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Reaction Kinetics and Critical Phenomena: Saponification of Ethyl Acetate at the Consolute Point of 2-Butoxyethanol + Water[1]

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The rate of sponification of ethyl acetate by sodium hydroxide was measured near the consolute point of the liquid mixture, 2-butoxyethanol + water. At temperatures far below the lower critical solution temperature, T_c, the apparent rate constant obeyed the Arrhenius equation. In the one-phase region just beneath T_c, the rate constant decreased below the Arrhenius background, indicating critical slowing down. Because the kinetics of this reaction are *second order*, the net reaction rate depends upon both $(\partial \Delta G/\partial \xi)_e$ and $(\partial^2 \Delta G/\partial \xi^2)_e$, where ΔG is the Gibbs free energy difference between products and reactants, ξ is the extent of reaction, and subscript "e" refers to chemical equilibrium. On the basis of the Principle of Universality, it is argued that as the temperature approaches T_c, both of these thermodynamic derivatives should go to zero, and the net reaction rate should slow down as is actually observed.

KEY WORDS: 2-butoxyethanol; critical slowing down; kinetics; saponification; water.

1. INTRODUCTION

The consolute point is an extremum in the temperature versus mole fraction phase diagram of a constant pressure binary liquid mixture where the homogeneous solution first begins to separate into two immiscible layers. The extreme value of the temperature along the boundary separating the two immiscible liquids is called the critical solution temperature, T_c^0.

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A binary mixture having a liquid–liquid phase boundary that is concave down is said to have an upper critical solution temperature (UCST), while a mixture having a liquid–liquid phase boundary that is concave up is said to have a lower critical solution temperature (LCST) [1]. Upon introduction of a reactant or a catalyst, a chemical reaction can often be initiated. This permits liquid mixtures to be used to study the effect of a critical point on the net rate of reaction.

Using conductivity as a measure of the extent of reaction, we have observed slowing down in the net rates of hydrolysis of five different organic halides near the equilibrium consolute points of three water-based binary liquid mixtures [2, 3]. These five reactions have the common feature that they all proceed by the S_N1 mechanism with rate laws that are first order in the concentration of the organic halide [4]. To explore these effects in more detail, we have carefully measured the S_N1 hydrolysis rate of 2-chloro-2-methylbutane in the critical region of isobutyric acid + water (UCST) using strong stirring in order to keep any coexisting phases well mixed [5, 6]. To distinguish the effect of an UCST from that of a lower, we also carefully determined the rate of hydrolysis of 2-bromo-2-methylpropane in triethylamine + water (LCST) [6]. In both cases, we observed *slowing down* above the critical temperature and *speeding up* below it. Because two phases coexist *below* an UCST, while they coexist *above* an LCST, these experiments combine to demonstrate that the reaction rate effects which we have observed are intimately associated with the critical point and are not an artifact of the coexistence of immiscible liquid phases [6].

The results of these S_N1 hydrolysis reaction experiments have led us to pose the following question: *Do reaction rate critical effects depend upon the reaction mechanism? To be more specific, can reaction rate critical effects be observed when the mechanism is other than S_N1, and the kinetics are no longer first order?* To answer this question, we have measured the rate of the saponification of ethyl acetate by NaOH in 2-butoxyethanol + water (LCST). In contrast to the S_N1 hydrolysis reactions, where the rate controlling step is unimolecular, the rate-controlling step in the saponification of ethyl acetate is the bimolecular encounter of OH^- with $CH_3COOC_2H_5$ to form the hemiorthocarboxylate ion intermediate, $CH_3(C_2H_5O)(OH)CO^-$, which then subsequently decays into the products [4].

