Thermokinetics of Reactions with Liquid-Liquid Phase Separation

Christian Baumann and Friedrich Becker†

Institut für Physikalische und Theoretische Chemie der Universität Frankfurt am Main, Marie-Curie-Straße 11, D-60439 Frankfurt, Germany

Key Words: Chemical Kinetics / Critical Phenomena / Heat Flow Colorimetry

Isothermal heat flow calorimetry with controlled thermoelectric cooling resp. heating is applied to study the critical slowing down of the kinetics of reactions with liquid-liquid phase separation. Results (i) on the acid-catalysed hydrolysis of chloromethyloxirane by water, and (ii) on the ring-opening and esterification of bromomethyloxirane by dichloroacetic acid in the presence of cyclohexane as an inert solvent, both at 298.15 K, are presented. The heat production $w(t)$ which is proportional to the reaction rate $\partial\zeta/\partial t$ (where ζ is the reaction coordinate) exhibits a funnel-like fall-off when the reaction path intersects the binodal curve at the critical solution point CP. From the shape of this part of the $w(t)$ curves an average value of the critical exponent $\varphi = 0.72 \pm 0.003$, which refers to the change of ζ with t at constant T and p, is calculated. This result is to be compared with the theoretical value of $\varphi = 0.708$ obtained from a modification of the Griffiths and Wheeler theory of critical points in multicomponent systems to chemically reacting systems far from equilibrium by introducing ζ as an additional extensive variable. This allows the critical slowing down of the reaction rates to be interpreted as resulting from the divergence of the correlation length ξ resp. from the convergence of the transport phenomena to zero at the CP.

1. Introduction

In this paper we continue our earlier thermokinetic investigations on the influence of the liquid-liquid phase transition on the kinetics of chemical reactions [1]. In the case of the esterification of 1,2-ethanediol by acetic anhydride, we have shown that the intersection of the coexistence curve by the reaction path is indicated by a jump of the heat production $w(t)$ which is proportional to the reaction rate. Near the critical solution point (CP) this jump is superposed by a symmetrical funnel-like fall-off of $w(t)$, the shape of which allows the critical exponent to be determined. We now present new experimental data on two more reactions in the liquid phase, whose reaction path begins either in the heterogeneous and ends in the homogeneous region, or vice versa [2]. These reactions, too, exhibit the funnel-like fall-off in the immediate neighbourhood of CP indicating the critical slowing down of the reaction rate. For an improved discussion of these results, we apply the theory of critical phenomena in multi-component systems as developed by Griffiths and Wheeler [3]. In chemically reacting systems, this theory must be modified by introducing the reaction coordinate ζ $(0 \le \zeta \le 1)$ as an additional extensive variable. The relevant critical exponent needed for the interpretation of our experiments refers to the divergence of the correlation length ξ with the reaction coordinate ζ, resp. with the reaction time t, at constant T and p.

2. Experimental

2.1 Thermokinetics of Reactions with Liquid-Liquid Phase Transition

No information is to be found in the literature on the kinetics of reactions which exhibit liquid-liquid phase transition, mainly because the classical kinetic methods fail in non-homogeneous systems. Thermokinetics, however, using a heat flow calorimeter with fast thermal response, yields equally reliable data on the heat production, both in homogeneous and heterogeneous liquid systems. The contribution of stirring to the total heat flow is contained in the base-line voltage signal and can be easily subtracted.

An interesting aspect of the kinetics in two-phase liquids is that the reaction rates in both phases depend on each other. If, by intensive stirring, the rate of exchange of matter through the phase boundary is made faster than the rather slow change of composition by the chemical reaction, both phases are virtually in material equilibrium at any time, so that its compositions are given by the end-points of the corresponding tie-lines. As a consequence, the reaction path in the two-phase region consists of two branches which follow the coexistence curve. In other words, the reaction in phase "'knows' of the degree of advancement of the reaction in phase" such that the slower reaction delays the faster one as long as two phases exist. Homogenisation is indicated by a drop, or a jump, of the heat production depending on whether the faster or the slower reacting phase vanishes.

