

THEORY OF FEED REACTOR FOR SECOND ORDER REACTIONS

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A complete solution of kinetic equations has been obtained for isolated second order reactions at feeding one compound into the solution of the second and at feeding both compounds into the empty solution (pure solvent). On basis of these solutions, simple methods for determination of rate constants have been proposed for both feed alternatives.

The feed reactor is characterized by a continual inlet of reaction components (one or several) and by the zero outlet of the reaction mixture from the reactor.

Theoretical description of the feed reactor can be based on equations valid for the backmix flow reactor with the outlet rate chosen equal to zero. Except of the study by Kirilov¹, the majority of available studies for the backmix reactor are based on the assumption of equal inlet and outlet²⁻⁴ rates. In all cases the solution is given only for the first and pseudofirst reaction order while for more complex cases the discussion is limited to the stationary state. Two studies^{5,6} which can be considered as the first practical application of the feed reactor with a constant feed rate of one compound are again limited to isolated first order reactions. This technique has been attempted by other authors^{7,8} for more complex reactions with use of the analog computer^{9,10} and rate constants have been evaluated. Feeding one component at a constant rate into the solution of the second component is theoretically studied in other papers^{11,12}. There the problem is simplified up to the infinitely high rate of the basic reaction and the side reaction of the non-fed component or its reaction product is studied and approximate solutions of kinetic equations are given. Practical application is represented by the study on dismutations¹³. Feed reactor with a variable feed rate, chosen so that the final concentration of some of the components be a linear function of time, is solved theoretically on an analog model by Cover¹⁴. Practical application of these studies has not yet been published; its main difficulty obviously lies in a complex programmed feeding device and in the necessity to perform a number of experiments till the suitable feed rate is found.

All so far quoted studies have considered the feed of one component. The feed reactor with the feed of both components has not yet been described.

In this study we have made an attempt to solve completely the feed reactor for second order reactions with arbitrarily constant feed rates of both components and to demonstrate how the rate constants can be simply determined.

* Part I in the series New Methods in Homogeneous Reaction Kinetics.

The feed reactor can be operated basically in two ways: *a*) by feeding one component into the basical solution of the second component, *b*) by feeding individually, both components into the media in which the reaction takes place (so-called empty solution).

Both procedures can be described by a common system of kinetic equations with different feed rates and initial conditions. If we consider the second order reaction



with the feed rates r_A, r_B ($M s^{-1}$), for changes of molarities of reaction components with time holds

$$-d[A]/dt = k[A][B] - r_A = d[P]/dt, \quad (1a)$$

$$-d[B]/dt = k[A][B] - r_B, \quad (1b)$$

while $r_X = [X]_0 v q/V$ and where $[X]_0$ is molarity of the fed component, v rate of motion ($cm s^{-1}$) of syringe pistons with the area $q(cm^2)$ and V is the volume (ml) of solution in the reactor. At feeding sufficiently concentrated solutions, the effect of dissolution can be neglected; in practice *e.g.* when feeding the total volume of 2 ml into 100 ml of basical solution.

For solution of the system of Eqs (1a, b), at first the differential relations between the concentrations [A] and [B] are obtained by equating the product $k[A][B]$ from both equations and by comparison of both relations

$$-v(d[A]/dt) + \nu r_A = -d[B]/dt + r_B. \quad (2a)$$

After integration in the range 0 to t , $[A(0)]$ to $[A]$ and $[B(0)]$ to $[B]$ we obtain

$$-v\{[A] - [A(0)]\} = -\{[B] - [B(0)]\} + (r_B - \nu r_A) t. \quad (2b)$$

After substitution from (2b) into (1a), for [B] or into (1b) for [A] we obtain

$$d[A]/dt = -\nu k[A]^2 + k[A]\{(r_B - r_A) t + \nu[A(0)] - [B(0)]\} + r_A, \quad (3a)$$

$$d[B]/dt = -k[B]^2 + k[B]\{(r_B - \nu r_A) t + [B(0)] - \nu[A(0)]\} + r_B, \quad (3b)$$

which are differential equations of the Riccati's type for which the solution in the closed type can be found. In the following the feed alternatives *a*) and *b*) are considered separately.

