

14.10: Chemical Activity

In [Section 5.17](#), we use mathematical models for the rates of chemical reactions to find the equilibrium constant equation, which specifies the equilibrium position of a reacting system. The variables in the reaction-rate models are the concentrations of reactants and products. Consequently, these concentrations are also the variables in the equilibrium constant equation. We develop our reaction-rate models from simple arguments about the dependence of collision frequencies on reagent concentrations. These arguments ignore the possibility that the effects of intermolecular forces on collision frequencies can change as the composition of the system changes. For a great many purposes, the concentration-based models describe experimental results with sufficient accuracy. However, as we note in our introductory discussion in [Section 1.6](#), the concentration-based equilibrium constant equation proves to be only approximately constant: To obtain rigorously accurate results, we must introduce new quantities, having the character of “corrected concentrations”, that we call activities.

We are now in a position to define the **chemical activity** of a substance more precisely. We introduce the activity concept in the particular context of chemical equilibria, but its scope is broader. The activity of a component is a wholly new thermodynamic quantity. We view it as the property that determines the chemical potential, μ , of a substance in a particular system at a given temperature. As such, the activity directly links the properties of the substance to the behavior of the system. Introducing the activity makes our equations for μ and $d\mu$ more compact. It also provides an avenue to relate qualitative ideas about the properties of the substance—ideas that we may not be able to express in mathematical models—to the effects that the substance has on the properties of the system.

The heuristic idea that an activity is a corrected concentration arises in the first instance because we use the pressure-dependence of the Gibbs free energy of an ideal gas as the model for our definition of activity. In [Section 15.7](#), we find that the equilibrium constant for a chemical reaction can be specified using the activities of the reactants and products and that the form of the equilibrium constant is the same for activities as it is for concentrations. In [Chapter 16](#) we see that assuming ideal behavior for solutions enables us to equate the activity and the mole fraction of a component in such solutions.

Our consideration of the chemical reactions of gases in [Chapter 13](#) introduces the basic ideas that we use: The Gibbs free energy of reaction is the same thing as the change in the chemical potential of the system; a reaction reaches equilibrium when the Gibbs free energy of the system cannot decrease further; the Gibbs free energy of reaction is a function of the chemical potentials of the reactants and products; and the chemical potential of a gas is a function of its partial pressure. In ideal gas mixtures, the chemical potential of a component depends on the partial pressure of that component, but not on the partial pressures of other species that may be present. The model we develop for ideal gases becomes unsatisfactory for real gases under the kinds of conditions that cause the experimentally observed properties of gases to depart from ideal gas behavior—conditions in which intermolecular forces cannot be neglected.

In [Section 14.9](#), we observe that the chemical potential of substance A can be expressed as a function of temperature, pressure, and its molar composition:

$$\mu_A(P, T, n_1, n_2, \dots, n_A, \dots, n_\omega)$$

The total differential becomes

$$d\mu_A = -\bar{S}_A dT + \bar{V}_A dP + \sum_{j=1}^{\omega} \left(\frac{\partial \mu_A}{\partial n_j} \right)_{PT} dn_j$$

We can write this as

$$d\mu_A = -\bar{S}_A dT + \bar{V}_A dP + (d\mu_A)_{PT}$$

where

$$(d\mu_A)_{PT} = \sum_{j=1}^{\omega} \left(\frac{\partial \mu_A}{\partial n_j} \right)_{PT} dn_j$$

In general, the change in the chemical potential of A depends on partial derivatives with respect to the amount of every substance present. The dependence on the amount of substance j is given by

$$\left(\frac{\partial \mu_A}{\partial n_j}\right)_{P,T,n_{m \neq j}}$$

and the dependence on the amount of A is given by

$$\left(\frac{\partial \mu_A}{\partial n_A}\right)_{P,T,n_{m \neq A}}$$

In a multi-component system whose components do not interact, $(\partial \mu_A / \partial n_A)_{P,T,n_{m \neq A}}$ is not zero, but all of the other partial derivatives $(\partial \mu_A / \partial n_j)_{P,T,n_{m \neq j}}$ must, by definition, vanish. This is exemplified in an ideal-gas system, in which the chemical potential of component A is given by

$$\mu_A(P_A) = \Delta_f G^\circ(A, P^\circ) + RT \ln(P_A / P^\circ)$$

and the partial pressure of A depends only on the mole fraction of A in the system, $P_A = x_A P_{\text{system}}$. For an ideal gas at constant temperature, changes in the chemical potential do not depend on the amounts of other substances that may be present:

$$(d\mu_A)_T = RT(d \ln P_A)_T$$

In the special case that the system pressure is constant, this becomes:

$$(d\mu_A)_T = RT(d \ln x_A)_T$$

foreshadowing our eventual recognition that mole fraction is the most natural concentration unit for theoretical modeling of the chemical potential.