The problem we are mostly interested in is the so-called "critical slowing down" of reaction rates being predicted by theories of critical phenomena [4]. Until now, all experiments reported in the literature on this issue refer to the behaviour of systems very close to the chemical equilibrium, and to extremely small perturbations of equilibria by critical phenomena [5], but not to directly measured reaction rates far from equilibrium. Moreover, knowledge of the value of the critical exponent from reaction rate data in the critical region will allow us to answer the question of whether the divergence of the thermodynamic coefficients being correlated with this exponent is weak or strong, and which are the reasons of the critical slowing down.

2.2 Reactions, Phase Diagrams, and Calorimetric Procedure

The first problem to be solved was to choose liquid phase reactions being suited for our investigations. These reactions should meet the following conditions:

0005-9021/96/0808-1335 $ 15.00+.25/0

1. It must start in the one-phase, and end in the two-phase region, or vice versa, and the reaction path must intersect the liquid-liquid coexistence curve far from equilibrium.
2. The half-life of the reaction near room temperature should be of the order of one hour to obtain (i) a very high resolution of the change of composition on the mole fraction scale, and (ii) to allow establishing of the phase diagram and of the liquid-liquid coexistence curve, at least approximatively. Reactions the rate of which may be adjusted by addition of small amounts of a catalyst are to be preferred.
3. The enthalpy change of these rather slow reactions must be large enough (20 to 30 kJ/mol or more) to obtain a heat flow signal which exceeds sufficiently the noise level of about ± 1 mW of our heat flow measurements.

After many preliminary tests, the following reactions were chosen:

(i) The acid-catalysed hydrolysis of chloromethyloxirane by water at 298.15 K, (ii) the ring-opening and esterification of bromomethyloxirane by dichloroacetic acid in the presence of cyclohexane as an inert component at 298.15 K.

The path of reaction (i) starts in the heterogeneous and ends in the homogeneous region, the path of reaction (ii) is inversely directed. In both reactions, the thermodynamic equilibrium at 298.15 K corresponds to virtually 100 per cent product formation, i.e. intersection of the coexistence curve takes place far from equilibrium.

If the phase diagrams of the systems consisting of educts and products are known, the reaction path may be easily constructed from the initial composition and from stoichiometry. Representation by a Gibbs phase triangle is possible even when more than three components are present in the reacting mixture by uniting formally to one single species all those educts resp. products the molar ratio of which is kept constant during the reaction by stoichiometry.

Mixtures of the educts were prepared by introducing weighted amounts of the components from a syringe into the inlet capillary of the calorimeter. For comparison, a second probe of the mixture of equal composition and temperature was prepared simultaneously in a graduated glass cylinder with magnetic stirrer and thermostating jacket. This method allows the time elapsed until phase transition occurs to be determined visually and to estimate the volume ratio of the coexisting phases. Mixtures the reaction path of which intersects the binodal curve very close to the CP exhibit a strong critical opalescence, and its phase volumes are virtually equal.

The CP can be precisely located by comparison of the shapes of the heat flow curves of the reactions. Only in the critical region, which is very narrow and comprises less than one per cent on the mole fraction scale, a funnel-like fall-off of the heat production is observed.

We use – with some improvements of the electronic equipment – the heat flow calorimeter with controlled thermoelectric cooling resp. heating which has been developped earlier for the continuous determination of heats of mixing by the overflow method [6]. On-line data acquisition using an AD transformer (PREMA DMM 4000, 5 1/2 digits) and a digital computer with an IEEE bus allows recording of the heat flow data in 1s intervals. To reduce the scatter by fluctuations, each 10 successive points are averaged so that the resulting heat flow curve consists of about 1000 data points or more.

Products: Chloromethyloxirane (Janssen, p.a.) was distilled at reduced pressure on a Vigreux column with 10 theoretical plates: Kp_{85} 57 °C, d_{20} 1.17908, n_D^{20} 1.4377. *Bromomethyloxirane* (Merck, ≥97 per cent) was treated likewise: Kp_{32} 54 °C, d_{20} 1.67216, n_D^{20} 1.4823. *Dichloroacetic acid* (Aldrich, >99.8 per cent) was treated in the same way: Kp_8 85 °C, d_{20} 1.5701, n_D^{20} 1.4660. *Cyclohexane* (Janssen, p.a.) was distilled on an automatic column filled with Dixon rings and 80 theoretical plates, and afterwards dried on mole sieves 0.4 nm: Kp_{760} 80.7 °C, d_{20} 0.77857, n_D^{20} 1.4264. *Water* was distilled twice on a quartz column and degassed.