Feed of the Component B into the Basic Solution of Component A

This alternative is characterized by the following feed rates and initial conditions:

$$r_A = 0, \quad r_B \neq 0, \quad [A(0)] = a, \quad [B(0)] = 0. \quad (4a)$$

Eq. (3a) of the Riccati's type is simplified by the conditions (4a) to the equation of the Bernoulli's type which can be easily integrated¹⁵ with the result

$$\frac{[A]}{a} = \exp(-\tau^2/2\sigma) / [\exp(-1/2\sigma) + (1/\sigma) \int_{-1}^{\tau} \exp(-x^2/2\sigma) dx], \quad (4b)$$

where

$$\tau = (r_B t / v \cdot a) - 1; \quad \sigma = r_B / v^2 a^2 k. \quad (4c, d)$$

By substituting Eq. (4b) into Eq. (2b) under conditions (4a), relation for the dependence of concentration of B on time is obtained

$$[B]/av = \tau + [A]/a, \quad (5a)$$

and from the condition of total concentration of compound A the dependence of concentration of product P on time is given by

$$[P]/a = 1 - [A]/a. \quad (5b)$$

Several calculated dependences of relative concentrations $[A]/a$, $[B]/a$, $[P]/a$ on

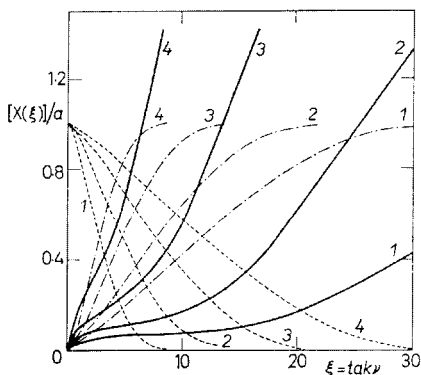


FIG. 1

Relative Concentrations of Reactants at Feeding the Compound B into Solution of Compound A

————— $[B(\xi)]/a$, - - - - - $[P(\xi)]/a$, ······ $[A(\xi)]/a$; σ : 1 0.0494, 2 0.08, 3 0.15, 4 0.3.

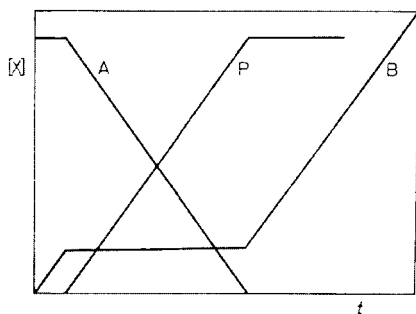


FIG. 2

Concentration in Schematical Dependence on Time for Feed of Component B into Solution of A

quantity* $(\tau + 1)/\sigma = \tau \nu k = \xi$ for different parameters σ of practical importance are given in Fig. 1.

The dependence concentration-time (Fig. 2) can be qualitatively explained as follows: At the beginning of reaction the concentration $[B]$ is small and thus the product $k[A][B]$ is small as well and the reaction is practically at standstill. In relations (1a, b) in the initial region of reaction the products $k[A][B]$ can be neglected so that $[A]$ remains constant ($d[A]/dt = 0$), $[A] = a$, $[P]$ is equal to zero and B increases linearly with time ($d[B]/dt = r_B$) according to relation $[B] = r_B t$.

The central part of curves is characterized by the feed rate r_B of the same magnitude as the product $k[A][B]$ and at a certain time interval they even compensate each other so that according to (1b) is $d[B]/dt = 0$ and concentration $[B]$ in the stationary state is given by the value $r_B/\nu k[A]$. At the same time, according to (1a) the reaction rate $-d[A]/dt$ is constant and equal to r_B as well as the rate of product formation $d[P]/dt$.

