

Paper : Physical Chemistry

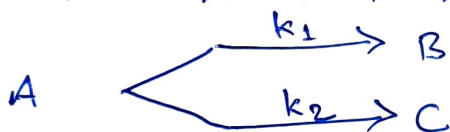
Topic : Chemical Kinetics

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3. Side or Parallel Reactions :-

In these reactions, the reacting substance follows two or more paths to give two or more products. The reaction in which the maximum yield of the products is obtained is called the main or major reaction ~~etc~~ while the other reaction (or reactions) are called side or parallel reactions. Consider a reaction



where A is the reactant which undergoes two reactions having velocity constants k_1 and k_2 respectively, to form independent products B and C. If in the above reaction

$$k_1 \gg k_2$$

then the path $A \rightarrow B$ is main reaction and the path $A \rightarrow C$ is side reaction.

It is to be noted that it is possible to convert any of side reactions into main (or major) reaction by adjusting the favourable experimental conditions of temperature, pressure and catalyst. Such side reactions are very common in organic chemistry.

Suppose 'a' is the initial concentration of A.

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Let x of A decomposes in time t to form partly as B and partly as C. If y and z are the amounts of B and C formed in time t , then we can write

$$\text{Rate of disappearance of A} = -\frac{dx}{dt}$$

$$\text{Rate of formation of B and C together} = \frac{dx}{dt}$$

$$\text{Rate of formation of B} = \frac{dy}{dt}$$

$$\text{Rate of formation of C} = \frac{dz}{dt}$$

As both B and C are formed from A, we can write

$$\frac{dx}{dt} = \frac{dy}{dt} + \frac{dz}{dt} \quad \text{--- (1)}$$

Since $(a-x)$ is the amount of A left unreacted after time t , then

$$\text{Rate of formation of B} = \frac{dy}{dt} = k_1(a-x)$$

$$\text{and Rate of formation of C} = \frac{dz}{dt} = k_2(a-x)$$

Substituting these values in equation (1) we get

$$\text{Overall rate of reaction, } \frac{dx}{dt} = k_1(a-x) + k_2(a-x)$$

$$\text{or } \frac{dx}{dt} = (a-x)(k_1 + k_2) \quad \text{--- (2)}$$

$$\text{or } \frac{dx}{dt} = (a-x)k \quad \text{--- (3)}$$

where $k = k_1 + k_2$

Separating the variables of equation (3) we get

$$\frac{dx}{(a-x)} = k \cdot dt \quad \text{--- (4)}$$

and integrating it under the condition that at $t=0$, $x=0$, we obtain

$$\ln \frac{a}{a-x} = kt$$

$$\text{or } k = \frac{1}{t} \ln \left(\frac{a}{a-x} \right) \quad \text{--- (5)}$$

The value of k can be obtained by noting the concentration changes in A with time.

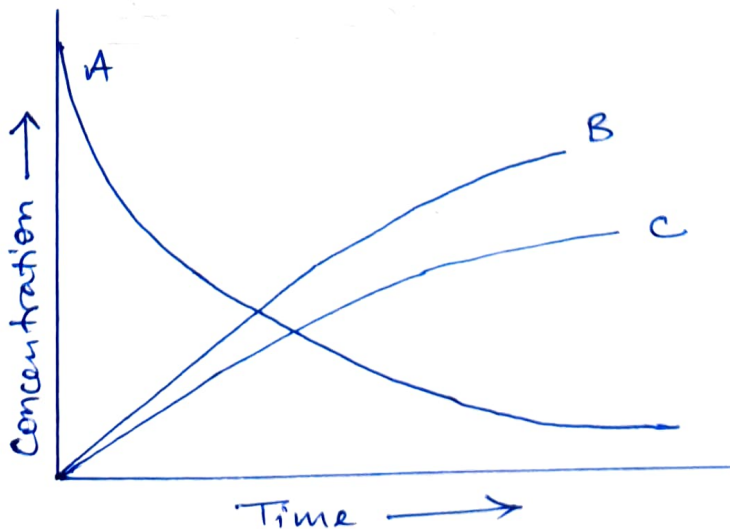
But the separate evaluations of k_1 and k_2 require some relationship between them. We can write

