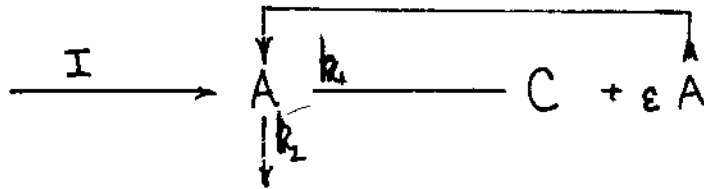
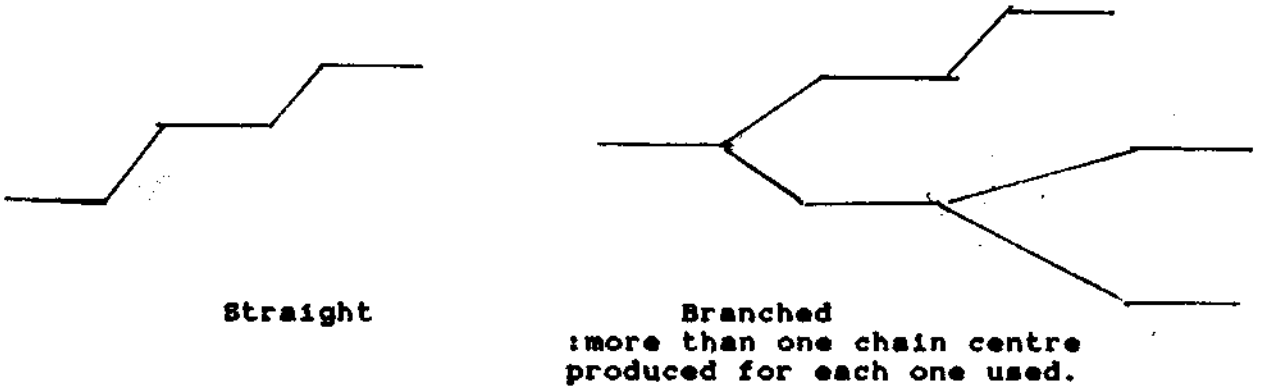


Fig. 1. Rate constants for reaction H<sub>2</sub>+2I·→2HI from thermal and photochemical data: ●, thermal results; ○, photochemical results.

Skaggs chain  $H_2/Cl_2$  rxn (repeat)  
+ thermal explosion  
Branched chain reactions



$$\frac{d[A]}{dt} = I + [k_2(\epsilon - 1) - k_2][A] = I + \phi[A]$$

(reduces to straight chain version if  $\epsilon = 1$ )

$\phi$ : "net branching factor"  
Just go to result

Integration  $\rightarrow [A] = \frac{I}{\phi} (e^{\phi t} - 1)$

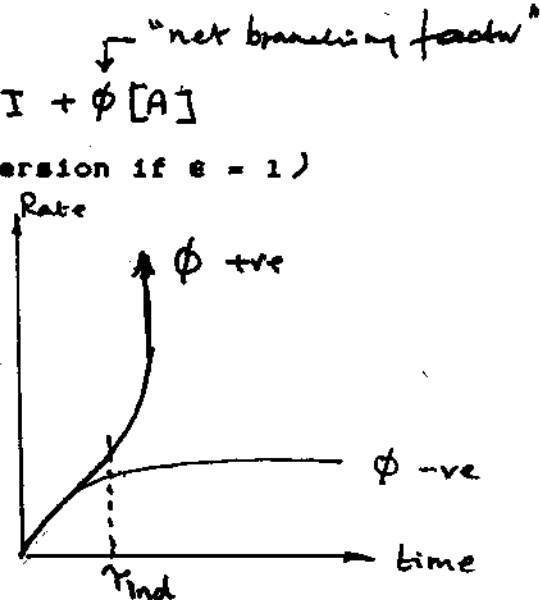
$$\rightarrow \omega = k_2[A] = \frac{I k_2}{\phi} (e^{\phi t} - 1)$$