In the final state when A is nearly consumed, the product $k[A][B]$ is again negligible so that $[B]$ increases linearly with time, $[A]$ is nil and $[P]$ is constant and equal to a .

If on the curve $[B(t)]$ is the horizontal extrapolated by the corresponding stationary concentration up to the initial region and the intersection with the initial linear branch is made, (to which is related the value $[A] = a$), the relations are obtained

$$[B] = r_B t; \quad [B] = r_B/\nu k a; \quad t^+ = 1/\nu k a. \quad (6a, b, c)$$

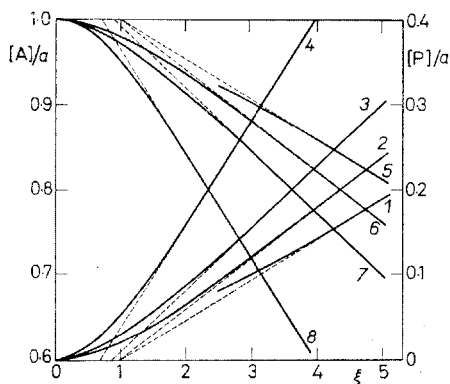


FIG. 3

Extrapolation of Linear Branches of Curves Relative Concentration-Time for the Non-fed Reactant and Product

$[P]/a, \sigma$: 1 0.0494, 2 0.0625, 3 0.08, 4 0.15; $[A]/a, \sigma$: 5 0.0494, 6 0.0625, 7 0.08, 8 0.15.

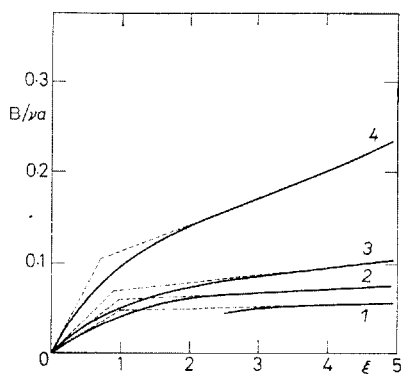


FIG. 4

Extrapolation of Initial and Central Branches of Curves Relative Concentration-Time for the Fed Component

For values of parameter δ see Fig. 3.

* This transformation shifts origin of the coordinate system to $t = 0$ and the relation for determination of the rate constant (see (6c)) to the point $\tau \nu k = 1$.

The time coordinate of the intersection t^+ is thus independent of the feed rate and according to (6c) enables to determine from the known initial concentration of the not-fed component and from the known stoichiometry the rate constant k . Similarly, the intersection of the linear decrease of $[A(t)]$ with the horizontal $[A] = a$ or of the linear increase $[P(t)]$ with the horizontal $[P] = 0$ gives the value t^+ .

Verification of these qualitative considerations on actual dependences $[A(t)]$, $[B(t)]$, $[P(t)]$ have demonstrated (Figs 3,4) that they are correct up to the value of parameter $\sigma = 0.06$, despite the central part of $[B(t)]$ curves is not horizontal. Simultaneously the independence of t^+ on different feed rates represents a criterion (since the rate constant for calculation of a suitable value σ is not known in advance) if conditions for application of the described simple method for determination of the rate constant are satisfied.

It is obvious from Fig. 4 that if the relation $t^+ = 1$ does not hold there appears on the $[B(t)]$ curves an inflex which can be also used for determination of the rate constant: If $d^2[B]/dt^2$ is expressed from (1b) and put equal to zero, in the inflex point is obtained the relation

$$k[B]([B] + v[A]) = r_B. \quad (6d)$$

If A is substituted from Eq. (5a) the following relations are obtained

$$([B]/va)(2[B]/va - \tau_i) = \sigma, \quad (6e)$$

$$k = r_B(2[B] - r_B t_i + va)/[B]. \quad (6f)$$

The accuracy, with which this relation can be used for determination of the rate constant, is given by the accuracy of the position of the inflex point. Information on this can be given *e.g.* from comparison of theoretical values of σ and those calculated from Eq. (6e) at the visually determined position of the inflex point on the theoretical $[B(t)]$ curves as demonstrates Table I.

