

## Chapter 1

# Criticality and Chemistry

### 1.1 Critical phenomena

Phase transitions occur in Nature in a great variety of systems and under a very wide range of conditions. For instance, the paramagnetic-ferromagnetic transition occurs in iron at around 1000 K, the superfluid transition occurs in liquid helium at 2.2 K, and Bose-Einstein condensation occurs at  $10^{-7}$  K. In addition to this enormous temperature range, phase transitions occur in a wide variety of substances, including solids, classical fluids and quantum fluids. Therefore, phase transitions are a very general phenomenon, associated with the basic properties of many-body systems. The thermodynamic functions become singular at the phase transition points, and these mathematical singularities lead to many unusual properties of the system which are called “critical phenomena.” We first consider the different types of the phase transition points (“critical points”) and then we introduce a qualitative method for describing the behavior of various parameters of the system in the vicinity of critical points.

The liquid-gas critical point of an one-component fluid is determined by the condition [4]

$$\left(\frac{\partial p}{\partial \rho}\right)_T = \left(\frac{\partial^2 p}{\partial \rho^2}\right)_T = 0 \quad (1.1)$$

where  $p$  is the pressure,  $\rho$  is the density, and  $T$  is the temperature. Similarly, the liquid-gas critical points of binary mixtures are characterized by the vanishing of the first and second derivatives of the chemical potential  $\mu$  with respect to the concentration  $x$ ,

$$\left(\frac{\partial \mu}{\partial x}\right)_{T,p} = \left(\frac{\partial^2 \mu}{\partial x^2}\right)_{T,p} = 0. \quad (1.2)$$

Here  $\mu = \mu_1/m_1 - \mu_2/m_2$ , where  $\mu_1$ ,  $\mu_2$  and  $m_1$ ,  $m_2$  are the chemical potentials and masses of the two components.

The close relation between (1.1) and (1.2) is evident from the equivalent form of Eq. (1.2), which can be rewritten as

$$\left(\frac{\partial p}{\partial \rho}\right)_{T,\mu} = \left(\frac{\partial^2 p}{\partial \rho^2}\right)_{T,\mu} = 0. \quad (1.3)$$

The critical conditions for a binary mixture (1.3) are the same as those for a pure system (1.1) when the chemical potential is kept constant. Analogously, the critical points for an  $n$ -component mixture are determined by the conditions

$$\left(\frac{\partial p}{\partial \rho}\right)_{T,\mu_1,\dots,\mu_{n-1}} = \left(\frac{\partial^2 p}{\partial \rho^2}\right)_{T,\mu_1,\dots,\mu_{n-1}} = 0 \quad (1.4)$$

where  $n - 1$  chemical potentials are held constant.

In addition to the above-mentioned thermodynamic peculiarities, relaxation processes slow down near the critical points resulting in singularities in the kinetic coefficients. An example is the slowing-down of diffusion near the critical points of a binary mixture. Nothing happens to the motion of the separate molecules when one approaches the critical point. It is the rate of equalization of the concentration gradients by diffusion which is reduced near the critical points. In fact, the excess concentration  $\delta x$  in some part of a system does not produce diffusion by itself. Usually a system has no difficulty in “translating” the change in concentration into a change in the chemical potential  $\delta\mu \sim (\partial\mu/\partial x)\delta x$ , which is the driving force for diffusion. However, near the critical point, according to (1.2),  $\partial\mu/\partial x$  is very small, and the system becomes indifferent to changes in concentration. This is the simple physical explanation of the slowing-down of diffusion near the critical point.

Since the states of a one-component system and a binary mixture are defined by the equations of state  $p = p(T, \mu)$  and  $\mu = \mu(T, \rho, x)$ , respectively, Eqs. (1.1) and (1.2) define the isolated critical point for an one-component system, and the line of critical points for a binary mixture. Another distinction between one-component systems and binary mixtures is that there are two types of critical points in the latter: the above considered liquid-gas critical points and liquid-liquid critical points, whereas two coexisting liquid phases are distinguished by different concentrations of the components. Both critical lines are defined by Eq. (1.2).

Different binary liquid mixtures show either concave-down or concave-up coexistence curves in a temperature-concentration phase diagram (at

fixed pressure) or in a pressure-concentration phase diagram (at fixed temperature). The consolute point is an extremum in the phase diagram where the homogeneous liquid mixture first begins to separate into two immiscible liquid layers. For the concave-down diagram, as for a methanol-heptane mixture, the minimum temperature above which the two liquids are miscible in all proportions is called the upper critical solution temperature (UCST). By contrast, for a concave-up diagram, such as the water-triethylamine solution, the maximum temperature below which the liquids are miscible in all proportions is called the lower critical solution temperature (LCST). Under the assumption of analyticity of the thermodynamic functions at the critical points, one can obtain the general thermodynamic criterion for the existence of UCST and LCST [3]. We will discuss this calculation in the next section when examining the influence of chemical reactions on UCST and LCST. Here we will consider chemical reactions occurring between solutes near the critical points of the solvent.

