U.D.C. 543.226

Methods of Thermokinetic Analysis of Chemical Reactions

V.S.Livshits

The theoretical foundations of the thermokinetic method of investigating chemical reactions are discussed. An analysis is made of the method as applied to the kinetics of adiabatic and non-adiabatic reactions, including heterogeneous catalysis. Methods of calculating kinetic parameters from experimental thermokinetic curves by different versions of the method are discussed. New ways of applying the thermokinetic method to studies of heterogeneous catalysis in flow systems are proposed. Examples are given of the use of the thermokinetic method in studies of a wide range of chemical reactions. The advantages of the thermokinetic method are briefly assessed. 50 references.

CONTENTS

I.	Introduction	812
II.	Homogeneous reactions	812
III.	Heterogeneous exothermic reactions	815
IV.	Special features of thermokinetic methods for the study of fast reactions	815
V.	Non-stationary thermokinetic methods	816
VI.	Examples of the use of thermokinetic methods	817
VII.	Advantages of thermokinetic methods	817

I. INTRODUCTION

Whenever possible, kinetic measurements are made under isothermal conditions: this tendency is fully justifiable, since isothermal kinetics are usually easy to treat mathematically.

However, there is a large group of reactions which cannot be made to take place isothermally because of the large thermal effects involved. These include reactions in media of low thermal conductivity and fast reactions with high initial concentrations of reactant and leading to explosion or ignition.

Most of the industrially important polymerisation and polycondensation reactions are strongly exothermic and usually proceed with appreciable self-heating. A number of variants of the thermometric method, based on measurements of temperature as a function of time, have been proposed for kinetic studies of reactions of this type.

There are also reactions (for example, the formation of condensation oligomers) which can only be taken to completion by gradually raising the temperature. These reactions can be investigated by thermokinetic methods, based on programmed heating[1].

Theoretical and experimental results relating to the thermokinetic method are scattered among journals for different fields, depending on the type of reaction being studied. Hence, there was a need for a review article and for a systematisation of existing methods.

The present article is devoted to an analysis of methods of treating experimental thermokinetic data so as to extract from the data the variation with time of the extent of reaction, the rate constants, and the activation energies. We shall review the most important publications up to 1968, and we shall briefly characterise the thermal regime and the current applications of thermokinetic methods. We shall be little concerned with the design of detectors used in the thermokinetic method, of calorimeters, and with other experimental problems, because they are exhaustively discussed in a number of monographs[2-5].

II. HOMOGENEOUS REACTIONS

1. Adiabatic Regime

The simplest relationship between ΔT and the extent of reaction is obtained with adiabatic reactors, and also with pseudo-adiabatic calorimeters provided with automatic compensation for the heat losses which occur when a temperature difference arises between the wall of the reaction vessel and the mass of reactant[6].

In these instances, as may be shown from the heat balance equation for an adiabatic reaction, the relationship between the conversion α and the temperature T at time t is of the form

$$\alpha = \frac{T - T_0}{T_{ad} - T_0} = \frac{\Delta T}{\Delta T_{ad}} \qquad (1)$$

where

$$\Delta T_{ad} = T_{ad} - T_0 = \frac{Q_p}{\bar{C}_p}$$

where Q_p is the heat of reaction, cal mole^{-1}; $\bar{C}_p$ the mean heat capacity of the reaction mixture, cal mole^{-1} deg^{-1}; and T_0 the initial temperature of the surrounding medium.

In the absence of reliable values for Q_p and $\bar{C}_p$, the experimenter can determine only the conversion α_{max}, corresponding to the maximal observed value of ΔT. Then,

$$\Delta T_{ad} = \Delta T_{max}/\alpha_{max}.$$

The steepness of the experimental plots of ΔT against t depends, as can readily be seen, not only on the rate constant at $T = T_0$ but also on the activation energy E. This follows from the kinetic equation for an adiabatic reaction[7]:

$$\frac{dT}{dt} = k_0 (T_{ad} - T)^n \exp(-E/RT) \left(\frac{x_0}{T_{ad} - T_0}\right)^{n-1}, \qquad (2)$$

or

$$\frac{dT}{dt} = k_0 \left(\frac{\bar{C}_p}{Q_p}\right)^{n-1} (T_{ad} - T)^n \exp\left(-\frac{E}{RT}\right), \qquad (2a)$$

where n is the order of the reaction, k_0 the pre-exponential factor, and x_0 is the initial concentration of reactant.

An expression for the activation energy can be obtained from the logarithmic form of this equation[6,8,9]. The activation energy is then given by the slope of the linear plots of $\ln \frac{dT/dt}{(T - T_0)^n}$ against $1/T$ or $\ln \frac{dT}{dt}$ against $1/T$, which is equal to $-E/R$.

It should be noted that the integral form of Eqn. (2) cannot be expressed[10] in simple functions in the general case, even with $n = 1$.

Livshits suggested[11] that the activation energy of non-isothermal (including adiabatic) reactions could be determined from the position of the point of inflection of experimental plots of T against t. This point, corresponding to maximal reaction rate, is reached when the "temperature" acceleration (or retardation) of the adiabatic reaction is fully compensated by the "concentration" retardation (or acceleration).

