CHAPTER NINE

SOLUTIONS OF NONELECTROLYTES

9-1 Introduction

We introduce, with this chapter, the physical chemistry of systems for which composition is a state variable. A solution is a mixture at the molecular level of two or more chemical species; it may be gaseous, liquid, or solid. If clusters of molecules are present, the situation becomes more complex. If the clusters are of the order of $100 \text{ Å}$ to a few thousand $\text{Å}$ or around $10^{-4}$ cm in size, the system is colloidal in nature. If they reach to $10^{-4}$ to $10^{-3}$ cm, we speak of the mixture as a suspension, an emulsion, or an aerosol. Beyond this, we simply have a mechanical mixture of two or more bulk phases.

There are no sharp natural boundaries in this sequence, but there are practical ones. Most physical chemists have concentrated on the extremes, that is, on molecular solutions or on systems having well-defined bulk phases which themselves may be solutions. On the other hand, much of the biological and physical world involves mixtures of the colloidal or intermediate type of dispersity. The physical chemistry of these last systems is difficult, and its introduction is reserved for Chapter 21. We confine ourselves here to the simpler case of molecular solutions.

A solution or mixture of gases presents little problem, at least at the level of complexity of this text. Unless very dense, gases are always fully miscible and, in the usual laboratory pressure range of around 1 atm, form essentially ideal solutions. Dalton's law of partial pressures [Eq. (1-18)] is well obeyed. We will consider the entropy and free energy of formation of gaseous mixtures in Section 9-4.

Solid solutions, that is, molecular dispersions of two or more species in a solid phase, are quite common. Alloys are one example; also, many ionic crystals are able to substitute one type of ion for another (of the same charge) almost randomly within their crystal lattices. Solid solutions are more difficult to study experimentally, however, and are less studied than liquid ones. Their behavior is also more subject to eccentricities. Most of our data are from, and most of our common experience is with, liquid solutions. For these reasons, the material that follows
refers mainly to liquid solutions. It should be remembered, however, that the formal thermodynamics is the same for both types of solutions.

It is now desirable to define the term composition more precisely. A phase may consist of a number of molecular species and yet still qualify thermodynamically as a pure substance. Liquid water, for example, contains not only a large assortment of transient clusters (see Section 8-CN-2), but also definite concentrations of hydrogen and hydroxide ions. These are all in equilibrium with each other, however, and their relative proportions are not subject to arbitrary change. Composition with respect to these species is not an independent variable; once we fix the temperature and pressure of a sample of water, we automatically also fix the various equilibrium constants and hence compositions. It is therefore not necessarily the number of species present that serves to characterize a solution. Nor is it necessarily the number of constituents. By constituents, we mean chemical species that we can physically measure out in making up a solution. The term formal composition denotes the composition calculated in terms of what is weighed out and mixed. We may, for example, prepare a mixture of hydrogen, nitrogen, and ammonia. In the presence of a catalyst, these would be in equilibrium, and it would be sufficient to specify the formal composition with respect to only two of the three species. In the absence of the catalyst, however, all three compositions are independently variable, and the formal composition with respect to all three would have to be specified.

We meet this type of complication by using the term component. The number of components of a solution (or of any mixture) is the least number of independently variable chemical species required to define the composition of the solution (and of all phases present, if there is more than one). Hydrogen plus nitrogen plus ammonia plus catalyst is a two-component system; without the catalyst, it becomes a three-component system. Ordinary water is a one-component system; water plus solute is a two-component system, and so forth.

As to compositions themselves, various measures are used. A common one for this chapter will be the mole fraction, denoted by $x_i$ for a liquid solution and, for clarity, by $y_i$ for a gaseous solution. Mole fractions are strictly additive. That is, the total number of moles of a solution is just the sum of the numbers of moles of each species, and the mole fraction composition of a solution formed when two others are mixed is strictly obtainable on this basis. Volume fractions $\phi_i$ are sometimes used, but the volume of a solution is not in general equal to the sum of the volumes of the constituents mixed, and care must be taken in the definition of the exact experimental basis for a volume fraction.

The term molality, $m$, denotes a kind of mole fraction which is well suited to aqueous solutions. It means the number of moles of the dilute or solute component per 1000 g of the major or solvent component. Finally, it is convenient both for the laboratory chemist and in certain theoretical treatments to use volume concentration. The term molarity, $M$, will be used here to denote moles per liter of solution (not of solvent alone), and $n$ to denote the rational concentration unit of molecules per cubic centimeter of solution.

Finally, we will deal with solutions mainly from the phenomenological or classical thermodynamic point of view. Much formal statistical thermodynamics has been developed for solutions, but the complications are such that this approach is not as yet a powerful one in actual application. The statistical thermodynamic point of view is therefore discussed only briefly, in the Commentary and Notes section.
9-2 The Vapor Pressure of Solutions. Raoult’s and Henry’s Laws

The vapor pressure and vapor composition in equilibrium with a solution of volatile substances constitute important and very useful information. The practical usefulness lies in the application to distillation processes, and the physical chemical importance, in the provision of a means of studying the thermodynamic properties of liquids and of testing models for the structure of liquids. One function of this section is therefore to introduce characteristic data and behavior as a preliminary to the thermodynamic treatments.

A. Vapor Pressure Diagrams

Vapor pressure data are customarily displayed in the form of vapor pressure–composition diagrams for some particular temperature, as illustrated schematically in Fig. 9-1. Here $P_{\text{tot}}$ is the total combined vapor pressure above varying compositions of a solution of liquids A and B. The liquids are, in this example, taken to be fairly similar, and the $P_{\text{tot}}$ curve, although not linear, decreases steadily from $P_A^\circ$, the vapor pressure of pure A, to $P_B^\circ$, that of pure B, as $x_B$ is varied from 0 to 1. The vapor is a mixture of gaseous A and B, and the variations of the partial pressures $P_A$ and $P_B$ are also shown. We assume that no other gases are present and that the vapors are ideal, so that

$$P_{\text{tot}} = P_A + P_B.$$  \hspace{1cm} (9-1)

If A and B are very similar, the limiting case being one of two substances differing only in isotopic content, then the vapor pressure diagram takes on an especially simple appearance. A good example is provided by the benzene–toluene system, shown in Fig. 9-2. The values of $P_{\text{tot}}$, $P_b$, and $P_t$ are now given by nearly
FIG. 9-2. The benzene–toluene system at 20°C: (a) vapor pressure–liquid composition diagram; (b) liquid and vapor composition diagram.

straight lines. Thus we have

\[ P_t = P_t^\circ x_t, \quad P_b = P_b^\circ (1 - x_t) = P_b^\circ x_b, \tag{9-2} \]

where \( x_t \) and \( x_b \) denote the mole fractions of toluene and of benzene, respectively, and the degree superscript indicates a pure phase. Then \( P_{\text{tot}} \) is simply

\[ P_{\text{tot}} = P_t + P_b = P_b^\circ + (P_t^\circ - P_b^\circ) x_t, \tag{9-3} \]

which is the equation of the straight line connecting \( P_b^\circ \) with \( P_t^\circ \). A solution with this behavior is called an ideal solution, and the general form corresponding to Eqs. (9-2) is called Raoult's law (1884):

\[ P_i = P_i^\circ x_i. \tag{9-4} \]

For simplicity, we will largely restrict the discussion to two-component systems, for which the Raoult’s law statements are

\[ P_1 = P_1^\circ x_1, \quad P_2 = P_2^\circ x_2, \tag{9-5} \]
with the corollary that

\[ P_{\text{tot}} = P_1^\circ + (P_2^\circ - P_1^\circ) x_2. \]  

(9-6)

As will be seen in the Commentary and Notes section, Raoult's law corresponds to a particularly simple picture of a solution—essentially one in which the components are distinguishable, but just barely, so that their physical properties are virtually identical. The situation is rather analogous to that of the ideal gas; the ideal gas law also corresponds to a particular, very simple picture. The ideal gas law is, moreover, the limiting law for all real gases, and, in this respect, is not hypothetical or approximate at all. The same is believed to be true for Raoult's law. Experimental evidence suggests that Raoult's law is the limiting law for all

**FIG. 9-3.** The acetone–chloroform system at 35°C, showing negative deviation from ideality; (a) vapor pressure–liquid composition diagram; (b) liquid and vapor composition diagram.
solutions, approached by each component as its mole fraction approaches unity. That is, as a limiting law statement, Eq. (9-4) reads

$$\lim_{x_i \to 1} P_i = P_i^0 x_i.$$  \hspace{1cm} (9-7)

Notice that the curves for $P_A$ and $P_B$ are drawn in Fig. 9-1 so that they approach the Raoult’s law line as $x_A$ and $x_B$ approach unity. The acetone–chloroform system shown in Fig. 9-3 provides a specific illustration. In this case, the partial pressure curves lie below the Raoult’s law lines, whereas in Fig. 9-1, they lie above the Raoult’s law lines. We speak of the first situation as one of negative deviation, and the second, as one of positive deviation (from ideality).

Raoult’s law as an ideal law is easy to understand theoretically. It is the expected behavior if there is complete uniformity of intermolecular forces, just as the ideal gas law is the expected behavior in the complete absence of intermolecular forces. Raoult’s law as a limiting law, Eq. (9-7), is a statement of experimental observation. While we assume that it is the limiting law for all systems, there is no rigorous theoretical proof. By contrast, the ideal gas law can be shown to be the expected limiting law for all real gases.

