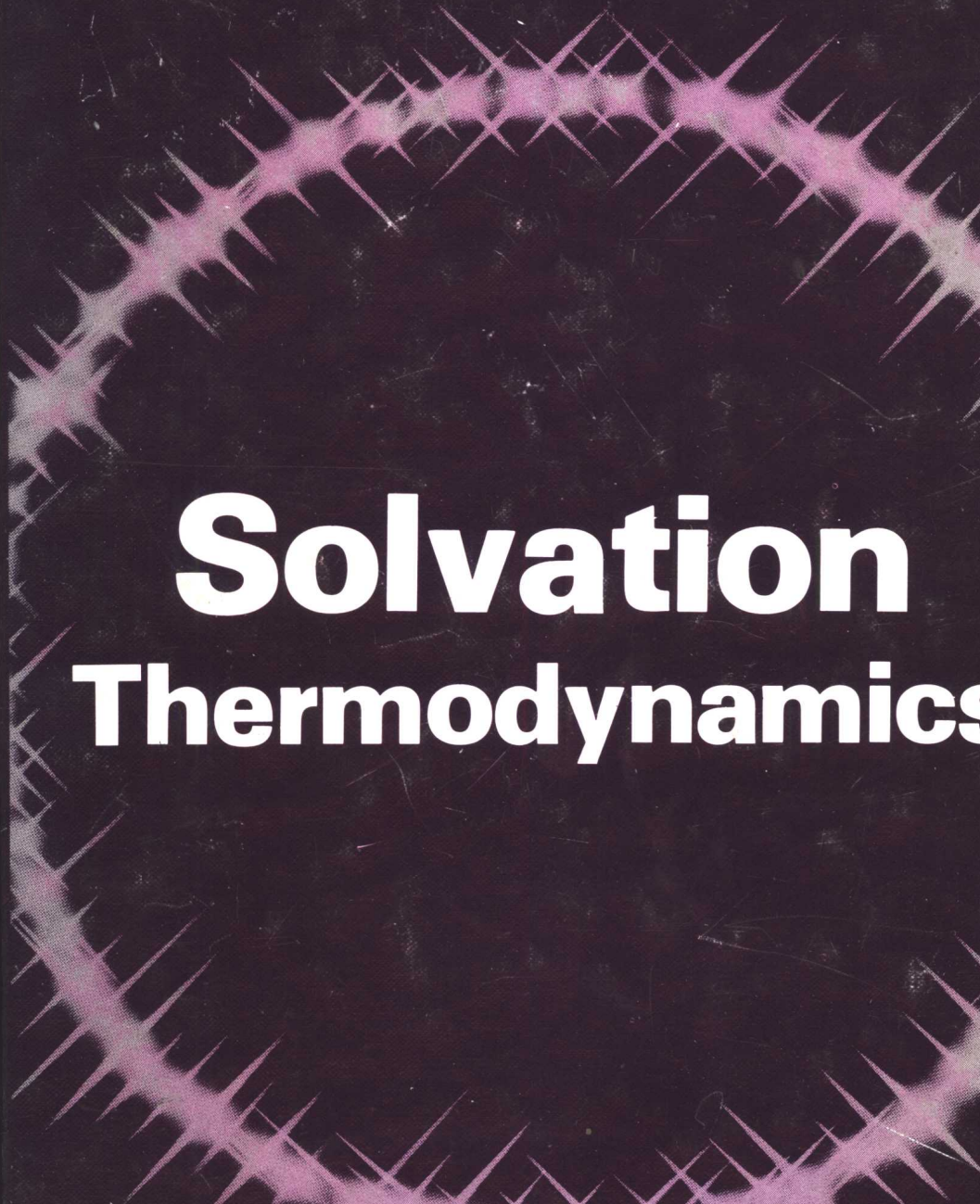

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Solvation Thermodynamics

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Preface

This book deals with a subject that has been studied since the beginning of physical chemistry. Despite the thousands of articles and scores of books devoted to solvation thermodynamics, I feel that some fundamental and well-established concepts underlying the traditional approach to this subject are not satisfactory and need revision.