Table 1. Types of non-isothermal reaction with extreme dependence of rate upon time.

Type of reaction and $\varphi(\alpha)$	$\frac{d\varphi(\alpha)}{dt}$	Thermal effect, Q_p	Thermal regime up to point of inflection (dT/dt)
nth order reaction, $(1-\alpha)^n$ with $n > 0$*	<0	>0	>0
nth order reaction with retardation, $(1-\alpha)^n$ with $n < 0$*	>0	<0	<0
Autocatalytic first-order reaction, $(1-\alpha)\alpha$ with $0.5 < \alpha < 1$	<0	>0	>0
Ditto, $(1-\alpha)\alpha$, with $0.5 > \alpha > 0$	>0	<0	<0
α^n; $n > 0$	>0	<0	<0
α^n; $n < 0$	<0	>0	>0
First-order reaction with retardation, $(1-\alpha)/\alpha$	<0	>0	>0

* With zero-order reactions $n = 0$, and the rate of non-isothermal reaction continuously increases ($Q_p > 0$) or decreases ($Q_p < 0$). In this case the activation energy is determined by the slope of the linear plot $\ln(dT/dt) = f(1/T)$, which is equal to $-E/R$.

To analyse this method, we note that the kinetic equation of an adiabatic reaction can be expressed in the general form;

$$\frac{d\alpha}{dt} = k_0 \varphi(\alpha) f(T). \qquad (3)$$

The quantity $d\alpha/dt$ goes through a maximum if the time changes of $\varphi(\alpha)$ and $f(T)$ are equal and opposite. It can be shown that this condition is realised in a number of instances, listed in Table 1.

Since $f(T) = \exp(-E/RT)$, and k_0 is not a function of T, E can be determined at the instant corresponding to the point of inflection (that is, $d^2\alpha/dt^2 = 0$) if the form of $\varphi(\alpha)$ is known.

Hence, by differentiating Eqn. (3) and equating the second differential to zero, a direct relationship is obtained between the activation energy and the temperature T_i of the reaction mixture at the point of inflection of the thermokinetic curve. Expressions for the activation energy of reactions obeying different kinetic laws are given in Table 2.

2. Non-adiabatic Non-isothermal Reactions

The heat balance equation for a non-isothermal reaction is of the form

$$m_0 Q_p \frac{d\alpha}{dt} - H\frac{dT}{dt} - \beta(T - T_0) = 0 \qquad (4)$$

where H is the effective heat capacity of the system, cal deg^{-1}; β the heat transmission coefficient, cal deg^{-1} s^{-1}; and m_0 the number of moles of reactant.

Table 2. Activation energy of various adiabatic reactions.

Kinetic law	Expression for the activation energy	Kinetic law	Expression for the activation energy
$(1-\alpha)^n$ $n \neq 0$	$E = \frac{nRT_i^2}{\Delta T_{ad} - \Delta T_i}$	α^n; $n \neq 0$	$E = -\frac{nRT_i^2}{\Delta T_i}$
$(1-\alpha)\alpha$	$E = \frac{RT_i^2(2\Delta T_i - \Delta T_{ad})}{\Delta T_i (\Delta T_{ad} - \Delta T_i)}$	$(1-\alpha)/\alpha$	$E = \frac{RT_i^2 \Delta T_{ad}}{\Delta T_i (\Delta T_{ad} - \Delta T_i)}$

Integration of Eqn. (4) for the initial conditions $\alpha = 0$, $t = 0$, and $T = T_0$ gives

$$m_0 Q_p \alpha = \int_0^T \beta(T - T_0)\, dt + H(T - T_0). \qquad (5)$$

For the condition[12,13] $T_0 = \text{const}$ the T–t curve can be transformed into an α–t curve by graphical integration once H and β have been evaluated. For relatively small values of ΔT it can be assumed that β and H are constant.

In the more general case we can assume

$$\beta = \beta_0 T_0^l; \quad H = H_0 + a(T - T_0),$$

where β_0, H_0, l, and a are constant.

Using Newton's law of cooling it can be shown[12] that the extent of conversion at time t is given by

$$\alpha = \frac{\int_t^\infty (T - T_0)\, dt + \int_0^t (T - T_0)\, dt}{\int_0^\infty (T - T_0)\, dt}. \qquad (6)$$

The integral $\int_t^\infty (T - T_0) dt$ is evaluated from the cooling curve by measuring the area under the curve between T and T_0. The second integral is equal to the area under the thermokinetic curve between 0 and t, and the integral in the denominator is equal to the area under the whole of the experimental curve, including the cooling period, up to the temperature T_0.

Evreinov and Entelis[13] used this method[12] in a modified form, which required the determination of β and H using Eqn. (5).

The β coefficient is evaluated from the cooling of copper specimens[14] or by electrical heating to the temperature T_{lim} at which the rate of heat evolution is equal to the rate of heat loss. Hence

$$\beta = \frac{0.2390\, N}{T_{lim} - T_0},$$

where N is the power dissipation of the heater in joules.