Acceptance of Raoult’s limiting law provides a basis for the understanding of a second limiting law, Henry’s law. Henry’s law states that the partial pressure of a component becomes proportional to its mole fraction in the limit of zero concentration:

$$\lim_{x_i \to 0} P_i = k_i x_i.$$  \hspace{1cm} (9-8)

This is illustrated in Fig. 9-4, in which the vapor pressure curves of Fig. 9-1 are shown approaching the limiting slopes $k_A$ and $k_B$; these slopes define straight lines whose intercepts are $k_A$ and $k_B$. Under the limiting Henry’s law condition each molecule of component A has become surrounded by B molecules. The environment is thus not one of pure A, but another environment determined by

FIG. 9-4. System showing positive deviation from ideality; illustration of Henry’s and Raoults laws.
the nature of the A–B interactions. We can regard $k_A$ as the hypothetical vapor pressure that pure A would exert if the molecules all had this different environment, and similarly, $k_B$ as the hypothetical vapor pressure that pure B would exert in an environment consisting of A molecules.

Like Raoult’s law, Henry’s law applies as a limiting law to systems of both positive and negative deviation from ideality. The partial pressure curves in Figs. 9-3 and 9-4 obey both limiting laws.

### B. Solubility of Gases

Henry's law is approximately valid for any solute in a dilute solution, and a particular application is to the solubility of gases in liquids. As an approximate law, Eq. (9-8) becomes

$$P_2 = k_2x_2,$$  \hspace{1cm} (9-9)

where species 2 in a two-component system will, by convention, be taken to refer to the solute. The solubilities of permanent, inert gases (such as N$_2$, O$_2$, CO, and CH$_4$) in water at 25°C give $k_2$ values of $\sim 10^5$ atm. Thus $k_2$ is $0.426 \times 10^5$ atm for O$_2$ in water; the solubility is then $x_{o_2} = 1/(0.426 \times 10^5) = 2.35 \times 10^{-5}$ at 1 atm. Since there are 55.5 moles of water per liter, this solubility corresponds to $1.30 \times 10^{-3} \ M$ per atm at 25°C. The partial pressure of oxygen in air is 0.2 atm, so the actual concentration, due to equilibration with air, is $(1.30 \times 10^{-3})(0.2) = 2.61 \times 10^{-4} \ M$. In this case, there will also be dissolved nitrogen present, corresponding to its $k_2$ value of $0.86 \times 10^5$ atm.

Some of the literature report Henry’s law constants for gases in terms of the volume of gas dissolved, measured at the temperature and pressure in question, per unit volume of solvent. The Henry’s law constant for oxygen becomes, on this basis, $(1.30 \times 10^{-3})(0.082)(298)/1.0$ or $0.032$ liter of O$_2$ per liter of water.

### C. Vapor Composition Diagrams

A vapor pressure diagram also contains the information to give the composition of the vapor in equilibrium with a given composition of solution. Thus, for the system of Fig. 9-1, we have

$$y_A = \frac{P_A}{P_{\text{tot}}} = \frac{P_A}{P_A + P_B}, \quad y_B = \frac{P_B}{P_{\text{tot}}} = \frac{P_B}{P_A + P_B},$$  \hspace{1cm} (9-10)

where $y_A$ and $y_B$ denote the mole fractions of A and B in the vapor, respectively. A conventional way of supplying this information is to plot the vapor composition corresponding to each value of $P_{\text{tot}}$, along with $P_{\text{tot}}$ versus liquid composition, as shown in Fig. 9-5. For example, for a liquid of composition $x_1$, $P_{\text{tot}}$ has the value $P_1$, and the solution is in equilibrium with vapor of composition $y_1$. The corresponding vapor composition plots are included in Figs. 9-2(b) and 9-3(b).

Vapor composition diagrams are in effect phase maps or phase diagrams. If the system is contained in a piston and cylinder arrangement thermostated to the given temperature, then from Fig. 9-5, liquid of composition $x_1$ cannot vaporize if the pressure is greater than $P_1$; the system will consist of liquid phase only. The same
FIG. 9-5. Use of vapor pressure and vapor composition diagrams—the lever principle.

will be true for any composition and pressure defining a point lying above the liquid line. The upper region of the diagram is one of liquid phase only. Similarly, a system of composition \( x_1 \) at a pressure less than \( P_3 \) will consist of vapor phase only. The lower region of the diagram must be one of vapor phase only. The liquid and vapor composition lines thus mark the boundaries of the liquid-only and vapor-only regions, respectively. Finally, a system whose overall composition and pressure locate a point between the two lines will consist of a mixture of phases.

A diagram such as that of Fig. 9-5 allows a complete tracing of the sequence of events as the pressure of a system is changed at constant temperature. Suppose, for example, that a system of composition \( \chi \) is initially under some high pressure. As the pressure is reduced vaporization will begin at \( P_1 \), producing vapor of composition \( y_1 \). With further decrease in pressure more and more vaporization must occur, and since the vapor is richer in A than is the liquid, the latter must move to the right in composition. When the pressure has reached \( P_2 \), liquid of composition \( x_2 \) is now in equilibrium with vapor of composition \( y_2 \). Finally, when the pressure has been reduced to \( P_3 \) all the liquid will be vaporized and further reduction in pressure will merely expand the mixed vapors.

Since the entire system is a closed one, the vapor and liquid phases are always of some uniform relative composition, and their relative amounts can be calculated by material balance. For example, if the system consists of \( n \) moles total, then at any point

\[
n = n_v + n_l,
\]

where \( n_l \) and \( n_v \) are the number of moles of liquid phase and of vapor phase, respectively. Thus for a system of overall composition \( x_1 \) and at pressure \( P_2 \) the material balance in B is

\[
n x_1 = n_v y_2 + n_l x_2 = n_v y_2 + (n - n_v) x_2. \]  

(9-12)
Equation (9-12) rearranges to give

\[
\frac{n_v}{n} = \frac{x_2 - x_1}{x_2 - y_2}.
\]  

Equation (9-13) can be given a very simple and useful graphical interpretation. The horizontal line connecting the points \( y_2 \) and \( x_2 \) is known as a "tie-line." In general, a tie-line connects the compositions of equilibrium phases. The difference \( x_2 - y_2 \) corresponds to the length of the tie-line at \( P_2 \) and the difference \( x_2 - x_1 \), the length of the right-hand section of the line. Alternatively, if the tie-line is regarded as a balance pivoted at the point \( x_1 \), then weights proportional to \( n_v \) and \( n_t \) will just balance if placed at the \( y_2 \) and \( x_2 \) ends, respectively. Equation (9-13) with its associated graphical interpretation is known as the "lever principle."

D. Maximum and Minimum Vapor Pressure Diagrams

The acetone–chloroform system of Fig. 9-3 shows a minimum in \( P_{\text{tot}} \). The physical interpretation is along the lines of Fig. 8-5, where for a pure liquid the energy of vaporization was attributed to \( n \phi / 2 \), where \( n \) is the number of nearest neighbors and \( \phi \) is the interaction energy. A negative deviation then suggests that \( \phi_{\text{AB}} \) is greater than \( \phi_{\text{AA}} \) or \( \phi_{\text{BB}} \), so that the ease of vaporization is reduced if \( A \) and \( B \) molecules mutually surround each other.

Such an increase in interaction energy between unlike molecules would, as an extreme, lead to the formation of an actual compound. In the case of Fig. 9-3 the appearance is more that of a tendency toward association. The fact that the deviation of \( P_{\text{tot}} \) from the ideal or Raoult’s law line is at a maximum at about 50% mole fraction suggests that the association is of the AB type (and not \( A_2B \) or \( AB_2 \), and so on).

The extreme case, in terms of this picture, would be one in which a very stable AB compound actually formed, as illustrated in Fig. 9-6. Systems in which the overall composition \( x_B \) is less than 0.5 consist of a solution of A and AB, those of

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**FIG. 9-6.** Formation of a stable compound AB, but with the solutions A + AB and B + AB ideal.
composition greater than 0.5 consist of a solution of B and AB. These two solutions are shown as ideal but need not be. Note that there is a discontinuity in the slope of the $P_{\text{tot}}$ line at $x_B = 0.5$. In the acetone–chloroform system, however, the $P_{\text{tot}}$ line is rounded at the minimum—an indication that no very stable AB complex forms. One may, in fact, estimate the dissociation constant of such a complex from the degree of curvature around this minimum.

Deviations from ideality may, of course, be positive. This is illustrated in Fig. 9-7 for the system benzene–ethanol. The physical argument is now reversed; we conclude that $\phi_{AB}$ is less than $\phi_{AA}$ or $\phi_{BB}$. The extreme of this situation is that in which the two liquids have limited solubility in each other. This means that two phases $\alpha$ and $\beta$ of different composition can coexist, and that therefore

$$P_{\alpha}^\alpha = P_{\alpha}^\beta = P_{\alpha}^{\beta\alpha}, \quad P_{\beta}^\alpha = P_{\beta}^\beta = P_{\beta}^{\alpha\beta}, \quad P = P_{\alpha} + P_{\beta},$$

(9-14)

where the superscript $\alpha$ or $\beta$ refers to a quantity for a single phase and the superscript $\alpha\beta$ stands for a quantity when both phases are present.

