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Chemical Reactions and Phase Transitions[1]

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We consider the questions of what effects the fluctuations in fluids near critical points have on the rates and extents of chemical reactions taking place in those fluids and of whether equilibrium polymerizations can be profitably viewed as phase transitions. We find that reaction rates are expected to be affected by critical points only in rare circumstances and that, indeed, there is no compelling experimental evidence for such effects. On the other hand, there is evidence for an effect of critical fluctuations on the extents of chemical reactions at equilibrium, but the effect is not (and is, in general, not expected to be) dramatic. We find that the experimental data on equilibrium polymerizations are in qualitative agreement with predictions based on the $n = 0$ magnet model but that closer consideration and further experimental work are in order.

KEY WORDS: chemical reactions; critical phenomena; equilibrium polymerization; reaction extent; reaction rate.

1. INTRODUCTION

How do the fluctuations in fluids at critical points affect chemical reactions taking place in those fluids? How do the fluctuations affect the *rates* of chemical reactions? How do the critical fluctuations affect the *extents* of chemical reactions taking place in the fluids? Early work, experimental and theoretical, indicated dramatic effects of critical fluctuations on reaction rates. More recent experiments and more careful theoretical analysis indicate that such effects will be small and will occur only in rare circumstances. An effect of critical fluctuations on the extent of conversion from products to reactants has recently been measured and shown to be consistent with theoretical expectations.

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Are there chemical reactions which can be viewed *as* phase transitions, and is such a point of view a productive one? Polymerization reactions which are reversible upon change in temperature are predicted by J. C. Wheeler and collaborators to behave as if the polymerization were a second-order phase transition. The theoretical predictions for these polymerizations are in qualitative agreement with experiments, but the comparison of theory and experiment raises some interesting issues.

2. THE EFFECT OF CRITICAL FLUCTUATIONS ON THE RATE OF A CHEMICAL REACTION

Procaccia and Gitterman studied critical-point effects on chemical reaction rates in 1981 [1, 2]. They made the phenomenological argument that the reaction rate will be [3]

$$\text{rate} = L(\partial A/\partial \xi)_{X, Y, \ldots}(\xi - \xi_0) \tag{1}$$

where L is a self-diffusion coefficient which has no critical anomaly, and A is the affinity of the reaction

$$A = -\sum_i \nu_i \mu_i \tag{2}$$

where ν_i is the signed stoichiometric coefficient of species i (positive for products and negative for reactants), μ_i is the chemical potential of species i, ξ is the extent of the reaction, and ξ_0 is the extent at equilibrium. The subscripts X, Y, etc., in Eq. (1) refer to those thermodynamic parameters held constant under the particular experimental conditions.

Derivatives such as the one in Eq. (1) have been considered by Griffiths and Wheeler [4]. In general, such derivatives will go to zero strongly (with a critical exponent $\gamma = 1.25$) if all quantities held constant are fields:

$$(\partial A/\partial \xi)_{X, Y} \approx t^{\gamma} \tag{3}$$

where $t = |T - T_c|/T_c$, and T_c is the critical temperature. The derivative will go to zero weakly (with an exponent $\alpha = 0.11$) if only one quantity held constant is a density and the rest are fields, and it will be regular if more than one quantity held constant is a density.

Procaccia and Gitterman [1] asserted that there will be reacting systems for which only fields are held constant. An example of such a system is a reaction in a one-component system for which the pressure and temperature are held constant. For such a system, Procaccia and Gitterman predicted a dramatic slowing down of the chemical reaction as the temperature nears the liquid–gas critical temperature of the system. They noted that the addition of nonreacting components to the system will mean that the concentrations of those components are held constant and that, therefore, densities are held constant in Eq. (1); one such extra component will change a strong effect to a weak one, and two such components will completely suppress the strong effect. They found the same behaviors to be predicted by linear and nonlinear hydrodynamic analyses.

Milner and Martin [5] reconsidered Eq. (1) and came to different conclusions. They pointed out that one must carefully consider the relaxation times for heat and sound in order to determine exactly what quantities should be considered to be constant. If the reaction rate is much faster than either the speed of sound or the thermal diffusivity, then the mass density and the entropy, both density variables, are both effectively constant, and there is no expectation of any effect of the critical fluctuations on the reaction rate. If the reaction is somewhat slower, slow enough for mass density to relax but not slow enough for heat to diffuse, then the system is at constant pressure (a field) and constant entropy (a density), leading to a weak slowing down of the reaction rate as a function of temperature. If the reaction is so slow that both sound and heat relax faster than the reaction can take place, then pressure and temperature (both fields) can be said to be constant and a strong slowing down is expected. We must recall, however, that both the speed of sound and the thermal diffusivity slow near critical points [6]. This will make it difficult to find reactions for which the above conditions are satisfied.