Also, the value of H/β, equal to

$$\frac{\int_t^\infty (T - T_0)\,dt}{T - T_0}$$

is obtained from the cooling curve. It is important to note that separate determination of H and β is not necessary: the first integral in the numerator of Eqn. (6) can be replaced by $H/\beta(T - T_0)$.

This type of treatment can be used as long as $T_0 = \text{const}$. If on the other hand the reaction is carried out under programmed heating, the quantity T_0 in Eqn. (6) must be replaced by the temperature of the surroundings for which the function $(T - T_0)$ is a maximum[15].

Methods of integration of non-isothermal kinetic equations with arbitrary temperature laws are given by Emanuel' and Knorre[16].

The more complicated case when the effective activation energy varies with extent of conversion has also been considered[14,17]. In this case, the functions $T = f(\alpha)$ and $\frac{d\alpha}{dt} = \varphi(\alpha)$ are obtained from Eqn. (6) and by graphical differentiation of the experimental T–t curve. The variation of the non-isothermal rate with reciprocal temperature is then determined for a number of values of α. Hence, using the equation $\frac{d\alpha}{dt} = k_0 \exp\left[-\frac{E(\alpha)}{RT}\right]\varphi(\alpha)$, the activation energy can be evaluated for the chosen values of α.

The non-isothermal rate is related to the isothermal rate of reaction at temperature $T = T_*$ by the equation

$$\left(\frac{d\alpha}{dt}\right)_{\substack{\text{isot} \\ T=T_*}} = \left(\frac{d\alpha}{dt}\right)_T \exp\left[\left(E/R\left(\frac{1}{T} - \frac{1}{T_*}\right)\right)\right]. \qquad (7)$$

An original method of treating thermokinetic data has been described by Korolev and coworkers[18]. Since the most commonly used reaction vessels are cylindrical, these authors considered the heat balance equation for an infinite cylinder of radius r:

$$\rho C \frac{dT}{dt} = \lambda\left(\frac{d^2T}{dr^2} + \frac{1}{r}\frac{dT}{dt}\right) + q(t)\,, \qquad (8)$$

where $q(t)$ is the rate of heat evolution, ρ is the density, λ is the thermal conductivity, and C is the heat capacity.

Eqn. (8) can readily be solved by a Laplace transform. Putting

$$\bar{z} = \int_0^\infty e^{-pt} T\,dt$$

and

$$\bar{q}(p) = \int_0^\infty q(t)\,e^{-pt}\,dt$$

and integrating Eqn. (8) multiplied by e^{-pt} between the limits $0 < t < \infty$, we obtain

$$C\rho\bar{z} = \lambda\left(\frac{d^2z}{dr^2} + \frac{1}{r}\frac{dz}{dr}\right) + \bar{q}(p). \qquad (9)$$

The solution which satisfies the condition of symmetry with respect to $z\frac{dz}{dt}$ at $r = 0$ is a Bessel function of the first kind, of purely imaginary argument. Carrying out the series expansion, and after some transformations, we obtain

$$q(t) = \frac{4\lambda}{r_0^2}\left(T + \frac{r_0^2}{4}t_r\frac{dT}{dt}\right) \qquad (10)$$

where t_r (the relaxation time) is of the order of several minutes, and can be determined experimentally from the cooling and heating curves of the reaction mixture.

When applied to an adiabatic process, Eqn. (8) takes the form

$$q(t) \simeq \rho C \frac{dT}{dt}\,. \qquad (11)$$

In the proposed method[18], the portions of the thermokinetic curve for which $dT/dt = \text{const}$ are analysed. Under these conditions the reaction rate w is

$$w = \frac{dT}{dt}\cdot\frac{\bar{C}_p}{Q_p}\,.$$

If the rate of heat removal is equal to the rate of heat evolution (isothermal process), Eqn. (10) takes the form

$$q(t) = \frac{4\lambda}{r_0^2}T\,. \qquad (12)$$

In the case of a non-isothermal, non-adiabatic process the quantity $\frac{\rho C}{\lambda}r_0^2$ needed for the calculation is evaluated from the cooling rate of the reaction mixture from temperature T to T_0. Thus for a cylinder,

$$T = T_0 \exp\left(-\frac{\mu_1^2\chi t}{r_0^2}\rho C\right) \qquad (13)$$

where μ_1 is the first root of the zero order Bessel function of the first kind ($\mu_1 = 2.401$).

Since the temperature [difference] falls by a factor of e in time t_r,

$$t_r = \frac{\mu_1^2\lambda}{r_0^2\rho C} = 1,$$

whence the desired quantity is

$$\frac{\rho C}{\lambda}r_0^2 = \mu_1^2 t_r\,.$$

In another group of methods of thermokinetic analysis of reactions, the heat evolution in the reaction mixture is reproduced by the application of current pulses of known power.

The design proposed by Skuratov and coworkers[19] is based on a double calorimeter, with cells of identical heat capacity. Current pulses of power equivalent to the rate of heat evolution in the working cell are applied to the reference cell. The kinetic curve is a plot of the square of the current in the reference cell against time. The area under the kinetic curve, multiplied by the appropriate proportionality factor, is a measure of the total heat evolution during the experiment.

