

Preface

In this book we attempt to trace the connection between chemical reactions and the physical forces of interaction manifested in critical phenomena. The physical and chemical descriptions of matter are intimately related. In fact, the division of forces into “physical” and “chemical” is arbitrary. It is convenient [1] to distinguish between strong attractive (chemical) forces leading to the formation of chemical species, and weak attractive (physical) forces, called van der Waals forces. It should be remembered, therefore, when one considers the “ideal” ternary mixture A , B and A_mB_n , that the strong chemical bonding interaction between A and B atoms has already been taken into account via the formation of the chemical complex A_mB_n , and the term “ideal” only means that there are no “physical” forces present. The growth of clusters in a metastable state is an example of the fuzzy distinction between physical and chemical forces. In numerical simulations a rather arbitrary decision has to be made whether a given particle belongs to a “chemical” cluster.

The usefulness of a “chemical” approach to physical problems can be seen from the mean-field theory of the phase transition on an Ising lattice of non-stoichiometric AB alloys [2]. The temperature dependence of the long-range and short-range order parameters is found from the “law of mass action” for the appropriately chosen “chemical reaction.” The latter is the exchange of position of an atom A from one sublattice and an atom B from the second sublattice. The change of the interaction energy for such a transition when both atoms are or are not nearest neighbors determines the “constant of chemical reaction.” Such an approach allows one to avoid the calculation of entropy provided that one is interested only in the value of the critical temperature, rather than in the behavior of all thermodynamic quantities, which are determined by the same classical critical indices in

all versions of mean-field theory. The latter example is, in fact, a special case of chapter 15 in [3], where the typical “physical” process of diffusion is considered as a “chemical reaction” in which some amount of substance A passes from volume element a to b while a different amount of B passes from b to a .

The “chemical” method, in which a given atom with all its neighbors is considered as the basic group, gives better results than the Bragg-Williams or Bethe-Peierls method. In the Bragg-Williams method, each atom is exposed to the (self-consistent) average influence of all other atoms, whereas in the Bethe-Peierls method, a pair of adjacent atoms is considered as the basic group.

Even though the border between chemical and physical forces is arbitrary, one usually considers first the “physical” forces in the equation of state, and then the “chemical” forces in the law of mass action based on the non-ideal equation of state. I shall follow this approach.

One can also trace the common features of phase transitions and chemical reactions by analyzing the time evolution of the state variables ψ described by the equation

$$d\psi/dt = F[\psi, \lambda], \quad (0.1)$$

where λ is the set of internal and external parameters, and F is a nonlinear functional in ψ . In the case of a phase transition, Eq. (0.1) may be the Landau-Ginzburg equation for the order parameter, while in the case of a chemical reaction — the equation for the rate of reaction. The steady state of the system is described by $\psi^0(\lambda)$ which is the solution of equation $F[\psi^0, \lambda] = 0$. For nonlinear F , more than one steady state solution is possible, and for some values of λ , at the so-called transition point, bifurcation may occur, when a system goes from the original steady state to the new steady state. Such a transition might be of first or second order in the case of a phase transition, and, analogously, the hard or soft transition for a chemical reaction.

I have kept this book as simple as possible, so that it will be useful for a wide range of researchers, both physicists and chemists, as well as teachers and students. No preliminary knowledge is assumed, other than undergraduate courses in general physics and chemistry. In line with this approach, I have favored a phenomenological presentation, thus avoiding the details of both microscopic and numerical approaches. There are a tremendous number of published articles devoted to this subject, and it proved impossible to include many of them in this book of small size. I ask

the forgiveness of the authors whose publications were beyond the scope of this book.

The organization of the book is as follows.

After the Introduction, Chapter 1 contains a short review of phase transitions and chemical reactions and their interconnection, which is needed to understand the ensuing material. Chapter 2 is devoted to the specific changes in a chemical reaction occurring near the critical point. The effect of pressure and phase transformation on the equilibrium constant and rate of reaction is the subject of Secs. 2.1–2.2. The hallmark of critical phenomena — the slowing down of all processes — leads also to the slowing-down of the rates of chemical reactions. This phenomenon is described in Sec. 2.3, while the opposite peculiar phenomenon of speeding-up of a chemical reaction near the critical point provides the subject matter for Sec. 2.4. It is shown that all three types of behavior (slowing-down, speeding-up and unchanged) are possible depending on the given experiment. In Sec. 2.5, we consider another influence of criticality — the anomalies in chemical equilibria including supercritical extraction. The appropriate experiments are described in Sec. 2.6.

The reverse process — influence of chemistry on critical phenomena — forms the content of Chapter 3, including the change in the critical parameters (Sec. 3.1), critical indices (Sec. 3.2), transport coefficients (Sec. 3.5) and degree of dissociation (Sec. 3.3). Section 3.4 is devoted to the isotope exchange reaction in near-critical systems.

Chapter 4 deals with the problem of the phase separation in reactive systems. The occurrence of multiple solutions of the law of mass action is described in Sec. 4.1. The mechanism of phase separation depends on whether it starts from a metastable or a non-stable state. The former case, where phase separation takes place through nucleation, and the spinodal decomposition for the latter case are considered in Secs. 4.2 and 4.3, respectively. Section 4.4 is devoted to the special case of a dissociation reaction in a ternary mixture.

Chapter 5 contains a description of chemical reactions near some specific regions of the phase diagram. An account of the supercritical fluids is given in Sec. 5.1, while the vicinities of the azeotrope, melting and double critical points are considered in Secs. 5.2, 5.3 and 5.4, respectively. The main experimental methods of analysis of near-critical fluids — sound propagation and light scattering — are considered in Chapter 6. Finally, in Chapter 7 we present our conclusions.