In real systems, the chemical potential of a component depends on its own concentration, but it also depends—more weakly—on the concentrations of the other species present. To treat real systems adequately, we need a general method to express the chemical potential of a component as a function of the component's concentration, in a way that fully accounts for the effects of the other species. Our grand strategy is to develop the activity of a component as an abstract, dimensionless quantity. We do this by choosing a simple function to define the activity of a component in terms of its chemical potential. This makes it possible to express the thermodynamic properties of any system as relatively simple functions of the activities of its components. To apply these results to specific systems, we must then find empirical equations that express the component activities as functions of component concentrations. So, from one perspective, the activity is merely a convenient intermediary in our overall effort to express the chemical potential as a function of composition.

To begin expressing this strategy in mathematical notation, let us represent the activity and concentration of a component, A , as \tilde{a}_A and c_A , respectively. For simplicity, we consider systems in which pressure–volume work is the only work. The chemical potential is a function of pressure, temperature, and composition; that is $\mu_A = \mu_A(P, T, c_A, c_B, c_C, \dots)$. We suppose that we have a large volume of such data available; that is, we have measured μ_A at many conditions represented by widely varying values of the variables $P, T, c_A, c_B, c_C, \dots$. Our strategy is to find two empirical functions. The first empirical function expresses the chemical potential of A as a function of its activity and the temperature of the system, $\mu_A = \mu_A(T, \tilde{a}_A)$. The second expresses the activity of A as a function of the concentrations of the species present and of the pressure and temperature of the system, $\tilde{a}_A = \tilde{a}_A(P, T, c_A, c_B, c_C, \dots)$. The mathematical composition of these two functions expresses the chemical potential as a function of $P, T, c_A, c_B, c_C, \dots$; that is, the mathematical composition is the function $\mu_A = \mu_A(P, T, c_A, c_B, c_C, \dots)$.

If we focus only on finding a function, $\mu_A(P, T, c_A, c_B, c_C, \dots)$, that fits the data, we can let the dependence of chemical potential on activity be anything we please. All we have to do is fix up the activity function, $\tilde{a}_A = \tilde{a}_A(P, T, c_A, c_B, c_C, \dots)$, so that the mathematical composition of the two accurately reproduces the experimental data. This is just another way of saying that, if all we want is an empirical correlation of the form $\mu_A = \mu_A(P, T, c_A, c_B, c_C, \dots)$, we do not need to introduce the activity at all.

However, our goal is more exacting. We want to construct the activity function so that it behaves as much like a concentration as possible. In particular, we want the activity of a component to become equal to its concentration in cases where intermolecular interactions vanish—or become independent of the component's concentration for some other reason. To achieve these objectives, we must choose the form of the function $\mu_A = \mu_A(T, \tilde{a}_A)$ carefully. Here the behavior of ideal gases provides a valuable template. Our observation that the chemical potential is related to the partial pressure by the differential expression

$(d\mu_A)_T = RT(d\ln P_A)_T$ suggests that it might be possible to develop the activity function using a relationship of the same form. In fact, this strategy proves to be successful.

We relate the chemical potential of a component to its activity by the differential expression

$$(d\mu_A)_T = RT(d\ln \tilde{a}_A)_T$$

The activity becomes a single function that captures the dependence of $(d\mu_A)_T$ on the number of moles of each of the components of the system:

$$RT(d\ln \tilde{a}_A)_T = \sum_{j=1}^{\omega} \left(\frac{\partial \mu_A}{\partial n_j} \right)_{PT} dn_j$$

If we hold the temperature constant, we can integrate between some arbitrary base state (in which the activity and chemical potential are $\tilde{a}_A^\#$ and $\mu_A^\#$) and a second state (in which these quantities are \tilde{a}_A and μ_A). That is, at any given temperature, we can select a particular state that we define to be the base state of A for the purpose of creating an activity scale. We denote the activity in the base state as $\tilde{a}_A^\#$. We let the chemical potential of A be $\mu_A^\#$ when A is in its base state at this temperature. At a fixed temperature, $\mu_A^\#$ is fixed. However, even if we keep all the other variables the same, the properties of the base state change when the temperature changes. This means that the chemical potential in the base state is a function of temperature—and only of temperature.