The automatic calorimeter used by Anderson for emulsion polymerisation studies[20] is even more convenient. This calorimeter operates on the following principle. The adiabatic heating produced by the reaction and measured by a sensitive thermocouple is converted into electrical power, which is applied to the reactor in the form of pulses and measured by a wattmeter. The power of the pulses is automatically controlled at the level corresponding to constant total rate of heat evolution, that is, to the difference between the power in the absence of chemical reaction and the rate of thermochemical heat evolution. Special calibration is not needed to calculate the conversion at a given instant and the heat of polymerisation, since a power of 1 W is equivalent to a rate of heat evolution of 0.2390 cal s^{-1}.

III. HETEROGENEOUS EXOTHERMIC REACTIONS

The thermal regime of heterogeneous exothermic reactions was first discussed by Frank-Kamenetskii[21]. Depending on the rate of removal of heat, two stable temperature regimes were shown to be possible: the lower in the activation-controlled and the upper in the diffusion-controlled region. The steady-state heating of the surface in the upper regime can be used to evaluate the kinetic parameters.

The critical condition[21] leading to ignition for a first-order surface reaction is of the general form

$$\delta_{\text{crit.}} = \theta^2 e^{\theta} \tag{14}$$

and

$$\nu = e^{-\theta}(\theta - 1) \tag{15}$$

where

$$\delta = \frac{Q_p}{\beta}\,\frac{E}{RT_0^2}\,k_0 \exp(-E/RT_0)\,x_v$$

$$\theta = \frac{E}{RT_0^2}(T - T_0)$$

$$\nu = \frac{k_0 \exp(-E/RT_0)}{\gamma}.$$

Here x_v is the molar concentration of reactant in the bulk, γ is the mass transfer coefficient, defined by the expression

$$\gamma = \frac{(Nu)D}{d}$$

where (Nu) is the Nusselt criterion, D is the diffusion coefficient of the reactant, and d is the characteristic linear dimension of the system.

Rozovskii and coworkers have shown that the kinetic parameters of heterogeneous reactions of zero[22] and non-zero[23] order can be determined from the critical ignition condition.

For a zero-order reaction the critical ignition condition has the form

$$\delta_{\text{crit.}} = \frac{Q_p k_0 \exp(-E/RT_0')\,E}{\beta' R (T_0')^2}, \tag{16}$$

where the primes denote the values of the parameters corresponding to the onset of ignition.

By experimenting with different heat evolution conditions (through changes in linear velocity, which in turn produce a change in the ignition temperature T_0'), the following relationship between T_0 and δ_{crit} can be obtained:

$$\frac{\beta'_{(1)}\,\delta_{\text{crit (1)}}\,(T'_{0(1)})^2}{\beta'_{(2)}\,\delta_{\text{crit (2)}}\,(T'_{0(2)})^2} = \exp E/R\,(T'_{0(1)} - T'_{0(2)}). \tag{17}$$

Taking logarithms, and ignoring the term $\ln \frac{\delta_{\text{crit}(1)}}{\delta_{\text{crit}(2)}}$, we arrive at an expression for the activation energy involving only the ignition temperatures and the ratio of the heat transmission coefficients, which can be replaced by the ratio of the linear velocities raised to the power $s = 0.65$:

$$E = \frac{RT'_{0(1)}T'_{0(2)}\left(\ln\frac{\beta'_1}{\beta'_2} + 2\ln\frac{T'_{0(1)}}{T'_{0(2)}}\right)}{T'_{0(1)} - T'_{0(2)}} \tag{18}$$

(where the numbers in brackets refer to the number of the experiment). The rate constants at the ignition temperature are calculated by the formula

$$k = \frac{\delta_{\text{crit}}\beta' R (T_0')^2}{Q_p E}. \tag{19}$$

The quantity δ_{crit} is evaluated by one of the approximate formulae as a function of the parameter $b = \frac{RT_0}{E}$:

$$\delta_{\text{crit}} \simeq \frac{1+b}{e} \quad \text{or} \quad \delta_{\text{crit}} \simeq \frac{1+b+b^2}{e}.$$

The rate constants at any other temperature T are calculated by the formula

$$k_T = k_{T_0} e^{\frac{E(T-T_0)}{RTT_0}}$$

which is equivalent to Eqn. (7).

If the order of the reaction is not zero, the expression for the activation energy from the results of two experiments retains the form of Eqn. (18), but the pre-exponential factor is found from the equation

$$f(x_{i\,\text{surf}})\,k_0 = \frac{\delta'_{\text{crit}}\,\beta' k (T_0')^2}{Q_p E \exp(-E/RT_0')} \tag{20}$$

and the order n of the reaction with respect to the ith component is found from the variation of T_0' with $x_{i,\text{surf}}$ according to the equation

$$\lg \delta_{\text{crit}} + 2\lg T_0' + \frac{E}{4.575\,T_0'} = n_i \lg x_{i,\text{surf}} + A,$$

where A is a constant.