$$\begin{aligned} \frac{\text{Amount of B at any stage (say time } t)}{\text{Amount of C at the same stage}} &= \\ &= \frac{\text{Rate of formation of B (i.e. } dx/dt)}{\text{Rate of formation of C (i.e. } dz/dt)} \\ &= \frac{k_1(a-x)}{k_2(a-x)} = \frac{k_1}{k_2} = Z \text{ (say)} \end{aligned}$$

$$\therefore Z = \frac{k_1}{k_2} \quad \text{--- (6)}$$

The estimation of B and C at the end of the reaction would give the value of Z . Hence, the values of k_1 and k_2 can be evaluated separately using equations $k = k_1 + k_2$ and $Z = k_1/k_2$ since the values of k and Z are measured experimentally.

Variation of concentration of A, B and C with time can be shown graphically as given below:



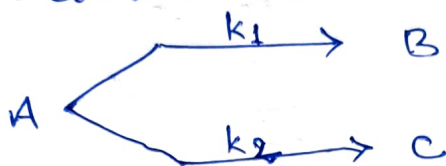
Wegscheider's Test for Side Reactions :-

This test is used to distinguish side reactions from opposing or consecutive reactions.

According to this test the ratio of amounts of substances formed in two side reactions is independent of time, provided that the order of two side reactions be the same.

This statement implies that this test is not applicable if the orders of two side reactions are different. The validity of the above statement can be tested as follows:

Case I :- When side reactions are of first order. Consider the reaction

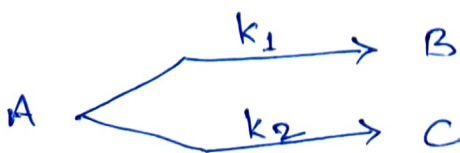


where both the side reactions are of the first order. Then

$$\begin{aligned}
 \frac{\text{Amount of B at any stage}}{\text{Amount of C at the same stage}} &= \frac{\text{Rate of formation of B}}{\text{Rate of formation of C}} \\
 &= \frac{k_1 (a-x)}{k_2 (a-x)} \\
 &= \frac{k_1}{k_2} = Z \quad \text{--- (7)}
 \end{aligned}$$

Since Z is a constant and is independent of time, Wegscheider's test is valid.

Case II :- When side reactions are of n th order. Consider the reaction



where both the side reactions are of the n th order. Then

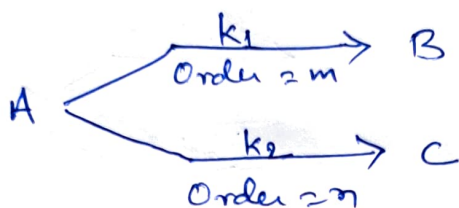
$$\frac{\text{Amount of B at any stage}}{\text{Amount of C at the same stage}} = \frac{\text{Rate of formation of B}}{\text{Rate of formation of C}}$$

$$= \frac{k_1 (a-x)^m}{k_2 (a-x)^n}$$

$$= \frac{k_1}{k_2} = Z \quad \text{--- (8)}$$

Since Z is a constant (i.e., independent of time), Wegscheider's test is valid.

Case III :- When side reactions are of different order. Consider the case in which the first side reaction is of m th order and the second of n th order.