3. Results

3.1 Acid-Catalysed Hydrolysis of Chloromethyloxirane

Chloromethyloxirane is slowly hydrolysed by water. In this reaction, the oxirane ring is opened and 1-chloro-2,3-dihydroxypropanol is formed. At room temperature, the reaction rate must be enhanced by acid catalysis. We use perchloric acid as a catalyst in amounts of 0.8 to 1.0 mole per cent of the total reacting mixture. In Fig. 1 an isothermal section at 298.15 K of the phase diagram of this system is shown, with the binodal curve and the critical solution point C. Determination of the educt composition the reaction path of which intersects the binodal curve exactly at C, is much facilitated by the fact that all paths start from a common operation point O. This point is situated outside of the Gibbs phase triangle because the number of moles decreases on the reaction:

$$C_3H_5ClO + H_2O = C_3H_7ClO_2 \ .$$

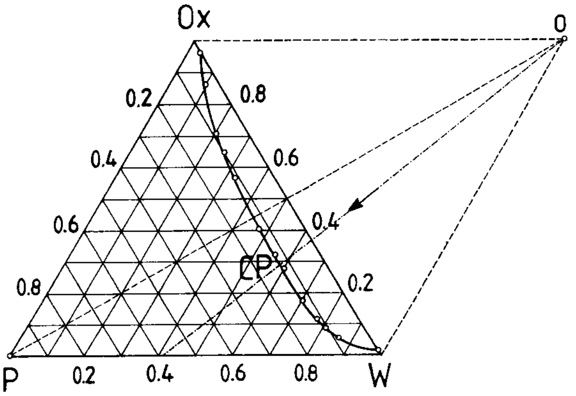


Fig. 1
Isothermal section at 298.15 K of the phase diagram of the system chloromethyloxirane (Ox) + water (W) with the operation point O and the reaction path which intersects the binodal curve at the critical solution point C (P = Product)

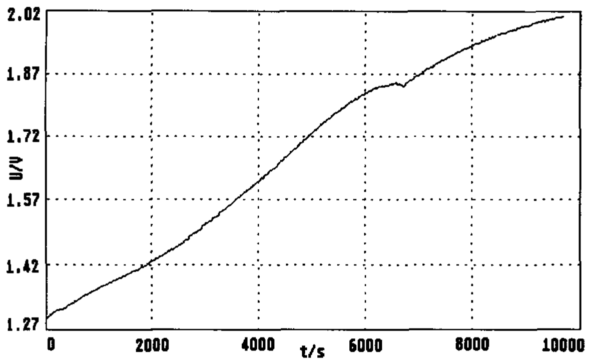
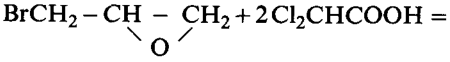


Fig. 2
Heat flow curve of the system chloromethyloxirane + water at 298.15 K, starting with the educt composition close to the critical composition

Any excess of water in the educt mixture, of course, remains unreacted so that the end-point of the reaction path corresponds to a mixture of 1-chloro-2,3-dihydroxypropane + water. In Fig. 2, an example of the heat flow curve of this reaction is shown, starting with the educt composition near the critical composition. The increase of the heat production during the first three hours indicates the autocatalytic nature of this reaction. After about two hours, phase transition with homogenisation occurs as revealed by a slight fall-off of the reaction rate. The high resolution on the time scale allows magnification of the critical region as shown in Fig. 3 which clearly demonstrates the funnel-like shape of the fall-off. The educt composition in this experiment was: *Epichlorohydrin* 17.287 g = 37.0 mole per cent, *water* 4.396 g = 61.62 mole per cent, *perchloric acid* 1.576 g = 0.88 mole per cent. The fall-off in the critical region corresponds to a drop of the voltage signal from $U = 0.006$ [V] to $U_{\min} = -0.029$ [V] at $t_c = 6758$ [s]. The parameters used for fitting Eq. (2) to the 473 data points in this region are: $A = 3.3 \cdot 10^{-4}$ [V], $B = -1.2 \cdot 10^{-5}$ [V/s], $\gamma = 4.37$, error square sum $= 9.5 \cdot 10^{-4}$ [V^2], yielding a value of $\varphi = 0.68$ for the critical exponent.