The properties of near-critical fluids range between those of gases and liquids (see Table 1). Near-critical fluids combine properties of gases and liquids. Their densities are lower than those of liquids, but much higher than the densities of gases, which makes the near-critical fluids excellent solvents for a variety of substances.

Table 1. Comparison of some physical properties of gases, liquids and near-critical fluids.

Physical Properties	Gas	Near-critical fluid	Liquid
Density ( $\text{kg}/\text{m}^3$ )	0.6–2	200–500	600–1000
Kinematic viscosity ( $10^{-6} \text{m}^2/\text{sec}$ )	5–500	0.02–0.1	0.1–5
Diffusion coefficient ( $10^{-6} \text{m}^2/\text{sec}$ )	10–40	0.07	$2 \times 10^{-4}$ – $2 \times 10^{-3}$

In Table 2 we list the critical parameters of the solvents in most common use. Water is the most abundant, cheap, safe and environmentally pure solvent. In spite of its high critical parameters which limits its application, in addition to the traditional uses, modern applications include the important problems of solving the environmental pollution problem and the fabrication of nanocrystalline materials with predictable properties [5]. Properties of near-critical water, such as the full mixing with oxygen and organic compounds, high diffusion and mass transfer coefficients, make water appropriate for efficient treatment of industrial wastes. The use of

near-critical water for detoxification of organic waste using the catalytic oxidation of pyridine was found [6] to be cheaper than other methods and also more effective, having almost no limitation on the concentration of the pyridine-containing solutions. The efficiency of hydrothermal detoxification of pyridine waste is substantially increased by the addition of a small amount of heterogeneous catalyst. For instance, the addition of 0.5% of  $\text{PtAl}_2\text{O}_3$  increases the oxidation of pyridine to 99% [7]. Other methods include dechlorination of chlorinate organic compounds, cleaning of polymers and plastic wastes, hydrolysis of cellulose, and the release of bromine for polymers and plastics.

Table 2. Critical parameters of fluids which are commonly used as solvents for chemical reactions.

Solvent	$T_{cr}$ (°C)	$p_{cr}$ (atm)	$\rho_{cr}$ (g/mL)
Water ( $\text{H}_2\text{O}$ )	373.9	220.6	0.322
Carbon dioxide ( $\text{CO}_2$ )	30.9	72.9	0.47
Sulfur hexafluoride ( $\text{SF}_6$ )	45.5	36.7	0.73
Ammonia ( $\text{NH}_3$ )	132.3	113.5	0.235
Methanol ( $\text{CH}_3\text{OH}$ )	239.4	80.9	0.272
Propane ( $\text{C}_3\text{H}_6$ )	96.6	41.9	0.22
Ethane ( $\text{C}_2\text{H}_6$ )	32.2	48.2	0.20
Pyridine ( $\text{C}_5\text{H}_5\text{N}$ )	347	55.6	0.31
Benzene ( $\text{C}_6\text{H}_6$ )	289	48.3	0.30

Nanocrystallines (particles whose size is a few interatomic distances) are new generation materials widely used as sensors, fuel cells, high-density ceramics, and semiconductors, among others. Hydrothermal synthesis in near-critical water is used to obtain nanocrystalline oxide powders with specified particle sizes and phase composition. Many references can be found [5] dealing with both nanotechnology and environmental problems.

Like water, carbon dioxide ( $\text{CO}_2$ ) has the advantage of being non-flammable, nontoxic and environment compatible. At the same time,  $\text{CO}_2$  has critical parameters more convenient than water, and is, therefore, the first choice for use as a near-critical solvent. Another advantage of  $\text{CO}_2$  lies in the fact that it does not attack enzymes and is therefore suitable for enzyme-catalyzed reactions. Some new applications include the use of two-phase reaction mixtures with high pressure carbon dioxide which are known as “ $\text{CO}_2$  — expanded fluids”. In fact, near-critical carbon dioxide is more frequently used in the laboratory and in technology than any other solvent. Hundreds of examples can be found in recent reviews [8], [9].