Milner and Martin further predicted that there are diffusive modes associated with pairs of components and that these modes are also expected to be slow compared to the chemical reaction. If there are i reactants and j products, then there are $i+j-2$ such conserved densities. If all $(i+j)$ species in the system take part in the reaction, then the reaction can slow strongly for $i+j \leqslant 2$, weakly for $i+j=3$, and not at all for $i+j>3$. Any components present but not participating in the reaction will have constant concentrations (densities), as noted by Procaccia and Gitterman. Thus a strong slowing down can happen only for a system of one or two species; when there are two species, both must take part in the reaction for the effect to be strong.

The conclusion is that the conditions predicted by theoretical considerations for a strong critical slowing down of a chemical reaction are not likely to be attained in most experimental situations.

Experimental investigations of the effect of critical points on chemical reaction rates are few. In 1946, Toriumi et al. [7] reported increases in the rates of oxidation of NH_3 and SO_2 near their respective liquid–vapor critical points; it is hard to assess those data in light of the many pitfalls we now know to exist near critical points. More recently, Krichevskii et al. reported a dramatic slowing down (from times of less than a picosecond to times of about an hour) of the recombination of chlorine atoms in chlorine near its liquid–vapor critical point [8] and a similar slowing down for the recombination of iodine atoms in carbon dioxide, near the carbon dioxide liquid–vapor critical point [9]. In 1985, Greer showed that Krichevskii et al. misinterpreted their experimental results and that the only slowing down observed for the halogen recombinations on the 1-h time scale was the slowing heat dissipation [10]. Greer's experiment did not probe time scales of less than a few minutes. The iodine/CO_2 experiment has three species (I_2, I, and CO_2), two of which take part in the reaction. The total concentration of the iodine and the total volume of the system, both densities, are constant; without even considering the hydrodynamic modes, no critical slowing down is expected. For the chlorine, however, only the overall volume is held constant, so an effect is not immediately precluded: it depends upon the relative relaxation rates of the hydrodynamic modes. However, since halogen recombinations are very fast, on a time scale of about a picosecond [11], we expect no effect on the reaction due critical fluctuations. In summary, there is no compelling experimental evidence of a critical effect on reaction rates near a liquid–gas critical point, nor has anyone suggested a real system for which such an effect might be expected.

Reactions near liquid–liquid critical points will generally involve more than two components, which makes it unlikely that an effect on the reaction rate can be found. Snyder and Eckert [12] studied two organic reactions near liquid–liquid critical points and claimed to see critical effects, but reconsideration of their data leads to the conclusion that the scatter in their results is large enough to invalidate their claim. Another reaction which has been studied near liquid–liquid critical points is the transfer of a proton from a weak acid to water. If the two components showing the liquid–liquid critical point are the reactants, then there are four species present, all participating in the reaction. The pressure (a field) and the overall composition (a density) are constant, reducing any effect to a weak one at most, depending on the hydrodynamic relaxation times. The electrical conductivity of the mixture isobutyric acid + water near its upper liquid–liquid critical point shows a weak anomaly which has been attributed to an anomaly in its proton transfer rate [13] but which could also be due to an anomaly in the extent of acid dissociation (see below). Dunker et al. [14] interpreted an absorption of sound near the isobutyric acid + water critical point as being due to the proton transfer reaction and observed a slowing down of its relaxation time with a critical exponent of about 1. This result of Dunker et al. is puzzling, since it is inconsistent with the Milner–Martin argument and yields an unexpected value of the exponent.

At this time we conclude that there is no compelling theoretical or experimental evidence for an effect of critical fluctuations on the rate of a chemical reaction. The work of Dunker et al. on the system isobutyric acid + water is intriguing and deserves corroboration by a complementary experimental technique.

3. THE EFFECT OF CRITICAL FLUCTUATIONS ON THE EXTENT OF A CHEMICAL REACTION

Procaccia and Gitterman considered the effect of critical fluctuations on the extents of chemical reactions in 1983 [15]. A more straightforward analysis was given by Wheeler and Petschek in the same year [16]. The simplest approach [16] is to consider the temperature dependence of the extent of the reaction at equilibrium:

$$(\partial\xi_0/\partial T)_{X,Y,\ldots} \approx t^{-p} \tag{4}$$

where p is a critical exponent. Here, as in the discussion above, the important consideration is the specification of the thermodynamic path for a given experiment.

For the dissociation of isobutyric acid + water near the liquid–liquid critical point of this mixture, the pressure (a field) and the total mole fraction of one of the components (a density) are held constant, so we expect a weak effect, an exponent $p = \alpha = 0.11$ in Eq. (4) [17]. The measurements of the conductivity of the mixture, which should be proportional to the concentrations of the ionic products of the reaction, are in agreement with this exponent [13, 18].

