

5.3: Simultaneous Processes

The number of moles of a substance in a system can change with time because several processes occur simultaneously. Not only can a given substance participate in more than one reaction, but also the amount of it that is present can be affected by processes that are not chemical reactions. A variety of transport process can operate to increase or decrease the amount of the substance that is present in the reaction mixture: A pure solid reactant could dissolve in a reacting solution, or a product could precipitate from it, as the reaction proceeds. A reacting species could diffuse into a reactor across a semi-permeable membrane. Controlled amounts of a reacting species could be added, either continuously or at specified intervals.

Each of the simultaneous processes contributes to the change in the number of moles of A present. At every instant, each of these contributions can be characterized by a rate. Over a short time interval, Δt , let $\Delta_i n_A$ be the contribution that the i^{th} process makes to the change in the amount of A in volume V . If, even though the i^{th} process may not be a reaction, we use $R_i(A)$ to represent its rate, its contribution to the rate at which the amount of A changes is

$$R_i(A) = \lim_{\Delta t \rightarrow 0} \left(\frac{\Delta_i n_A}{V(t) \Delta t} \right) = \frac{1}{V(t)} \frac{d_i n_A}{dt}$$

If there are numerous such processes, whose rates are $R_1(A)$, $R_2(A)$, ..., $R_i(A)$, ..., $R_\omega(A)$, the observed overall rate is

$$R(A) = \sum_{i=1}^{\omega} R_i(A) = \frac{1}{V(t)} \sum_{i=1}^{\omega} \frac{d_i n_A}{dt}$$

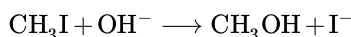
If the volume is constant,

$$R_i(A) = \frac{1}{V} \frac{d_i n_A}{dt} = \frac{d_i [A]}{dt}$$

and

$$R(A) = \sum_{i=1}^{\omega} R_i(A) = \sum_{i=1}^{\omega} \frac{d_i [A]}{dt} = \frac{d[A]}{dt}$$

To illustrate these ideas, let us consider the base hydrolyses of methyl and ethyl iodide. No intermediates are observed in these reactions. If we carry out the base hydrolysis of ethyl iodide of methyl iodide,



in a closed constant-volume system, we can express the reaction rate in several equivalent ways:

$$R(\text{CH}_3\text{I}) = \frac{1}{V} \frac{d\xi(\text{CH}_3\text{I})}{dt} = \frac{d[\text{CH}_3\text{OH}]}{dt} = \frac{d[\text{I}^-]}{dt} = -\frac{d[\text{CH}_3\text{I}]}{dt} = -\frac{d[\text{OH}^-]}{dt}$$

If a mixture of methyl and ethyl iodide is reacted with aqueous base, both hydrolysis reactions consume hydroxide ion and produce iodide ion. The rates of these individual processes can be expressed as

$$R(\text{CH}_3\text{I}) = \frac{1}{V} \frac{d\xi(\text{CH}_3\text{I})}{dt} = \frac{d[\text{CH}_3\text{OH}]}{dt} = -\frac{d[\text{CH}_3\text{I}]}{dt}$$

and

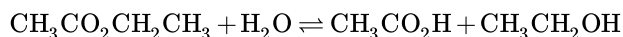
$$\begin{aligned} R(\text{CH}_3\text{CH}_2\text{I}) &= \frac{1}{V} \frac{d\xi(\text{CH}_3\text{CH}_2\text{I})}{dt} = \frac{d[\text{CH}_3\text{CH}_2\text{OH}]}{dt} \\ &= -\frac{d[\text{CH}_3\text{CH}_2\text{I}]}{dt} \end{aligned}$$

but the rates at which the concentrations of hydroxide ion and iodide ion change depend on the rates of both reactions. We have

$$\begin{aligned}\frac{d[I^-]}{dt} &= -\frac{d[OH^-]}{dt} \\ &= R(CH_3I) + R(CH_3CH_2I) \\ &= -\frac{1}{V} \frac{d\xi(CH_3I)}{dt} - \frac{1}{V} \frac{d\xi(CH_3CH_2I)}{dt}\end{aligned}$$

In principle, either of the reaction rates can be measured by finding the change, over a short time interval, in the number of moles of a particular substance present.

Simultaneous processes occur when a reaction does not go to completion. The [hydrolysis of ethyl acetate](#),



can reach equilibrium before the limiting reactant is completely consumed. The reaction rate, defined as $R = V^{-1} (d\xi/dt)$, falls to zero. However, ethyl acetate molecules continue to undergo hydrolysis; the extent of reaction becomes constant because ethyl acetate molecules are produced from acetic acid and ethanol at the same rate as they are consumed by hydrolysis. Evidently, the rate of the forward reaction does not fall to zero even though the net reaction rate does.

Let R_f represent the number of moles of ethyl acetate undergoing hydrolysis per unit time per unit volume. Let R_r represent the number of moles of ethyl acetate being produced per unit time per unit volume. The net rate of consumption of ethyl acetate is $R = R_f - R_r$. At equilibrium, $R = 0$, and $R_f = R_r > 0$. In such cases, it can be ambiguous to refer to “the reaction” or “the rate of reaction.” The rates of the forward and of the net reaction are distinctly different things.

So long as no intermediate species accumulate to significant concentrations in the reaction mixture, we can find the forward and reverse rates for a reaction like this, at any particular equilibrium composition, in a straightforward way. When we initiate reaction with no acetic acid or ethanol present, the rate of the reverse reaction must be zero. We can find the rate law for the forward reaction by studying the rate of the hydrolysis reaction when the product concentrations are low. Under these conditions, $R_r = 0$ and $R \approx R_f$. From the rate law that we find and the equilibrium concentrations, we can calculate the rate of the forward reaction at equilibrium. Likewise, when the ethyl acetate concentration is low, the rate of the hydrolysis reaction is negligible in comparison to that of the esterification reaction. We have $R_f \approx 0$ and $R = -R_r$, and we can find the rate law for the [esterification reaction](#) by studying the rate of the esterification reaction when the concentration of ethyl acetate is negligible. From this rate law, we can calculate the rate of the reverse reaction at the equilibrium concentrations.

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