At constant temperature, the relationship between chemical potential and activity in any other state becomes

$$\int_{\mu_A^\#}^{\mu_A} d\mu_A = RT \int_{\tilde{a}_A^\#}^{\tilde{a}_A} d\ln \tilde{a}_A$$

or

$$\mu_A = \mu_A^\# + RT \ln \left(\frac{\tilde{a}_A}{\tilde{a}_A^\#} \right)$$

where it is implicit in the last equation that the activity is a function of pressure, temperature, and the chemical composition of the system. The temperature and chemical potential are state functions, so this expression requires that the activity be a state function also.

It is convenient to let the activity be unity in the base state. When we do this, we give the base state another name; we call it the **activity standard state**. When we stipulate that the activity in the base state is unity, we use a superscript zero to designate the activity and chemical potential. That is, in the standard state, $\tilde{a}_A^\circ = 1$, and the value of the chemical potential of A is $\tilde{\mu}_A^\circ$ when A is in this state. (In many cases, it turns out to be convenient to choose a standard state that does not correspond to any physical condition that can actually be achieved. In such cases, the standard state is a hypothetical system, whose properties we establish by mathematical extrapolation of measurements made on a real system in non-standard states.) With this convention, the chemical potential and activity are related by the equation

$$\mu_A = \tilde{\mu}_A^\circ + RT \ln \tilde{a}_A$$

at the specified temperature. We adopt this equation as our formal definition of the **activity** of component A. The activity and the chemical potential depend on the same variables and contain equivalent information.

Note that we have done nothing to restrict the state we choose to designate as the activity standard state. This creates opportunity for confusion, because it allows us to choose an activity standard state for A in a particular system that is different from the standard state for pure A that we define for the tabulation of thermodynamic data for pure substances. This means that we choose to let the meaning of the words “standard state” be context dependent. The practical effect of this ambiguity is that, whenever we are dealing with a chemical activity, we must be careful to understand what state of the substance is being designated as the standard state—and thereby being assigned chemical potential $\tilde{\mu}_A^\circ$ and unit activity. Because the standard state is a fixed composition, $\tilde{\mu}_A^\circ$ is a function of temperature, but not of pressure or composition. At a given temperature, changes in the system pressure or the concentration of A affect the chemical potential, μ_A , only by their effect on the activity, \tilde{a}_A .

To complete our program, we define a function that we call the **activity coefficient**, $\gamma_A(P, T, c_A, c_B, c_C, \dots)$, of component A, in a system characterized by variables $P, T, c_A, c_B, c_C, \dots$, by the equation

$$\tilde{a}_A(P, T, c_A, c_B, c_C, \dots) = c_A \gamma_A(P, T, c_A, c_B, c_C, \dots)$$

This definition places only one constraint on the form of γ_A ; the function $\gamma_A(P, T, c_A, c_B, c_C, \dots)$ can be anything that adequately accounts for the experimental data, so long as $\gamma_A \rightarrow 1$ when the effects of intermolecular interactions are negligible.

Introducing the activity coefficient does not simplify the job of finding a suitable, empirical, activity function; it just imposes a condition on its form. In Chapters 15 and 16, we find that standard states are best described using mole fraction or molality as the concentration unit. (Note that mole fraction is dimensionless and molality is proportional to mole fraction for dilute solutes.)

In Section 16.6 we consider the use of molality when A is a solute in a solution whose other components are in fixed proportions to one another. At very low concentrations of A, the environment around every A molecule is essentially the same. The chemical potential of A is observed to be a linear function of $\ln m_A$, because a small increase in the concentration of A does not significantly change the intermolecular interactions experienced by A molecules. As the concentration of A increases further, intermolecular interactions among A molecules become increasingly important, and the chemical potential ceases to be a simple linear function of $\ln m_A$. The activity coefficient is no longer equal to one.

In the remainder of this chapter, we focus on some of the general properties of the activity function. In the next two chapters, we develop a few basic applications of these ideas. First, however, we digress to relate the ideas that we have just developed about activity to the ideas that we developed in Chapter 11 about fugacity.

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