The limiting situation of complete immiscibility is shown in Fig. 9-8. The possible types of sequences are those for the systems $x_2$ and $x_3$. All systems now consist of two liquid phases initially, and when the pressure is reduced to $P_{AB}$ vapor phase of composition $y_{AB}$ forms and continues to do so until one liquid or the other is gone. The remaining liquid then continues to vaporize along the appropriate vapor composition line. The composition $y_{AB}$ is in this case given by

$$y_{AB} = \frac{P_B^\circ}{P_A^\circ + P_B^\circ} = \frac{P_B^\circ}{P_{AB}}.$$

(9-15)

E. A Model for Nonideal Solutions

A fairly simple treatment developed by M. Margules in 1895 is still a very useful one. The difference between $\phi_{AB}$ and $\phi_{AA}$ can be regarded as an energy term which
enters as a Boltzmann factor modifying $P_A$ over its ideal value. This energy difference should be approximately proportional to $x_B^2$ on the basis of arguments about the proportion of A–A and A–B interactions, and one writes

$$P_A = P_A^0 x_A \exp(\alpha x_B^2), \quad (9-16)$$

where $\alpha$ is a characteristic constant (and is temperature-dependent). Since the A–B interaction is a mutual one, a similar equation applies to $P_B$:

$$P_B = P_B^0 x_B \exp(\alpha x_A^2), \quad (9-17)$$

where $\alpha$ is the same constant as in Eq. (9-16). Notice the Eqs. (9-16) and (9-17) give Raoult’s law as a limiting law, and reduce to Raoult’s law for all compositions if $\alpha = 0$.

The model also provides a relationship between the Henry’s law constants $k_A$ and $k_B$ [Eq. (9-8)]. Thus from Eq. (9-16) we have

$$\frac{dP_A}{d\alpha} = P_A^0 [\exp(\alpha x_B^2)](1 - 2\alpha x_A x_B) \quad (9-18)$$

and in the limit when $x_A \to 0$,

$$k_A = P_A^0 \alpha. \quad (9-19)$$

The situation is symmetric, and so

$$k_B = P_B^0 \alpha. \quad (9-20)$$

Thus the two Henry’s law constants are predicted to be in the ratio of the $P^0$ values. This rule is obeyed reasonably well except for strongly associated liquids ($\alpha$ very negative).

In the case of positive deviation $\alpha$ is positive, and if sufficiently so, the curve calculated from Eq. (9-17) will show a maximum and a minimum, as illustrated in Fig. 9-9. The situation is reminiscent of that with respect to the van der Waals
equation and the conclusion is that the experimental vapor pressure curve must show an equivalent horizontal portion and that the system is one of partial miscibility. The “critical temperature” is such that \( \alpha = 2 \). For this value of \( \alpha \) the system just fails to show a miscibility gap.

9-3 The Thermodynamics of Multicomponent Systems

Some aspects of the more formal thermodynamics of solutions, gaseous, liquid, or solid, must now be taken up. An important result will be the introduction of a new quantity, the chemical potential, which plays much the same role for solutions as \( G \) does for pure substances. The criterion for phase equilibrium is then expanded to the case of phases that are solutions, and an important new relationship, the Gibbs–Duhem equation, is introduced. Further developments are given in the Special Topics section, including the thermodynamic treatment of the surface tension of solutions. The principal new concept to be understood is that of partial molal quantities. Thermodynamics has become more complicated, but unavoidably so.

A. The Chemical Potential

The various thermodynamic functions must now include the amount of each component as a variable. That is, we consider what is called an open system, or one which may gain or lose chemical species. Thus the total energy \( E \) is a function of \( S, v, \) and now \( n_i \), where \( n_i \) denotes the number of moles of the \( i \)th species, and

![FIG. 9-9. Plot of \( P_B \) according to the Margules equation (9-17). (The plot of \( P_A \) is similar, but increases from right to left, of course.)](image-url)
sans serif \((E, S, \text{ and so on})\) denotes extensive quantities not on a per mole basis. The total differential for \(E\) is

\[
dE = \left(\frac{\partial E}{\partial S}\right)_{v,t_1} \, dS + \left(\frac{\partial E}{\partial v}\right)_{S,t_1} \, dv + \left(\frac{\partial E}{\partial n_1}\right) \, dn_1 + \left(\frac{\partial E}{\partial n_2}\right) \, dn_2 + \ldots
\]

(9-21)

Comparison with Eq. (6-12), to which Eq. (9-21) should reduce if the \(dn_i\) are zero, gives

\[
dE = T \, dS - P \, dv + \sum_i \left(\frac{\partial E}{\partial n_i}\right)_{S,v,n_j \neq n_i} \, dn_i.
\]

(9-22)

Similarly, free energy is now a function of \(T, P, \text{ and also } n_i\), so we have

\[
dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_i} \, dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_i} \, dP + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T,P} \, dn_i
\]

(9-23)

Comparison with Eq. (6-43) identifies the first two coefficients, so that

\[
dG = -S \, dT + v \, dP + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T,P} \, dn_i.
\]

(9-24)

Alternatively, however, we have

\[
dG = dH - d(TS) = dE + P \, dv + v \, dP - T \, dS - S \, dT,
\]

(9-25)

so, in combination with Eq. (9-22), it must also be true that

\[
dG = -S \, dT + v \, dP + \sum_i \left(\frac{\partial E}{\partial n_i}\right)_{S,v} \, dn_i.
\]

(9-26)

Thus we have

\[
\mu_i = \left(\frac{\partial E}{\partial n_i}\right)_{S,v} = \left(\frac{\partial G}{\partial n_i}\right)_{T,P},
\]

(9-27)

where \(\mu_i\) is a new quantity called the chemical potential.

Equations (9-22) and (9-26) can now be written

\[
dE = T \, dS - P \, dv + \sum_i \mu_i \, dn_i,
\]

(9-28)

\[
dG = -S \, dT + v \, dP + \sum_i \mu_i \, dn_i.
\]

(9-29)

The second of these is perhaps the more useful since it identifies the chemical potential \(\mu_i\) as the free energy change of a system per mole of added component \(i\), with temperature, pressure, and the other mole quantities kept constant. The chemical potential is a coefficient (like heat capacity) and we are really talking about the change \(dG\) for a small increment \(dn_i\). The added amount of the \(i\)th

\[\dagger\] To simplify the appearance of equations, the reminder \(n_j \neq n_i\) will be taken for granted in derivatives such as \((\partial G/\partial n_i)_{S,v,n_j \neq n_i}\).
component should not be sufficient to change the composition of the system appreciably since \(\mu_i\) will depend on composition as well as on temperature and pressure.

### B. Partial Molal Quantities

The chemical potential is one of a family of partial molal quantities. If, in general, we have some extensive property \(\mathcal{P}\), then for a solution \(\mathcal{P}_i\) is the partial molal property for the \(i\)th component:

\[
\mathcal{P}_i = \left(\frac{\partial \mathcal{P}}{\partial n_i}\right)_{T,P}
\]  

(9-30)

Thus

\[
\bar{V}_i = \left(\frac{\partial v}{\partial n_i}\right)_{T,P}
\]

(9-31)

\[
\bar{H}_i = \left(\frac{\partial H}{\partial n_i}\right)_{T,P}
\]

(9-32)

and

\[
\bar{S}_i = \left(\frac{\partial S}{\partial n_i}\right)_{T,P}
\]

(9-33)

Further, the various thermodynamic coefficients that were derived for a single substance retain the same form for the \(i\)th component of a solution if the corresponding partial molal quantities are used. As useful examples, we have

\[
\left(\frac{\partial \mu_i}{\partial P}\right)_T = \frac{\partial}{\partial P} \left(\frac{\partial G}{\partial n_i}\right)_{P,T} = \frac{\partial}{\partial n_i} \left(\frac{\partial G}{\partial P}\right)_T = \left(\frac{\partial v}{\partial n_i}\right)_{P,T} = \bar{V}_i
\]

(9-34)

and, similarly,

\[
\left(\frac{\partial \mu_i}{\partial T}\right)_P = -\bar{S}_i
\]

(9-35)

Equation (9-34) may be applied to a mixture of ideal gases. By Eq. (9-31),

\[
\bar{V}_i = \left(\frac{\partial v}{\partial n_i}\right)_{T,P} = \frac{RT}{P} \left(\frac{\partial n_i}{\partial P}\right)_{T,P} = \frac{RT}{P}
\]

Then

\[
\left(\frac{\partial \mu_i}{\partial P}\right)_T = \bar{V}_i = \frac{RT}{P}
\]

and

\[
d\mu_i = RT \frac{dP}{P} = RT \frac{dP_i}{P_i} = RT d\ln P_i \quad \text{(ideal gas)}
\]

(9-36)

since \(P_i = x_i P\) and, under the conditions of the differentiation, \(dP_i = x_i dP\). We thus have

\[
\mu_i(g) = \mu_i^0(g) + RT \ln P_i \quad \text{(ideal gas)}
\]

(9-37)
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where $\mu_i^*(g)$ is the chemical potential of the gas in its standard state, ordinarily taken to be 1 atm. (The same equation applies for a nonideal gas with fugacity $f_i$ replacing $P_i$—see Section 6-ST-2.) Since $\mu_i^*(g)$ refers to pure component $i$, it could just as well have been written $G_i^*(g)$; it seems preferable, however, to keep the notation symmetric. [See Robinson (1964) for a discussion of the preceding derivation.]