2. THEORY

2.1. Kinetics

We can define the extent of reaction, ξ, by considering a reversible elementary reaction written in the form

$$\nu_1\,(1) + \nu_2\,(2) \rightarrow \nu_3\,(3) + \nu_4\,(4)\,. \tag{1}$$

In Eq. (1), the reactants (1) and (2) are converted into products (3) and (4). The respective stoichiometric coefficients are ν_1, ν_2, ν_3, and ν_4. If we let $c_i(0)$ be the initial concentration of species i, then the concentration, c_i, at a later time t is $c_i = c_i\,(0) \pm \nu_i \xi$, where the upper sign applies to products while the lower sign applies to reactants. The initial value of ξ is zero, while its equilibrium value at the end of the reaction is ξ_e. The net rate of reaction is the time derivative, $d\xi/dt$.

In the saponification of ethyl acetate, the stoichiometry of the overall reaction is

$$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH. \tag{2}$$

Since both sodium hydroxide and sodium acetate are strong electrolytes, the measurement of electrical conductance can be used to follow the progress of the reaction. Because the hydroxide ion has a higher conductivity than the acetate ion, there is a net decrease in conductance as the reaction progresses.

If the initial concentrations of OH^- and $CH_3COOC_2H_5$ are the same and equal to c_0, the rate law governing the reaction in Eq. (2) is

$$\frac{d\xi}{dt} = k'\,(c_0 - \xi)^2 - k''\xi^2, \tag{3}$$

where the rate constant in the forward direction is k'. Even though this saponification reaction is essentially irreversible [4], we have included the rate of the reverse reaction, $k''\xi^2$, albeit slight, in the overall rate law in order to make contact between the kinetics and the thermodynamics. On the basis of what is known about the mechanism [4], we have taken the kinetics of the reverse reaction to be second order with rate constant, k''.

For comparison with thermodynamics, it will prove useful to express the right-hand side of Eq. (3) in terms of the position of equilibrium, ξ_e instead of the initial concentration, c_0, as shown. Since at equilibrium, $d\xi/dt = 0$, the value of ξ_e can be computed by first setting the right-hand side of Eq. (3) to zero and then solving the resulting quadratic equation. Because of the near irreversibility of the reaction in Eq. (2), we have $k''/k' << 1$, and the appropriate root is given by

$$\xi_e = \frac{c_0\left(1 - \left(k''/k'\right)^{1/2}\right)}{1 - (k''/k')}. \tag{4}$$

The right-hand side of Eq. (3) is the function, $f(\xi) = k'(c_0 - \xi) - k''\xi^2$, which we can expand in a Taylor series about $\xi = \xi_e$. Since $f(\xi_e) = 0$, and the third and higher derivatives of $f(\xi)$ are all identically zero, the right-hand side of Eq. (3) can be represented exactly by the first two non-zero terms of its Taylor series. When the coefficients in this series are evaluated using Eq. (4) and the results are substituted into Eq. (3), we have

$$\frac{d\xi}{dt} = -2k' c_0 \left(k''/k'\right)^{1/2} (\xi - \xi_e) + k' \left(1 - \left(k''/k'\right)\right) (\xi - \xi_e)^2 . \tag{5}$$

If we ignore terms first order and higher in $(k''/k')^{1/2}$, Eq. (4) becomes $\xi_e = c_0$, while Eq. (5) assumes the form,

$$\frac{d\xi}{dt} = k'(c_0 - \xi)^2. \tag{6}$$

Equation (6) is, of course, the appropriate rate law for a second-order irreversible reaction. With the initial condition, $\xi = 0$ at $t = 0$, the integral of Eq. (6) is

$$\xi\,(t) = \left(\frac{k' c_0 t}{1 + k' c_0 t}\right) c_0. \tag{7}$$

When at least one of the reactants or products is ionic, the progress of the reaction can be followed by measuring the conductance. The instantaneous value of the conductance, L, is given by

$$L = L^0 + \left(L^e - L^0\right) (\xi/\xi_e) , \tag{8}$$

where L^0 is the initial value, and L^e is the value at equilibrium [5]. After substitution of Eq. (7) into Eq. (8), we obtain

$$\frac{1}{L^0 - L} = \frac{1}{L^0 - L^e} + \frac{1}{\left(L^0 - L^e\right) k' c_0 t} . \tag{9}$$

Values of $\left(L^0 - L\right)^{-1}$ plotted versus t^{-1} produced a straight line, the slope of which was used to determine the value of the rate constant, k'.