The main reason for this need is that solvation thermodynamics has traditionally been treated in the context of classical (macroscopic) thermodynamics alone. However, solvation is inherently a molecular process, dependent upon local rather than macroscopic properties of the system. Therefore, the starting point should be based on statistical mechanical methods.

For many years it has been believed that certain thermodynamic quantities, such as the standard free energy (or enthalpy or entropy) of solution, may be used as measures of the corresponding functions of solvation of a given solute in a given solvent. I first challenged this notion in a paper published in 1978 based on analysis at the molecular level.

During the past ten years, I have introduced several new quantities which, in my opinion, should replace the conventional measures of solvation thermodynamics. To avoid confusing the new quantities with those referred to conventionally in the literature as standard quantities of solvation, I called these "nonconventional," "generalized," and "local" standard quantities and attempted to point out the *advantages* of these new quantities over the conventional ones.

It was just very recently that I not only became aware that the newly proposed quantities have *advantages* over the conventional ones and could be applied in a uniform manner to a wider range of systems, but also became convinced that these proposed quantities are actually the ones that deserve to be referred to as *bona fide* measures of solvation thermodynamics. This conviction has compelled me to risk claiming the term *solvation thermodynamics* for the newly proposed quantities.

I realize that the usage of these terms with their newly assigned meanings will initially cause some confusion, since the reader's notions of solvation thermodynamics have been inevitably biased by exposure to the previously assigned meanings. However, I hope that this book will convince the reader willing to discard prejudices that the quantities used in this book are in fact the best ones for studying solvation thermodynamics. As in biology, I believe that in the long run the concept that is the fittest will survive.

By using the term *solvation* in the present approach, we do make a minor semantic sacrifice. The very term *solvation* implies the traditional distinction between a *solute* and a *solvent*. The former is being *solvated* by the latter. In the present approach we shall apply the term *solvation* in a more general sense. Instead of speaking about "a solute being solvated by a solvent," we shall be talking about "a molecule being solvated by a medium," i.e., we shall abandon the traditional distinction between a solute and a solvent. I believe, however, that the cost of this minor sacrifice is more than compensated by the enormous increase in generality afforded by the present treatment. For example, the present treatment permits us an exact description of the thermodynamics of solvation not only in the limit of infinite dilution of solute, but over the entire physically realizable range of concentrations. Thus we shall be speaking of the solvation of, say, argon in water as well as the solvation of argon in any mixture of argon and krypton, including the case of the solvation of argon in pure argon. We shall also find that, once we have properly defined the solvation process, we may describe the thermodynamics of solvation without reference to *any* standard states. This is a considerable improvement relative to the present situation in the field.

The book is organized in four parts. The first presents the subject matter in an elementary, sometimes phenomenological manner. The reader who is interested in getting a general idea of the method and scope of applications could satisfy himself by reading this part only. However, for a deeper understanding of the ideas employed, it is necessary to consult various sections in Chapter 3. The latter chapter contains a more detailed treatment of subjects discussed, and referred to, in Chapters 1 and 2.

Chapter 2 includes various applications to specific systems, ranging from hard spheres to protein solutions. The selection of systems was done without any pretense at being exhaustive or up to date. In fact, while writing this work it became clear to me that there is an almost unlimited number of systems that could fit into the framework of this book. Obviously, some arbitrary decisions had to be made in including some systems while rejecting others.

The last chapter on mixing and assimilation was added because it has direct bearings on the correct interpretation of various components of the chemical potential. I believe that some of the fundamental misconceptions regarding the free energy and entropy of mixing that are so ubiquitous in the literature have led to various misinterpretations in the traditional approach to solvation thermodynamics. Reading this chapter, though not essential to understanding the rest of the book, could be quite useful for the comprehension of the various ingredients that contribute to the chemical potential.