When Eq. (6f) is applied, the time of the inflex must be measured together with the concentration of the fed component at this point. However, by elimination of $[B]/va$ from (6d) by use of Eqs

TABLE I

Comparison of Theoretical and Calculated Parameters σ According to Eq. (6e)

ξ_i	1.6	1.75	2.0	2.50	3.0	4	4.6	5	6
$-\tau_i$	0.20	0.30	0.40	0.50	0.55	0.60	0.63	0.687	0.706
$[B]/av$	0.46	0.375	0.30	0.21	0.17	0.12	0.10	0.075	0.06
σ	0.515	0.394	0.30	0.193	0.151	0.1008	0.083	0.0627	0.0495
σ_{teor}	0.5	0.4	0.3	0.2	0.15	0.1	0.08	0.0625	0.0494
Deviation, %	+3.0	-1.5	0.0	-3.5	+0.8	+0.8	+3.7	-0.3	0.0

(5a) and (4b) the relation relating τ_i with the parameter σ can be obtained which is only the relation between the time of inflex t_i and the rate constant k . But, unfortunately, this relation is transcendental and so it can be solved only graphically as is demonstrated in Fig. 5. For a practical application the quantity $\tau_i = (t_i r_B / v a) - 1$ is determined from the experimentally obtained value of t_i , the respective value of σ is read off from the graph and the rate constant $k = (\tau_i + 1) / v a t_i \sigma$ is calculated. This procedure is advantageous especially in those cases when instead of concentration $[B]$ is measured the quantity H which is in a linear dependence on concentrations of all reactants (e.g. absorbance). In such case the time coordinate of the inflex of curve $H(t)$ is the same as that of the curve $[B(t)]$ because from (1a, b) results that with the condition $d^2[B]/dt^2 = 0$ is simultaneously fulfilled $d^2[A]/dt^2 = 0$ and $d^2[P]/dt^2 = 0$ and so $d^2H/dt^2 = 0$ holds as well.

From analogous $[B(t)]$ curves obtained by the electrolytic supply of the component B in literature^{16,17} were already described methods for determination of the rate constant which were based on the differential kinetic equation where at first the derivative $d[(B)]/dt$ had to be determined graphically and for the actual concentration $[B]$ calculated $[A]$ which represented a cumbersome and a very time-consuming procedure where the total accuracy of the result was small as so many parameters had to be determined.

Feeding of Both Components A and B into the Empty Solution

This situation is characterized by the following feed rates with the initial conditions:

$$r_A \neq 0, \quad r_B \neq 0, \quad [A(0)] = 0, \quad [B(0)] = 0. \quad (7a)$$

For both non-zero feed rates it is still advisable for further interpretation to differ two cases *i.e.* the stoichiometric and nonstoichiometric feed.

Stoichiometric feed. Especially simple solution of Eq. (3a) or (3b) can be obtained by a choice of the feed rates $v r_A - r_B = 0$ at which the reactants are fed at the stoichiometric ratio. Then the Riccati's equations (3a, b) are reduced to the case in which the separation of variables can be easily made and the integration performed by separation to partial fractions with the result:

$$[A] = (r_A / v k)^{1/2} \{ [\exp [2t(v k r_A)^{1/2}] - 1] / [\exp [2t(v k r_A)^{1/2}] + 1] \};$$

$$[B] = (r_B / k)^{1/2} \{ [\exp [2t(k r_B)^{1/2}] - 1] / [\exp [2t(k r_B)^{1/2}] + 1] \}. \quad (7b, c)$$

$$[P] = r_A \cdot t - [A(t)]. \quad (7d)$$

The dependence of $[A(t)]$ and $[P(t)]$ is plotted in Fig. 6. For the intersection of the initial linear branch* $[A] = r_A t$ with the asymptote $[A] = (r_A / v k)^{1/2}$ (or for the