2.2. Thermodynamics

The rate law expressed by Eq. (5) provides no clues by itself concerning the effects to be anticipated in applying it to a second order, irreversible reaction near a critical point. To take into account the large deviations from solution ideality expected near a critical point, $d\xi/dt$ needs to be expressed in terms of the Gibbs free energy difference, ΔG, that separates products from reactants. The rate law in these terms assumes the form [7]

$$\frac{d\xi}{dt} = \frac{\kappa' a_1^{\nu_1} a_2^{\nu_2}}{y_*}\left[1 - \exp(\Delta G/RT)\right], \tag{10}$$

where a_i ($i = 1, 2$) are the thermodynamic activities and $\nu_1 = \nu_2 = 1$ are the stoichiometric coefficients of the reacting species, ethyl acetate and OH^-, respectively, y_* is the activity coefficient of the transition state, κ' is the rate coefficient for reaction in the forward direction in the case of dilute ideal solution, R is the universal gas constant, and T is the absolute temperature. The factor

$$r' = \kappa' a_1^{\nu_1} a_2^{\nu_2}/y_* \tag{11}$$

that multiplies the bracket in Eq. (10) is the forward rate of reaction.

To make contact with Eq. (5), we begin by expanding the right-hand side of Eq. (10) in powers of $\Delta G/(RT)$. After retaining terms up to second order, we have

$$\frac{d\xi}{dt} = -r'\left[\left(\frac{\Delta G}{RT}\right) + \frac{1}{2}\left(\frac{\Delta G}{RT}\right)^2\right]. \tag{12}$$

Because equilibrium is the reference point for analyzing the effects of the consolute point on chemical reactions, we next expand r' and ΔG as functions of ξ in Taylor series about $\xi = \xi_e$. To second order in $(\xi - \xi_e)$, we have

$$r'(\xi) = r'(\xi_e) + \left(\frac{\partial r'}{\partial \xi}\right)_e (\xi - \xi_e) + \frac{1}{2}\left(\frac{\partial^2 r'}{\partial \xi^2}\right)_e (\xi - \xi_e)^2, \tag{13}$$

and

$$\Delta G(\xi) = \Delta G(\xi_e) + \left(\frac{\partial \Delta G}{\partial \xi}\right)_e (\xi - \xi_e) + \frac{1}{2}\left(\frac{\partial^2 \Delta G}{\partial \xi^2}\right)_e (\xi - \xi_e)^2, \tag{14}$$

respectively, where the supscript, "e", refers to chemical equilibrium. Noting that $\Delta G(\xi_e) = 0$, we can substitute Eqs. (13) and (14) into Eq. (12) and collect terms up to order $(\xi - \xi_e)^2$. The result is

$$\frac{d\xi}{dt} = -\frac{r'(\xi_e)}{RT}\left(\frac{\partial \Delta G}{\partial \xi}\right)_e (\xi - \xi_e) - \left[\frac{r'(\xi_e)}{2(RT)^2}\left(\left(\frac{\partial \Delta G}{\partial \xi}\right)_e\right)^2 + \frac{1}{RT}\left(\frac{\partial r'}{\partial \xi}\right)_e \times \left(\frac{\partial \Delta G}{\partial \xi}\right)_e + \frac{r'(\xi_e)}{2RT}\left(\frac{\partial^2 \Delta G}{\partial \xi^2}\right)_e\right](\xi - \xi_e)^2. \tag{15}$$