The book is addressed primarily to experimentalists in the field of solution chemistry. Although most of the results derived in this book were obtained from thermodynamic quantities, this is not true for *all* the systems, as will be clear from Sections 1.6, 2.17, and 3.12 dealing with ionic solutions. The reason is that the fundamental relationships between solvation thermodynamics and experimental quantities have their origin in statistical mechanics, not in thermodynamics. In a sense, the whole approach as presented in this book may be viewed as being a hybrid between a pure thermodynamic approach and a statistical mechanical approach. We rely from the very outset on statistical mechanics, yet it is not a pure statistical mechanical approach in the sense that we do not attempt to compute solvation quantities using first-principle techniques of statistical mechanics.

The book was conceived in Jerusalem, Israel. The first draft was written in La Plata, Argentina, the second draft was written in Manila, Philippines, and the final draft and typing were completed in Bethesda, Maryland. I would like to express my indebtedness to my colleagues and hosts, Dr. Raul Grigera in La Plata and Dr. Claro Llaguno in Manila, who provided the favorable atmosphere in which to write the book while visiting their countries.

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Jerusalem, Israel

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Chapter 1

Elementary Background

1.1. THE FUNDAMENTAL EXPRESSION FOR THE CHEMICAL POTENTIAL

In thermodynamics the chemical potential (CP) of a component s in a system may be defined in various ways. The most common and useful definitions are

$$\mu_s = \left(\frac{\partial G}{\partial N_s} \right)_{P,T,N'} = \left(\frac{\partial A}{\partial N_s} \right)_{T,V,N'} \quad (1.1)$$

where G is the Gibbs energy of the system, A is the Helmholtz energy, N_s is the number of s molecules in the system, T is the absolute temperature, P is the pressure, V is the volume, and N designates the set of numbers N_1, \dots, N_c , where N_i is the number of molecules of the i th species in the system. The set N' is the same as N but excludes the number N_s for the species s .

In thermodynamics the CP is usually defined *per mole* rather than *per molecule*. However, since our fundamental expression for the CP will be derived from statistical mechanics, it will be more convenient to define the CP, as well as other partial molecular quantities, per molecule rather than per mole. The conversion between the two quantities involves the Avogadro number $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$. However, when presenting values of the thermodynamic quantities of solvation in Chapter 2, they will all be *per mole* of the corresponding component. The first derivative on the right-hand side (rhs) of equation (1.1) is taken at constant temperature and pressure. These variables are the most easily controllable in actual experimental work. Hence, this definition of the CP is the more useful from the practical point of view. However, from the theoretical point of view it is somewhat easier to work with the second

derivative on the rhs of equation (1.1). Here the temperature and volume are kept constant. The corresponding thermodynamic potential A is conveniently related to the canonical partition function of the system (see Section 3.1).

It is well known that thermodynamics alone does not provide the functional dependence of the CP on the temperature, pressure, or composition of the system. In principle, this is obtainable from statistical mechanics. Moreover, statistical mechanics is presumed to furnish an explicit dependence of μ_s on all the relevant molecular parameters pertinent to all the molecules present in the system.

In some very special cases a partial dependence of the CP on pressure or composition is handled within the framework of thermodynamics. For instance, if the system is an ideal gas then the CP of component s may be written as

$$\mu_s = \mu_s^{\circ g} + kT \ln P_s \quad (1.2)$$

where P_s is the partial pressure of the component s in atmospheric units, k is the Boltzmann constant, and $\mu_s^{\circ g}$ is a constant independent of the partial pressure P_s .

A second case is a very dilute solution of a nonionic solute s in a solvent. In this case, Henry's law is observed and the CP of s may be expressed in the form

$$\mu_s = \mu_s^{\circ l} + kT \ln x_s \quad (1.3)$$

where x_s is the mole fraction of s and $\mu_s^{\circ l}$ is referred to as the standard CP, a quantity independent of x_s .