3.2 Ring-Opening and Esterification of Bromomethyloxirane by Dichloroacetic Acid

In Fig. 4, the phase diagram of the system bromomethyloxirane + dichloroacetic acid + cyclohexane is presented. This reaction starts in the homogeneous and ends in the heterogeneous region. By addition of the inert solvent cyclohexane, phase separation on water formation during the reaction is induced:



$$BrCH_2-\underset{\diagdown O \diagup}{CH - CH_2} + 2Cl_2CHCOOH =$$

$$BrCH_2-CH(OCOCHCl_2)-CH_2(OCOCHCl_2)+H_2O \ .$$

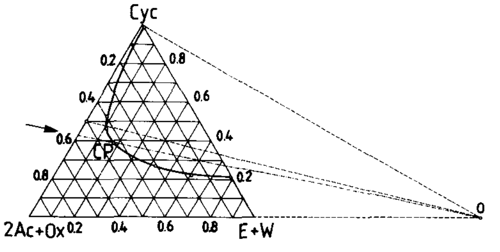


Fig. 4
Isothermal section at 298.15 K of the phase diagram of the system bromomethyloxirane (Ox) + dichloroacetic acid (Ac) + cyclohexane (Cyc) with the operation point O and the reaction path which intersects the binodal curve at the critical solution point C (E = Ester)

Because cyclohexane is an inert solvent, the operation point O is situated on the extrapolated baseline of the triangle. The reaction path starting from the stoichiometric mixture – two moles of dichloroacetic acid + one mole of bromomethyloxirane being considered as a single component – intersects the binodal curve very close to the CP. An example of the heat flow curve of this reaction is shown in Fig. 5. The decrease of heat flow with time is in accordance with a second-order time law. If the educt composition is very close to the critical composition, the jump on phase separa-

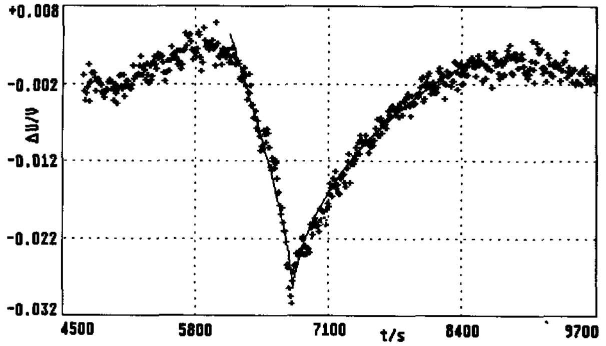


Fig. 3
Magnified presentation of the critical region of the heat flow curve (Fig. 2) showing the funnel-like fall-off. The continuous curve is calculated by fitting of Eq. (2) to the N data points with the parameters given in the text

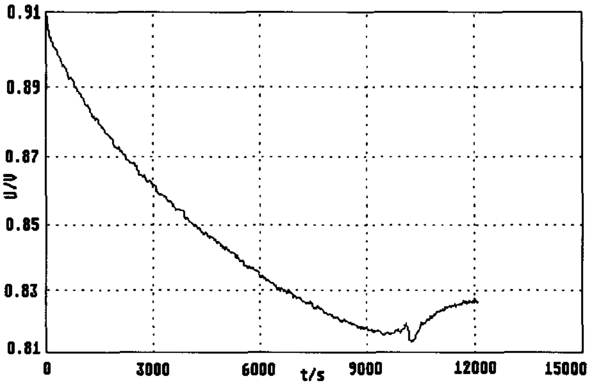


Fig. 5
Heat flow curve of the system bromomethyloxirane + dichloroacetic acid + cyclohexane with the educt composition very close to the critical composition

tion is superposed by a funnel-shaped fall-off of the reaction rate as shown in Fig. 5. A magnification of the critical region is presented in Fig. 6. The educt composition in this experiment was: *Epibromohydrin* 5.157 g = 16.7 mole per cent, *dichloroacetic acid* 9.620 g = 33.2 mole per cent, *cyclohexane* 9.488 g = 50.1 mole per cent. The fall-off in the critical region corresponds to a drop of the voltage signal from $U = 0.818$ [V] to $U_{\min} = 0.812$ [V] at $t_c = 10222$ [s]. The parameters used for fitting Eq. (2) to the 70 data points in this region are: $A = 1.6\cdot10^{-4}$ [V], $B = -1.4\cdot10^{-5}$ [V/s], $\gamma = 10.1$, error square sum = $1.2\cdot10^{-5}$ [V^2], yielding the critical exponent $\varphi = 0.741$.

