Chemical Kinetics at a Critical Point

The rate of the Diels-Alder reaction of isoprene with maleic anhydride has been measured in the vicinity of the upper critical solution points of two liquid-liquid mixtures, and the rate of the Menschutkin reaction of ethyl iodide and triethylamine has been investigated near a lower critical solution point. Anomalous behavior has been observed, with the former reaction rate augmented by up to 40% and the latter apparently running 25-30% too slow. A possible explanation for these results is presented in terms of transition state theory and the abrupt behavior of the solution activities of dilute solutes near a critical point.

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SCOPE

The purpose of this work was to investigate experimentally the effect of proximity to a critical point on the rate of a chemical reaction in solution. It is well established that upon approach to a thermodynamic critical point many of the equilibrium and transport properties of fluids (and solids as well) behave in an unusual fashion, even diverging as they appear to approach either zero or infinity. There has never previously been any clear experimental evidence of how the rate of a reaction would vary upon approach to the critical point. Chemical kinetics in solution is, of course, linked closely to the thermodynamic state of the system and can frequently be affected as well by transport phenomena. Therefore, experiments were devised to test as unambiguously as possible the behavior of a chemical reaction near a critical point. If unusual or anomalous behavior were to occur, a knowledge of its behavior could be quite useful in two respects: First, from the theoretical point of view such information could yield new insight into the nature of the critical phenomenon, a thermodynamic singularity which is itself rather imperfectly understood. Such new data, markedly different from any heretofore available, could contribute to the development of new statistical mechanical models of the critical state. Second, from a practical point of view, the development of such models would permit much better prediction of thermodynamic and transport properties in the critical region, important in many current processes. In addition, it is quite conceivable that such anomalous effects themselves could have important applications in chemical reaction engineering. If such effects occur, and especially if an adequate theory were available to predict them, then they could be put to work to increase reaction rates, optimize yields of desired products from competing reactions, optimize conversions, or perhaps to minimize product degradation.

CONCLUSIONS AND SIGNIFICANCE

In this paper we report clear experimental evidence for anomalous behavior of the rates of two simple bimolecular reactions in three different solutions at liquid-liquid critical points. A Diels-Alder addition was found to proceed as much as 30 to 40% faster than expected at the upper critical solution points of the hexane-nitrobenzene and hexane-nitroethane systems, while an alkylation reaction appeared to have a somewhat lower rate than expected at the lower critical solution point of the water-triethylamine system.

The observed results do not appear to be attributable in any way to the statistical mechanical concentration fluctuations known to occur near liquid-liquid critical points. Rather, the effects appear to be explicable in terms of variations in activities in the Brønsted-Bjerrum equation. This expression gives the variation of the rate constant for a reaction in a nonideal solution as the quotient of the activity coefficients of the reactants divided by that for the reaction transition state. The activities of dilute solutes vary quite sharply close to a critical point, thus causing the observed anomalies.

Based in part on these results, a new model of dilute solute behavior near a critical point (Wheeler, 1972) has been developed using a lattice gas approach. In addition to representing correctly a number of other critical anomalies, this model gives a good qualitative prediction of the effects observed.

Although the effects reported here are probably of insufficient magnitude to be of much practical application in chemical reaction engineering, it should be noted that the liquid-liquid and vapor-liquid critical points are mathematically equivalent in statistical mechanics. Although it would be most difficult to verify experimentally, it appears that analogous anomalies could occur at vapor-liquid critical points and might possibly be of sufficient magnitude to be of practical use.

The anomalous behavior of fluids in the region of a second-order phase transition—a critical point—is a well-accepted phenomenon. The classical analytical equations of state do not predict the scaling laws for thermodynamic properties correctly (Fisher, 1967; Heller, 1967; Rowlinson, 1969), and derivative properties, such as isothermal compressibility or heat capacity, actually diverge at a vapor-liquid critical point. Further, many transport coeffi-

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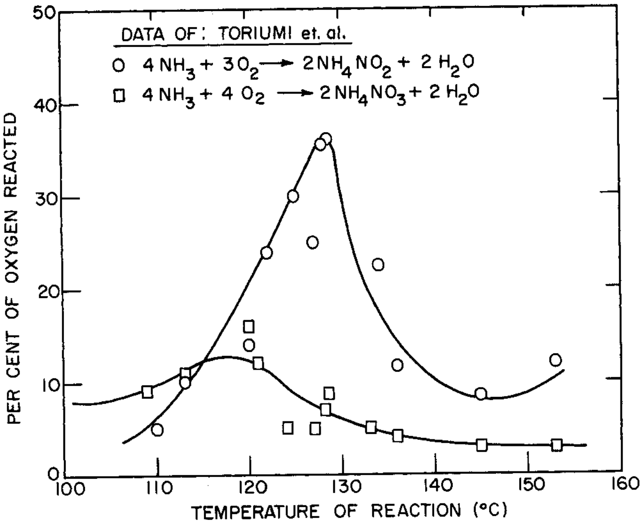

Fig. 1. Ammonia oxidation near the critical region; data of Toriumi et al. (1946).

cients have been observed to exhibit abrupt changes very close to the critical point. For example, both the kinematic viscosity and the thermal conductivity have been observed to have lambda-shaped maxima near vapor-liquid critical points (see, for instance, Guildner, 1958; Reed and Taylor, 1959; Fixman, 1962 and 1967; Kestin et al., 1964; Wood and Smith, 1964). Another property of great interest to chemical engineers is the rate of chemical reactions and the possible effect of proximity to a critical point, but very little unambiguous information has been reported on such behavior. However, the results of one study are shown in Figure 1 (Toriumi et al., 1946). Though the data scatter, the rate of the complex oxidation of ammonia was observed to go through a maximum in the vicinity of the critical temperature of NH_3, 132°C. These data, though hardly conclusive, do suggest that the rate of a chemical reaction may also exhibit anomalous behavior in the critical region, and the purpose of this work is to investigate experimentally such a possibility.