where  $\phi = k_2(\epsilon - 1) - k_2$

For  $\epsilon > 0$ ,  $\omega \rightarrow \infty$

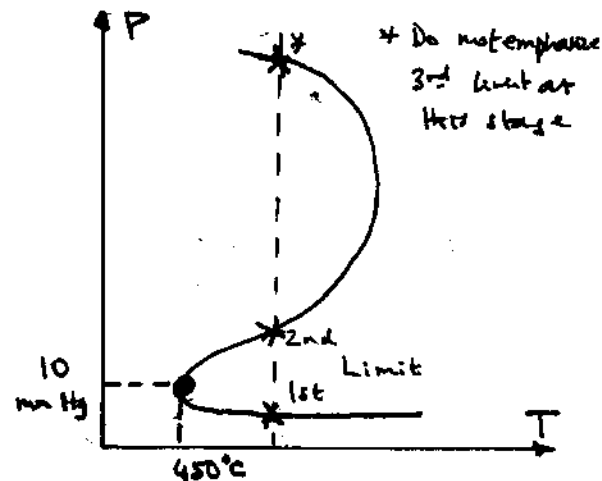
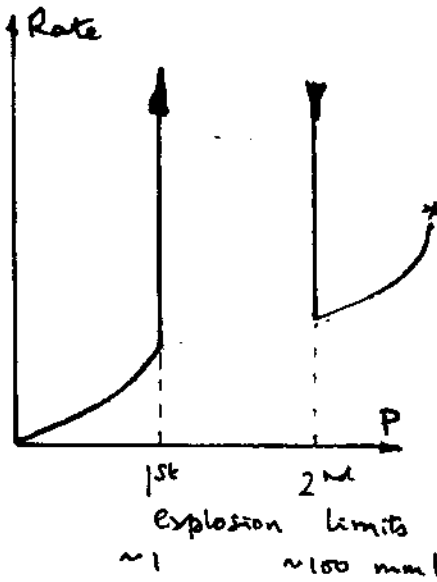
: acceleration occurs after  $\omega t > 1$

Thus  $t_{ind} = 1/\omega$



Branched chain explosion (cf. thermal exp.: combined behaviour) 0920

Behaviour



(0, \* for later diagrams)



Note how increase in pressure reduces rate, etc.

Critical pressure:

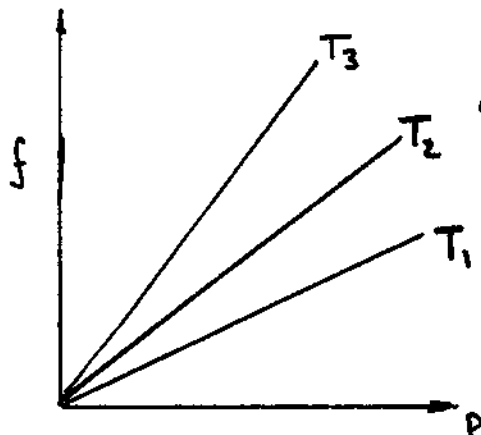
shown, e.g., by pumping out vessel from  $\geq 100$  mmHg  
glow limits for phosphorus

Explanation achieved by splitting  $\phi$  up into branching and breaking terms, and examining the P,T dependence of each.

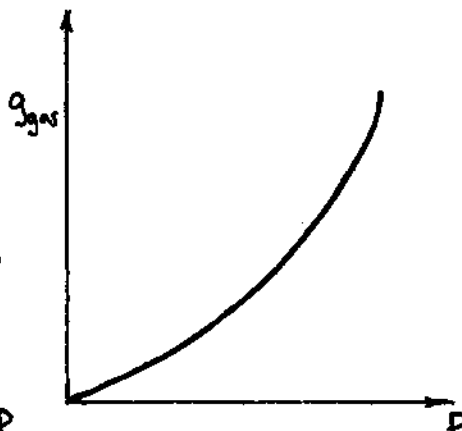
HANDOUT  
LIX/VI

H<sub>2</sub>/O<sub>2</sub> REACTION SCHEME

$$\phi = f - g_{wall} - g_{sw}$$



Large E<sub>a</sub>



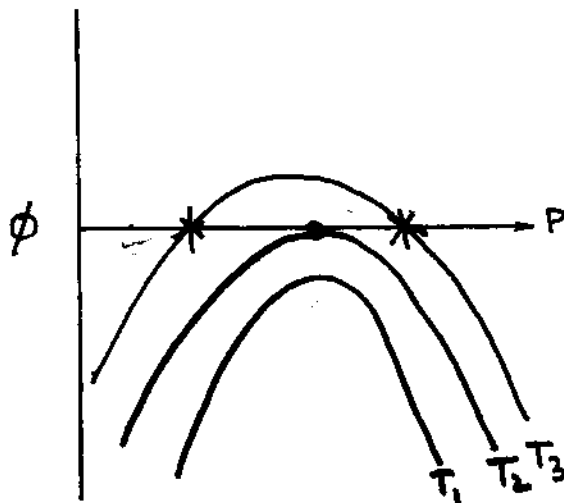
H+O<sub>2</sub>+M: p<sup>2</sup>  
T-independent