C. Criterion for Phase Equilibrium

We are dealing with equilibrium systems, and hence with systems for which no spontaneous change in temperature or pressure occurs. Equation (9-29) then reduces to

$$dG = \sum_i \mu_i \, dn_i.$$  \hfill (9-38)

If the system consists of a single phase and is chemically isolated, that is, if no chemical species can enter or leave, then the criterion for equilibrium given by Eq. (6-42) applies, so we have

$$dG = 0, \quad \sum_i \mu_i \, dn_i = 0. \hfill (9-39)$$

Alternatively, the system might consist of two (or more) phases in equilibrium. For each phase there will be an equation of the form of Eq. (9-38):

$$dG^\alpha = \sum_i \mu_i^\alpha \, dn_i^\alpha, \quad dG^\beta = \sum_i \mu_i^\beta \, dn_i^\beta, \hfill (9-40)$$

and so forth, where

$$dG = dG^\alpha + dG^\beta + \cdots. \hfill (9-41)$$

If the entire set of phases is in equilibrium and constitutes a chemically closed system overall, then again $dG$ is zero, and we now have

$$0 = \sum_i \mu_i^\alpha \, dn_i^\alpha + \sum_i \mu_i^\beta \, dn_i^\beta + \cdots. \hfill (9-42)$$

Suppose that some process occurs in this equilibrium system of phases whereby $dn_i$ moles of the $i$th species is transferred from phase $\alpha$ to phase $\beta$; all other $dn$ quantities are zero. For this process it follows that

$$\mu_i^\alpha \, dn_i^\alpha + \mu_i^\beta \, dn_i^\beta = 0. \hfill (9-43)$$

Since $dn_i^\alpha = -dn_i^\beta$ (the total number of moles of the $i$th species remains the same in the overall system), we have

$$\mu_i^\alpha = \mu_i^\beta. \hfill (9-44)$$

The very important conclusion is that for phase equilibrium between solutions the chemical potential of each species must be the same in every phase in which it is present. Equation (9-44) is a more general statement of the equilibrium condition for a pure substance, $G^\alpha = G^\beta$. 
D. The Gibbs-Duhem Equation

A very useful relationship may be obtained from Eq. (9-28). Since our applications will be restricted to two-component systems, we will make the derivation on that basis. The differentials of Eq. (9-28) are all of the form

(intensive property) \times d(\text{extensive property}).

We can therefore imagine that we introduce additional amounts of components 1 and 2, keeping the temperature, pressure, and composition (and hence \( \mu_1 \) and \( \mu_2 \)) constant. The result amounts to an integration giving

\[
E = TS - Pv + \mu_1 \eta_1 + \mu_2 \eta_2. \tag{9-45}
\]

Since

\[
G = E + Pv - TS,
\]

we can write

\[
G = n_1 \mu_1 + n_2 \mu_2. \tag{9-46}
\]

Differentiation of Eq. (9-46) gives

\[
dG = n_1 d\mu_1 + \mu_1 dn_1 + n_2 d\mu_2 + \mu_2 dn_2 \tag{9-47}
\]

and comparison with Eq. (9-38) leads to the result

\[
n_1 d\mu_1 + n_2 d\mu_2 = 0. \tag{9-48}
\]

We divide by the total number of moles to obtain

\[
x_1 d\mu_1 + x_2 d\mu_2 = 0. \tag{9-49}
\]

Equations (9-48) and (9-49) are alternative forms of the \textit{Gibbs-Duhem equation}. Its great usefulness is in relating the chemical potential change of one component (for a constant-temperature, constant-pressure process) to that of the other. The next section provides some specific applications.

An alternative way of obtaining Eq. (9-48) is as follows. Equation (9-45) is of general validity and may be differentiated to give

\[
dE = T dS + S dT - P dv - v dP + \mu_1 dn_1 + n_1 d\mu_1 + \mu_2 dn_2 + n_2 d\mu_2. \tag{9-50}
\]

Comparison with Eq. (9-28) gives

\[
0 = S dT - v dP + n_1 d\mu_1 + n_2 d\mu_2. \tag{9-51}
\]

For a process at constant temperature and pressure, Eq. (9-51) reduces to Eq. (9-48). We will find this type of procedure useful in obtaining the Gibbs adsorption equation (see Special Topics section).

9-4 Ideal Gas Mixtures

The chemical potential of a component of an ideal gas mixture is given by Eq. (9-37),

\[
\mu_i(g) = \mu_i^0(g) + RT \ln P_i.
\]
We can apply this equation to calculate the free energy and entropy change for the isothermal process

\[ n_1(\text{gas 1 at } P) + n_2(\text{gas 2 at } P) = \text{mixture (at } P, \text{ with } P_1 = x_1P \text{ and } P_2 = x_2P). \]  

(9-52)

The process, physically, corresponds to the procedure shown in Fig. 9-10. For pure gases, \( G_1 = n_1[\mu_1^\circ(g) + RT \ln P] \) and \( G_2 = n_2[\mu_2^\circ(g) + RT \ln P] \). The free energy of the mixture is, by Eq. (9-46),

\[ G_{\text{mix}} = n_1[\mu_1^\circ(g) + RT \ln P_1] + n_2[\mu_2^\circ(g) + RT \ln P_2], \]

or, since \( P_1 = x_1P \) and \( P_2 = x_2P \), substitution gives

\[ G_{\text{mix}} = n_1[\mu_1^\circ(g) + RT \ln P + RT \ln x_1] + n_2[\mu_2^\circ(g) + RT \ln P + RT \ln x_2]. \]

The free energy change for process (9-52) is \( G_{\text{mix}} - G_1 - G_2 \) or

\[ \Delta G_M = n_1RT \ln x_1 + n_2RT \ln x_2 \]  

(ideal gas).

(9-53)

The free energy of mixing per mole of mixture is

\[ \Delta G_M = x_1RT \ln x_1 + x_2RT \ln x_2 \]  

(ideal gas).

(9-54)

Since \( \Delta S = -\left[\partial(\Delta G/\partial T)\right]_P \), the entropy of mixing per mole of solution is

\[ \Delta S_M = -(x_1R \ln x_1 + x_2R \ln x_2) \]  

(ideal gas).

(9-55)

Notice that the free energy of mixing is independent of \( P \) and that the entropy of mixing is independent of both \( P \) and \( T \). The latter could have been obtained on the basis of the probability arguments of Section 6-8A (see Commentary and Notes section).

**9-5 Ideal and Nonideal Solutions. Activities and Activity Coefficients**

We can apply the criterion for equilibrium to the case of a solution and its vapor. The treatment will be in terms of a liquid solution, but it is equally applicable to solid solutions. The vapor phase is assumed, as usual, to be ideal, and for simplicity we consider only a two-component solution. The requirement that the chemical potential of a component be the same in two phases that are in equi-
Equilibrium may be combined with Eq. (9-37) to give
\[ \mu_1(l) = \mu_1(g) = \mu_1^\circ(g) + RT \ln P_1. \]  
(9-56)

In the case of a pure liquid \( \mu_1(l) \) becomes \( \mu_1^\circ(l) \) [or just \( G_1^\circ(l) \)] and Eq. (9-56) reduces to
\[ \mu_1^\circ(l) = \mu_1^\circ(g) + RT \ln P_1^\circ. \]  
(9-57)

Alternatively, we may add and subtract \( RT \ln P_1^\circ \) on the right-hand side of Eq. (9-56) to obtain
\[ \mu_1(l) = [\mu_1^\circ(g) + RT \ln P_1^\circ] + RT \ln \frac{P_1}{P_1^\circ}, \]
or
\[ \mu_1(l) = \mu_1^\circ(l) + RT \ln \frac{P_1}{P_1^\circ}. \]  
(9-58)

We thus have two ways of expressing the chemical potential of component one. Equation (9-56) does so in terms of \( \mu_1^\circ(g) \) and \( P_1 \), while Eq. (9-58) does so in terms of \( \mu_1^\circ(l) \) and \( P_1/P_1^\circ \). In the first case the standard or reference state is the vapor at unit pressure, 1 atm, and in the second case it is the pure liquid. The equations are symmetric with respect to the components and so a parallel set of relationships applies for component 2:
\[ \mu_2(l) = \mu_2^\circ(g) + RT \ln P_2, \]  
(9-59)
\[ \mu_2(l) = \mu_2^\circ(l) + RT \ln \frac{P_2}{P_2^\circ}. \]  
(9-60)

A. Ideal Solutions

Equations (9-58) and (9-60) take on a very simple form if Raoult's law is obeyed, since then \( P_1/P_1^\circ = x_1 \) and \( P_2/P_2^\circ = x_2 \). Thus
\[ \mu_1(l) = \mu_1^\circ(l) + RT \ln x_1 \quad \text{(ideal solution),} \]  
(9-61)
\[ \mu_2(l) = \mu_2^\circ(l) + RT \ln x_2 \quad \text{(ideal solution).} \]  
(9-62)

We can use Eq. (9-46) to obtain the total free energy of the solution:
\[ G = n_1 \mu_1^\circ(l) + n_2 \mu_2^\circ(l) + n_1RT \ln x_1 + n_2RT \ln x_2 \quad \text{(ideal solutions).} \]  
(9-63)

If we now consider the process of preparing the solution by mixing the pure liquids,
\[ n_1 \text{(component 1)} + n_2 \text{(component 2)} = \text{solution}, \]  
(9-64)
the corresponding free energy change is
\[ \Delta G_M = n_1RT \ln x_1 + n_2RT \ln x_2 \quad \text{(ideal solution).} \]  
(9-65)

or, per mole of solution,
\[ \Delta G_M = x_1RT \ln x_1 + x_2RT \ln x_2 \quad \text{(ideal solution).} \]  
(9-66)
We can also obtain the entropy of mixing. From Eqs. (9-35) and (9-61),
\[-\tilde{S}_i(l) = -S_i^\circ(l) + R \ln x_i \quad \text{(ideal solution)},\]
and similarly for component 2. The total entropy of the solution is then
\[S = n_1 S_1^\circ(l) + n_2 S_2^\circ(l) - (n_1 R \ln x_1 + n_2 R \ln x_2),\]
and, for the mixing process, per mole of solution,
\[\Delta S_M = -(x_1 R \ln x_1 + x_2 R \ln x_2).\]
Note that Eqs. (9-66) and (9-69) are identical to Eqs. (9-54) and (9-55) for the mixing of ideal gases (see Commentary and Notes section).