There are two related viewpoints from which one might discuss possible anomalies in a rate constant near a critical point. The first is a statistical mechanical evaluation of fluctuation theory applied essentially to a collision theory of reactions. From ensemble techniques we know that even in a fluid at equilibrium, fluctuations can occur in thermodynamic properties (Hill, 1956). Normally these are quite small, even vanishingly small for systems of finite size. However, near a critical point they can grow quite large. For example, the mean square relative deviation in the energy is given as

$$\frac{\overline{(E-\overline{E})^2}}{(\overline{E})^2} = \frac{k_B T^2 C_V}{(\overline{E})^2} \tag{1}$$

where the bars indicate average values. Normally the right-hand side of Equation (1) is very small, as the average energy $\overline{E}$ is proportional to the number of particles in the system, but at a vapor-liquid critical point, C_V becomes extremely large, and thus energy fluctuations become finite. These fluctuations must be evenly distributed about the equilibrium mean value, but since by the Arrhenius expression the reaction rate varies as an exponential of the energy, the net effect of averaging would be a large increase in the observed reaction rate.

A similar argument can be applied to concentration fluctuations near a liquid-liquid critical point. In a binary mixture $\overline{\xi_2^2}$ would be the mean square fractional fluctuation in concentration c of species 2 (Davidson, 1962)

$$\overline{\xi_2^2} = \frac{k_B T}{c^2 N_1 \, (\partial \mu_2 / \partial c)_{T,P}} \tag{2}$$

Again, normally the right-hand side vanishes as the number of particles N_1 is quite large, but the derivative of the chemical potential μ at the critical point can become small, and large finite concentration fluctuations occur, giving rise to readily observable turbidity. Calculations of this effect have been carried out for real systems, and it is shown to be appreciable sufficiently close to the critical point (Fürth and Williams, 1954). When applied to chemical reactions by simple collision theory, concentration fluctuations would, in principle, not affect a first-order reaction rate, but should certainly affect the rates of higher order reactions. For example, for a second-order reaction, the average of the square of the concentration need not be identical with the square of the average. From such considerations, however, one would expect that this effect on the rate would be a good deal smaller than that of energy fluctuations at a liquid-liquid critical point.

The alternate approach to fluctuation theory is a thermodynamic description of the system using transition state theory. Such an approach to a reaction in solution leads to the Brønsted-Bjerrum expression, relating the reaction rate constant in a real system k to that in a Raoult's law system k_0 by the activity coefficients γ. For a simple bimolecular reaction proceeding through transition state M, ($A + B \rightleftharpoons M^{\ddagger} \rightarrow$ Products) this expression gives (Eckert, 1967)

$$\frac{k}{k_0} = \frac{\gamma_A \, \gamma_B}{\gamma_M} \tag{3}$$

The activity coefficient in solution can behave quite anomalously in the critical region. Krichevskii and coworkers (1967, 1969) have measured fugacities and nonideal chemical equilibria in the critical region to attempt to define such behavior, and the results appear to indicate that at a critical point the activity coefficient in solution may be undefined or multivalued. Wheeler (1972) claims on theoretical grounds that the activity coefficient does not diverge at the critical point, but is finite. He does show, however, that it may appear to take on different values depending on the apparent direction of approach to the critical point, and the value is an extremum representing the tip of a cusp. In any event, from these results and Equation (3), it is clear that the ratio of activity coefficients can, in principle, vary quite rapidly very close to the critical point, resulting in apparent anomalies in the observed rate.

Thus the state of the theory is that while one may postulate effects, they certainly can be predicted neither quantitatively nor even qualitatively, and the only data available are ambiguous and for very complex systems. Therefore, we have undertaken a detailed study of simple reactions in precisely defined and controlled experiments. For experimental convenience, we chose to work at a liquid-liquid critical point; although the effects might be smaller than at a vapor-liquid critical point, the difficulty of holding a reacting mixture at its precise (and changing) critical temperature and pressure would appear to be experimentally quite difficult. Two reactions were studied, both clean, simple bimolecular events with no side reactions. These were the concerted four-center Diels-Alder addition of isoprene to maleic anhydride and the S_N2 Menschutkin reaction of triethylamine with ethyl iodide. These reactions were run very dilute in binary mixtures which exhibit critical points near room temperature—hexane-nitroethane, hexane-nitrobenzene, and triethylamine-water. The effect of reactants and products on the critical points were small (Snyder, 1971; Snyder *and Eckert, 1973*) but could be determined accurately and were accounted for experimentally over the course of these relatively slow reactions. The results then provide the first unambiguous example of the behavior of a chemical reaction at a well-defined critical point.

