The second principle accounts for the stability of systems, but its most natural statement in terms of entropy increases for isolated systems is too general to be practically useful. This leads to the definition of thermodynamic potentials, such as the Gibbs free energy, whose variations dictate the feasibility of transformations under given specific conditions. These potentials will form the main theme dealt with in this chapter. In preamble, the role of changes in chemical composition, due either to chemical reactions within the system or to exchange of matter with the surroundings, will be considered in order to arrive at the most general framework for the evolution criteria that will be presented. Finally, we will discuss the various ways the state of a system can be stable, paying particular attention to the notion of metastability.

2.1 INTERNAL ENERGY OF AN OPEN SYSTEM

2.1a INTERNAL ENERGY AND COMPOSITION

Consider a system made up of one mole of methane and two moles of oxygen. With a small spark or an adequate catalyst, let us start the combustion of methane according to the familiar reaction

\[ \text{CH}_4 + 2 \text{O}_2 \rightleftharpoons \text{CO}_2 + 2 \text{H}_2\text{O}. \quad (2.1) \]

What is the variation of the internal energy of the system if the combustion of methane is complete?
In fact, this question cannot be given any answer as long as the nature of the system has not been specified. For an isolated system, there is no exchange of matter or energy with the surroundings so that the internal energy remains constant. The chemical energy liberated by the combustion is transformed into heat but, since the volume is constant, the resulting temperature rise is associated with a pressure increase. Thermal and mechanical energies thus increase at the expense of chemical energy while the internal energy does not change.

If the combustion takes place in a closed system, the internal energy variation is the sum of the work and heat exchanged with the surroundings. This was the case considered in the first chapter, where it was not necessary to make the composition dependence of the internal energy explicit because we were not interested in the purely chemical effects of transformations. To address these effects now, we must consider not only the changes in internal energy due to chemical reactions, but also those resulting from exchange of matter with the surroundings. Let us imagine that a fraction of the gases produced through the combustion of methane is removed from the system. Thus, to establish the energy balance of the transformation, we also need to know the way in which the internal energy of an open system depends on chemical composition. This will be the first point treated in this chapter.

2.1b COMPONENTS OF A SYSTEM

Various kinds of variables can be used to describe the chemical composition of a system (see 4.1a). Here we will use the \( n_i \) numbers of moles of the \( N \) components. By component, we mean any chemical entity contributing to the constitution of the phases of a system. A mixture of methane and oxygen can be expressed in terms of the number of moles of methane and oxygen, but also as a function of the number of moles of elemental carbon, hydrogen and oxygen. The only constraint exerted concerns the number of independent components, namely, the smallest number of components required to describe the composition of the system. With elements, for instance, there are only two independent components, C and O, or H and O, because the \( \text{CH}_4 \) formula dictates that the abundances of carbon and hydrogen satisfy a 1:4 ratio.

Likewise, one usually considers the single component \( \text{H}_2\text{O} \) for water. It would be possible to chose instead H and O atoms, or \( \text{H}^+ \) and \( \text{OH}^- \) ions. To yield the \( \text{H}_2\text{O} \) stoichiometry, however, the abundances of the H and O components must be in a 2:1 ratio and those of \( \text{H}^+ \) and \( \text{OH}^- \) ions in a 1:1 ratio. In both cases the abundance of one component automatically determines that of the other. If we wanted to use a variety of subatomic entities as components, the same kind of constraints would reduce the number of independent components of water to one each time. Hence, for reasons of simplicity one usually considers water to be formed of the single component \( \text{H}_2\text{O} \).

2.1c CHEMICAL POTENTIALS

In the first chapter we have reviewed the internal energy variations due to the exchange of entropy (and heat), and of volume (and work). To examine the influence of chemical composition, let us modify the state of a system by changing the abundance of only one of its components. As long as the variation \( dn_i \) of the number of moles of this