Krichevskii et al. [19] attempted to study the dimerization of NO_2 in carbon dioxide, near the liquid–gas critical point of carbon dioxide. By the arguments of Wheeler and Petschek, we expect no critical effect, since the total volume and the total concentration of the NO_2 (in monomer and in dimer), both densities, were constant. Krichevskii et al. studied the scattering of light as a measure of the extent of reaction and saw a strong anomaly, but that effect was due entirely to the critical opalescence of the mixture and gave no information on the chemical reaction [16, 20]. The same reaction was studied by Tveekrem et al. in a mixture of perfluoromethylcyclohexane + carbon tetrachloride near its liquid–liquid critical point [21]. Both the total concentration of the solvent and the total concentration of NO_2 (densities) are constant, but the latter can be ignored if it is small, so that a weak effect is expected [16]. Tveekrem et al. followed the reaction by monitoring the static dielectric constant. They measured a decrease in dimerization of about 4% as T_c was approached;

the temperature dependence of the decrease was best described by an exponent α, as expected.

We conclude that the available experimental evidence shows an effect of critical fluctuations on the extent of chemical reactions at equilibrium and that the nature of the effect is consistent with theoretical expectations. Only weak effects on the extent have been observed. A strong effect would require a one-component system (thus a liquid–gas critical point) at constant pressure, in which the reaction is an intramolecular transformation. An example is a conformational change, such as the boat–chair transformation in cyclohexane, near the liquid–gas critical point of cyclohexane.

4. CHEMICAL REACTIONS WHICH CAN BE VIEWED AS PHASE TRANSITIONS

Wheeler and his collaborators [22] have suggested that certain kinds of thermally reversible chemical reactions can profitably be viewed as phase transitions. In this view, the reactions fit into the theoretical framework developed for magnetic and fluid phase transitions, allowing immediate calculation of the thermodynamic properties.

The reaction to be seen as a phase transition is equilibrium polymerization. Equilibrium polymerization takes place in such a way that the ends of the polymer molecules remain active, an equilibrium exists between polymers and monomers, and monomers are continually adding to and breaking from the polymers. The equilibrium mixture is essentially all monomer above or below (depending upon the sign of the enthalpy of propagation) a particular temperature; at that temperature, polymerization propagates abruptly.

Wheeler et al. considered equilibrium polymerization in two kinds of systems, liquid sulfur [23, 24] and organic "living" polymers [25]. Liquid sulfur polymerizes from monomers of eight sulfur atoms in a ring to mostly chains of about 10^5 atoms (although polymeric rings are not precluded), upon heating to 159°C. The organic molecule α-methylstyrene polymerizes upon cooling to 60°C in the presence of a very small amount of initiator. Wheeler et al., noting the similarity between the partition function for equilibrium polymerization and that for the $n = 0$ magnet, where n is the dimension of the order parameter, predicted that equilibrium polymerizations producing only chain polymers will behave as do systems in the $n = 0$ universality class. They calculated properties such as the density and the heat capacity.

However, Cordery and others [26, 27] predicted that if the polymers are rings rather than chains, then the universality class must be $n = 1$ rather than $n = 0$. Furthermore, if the rings are directed rings (the monomers always adding in a certain direction), then the universality class becomes $n = 2$. When chains and rings are present, bicritical phenomena develop [28]. When a second component is added to the polymerizing component, then tricritical phenomena develop [29].

Some work has been done in testing these predictions by measuring experimental properties of polymerizing systems. For pure sulfur, data on the density [30] and the heat capacity [31] from the literature are in qualitative agreement with the theory [23, 24], as are new measurements of the static dielectric constant [32] and the viscosity [33]. However, there are intriguing qualitative differences which suggest that sulfur may contain rings as well as chains. Work with sulfur mixtures has been difficult because the sulfur tends to react with the second component [34]. New work with sulfur + biphenyl [35] supports the view [36] that the reaction between the sulfur and the other component (biphenyl) leads to a nonsymmetrical tricritical point.

Published data on the amount of polymer as a function of temperature are available for tetrahydrofuran [37] and agree well with the predictions [25]. No measurements are available for such properties as the heat capacity and the density near the ceiling temperature for any living polymers. There are no published studies of the phase diagrams of living polymers mixed with a second component.

5. CONCLUSIONS

We conclude that (i) reaction rates are not, in general, affected by critical fluctuations; (ii) extents of reaction can sometimes be weakly affected by critical fluctuations, but strong effects will be very rare; and (iii) equilibrium polymerization behaves qualitatively like a chemical reaction, but the quantitative behavior requires more consideration.

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