EXPERIMENT

Materials

The purifications of *n*-hexane, nitrobenzene, nitroethane, isoprene, maleic anhydride, and 4-methyl-*cis*-4-cyclohexene-1,2-*dicarboxylic* anhydride (MCDA) have been described previously (Snyder and Eckert, 1973). Ethyl acetate was washed with 5% Na_2CO_3, then neutralized with saturated aqueous $CaCl_2$, and dried with molecular sieves. It was then distilled in a 1-m column (about 36 theoretical plates) packed with *nichrome helices* and a center cut was taken.

Ethyl iodide was shaken with aqueous sodium thiosulfate until colorless. It was then washed with deionized water, shaken with 5% Na_2CO_3, and rewashed with deionized water. The ethyl iodide was predried with $CaCl_2$ and then distilled from fresh $CaCl_2$ in the same 1-m column. A center cut was taken of boiling point range less than 0.4°C. It was stored in a brown glass bottle in contact with metallic copper at − 10°C.

Triethylamine was dried with solid KOH and then distilled from fresh KOH in the same 1-m column. The boiling range of the fraction kept was less than 0.5°C, and it was stored in brown bottles at − 10°C.

Water used was laboratory deionized water which, after degassing, had a specific resistance of greater than 500,000 ohms.

Tetraethyl pyridinium iodide was prepared by refluxing triethylamine and ethyl iodide in acetone for 48 hours. The solution was then cooled to precipitate the product, which was washed, dried, and twice recrystallized from acetone. It was dried under vacuum at 25°C for three days and stored in the dark in a dessicator.

Procedure

The reaction of isoprene-maleic anhydride was run very dilute in a series of hexane-nitrobenzene solvent mixtures by the conventional batch method. Reactants were weighed into a 10-ml round bottom flask into which a magnetic stirrer had been placed. The flask, fitted with a septum, was placed in a thermostatted water bath, which could be held to ±0.01°C and measured to the same accuracy with thermometers calibrated against National Bureau of Standards thermometers. At the low concentrations used (about 10^{-2} M), the reaction half-life generally exceeded 24 hours. Samples were taken at 30-min. intervals for a period of several hours by a microliter syringe fitted with a Chaney adapter. This method permitted sampling without removing the flask from the bath and gave a sample size reproducible to better than 1%. Samples were analyzed by gas chromatography for isoprene concentration as a function of time. This method was used because of interference of the nitrobenzene and product peaks and to give an accurate initial concentration of isoprene, which was often difficult to obtain gravimetrically because of high volatility. The chromatograph used was a Beckman GC-5 equipped with a dual hydrogen-flame ionization detector. Two ⅛-in. O.D. columns 6 ft. long, packed with 3% SE-30 on a gas-pack F support were used. Output was to a Sargent SR millivolt recorder with a disc integrator. The detector temperature was set at 250°C, the inlet and detector line temperatures were set at 225°C, and the column temperature was 25°C. Peak area reproducibility was found to be within 1% after suitable calibration.

For reactions of this type run at the liquid-liquid critical point of the mixture, two methods were used to ascertain the exact critical temperature of the reaction mixture. First, visual observation of meniscus occurrence was employed. In addition, the critical point of the reaction mixture was calculated by assuming that the effects of dilute solutes 3, 4, etc. on the critical solution temperature T_c of a binary mixture of solvents 1 and 2 could be expressed as a Taylor series in the form:

$$dT_c = \left(\frac{\partial T_c}{\partial x_3}\right)dx_3 + \left(\frac{\partial T_c}{\partial x_4}\right)dx_4 + \ldots \qquad (4)$$

For example, components 1 and 2 are the hexane and nitrobenzene in the mole ratio of their binary critical point, and components 3, 4, etc. are the reactants and product, all very dilute. The coefficients in Equation (4) have been measured for this system by Snyder and Eckert (1973) and shown to be constant and additive for dilute solutions (up to one mole %). The calculated and observed critical temperatures agreed to about ± 0.02°C, which is probably the limit of accuracy for these determinations.

For the other experiments a more sophisticated system was devised to achieve three goals: These were better temperature control of the reactor, more sensitive detection of the critical point, and more accurate analysis of the reaction rate. The apparatus used to achieve these goals is shown in Figures 2 and 3. It consisted of two nested temperature baths with the outer bath thermostatted to better than ±0.005°C with a three-mode controller, and the inner bath a stainless-steel container within it. Small temperature changes in both the inner and outer baths were monitored with a Hewlett-Parkard quartz crystal thermometer, sensitive to changes of ± 0.0001°C. Fluctuations of the inner bath were less than ± 0.001°C, although the accuracy of measurement of the temperature was no better than ± 0.01°C.

The actual reaction was carried out inside the inner bath in a 10-ml cell fitted with flat windows at 90° angles with each other. In this cell, the proximity to the critical temperature could be monitored continuously by a light scattering technique. Light may be scattered in a liquid-liquid mixture by fluctuations in the refractive index of the fluid. At the critical point such fluctuations become extremely large and