Since \(\Delta G = \Delta H - T \Delta S\) for a constant-temperature process, it follows from Eqs. (9-66) and (9-69) that
\[\Delta H_M = 0.\]
The heat of mixing for an ideal solution (and for ideal gases) is zero.

**B. Nonideal Solutions**

Equations (9-58) and (9-60) could be used for nonideal solutions, but it would be inconvenient always to have to refer to vapor pressures. A more general form, preferably analogous to Eqs. (9-61) and (9-62) for ideal solutions, would be very advantageous. We obtain this form by introducing the effective or thermodynamic concentration, called the *activity*. Activity or effective mole fraction \(a_i\) is defined so as to retain the form of Raoult's law:
\[P_i = a_i P_i^\circ.\]
Equation (9-58) becomes
\[\mu_i(l) = \mu_i^\circ(l) + RT \ln a_i,\]
and similarly for component 2. Since Raoult's law is the limiting law for all solutions, as \(x_i \to 1\), \(a_i\) must approach \(x_i\). We may retain the Raoult's law form even more explicitly by using the term activity coefficient \(\gamma_i\), defined as the factor by which \(a_i\) deviates from \(x_i\):
\[a_i = \gamma_i x_i.\]

Since \(a_i \to x_i\), \(\gamma_i \to 1\) as \(x_i \to 1\). Equation (9-72) becomes
\[\mu_i(l) = \mu_i^\circ(l) + RT \ln x_i + RT \ln \gamma_i.\]

The equation for the free energy of mixing, corresponding to the process of Eq. (9-64), can be put in a form that allows \(\Delta G_M\) to be expressed as the sum of an ideal and a nonideal contribution. Equation (9-65) becomes
\[\Delta G_M = x_1 RT \ln a_1 + x_2 RT \ln a_2\]
or
\[\Delta G_M = x_1 RT \ln x_1 + x_2 RT \ln x_2 + x_1 RT \ln \gamma_1 + x_2 RT \ln \gamma_2.\]
Alternatively,
\[
\Delta G = \Delta G_{\text{M}} - \Delta G_{\text{M(ideal)}} = x_1 RT \ln \gamma_1 + x_2 RT \ln \gamma_2.
\] (9-76)

The difference \(\Delta G_{\text{M}} - \Delta G_{\text{M(ideal)}}\) is known as the excess free energy of mixing \(\Delta G_{\text{E}}\).

Similarly,
\[
\Delta S = \Delta S_{\text{M}} - \Delta S_{\text{M(ideal)}}.
\] (9-77)

The evaluation of \(\Delta S_{\text{E}}\) involves the change in activity coefficients with temperature or, alternatively, a measurement of \(\Delta H_{\text{M}}\) (see Special Topics section). Also,
\[
\Delta G_{\text{E}} = \Delta H_{\text{E}} - T \Delta S_{\text{E}},
\] (9-78)

since \(\Delta H_{\text{M(ideal)}}\) is zero.

Note that if the vapor pressure shows a positive deviation from ideality, then \(a_1\) and \(a_2\) will be greater than the corresponding mole fractions and the \(\gamma\)'s will be greater than unity. Conversely, if the deviation is negative, the \(\gamma\)'s will be less than unity. The Gibbs–Duhem equation provides some important conclusions in this respect. If we evaluate \(d\mu_{\text{a}}(l)\) from Eq. (9-72), then, by Eq. (9-49),
\[
x_1 d(\ln a_1) + x_2 d(\ln a_2) = 0
\] (9-79)
or
\[
\int d(\ln a_2) = - \int \frac{x_1}{x_2} d(\ln a_1).
\] (9-80)

Thus if the activities of component 1 are known for a range of concentrations, integration of Eq. (9-80) allows a calculation of the change in activity of component 2 (see Section 9-5C and Special Topics section). Further analysis shows that if component 1 has a positive deviation from ideality, so must component 2, and vice versa. That is, the deviation must be of the same type for both components.

### C. Calculation of Activities and Activity Coefficients

The preceding material is sufficiently complicated that we now offer a detailed numerical example to help clarify just how the various definitions and procedures are implemented. The data of Fig. 9-3 for the acetone-chloroform system will be used. Values for the two partial pressures, interpolated from the original data, are given in Table 9-1. There are a number of regularities and interrelations to notice. First, the activity coefficients are given either by \(\gamma_c = a_c/x_c\) and \(\gamma_a = a_a/x_a\) (c = chloroform and a = acetone) or by \(\gamma_c = P_c/P_{c(\text{ideal})}\) and \(\gamma_a = P_a/P_{a(\text{ideal})}\), where \(P_{a(\text{ideal})}\) is the Raoult's law value for the partial pressure. The two calculations are equivalent.

Next, the plot of the activity coefficients given in Fig. 9-11 shows that \(\gamma_c \to 1\) as \(x_c \to 1\), and \(\gamma_a \to 0\) as \(x_a \to 0\). The respective limiting values are actually 0.485 and 0.449, or about 8% different. The model is thus approximate in this case, but still is not too bad, considering its simplicity.

The data may also be used to illustrate the application of Eq. (9-80). Figure 9-12 shows the plot of \(x_a/x_c\) versus log \(a_a\). The shaded area corresponds to the integral between \(x_c = 0.9\) and
TABLE 9-1. *The Acetone (a)-Chloroform (c) System at 35°C*

<table>
<thead>
<tr>
<th>$x_c$</th>
<th>$P_a$</th>
<th>$P_o$</th>
<th>$P_c$</th>
<th>$P_a$</th>
<th>$a_c$</th>
<th>$a_a$</th>
<th>$\gamma_c$</th>
<th>$\gamma_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0</td>
<td>345</td>
<td>0</td>
<td>345</td>
<td>0</td>
<td>(1.00)</td>
<td>(0.485)</td>
<td>(1.00)</td>
</tr>
<tr>
<td>0.10</td>
<td>16.0</td>
<td>310</td>
<td>29.3</td>
<td>311</td>
<td>0.0546</td>
<td>0.899</td>
<td>0.546</td>
<td>0.998</td>
</tr>
<tr>
<td>0.20</td>
<td>35</td>
<td>270</td>
<td>59</td>
<td>276</td>
<td>0.119</td>
<td>0.783</td>
<td>0.597</td>
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</tr>
<tr>
<td>0.30</td>
<td>57</td>
<td>227</td>
<td>88</td>
<td>242</td>
<td>0.195</td>
<td>0.658</td>
<td>0.648</td>
<td>0.940</td>
</tr>
<tr>
<td>0.40</td>
<td>82</td>
<td>185</td>
<td>117</td>
<td>207</td>
<td>0.280</td>
<td>0.536</td>
<td>0.700</td>
<td>0.894</td>
</tr>
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<td>140</td>
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<td>173</td>
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<td>0.406</td>
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<td>0.296</td>
<td>0.808</td>
<td>0.739</td>
</tr>
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<td>104</td>
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<td>0.878</td>
<td>0.628</td>
</tr>
<tr>
<td>0.80</td>
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<td>69</td>
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<td>0.107</td>
<td>0.934</td>
<td>0.536</td>
</tr>
<tr>
<td>0.90</td>
<td>257</td>
<td>16.5</td>
<td>264</td>
<td>34.5</td>
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<td>0.048</td>
<td>0.975</td>
<td>0.478</td>
</tr>
<tr>
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<td>293</td>
<td>0</td>
<td>293</td>
<td>0</td>
<td>(1.00)</td>
<td>0</td>
<td>(1.00)</td>
<td>(0.449)</td>
</tr>
</tbody>
</table>


$b a_c = P_c/P_o, a_a = P_a/P_o.$

c $\gamma_c = a_c/x_c, \gamma_a = a_a/x_a.$

$x_c = 0.3:

$$\log a_c(x_c=0.3) - \log a_c(x_c=0.9) = \int_{x_c=0.3}^{x_c=0.9} \frac{x_c}{x_c} d(\log a_c).$$ \hspace{1cm} (9-81)

The area is approximately \(-0.66\), so

$$\log a_c(x_c=0.3) = \log a_c(x_c=0.9) - 0.66 = \log(0.877) - 0.66$$ \hspace{1cm} (9-82)

whence $a_c = 0.192$, in good agreement with the observed value of 0.195.

Finally, we can calculate the free energy and excess free energy of mixing, using Eqs. (9-75)

![Activity coefficient plot for the acetone–chloroform system at 35°C.](image)
and (9-76). We have

$$
\Delta G = (1.987)(308)(x_c \ln y_c + x_a \ln y_a) = 612(x_c \ln y_c + x_a \ln y_a).
$$

The calculated values for $\Delta G$ are plotted in Fig. 9-13 for 25°C. Here $\Delta G$ is negative and goes through a minimum at about $x_c = 0.6$; it is zero, of course, for either pure liquid. We must know the temperature dependence of $\Delta G$ in order to obtain $\Delta S_M$ and hence $\Delta S_E$ or, alternatively, calorimetric heat of mixing data so as to obtain $\Delta H_E$. These quantities have been obtained, and are included in the figure. Notice that $T \Delta S_E$ and $\Delta H_E$ are both relatively large but partially cancel to give a much smaller $\Delta G$. This often happens.

FIG. 9-12. Application of the Gibbs–Duhem equation to the acetone–chloroform system at 35°C.