All the formulae used in this Section have been derived from the heat balance equation

$$\beta(T - T_0) = Q_p k_0 \exp(-E/RT) f(x_{i,\text{surf}}),$$

where $i = 0, 1, 2$.

It must be stressed that only the critical ignition temperature depends on the value of the heat transmission coefficient, which varies with the flow velocity. However, the steady state heating of the surface is independent of the gas flow velocity, as shown by Buben for the catalytic oxidation of hydrogen and ammonia on platinum[24].

In conclusion, we note that the thermokinetic methods of investigation of heterogeneous catalytic reactions lead to equations of the same mathematical form as those obtained for homogeneous processes. However, in the latter case one makes experimental plots of T against t, whereas in catalytic reactions the steady state heating of the surface at a particular point is observed as a function of the position of that point along the layer of catalyst.

It is evident that a definite contact time and extent of conversion must correspond to each cross-section of the catalyst in an integral reactor once a steady state is established. Thus, having determined the temperature distribution (in a uniform thermal field from the electric heater) along the catalyst column, the required kinetic parameters can be calculated from the formula given in Section II.

IV. SPECIAL FEATURES OF THERMOKINETIC METHODS FOR THE STUDY OF FAST REACTIONS

When applied to fast reactions, in which the half-life $\tau_{1/2}$ is of the order of 1 s or less, thermokinetic methods exhibit some specific features both in apparatus design and in the significance of the mathematical equipment.

We shall briefly discuss the thermometric methods of monitoring fast reactions, originally put forward in both a static and a flow variant.

In the first variant[25], the gas mixture in the reaction vessel is irradiated through a special window with ultraviolet light capable of initiating the reaction and of specific

intensity I_0 at the entry window. The absorption of light by the gas creates an intensity gradient in the vessel, and therefore the rate of thermochemical heat evolution decreases with increasing distance from the entry window. With a finite rate of heat transfer over the cross-section of the reactor, an easily detectable temperature gradient arises. An expression relating the temperature rise ΔT in the central zone of the reactor to the extinction coefficient ϵ and to the distance X from the window for an initial pressure P can easily be obtained from the heat balance condition:

$$\Delta T = \frac{I_0 h\nu\,[1-\exp(-\varepsilon X)]}{\lambda\varepsilon} \qquad (21)$$

where h is Planck's constant, ν is the frequency of the light used to initiate the reaction, λ is the thermal conductivity of the gas. A modification of the static variant, known as the thermal maximum method, has been developed for fast liquid-phase reactions.

In this method[26] a bulb containing one of the reactants is broken in a solution of the second reactant under standard conditions of fast stirring. If the reaction is exothermic, we observe a temperature rise determined by the value of the rate constant and by the efficiency of the heat exchange. This rise goes through a maximum, with time, if the order of the reaction differs from zero. The rate constant k_1 for a first-order reaction† is calculated from the equation[26]

$$\frac{\Delta T_{max}}{\Delta T_{ad}} = (k_1/k_2)^{\frac{k_2}{k_2-k_1}} \qquad (22)$$

where the cooling constant k_2 is defined by Newton's law

$$-\frac{dT}{d\tau} = k_2(T - T_0). \qquad (23)$$

If the heat of the reaction is not known, the adiabatic heating is obtained by measuring ΔT_{max} for a series of increasing concentrations of the first reactant and extrapolating to infinity. The rates of reactions with $\tau_{1/2}$ of the order of 0.2 s can be studied by this method[27].

The flow variant of the method is applicable both to liquid-phase[28] and to gas-phase[29] reactions: it is usually called the continuous flow method.

In the method developed by Roughton[28]‡ two streams of liquid reactants moving with a linear velocity of the order of metres per second are efficiently mixed and led into a capillary provided with a sensitive thermocouple whose junction can be moved controllably. Under the given conditions the reaction proceeds adiabatically§. Hence, the temperature rise (of the order of 0.2–0.3 deg) can easily be correlated with the extent of conversion. The variation of the conversion along the length of the capillary allows the rate constant to be determined to a reproducibility of ±7% at the lowest values of $\tau_{1/2}$ investigated (~ 0.1 s). When the flow method is applied to gas-phase reactions, substantial changes are necessary not only in the dimension of the apparatus and in the linear velocity, but also in the method of treatment of the results of the measurements: this is because of the non-adiabaticity of the process and of the need to use heat transfer equations in partial differential form (Laplace transform)[29].

† For a second-order reaction the equation involves complex functions.

‡ Sometimes wrongly transliterated in Russian as 'Роутон'.

§ Control experiments must be made to test whether the heat of mixing of the reactants is zero.

V. NON-STATIONARY THERMOKINETIC METHODS

Non-stationary kinetic methods are used when the number of kinetic constants to be determined is greater than the number of kinetic equations which can be written in the quasi-stationary approximation. We shall discuss the application of non-stationary thermokinetic methods by considering two examples: radical polymerisation and enzyme catalysis with Michaelis–Menten kinetics.

1. Radical Polymerisation of Vinyl Monomers

According to the kinetic equations for radical polymerisation, the rate of decrease of the monomer concentration is

$$-\frac{d[M]}{dt} = w_i^{1/2}\frac{k_p}{k_t^{1/2}}[M] \qquad (24)$$

where [M] is the monomer concentration, w_i is the rate of initiation, and k_p and k_t are the rate constants for chain propagation and chain termination respectively.