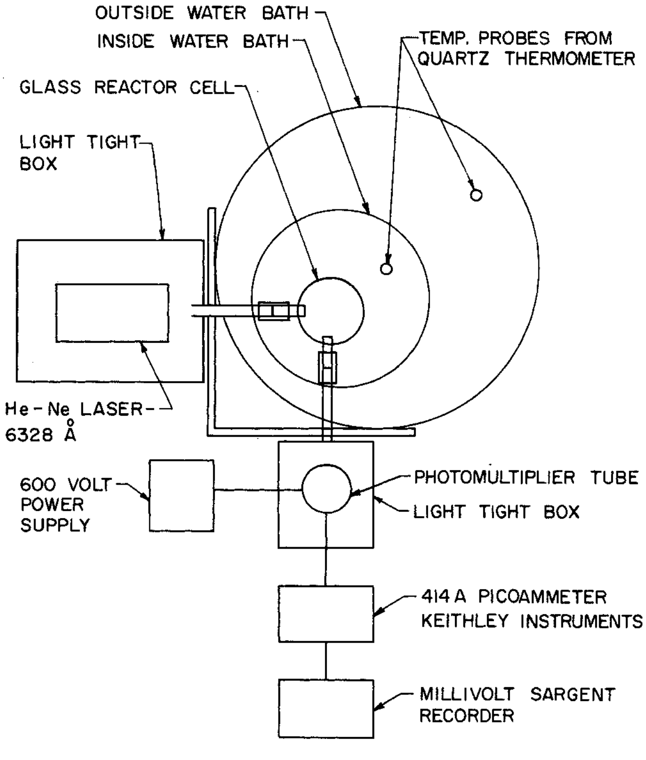

Fig. 2. Schematic diagram of light-scattering cell in nested temperature baths.

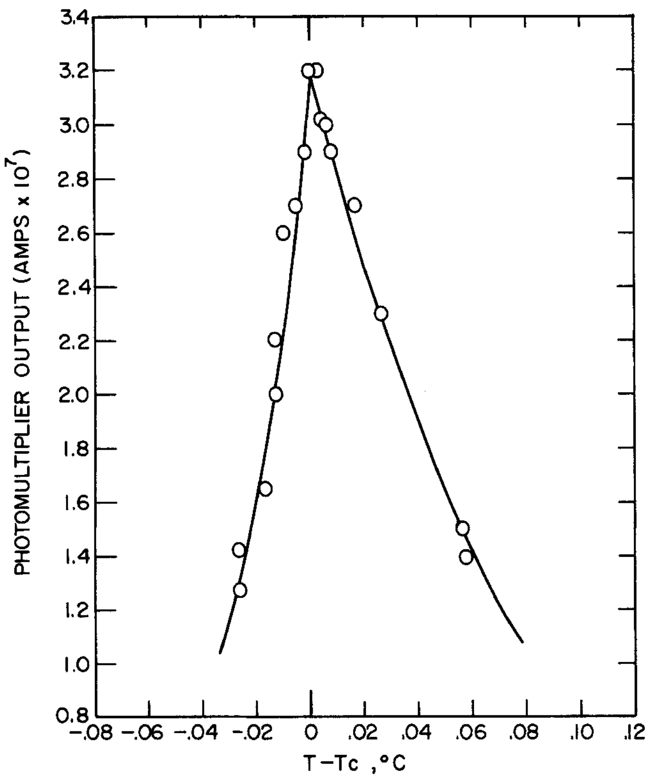

Fig. 3. Side view of reactor, inside light-scattering apparatus.

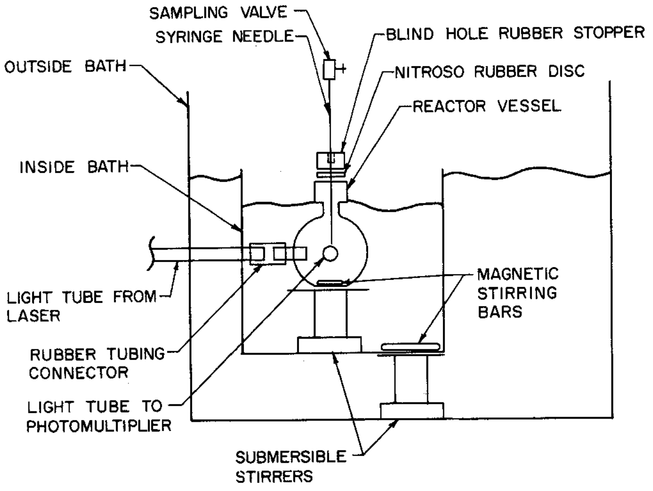

Fig. 4. Typical response curve of light-scattering technique showing sensitivity of critical point determination.

the intensity of scattered light becomes a maximum. A LAS-101A helium-neon gas laser from Electro Optics Associates, Inc. was used to direct light (6328Å) through the reactor cell. A 1P28 electron tube monitored the scattered light from the reactor cell at 90° from the directed light source. The laser and electron tube were kept in light-tight boxes, which were connected to the reactor cell in the inner bath by light tubes. The inner bath was also light tight and blackened on the inside to keep reflected light to a minimum. With this experimental arrangement only scattered light from the laser source was detected by the electron tube.

The power supply was two 300-volt batteries. The output of the tube was monitored by a model 414A picoammeter from Keithley Instruments. A Sargent SR millivolt recorder was connected to the picoammeter for continuous monitoring of the electron tube's output.

Figure 4 represents a typical current output of the electron tube near the critical temperature of the reacting liquid mixture. Using this light scattering method, reactions were held continuously within about 0.01°C of the critical temperature.