The infinite increase of the compressibility  $\rho^{-1}(\partial\rho/\partial p)_T$  or  $(\partial x/\partial\mu)_{T,p}$  as the critical point is approached, leads to a number of peculiarities in the behavior of a substance near its critical point. The specific heat at constant pressure  $C_p$  and the expansion coefficient  $\beta = -\rho^{-1}(\partial\rho/\partial T)_p$  also increase near the critical point of a one-component system, as follows from Eq. (1.1) and the appropriate thermodynamic relations.

A sharp increase in the mean square fluctuations of the density (or concentration) and of the integral of the correlation function  $g_{\rho\rho}$  follows from the well-known thermodynamic relations

$$\overline{(\rho(r) - \bar{\rho})^2} \sim \left(\frac{\partial\rho}{\partial p}\right)_T \rightarrow \infty; \quad \int g_{\rho\rho} d^3r \sim \left(\frac{\partial\rho}{\partial p}\right)_T \rightarrow \infty. \quad (1.5)$$

The large increase of the correlations between the positions of different particles is given by the second expression in (1.5), which is closely connected with the first expression. In other words, widely separated particles have to be strongly correlated to cause great changes in density.

The correlation radius  $\xi$ , which characterizes the distance over which correlations are significant, increases sharply near the critical temperature  $T_C$ ,

$$\xi_{T \rightarrow T_C} \rightarrow \infty. \quad (1.6)$$

According to estimates from scattering experiments,  $\xi$  reaches  $10^{-4} - 10^{-5}$  cm near the critical point. Thus, the specific nature of the critical region consists of the appearance of a new characteristic distance  $\xi$ , satisfying the condition

$$a \ll \xi \ll R \quad (1.7)$$

where  $a$  is the average distance between particles and  $R$  is a characteristic macroscopic length.

As an illustration of the crucial importance of the new characteristic length  $\xi$ , let us consider the singular part of the transport coefficients near the critical point for a model fluid consisting of spheres with a characteristic radius  $\xi$ . Particles inside such spheres are strongly correlated, and we can assume that under the influence of an external force, they move together with a mean velocity  $v$  and a mean free path  $\xi$ . One finds the following results [10]:

1. **Diffusion coefficient** [11]. When an external force  $F$  is applied, the spheres move according to Stoke's law,  $F \sim \eta\xi v$ , where  $\eta$  is the viscosity, i.e., the mobility  $b \equiv v/F \sim (\eta\xi)^{-1}$ . Using the Einstein relation  $D = k_B T b$ ,

where  $D$  is the diffusion coefficient and  $k_B$  is the Boltzmann constant, we have  $D \sim (\eta\xi)^{-1}$  or  $D\eta \sim \xi^{-1}$ , a result confirmed by the more rigorous theory and by experiment.

**2. Heat conductivity.** The usual arguments of molecular-kinetic theory give the heat flux  $q$  passing through unit area per unit time,  $q \sim vn(\epsilon_1 - \epsilon_2)$ . Here,  $n$  is the total number of spheres, and  $\epsilon_1 - \epsilon_2$  is the difference in their energies on two sides of a selected area, arising from the temperature difference  $T_1 - T_2 \sim \xi\nabla T$ :  $\epsilon_1 - \epsilon_2 \sim VC_p\xi\nabla T$ , where  $V$  is the total volume of the spheres, so that  $nV = 1$ . Thus,  $q \sim vC_p\xi\nabla T$ . One can find the velocity  $v$  from the estimate for the diffusion coefficient given above:  $v \sim D/\xi \sim 1/\xi^2\eta$ . Finally, the heat conductivity  $\lambda \sim q/\nabla T \sim vC_p\xi \sim C_p/\eta\xi$ . This result is supported by more rigorous theory and also by experiment.

The qualitative description of the singularity of the quantity  $a$  at the critical point is given by the non-integer critical index  $x$ , where  $a \sim |T - T_C|^x$ . If  $x \neq 0$ , this critical index is given by  $x = \ln(a)/\ln|T - T_C|$ , whereas if  $x = 0$ , there are two possibilities. In one case,  $a$  becomes constant at the critical point, with the possibility of different values of this constant on the two sides of the transition, which is called a jump singularity. In the other case,  $a$  exhibits a logarithmic singularity,  $a \sim \ln|T - T_C|$ .