diffusion controlled

$$g_{wall} \propto P^{-1} \quad \left( \propto \frac{k_1 D}{Pr^2} \right)$$

- n.b.:
- (i) Increase in  $\underline{g}$  lowers 1st limit  
( $g_{wall} \uparrow$ )
  - (ii) Addition of inert gas lowers both limits  
( $g_{wall} \uparrow$ ) ( $g_{sw} \uparrow$ )
  - (iii) Nature of wall affects 1st limit  
( $k_w$  altered,  $\longleftrightarrow$   $g_{wall}$ )



Third limit: point out now

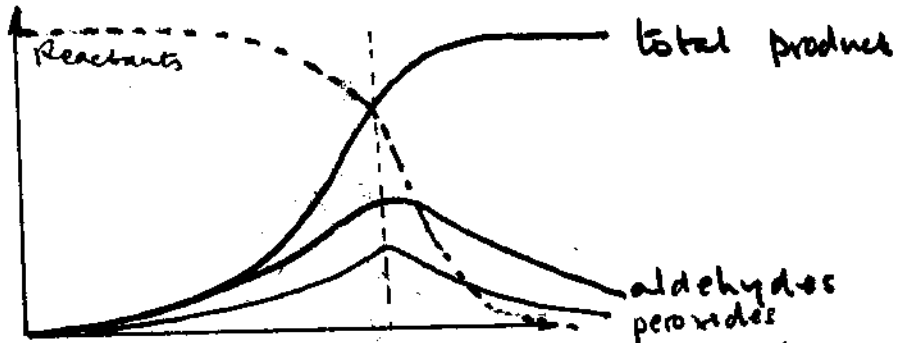


# Oxidation of hydrocarbons

## Degenerate branching

Top of H/O

Long  $\tau_{ind}$  suggests that  $\beta$  only just  $> 1$  in oxidation of hydrocarbons. Hence if  $f/g$  same as for  $H_2/O_2$ , absolute rates must be  $10^3$  less  $\rightarrow$  HIGH CONCENTRATIONS OF INTERMEDIATES, as observed.



Semenov suggested relatively high concentrations of intermediates that take part in BOTH BRANCHING AND ~~BRANCHING~~ <sup>NON-BRANCHING</sup> PROCESSES:

### 'Degenerate Branching'

HANDBOUT

LIII / V2

## COMPARISON OF $H_2/O_2$ and $RCH_3/O_2$ REACTIONS

Rare production of  $\alpha$  needed for branching ~~chain~~ from  $RO_2$



Note that  $RCH_2$  is degraded to  $R$ , next lower member of series. Experimental observation: e.g., in the oxidation of hexane, find all aldehydes down to  $HCHO$ .

Meaning of "explosion" altered here: rate may accelerate, but not go to  $\infty$ , because reactants are consumed substantially before end of induction period.

"Infinite" rates are possible with right chain-thermal conditions (i.e. a thermal explosion ensues).

Important observation confirms aldehyde hypothesis —  $\tau_{ind}$  interpreted as time taken to build up critical concentration. Add aldehyde to initial mixture,  $\tau_{ind} + zero$ . (Therefore don't add aldehydes to petrol!).

0940

nb. Aldehydes are not crucial intermediates in updated scheme: (but they are sources of products)

SLIDES (3)

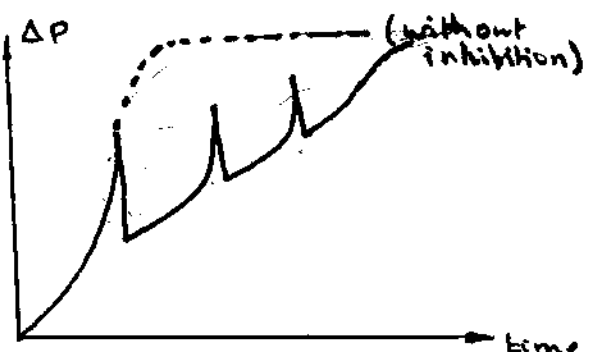
Antiknock agents (e.g. LTE): delay induction period.