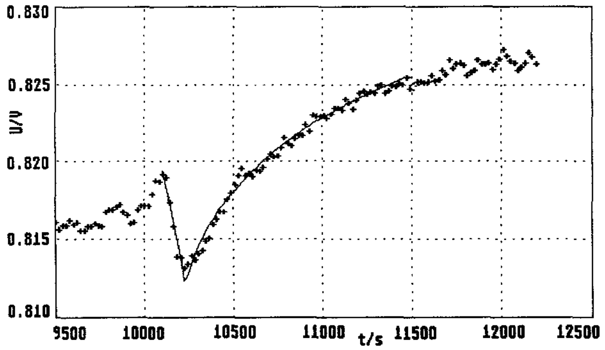


Fig. 6
System bromomethyloxirane + dichloroacetic acid + cyclohexane. Magnified presentation of the critical region of the heat flow curve (Fig. 5) with the funnel-like fall-off. The full line is calculated by fitting of Eq. (2) to the N data points using the parameters given in the text

3.3 Calculation of the Critical Exponent φ

The theory of critical phenomena predicts convergence to zero of the transport phenomena in the critical region on approaching the critical temperature T_c according to the power law:

$$f(\varepsilon) = A\,|\varepsilon|^{\nu} > 0\ , \quad \text{with} \quad \varepsilon \equiv (T - T_c)/T_c\ , \tag{1}$$

where $\nu = 0.63$ is the critical exponent of the correlation length ξ [7]. $f(\varepsilon)$ has a funnel-like shape with infinite slopes at $\varepsilon \to 0$. Because of the non-zero time-lag of the response of the signal being measured and its finite resolution on the ε scale, the experimental curves, however, differ from Eq. (1) in two respects: (i) No convergence of $f(\varepsilon)$ to zero but only a drop by some per cent is obtained; (ii) the limiting slope of $f(\varepsilon)$ at $\varepsilon \to 0$ is not infinity, as required by Eq. (1), but zero. Hence, it is reasonable to modify Eq. (1) into a more realistic fitting curve, without affecting the term $|\varepsilon|^{\nu}$. As we have shown in the case of the measurement of the electrolytic conductance in the critical region of partially miscible ternary liquid mixtures [8], this can be successfully done by introducing a 'delay factor', $[1 - \exp(-\gamma|\varepsilon|)]$, which reduces the slope of $f(\varepsilon)$ the more the smaller ε becomes, but leaves the upper part of the funnel virtually unchanged.

In our thermokinetic experiments, however, the CP is not approached by change of the temperature, but by change of the composition with the reaction time t at constant temperature, so that ε in Eq. (1) must be replaced by $(t_c - t)/t_c$, where the CP is attained at $t = t_c$. Denoting the empirical critical exponent by φ, the function to be used for fitting the data points in the critical region reads

$$q(t) = q(t_c) + A\,|(t_c - t)/t_c|^{\varphi} \cdot [1 - \exp(-\gamma\,|(t_c - t)/t_c|)] + Bt\ . \tag{2}$$

The linear term Bt in Eq. (2) is added for taking account of the skewness of the $w(t)$ curve by the decrease of the educt concentrations on reaction. The range of validity of Eq. (2) is confined to the critical region where the $w(t)$ curve displays its anomaly. The average value of φ obtained by fitting of Eq. (2) to the whole body of our experimental data is

$$\varphi = 0.72 \pm 0.03\ . \tag{3}$$

This result agrees fairly well with the theoretical value of the critical exponent $\varphi = 0.708$ of the correlation length ξ on the reaction coordinate scale ζ at constant temperature (cf. Eq. (9)) which suggests that the critical slowing down of the reaction rate, too, is governed by the slowing down of the transport phenomena.