As can be seen from Eqn. (24), a study of the stationary radical polymerisation kinetics can only lead to a combination of the k_p and k_t constants ($k_p/k_t^{1/2}$).

Bengough and Melville[30] developed an inertia-free method involving measurements of the adiabatic heating of the mixture undergoing polymerisation during the initial period of the reaction under continuous illumination (photoinitiation), and calculation of the mean lifetime τ of the radicals. The extent of conversion at time t after the beginning of irradiation such that $t \gg \tau$ (in practice, $t > 5\tau$) is given by the expression

$$\alpha = \frac{\Delta T}{\Delta T_{ad}} = \frac{k_p}{k_t}\left(\frac{t}{\tau} - \ln 2\right). \qquad (25)$$

The quantity $\tau \ln 2$, and hence τ, is evaluated from the intercept of the linear plot of α against t (of slope $k_p/k_t\tau$) on the ordinate axis. From a knowledge of k_p/k_t and $k_p/k_t^{1/2}$, the two kinetic constants can be evaluated separately. One advantage of this method is the possibility of measuring conversions of the order of 10^{-4} mol.%.

Bagdasar'yan and Revzin[31] developed an original non-stationary kinetic method of determining k_p and k_t by observing the change in the adiabatic temperature rise accompanying a sudden decrease in the intensity of the irradiation responsible for initiation after a steady rate of polymerisation has been set up (background initiation method), In this method, the steady-state rate before and after the decrease in the rate of initiation must be known, as well as ΔT_{ad}. Thus, the non-stationary kinetic method can be used both in the early stages and in the late stages of a polymerisation reaction.

2. Enzyme Catalysis

The classical scheme of enzyme catalysis includes the formation of an intermediate enzyme–substrate (ES) complex, which subsequently decomposes with formation of the product P and can also partially dissociate into the starting components:

$$E + S \underset{k_{-1}}{\overset{k_{+1}}{\rightleftarrows}} ES \xrightarrow{k_2} E + P, \text{ with } k_{+1} \gg k_2.$$

By the conventional methods[32], only k_2 and the Michaelis constant K_m can be determined:

$$K_m = \frac{k_{-1} + k_2}{k_{+1}}.$$

By using low-inertia (including thermometric) methods of monitoring the reaction, the continuous flow method can detect the formation of the enzyme–substrate complex when the reaction leading to product formation is in a non-stationary (accelerating) regime. By extrapolating the linear (stationary) portion of the kinetic curve to the time axis, the mean lifetime τ of the enzyme–substrate complex can be determined. Knowing τ and the initial concentration of the substrate $[S_0]$, we can determine k_{+1} from the equation

$$\tau = \frac{1}{k_{+1}[S]_0},$$

and hence arrive at k_{-1} from the value of K_m.[33]

Another variant of the treatment of the experimental data, proposed by Roughton[34], yields the product $k_{+1}k_2$ from the curve for product accumulation during the non-stationary period.

To conclude this section, we note that the temperature jump method proposed by Eigen[35], which can be applied to systems at equilibrium, is sometimes classified among the non-stationary thermokinetic methods. The method relies on the practically instantaneous (10^{-6}–10^{-7} s) rise in temperature by 10–12 deg obtained by discharging a high-voltage condenser or by a laser flash, followed by observation of the relaxation of the system, that is, its approach to a new equilibrium. The method has also been applied to enzyme reactions, but even in the case of unimolecular reactions the measured relaxation time is a measure only of the sum of the rate constants for the forward and the reverse reaction.

VI. EXAMPLES OF THE USE OF THERMOKINETIC METHODS

Thermokinetic methods have been used to study the kinetics of a number of liquid-phase reactions (hydrolysis of esters[12,26], polycondensation of diacyl chlorides and glycols[13], polymerisation of styrene[15], alkene oxides[36], ethylenediamine[50], and oligoacrylates[37] in bulk). The polymerisation kinetics of styrene have been studied[20] by compensation calorimetry.

Thermokinetic studies of fast gas reactions include the photochemical dissociation of ethylene[25] and the reaction of boron trifluoride with aliphatic amines[29].

The adiabatic nature of thermal explosion and thermal ignition was established by Semenov[40], and the use of the adiabatic regime for studying these reactions has been discussed in monographs by Zel'dovich and Voevodskii[7], Frank-Kamenetskii[21], and Kondrat'ev[41]. A great deal of work has been devoted to the application of thermokinetic methods in studies of topochemical reactions (thermal decomposition of inorganic compounds, using differential thermography[8], decomposition of explosives[6,42], and thermal degradation of polymers[43]). The kinetics of various heterogeneous processes (adsorption, dissolution) have been investigated calorimetrically[2]. Critical ignition conditions have been used to study the kinetics of a heterogeneous catalytic reaction (the synthesis of alcohols from CO and H_2[44]).

