Journal of Thermal Analysis, Vol. 30 (1985) 627–640

APPLICATION OF THERMOKINETICS IN CHEMICAL PROCESS ANALYSIS, AS ILLUSTRATED BY THE REACTION OF PHENYL ISOCYANATE AND *n*-BUTANOL

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(Received November 15, 1984)

Shortening the time required for chemical process development from the first laboratory trial through technical and pilot plants to industrial installation is a long-standing aim. Knowledge of the reaction kinetics is of major importance for this purpose. The usefulness of thermokinetics in chemical process engineering is illustrated by reaction of phenyl isocyanate and *n*-butanol.

The conventional method of eliciting the kinetics of formation of urethanes in the chemical industry is to take samples at given intervals during the reaction, which are then analysed immediately (or in some cases after appropriate handling) by means of conventional analysis methods such as titration, refractometry, spectrophotometry, etc. From the dependence of the estimated concentrations of the educts and the products on time which is thus established, the technically oriented reaction mechanism and the appertaining rate law are then elicited on the basis of graphic or numeric operations [1]. Technically oriented means that it does not concern microkinetics in the sense of academic basic research, but a phenomenological characterization of the processes in the reaction mixture, which allows quantitative predictions of the range of products and regarding influences on the reaction due to chemical species concentrations, temperature, pressure, solvent and catalysts.

The conventional approach is clearly time-consuming and subject to error, particularly when rapid reactions are being investigated. Moreover, classical analysis of samples with the chemical milieu of a technical mix yield (more often than generally known) either no result or only an unsatisfactory one. Patently, therefore, an analysis method must be used which is always applicable, operates continuously and without interfering with the course of the reaction, in simple cases gives immediately the reaction rate or a value directly proportional to it, and in very complex cases indicates at least the gross kinetics, i.e. the pulse rate of the reaction.

Thus, it stands to reason that thermal analysis should be employed, for everyone knows that any chemical reaction is accompanied by the liberation of more or less heat. In doing so, preference should be given to the direct measurement of thermal reaction power (rate of heat evolution) q because of the well-known relation between the reaction rate r and the thermal reaction power q: $q = r\cdot(-\Delta H)\cdot V = k\cdot f(c_i, p_i)\cdot(-\Delta H)\cdot V$ for an elementary reaction and $q = \sum q_j = \sum r_j\cdot(-\Delta H_j)\cdot V$ for a system of elementary reactions j. (List of symbols at the end of the paper.) The measurement of q should preferably be performed under virtually isothermal conditions, since otherwise the analysis becomes unnecessarily complicated due to the complex dependence both of the rate constants $k(T)_j$ and of the reaction enthalpies $\Delta H(T)_j$ on temperature. Moreover, the rate functions $f_j(c_i, p_j)$ can be elicited much more easily and accurately with an isothermal than with a nonisothermal procedure.

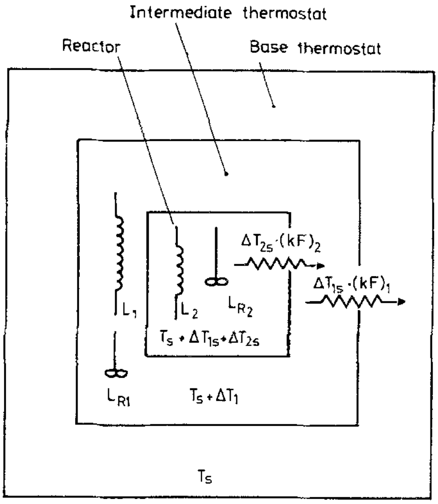

Fig. 1 Working principle [2]

Apparatus [2]

The apparatus used for this purpose functions essentially on the compensation principle: A reactor chamber is surrounded by the fluid of a turbulently stirred thermostat, which strictly speaking is an intermediate thermostat, since it is in turn immersed in a base thermostat the fluid of which is subject to turbulent stirring (Fig. 1). The reactor chamber is equipped with a stirrer, a current breaker, a controlled electric heater and a temperature sensor. The intermediate thermostat is equipped in the same way. The temperature T_s of the base thermostat is controlled at a constant level. The controlled heating power L_1 of the intermediate thermostat maintains a constant set temperature difference ΔT_{1s} between the intermediate thermostat and the base thermostat, and the controlled heating power L_2 in the reactor maintains a constant set temperature difference ΔT_{2s} between the reactor and the intermediate thermostat. The reactor involves the highest temperature, $T_s + \Delta T_{1s} + \Delta T_{2s}$, the intermediate thermostat the medium temperature, $T_s + \Delta T_{1s}$, and the base thermostat the lowest temperature, T_s.