When the Diels-Alder reaction was run in the hexane-nitroethane solvent system in this apparatus, a superior sampling and gas chromatographic analysis system was employed. As shown in Figure 3, the flask was fitted with an adapter containing a nitroso rubber disk insert below a blind-hole silicone rubber stopper. Nitroso rubber is particularly resistant to the absorption of most organics and, therefore, minimized the loss of isoprene by absorption into the silicone rubber stopper. A number 23-gauge syringe needle was placed permanently in the reactor during the reaction, long enough so that the top was above the cover on the outer bath. Samples were taken through a microvalve placed on top of the syringe needle by inserting the needle of the microliter syringe completely through the valve and through the larger needle down inside the reactor itself.

The analysis was improved in that the nitroethane peak did not interfere, so separate peak areas could be determined for both reactants and the adduct (MCDA) for each sample and the extent of reaction determined by a ratio. This relieved the dependence on a known size sample, and to a great extent, minimized errors due to the volatility of the isoprene. In addition, it provided an internal check on the precision of the analyses, such that with this improved procedure, the precision was generally better than ± 1%.

The Menschutkin reaction was also run in the double-bath laser-diffraction apparatus, with the actual reaction vessel modified for in situ conductometric analysis. The reaction vessel still had light tubes with flat windows at 90° angles, but above the light path two platinum flag electrodes, about 1 cm square, were placed in the reacting solution. Concentrations were monitored by following the solution conductivity using a Beckman model RC-18 conductivity bridge, with a CRO null detector, capacitance balancing and a Wegner ground. By the use of precalibration with gravimetrically prepared solutions of the quarternary ammonium product salt, this technique has been shown to be accurate to better than 0.1% for such reactions (Eckert et al., 1973).

It is interesting to note that in both the calibration runs and reaction runs, no anomalous behavior of the conductivity was observed. The conductivity of the tetraethylammonium iodide in the critical mixture appeared to be a continuous, relatively smooth function right up to the phase separation point.

RESULTS

The rate of isoprene-maleic anhydride condensation in ethyl acetate at 35.00°C has been reported to be 0.436 l/mole-hr. (Grieger and Eckert, 1970a). As a check this reaction was run in the same solvent and at the same concentrations in the apparatus reported here, and the second-order rate constant found was 0.434 ± 0.005 l/mole-hr., in satisfactory agreement.

This reaction was run in a series of hexane-nitrobenzene mixtures at two temperatures, 35.00°C and 20.73°C, the latter being the upper critical solution temperature of the reaction mixture.

The results are shown in Figure 5 and presented along with experimental uncertainties in Table 1. The uncertainties represent the scatter of the data about the straight line plot for the integrated rate expression. Calculations were made of the kinetic solvent effect in a mixed solvent, using the molecular thermodynamic approach of Wong and Eckert (1968), and the agreement with the data at 35.00°C, well away from criticality, verify the applicability of this method to this reaction. The same calculation (which ignores the existence of a critical solution point) was made along the critical isotherm, 20.73°C, and as shown in Figure 5, predicts no rate augmentation at the critical point, around a composition of $x_N = 0.43$. The experimental rate data are 30 to 40% higher than the curve in this region. Note, however, that the estimated uncertainty in the rate, generally well under 5% away from the critical point, is a good deal larger near the critical point, about 15 to 20%, probably representing uncertainties introduced by disturbing the system for sampling. The second technique used was designed specifically to eliminate such uncertainties.

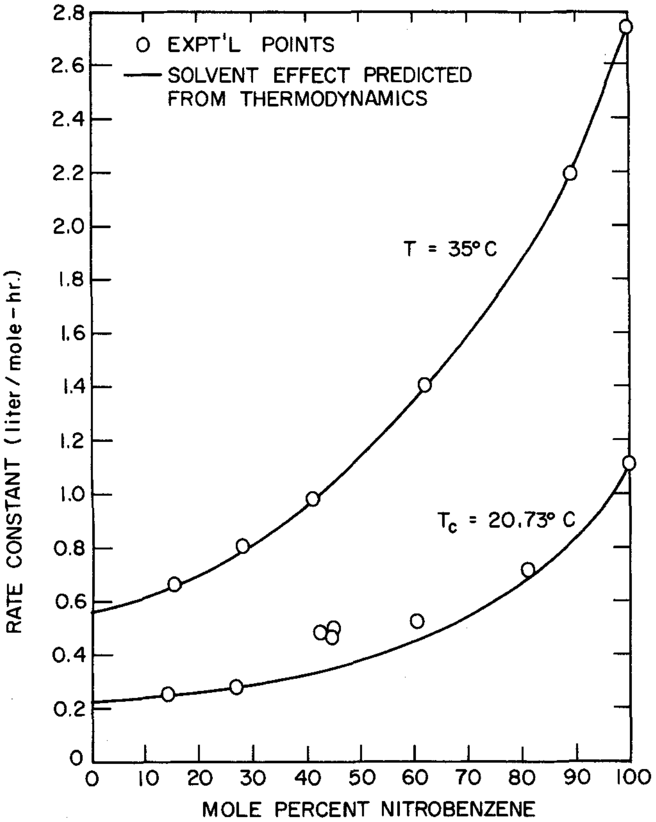

Fig. 5. Rate of the Diels-Alder addition of isoprene to maleic anhydride in dilute solution in hexane-nitrobenzene mixtures.