Although there are general properties which define the values of the critical indices (dimension  $d$  of space, symmetry and the presence of long-range interactions), according to the universality principle, these values are defined by the general statistical properties of the many-body system, rather than by the details of the microscopic interactions. This implies that different isomorphic systems will have the same indices for the appropriate parameters. Using the language of fluids, the commonly accepted symbols  $\alpha, \beta, \gamma, \delta, \eta$ , and  $\nu$  describe, respectively, the asymptotic behavior near the one-component liquid-gas critical point of the specific heat at constant volume, order parameter (deviation of the density from its critical value), compressibility, pressure-density relation at the critical isotherm, the correlation function at the critical temperature, and the correlation length. Of these indices, one ( $\beta$ ) is determined only below the critical temperature and two ( $\delta, \eta$ ) exist only at the critical temperature. The remaining three indices can be defined for temperatures above critical ( $\alpha, \gamma, \nu$ ) as well as below ( $\alpha', \gamma', \nu'$ ). According to scaling theory [12],  $\alpha = \alpha', \gamma = \gamma', \nu = \nu'$  and the following relations exist between critical indices:  $\alpha + 2\beta + \gamma = 2$ ,  $d\nu = 2 - \alpha$ ,  $(2 - \eta)\nu = \gamma$ , and  $\beta(\delta - 1) = \gamma$ .

The values of the critical indices depend on the proximity to the critical point. In the approach to the critical point, the indices have their “classical” mean-field values, obtained by assuming the analyticity of thermodynamic functions at the critical points which allows the expansion of these functions in a power series in the deviation from the critical parameters. However, the singularity in the critical points makes the series expansion inapplicable very close to the critical point, leading to “non-classical” values of the critical indices (non-integer powers, logarithmic dependence, etc.). Since the difference between the results of mean-field theory and the exact theory is due to fluctuations of the order parameter, we expect that the mean-field approximation will be accurate when these fluctuations are small. Ginzburg proposed [13] that the mean field theory is applicable when the fluctuations are small compared to the thermodynamic values. The Ginzburg criterion divides the region near the critical point into two parts, giving the crossover from classical to non-classical behavior. An interesting idea has been proposed recently [14] of the existence of the second crossover in the immediate vicinity of the critical point, where the non-classical critical indices regain their classical values. Indeed, according to Eq. (1.5), the development of large-scale fluctuations is accompanied by a continuous increase of the sus-

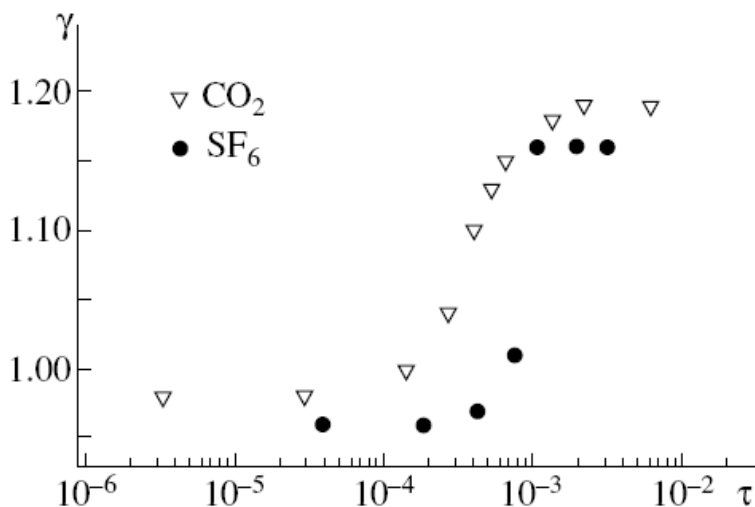


Fig. 1.1 Variation of critical exponent for the isothermal compressibility in the immediate vicinity of the critical point for CO<sub>2</sub> and SF<sub>6</sub>. The experimental points are taken from [16], [17]. Reproduced from Ref. [14] with permission, copyright (2002), Springer.

ceptibilities of the critical system, in particular, the susceptibility to varies external perturbations (gravitational and Coulomb fields, surface forces, shear stresses, turbulence, presence of boundaries). As a consequence, classical mean-field behavior must be restored. This transition occurs in the direction opposite to the Ginzburg criterion direction and defines the second crossover. Such behavior was found experimentally as early as 1974 [15] by taking  $p - V - T$  measurements of very pure SF<sub>6</sub> in the immediate vicinity ( $\tau = \frac{T - T_C}{T_C}$ ) of the critical point with  $2 \times 10^{-4}K$ ,  $\pm 0.01\%$ , and  $\pm 0.02\%$  accuracy, respectively in the temperature, dimensionless pressure and density.

As an example, we show [14] in Fig. 1.1 the crossover to the classical value of the critical index of the isothermal compressibility in the immediate vicinity of the critical point for CO<sub>2</sub> and SF<sub>6</sub>. The author of [14] states his belief that the analogous second crossover has been seen in other experiments under the influence of gravity, impurities, and shear flows. This problem certainly deserves further investigation.