Clearly, both equations (1.2) and (1.3), though useful, are valid for very restrictive cases (ideal gases and solutions). Most real systems studied in the laboratory are neither ideal gases nor ideal solutions.

Throughout this book we shall use a very general expression for the CP that is not accessible from thermodynamics. It is based on some simple statistical mechanical considerations. Here we shall present only a qualitative description of the various factors involved in this expression. A more detailed derivation is deferred to Section 3.1.

For simplicity, we consider a two-component system at some temperature T and pressure P with N_A and N_B the number of molecules of components A and B, respectively. The extensive character of the Gibbs energy enables the mathematical derivative in equation (1.1) to be replaced by a difference, namely

$$\mu_A = G(T, P, N_A + 1, N_B) - G(T, P, N_A, N_B) \quad (1.4)$$

i.e., the CP of component A is the change in the Gibbs energy caused by the addition of *one* A molecule to the system while keeping T , P , and N_B unchanged. This statement is valid for a macroscopic system, where the addition of *one* molecule may be viewed as an infinitesimal change in the variable N_A .

For the purpose of interpreting the various contributions to the CP, it is useful to introduce an auxiliary quantity which we shall refer to as the pseudochemical potential (PCP). This quantity is defined similarly to equation (1.4) but with the additional restriction that the center of mass of the newly added molecule be placed at a *fixed* position, say \mathbf{R}_0 , within the system. We thus define the PCP of component A as

$$\mu_A^* = G(T, P, N_A + 1, N_B; \mathbf{R}_0) - G(T, P, N_A, N_B) \quad (1.5)$$

Clearly, the difference between the definitions of μ_A and μ_A^* is only in the constraint imposed on the location of the center of mass of the newly added molecule.

We note that since our system is presumed to be macroscopic and homogeneous (no external fields), all the points in the system should be equivalent (except for a small region near the surface of the system that may be neglected for macroscopically large systems). Therefore, we use the notation μ_A^* rather than the more explicit one $\mu_A^*(\mathbf{R}_0)$ to stress the fact that μ_s^* is independent of the particular choice of \mathbf{R}_0 . The asterisk is sufficient to indicate that we are dealing with a PCP and that we are constrained to a fixed point; the exact location of the selected point \mathbf{R}_0 is of no relevance to any of the following considerations.

Classical statistical mechanics provides us with a very useful relation between the CP, μ_s of a molecule s , and the corresponding PCP, μ_s^* of the same molecule in the same system. This relation is

$$\mu_s = \mu_s^* + kT \ln \rho_s \Lambda_s^3 \quad (1.6)$$

A full derivation of this relation is given in Section 3.1. In equation (1.6), ρ_s is the number density of the component s , $\rho_s = N_s/V$, and Λ_s^3 is referred to as the momentum partition function. The product $\rho_s \Lambda_s^3$ is a dimensionless quantity. The applicability of classical statistical mechanics for our systems is based on the assumption that $\rho_s \Lambda_s^3 \ll 1$. Indeed, for most systems of interest in solution chemistry, this condition is fulfilled.[†]

[†] Liquid water might be an exception. At present it is not clear to what extent the translational degrees of freedom of a water molecule are separable and can be treated classically.