Corresponding to the constant temperature difference ΔT_{2s}, the heat $(kF)_2 \cdot \Delta T_{2s}$ flows from the reactor to the intermediate thermostat and, corresponding to the constant temperature difference ΔT_{1s}, the heat $(kF)_1 \cdot \Delta T_{1s}$ flows from the intermediate thermostat to the base thermostat. In controlled thermal equilibrium, the balance of thermal power is given by

a) reactor

$$q + L_2 + L_{R2} = (kF)_2 \cdot \Delta T_{2s} \tag{1}$$

b) intermediate thermostat

$$(kF)_2 \cdot \Delta T_{2s} + L_1 + L_{R1} = (kF)_1 \cdot \Delta T_{1s} \tag{2}$$

$(kF)_2$ and L_{R2} are, in a manner of speaking, apparatus constants; ΔT_{1s} and ΔT_{2s} are maintained unchanged by appropriately adjusting L_1 and L_2 via two PID control loops to the evolved thermal reaction power q, as well as to the stirring power L_{R2} within the reactor and to the heat flow $(kF)_2 \cdot \Delta T_{2s}$ from the reactor to the intermediate thermostat, which both change inevitably as a result of the changing physical properties of the reaction mix (viscosity, density, etc.).

Therefore, Eqs (1) and (2) result in

$$q(t) = \underbrace{[L_1 + L_2 + L_{R2}]}_{\substack{\text{prior}\\ \text{to start}\\ \text{of reaction}}} - \underbrace{[L_1(t) + L_2(t) + L_{R2}(t)]}_{\substack{\text{after}\\ \text{start of}\\ \text{reaction}}} \tag{3}$$

It is ensured that the bearing of the stirrer arrangement is not fouled by the reaction mix during the reaction, and that the stirrer rotational velocity is kept constant via a control loop, i.e. that the friction loss remains unchanged, so that the following relationship exists between the stirring power L_{R2} and the motor power L_{M2}:

$$L_{R2} = L_{M2} - \text{const.} \tag{4}$$

It therefore follows from Eq. (3) that

$$\begin{aligned} q(t) &= \underbrace{[L_1 + L_2 + L_{M2}]}_{\substack{\text{prior}\\ \text{to start}\\ \text{of reaction}}} - \underbrace{[L_1(t) + L_2(t) + L_{M2}(t)]}_{\substack{\text{after}\\ \text{start of}\\ \text{reaction}}} \qquad (5)\\ &= L_p - L(t) \end{aligned}$$

with $L_p = \text{const.}$ (Fig. 2).