0945

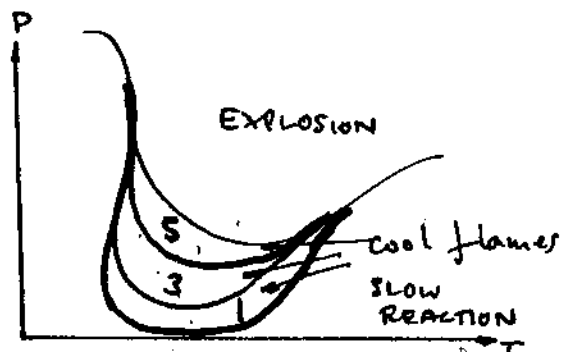
Cool Flames

For C<sub>2</sub>H<sub>6</sub> and higher alkanes  
For C<sub>2</sub>H<sub>4</sub> and higher alkenes

Observe "cool flames", associated with pulses of increased pressure.



Pressure changes associated with 3 cool flames



Flame/Explosion Peninsula

Light is fluorescence of aldehydes.  
One photon is produced for about 10<sup>6</sup> CO molecules formed.  
Secondary process



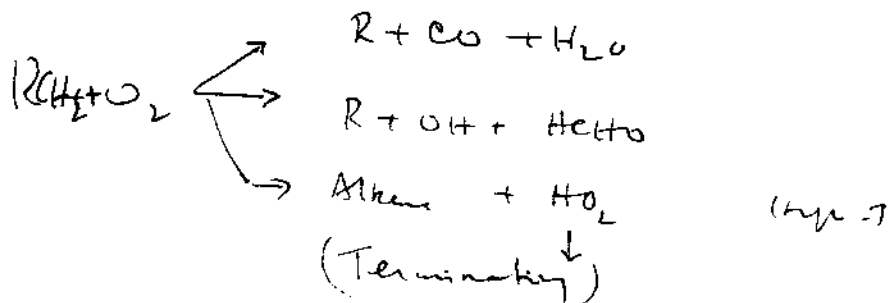
is responsible.

~~Negative temperature coefficient: I drops with increasing T. Aldehydes unstable with increase in T, so they decompose and remove the very substance responsible for degenerate branching. As reaction proceeds, I increases and aldehydes are destroyed. The reaction is thus slowed down. Process repeats until there is not enough reactant to give  $\sigma > 1$  at all.~~

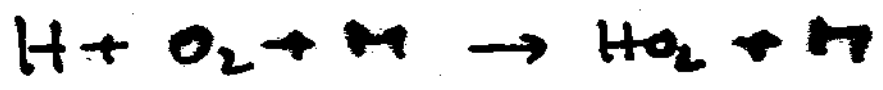
LIII/V3

0955

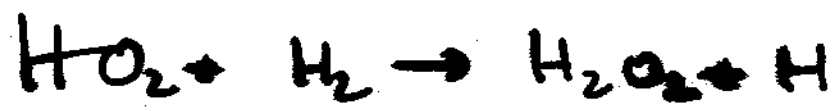
replace by competition in



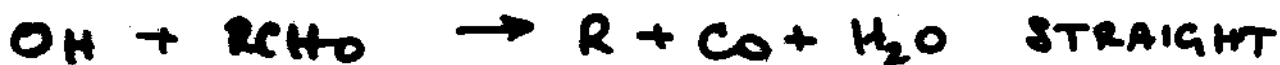
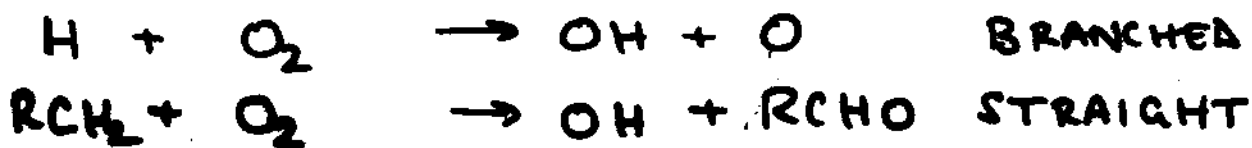
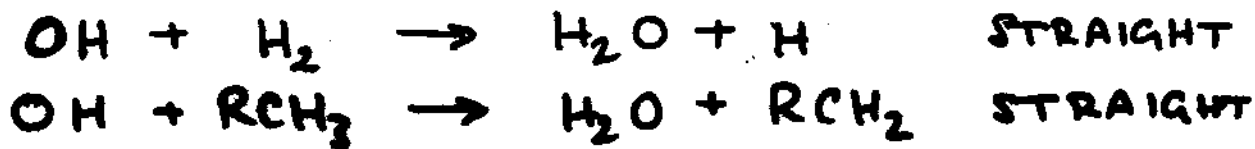
H<sub>2</sub> + O<sub>2</sub> scheme



