

16.19: Finding Solute Activity Using the Hypothetical One-molal Standard State

In this chapter, we introduce several ways to measure the activities and chemical potentials of solutes. In Sections 16.1–16.6 we consider the determination of the activities and chemical potentials of solutes with measurable vapor pressures. To do so, we use the ideal behavior expressed by Raoult's Law and Henry's Law. In Section 16.15 we discuss the determination of solvent activity coefficients from measurements of the decrease in the freezing point of the solvent. In Section 16.7 we discuss the mathematical analysis by which we can obtain solute activity coefficients from measured solvent activity coefficients. Electrical potential measurements on electrochemical cells are an important source of thermodynamic data. In Chapter 17, we consider the use of electrochemical cells to measure the Gibbs free energy difference between two systems that contain the same substances but at different concentrations.

We define the activity of substance A in a particular system such that

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

In the activity standard state the chemical potential is $\tilde{\mu}_A^\circ$ and the activity is unity, $\tilde{a}_A = 1$. It is often convenient to choose the standard state of the solute to be the hypothetical one-molal solution, particularly for relatively dilute solutions. In the hypothetical one-molal standard state, the solute molality is unity and the environment of a solute molecule is the same as its environment at infinite dilution. The solute activity is a function of its molality, $\tilde{a}_A(\underline{m}_A)$. We let the molality of the actual solution of unit activity be \underline{m}_A° . That is, we let $\tilde{a}_A(\underline{m}_A^\circ) = 1$; consequently, we have $\mu_A(\underline{m}_A^\circ) = \tilde{\mu}_A^\circ$ even though the actual solution whose molality is \underline{m}_A° is not the standard state. To relate the solute activity and chemical potential in the actual solution to the solute molality, we must find the activity coefficient, γ_A , as a function of the solute molality,

$$\gamma_A = \gamma_A(\underline{m}_A)$$

Then

$$\tilde{a}_A(\underline{m}_A) = \underline{m}_A \gamma_A(\underline{m}_A)$$

and

$$\tilde{a}_A(\underline{m}_A^\circ) = \underline{m}_A^\circ \gamma_A(\underline{m}_A^\circ) = 1$$

To introduce some basic approaches to the determination of activity coefficients, let us assume for the moment that we can measure the actual chemical potential, μ_A , in a series of solutions where \underline{m}_A varies. We have

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

We know \underline{m}_A from the preparation of the system—or by analysis. If we also know $\tilde{\mu}_A^\circ$, we can calculate $\gamma_A(\underline{m}_A)$ from our experimental values of μ_A . If we don't know $\tilde{\mu}_A^\circ$, we need to find it before we can proceed. To find it, we recall that

$$\lim_{\underline{m}_A \rightarrow 0} RT \ln \gamma_A = 0$$

Then

$$\lim_{\underline{m}_A \rightarrow 0} (\mu_A - RT \ln \underline{m}_A) = \lim_{\underline{m}_A \rightarrow 0} (\tilde{\mu}_A^\circ + RT \ln \gamma_A) = \tilde{\mu}_A^\circ$$

and a plot of $(\mu_A - RT \ln \underline{m}_A)$ versus \underline{m}_A will intersect the line $\underline{m}_A = 0$ at $\tilde{\mu}_A^\circ$.

Now, in fact, we can measure only Gibbs free energy differences. In the best of circumstances what we can measure is the difference between the chemical potential of A at two different concentrations. If we choose a reference molality, $\underline{m}_A^{\text{ref}}$, the chemical potential difference $\Delta\mu_A(\underline{m}_A) = \mu_A(\underline{m}_A) - \mu_A(\underline{m}_A^{\text{ref}})$ is a measurable quantity. A series of such results can be displayed as a plot of $\Delta\mu_A(\underline{m}_A)$ versus \underline{m}_A —or any other function of \underline{m}_A that proves to suit our purposes. The reference molality, $\underline{m}_A^{\text{ref}}$, can be chosen for experimental convenience.