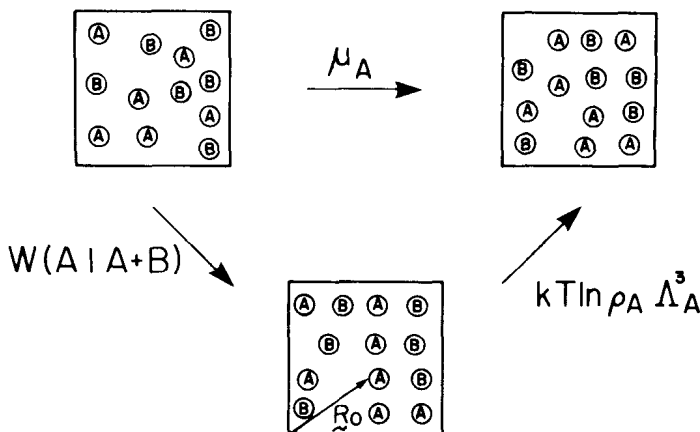


Figure 1.1. A schematic description of the process of adding one simple spherical molecule A to a mixture of A and B. First, the center of mass of the particle is placed at a fixed position in the system, and then the particle is released to wander in the entire volume. The corresponding contributions to the chemical potential of A are indicated next to each arrow.

Equation (1.6) for the chemical potential may be interpreted as follows. The chemical potential is a measure of the change in the Gibbs energy caused by the addition of one s particle to the system (at constant P , T , and composition). The split of μ_s into two parts corresponds to a splitting of the process of adding the particle s in two steps. First, we place the molecule at a *fixed* position, say \mathbf{R}_0 , and the corresponding change in the Gibbs energy is μ_s^* . Next, we release the constraint imposed on the fixed position; this results in an additional change in the Gibbs energy, $kT \ln \rho_s \Lambda_s^3$. Since we are dealing with classical systems,[†] $\rho_s \Lambda_s^3 \ll 1$, the quantity $kT \ln \rho_s \Lambda_s^3$ is always negative. This quantity has been referred to as liberation Gibbs energy.^{(1)‡} The two steps are described schematically in Figure 1.1 for a two-component system of A and B.

[†] More precisely, we should refer to systems for which the classical limit of statistical mechanics is applicable.

[‡] This term could also be referred to as the “translational Gibbs energy.” However, there are cases where there exists no proper translation, yet an analogue of the liberation Gibbs energy term in the chemical potential does appear. Examples are discussed in Sections 3.16 and 3.17. In these cases the term $kT \ln \rho_s \Lambda_s^3$ is replaced by a term $kT \ln N/M$, where M is the total number of available sites. The latter term may be referred to as liberation Gibbs energy, but not translational Gibbs energy, since no proper translation exists in these systems. In this sense the term “liberation” has more general applicability, and the “translational Gibbs energy” is only a particular example of the “liberation Gibbs energy.”

Although we did not offer a proof of relation (1.6) (see, however, Section 3.1), it is helpful to obtain a qualitative idea of the significance of the various factors that contribute to the liberation term $kT \ln \rho_s \Lambda_s^3$. When we release the particle that was constrained to a fixed position, it acquires translational kinetic energy; the corresponding contribution to the Gibbs energy of the releasing process is $kT \ln \Lambda_s^3$. Furthermore, once released, the particle may wander throughout the entire volume V of the system, giving rise to the term $-kT \ln V$. Finally, the particle that is at a fixed position is distinguishable from all other s particles in the system. Once it is released, it is assimilated[†] by all the N_s particles and therefore loses its distinguishability. This, together with the previous contributions, gives rise to the term $kT \ln \rho_s \Lambda_s^3$.

The most important property of equation (1.6), which constitutes the cornerstone of the entire content of this book, is its generality. It is valid for any kind of molecule (argon, benzene, or a protein), in any fluid mixture (i.e., in a multicomponent system), and for any concentration of s (from very dilute systems up to pure liquids). The only assumption that has been introduced to render equation (1.6) valid is the applicability of classical statistical mechanics. As noted above, we shall deal in this book only with systems that obey classical statistical mechanics.

In equation (1.6) we have defined ρ_s as N_s/V in the canonical ensemble, i.e., when N_s and V are fixed variables. However, this equation and the significance of the two terms as interpreted above hold true for any other ensemble. For instance, in the T, P, N ensemble, we should read $\rho_s = N/\langle V \rangle$, where $\langle V \rangle$ is the average volume of the system. In the T, V, μ ensemble we should read $\rho_s = \langle N_s \rangle/V$, where $\langle N_s \rangle$ is the corresponding average number of s particles in the system (for more details, see Section 3.1).