The first-order term in $(\xi - \xi_e)$ on the right-hand side of Eq. (15) is adequate by itself to describe the net rate of any reaction close to equilibrium. In addition, it is an exact expression for the rate of a reversible reaction that is first-order in both directions, and serves as an approximate expression for the net rate of an irreversible first-order reaction [5]. By contrast, both the linear and quadratic terms in $(\xi - \xi_e)$ in Eq. (15) are required to represent the net rate of a reaction that is sufficiently far from equilibrium and no more than second order or higher in either direction. If the reaction is irreversible and second-order in the forward direction, we have seen in Section 2.1 that the coefficient of the term in $(\xi - \xi_e)$ is negligible, and only the term in $(\xi - \xi_e)^2$ is important. Because Eq. (15) expresses the net rate of reaction in the form of an expansion about equilibrium, the Griffiths–Wheeler rules [8] that govern the critical properties of thermodynamic derivatives can be used to predict the critical behavior of $(\partial \Delta G/\partial \xi)_e$ and $\left(\partial^2 \Delta G/\partial \xi^2\right)_e$ which appear in the coefficient of $(\xi - \xi_e)^2$.

3. EXPERIMENT

In our previous experiments, we have encountered several phenomena that are characteristic of chemically reacting mixtures near a consolute point:

First, the dissolution of reactants and reaction products in a binary liquid mixture with a consolute point usually causes a noticeable shift in the critical temperature [3]. As a consequence, it becomes necessary to draw a distinction between the critical solution temperature, T_c^0, of the original binary mixture and the equilibrium critical solution temperature, T_c, of the multicomponent reaction mixture in which the binary mixture plays the role of the solvent. We have observed experimentally that

$$T_c = T_c^0 + ac, \tag{16}$$

where a is an empirical coefficient, which has a different value for each mixture, and c is the initial molar concentration of the added reactant [9]. Although technically the value of T_c is determined by the value of ξ_e, T_c can be connected to the *initial* concentration of the reactants as in Eq. (16), because of the stoichiometric relation that links reactants to products and because all of the reactions mentioned above go essentially to completion. Since each saponification kinetics run started with fixed, identical concentrations of ethyl acetate and sodium hydroxide, the value of T_c was a constant for our experiment.

Second, when the thermostat temperature, T, happens to lie between T_c^0 and T_c, a liquid–liquid phase transition will occur in the mixture during the course of the reaction [5, 9]. The elapsed time, t, after the start of a run when the phase separation appears, is revealed by a change in the slope, $d\xi/dt$, of a plot of $\xi(t)$ versus t [5, 6]. As equilibrium is the reference state for the theory of critical effects on the reaction rate [3, 5, 6], we have ignored in a kinetics run any data collected prior to the occurrence of the phase transition.

Third, because of the dependence of the critical solution temperature upon composition, we should expect during the course of a kinetics run that this temperature will have an instantaneous value that depends upon $\xi(t)$. With a fixed thermostat temperature, T, this drift in the critical temperature might cause critical slowing down of the conductance, which is known to depend upon the difference between T and the critical temperature [10]. The response of the conductance probe to this temperature difference might be mistaken for its response to the concentrations of sodium acetate and sodium hydroxide. In calibration experiments, however, we have made sure that our conductance probe continues to respond linearly to concentration despite the drift in T_c with time [6, 9]. Indeed, as a part of this calibration procedure, a reaction mixture that had reached chemical equilibrium was warmed (or cooled) through the suspected critical region. We observed the residual conductance, L^e, to pass through a sharp minimum as a function of T. Opalescence could be observed in the liquid at this conductance minimum, which demonstrated that the corresponding temperature equaled T_c [6, 9]. We used the location of this conductance minimum as the operational definition of the equilibrium critical temperature for all our mixtures.