9-6 The Temperature Dependence of Vapor Pressures

We can obtain a relationship analogous to the Clausius–Clapeyron equation by proceeding as follows. Differentiation of

\[ \mu_i(l) = \mu_i^\circ(g) + RT \ln P_i \quad \text{[Eq. (9-56)]} \]

with respect to temperature, and use of Eq. (9-35), gives

\[ -\delta S_i(l) = -S_i^\circ(g) + R \ln P_i + RT \frac{d(ln P_i)}{dT}. \]

The term \( R \ln P_i \) is replaced by \( [\mu_i(l) - \mu_i^\circ(g)]/T \) to give

\[ RT \frac{d(ln P_i)}{dT} = \left[ \frac{[\mu_i^\circ(g) + TS_i^\circ(g)]}{T} - \frac{[\mu_i(l) + TS_i(l)]}{T} \right]. \quad (9-84) \]

The defining equation for \( G \),

\[ G = H - TS \quad \text{[Eq. (6-31)]} \]

becomes, for a component of a solution,

\[ \mu_i = \bar{H}_i - TS_i \quad (9-85) \]

[obtained by differentiating Eq. (6-31) with respect to \( dn_i \) at constant \( T \) and \( P \)]. The terms in brackets in Eq. (9-84) may next be replaced by the corresponding enthalpies to give, on rearrangement,

\[ \frac{d(ln P_i)}{dT} = \frac{\Delta H_{v,i}}{RT^2}, \quad (9-86) \]

where

\[ \Delta H_{v,i} = H_i^\circ(g) - \bar{H}_i(l). \quad (9-87) \]

and is the partial molal heat of vaporization for the \( i \)th component. In the case of pure liquid \( \bar{H}_i(l) \) becomes \( H_i^\circ(l) \) and Eq. (9-86) reduces to the Clausius–Clapeyron equation. The same is true for an ideal solution, since \( \Delta H_M \) is zero.

The ideal solution form of Eq. (9-86) may be developed more explicitly. First, for a pure liquid the Clausius–Clapeyron equation can be written

\[ P_i^\circ = \exp \left[ \frac{\Delta H_{v,i}^\circ}{R} \left( \frac{1}{T_{b,i}^\circ} - \frac{1}{T} \right) \right]. \quad (9-88) \]

where \( T_{b,i}^\circ \) is the normal boiling point of liquid \( i \); Eq. (9-88) follows from Eq. (8-10) when we set the vapor pressure equal to 1 atm at \( T_{b,i}^\circ \). For an ideal solution, \( P_i = x_i P_i^\circ \), so Eq. (9-88) becomes

\[ P_i = x_i \exp \left[ \frac{\Delta H_{v,i}^\circ}{R} \left( \frac{1}{T_{b,i}^\circ} - \frac{1}{T} \right) \right]. \quad (9-89) \]

Equations (9-87) and (9-89) apply equally well to the vapor pressure of the \( i \)th component of a solid solution, ideal in the case of Eq. (9-89). The enthalpy quantities are then those for sublimation, of course.
9-7 Boiling Point Diagrams

A. General Appearance

The material of Section 9-2 is now extended to show the various types of boiling point diagrams that one finds for a solution of two volatile liquids. It is first necessary to consider how the total vapor pressure of the solution should vary with composition and temperature. This is most easily done for the case of an ideal solution, for which the two partial pressures are, from Eq. (9-89),

\[ P_A = x_A \exp \left[ \frac{\Delta H_{v,A}}{R} \left( \frac{1}{T_{b,A}} - \frac{1}{T} \right) \right] \]  \hspace{1cm} (9-90)

and

\[ P_B = x_B \exp \left[ \frac{\Delta H_{v,B}}{R} \left( \frac{1}{T_{b,B}} - \frac{1}{T} \right) \right]. \]  \hspace{1cm} (9-91)

The total pressure \( P \) is just

\[ P = P_A + P_B. \]  \hspace{1cm} (9-92)

Substitution of the expressions for \( P_A \) and \( P_B \) into Eq. (9-92) gives the equation for the variation of \( P \) with composition and temperature.

The general appearance of this function is shown in Fig. 9-14; it is assumed that component A is the one with the lower boiling point.

The upper surface gives the total vapor pressure and the lower one the vapor composition for solutions of a given composition and temperature. The front of the projection corresponds to a cross section at constant temperature, and thus constitutes the vapor pressure-composition diagram for that temperature, as shown in Fig. 9-15(a). The top surface in Fig. 9-14 corresponds to a cross section at constant pressure and therefore to the boiling point diagram for that pressure, as shown in Fig. 9-15(b). Notice that the liquid composition line is now curved and lies below rather than above the vapor composition line.

![Fig. 9-14. Variation of \( P \) with temperature and composition for an ideal solution.](image)
The normal boiling point diagram is given by a cross section at \( P = 1 \text{ atm} \).

We can obtain the boiling point versus composition line analytically by setting \( P = 1 \) in Eq. (9-92):

\[
1 = x_A \left\{ \exp \left[ \frac{\Delta H_{v,A}^o}{R} \left( \frac{1}{T_{b,A}} - \frac{1}{T_b} \right) \right] \right\} + x_B \left\{ \exp \left[ \frac{\Delta H_{v,B}^o}{R} \left( \frac{1}{T_{b,B}} - \frac{1}{T_b} \right) \right] \right\}.
\]  

Equation (9-93) reduces to two variables since \( x_A + x_B = 1 \). Since it is transcendental, it is best solved by picking successive choices for \( T_b \) and solving for corresponding \( x_A \) or \( x_B \). The resulting plot is shown in Fig. 9-15(b). The vapor line gives the compositions of vapor in equilibrium with boiling solutions and is calculated from the corresponding \( P_A \) and \( P_B \) values:

\[
y_A = \frac{P_A}{P}, \quad y_B = \frac{P_B}{P}.
\]
The boiling point diagram is again a phase map. Referring to 9-15(b), we see that if a system of composition \( x_0 \) is contained in a cylinder with a piston arranged so that the pressure is always 1 atm, the system consists entirely of vapor if \( T > T_1 \). On cooling to \( T_1 \), liquid of composition \( x_1 \) begins to condense out and by temperature \( T_2 \) the system consists of liquid of composition \( x_2 \) and vapor of composition \( y_2 \). The relative amounts are given on application of the lever principle to the tie-line at \( T_2 \). At \( T_3 \) the last vapor, of composition \( y_3 \), has condensed, and below \( T_3 \) the system is entirely liquid.

Figure 9-15 illustrates another point, namely, that the boiling point diagram is (roughly) similar in appearance to that of the vapor pressure diagram turned upside down: The higher vapor pressure liquid is the lower boiling one, and the relative positions of the phase regions are reversed. A similar situation holds for nonideal systems as shown in Fig. 9-16. Positive deviation, leading to a maximum in the vapor pressure diagram, will usually give a minimum boiling system as in Fig.

\[ P = 750 \text{ Torr} \]

\[ T, ^\circ C \]

\[ x_0 \quad y_1 \quad y_1' \quad x_0' \]

\( P = 1 \text{ atm} \]

\[ T, ^\circ C \]

\[ x_0 \quad x_{max} \quad x_0' \]

**FIG. 9-16.** Vapor pressure and boiling point diagrams: (a) Positive deviation from Raoult's law, giving a minimum boiling diagram. (b) Negative deviation from Raoult's law, giving a maximum boiling diagram.
9-16(a), whereas a negatively deviating system with a minimum in the vapor pressure diagram usually shows maximum boiling behavior, as in Fig. 9-16(b). Compare with Figs. 9-7 and 9-3.

B. Distillation

If a boiling system is arranged so that the vapors are continuously removed rather than being contained as in the cylinder and piston arrangement, a somewhat different sequence of events occurs. Referring to the case of Fig. 9-15(b), we see that liquid of composition \( x_0 \) would first boil at \( T_3 \), producing vapor of composition \( y_3 \). Since the vapor is richer in \( A \) than is the liquid, and is steadily being removed, the liquid composition progressively becomes richer in \( B \), passing compositions \( x_2 \) and \( x_1 \), respectively. Unlike the situation with the closed system, however, liquid remains when \( T_1 \) is reached. This is because the overall vapor composition is not \( x_0 \), but rather the average of the compositions of the succession of vapors produced, ranging from \( y_3 \) to \( x_0 \). For example, this average vapor composition might be about equal to \( y_2 \), in which case the relative amount of liquid remaining would be given by the lever \((y_2 - x_0)/(y_2 - x_1)\), or about 50%. Continued boiling would continue to shift the liquid composition to the right, and the last drop of liquid remaining would be essentially pure \( B \).

A similar analysis applies to Fig. 9-16(a). Liquids of composition either \( x_0 \) or \( x_0' \) produce initial vapors of composition \( y_1 \) or \( y_1' \); in both cases the vapor composition is closer to the minimum boiling composition than is the liquid composition. As a consequence, continued boiling of system \( x_0 \) moves the liquid composition progressively toward pure benzene, and continued boiling of system \( x_0' \) moves it toward pure ethanol. If there is a maximum boiling point, the vapor compositions might be about equal to \( y_2 \), in which case the relative amount of liquid remaining would be given by the lever \((y_2 - x_0)/(y_2 - x_1)\), or about 50%. Continued boiling would continue to shift the liquid composition to the right, and the last drop of liquid remaining would be essentially pure \( B \).

Fractional distillation comprises a series of evaporation-condensation steps. It is helpful at this point to refer to a diagram of the type shown in Fig. 9-17, in which vapor composition \( y \) is plotted against liquid composition \( x \). The case illustrated is that of a relatively ideal solution. Liquid of composition \( x_0 \) produces some vapor of composition \( y_1 \). If this vapor is condensed, the effect is to locate a new liquid composition \( x_1 \) on the diagonal. Liquid \( x_1 \) produces vapor \( y_2 \) and on its condensation, liquid \( x_2 \) results. The series of steps gives the number of operations needed to reach the final liquid composition \( x_5 \). This analysis assumes that only a small amount of each liquid is vaporized; in actual practice the fraction is appreciable and so the vapor compositions are always less enriched in the more
volatile component than in the ideal situation. The detailed treatment of fractional
distillation constitutes a major subject in chemical engineering and is beyond the
scope of this text.