In some special cases we may rewrite equation (1.6) in a somewhat more detailed form. The simplest case is an ideal gas. If the internal partition function (i.e., rotational, vibrational, electronic, and nuclear) is denoted by q_s , then equation (1.6) reduces to

$$\begin{aligned} \mu_s &= -kT \ln q_s + kT \ln \rho_s \Lambda_s^3 \\ &= (-kT \ln kT q_s / \Lambda_s^3) + kT \ln P_s \\ &= \mu_s^{\text{og}} + kT \ln P_s \end{aligned} \quad (1.7)$$

where in the last expression on the rhs of equation (1.7) we have also written the CP of s in the conventional thermodynamic form.

[†] The term assimilation will be discussed in more detail in Chapter 4. It is used here only to stress the fact that the term $kT \ln \rho_s \Lambda_s^3$ is *not* a mixing term, as is so often referred to in the literature.

Clearly, when there are no interactions among the particles the PCP is simply

$$\mu_s^* = -kT \ln q_s \quad (1.8)$$

The liberation term is the same as in equation (1.6).

In a condensed phase the internal degrees of freedom may or may not be affected by the interaction of s with its surrounding molecules. First, we consider a simple structureless particle, say a hard sphere or argon. In this case we assume that $q_s = 1$ and hence equation (1.6) reduces to

$$\mu_s = W(s | l) + kT \ln \rho_s A_s^3 \quad (1.9)$$

In equation (1.9) we use the notation $W(s | l)$ to designate the average Gibbs energy of interaction of s with its entire surroundings. This is also referred to as the coupling work of s to the system. A more explicit expression for $W(s | l)$ is derived in Section 3.1.

The more general case is when s does have internal degrees of freedom. If these are unaffected by the interactions, we may simply add the term $-kT \ln q_s$ to equation (1.9). However, it is expected that in most cases the internal degrees of freedom will be affected by the interactions. A simple example where an internal rotational degree of freedom is affected is discussed in Section 3.2. In the most general case we shall use relation (1.6), in which μ_s^* includes both the coupling work (actually an average coupling work) and whatever effect the surroundings have on the internal partition function of s . We shall never need to spell out the details of μ_s^* ; however, one should keep in mind the various factors that might contribute to its value in a condensed phase.

1.2. DEFINITION OF THE SOLVATION PROCESS AND THE CORRESPONDING SOLVATION THERMODYNAMICS

The term "solvation" or its more specific predecessor "hydration" has been used in physical chemistry probably since the creation of this branch of science. In the *Encyclopaedia Britannica* we find the following description of this term: "When a solvent and a solute molecule link together with weak bonds, the process is called solvation."⁽²⁾ In another, now classical monograph by Gurney, we find: "The interaction that takes place when an ion is introduced into a solvent is called the solvation of the ion."⁽³⁾

It is evident from the above quotations that "solvation" is a term

that is associated with the *interaction* between a *solute* and a *solvent*. This quite general description leaves, however, a great deal of freedom when we attempt to translate the term "solvation" into a more precise definition. What exactly is the "process of interaction?" What are the phenomena that are manifested by the solvation process? Which molecules shall we consider as "solute" and which as "solvent?" What do we mean by entropy, enthalpy, volume, etc., of solvation?