Organic materials were purchased from Aldrich and used as received. Water was once distilled from a glass system. The solvent was prepared at the critical composition of 24.78 mass% 2-butoxyethanol in water [11]; this mixture had an LCST at $T_c^0 = 50.11°\mathrm{C}$. To 100 mL of this binary mixture, enough ethyl acetate and sodium hydroxide were added to make the concentration, c_0, of each reactant equal to 0.001 M. Once this mixture had reached chemical equilibrium, the critical temperature was $T_c = 48.4°\mathrm{C}$. The corresponding value for a in Eq. (16) was $-1710°\mathrm{C\,mol^{-1}\,L}$.

The thermostat bath, temperature controller, temperature measuring equipment, and reaction cell were as previously described [2, 3, 5, 6]. The reaction mixture was well stirred with a magnetically driven stirring bar. The conductance was measured with a Hanna Instruments Inc. Model HI 9032 conductivity meter. The software of the Hanna meter recorded the time, t, and difference, $L^0 - L$; hence, Eq. (9) was fitted to the data from each run with $L^0 - L^e$ and k' taken as adjustable parameters. From the slope and intercept, the value of k' could be computed.

Table I summarizes our measurements of k' as a function of temperature (in °C). In Fig. 1, we show an Arrhenius plot of this data where T is the temperature (in K). The straight line, which was fitted to the data collected at temperatures outside the critical region, had the equation,

$$\ln k' = 18.9 - 48,900/RT, \tag{17}$$

where $R = 8.314\,\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, and the units of k' are $\mathrm{L \cdot mol^{-1} \cdot min^{-1}}$. This line serves to establish the "background" for determining the existence of a critical effect. In the region just below the critical temperature, slowing down of the reaction rate is apparent. Because of the limited ability of our thermostat to maintain a constant temperature that was more than about 30°C above ambient, all of the data, except for six points, were collected in the one-phase region below $T_c = 48.4°\mathrm{C}$.

4. DISCUSSION AND CONCLUSIONS

Griffiths and Wheeler [8] separate the thermodynamic variables into two classes. In the first class are the "fields," such as temperature, pressure, the component chemical potentials, and ΔG. The value of a given field variable is the same in all phases coexisting in equilibrium. In the second class are the "densities," such as entropy, the concentrations of the chemical components, and ξ, which have different values in each coexisting phase. Griffiths and Wheeler argue that when the experimental conditions are such that the fixed variables consist of fields and no more than one density, then the derivative of a field with respect to a density, such as $(\partial \Delta G/\partial \xi)_e$, should go to zero as the power law, $|T - T_c|^x$, as T approaches T_c. The order of magnitude of the exponent, x, depends on whether the number of densities held fixed is zero or one. In the case where no densities are held fixed, the value of x is expected to be of order unity, and the derivative is said to go to zero "strongly". When one density is fixed, the value of x is expected to be of the order of 1/10, and the derivative is said to go to zero "weakly." In both cases, the specific value of the exponent depends upon whether the critical point is approached along the critical isotherm or the critical isobar [12]. When two or more densities are fixed, the value of the derivative should be continuous.

In applying the Griffiths–Wheeler rules to the saponification of ethyl acetate in 2-butoxyethanol + water, we need first to enumerate the number of fixed densities. In a homogeneous reacting mixture, the fixed densities

Table I. Rate Coefficient k' versus Temperature for the Saponification of Ethyl Acetate in 2-Butoxyethanol (2BE) + Water at its Consolute Composition of 24.78 Mass Percent 2BE. (The Initial Concentration of Sodium Hydroxide and Ethyl Acetate was 0.001 M. The Critical Temperature at Chemical Equilibrium was 48.4 °C)