* It is not necessary to obtain these branches by constructing the tangents $[A(t)]$ or $[P(t)]$ of the curve at the origin or in the curved part (which always are affected by a certain error) but directly since the slope r_A is known. Eventually the direct line $[A] = r_A t$ can be directly registered if $r_B = 0$ is chosen.

curve $[(B(t))]$ the intersection of the branch $[B] = r_B t$ and the asymptote $B = (r_B/k)^{1/2}$ the relations hold

$$t^+ = (1/vkr_A)^{1/2}; \quad [A]^+ = (r_A/vk)^{1/2} \text{ event. } t^+ = (1/r_B k)^{1/2}; \quad [B]^+ = (r_B/k)^{1/2}. \quad (8a, b)$$

The intersection of the linear, ascending part of the $[P] - t$ curve (*i.e.* valid for $t \rightarrow \infty$) extrapolated to the axis $[P] = 0$ is obtained by use of Eq. (7d) in the form

$$t^+ = [A(t = \infty)]/r_A = (1/vkr_A)^{1/2}. \quad (8d)$$

The relations for t^+ as well as for $[A]^+$ for the reactants and the products are not based on any approximations and are suitable for calculation of the rate constant.

The qualitative expression of the dashed part of plotted branches from Fig. 6 again results from the considerations and significance of the product $k[A][B]$ in (1a, b): in the initial state this product is negligible as $[A(t)] \approx 0$; and $[B(t)] \approx 0$, and the concentrations of $[A]$ and $[B]$ are increasing linearly with time. In the final state $k[A][B]$ is compensated by r_A and simultaneously $k[A][B]$ by r_B , as at the stoichiometric feed $r_B = vr_A$; thus derivations $d[A]/dt$ and $d[B]/dt$ are equal to zero.

Nonstoichiometric feed. If the condition $vr_A = r_B$ is not satisfied, Eqs (3a, b) remain of the Riccati's type.

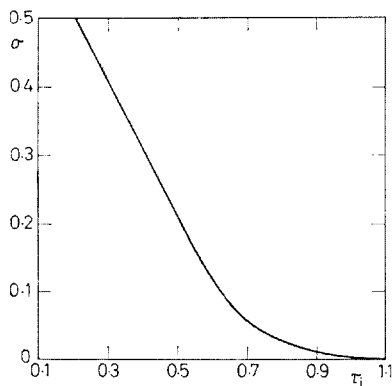


FIG. 5
Theoretical Dependence of Coordinate of the Inflex Point τ_1 on Parameter σ

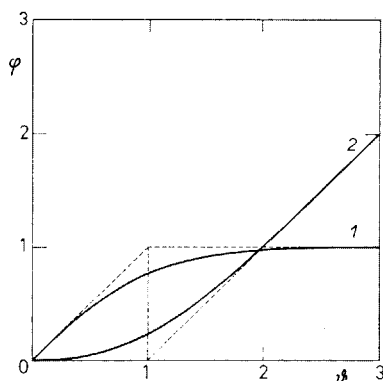


FIG. 6
Theoretical Curves Concentration–Time at Stoichiometric Feed of Both Reactants
Curve 1: $\varphi = [A] (vk/r_A)^{1/2}$ or $[B] (k/r_B)^{1/2}$; curve 2: $\varphi = [P] (vk/r_A)^{1/2}$, $\vartheta = t(vkr_A)^{1/2}$.