If our theoretical structure is valid, the results are represented by the equations

$$\Delta\mu_A(\underline{m}_A) = \mu_A(\underline{m}_A) - \mu_A(\underline{m}_A^{\text{ref}}) = RT \ln \frac{\tilde{a}_A(\underline{m}_A)}{\tilde{a}_A(\underline{m}_A^{\text{ref}})} = RT \ln \underline{m}_A + RT \ln \gamma_A(\underline{m}_A) - RT \ln \tilde{a}_A(\underline{m}_A^{\text{ref}})$$

When $\underline{m}_A = \underline{m}_A^o$, we have

$$\Delta\mu_A(\underline{m}_A^o) = \mu_A(\underline{m}_A^o) - \mu_A(\underline{m}_A^{\text{ref}}) = \tilde{\mu}_A^o - \mu_A(\underline{m}_A^{\text{ref}}) = RT \ln \frac{\tilde{a}_A(\underline{m}_A^o)}{\tilde{a}_A(\underline{m}_A^{\text{ref}})} = -RT \ln \tilde{a}_A(\underline{m}_A^{\text{ref}})$$

and

$$\Delta\mu_A(\underline{m}_A) - \Delta\mu_A(\underline{m}_A^o) = RT \ln \underline{m}_A + RT \ln \gamma_A(\underline{m}_A)$$

so that

$$RT \ln \gamma_A(\underline{m}_A) = -\Delta\mu_A(\underline{m}_A^o) + \Delta\mu_A(\underline{m}_A) - RT \ln \underline{m}_A$$

Since $\lim_{\underline{m}_A \rightarrow 0} \gamma_A(\underline{m}_A) = 1$, we have

$$0 = \lim_{\underline{m}_A \rightarrow 0} RT \ln \gamma_A(\underline{m}_A) = -\Delta\mu_A(\underline{m}_A^o) + \lim_{\underline{m}_A \rightarrow 0} [\Delta\mu_A(\underline{m}_A) - RT \ln \underline{m}_A]$$

Letting

$$\beta(\underline{m}_A) = \Delta\mu_A(\underline{m}_A) - RT \ln \underline{m}_A$$

and

$$\beta^o = \lim_{\underline{m}_A \rightarrow 0} [\Delta\mu_A(\underline{m}_A) - RT \ln \underline{m}_A]$$

we have

$$\Delta\mu_A(\underline{m}_A^o) = \beta^o$$

Then

$$RT \ln \gamma_A(\underline{m}_A) = -\Delta\mu_A(\underline{m}_A^o) + \Delta\mu_A(\underline{m}_A) - RT \ln \underline{m}_A = -\beta^o + \Delta\mu_A(\underline{m}_A) - RT \ln \underline{m}_A$$

so that we know both the activity coefficient, $\gamma_A = \gamma_A(\underline{m}_A)$, and the activity, $\tilde{a}_A(\underline{m}_A) = \underline{m}_A \gamma_A(\underline{m}_A)$, of A as a function of its molality. Consequently, we know the value of $\Delta\mu_A(\underline{m}_A) - \Delta\mu_A(\underline{m}_A^o)$ as a function of molality. Since this difference vanishes when $\underline{m}_A = \underline{m}_A^o$, we can find \underline{m}_A^0 from our experimental data. Finally, the activity equation becomes

$$RT \ln \tilde{a}_A(\underline{m}_A) = \Delta\mu_A(\underline{m}_A) - \beta^o$$

This procedure yields the activity of A as a function of the solute molality. We obtain this function from measurements of $\Delta\mu_A(\underline{m}_A) = \mu_A(\underline{m}_A) - \mu_A(\underline{m}_A^{\text{ref}})$. These measurements do not yield a value for $\mu_A(\underline{m}_A)$; what we obtain from our analysis is an alternative expression,

$$RT \ln \frac{\tilde{a}_A(\underline{m}_A)}{\tilde{a}_A(\underline{m}_A^{\text{ref}})}$$

for the chemical potential difference, $\mu_A(\underline{m}_A) - \mu_A(\underline{m}_A^{\text{ref}})$ between two states of the same substance. $\mu_A(\underline{m}_A)$ is the difference between the chemical potential of solute A at \underline{m}_A and the chemical potential of its constituent elements in their standard states at the same temperature. To find this difference is a separate experimental undertaking. If, however, we can find $\mu_A(\underline{m}_A^*)$ for some \underline{m}_A^* , our activity equation yields $\tilde{\mu}_A^o$ as

$$\tilde{\mu}_A^o = \mu_A(\underline{m}_A^*) - RT \ln \tilde{a}_A(\underline{m}_A^*)$$

