THE THEORY OF NON-BRANCHING CHAIN REACTIONS WITH ALTERNATING CENTRES

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A general expression is derived for the mean chain length of a reaction involving two types of chain centre each of which can be removed in a termination reaction. The treatment is applied to the system hydrogen + chlorine + nitrosyl chloride as an example.

In order to derive an expression for the rate of a non-branching chain reaction, it is customary to write down a series of initiating, propagating, and terminating steps and to set up the equations for the rate of production of each type of chain centre. Each equation is then put equal to zero with appeal to *ein stationärer* Zustand of Bodenstein.¹ The solution of the resulting simultaneous equations is often very tedious. If the reaction involves only one type of chain centre, there are general expressions for the rate which can save much algebra. Where the centre is removed in a terminating reaction which is first order with respect to the centre, the general expression is

$$rate = \frac{rate of initiating reaction}{rate of terminating reaction} \times rate of propagating reaction.$$
(1)

When the centres are destroyed mutually, in a second-order reaction, the expression becomes

rate =
$$\sqrt{\frac{\text{rate of initiating reaction}}{\text{rate of terminating reaction}}} \times \text{rate of propagating reaction.}$$
 (2)

In many chain reactions, however, there are two types of centre. This occurs, for example, in the hydrogen + chlorine reaction where chlorine and hydrogen atoms alternate as chain carriers,

$$Cl + H_2 \xrightarrow{\kappa_1} HCl + H$$
 (i)

$$\mathbf{H} + \mathbf{Cl}_2 \xrightarrow{\kappa_2} \mathbf{H}\mathbf{Cl} + \mathbf{Cl} \tag{ii}$$

Often it is assumed that only chlorine atoms are removed in a terminating step; the rate can then be written down as (1) or (2) with a factor 2 showing that two product molecules (HCl) are produced for each propagating reaction of a

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chlorine atom. In effect the problem is treated as a single centre propagating according to the step

$$Cl + H_2 + Cl_2 \longrightarrow 2HCl + Cl.$$

However, it is quite possible that both chlorine and hydrogen atoms could be removed in separate terminating steps, for example, by reaction with the wall or with an inhibitor. The rate can be derived for this case by the Bodenstein method of stationary states, but the elegant treatment of non-branching chain reactions developed by Semenov can be amplified to give a neat general expression for the case where both centres can be removed, each in a reaction which is firstorder with respect to the centre concerned.

In dealing with chains of type (1) involving a single centre, Semenov supposed that there is a probability α that any centre will regenerate itself in a propagating step, and a probability $(1 - \alpha)$ that it will be removed and the chain so stopped. It can then be shown² that the average number of successful links in the chain, that is the mean chain length v, is

$$\nu = \alpha/(1-\alpha). \tag{3}$$

The probability that the chain will contain only one link is $\alpha(1 - \alpha)$. The probability of two links is $\alpha^2(1 - \alpha)$ and so on. The mean chain length is then

$$1\alpha(1-\alpha)+2\alpha^2(1-\alpha)+\ldots+s\alpha^s(1-\alpha)+\ldots=\alpha/(1-\alpha).$$

The rate of the reaction is then equal to the rate at which centres are generated multiplied by the number of successful links per initial centre, because each successful link generates a product molecule.

Hence the rate = rate of generation of centres $\times v$ = rate of initiation reaction $\times \alpha/(1 - \alpha)$.

Now α is given, in terms of the usual elementary reactions, by

$$\alpha = \frac{\text{fate of propagating reaction}}{\text{rate of propagating reaction} + \text{rate of terminating reaction}}$$

Hence the rate = rate of initiation $\times \frac{\text{rate of propagating reaction}}{\text{rate of terminating reaction}}$

which is identical with (1) as it should be.

The two-centre case can now be treated similarly, using the hydrogen + chlorine chain as a model. Let it be supposed that chlorine atoms initiate the chain, for convenience, and that the chance that the chlorine atom will generate a hydrogen atom is α , and that the chance that the hydrogen atom will generate a chlorine atom is β . Let it also be supposed that hydrogen chloride is produced only by (i) and (ii) and not by any other reactions.