The application of fast thermokinetic methods has been described in conjunction with the hydration of acetaldehyde[27], the preparation of polyamides[45] and polyesters[46], etc. Non-stationary thermokinetic methods have been used to study the polymerisation of vinyl acetate, acrylates[30], and oligoacrylates[47]. The kinetics of the formation of the enzyme–substrate complex in the cataly is of ribonuclease[58] and of chymotrypsin[49] have bee investigated by the temperature step method.

There can be no doubt that the number of investigations by thermokinetic methods will increase rapidly, in parallel with advances in the experimental techniques of this rapidly developing branch of chemical kinetics.

VII. ADVANTAGES OF THERMOKINETIC METHODS

Thermokinetic methods have unique advantages in the study of the kinetics of strongly exothermic reactions, in which isothermal conditions cannot be maintained, and of reactions in highly viscous media, which preclude effective stirring. In most of the variants of the thermokinetic method the whole of the kinetic curve can be obtained in a single experiment. The use of rising temperature conditions for the reaction (by exothermic self-heating or by programmed heating) enables the kinetics to be studied at extreme stages of the reaction, which is not always possible under isothermal conditions. Lastly, the thermometric method (applied to reactions of known kinetic law) allows the effective activation energy to be evaluated from a single experimental curve[11].

REFERENCES

1. A.G.Merzhanov and V.G.Abramov, Zhur.Fiz.Khim., 38, 2640 (1964) [Russ.J.Phys.Chem., 1431 (1964)].
2. E.Calvet and R.Prat, "Microcalorimétrie: Applications physico-chimiques et biologiques" (Translated into Russian), Inostr.Lit., Moscow, 1963.
3. M.M.Popov, "Termometriya i Kalorimetriya" (Thermometry and Calorimetry), 2nd Edition, Izd.Moskov.Univ., Moscow, 1954.
4. E.Caldin, "Fast Reactions in Solution" (Translated into Russian), Izd.Mir, Moscow, 1966.
5. S.M.Skuratov, V.P.Kolesov, and A.F.Vorob'ev, "Termokhimiya" (Thermochemistry), Parts I and II, Izd.Moskov.Gos.Univ., Moscow, 1964–1966.
6. D.Cross and A.B.Amster, in "8th International Symposium on Combustion, Pasadena, California, Aug.28–Sept 3 1960", Williams and Wilkins, Baltimore, 1962, p.728.
7. Ya.B.Zel'dovich and V.V.Voevodskii, "Teplovoi Vzryv i Rasprostranenie Plameni v Gazakh" (Thermal Explosion and Flame Propagation in Gases), Izd.Moskov.Mekhanicheskogo Inst., Moscow, 1947, pp.90, 107.
8. B.M.Moiseev, Zhur.Fiz.Khim., 37, 685 (1963) [Russ.J.Phys.Chem., 357 (1963)].
9. G.I.Likhtenshtein, Yu.M.Sivergin, and A.A.Berlin, Teort. i Eksper.Khim., 1, 690 (1965).
10. I.Gol'dman, Zhur.Fiz.Khim., 21, 1293 (1947).
11. V.S.Livshits, Kinetika i Kataliz, 9, 712 (1968).
12. P.Baumgartner and P.Duhaut, Bull.Soc.chim.France, 1187 (1960).
13. V.V.Evreinov and S.G.Entelis, Kinetika i Kataliz, 6, 922 (1965).
14. V.N.Kondrat'ev, "Teplovye Izmereniya" (Thermal Measurements), Mashgiz, Moscow–Leningrad, 1957.
15. A.G.Merzhanov, V.G.Abramov, and L.T.Abramova, Zhur.Fiz.Khim., 41, 179 (1967) [Russ.J.Phys.Chem., 90 (1967)].