In this case Eq. (3a) can be transformed by substitution from Eq. (9a) to the linear differential second order equation with inconstant coefficients (9b)

$$A(t) = u'(t)/vku(t); \quad u'' + u'kt(r_B - vr_A) - ur_Avk = 0, \quad (9a, b)$$

which can be transformed by transformation (10a) of the independent variable t into the region of purely imaginary numbers, into the equation for which the solution for integer n are¹⁵ the Hermit's polynomials $H_n(x)$ defined by relation

$$x = it[k(r_B - vr_A)/2]^{1/2}; \quad n = vr_A/(r_B - vr_A) \quad (10a)$$

$$u(x) = H_n(x) = (-1)^n \exp(x^2) d^n \exp(-x^2)/dx^n. \quad (10b)$$

This means that if the ratio of feed rates is in the ratio of two successive integers $r_B/vr_A = (n+1)/n$, the solution for $[A(t)]$ can be obtained by use of the Hermit's polynomials. If the reversed substitutions are made, particular integral (for $n = 1, 2, \dots$) in the form

$$[A_1(t)] = (1/vk) 2n H_{n-1}(t)/H_n(t). \quad (11)$$

is obtained. If the general integral for $[A]$ is given as the sum of particular $[A_1]$ and of the unknown function $\omega(t)$ and is introduced into Eq. (3a), for the unknown function $\omega(t)$ results

$$\omega' = -\omega^2 k - \omega k(2[A_1] + tvr_A/n), \quad (12)$$

which is an equation of the Bernoulli's type and by substitution $z = 1/\omega$ is transformed into the linear differential equation with the right hand side that can be solved by the method of variation of the constant. After reversed substitutions the general solution for $[A(t)]$ is finally obtained in the form

$$[A] = [A_1] + \left\{ (vkJ + L) \exp(2vk \int_0^t [A_1] dt) \exp(vkr_A t^2/2n) \right\}^{-1}, \quad (13)$$

where

$$J = \int \exp(-2vk \int [A_1] dt - vkr_A t^2/2n) dt, \quad \text{and } L = 0 \text{ for}$$

odd n , and $L = \infty$ for even n .

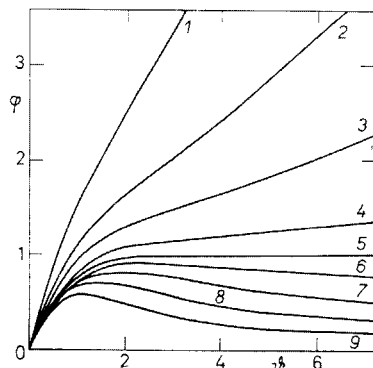


FIG. 7

Curves Concentration-Time at Nonstoichiometric Feed of Both Reactants

γ : 1 1/2; 2 2/3; 3 4/5; 4 12/13; 5 1; 6 13/12;
7 5/4; 8 3/2; 9 2.

Values of the integration constant L result from the requirement that for all $n[A(t=0)] = 0$ when we realize that for even n is $\lim_{t \rightarrow 0} [A_1]$ and also $\lim_{t \rightarrow 0} J = 0$ while for odd n for $t \rightarrow 0$ $[A_1(t)] \approx \approx -1/vkJ(t)$.

The dependence of concentration of the second component on time $B(t)$ can be calculated from known $[A(t)]$ on basis of (2b):

$$[B(t)] = (r_B - vr_A)t + v[A(t)]. \quad (14a)$$

The dependence $[P(t)]$ is given similarly as Eq. (7d) by the relation

$$[P(t)] = r_A t - [A(t)]. \quad (14b)$$

As the solution $[A(t)]$ is known only for the feed conditions $r_B/vr_A = (n+1)/n > 1$, it means that the $[A(t)]$ curves can be calculated from Eq. (13) only for conditions $r_B > vr_A$ i.e. for the feed of component A lower than stoichiometric. For the stoichiometric feed $[A(t)]$ is given by Eq. (7b). The dependences $[A(t)]$ at greater feed of component A than corresponds to the stoichiometric ratio (i.e. for the above equivalent curves $[A(t)]$) can be solved as follows: From Eq. (3b) is expressed $[B(t)]$ for feed of B in the lower than stoichiometric ratio and then by use of Eq. (14) from the known lower than equivalent dependence of $[B(t)]$ the above equivalent dependences of $[A(t)]$ are calculated.