Temp. (°C)	k' (L · mol^{-1} · min^{-1})	Temp. (°C)	k' (L · mol^{-1} · min^{-1})
48.58	1.67	47.62	1.66
48.56	1.72	47.55	1.66
48.50	1.68	47.43	1.67
48.44	1.72	47.27	1.65
48.43	1.63	47.18	1.66
48.42	1.65	47.07	1.64
48.33	1.61	46.96	1.64
48.29	1.64	46.87	1.62
48.21	1.64	46.74	1.59
48.13	1.64	46.68	1.60
48.11	1.65	46.51	1.59
48.11	1.67	46.49	1.59
48.06	1.66	46.42	1.60
48.03	1.67	45.63	1.51
48.03	1.66	45.37	1.50
48.03	1.64	45.01	1.46
48.00	1.66	44.79	1.44
47.90	1.65	44.66	1.44
47.82	1.64	44.19	1.39
47.79	1.64	43.88	1.36
47.70	1.66	42.77	1.29

are the concentrations of any components that are inert in the sense of not participating in at least one chemical equilibrium. Neither the reactants, ethyl acetate and sodium hydroxide, nor the products, sodium acetate and ethanol, can be considered to be inert, because they are involved in the main reaction. Since the concentration of 2-butoxyethanol is much greater than that of the sodium hydroxide, this solvent alcohol can be expected to partly displace ethanol from ethyl acetate to form 2-butoxyethyl acetate in a side reaction called transesterification [13]. Although ethyl acetate does not hydrolyze effectively in pure water [4], the water in our mixture is, nevertheless, not completely inert. When Eq. (2) is at equilibrium, the acetate ion will participate with the water in a Bronsted-Lowry acid-base reaction to form a small amount of hydroxide ion and acetic acid [14]. With all components apparently involved in at least one reaction, the Griffiths–Wheeler rules predict that $(\partial \Delta G/\partial \xi)_e$ should go to zero "strongly" as T

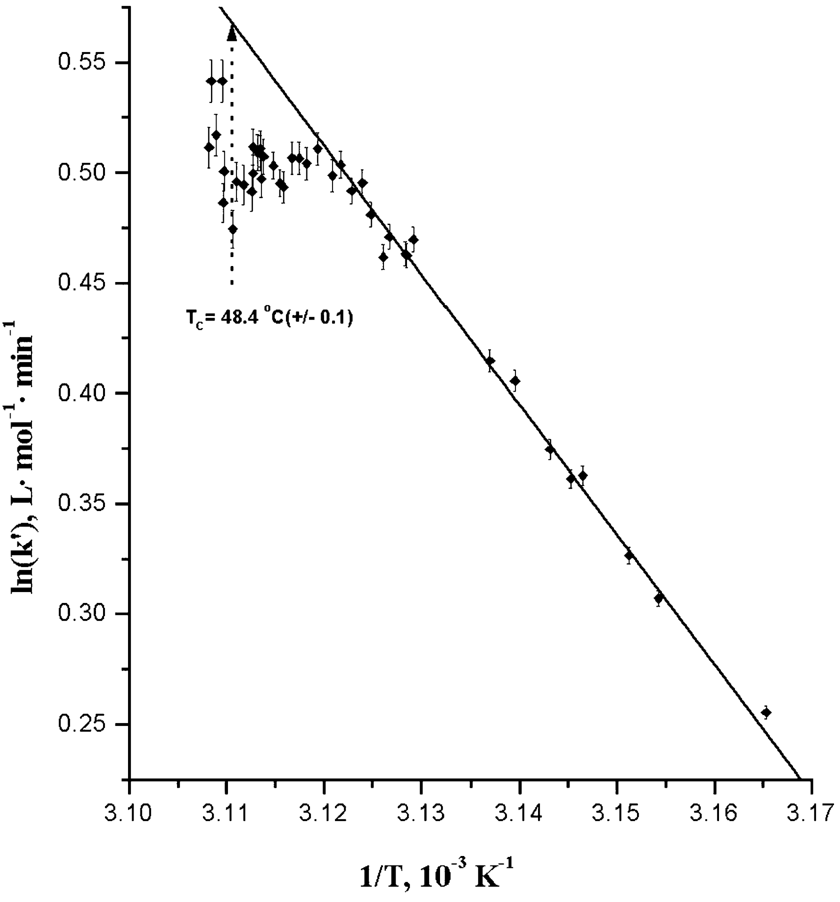

Fig. 1. Arrhenius plot of the second-order rate coefficient, k', for saponification of ethyl acetate in 24.78 mass% 2-butoxyethanol in water. The reciprocal of the absolute temperature is $1/T$, while the reciprocal of the equilibrium temperature is labeled T_c. This temperature corresponds to 48.4 °C.