This analysis of the $\Delta\mu_A(\underline{m}_A)$ data assumes that we can find $\beta^o = \lim_{\underline{m}_A \rightarrow 0} [\Delta\mu_A(\underline{m}_A) - RT \ln \underline{m}_A]$. To find an accurate value for β^o , it is important to collect data for $\Delta\mu_A(\underline{m}_A)$ at the lowest possible values for \underline{m}_A . Inevitably, however, the experimental error in $\Delta\mu_A(\underline{m}_A)$ increases as \underline{m}_A decreases. Our theory requires that $\beta(\underline{m}_A) = \beta^o + f(\underline{m}_A)$, where $\lim_{\underline{m}_A \rightarrow 0} f(\underline{m}_A) = 0$, so that the graph of $\beta(\underline{m}_A)$ versus $f(\underline{m}_A)$ has an intercept at β^o . Accurate extrapolation of the data to the intercept at $\underline{m}_A = 0$ is greatly facilitated if we can choose $f(\underline{m}_A)$ so that the graph is linear. In practice, the increased experimental error in $\beta(\underline{m}_A)$ at the lowest values of \underline{m}_A causes the uncertainty in the extrapolated value of β^o for a given choice of $f(\underline{m}_A)$ to be similar to the range of β^o values estimated using different functions. For some p in

the range $0.5 < p < 2$, letting $f(\underline{m}_A) = \underline{m}_A^P$ often provides a fit that is as satisfactorily linear as the experimental uncertainty can justify.

This procedure yields the activity of A as a function of the solute molality. We obtain this function from measurements of $\Delta\mu_A(\underline{m}_A) = \mu_A(\underline{m}_A) - \mu_A(\underline{m}_A^{\text{ref}})$. These measurements do not yield a value for $\mu_A(\underline{m}_A)$; what we obtain from our analysis is an alternative expression,

$$RT \ln \frac{\tilde{a}_A(\underline{m}_A)}{\tilde{a}_A(\underline{m}_A^{\text{ref}})}$$

for the chemical potential difference, $\mu_A(\underline{m}_A) - \mu_A(\underline{m}_A^{\text{ref}})$ between two states of the same substance. $\mu_A(\underline{m}_A)$ is the difference between the chemical potential of solute A at \underline{m}_A and the chemical potential of its constituent elements in their standard states at the same temperature. To find this difference is a separate experimental undertaking. If, however, we can find $\mu_A(\underline{m}_A^*)$ for some \underline{m}_A^* , our activity equation yields $\tilde{\mu}_A^o$ as

$$\tilde{\mu}_A^o = \mu_A(\underline{m}_A^*) - RT \ln \tilde{a}_A(\underline{m}_A^*)$$

Finally, let us contrast this analysis to the analysis of chemical equilibrium that we discuss briefly in [Chapter 15](#). In the present analysis, we use an extrapolation to infinite dilution to derive activity values from the difference between the chemical potentials of the same substance at different concentrations. In the chemical equilibrium analysis for $aA + bB \rightleftharpoons cC + dD$, we have

$$\Delta_r \mu = \Delta_r \tilde{\mu}^o + RT \ln \frac{\tilde{a}_C^c \tilde{a}_D^d}{\tilde{a}_A^a \tilde{a}_B^b} = \Delta_r \tilde{\mu}^o + RT \ln \frac{m_C^c m_D^d}{m_A^a m_B^b} + RT \ln \frac{\gamma_C^c \gamma_D^d}{\gamma_A^a \gamma_B^b}$$

When the system is at equilibrium, we have $\Delta_r \mu = 0$. Since $\lim_{m_i \rightarrow 0} \gamma_i = 1$, we have, in the limit that all of the concentrations go to zero in an equilibrium system,

$$0 = \lim_{m_i \rightarrow 0} RT \ln \frac{\gamma_C^c \gamma_D^d}{\gamma_A^a \gamma_B^b} = \Delta_r \tilde{\mu}^o + \lim_{m_i \rightarrow 0} RT \ln \frac{m_C^c m_D^d}{m_A^a m_B^b}$$

Letting

$$K_c = \frac{m_C^c m_D^d}{m_A^a m_B^b}$$

We have

$$\Delta_r \tilde{\mu}^o = -RT \lim_{m_i \rightarrow 0} K_c$$

Since $\Delta_r \mu = 0$ whenever the system is at equilibrium, measurement of K_c for any equilibrium state of the reaction yields the corresponding ratio of activity coefficients:

$$RT \ln \frac{\gamma_C^c \gamma_D^d}{\gamma_A^a \gamma_B^b} = -\Delta_r \tilde{\mu}^o - RT \ln K_c$$

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