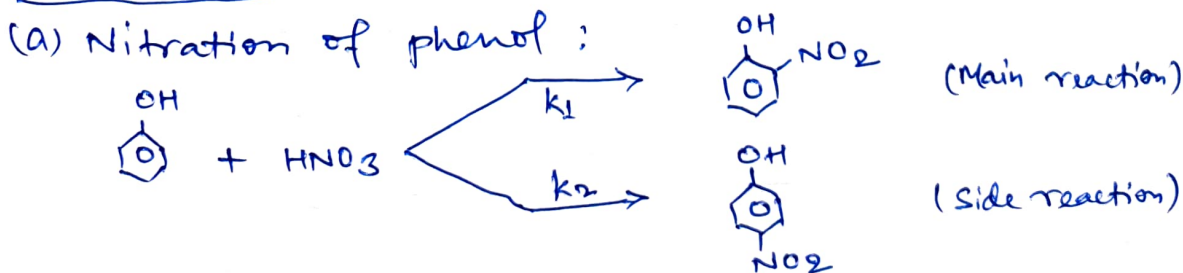


Therefore,

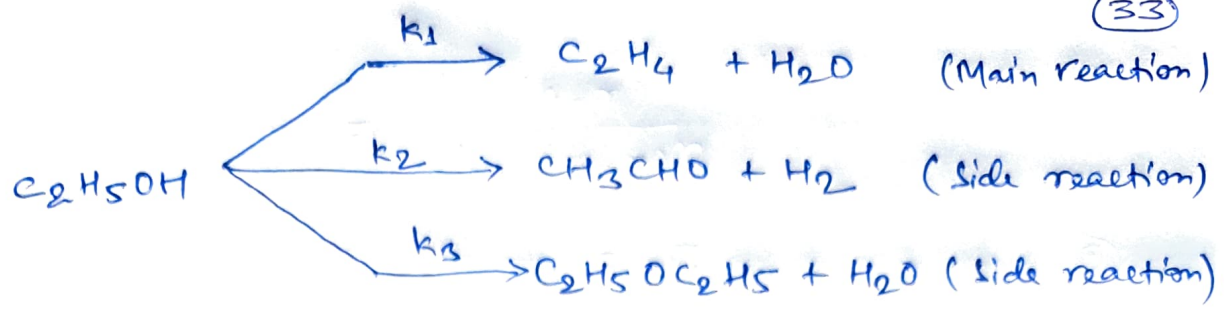
$$\begin{aligned}
 \frac{\text{Amount of B at any stage}}{\text{Amount of C at the same stage}} &= \frac{\text{Rate of formation of B}}{\text{Rate of formation of C}} \\
 &= \frac{k_1 (a-x)^m}{k_2 (a-x)^n} \\
 &= \frac{k_1}{k_2} (a-x)^{m-n} \quad \text{--- (9)}
 \end{aligned}$$

But since $(a-x)$ depends of time, hence $\frac{k_1}{k_2} (a-x)^{m-n}$ is not independent of time. So, Wegscheider's test fails in such cases.

Examples :-

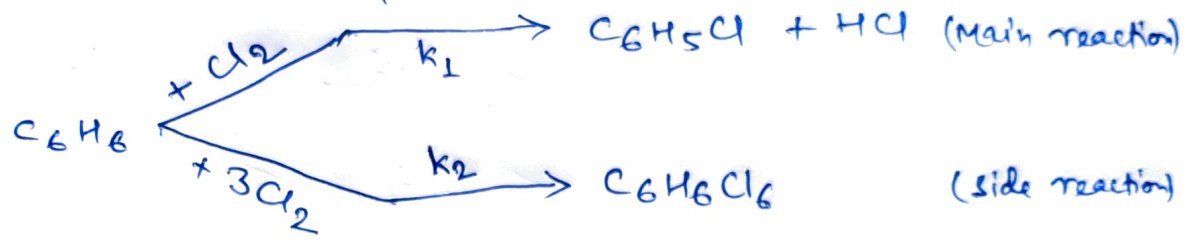


(b) When ethyl alcohol is made to react under different conditions :



It is important to note here that it is possible to convert any of the side reactions into the main reaction by adjusting the favourable experimental conditions.

(c) Chlorination of benzene :



(d) Nitration of benzoic acid :

It gives a mixture of ortho, meta and para nitrobenzoic acids.

(e) Dual decay of some radioactive elements.



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