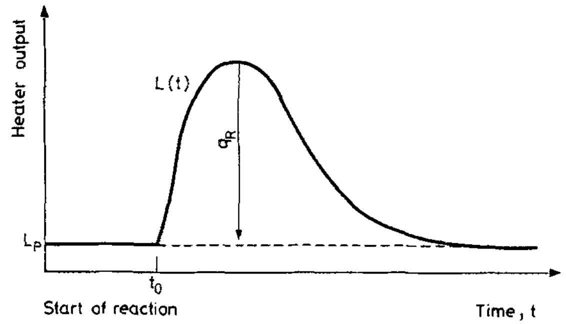

Fig. 2 For evaluation of the thermal reaction power q from the measured curve

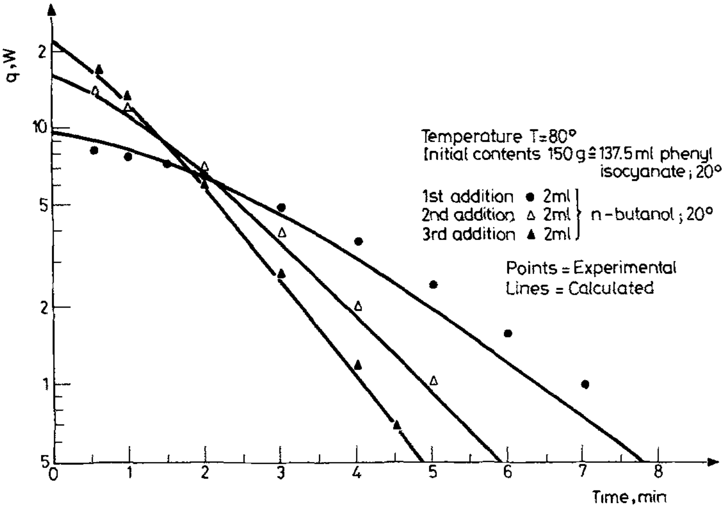

Fig. 3 Thermal power of the reaction between phenyl isocyanate and *n*-butanol

The reaction between phenyl isocyanate and n-butanol

To carry out the measurements, for instance, 150 g phenyl isocyanate is placed in the reactor and 2 ml *n*-butanol is injected to start the reaction. As a monoisocyanate/monoalcohol reaction system is involved, the appertaining stoichiometry indicates one overall reaction step, from which it can be assumed, in light of the large excess of monoisocyanate, that it proceeds in accordance with a pseudo-first-order rate law, i.e. the logarithmic representation of the measured thermal power $q(t)$ over time should give a straight line. However, this is not the case, a concave curve being produced initially, which only becomes a straight line later during the reaction (Fig. 3). When (after completion of the conversion of the injected

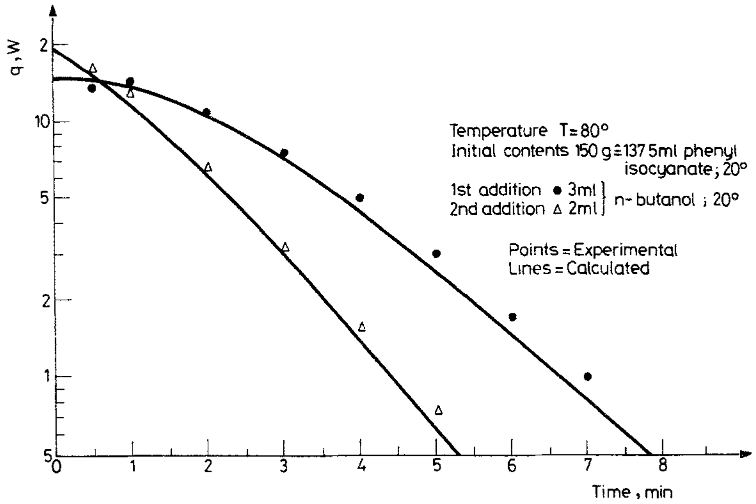

Fig. 4 Thermal power of the reaction between phenyl isocyanate and *n*-butanol

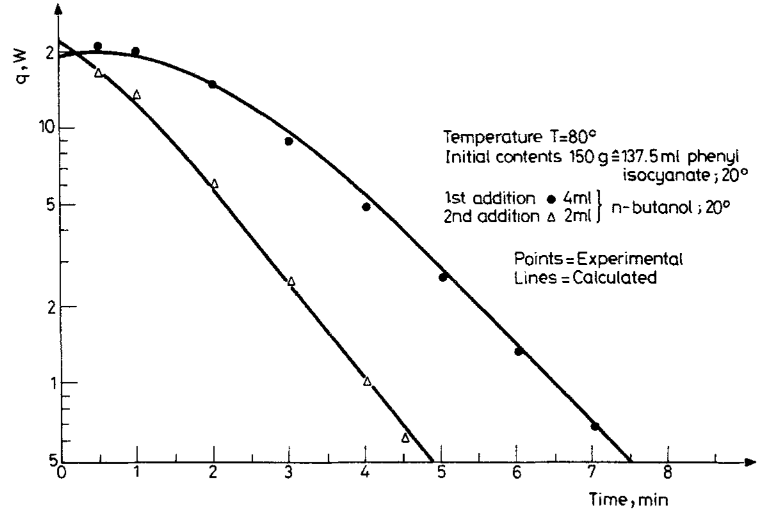

Fig. 5 Thermal power of the reaction between phenyl isocyanate and *n*-butanol

small amount of alcohol) a second small amount of alcohol is injected into this prereacted mix, which now contains products, the reaction runs more quickly. From (repeated) alcohol injection to injection, the reaction becomes quicker and quicker.

The experimental results which are represented in Figs 3–12 clearly show that the phenyl isocyanate/*n*-butanol reaction proceeds in an autocatalytically accelerated manner. It can be assumed that the produced urethane (or a proportional amount of by-product) acts as catalyst.