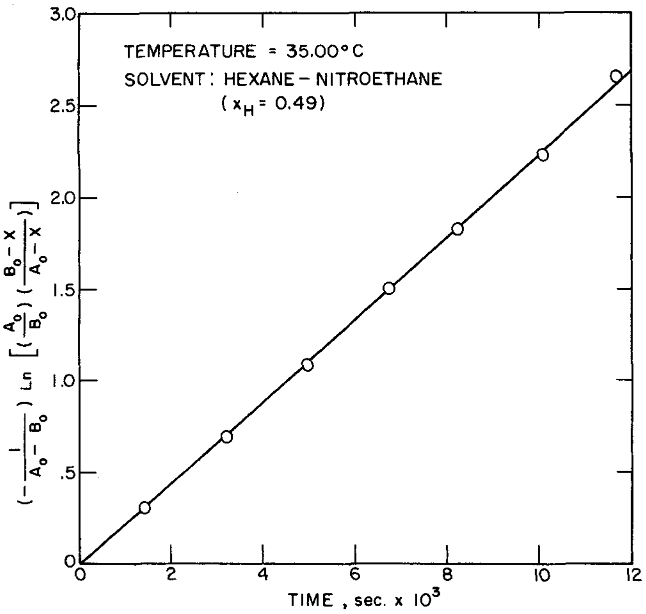

Fig. 6. Typical rate plot for the reaction of isoprene with maleic anhydride in a hexane-nitroethane mixture—integrated second-order rate expression as a function of time.

The reactions run in the hexane-nitroethane system were all run at the critical composition, but over a temperature range from the upper critical solution temperature to about 30°C higher. An integrated rate plot for a typical run is shown in Figure 6. The standard deviation of these plots averaged less than 3%, and replicate runs away from the critical point agreed to approximately this precision as well. An Arrhenius plot (see Figure 7) of the points in noncritical solutions shows good linearity and gives a very reasonable value of 12.6 kcal/mole for the activation energy, in good agreement with the values of 12 to 14 kcal/mole found in other solvents (Grieger and Eckert, 1970b). As shown in Table 2, the rate constant at the critical point itself varied widely, by about 30%, well beyond the possible extent of experimental error. This variation is depicted in Figure 8 where the rate deviation expressed as the rate relative to the Arrhenius plot line in Figure 7 is shown as a function of the difference $(T - T_c)$. This relative temperature measurement is used in place of absolute temperature as the

TABLE 1. RATE CONSTANTS FOR ISOPRENE-MALEIC ANHYDRIDE REACTION

Solvent: Hexane-nitrobenzene mixtures

T, °C	Mole fraction Nitrobenzene x_N	Rate constant, k 1/mole-hr. ± uncertainty
35.00	1.000	2.73 ± 0.08
		2.72 ± 0.21
	0.882	2.19 ± 0.07
	0.662	1.40 ± 0.04
	0.416	0.98 ± 0.05
	0.287	0.80 ± 0.03
	0.158	0.66 ± 0.02
20.73	1.000	1.11 ± 0.06
	0.816	0.71 ± 0.02
	0.607	0.52 ± 0.03
	0.455*	0.50 ± 0.08
	0.443*	0.47 ± 0.11
	0.430*	0.48 ± 0.08
	0.268	0.28 ± 0.02
	0.142	0.25 ± 0.01

* Runs very close to the critical composition.

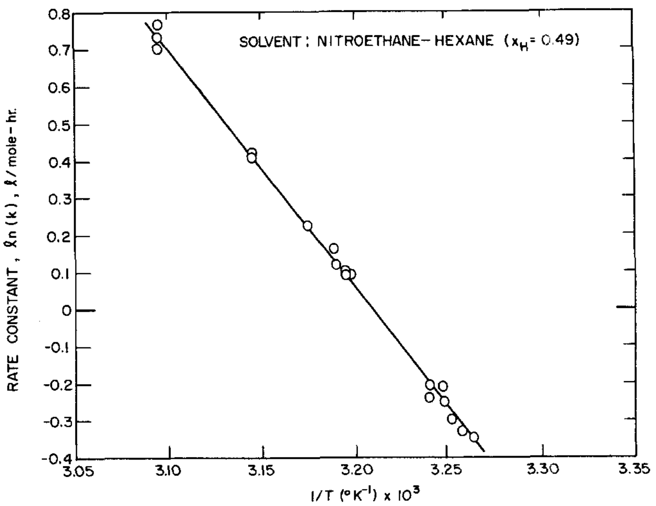

Fig. 7. Arrhenius plot for isoprene-maleic anhydride addition at temperatures above the critical solution temperature but at the critical composition of the hexane-nitroethane solvent system.

actual critical solution temperature T_c varied slightly with the concentrations of reactants as well as the extent of reaction (Snyder and Eckert, 1973).

Finally, the results for the Menschutkin alkylation reaction are given in Table 3 and shown in Figure 9 where all points represent kinetic runs at the critical composition. The Arrhenius plot line is fit through data at temperatures below the lower critical solution temperature, in the single-phase region. These results correspond to an activation energy of 17 kcal/mole, somewhat higher than that reported for the same reaction in an aprotic solvent, benzene, by Winkler and Hinshelwood (1935), 11.4 kcal/mole. This difference is quite reasonable in the highly protic solvent system used here, as the activation barrier for the unsolvated reaction would be augmented by the energy required to break the hydrogen bonds involved in solvating the amine, and an energy of about 4 to 10 kcal/mole is quite reasonable for such interactions. Hartmann and co-workers (1965) did observe such an increase in the activation energy for a similar Menschutkin reaction in a protic solvent. Thus it appears that at the lower critical solution point of the triethylamine-water system, the rate of the reaction is anomalously slow by about 30%. Although again there is some scatter of the rates observed at the critical temperature, the observed anomaly lies outside the error bars.