The dependence of $[A(t)]$ curves for different ratios $\gamma = r_B/vr_A$ is given for illustration in Fig. 7.

The qualitative shape of curves can be derived from the dependence at the stoichiometric feed: the ascending initial region where the rate of chemical reaction is small is similar, but in the next region instead of the steady state either the component B is in excess and consequently A is continually removed (lower than equivalent $[A(t)]$ curves), or on the contrary the component B is removed and thus A is continually increasing (above-equivalent $[A(t)]$ curve).

The important point on the lower than equivalent curves is the extreme in which according to (3a) holds

$$k = r_A/[v[A]^2 + [A]t(r_B - vr_A)]. \quad (15)$$

For $vr_A \approx r_B$ the maximum is relatively flat and it is difficult to determine the corresponding time coordinate. It is better to use in these cases for determination of the rate constant the relations (6b or 6c) which were derived for $vr_A = r_B$. As was verified by theoretical curves, the error made in this way was not greater than 4% as long as r_B was situated within the interval $0.923 r_A v$ to $1.083 r_A v$.

Aside from an extreme, the subequivalent curves have also the inflex point, where on the basis of the once more differentiated Eq. (3a) holds

$$k = r_A/[v[A]^2 - [A](vr_A - r_B)t] + (vr_A - r_B)/\{v[A] - (vr_A - r_B)t\} \cdot \{(vr_A - r_B)t - 2v[A]\}. \quad (16)$$

In practice it is rather difficult to determine accurately the coordinates of this inflex point.

If the rate constant is to be determined from the dependence of product concentration on time then from the derivative of Eq. (14b) in time results that in the point of the extreme of the $[A(t)]$ curve the $[P(t)]$ curve has the slope r_A which makes possible to determine the time of the extreme t , calculate $[A(t)]$ from Eq. (14b) and to substitute it into Eq. (15). Or we determine by a double differentiation of (14b) in time that the time coordinates of the inflex on the $[P(t)]$ and $[A(t)]$ curves are identical. The $[A(t)]$ calculated from (14b) can be then substituted into Eq. (16) and k can be calculated.

Curves Absorbance–Time and Their Relation to Curves Concentration–Time

Concentration in practical cases is never determined directly, but by a quantity which is proportional to it or more generally by a quantity which is linearly dependent on concentrations of all reactants. Thus the question arises how valid are relations for calculation of the rate constant derived from the curves concentration–time.

If for calculation of the rate constant is chosen the relation based only on the time coordinate *i.e.* Eq. (6c) at the feed of one component or (8a, b, c) at the stoichiometric feed of both components, then the only concern is as accurate calculation as possible of the time coordinate of the intersection of two concentration–time branches. The linear transformation of these extrapolated branches from the dependence concentration–time on dependence absorbance–time does not alter the value of the intersection t^+ , only the slope of individual branches and so these fed branches can be used for calculation of the rate constant even in cases when both the reactants and the products are coloured. If only one component of the mixture is coloured, its extinction coefficient can be determined and for calculation of the rate constant also Eqs (8a, b) can be used which are based on measurements of the stationary concentration.

At the nonstoichiometric feed the relation (15) includes the term for calculation of the rate constant together with the time constant of the extreme and the actual concentration of the component fed in the lower, than stoichiometric ratio. If only one component in the reaction mixture is coloured regardless of the reactant or product the concentration can be calculated from the measured absorbances and Eq. (15) can be also applied. If there are several coloured components the alternative with the nonstoichiometric feed has no practical significance.

The derived theoretical relations were verified on a number of model reactions. The obtained results proved fully satisfactory and they represent a simple method for determination of the rate constant. The obtained rate constants are in a very good agreement with their values calculated by another, independent method as we shall demonstrate in our next study.

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