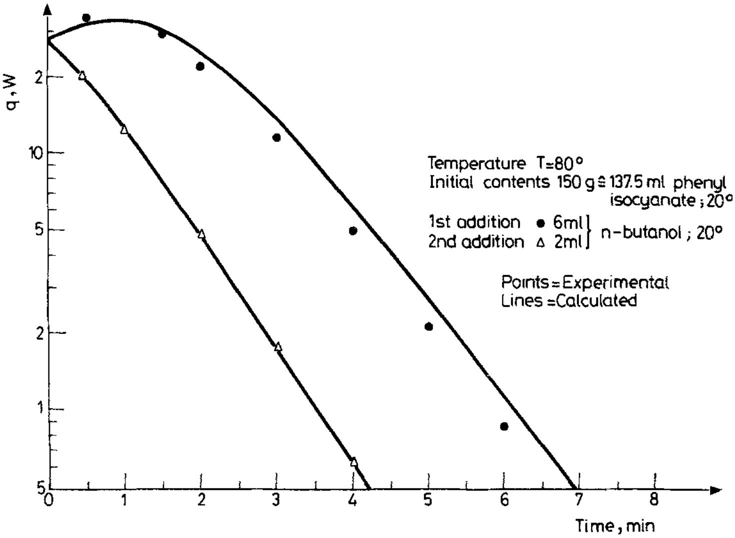

Fig. 6 Thermal power of the reaction between phenyl isocyanate and *n*-butanol

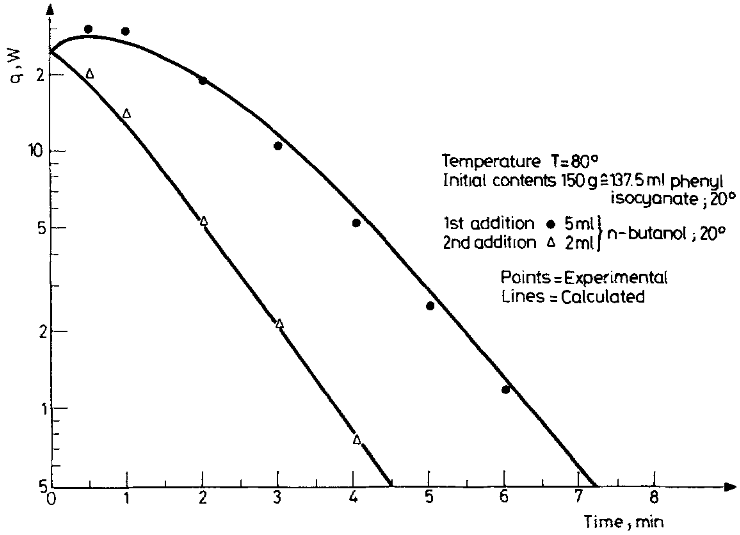

Fig. 7 Thermal power of the reaction between phenyl isocyanate and *n*-butanol

For a reaction-kinetic treatment of the results, with a view to compilation of a technically oriented reaction equation, it must be assumed that the measured thermal reaction power is not solely caused by the autocatalytic reaction mechanism, but that an additional parallel uncatalysed reaction step also occurs.