## 1.2 Chemical reactions

The equilibrium numbers of particles of the different substances taking part in a chemical reaction are connected by the law of mass action. This law results from a relation between the chemical potentials  $\mu_i$  of the various components [3]. Thus, for the reaction  $\sum \nu_i A_i = 0$ , where  $A_i$  are the chemical symbols of the reagents and  $\nu_i$  are positive or negative integers, the equation for chemical equilibrium has the form  $\sum \nu_i \mu_i = 0$ . For the simplest case of the isomerization reaction, the reaction equation and the law of mass action have the form  $A_1 - A_2 = 0$  and  $\mu_1 = \mu_2$ , respectively.

Thus, binary mixtures undergoing a chemical reaction are characterized by their concentration, as in a non-reactive mixture. However, according to the law of mass action, this concentration is a function of other thermodynamic variables. Therefore, the number of thermodynamic degrees of freedom of a binary system undergoing a chemical reaction is the same as for a non-reactive, one-component system.

Chemical reactions influence all properties of many-component systems. As an example, we shall show that the existence of the chemical reaction may lead to the replacement of UCST by LCST and vice versa [18]. Moreover, the Clapeyron-Clausius equation for a binary mixture is determined by the chemical reaction, in addition to the latent heat and the volume difference between the two phases.

Consider a mole of a binary mixture which separates into two phases,  $B'$  and  $B''$ . The system can be described by four parameters,  $p, T, x'_2$ , and  $x''_2$ , which satisfy the following conditions:

$$\mu'_1(T, p, x'_2) = \mu''_1(T, p, x''_2); \quad \mu'_2(T, p, x'_2) = \mu''_2(T, p, x''_2). \quad (1.8)$$

One can differentiate the equilibrium conditions (1.8) along the equilibrium surface between  $B'$  and  $B''$ . Using simple thermodynamic relations, one obtains [3]

$$\begin{aligned} \Delta v_1 dp - \Delta h_1 dT/T + x'_2 g'_{2x} dx'_2 - x''_2 g''_{2x} dx''_2 &= 0, \\ \Delta v_2 dp - \Delta h_2 dT/T + (1 - x''_2) g''_{2x} dx''_2 - (1 - x'_2) g'_{2x} dx'_2 &= 0 \end{aligned} \quad (1.9)$$

where  $v_i$  and  $h_i$  are the partial molar volume and enthalpy,

$$\Delta v_i = v''_i - v'_i; \quad \Delta h_i = h''_i - h'_i; \quad g'_{2x} \equiv \left( \frac{\partial^2 g'}{\partial x_2'^2} \right)_{T,p}; \quad g''_{2x} \equiv \left( \frac{\partial^2 g''}{\partial x_2''^2} \right)_{T,p}. \quad (1.10)$$

The partial derivatives of the intensive variables are given by Eq. (1.9) at constant pressure (temperature) and at constant concentration [3]. However, there is no need to consider these special sections of the coexistence surface when we deal with a reactive system. Indeed, for a reaction  $\nu_1 A_1 \rightleftharpoons \nu_2 A_2$ , an additional restriction to (1.9) exists in the form of the law of mass action

$$\nu_1 \mu'_1 + \nu_2 \mu'_2 = 0. \quad (1.11)$$

Differentiating the latter equation along the equilibrium surface, yields

$$\begin{aligned} (\nu_1 v'_1 + \nu_2 v'_2) dp - (\nu_1 h'_1 + \nu_2 h'_2) dT/T \\ + [\nu_1 x'_2 g'_{2x} - \nu_2 (1 - x'_2) g'_{2x}] dx'_2 = 0. \end{aligned} \quad (1.12)$$

Combining Eqs. (1.9) and (1.12) yields the slope of the equilibrium line of a two-phase reactive binary mixture,

$$T \left( \frac{\partial p}{\partial T} \right)_{chem} = \frac{h'_{2x} (\Delta x_2)^2 - (2\Delta x_2/n') (\nu_1 v'_1 + \nu_2 v'_2)}{v'_{2x} (\Delta x_2)^2 - (2\Delta x_2/n') (\nu_1 h'_1 + \nu_2 h'_2)} \quad (1.13)$$

$$\left( \frac{\partial T}{\partial x_2} \right)_{chem} = \frac{2T g'_{2x} \Delta x_2 + T n' v'_2 (\Delta x_2)^2 (\nu_1 v'_1 + \nu_2 v'_2)^{-1} g'_{2x}}{h'_{2x} (\Delta x_2)^2 - v'_2 (\Delta x_2) (\nu_1 h'_1 + \nu_2 h'_2) (\nu_1 v'_1 + \nu_2 v'_2)^{-1}} \quad (1.14)$$

where  $n' \equiv \nu_1 x'_2 - \nu_2 (1 - x'_2)$  and  $h' \equiv (1 - x'_2) h'_1 + x'_2 h'_2$ ;  $v' \equiv (1 - x'_2) v'_1 + x'_2 v'_2$  are the heat of reaction and the volume change of reaction in phase  $B'$ .