16. N.M.Emanuel' and D.G.Knorre, "Kurs Khimicheskoi Kinetiki" (Course in Chemical Kinetics), Izd.Vys.Shkola, Moscow, 1962, p.390.
17. A.G.Merzhanov, V.G.Abramov, and L.T.Abramova, Dokl. Akad.Nauk SSSR, 171, 901 (1966).
18. G.V.Korolev, B.V.Pavlov, and A.A.Berlin, Vysokomol. Soed., 1, 1396 (1959).
19. G.M.Chil'-Gevorgyan, A.K.Bonetskaya, and S.M.Skuratov, Zhur.Fiz.Khim., 39, 1794 (1965) [Russ.J.Phys.Chem., 956 (1965)].
20. H.M.Anderson, J.Polymer Sci., A1, 783 (1966).
21. D.A.Frank-Kamenetskii, "Diffuziya i Teploperedacha Khimicheskoi Kinetike" (Diffusion and Heat Transfer in Chemical Kinetics), 2nd Edition, Izd.Nauka, Moscow, 1967, pp.393, 398, 301.
22. Yu.B.Kagan, A.Ya.Rozovskii, M.G.Slin'ko, and A.T.Ponomarenko, Kinetika i Kataliz, 5, 920 (1964).
23. Yu.B.Kagan, A.Ya.Rozovskii, M.G.Slin'ko, and A.T.Ponomarenko, Kinetika i Kataliz, 5, 1111 (1964).
24. N.Ya.Buben, "Sbornik Rabot po Fizicheskoi Khimii" (Collected Papers on Physical Chemistry), Izd.Akad.Nauk SSSR, Moscow, 1947, pp.148, 154.
25. A.B.Callear and J.C.Robb, Discuss.Faraday Soc., No.17, 21 (1954).
26. R.P.Bell and J.C.Clunie, Proc.Roy.Soc., 212A, 16 (1952).
27. R.P.Bell, M.H.Rand, and K.M.A.Wynne-Jones, Trans. Faraday Soc., 52, 1093 (1956).
28. L.Pearson, B.R.Pinsent, and F.J.Roughton, Discuss. Faraday Soc., No.17, 141 (1954).
29. D.Garvin, V.P.Guinn, and G.B.Kistiakowsky, Discuss. Faraday Soc., No.17, 32 (1954).
30. W.J.Bengough and H.W.Melville, Proc.Roy.Soc., 225A, 330 (1954); 230A, 429 (1955).
31. Kh.S.Bagdasar'yan and A.F.Revsin, Kinetika i Kataliz, 4, 844 (1963).
32. V.Ya.Yakovlev, "Kinetika Fermentativnogo Kataliza" (Kinetics of Enzyme Catalysis), Izd.Nauka, Moscow, 1965, pp.41, 42.
33. M.Dixon and E.Webb, "Enzymes" (Translated into Russian), 2nd Edition, Izd.Mir, Moscow, 1966, pp.101, 102.
34. F.J.Roughton, Discuss.Faraday Soc., No.17, 116 (1954).
35. M.Eigen, Discuss.Faraday Soc., No.17, 194 (1954).
36. K.S.Kazanskii, V.V.Evreinov, and S.G.Entelis, Izv.Akad. Nauk SSSR, Ser.Khim.Nauk., 274 (1964).
37. G.V.Korolev, Thesis, Inst.Khim.Fiz.Akad.Nauk SSSR, Moscow, 1965.
38. O.B.Solomatina, A.K.Bonetskaya, S.M.Skuratov, and I.S.Enikolopyan, Vysokomol.Soed., 9B, 313 (1967).
39. G.M.Chil'-Gevorgyan, A.K.Bonetskaya, S.M.Skuratov, and N.S.Enikolopyan, Vysokomol.Soed., 9A, 1363 (1967).
40. N.N.Semenov, "Tsepsnye Reaktsii" (Chain Reactions), ONTI, Leningrad, 1934.
41. V.N.Kondrat'ev, "Kinetika Khimicheskikh Gazovykh Reaktsii" (Kinetics of Chemical Gas Reactions), Izd.Akad. Nauk SSSR, 1958, p.547.
42. A.G.Merzhanov and A.G.Strunina, "Nauchno-tekhnicheskie Problemy Goreniya i Vzryva" (Scientific and Technological Problems in Combustion and Explosion), 1, 59 (1965).
43. L.Reich, J.Appl.Polymer Sci., 9, 3033 (1965); 10, 465 (1966).
44. Yu.B.Kagan, A.T.Ponomarenko, and A.Ya.Rozovskii, Kinetika i Kataliz, 7, 679 (1966).
45. S.G.Entelis, E.Yu.Bekhli, and O.V.Nesterov, Kinetika i Kataliz, 6, 331 (1965).
46. E.Yu.Bekhli, O.V.Nesterov, and S.G.Entelis, J.Polymer Sci., C1, 209 (1967).
47. N.N.Tvorogov and G.V.Korolev, Vysokomol.Soed., 6, 877 (1964).
48. R.E.Kathou and G.G.Hammes, J.Amer.Chem.Soc., 86, 3240 (1964).
49. A.Yapel and R.Lumry, J.Amer.Chem.Soc., 86, 4499 (1964).
50. O.O.Bartan, Candidate's Thesis, Inst.Khim.Fiz.Akad.Nauk SSSR, Moscow, 1966.

Central Scientific Institute for the Sewing Industry, Moscow

U.D.C. 543.241.5

The Differentiating Action of Oxygen-containing Solvents on the Strengths of Acids

V.I.Dulova, N.V.Lichkova, and L.P.Ivleva

The present review examines the differentiating action of various oxygen-containing solvents on the strength of acids, chiefly carboxylic acids, and nitrophenols. The strength of the acids in these solvents is characterised by the dissociation constants (dielectric constant of solvent > 10) or by the conversion constants (dielectric constant of solvent < 10). The constants were determined by the buffer-free indicator method. The bibliography contains 143 references.

CONTENTS

I. Introduction 818
II. Determination of the strength of acids in solution 819
1. Alcohols and ethers 821
2. Ketones 827
3. Esters 828

I. INTRODUCTION

In the study of electrolytes in non-aqueous solvents, it is often found that the change in their strength is different from that observed in water. This effect of the solvents is called their "differentiating action".

The differentiating action of solvents on the strength of electrolytes, in particular acids, is an important problem in the general theory of solutions. This problem is also of considerable importance in the examination of the reactivities of substances and the mechanisms of reactions in solution. The ability of various non-aqueous solvents to