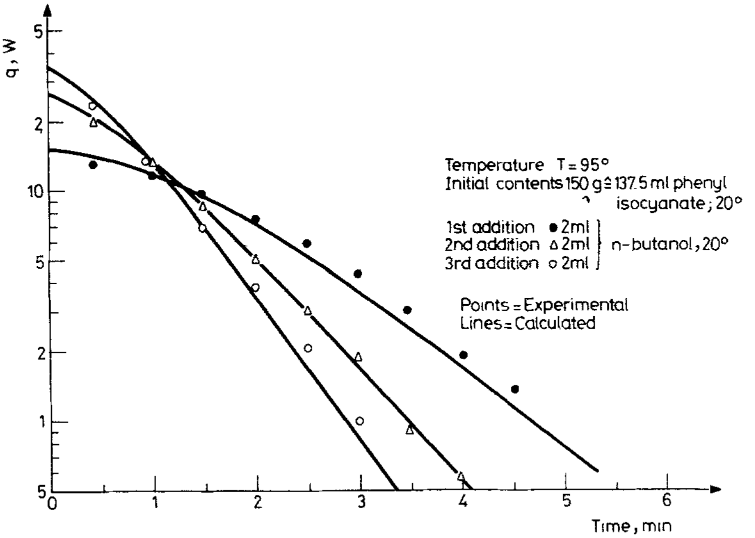

Fig. 8 Thermal power of the reaction between phenyl isocyanate and *n*-butanol

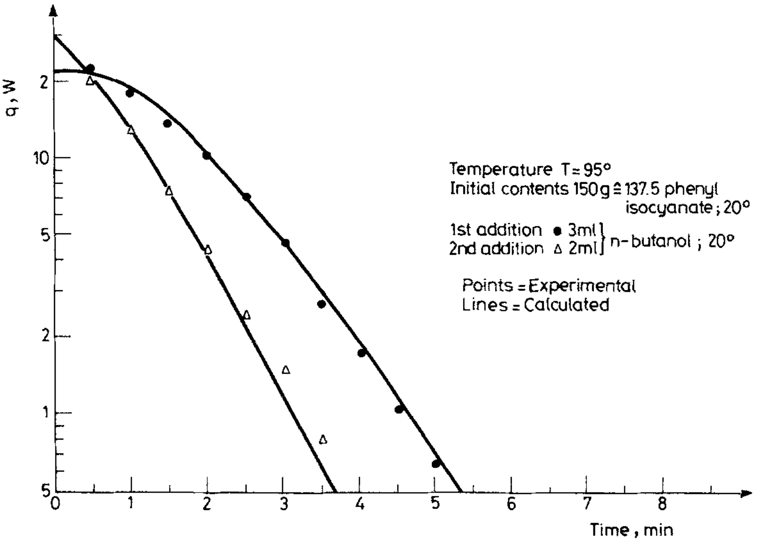

Fig. 9 Thermal power of the reaction between phenyl isocyanate and *n*-butanol

Otherwise, the reaction at the beginning of the test series (in the absence of urethane) would not start.

The following reaction mechanism is therefore suggested:

$$A + I \xrightarrow{k_1} U \text{ uncatalysed}$$

$$A + I \xrightarrow{k_2(U)} U \text{ catalysed}$$

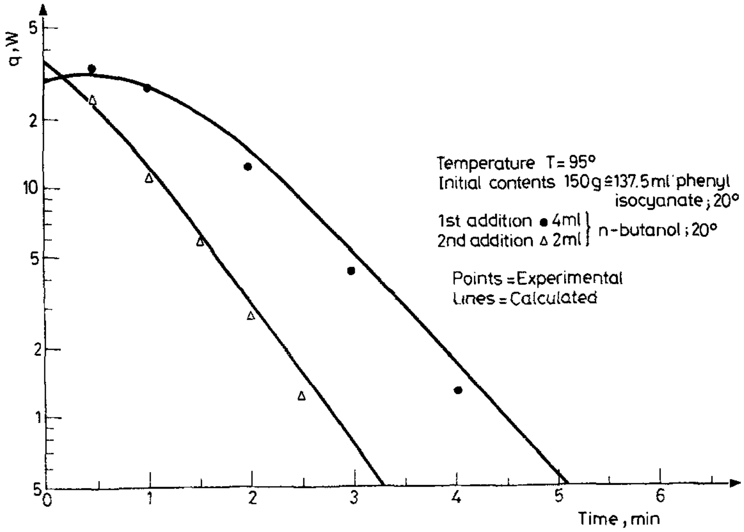

Fig. 10 Thermal power of the reaction between phenyl isocyanate and *n*-butanol

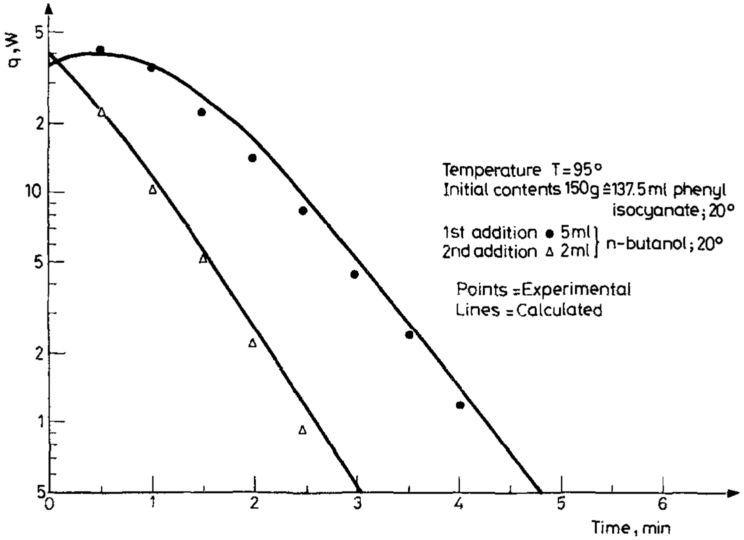

Fig. 11 Thermal power of the reaction between phenyl isocyanate and *n*-butanol

The first step represents the uncatalysed mechanism, and the second step the additional catalysed one. The overall effects of both mechanisms are the same, so that both conversions have the same reaction enthalpy ΔH.