In the absence of a chemical reaction, all terms vanish, except the first term in the denominators and numerators of Eqs. (1.13) and (1.14), and these terms reduce to the well-known form [3]

$$T \left( \frac{\partial p}{\partial T} \right)_{x'_2} = \frac{h'_{2x}}{v'_{2x}} \quad (1.15)$$

$$\left( \frac{\partial T}{\partial x'_2} \right)_p = \frac{2Tg'_{2x}\Delta x_2}{h'_{2x}(\Delta x_2)^2}. \quad (1.16)$$

Equation (1.13) is the generalized form of the Clapeyron-Clausius equation (1.15) for a reactive mixture, while Eq. (1.14) determines the criterion for UCST and LCST. The latter can be obtained in the same way as for a nonreactive mixture [3].

The “classical” expansion near the critical points  $g'_{2x} \approx \frac{1}{8}g'_{4x}(\Delta x_2)^2$ , yields

$$\left( \frac{\partial T}{\partial x'_2} \right)_p = \frac{Tg'_{4x}(x'_2 - x''_2)}{4h_{2x,cr}}. \quad (1.17)$$

If  $x''_2 > x_{2,cr} > x'_2$ , then  $(\partial x'_2/\partial T)_p$  is positive if  $h_{2x,cr} \equiv (\partial^2 h/\partial x^2)_{cr}$  is negative. These signs define UCST. Analogously, LCST corresponds to  $(\partial^2 h/\partial x^2)_{cr} > 0$ .

Performing a similar expansion near the single critical point of a reactive binary mixture, one obtains from (1.13) and (1.14),

$$T \left( \frac{\partial p}{\partial T} \right)_{chem} \sim \frac{v_1 h_{1,cr} + v_2 h_{2,cr}}{v_1 v_{1,cr} + v_2 v_{2,cr}} \quad (1.18)$$

$$\begin{aligned} \left( \frac{\partial T}{\partial x'_2} \right)_{chem} &\sim Tg'_{4x}(x'_2 - x''_2) \left( h_{2x,cr} - v_{2x,cr} \frac{v_1 h_{1,cr} + v_2 h_{2,cr}}{v_1 v_{1,cr} + v_2 v_{2,cr}} \right)^{-1} \\ &\sim Tg'_{4x}(x'_2 - x''_2) h_{2x,cr} \left( 1 - \frac{v_1 h_{1,cr} + v_2 h_{2,cr}}{T_c(v_1 v_{1,cr} + v_2 v_{2,cr})} dT_C/dp \right)^{-1}. \end{aligned} \quad (1.19)$$

Equation (1.15) was used in the last relation in (1.19). It follows from (1.19) that the existence of a chemical reaction may change the type of critical point (UCST to LCST and vice versa) if the last bracket in (1.19) is negative. The ratio of the second derivatives  $v_{2x,cr}/h_{2x,cr}$  can be replaced by the ratio of excess volume  $V_E$  and excess enthalpy  $h_E$  at the critical point.

Thus, a chemical reaction will change the nature of the critical point if the following (equivalent) inequalities are satisfied:

$$\frac{v_1 h_{1,cr} + v_2 h_{2,cr}}{v_1 v_{1,cr} + v_2 v_{2,cr}} \frac{V_E}{h_E} > 1 \text{ or } \frac{v_1 h_{1,cr} + v_2 h_{2,cr}}{v_1 v_{1,cr} + v_2 v_{2,cr}} \frac{1}{T_C} \frac{dT_C}{dp} > 1. \quad (1.20)$$

One can find [19], [20] the form of the critical line near the critical point  $dT_C/dp$  as well as  $V_E$  and  $h_E$ . Typical examples of positive  $V_E$  and  $h_E$  are shown in Fig. 1.2.