TABLE 2. RATE CONSTANTS FOR THE ISOPRENE-MALEIC ANHYDRIDE REACTION

Solvent: Hexane (49 mole %)-nitroethane (51 mole %)

Temp., relative to crit. solution temp., $T - T_c$, °C	Rate constant k 1/mole-hr. ± uncertainty
28.8	3.99 ± 0.08
16.3	2.21 ± 0.07
	2.17 ± 0.04
10.3	1.25 ± 0.06
6.9	1.10 ± 0.03
6.3	1.12 ± 0.06
	1.13 ± 0.01
6.0	1.19 ± 0.05
	1.13 ± 0.02
3.4	0.817 ± 0.033
1.54	0.784 ± 0.028
1.50	0.699 ± 0.019
1.30	0.782 ± 0.018
0.90	0.725 ± 0.009
0.50	0.737 ± 0.038
0	0.899 ± 0.018
	0.874 ± 0.037
	0.868 ± 0.043
	0.651 ± 0.017
	0.678 ± 0.006
	0.678 ± 0.007
	0.674 ± 0.040
	0.626 ± 0.013
	0.719 ± 0.014
	0.713 ± 0.014
	0.758 ± 0.053
	0.794 ± 0.022
	0.639 ± 0.018
	0.719 ± 0.029
	0.667 ± 0.005

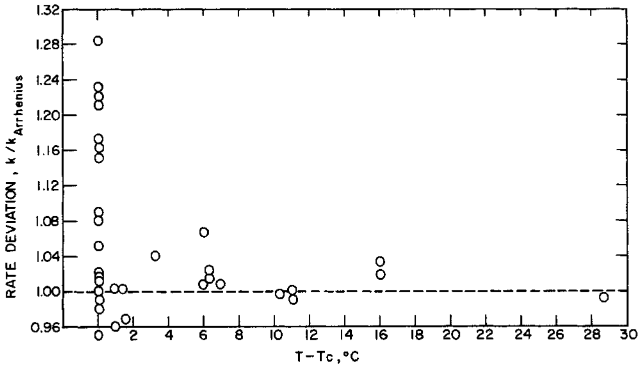

Fig. 8. Relative rate deviation of the isoprene-maleic anhydride reaction (that is, deviation from the Arrhenius plot in Figure 7) as a function of proximity to the critical solution temperature in the hexane-nitroethane system, all data at the critical composition.

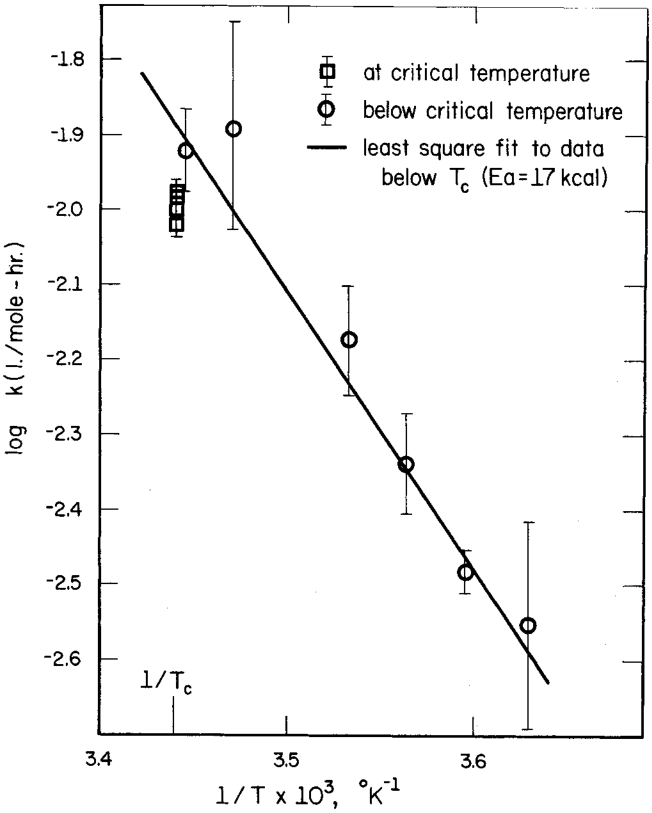

Fig. 9. Rate constant for the Menschutkin reaction of triethylamine with ethyl iodide at temperatures above and at the lower critical solution temperature of the triethylamine-water system, all data at the critical composition.

TABLE 3. RATE CONSTANTS FOR THE TRIETHYLAMINE-ETHYL IODIDE REACTION

Solvent: Triethylamine-water, critical composition

T, °C	Rate constant, k 1/mole-hr. ± uncertainty
2.50	0.0028 ± 0.0010
5.00	0.0033 ± 0.0002
7.50	0.0046 ± 0.0007
10.00	0.0067 ± 0.0012
15.00	0.0129 ± 0.0048
17.20	0.0120 ± 0.0016
17.45*	0.0100 ± 0.0014
	0.0106 ± 0.0003
	0.0096 ± 0.0006
	0.0104 ± 0.0005

* Lower critical solution temperature.