The reaction rate r_1 of the uncatalysed reaction step is expressed as proportional to the product of the concentrations of isocyanate i and alcohol a, while the rate r_2 of

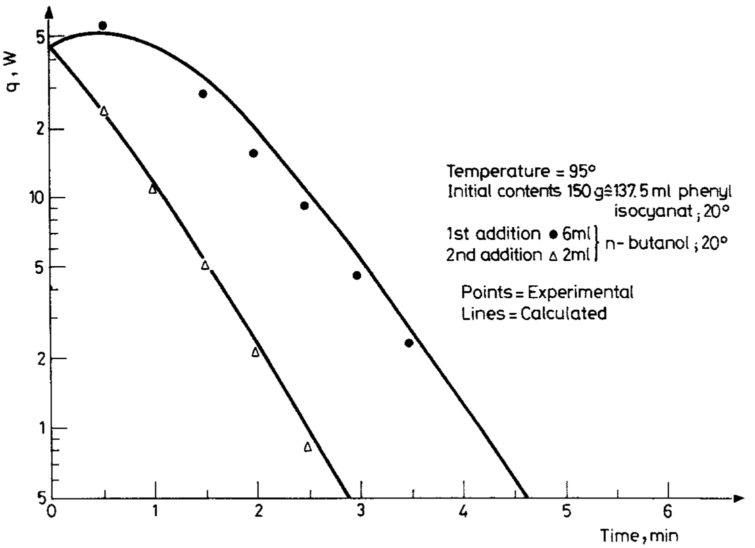

Fig. 12 Thermal power of the reaction between phenyl isocyanate and *n*-butanol

the urethane-catalysed reaction step is also expressed as proportional to the product of the concentrations of isocyanate i and alcohol a, but where the proportionality factor k_2 is a function of the urethane (or by-product) concentration u:

$$\begin{aligned} r_1 &= k_1 \cdot i \cdot a \\ r_2 &= k_2(u) \cdot i \cdot a \end{aligned} \tag{6}$$

To a first approximation it is assumed that $k_2(u)$ is a linear function of the urethane concentration: $k_2(u) = k_2 \cdot u$.

Therefore, Eq. (6) gives:

$$\begin{aligned} r_1 &= k_1 \cdot i \cdot a \\ r_2 &= k_2 \cdot u \cdot i \cdot a \end{aligned} \tag{7}$$

The thermal reaction power q of the reaction phenyl isocyanate/*n*-butanol is therefore expressed by

$$q = (r_1 + r_2) \cdot V \cdot (-\Delta H) = (k_1 \cdot i \cdot a + k_2 \cdot u \cdot i \cdot a) \cdot V \cdot (-\Delta H) \tag{8}$$

where the reaction volume V is a function of the composition, $V = V(i, u, a)$: volume changeability during conversion.

As a large excess of isocyanate is used, the following simplifications are possible:

1. During each individual experiment (ν), the reaction proceeds without a change in volume:

$$V_\nu \simeq \text{const} = V_{0\nu}{}^{*}$$

2. During each individual experiment (ν), the isocyanate concentration remains unchanged:

$$\begin{aligned} i_\nu \simeq \text{const.} = i_{0\nu},\ \text{i.e. } & k_1 \cdot i_\nu \simeq k_1 \cdot i_{0\nu} = K_{1\nu} \text{ and} \\ & k_2 \cdot i_\nu \quad k_2 \cdot i_{0\nu} = K_{2\nu} \end{aligned}$$

$K_{1\nu}$ and $K_{2\nu}$ therefore represent constants for each individual experiment; they differ from one individual experiment to the next through the alcohol quantity ΔV_A added and the quantity of isocyanate already converted.

On the basis of the given simplifications, the following is valid for the thermal reaction power q during each individual experiment ν:

$$q_\nu = (K_{1\nu} \cdot a + K_{2\nu} \cdot a \cdot u) \cdot V_\nu \cdot (-\Delta H)$$

On account of the mole balance $u = a_0 - a + u_0$, it follows that

$$q_\nu = (K_{1\nu} + K_{2\nu} \cdot (a_{0\nu} + u_{0\nu}) \cdot a_\nu - K_{2\nu} \cdot a_\nu^2) \cdot \\ \cdot V_{0\nu} \cdot (-\Delta H) \tag{9}$$

If Q_ν is the quantity of heat evolved up to time t and $Q_{00\nu} = a_{0\nu} \cdot V_{0\nu} \cdot (-\Delta H)$ the total reaction heat, the concentration a_ν can be expressed in terms of Q_ν:

$$a_\nu = \frac{a_{0\nu}}{Q_{00\nu}} (Q_{00\nu} - Q_\nu)$$

The following therefore applies for the thermal reaction power q for each individual experiment (ν):

$$q_\nu = \alpha_\nu \cdot (Q_{00\nu} - Q_\nu) - \beta_\nu / Q_{00\nu} \cdot (Q_{00\nu} - Q_\nu)^2 \tag{10}$$

where $\alpha_\nu = K_{1\nu} + K_{2\nu} \cdot (a_{0\nu} + u_{0\nu})$ and $\beta_\nu = K_{2\nu} \cdot a_{0\nu}$. On account of the identity $q \equiv dQ/dT$, the above equation represents a differential equction for Q as a function of