A special case in distillation is that of two immiscible liquids. A mixture of two
such liquids will boil when their combined vapor pressure reaches 1 atm. We thus
write the separate Clausius–Clapeyron equations for each pure liquid:

\[
\begin{align*}
P_A^o &= \exp\left[\frac{\Delta H_{v,A}^o}{R} \left( \frac{1}{T_{b,A}} - \frac{1}{T} \right) \right], \\
P_B^o &= \exp\left[\frac{\Delta H_{v,B}^o}{R} \left( \frac{1}{T_{b,B}} - \frac{1}{T} \right) \right].
\end{align*}
\]

The normal boiling point of the mixture of liquid phases is given by

\[
1 = \exp\left[\frac{\Delta H_{v,A}^o}{R} \left( \frac{1}{T_{b,A}} - \frac{1}{T} \right) \right] + \exp\left[\frac{\Delta H_{v,B}^o}{R} \left( \frac{1}{T_{b,B}} - \frac{1}{T} \right) \right],
\]

since we require that \( P_A^o + P_B^o = 1 \). The situation is illustrated in Fig. 9-18.

Boiling of such a mixture produces vapor of composition

\[
y_B = \frac{P_B^o}{P_A^o + P_B^o} \quad (= P_B^o \text{ if } P = 1),
\]

where \( P_A^o \) and \( P_B^o \) are the vapor pressures of the pure liquids at \( T_b \). On continued
boiling, one or the other liquid phase will eventually disappear and the boiling
point will then revert to that of the remaining liquid.

A procedure of this type is often known as a steam distillation, since a frequent
application is the distillation of a mixture of water and an insoluble organic liquid
or oil. The advantage is that the oil is thereby distilled at a much lower temperature
than would otherwise be needed and with less danger of decomposition. It is also
possible to obtain the molecular weight of the oil from Eq. (9-98). If component
A is water, then $P_A^\circ$ is given by the measured $T_b$ and $P_B^\circ$ is then the ambient or barometric pressure minus $P_A^\circ$ and $y_B$ is given by Eq. (9-98). With $y_B$ and the weight fraction of the distillate known, $M_B$ can be calculated.

As an example, suppose that a mixture of an insoluble organic liquid and water boiled at 90.2°C under a pressure of 740.2 Torr. The vapor pressure of pure water is 530.1 Torr at this temperature. The condensed distillate is 71 % by weight of the oil. Evidently $P_B^\circ$ is $740.2 - 530.1$ or 210.1 Torr; therefore $y_B = 210.1/740.2 = 0.2838$. Since

$$y_B = \frac{W_B/M_B}{(W_B/M_B) + (W_A/M_A)},$$

where $W$ denotes weight of substance, or

$$\frac{W_B}{M_B} = y_B \frac{W_A}{1 - y_B M_A},$$

then, per 100 g of distillate,

$$\frac{W_B}{M_B} = \frac{0.2838}{0.7162} = \frac{29}{18.02} = 0.638$$

and $M_a = 71/0.638 = 111.2$ g mole$^{-1}$.

### 9-8 Partial Miscibility

The equilibrium between a liquid solution and a pure solid phase of one of the components is treated in Chapter 10 and that between liquid and solid solutions in Chapter 11. There remains the case of two partially miscible liquid phases. If liquid phases $\alpha$ and $\beta$ are in equilibrium, then if the system is one of two compo-
nents A and B, the condition for equilibrium is that

\[ \mu_A^\alpha = \mu_A^\beta \quad \text{and} \quad \mu_B^\alpha = \mu_B^\beta. \] (9-99)

As discussed in the Special Topics section, this means that a plot of the molar free energy of the solution, \( G/(n_A + n_B) \), versus composition shows a double minimum, and therefore so, too, does a plot of \( \Delta G_{\text{mix}} \) versus composition.

The situation is one in which there is a limited solubility of B in A, giving A-rich solutions designated as \( \alpha \) phase, and a limited solubility of A in B, giving B-rich solutions designated as \( \beta \) phase. The maximum solubilities may then be designated as \( S^\alpha \) and \( S^\beta \), where \( S^\alpha \) is the composition of a solution saturated with respect to B and \( S^\beta \) is that of a solution saturated with respect to A. The compositions \( S^\alpha \) and \( S^\beta \) are not very dependent on pressure; quite large pressures are needed to change the free energies of liquids appreciably. They are temperature-dependent, however, and this dependence is customarily shown in plots of solubility versus temperature at 1 atm pressure.

![Figure 9-19. Miscibility gap between two liquids with an upper consolute temperature.](image-url)
two liquid phases. The compositions are given by the ends of the tie-line as \( x_1^a \) and \( x_1^\beta \), and the relative amounts present may be obtained by means of the lever principle. Thus we have

\[
\frac{n^\alpha}{n^\alpha + n^\beta} = \frac{x_0 - x_1^\beta}{x_1^\alpha - x_1^\beta},
\]

where \( n^\alpha \) and \( n^\beta \) are, respectively, the number of moles of phase \( \alpha \) of composition \( x_1^a \) and of phase \( \beta \) of composition \( x_1^\beta \). When the system is warmed to \( T_2 \) the two phases are of composition \( x_2^a \) and \( x_2^\beta \) and application of the lever principle shows that the proportion of phase \( \alpha \) has increased. At \( T_3 \) phase \( \beta \) disappears and the system consists of phase \( \alpha \) of composition \( x_0 \).

One may, alternatively, make a horizontal traverse of the diagram. Thus addition of liquid B to pure liquid A at \( T_1 \) gives a phase of increasing mole fraction of B. When composition \( x_1^a \) is reached phase of composition \( x_1^\beta \) begins to appear, and further addition of B steadily increases the proportion of \( \beta \) phase. When the system composition reaches \( x_1^\beta \) no more \( \alpha \) phase remains and continued addition of B now merely increases the concentration of B in the \( \beta \) phase.

The phenol–water system shows this type of behavior, as illustrated in Fig. 9-20(a). The upper consolute temperature in this case is about 70°C. It can also happen that the solubilities increase with decreasing temperature, as illustrated by the water–

![Fig. 9-20](image-url)
triethylamine system of Fig. 9-20(b). There is now a lower consolute temperature. Finally, both types of behavior may be shown, as in the case of the water–nicotine system of Fig. 9-20(c). The compositions are given in weight fraction in all these figures and application of the lever principle will therefore give the relative weights of the two phases that are present.

**COMMENTARY AND NOTES**

**9-CN-1 Other Properties of Solutions**

The emphasis of this chapter has been almost entirely on the vapor pressure of solutions. Vapor pressures provide experimental access to the thermodynamic quantities for solutions, solid or liquid, as well as vapor pressure and boiling point diagrams of great general utility. These topics have therefore received first priority. Unfortunately, anything approaching a complete outline of the physical chemistry of solutions would take entirely too much space. Actually, all of the various types of properties mentioned in previous chapters have been measured for solutions. Examples are molar refractions and polarizations, usually with additivity of the solvent and solute contributions assumed, density, compressibility, thermal expansion, and surface tension.

The molar volume of a solution might be discussed briefly, however. At constant temperature and pressure, volume is a function of composition only, and for a two-component system we have

\[
dv = \left( \frac{\partial v}{\partial n_1} \right)_{T,P,n_2} dn_1 + \left( \frac{\partial v}{\partial n_2} \right)_{T,P,n_1} dn_2
\]

or

\[
dv = \bar{V}_1 dn_1 + \bar{V}_2 dn_2
\]

where \( \bar{V}_1 \) and \( \bar{V}_2 \) are the partial molal volumes. Integration at constant composition gives

\[
v = n_1 \bar{V}_1 + n_2 \bar{V}_2 \quad \text{or} \quad V_{av} = x_1 \bar{V}_1 + x_2 \bar{V}_2,
\]

where \( V_{av} \) is the average molar volume.

Differentiation, and subtraction of Eq. (9-102), leads to the important relation

\[
n_1 d\bar{V}_1 + n_2 d\bar{V}_2 = 0
\]

or

\[
x_1 d\bar{V}_1 + x_2 d\bar{V}_2 = 0.
\]

The procedure is analogous to that used in obtaining the Gibbs–Duhem equation [Eq. (9-48)] and, in fact, is one that can be applied to any extensive property (see Special Topics section).

The partial molal volume of a component of an ideal solution will be the same as the molar volume of the pure substance. For most ordinary organic liquids the average molar volume \( v/n \) varies almost linearly with composition. In the acetone–chloroform system, for example, the volume change on mixing amounts to a few
tenths of a percent at the most. The molar volume of acetone is 72.740 cm$^3$ mole$^{-1}$ at 25°C and the partial molal volume increases slightly on dilution with chloroform to a limiting dilute solution value of 73.993 cm$^3$ mole$^{-1}$. Solutions involving water are often anomalous; there is almost a 3% volume change when a water-methanol solution is made up, and an actual shrinkage in total volume may occur when an electrolyte is dissolved in water. The explanation for this last is that ions attract water molecules so strongly that the resulting compaction more than compensates for the added volume of the ions themselves. The existence of negative partial molal volumes serves to emphasize that $F_i$ and other partial molal quantities are coefficients of the system and do not have the same literal meaning as do the corresponding properties of a pure substance.