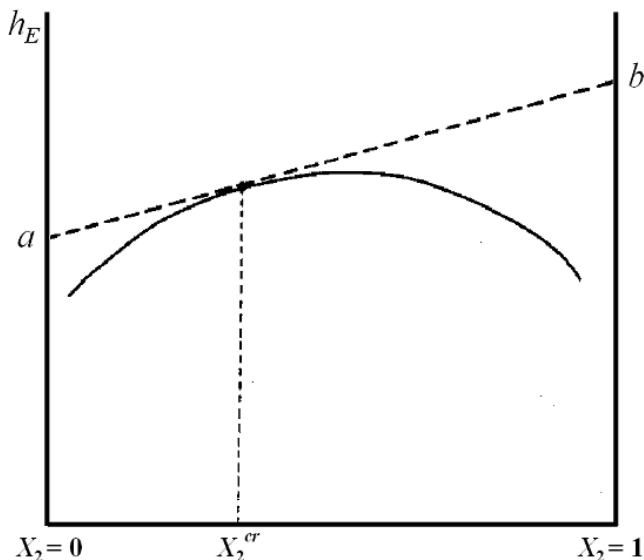


Fig. 1.2 Typical form of the excess enthalpy  $h_E$  (or excess volume  $V_E$ ) for a binary mixture as a function of concentration. Points  $a$  and  $b$  correspond to the critical molar enthalpy of pure substances. Reproduced from Ref. [18] with permission, copyright (1990), Springer.

Using the definition of the partial molar quantity  $y_1 = y - x_2 (\partial y / \partial x_2)_{T,p}$ , where  $y \equiv (h, v)$ , one can see that the points  $a, b$  in Fig. 1.2 give  $h_{1,cr}$  and  $h_{2,cr}$  (or, analogously,  $v_{1,cr}$  and  $v_{2,cr}$ ). For an isomerization reaction,  $\nu_1 = -\nu_2 = 1$ , and Eq. (1.20) becomes

$$\frac{h_{1,cr} - h_{2,cr}}{h_E} \frac{V_E}{v_{1,cr} - v_{2,cr}} > 1. \quad (1.21)$$

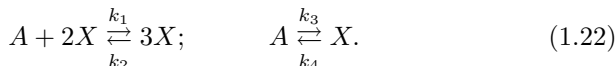
There is no physical reason why criterion (1.21) should not be satisfied for some mixtures. Then, the presence of a chemical reaction will change UCST to LCST and vice versa.

### 1.3 Analogy between critical phenomena and the instability of chemical reactions

Critical phenomena describe the behavior of closed thermodynamic systems whereas chemical reactions occur in the systems open to matter transport from the environment. The former are described by the well-known Gibbs technique, but there is no universal approach to non-equilibrium chemical reactions which are defined by the equation of the reaction rate. However, as already mentioned in the Introduction, there is a close analogy between these two phenomena (in fact, article [21] is entitled “Chemical instabilities as critical phenomena”).

One distinguishes between phase transitions of first and second orders. First-order transitions involve a discontinuity in the state of the system, and, as a result, a discontinuity in the thermodynamic variables such as entropy, volume, internal energy (first derivatives of the thermodynamic potential). In second-order phase transitions, these variables change continuously while their derivatives, which are the second derivatives of the thermodynamic potentials (specific heat, thermal expansion, compressibility), are discontinuous. Analogously, in the theory of instability of nonlinear differential equations, which describe the rate of chemical reactions, one distinguishes between hard and soft transitions. These are similar in nature to first-order and second-order phase transitions [22].

As an example, consider the following chemical reactions [23]



These rate equations describe the conversion of the initial reactant  $A$  into  $X$  by two parallel processes: a simple monomolecular degradation or an autocatalytic trimolecular reaction. Both these reactions are reversible with reaction constants  $k_i$ ,  $i = 1, \dots, 4$ . The system is open to interaction with an external reservoir of reactant  $A$ , so that the concentration of  $A$  remains constant. The macroscopic equation for the number of molecules  $X$  has the following form

$$\frac{dX}{dt} = -k_2 X^3 + k_1 A X^2 - k_4 X + k_3 A. \quad (1.23)$$

The solution of Eq. (1.23) with the initial condition  $X(0) = X_0$  is

$$\begin{aligned} & \left( \frac{X - X_1}{X_0 + X_1} \right)^{k_3 - k_2} \left( \frac{X - X_2}{X_0 - X_2} \right)^{k_1 - k_3} \left( \frac{X - X_3}{X_0 - X_3} \right)^{k_2 - k_1} \\ & = \exp[-k_2 (X_1 - X_2) (X_2 - X_3) (X_3 - X_1) t] \end{aligned} \quad (1.24)$$

where  $X_1$ ,  $X_2$  and  $X_3$  are the three roots of

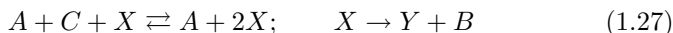
$$k_2X^3 - k_1AX^2 + k_4X - k_3A = 0 \quad (1.25)$$

with  $X_3 \geq X_2 \geq X_1$ . The steady state solutions  $X_s$  of Eq. (1.24) are

$$\begin{aligned} X_s &= X_1 \text{ for } X_0 < X_2; \\ X_s &= X_2 \text{ for } X_0 = X_2; \\ X_s &= X_3 \text{ for } X_0 > X_2. \end{aligned} \quad (1.26)$$