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* $V_{0\nu} = V_I$ — initial content $\sum_1^\nu \Delta V_{A\nu}$-injections

$a_{0\nu} = A_\nu$-injection$/V_{0\nu}$

$i_0 = I$-initial content $- \sum_1^{\nu-1} A_\nu$-injections$/V_{0\nu}$

for $\nu = 1$: sum term $\sum A_\nu = 0$

$u_0 = \sum_1^{\nu-1} A_\nu$-injections$/V_{0\nu}$

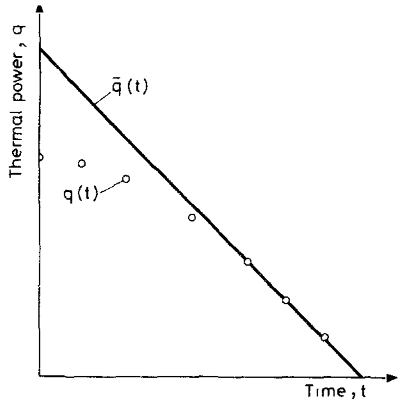

Fig. 13 Measured curve $q(t)$ and auxiliary curve $q(t)$

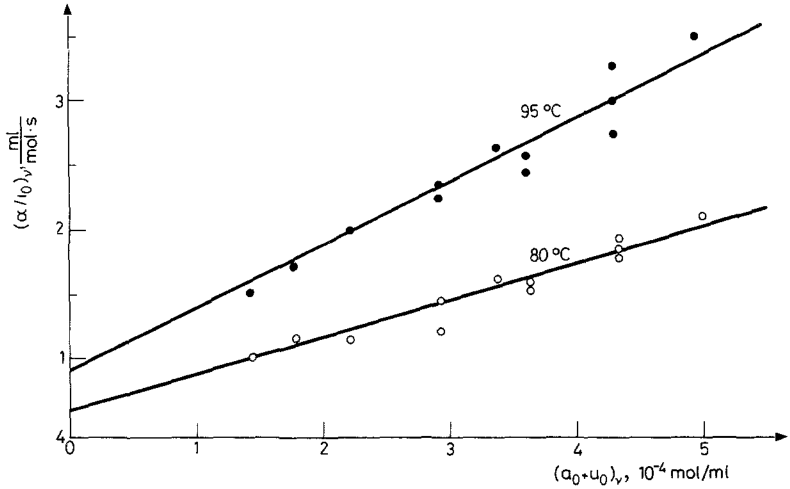

Fig. 14 For determination of the rate constants k_1 and k_2 from $(\alpha/i_0)_v = k_1+k_2(a_0+u_0)_v$

time; integration and rearrangement yields $Q = f(t)$. Inserting $Q(t)$ in (10) yields the thermal reaction power as a function of time:

$$q_v(t) = \frac{Q_{00v}\cdot\alpha_v(1-\beta_v/\alpha_v)\,e^{\alpha_v t}}{[\beta_v/\alpha_v+(1-\beta_v/\alpha_v)\,e^{\alpha_v t}]^2}$$

For $t \gg 0$, the following applies:

$$q_v(t \gg 0) \simeq Q_{00v}\cdot\alpha_v^2\cdot e^{-\alpha_v t}/(\alpha_v-\beta_v) = \bar{q}_v(t) \quad \text{(Fig. 13)}$$

i.e. when plotted logarithmically, $q_v(t)$ for $t \gg 0$ becomes, in accordance with the results, a straight line with slope α_v and ordinate intercept $Q_{00v}\cdot\alpha_v^2(\alpha_v+\beta_v)$.

The slopes of the straight lines from the individual experimental results (v) are different, in accordance with

$$\alpha_v = K_{1v}+K_{2v}\cdot(a_{0v}+u_{0v}) = k_1\cdot i_{0v}+k_2\cdot i_{0v}\cdot(a_{0v}+u_{0v})$$

as pointed out.

If $(\alpha/i_0)_v$ is plotted against $(a_0+u_0)_v$, a straight line must be obtained whose slope represents the k_2 value and whose ordinate intercept represents the k_1 value (Fig. 14).