No wonder the term "solvation" has been used in a multitude of meanings. At present there seems to be no universal agreement on the very definition of the solvation process. Instead, it has been commonly assumed that some standard thermodynamic process, e.g., the transfer of argon from the gaseous phase at 1 atm pressure to a solution at some specified concentration, could serve as a definition of the solvation process and hence provide the grounds for defining all the corresponding thermodynamic quantities. A close examination of this approach⁽¹⁾ reveals that the various "standard processes" indeed *include* the "solvation process," and the pertinent standard thermodynamic quantities *include* the thermodynamic quantities of solvation. However, we shall see in Section 1.4 that the traditional standard thermodynamic quantities are, in principle, inadequate measures of the solvation phenomenon.

We now define the solvation *process* of a molecule *s* in a fluid *l* as the process of transferring the molecule *s* from a *fixed* position in an ideal gas phase *g* into a fixed position in the fluid or liquid phase *l*. The process is carried out at constant temperature *T* and pressure *P*. Also, the composition of the system is unchanged.

When such a process is carried out, we shall say that the *molecule s* is being solvated by the liquid phase *l*. If *s* is a simple spherical molecule, it is sufficient to require that the center of the molecule be fixed. On the other hand, if *s* is a more complex molecule, such as *n*-alkane or a protein, we require that the center of mass of the molecule be at a fixed position. We note, also, that in complex molecules the geometrical location of the center of mass might change upon changing the conformation of the molecule. In such cases we need to distinguish between the process of solvation of the molecule at a particular conformation and an average solvation process over all possible conformations of the molecule. A detailed example is worked out in Section 3.2.

One could also define the solvation process as above, but at constant volume rather than constant pressure. The definition given above is the one which may be related more directly to experimental quantities. However, for some theoretical considerations it might be more convenient to treat the constant-volume solvation process. The relation between the two is discussed in Section 3.1.

In defining a particular solvation process of a molecule *s*, we must

specify the temperature, the pressure, and the composition of the liquid phase. There is no restriction whatsoever on the concentration of s in the system. This may be very dilute s in l , in which case the term *solute* in its conventional sense might apply for s . It may be a concentrated solution of s in l , or even a pure liquid s . Clearly, in the latter cases the conventional sense of the term *solute* becomes inappropriate. However, what remains unchanged is the conceptual meaning of the term *solvation* as a measure of the interaction between s and its entire surroundings l . This point will be clarified further when we introduce the various thermodynamic quantities of solvation below. As we shall see in Section 1.4, in the limit of very dilute solutions some of the thermodynamic quantities of *solvation*, as defined above, coincide with the conventional quantities of solvation. This is not the case, however, for higher concentrations of s in l . While conventional thermodynamics cannot be applied to these systems, the new definition, along with the pertinent thermodynamic quantities, can be applied without any restrictions on the concentration of s . In this sense the new definition generalizes the concept of *solvation* beyond its traditional limits. In fact this generalization extends the applicability of the concept of solvation from one concentration to an infinite range of concentrations.

It will be useful to introduce at this point the concept of a *solvaton*. The solvaton s is that particular molecule s the solvation of which is studied. This term is introduced to stress the distinction between the molecule serving as our “test particle” and other molecules of the same species that might be in the surroundings of the solvaton. In Section 3.18 we shall also require that solvatons do not interact with each other, but that they do interact with the rest of the system in exactly the same manner as a regular molecule of the same species.

Once we have defined the *process of solvation*, we may proceed to introduce the corresponding thermodynamic quantities. We shall henceforth talk about *solvation entropy*, *solvation energy*, *solvation volume*, and so on, meaning the change in the corresponding thermodynamic quantity associated with the solvation process as defined above.

First, and of foremost importance, is the Gibbs energy of solvation of s in l . This is defined as

$$\Delta G_s^* = \mu_s^{*l} - \mu_s^{*ig} \quad (1.10)$$

where μ_s^{*l} and μ_s^{*ig} are the PCP of s in the liquid and in an ideal-gas (ig) phase, respectively. From the definition of the PCP given in the previous section, it is clear that ΔG_s^* is the Gibbs energy change for transferring s from a *fixed* position in an ideal-gas phase into a *fixed* position in the liquid phase l .