removed by



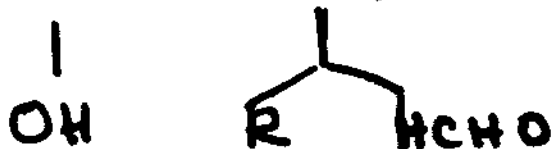
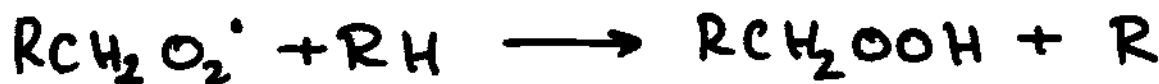
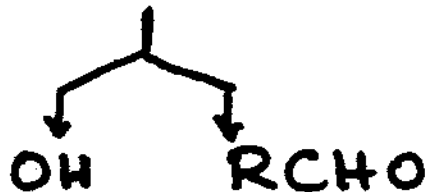
H<sub>2</sub> + O<sub>2</sub> AND RCH<sub>3</sub> + O<sub>2</sub>



MORE RARELY, THE RCH<sub>2</sub> + O<sub>2</sub> REACTION  
PROCEEDS THROUGH A **BRANCHING** CHANNEL



MECHANISMS FOR RCH<sub>2</sub> - O<sub>2</sub> INTERACTIONS:



COOL FLAMES

EMISSION IS OF  $\text{HCHO}^*$

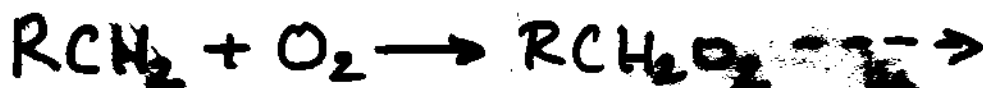
FORMED IN MINOR SECONDARY PROCESS



AS DISCUSSED EARLIER, BOTH

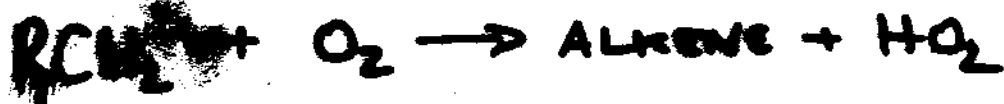
$\text{OH}$  AND  $\text{CH}_3\text{O}$

ARE PRODUCTS OF THE REACTION



AND THE ALKOXY ( $\text{RCH}_2\text{O}$ ) RADICALS  
ARE INVOLVED IN THE ~~BRANCHED~~ STEPS

AT HIGH TEMPERATURES, A FURTHER  
CHANNEL



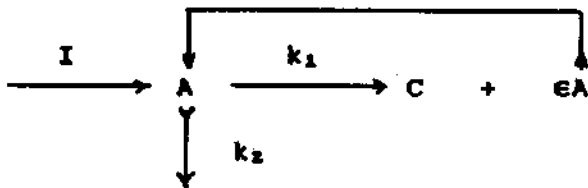
BEGINS TO DOMINATE. THE  $\text{HO}_2$

IS A TERMINATING SPECIES IN GENERAL

THUS AN INCREASE IN TEMPERATURE  
MAY QUENCH THE REACTION

## Branched Chain Kinetics

Formal Chain:



Let there be  $[A]$  chain centres at time  $t$ . Then

$$\begin{aligned} \frac{d[A]}{dt} &= I + (k_1(\epsilon - 1) - k_2)[A] \\ &= I + \phi[A] \end{aligned}$$

where  $\phi$  is the 'net branching factor'. If

$[A] = 0$  at  $t=0$ , then integration yields

$$[A] = \frac{I}{\phi} (e^{\phi t} - 1)$$

so that the rate of reaction is given by

$$w = k_1[A] = \frac{Ik_1}{\phi} (e^{\phi t} - 1)$$

Thus, if  $\phi > 0$  (which requires that  $\epsilon > 1$ ), rate increases with time. Effective 'induction period' is the time taken for the product  $\phi t$  to become greater than unity. That is:

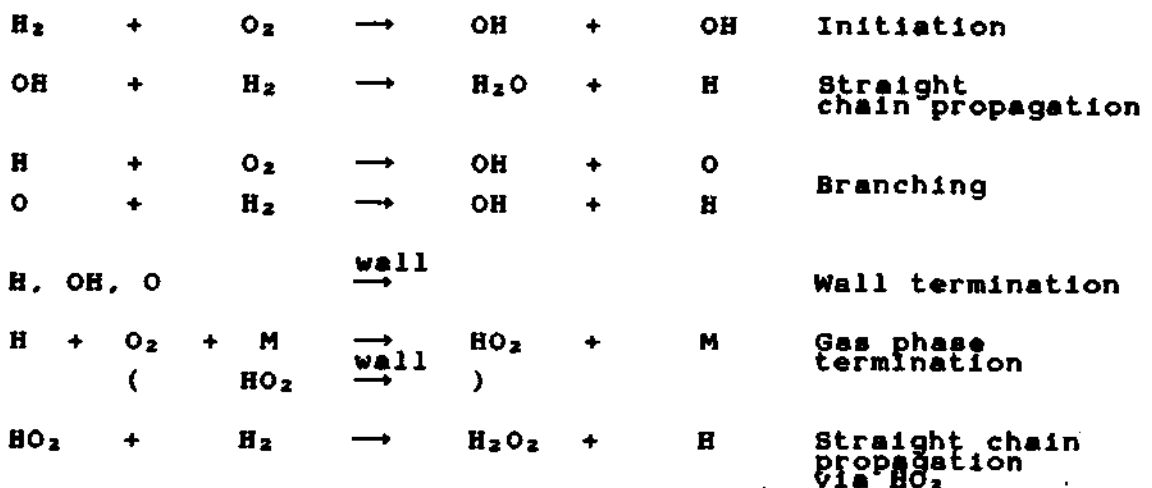
$$\tau_{ind} = 1/\phi$$

We shall split  $\phi$  into a branching term,  
 $f (= k_1(\epsilon - 1))$

and a breaking term,  
 $g (= k_2)$ ,

and further divide  $g$  into  $g_{wall}$  and  $g_{gas}$

### Processes in the $H_2 + O_2$ reaction



Oxidation of Hydrogen and Hydrocarbons

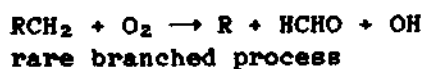
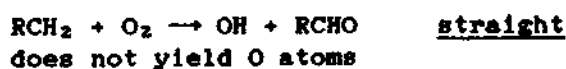
$H_2 + O_2$	Hydrocarbon + $O_2$
$t_{ind} < 1$ second	$t_{ind} = 10^2$ to $10^3$ seconds
$\phi > 1$	$\phi = 10^{-2}$ to $10^{-3}$

Hence, for given rate of reaction

Relatively low concentrations of intermediates (H, O, OH,  $HO_2$ )

Relatively high concentrations of intermediates (R,  $RO_2$ , OH, and aldehydes and peroxides, etc)

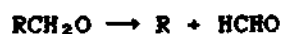
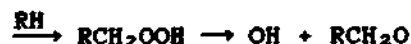
Schemes



Two routes for reaction of  $RCH_2$  with  $O_2$ , the minor one of which leads to branching:

DEGENERATE BRANCHING

Typical mechanisms for these steps are



Note that the radical R is formed in this scheme (in two ways), so that similar chemistry to that described for  $RCH_3$  with intermediates  $RCH_2$ ,  $RCH_2O_2$ ,  $RCHO$ , etc, follows with R,  $RO_2$ , the lower aldehyde, and so on