The Arrhenius plot of the elicited rate constants yields for the activation energy E:

$E_1 = 31.4$ kJ/mol
$E_2 = 39.4$ kJ/mol

and for the pre-exponential factor k_p:

$k_{p1} = 2.6\cdot 10^4$ ml/(mol·s)
$k_{p2} = 2.3\cdot 10^4$ ml/(mol^2·s)

The reaction enthalpy is calculated using the rate constants k_1 and k_2 in accordance with the following equation from the ordinate intersection $\bar{q}(0)_v$ of the extrapolated straight line $(q_v(t \gg 0) = \bar{q}(t)_v$:

$$-\Delta H = \bar{q}(0)_v\cdot(k_1\cdot i_{0v}+k_2\cdot i_{0v}\cdot u_{0v})/(k_1\cdot i_{0v}+k_2\cdot i_{0v}(a_{0v}+ +u_{0v})^2\cdot A_{0v})$$

The arithmetic average of the scattered values of the reaction enthalpy calculated from the variety of ordinate sections $\bar{q}(0)_v$ yields

$$-\Delta H = 87.4 \text{ kJ/mol } n\text{-butanol}$$

To verify the quality of the kinetic approach, Eq. (7), the thermal reaction power is calculated under the factual conditions, i.e. in accordance with Eq. (8), with only the assumption of the unchangeability of the reaction volume, because the volume changeability v (u, c, a) is unknown.

The calculated curves are shown in Figs 3–12. The agreement between calculation and experiment is satisfactory enough to allow for the chemical engineering/design of reactors, etc.

Nevertheless, a systematic deviation between the calculated and the experimental results cannot be overlooked: with additions of a lower alcohol volume, the calculated curves lie below the measured curves, whilst on greater alcohol volume additions the calculated curves lie above the measured one. This indicates that the linear dependence of the rate factor k_2 on the urethane concentration is not exactly valid; this is not surprising when it is considered that the autocatalysis certainly does not proceed via one step, but via intermediate steps which involve initial binding and subsequent release of the urethane. However, as the change of deviations between the calculated and the experimental results is only small, it can be concluded that the deviation from the linear dependence of k_2 on the urethane (or by-product) concentration is also small. Moreover, an exact determination of $k_2 = f(u)$ is only reasonable and can only be successfully carried out when the complex volume changeability of the reaction volume $V = V(i, u, a)$ is exactly known, because strictly speaking, for the mentioned aim, it must be accurately considered in the eliciting of the kinetic parameters.

List of symbols

A	characterizing alcohol
a	concentration of alcohol
c_i	concentration of chemical species i
E	activation energy
$f(ci, pi)$	functionality of the rate equation on concentration and partial pressure of species
F	heat exchange area
I	characterizing isocyanate
i	concentration of isocyanate
ΔH	reaction enthalpy
k	heat exchange coefficient
K_1, K_2, k_1, k_2	rate constants
L_1, L_2	heating powers of intermediate thermostat and reactor
L_{R1}, L_{R2}	stirring powers of intermediate thermostat and reactor
L_{M2}	power of reactor motor
o	index characterizing facts at start of reaction
p_i	partial pressure of chemical species i
q_j	thermal reaction power of elementary reaction j
q	total reaction power
$\bar{q}$	auxiliary quantity
$Q(t)$	heat of reaction evolved up to time t
Q_{00}	total heat of reaction
r	reaction rate
T_s	temperature of base thermostat
ΔT_{1s}	set temperature difference intermediate/base thermostat
ΔT_{2s}	set temperature difference reactor/intermediate thermostat
t	time as from start of reaction

U	characterizing urethane
u	concentration of urethane
V	volume of reaction mix
ΔV_A	volume of injected alcohol
α	auxiliary rate factor
β	auxiliary rate factor
ν	characterizing individual measurement

References

1 K. C. Frisch, S. L. Rugan: Advances in Urethanes, 1962, Interscience Publ., New York.

2 W. Litz, J. Thermal Anal., 27 (1983) 215.

Zusammenfassung — Die Abkürzung der Verfahrensentwicklung vom ersten Laborversuch über Technikums- und Pilotanlagen bis zur großtechnischen Anlage ist ein seit langem erstrebtes Ziel. Dabei ist bekanntlich die Kenntnis der Reaktionskinetik von großer Bedeutung. Am Beispiel der Reaktion Phenylisocyanat und *n*-Butanol wird die Nützlichkeit der Thermokinetik in der chemischen Verfahrensentwicklung aufgezeigt.

Резюме — Сокращение времени, требуемого для протекания химического процесса, начиная от первоначальных лабораторных испытаний на опытных и пилотных установках до промышленных установок, является давнишней мечтой. Для достижения этой цели главным является знание кинетики реакций. Полезность термокинетики в химической технологии показана на примере реакции фенилизоцианата с н-бутанолом.