4. Discussion

Chemically reacting systems are multi-component systems which means that the theory of critical phenomena in these systems, as developed by Griffiths and Wheeler in 1970 [3], has to be applied. In non-reacting systems, the CP is usually approached by variation of $\varepsilon \equiv (T - T_c)/T_c$ at constant composition and pressure. Isothermal reaction kinetics, however, is performed at constant ε by change of the composition along the reaction coordinate ζ, so that ε must be replaced by $[(\zeta - \zeta_c)/\zeta_c]^{1.124}$ (see Eq. (7)). If we attribute the critical slowing down of the chemical reactivity to the divergence of the correlation length ξ, the quantity to be calculated is the critical exponent which governs the change of ξ on approaching the CP along the reaction coordinate, i.e. with $(\zeta - \zeta_c)/\zeta_c \to 0$. We give here only a very short outline of the main theoretical ideas on which this calculation is based; a more detailed treatment is presented in [2], Chap. 2.

We start from the Gibbs stability conditions of a critical point in a n-component system (see Tisza [9]):

$$\partial\mu_n/\partial c_n = \partial^2\mu_n/\partial c_n^2 = 0 \quad (\mu_1, \mu_2, \ldots \mu_{n-1}, T, V = \text{const.}) \tag{4}$$

and expand μ_n into a Taylor series with respect to the order parameter $\Delta c_n = c_n - c_{n_c}$. On introducing the critical fluctuations we obtain an effective Hamiltonian which is analogous to the Landau functional for magnetic phase transitions [10]. By this analogy it is shown that phase transitions in n-component systems belong to the same universality class 3, with a one-dimensional order parameter, as one- and two-component systems. Therefore, the singular part Ω_{sing} of the thermodynamic potential Ω depends only on two parameters ε and h, which, to a first approximation, are linear functions of the intensive variables $T, \mu_1, \ldots, \mu_n$ [11]:

$$\Omega_{\mathrm{sing}} = A \cdot |\varepsilon|^{2-\alpha} + B \cdot |h| \cdot |\varepsilon|^{\beta} + C \cdot h^2 \cdot |\varepsilon|^{\alpha-2\beta-2} \ . \quad (5)$$

In the space of the intensive variables, the coexistence surface CXS is given by ($h = 0, \varepsilon < 0$), and the critical surface CRS by ($h = 0, \varepsilon = 0$). From [5], all singular thermodynamic quantities may be calculated. We now define the two extensive quantities

$$\Delta Y_{\mathrm{h}} = \partial \Omega_{\mathrm{sing}} / \partial n \quad \text{and} \quad \Delta Y_{\varepsilon} = \partial \Omega_{\mathrm{sing}} / \partial \varepsilon \ ,$$

which are interrelated by

$$\Delta Y_{\mathrm{h}} \sim \Delta Y_{\varepsilon}^{\beta/(1-\alpha)} \ . \quad (6)$$

From a geometrical discussion of the CXS and the CRS, it can be shown that Eq. (6) represents the coexistence curve in the Gibbs phase triangle with appropriately chosen variables. It can be further shown that ΔY_{ε} depends linearly on the reaction coordinate ζ, so that Eq. (5) can be transformed into

$$\varepsilon \sim \Delta\zeta^{1/(1-\alpha)} = \Delta\zeta^{1.124} \ , \quad \text{with} \quad \Delta\zeta \equiv (\zeta - \zeta_c)/\zeta_c \ . \quad (7)$$

The critical exponent of the correlation length ξ is [12]

$$\xi \sim \varepsilon^{-\nu} = \varepsilon^{-(2-\alpha)/3} = \varepsilon^{-0.63} \ . \quad (8)$$

Replacing ε in (8) by ζ using (7) yields

$$\xi \sim \zeta^{-(2-\alpha)/3(1-\alpha)} = \zeta^{-0.708} \ . \quad (9)$$

We finally need the relationship between the reaction rate $\partial\zeta/\partial t$ and the reaction time t which may be expressed by

$$\partial\zeta/\partial t \sim t^{\varphi} \quad \text{resp.} \quad \partial\zeta/\partial t \sim \xi^{x} \ , \quad (10)$$

with the critical exponent φ from the fitting curve (2). The right-hand side of (10) is valid if the change of ξ with t is made responsible for the convergence to zero of $\partial\zeta/\partial t$. The numerical value of the unknown exponent x follows from comparison of (9) and (10):

$$x = -3\varphi(1-\alpha)/(2-\alpha) = -1.41\,\varphi \ . \quad (11)$$

Putting $x = 1$ means that no other effect than the divergence of ξ contributes to the slowing down of $\partial\zeta/\partial t$. In this case we obtain $\varphi = 0.708$ (Eq. (9)) which has to be compared with the average value of $\varphi = 0.72 \pm 0.03$ (cf. Eq. (3)) obtained by fitting of our experiments to Eq. (2).