Stability analysis shows that the solution  $X_2$  is unstable with respect to small perturbations, whereas the solutions  $X_1$  and  $X_3$  are stable. Moreover, it follows from Eq. (1.26) that hysteresis may occur as  $X$  is varied [23]. The last two results are typical of equilibrium phenomena which are described near the liquid-gas critical point by the classical equation of state, say, the van der Waals equation of the form (1.25). This establishes the link between first-order phase transitions in equilibrium systems and so-called hard transitions in reactive systems.

As an example of different behavior, consider the chemical reaction



where the second reverse reaction is neglected. The rate equation for the number of molecules  $X$  has the following form

$$\frac{dX}{dt} = -AX^2 + (AC - 1)X \quad (1.28)$$

or, introducing  $\tau = At$  and  $\lambda = (AC - 1)/A$ ,

$$\frac{dX}{d\tau} = -X^2 + \lambda X. \quad (1.29)$$

The solution of this equation has the typical features of second-order phase transitions: the soft transition points  $X_s(\lambda)$  are continuous at the transition point  $\lambda = 0$ , but the derivatives are not.

The foregoing equations have to be generalized to include fluctuations from the steady state. No first-principle microscopic theory exists for fluctuations in reactive chemical systems. One usually uses a phenomenological master equation based on the macroscopic rate equations or a Langevin equation obtained by adding a stochastic term to the rate equations. The details can be found in [22]. Here we bring a fascinating example of the influence of noise on the chemical reaction [24], which is illustrated by the so-called ecological model. In this model, one considers two biological species with densities  $n_1(t)$  and  $n_2(t)$ , which decrease with rates  $a_1$  and

$a_2$  and compete with rates  $b_1$  and  $b_2$  for the same renewable food  $m$ . The birth-death equations for these species have the following form

$$\frac{dn_1}{dt} = (b_1 m - a_1) n_1; \quad \frac{dn_2}{dt} = (b_2 m - a_2) n_2. \quad (1.30)$$

The amount of food decreases both naturally (at a rate  $c$ ), and according to Eq. (1.30). Assume that the amount  $m$  of the food increases at rate  $q$ , i.e.,

$$\frac{dm}{dt} = q - cm - d_1 n_1 - d_2 n_2. \quad (1.31)$$

Assume now that the species  $n_1$  is strong and species  $n_2$  is weak, which occurs when the ratio  $a_1/b_1$  is smaller than both  $a_2/b_2$  and  $q/c$ . Under these conditions, the asymptotic  $t \rightarrow \infty$  solutions of Eqs. (1.30) and (1.31) are

$$m = \frac{a_1}{b_1}; \quad n_2 = 0; \quad n_1 = \frac{qb_1 - ca_1}{b_1 d_1} \quad (1.32)$$

which means that in the long run, the strong species survives and the weak species becomes extinct. The question arises regarding which changes can help the weak species to survive. One can easily see [24] that if one allows the food growth rate  $q$  to fluctuate in time (replacing  $q$  in Eq. (1.31) by  $q + f(t)$  with  $\langle f \rangle = 0$ ) or to allow the weak (but not the strong!) species to be mobile (adding the diffusive term  $D\nabla^2 n_2$  term in the second of Eqs. (1.30)), the weak species will finally become extinct. This result can be formulated as the “ecological theorem”: the long-term coexistence of two species relying on the same renewable resources is impossible. However, it has been shown [24] that if both these factors occur together with not-too-small food growth fluctuations, the corrected equations (1.30) and (1.31) have non-zero asymptotic solutions for both  $n_1$  and  $n_2$ . This result has an important ecological interpretation. In a fluctuating environment, high mobility gives an evolutionary advantage that makes possible the coexistence of weak and strong species. The individuals of the mobile weak species survive since they can utilize the food growth rate fluctuations more effectively.

The effect outlined above, which is called a “noise-induced phase transition” [25], also occurs in systems undergoing chemical reactions [24], as well as in many other phenomena.