In order to preclude the possibility that the observed anomalies were caused by the unexpected presence of two liquid phases, the effect of running reactions just within the two-phase region was investigated. First, for the Diels-Alder reaction in the hexane-nitrobenzene system, distribution coefficients in the two-phase region were determined for the two reactants, which showed that the maleic anhydride went preferentially into the more polar nitrobenzene-rich phase, and the isoprene was concentrated in the less polar hexane-rich phase (Snyder, 1971). Thus for a second-order reaction, this would cause a net decrease (not increase) in the observed rate and thus could not account for the anomaly.

Conversely, for the ethyl iodide-triethylamine reaction, the ethyl iodide is almost completely insoluble in water and in the two-phase region concentrates strongly in the triethylamine-rich phase. Thus if the observed effect in this case were due to concentration effects, the anomaly would be an increased rate, but for this system an anomalous rate decrease of about 30% was observed.

DISCUSSION AND CONCLUSIONS

Although the data scatter badly, especially for replicate runs at the critical point, it appears clear that distinct anomalies are occurring in the rate constant, well beyond the uncertainty limits of the data. It is the very scatter itself which gives some indication of what the nature of this anomaly might be.

First of all, it appears quite unlikely that the results can be explained on the basis of fluctuation theory. On the basis of the measured distribution coefficients for the reacting solutes between the two liquid phases, fluctuation theory would predict anomalous decreases in the cycloaddition rate and increases in the alkylation rates at the critical points; the converse was observed. Thus, although this approach may be aesthetically attractive, it seems unprofitable.

A better explanation is available in terms of the transition state approach, Equation (3). It is clear from both theory and experiment that the activity coefficients of dilute solutes may change very rapidly very close to the critical point. The reactants were always dilute except for triethylamine, and the transition state is certainly a dilute species. Since the rate appears as a quotient of the activity coefficients, sharp changes over narrow temperature regions could well result in the type of anomalies observed.

There are two possible explanations for the apparent multiplicity of values observed at the critical point. First, the abrupt changes in activity coefficient may occur over an extremely narrow temperature range, about 10^{-3} to 10^{-4}°C, or even less, and thus beyond the limits of resolution of this work. In other words there is no certainty that scaling law for the rate constant anomaly exists, but if it does, to study it considerably better control and measurement of temperature would be required, and one cannot be certain just how much better it need be. Thermal precisions of 10^{-3} to 10^{-4}°C have been achieved with difficulty for equilibrium systems, but the task of doing so for a reacting system where T_c is a function of time would be truly formidable. Alternatively, the activity coefficients may be undefined or multivalued at the critical point, as claimed by Krisehevskii et al. (1967, 1969).

Evidence in favor of the first viewpoint is given by the application of a decorated lattice-gas model, similar to that of Clark and Neece (1968), to reaction rates in a critical solution by Wheeler (1972). Using a reasonable set of values of the interaction energies, he showed that one could predict an anomalous increase in rate of the isoprene-maleic anhydride reaction at the critical point of both the hexane-nitrobenzene and hexane-nitroethane systems in qualitative agreement with the data.

In conclusion, we have demonstrated experimentally, anomalous behavior of the rates of two chemical reactions at both upper and lower critical solution points. The effects are not large, in the range of 20 to 40%, and require temperature control to ± 0.01°C. As such they probably have little practical application; however, they may lead to further understanding of the nature of the critical state.

One might predict greater effects in a more precisely controlled system. Also, following the application of the fluctuation approach to collision theory, one would predict a much greater effect at a vapor-liquid critical point. In either case, however, the difficulty of maintaining a reactor (of changing composition) at the exact critical temperature and pressure, would be immense. Nonetheless, such experiments would be useful additions to our experimental understanding of the critical point, and it is not completely inconceivable that practical applications of this anomaly might be discovered in the future.

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NOTATION

c = concentration
C_V = constant volume heat capacity
E = energy
k = reaction rate constant
k_0 = reaction rate constant, ideal system
k_B = Boltzmann constant
N = number of particles
P = pressure
T = temperature
T_c = critical solution temperature
x = mole fraction
γ = activity coefficient
μ = chemical potential
ξ = concentration fluctuation

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Gas Chromatographic Determination of Thermodynamic Properties of Polymer Solutions at High Pressure

The gas chromatographic (GC) method for thermodynamic measurements of polymer-solvent systems at finite concentration has been improved to extend its operating range from atmospheric pressure to over 70 atm and over 240°C. This paper describes the design and operation of the equipment and the mathematical treatment of the GC data, and presents experimental results for *n*-hexane and isooctane in high density polyethylene. These results include the solubility isotherms, activity coefficients, and polymer-solvent interaction parameters. The activity coefficients covering a range from 4 to 70 atm for *n*-hexane in the polymer solution were correlated successfully as a function of composition using a two-parameter segment interaction equation.

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SCOPE

There is a scarcity of solubility isotherms and other thermodynamic data for polymer-solvent systems at the elevated temperatures and pressures often encountered in commercial processing. One especially important area for which there is little data available is that of devolatilization of monomer or solvent remaining in a high temperature melt. This study reports the details of apparatus design and operation for a gas chromatographic method to acquire these data rapidly with sufficient accuracy for design purposes. The method, employing the elution of a solvent peak on a constant plateau of solvent concentration in the carrier gas, uses gas chromatographic equipment that is readily available and relatively easy to adapt to operation at high pressure. The flexibility of the apparatus permits measurements to be obtained for practically any thermally stable solvent that can be vaporized with any film-forming polymer.

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