By means of Eq. (5) it is possible to prove the hypothesis of Griffiths and Wheeler, which allows prediction of whether determinants of the second derivatives of μ exhibit a strong, medium-sized, weak, or even no divergence at the CP. The most interesting result is that the corresponding thermodynamic coefficients do not diverge if more than two extensive variables are kept constant. For the calorimetric experiments in systems of three or more components, the behaviour of the molar heat capacity, C_{p,n_1,n_2,n_3}, is most important. This quantity, however, does not diverge at the CP and thus cannot be made responsible for the observed fall-off of the heat flow curves. To understand this result which seems at first glance surprising, we must remember that the only response of a one-component system near the CP, resp. of a two-component system at p = const., to perturbations of temperature is phase transition, whereas a multicomponent system can respond by shifting the CP on the composition scale such that the critical temperature may be raised or lowered.

The critical slowing down of the transport phenomena, like diffusivity, viscosity, and thermal diffusivity, however, remains unaffected by the composition of the system. These phenomena are governed by the divergence of the correlation length ξ the critical exponent $\nu = -0.63$ (resp. $\varphi = 0.708$, see Eq. (9)) of which is equivalent to a medium-sized divergence [7]. Divergence of ξ, however, means that the transport phenomena converge to zero.

We must finally discuss which of the transport phenomena is to be made responsible for the fall-off of the heat production resp. of the rate of the chemical reactions in our experiments. Influence of thermal diffusivity can be ruled out because the reactions are performed at constant temperature. Divergence of viscosity should increase the heat production by stirring which, however, contributes only about 20 per cent to the total heat production. From experimental evidence, the divergence of viscosity is very small, so that its contribution to the heat production should be less than 5 per cent. Hence, the main contribution must be attributed to the slowing down of diffusion. How can diffusion influence a slow reaction the half-life of which is of the order of one hour? Any change of the molecular structure of the reacting species in solution, especially of its polarity, is accompanied by a rearrangement of its solvation shells. This implicates the change of place of many solvent molecules which is a diffusion-controlled process. Thus the slowing down of the reaction rate can be interpreted as slowing down of the rearrangement of the solvation shells of all involved species, including the educts, the transition state, and the products.

Financial support of this work by the Deutsche Forschungsgemeinschaft, Bonn-Bad Godesberg, and by the Fonds der Chemischen Industrie, Frankfurt, is gratefully acknowledged.

References

[1] Ch. Müller, A. Steiger, and F. Becker, Thermochim. Acta *151*, 131 (1989).

[2] Ch. Baumann, Diss. Frankfurt a. M., 1992.
[3] R.B. Griffiths and J.C. Wheeler, Phys. Rev. A *2*, 1047 (1970).
[4] I. Procaccia and M. Gitterman, Phys. Rev. A *27*, 555 (1983).
[5] E.M. Anderson and S.C. Greer, Phys. Rev. A *30*, 3129 (1984).
[6] D. Gauger-Borzek, Diss. Frankfurt a. M., 1986; F. Becker, Chem.-Ing.-Techn. *41*, 1060 (1969).
[7] J.V. Sengers, Ber. Bunsenges. Phys. Chem. *76*, 234 (1972).
[8] S. Flindt, A. Steiger, and F. Becker, Ber. Bunsenges. Phys. Chem. *95*, 1196 (1991).
[9] L. Tisza, Generalized Thermodynamics, The M.I.T. Press, Cambridge, Massachusetts, London, 1986.
[10] L.D. Landau and E.M. Lifschitz, Lehrbuch der Theoretischen Physik, Vol. V, Teil 1 (E.M. Lifschitz and L.P. Pitajewski, eds.) § 153, p. 484ff., Akademie-Verlag, Berlin, 1979.
[11] l.c. [10], p. 466, Eq. (149).
[12] J.M.H. Levelt-Sengers and J.V. Sengers, Phys. Rev. A *12*, 2622 (1975).

(Received: November 29, 1995
final version: May 21, 1996)
E 9080