approaches T_c. We thus conclude that the terms in Eq. (15) that involve $(\partial \Delta G/\partial \xi)_e$ must vanish at the critical point.

The net rate of reaction is then determined by the product, $\left(r'(\xi_e)/(2RT)\right)\left(\partial^2\Delta G/\partial\xi^2\right)_e$, which is all that remains of the coefficient multiplying $(\xi-\xi_e)^2$ in Eq. (15). The Griffiths–Wheeler rules, which are based upon the *Principle of Universality* [15, 16] that governs all critical phenomena, can be used to draw thermodynamic analogies between pure fluids and liquid mixtures. In a pure fluid, the pressure P is a field while the molar volume V is a density, and the second derivative $\left(\partial^2 P/\partial V^2\right)_T$ goes to zero at the critical point. Since ΔG is a field, while ξ is a density, we can perhaps argue by analogy that $\left(\partial^2 \Delta G/\partial\xi^2\right)_e$ should go to zero at the critical point of a mixture. Indeed, according to Eq. (15), the experimental results summarized in Fig. 1 can be understood if both the first and second derivatives of ΔG are small near the critical point. By contrast, the behavior of $r'(\xi_e)$ and its derivatives does not seem to be known as T approaches T_c.

None of the six points in Fig. 1 collected at temperatures above T_c lie above the straight line, as would be the case if speeding up of the net reaction rate occurred in this region. We cannot completely rule out speeding up, however, until we are able to repeat this experiment at concentrations of ethyl acetate and sodium hydroxide that are large enough to reduce T_c to a value closer to the center of the range of our thermostat. This strategy is not without its hazards, however, because as the gap between T_c^0 and T_c widens, a larger fraction of the kinetic runs will be interrupted by a liquid–liquid phase transition, since the thermostat temperature, T, will necessarily lie between T_c^0 and T_c.

In answer to the question posed in the Introduction, we can conclude on the basis of Fig. 1 that reaction rate critical effects are not confined to the S_N1 mechanism. Indeed, we have shown that Eq. (15) can be used to predict the effect of reaction mechanism on the critical behavior of $d\xi/dt$. In applying Eq. (15), we should distinguish between *dynamic* critical effects that depend upon $r'(\xi_e)$ and its derivatives, and *static* critical effects that depend upon the thermodynamic derivatives $(\partial\Delta G/\partial\xi)_e$ and higher. As pointed out, little is known about dynamic effects. So far as static critical effects in reactions with *first-order kinetics*, such as S_N1, are concerned, the net rate depends upon the derivative $(\partial\Delta G/\partial\xi)_e$, because all derivatives $\left(\partial^2\Delta G/\partial\xi^2\right)_e$ and higher are negligible. In the case of reactions with *second-order kinetics*, such as the saponification of ethyl acetate, the static effects depend upon both $(\partial\Delta G/\partial\xi)_e$ and $\left(\partial^2\Delta G/\partial\xi^2\right)_e$, because $\left(\partial^3\Delta G/\partial\xi^3\right)_e$ and higher are all negligible. In contrast to $d\xi/dt$, which can depend upon the first and higher derivatives of ΔG with respect to ξ, the average statistical fluctuation in ξ about ξ_e at chemical equilibrium near a critical point is determined solely by $(\partial\Delta G/\partial\xi)_e$ and is independent of the order of the kinetic rate law [17].

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