The probability of one and only one molecule of hydrogen chloride being produced is $\alpha(1-\beta)$

two and only two molecules of hydrogen chloride	e is	$\alpha\beta(1-\alpha)$
three and only three	is	$\alpha^2\beta(1-\beta)$
four and only four	is	$\alpha^2\beta^2(1-\alpha)$

and so on. The average number of molecules of hydrogen chloride formed for each initial chlorine atom is therefore

$$\begin{aligned} &1\alpha(1-\beta)+3\alpha^2\beta(1-\beta)+5\alpha^3\beta^2(1-\beta)+\ldots\\ &+2\alpha\beta(1-\alpha)+4\alpha^2\beta^2(1-\alpha)+6\alpha^3\beta^3(1-\alpha)+\ldots\\ &=\alpha(1+\beta)/(1-\alpha\beta). \end{aligned}$$

The asymmetry in the numerator is due to the fact that one type of centre must initiate the reaction; in the example given the initiating centre is concerned with α .

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The rate of production of hydrogen chloride is then

$$\frac{d[\text{HCl}]}{dt} = \text{the rate of generation of chlorine atoms} \times \frac{\alpha(1+\beta)}{1-\alpha\beta}.$$
 (4)

This general expression can be used for any kinetic scheme for which the simple conditions mentioned hold. A particular example may be given, which arose during an investigation ³ of the effect of nitrosyl chloride on the thermal reaction between hydrogen and chlorine. Certain experiments had shown that the nitric oxide, formed by the decomposition of nitrosyl chloride

$$2NOCl \rightarrow 2NO + Cl_2$$

played a major part in generating chain centres, while the nitrosyl chloride inhibited the reaction by some very effective terminating steps. The scheme finally selected for temperatures around 250° C was as follows:

initiation: $NO + Cl_2 \xrightarrow{k_0} NOCl + Cl$ (iii)

propagation: $Cl + H_2 \xrightarrow{k_1} HCl + H$ (i)

$$H + Cl_2 \xrightarrow{k_2} HCl + Cl$$
 (ii)

termination:
$$Cl + NOCl \xrightarrow{k_3} NO + Cl_2$$
 (iv)

$$H + NOCI \xrightarrow{\kappa_4} NO + HCl \qquad (v)$$

It will be noticed that (v) generates a molecule of product, hydrogen chloride, and so the expression (4) which assumed that only (i) and (ii) generate molecules of product has to be modified slightly. It can easily be shown that only even numbers of product molecules can be formed from each initial centre, and the expression for the rate is

$$\frac{d[HCl]}{dt} = \text{the rate of generation of chlorine atoms} \times \frac{2\alpha}{1 - \alpha\beta}.$$
 (5)

Now the rate of generation of chlorine atoms = $k_0[NO][Cl_2]$

while

$$\begin{aligned} & = k_1[\text{Cl}][\text{H}_2] + k_3[\text{Cl}][\text{NOCl}]' \\ & \beta = \frac{k_2[\text{H}][\text{Cl}_2]}{k_2[\text{H}][\text{Cl}_2] + k_4[\text{H}][\text{NOCl}]}. \\ & \therefore \frac{\text{d}[\text{HCl}]}{\text{d}t} = \frac{2\alpha}{1 - \alpha\beta} \times k_0[\text{Cl}_2][\text{NO}] \\ & = \frac{2k_0k_1[\text{NO}][\text{Cl}_2][\text{H}_2]}{k_1[\text{H}_2] + k_3[\text{NOCl}] - \frac{k_1k_2[\text{H}_2][\text{Cl}_2]}{k_2[\text{Cl}_2] + k_4[\text{NOCl}]} \\ & = \frac{2k_0k_1[\text{NO}][\text{Cl}_2][\text{H}_2]}{k_3[\text{NOCl}] + \frac{k_1k_4[\text{H}_2][\text{NOCl}]}{k_2[\text{Cl}_2] + k_4[\text{NOCl}]}. \end{aligned}$$

 $k_1[Cl][H_2]$

As this example shows, the rate expression can be derived rapidly from the general expression, and in a convenient form. Another advantage of this treatment is that other possible chain terminating steps can readily be incorporated in α or β , and the resulting rate equation derived from the general expressions (4) or (5) in a few lines.

¹ Bodenstein, Z. physik. Chem., 1910, 85, 329

- ² Semenoff, Chemical Kinetics and Chain Reactions (O.U.P., 1935), chap. 2.
- ³ Ashmore and Chanmugam, Trans. Faraday Soc, 1953, 49, 254.

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