The viscosity of a solution of similar substances will again vary nearly linearly with composition; often a better straight line is obtained if the reciprocals or fluidities are used instead. Deviations from linearity in the plot of viscosity versus mole fraction tend to correlate with such deviations in the corresponding vapor pressure diagrams. The acetone–chloroform system, which shows a minimum in the vapor pressure diagram attributable to greater $A$–$B$ than $A$–$A$ or $B$–$B$ types of interactions, has a maximum in the viscosity–composition plot. Diffusion has also been studied a good deal in binary liquid systems. There is a single mutual diffusion coefficient, but, in addition, self-diffusion coefficients may be obtained for each component separately by means of isotopic labeling. As with viscosity, there are a number of semiempirical models but no really satisfactory ones.

The surface tension of solutions constitutes a large subject. Figure 9-21 displays typical categories of surface tension versus composition plots. In the case of similar liquids the surface tension plot is roughly symmetric relative to a straight line connecting the values of $\gamma$ for the pure liquids, as exemplified by the data shown in Fig. 9-21(a). If the molecular areas $\sigma$ of the two species are similar, then a simple treatment based on the energy $\gamma\sigma$ required to bring a molecule into the surface gives the equation

$$e^{-\gamma_0/kT} = x_1e^{-\gamma_1/kT} + x_2e^{-\gamma_2/kT}. \quad (9-106)$$

The surface tensions of the respective pure liquids are given by $\gamma_1$ and $\gamma_2$. Another form, derived for regular solutions (Section 9-CN-2), is

$$\gamma = \gamma_1x_1 + \gamma_2x_2 - \beta x_1x_2, \quad (9-107)$$

where $\beta$ is an empirical constant related to the constant $\alpha$ of Eq. (9-16).

If the two liquids have rather different surface tensions, then the plot will look like that shown in Fig. 9-21(b) for the water–ethanol system. The surface tension drops rapidly over the first 10 or 20% of ethanol added and then approaches the value for pure ethanol more slowly. This type of behavior becomes accentuated in the case of a long-chain solutes having a polar end group, such as sodium lauryl sulfate. As illustrated in Fig. 9-21(c), there is a sharp drop in $\gamma$ even for very dilute solutions. Such long-chain solutes include the common soaps and detergents and belong to the class of so-called surface-active agents (surfactants). As discussed in the Special Topics section, the thermodynamic implication is that the surfactant concentrates at the solution–air interface. With sodium lauryl sulfate, there is nearly a monolayer or complete film of the surfactant by 0.01 M concentration. With a higher molecular weight and less soluble surfactant, the monolayer is usually formed simply by adding the material directly to the surface. One may drop
a hexane solution of stearic acid carefully onto a water surface and thus obtain a monolayer of the acid after the hexane has evaporated. The film may be compressed between movable barriers and its surface tension measured as a function of surface concentration (see Section 9-ST-2).

A fourth category of system is that of an electrolyte solution such as aqueous sodium chloride, shown in Fig. 9-21(d). The surface tension increases somewhat with concentration. The thermodynamic implication is that the surface region is more dilute in electrolyte than the bulk solution, or that negative adsorption occurs at the interface.

To return to the general sequence of this section, we see that yet another aspect of the physical chemistry of solutions is the somewhat special behavior of solution–vapor and solution–solid equilibria when only one component is present in both phases. This subject is taken up in the Chapter 10. Finally, electrolyte solutions constitute a large topic in their own right and are discussed in Chapter 12. For these solutions, the new property of electrical conductivity is very important.
### 9-CN-2 Ideal, Regular, and Athermal Solutions

Several of the attributes of an ideal solution have been introduced in the preceding sections. These, plus some further ones, are assembled here to provide an overall picture. The ideal solution obeys Raoult’s law, so that

\[ \mu_i(l) = \mu_i^\circ(l) + RT \ln x_i \quad \text{[ideal solution, Eq. (9-61)].} \]

The free energy of mixing to form an ideal solution is given, for the case of two components, by

\[ \Delta G_M = x_1 RT \ln x_1 + x_2 RT \ln x_2 \quad \text{[ideal solution, Eq. (9-65)],} \]

and the entropy of mixing by

\[ \Delta S_M = -(x_1 R \ln x_1 + x_2 R \ln x_2) \quad \text{[ideal solution, Eq. (9-69)].} \]

By definition, of course, the excess free energy and entropy of mixing are zero. Since \( \Delta H = \Delta G + T \Delta S \), it follows that the heat of mixing is zero for an ideal solution. Figure 9-13 shows the variations of \( \Delta G_M \), \( \Delta S_M \), and \( \Delta H_M \) with composition for a nonideal solution. It is necessarily also true that \( H_i = H_i^\circ \), that is, the partial molal enthalpy of an ideal solution component is equal to that of the pure species.

Differentiation of Eq. (9-61) with respect to \( P \) at constant \( T \), and with the use of Eq. (9-34), gives

\[ V_i - V_i^\circ = 0. \]

The partial molal volume of an ideal solution component is thus the same as that of the pure component. Consequently \( \Delta V_M \) is zero.

Nonideal solutions may be viewed in terms of the excess quantities of mixing \( \Delta G_E \), \( \Delta S_E \), and \( \Delta H_E = \Delta H_M \). If, for example, Eqs. (9-16) and (9-17) are obeyed, then

\[ \Delta G_E = x_1 x_2 \alpha RT. \quad (9-108) \]

Solutions obeying Eq. (9-108) have been called “simple” solutions by E. A. Guggenheim. One simple model for solutions concludes that \( \alpha \) is just an interaction energy divided by \( RT \). It follows that \( d(\Delta G_E)/dT \) and hence the excess entropy of mixing should be zero, but not, of course, \( \Delta H_M \). This type of solution is known, after J. H. Hildebrand, as a regular solution. The implication is that the two components are randomly distributed in the solution as though it were ideal, although their interaction energies with themselves and with each other are different.

Finally, an athermal solution is one for which \( \Delta H_M = 0 \), although \( \Delta S_E \) and \( \Delta G_E \) are not necessarily zero. This situation may occur with components rather similar in chemical nature but very different in molecular size. A simple treatment on this basis leads to the equation for the free energy of mixing:

\[ \Delta G_M = x_1 RT \ln \phi_1 + x_2 RT \ln \phi_2, \quad (9-109) \]
where \( \phi_1 \) and \( \phi_2 \) are the volume fractions. There is some statistical thermodynamic basis for the supposition that for a solution to be ideal the molar volumes of the components should be about the same (see the next section) and Raoult's law may in fact be less general, even as a limiting law, than is customarily thought.

**9-CN-3 Statistical Thermodynamics of Solutions**

Needless to say, the statistical thermodynamic treatment of solutions is difficult and fragmentary in its achievements. One may, in principle, set up the partition functions, which now involve the chemical potential of a component as a weighting factor. Useful in this connection is what is called the absolute or rational activity \( q \), given by

\[
\mu_i = RT \ln q_i .
\]  

(9-110)

Like the chemical potential, the absolute activity of a species is the same in all equilibrium phases in which the species is present.

Certain simple entropy calculations can be made. One consideration is the following. It will be recalled that the translational partition function for a gas required the factor \( \frac{1}{N!} Q_{\text{tot}}^{N_0} \) [Eq. (6-68)].

In the case of a crystalline solid each molecule is restricted to its own volume \( V/N_0 \) and the translational partition function becomes

\[
Q_{\text{tot}} = Q_{\text{tot}}^{N_0} \left( \frac{V}{N_0} \right)^{N_0} .
\]  

(9-111)

Equation (9-111) follows from Eq. (4-68) if the volume is made \( V/N_0 \) rather than \( v \), the volume of the whole system. The difference between the two corresponding entropies is, by Eq. (6-64), just \( k \ln(Q/Q') \), since the energies for the two situations are the same. Thus

\[
S(\text{gas}) - S(\text{lattice}) = k \ln \left( \frac{N_0^{N_0}}{N_0!} \right) = N_0k
\]  

(9-112)

[using Stirling's formula for \( \ln(N_0!) \)].

This entropy factor is known as the communal entropy, and is thought to develop by stages as a solid melts and the liquid is heated. The lattice model may be approximately applicable to the liquid, in other words. Although absolute calculations of thermodynamic quantities are most difficult, we can obtain the entropy of mixing. We assume the solution to consist of lattice sites, all equivalent, which may be occupied either by a molecule of component 1 or by a molecule of component 2. In addition to all other contributions there is now one which has to do with the ways in which \( N_1 \) molecules of species 1 and \( N_2 \) molecules of species 2 may be distributed, where \( N_1 + N_2 = N_0 \). The reasoning at this point is very similar to that of Section 2-2. There are \( N_0! \) ways in which \( N_0 \) molecules can be arranged among the sites, but we assume that those of component 1 are indistinguishable among themselves, and likewise for those of component 2. We
must then divide by the number of ways in which $N_1$ molecules can be arranged among themselves, and similarly for the $N_2$ molecules. The thermodynamic probability of the solution is

$$W = \frac{N_0!}{N_1! N_2!}. \quad (9-113)$$

The relationship between entropy and thermodynamic probability [Eq. (6-66)] now gives for the mixing entropy of the solution

$$\Delta S_M = k \ln \left( \frac{N_0!}{N_1! N_2!} \right). \quad (9-114)$$

Use of Stirling's approximation for factorials and some straightforward algebraic maneuvering yields the final form

$$\Delta S_M = -(x_1 R \ln x_1 + x_2 R \ln x_2) \quad [\text{Eq. (9-69)}],$$

which is the same as that previously obtained. The uniform lattice concept does seem to imply that the two species should be of about the same molecular size for ideal solution behavior to hold, as mentioned in the preceding section. This is only an implication, however, since the lattice picture is not essential to obtain a correct expression for the entropy of mixing. Thus Eq. (9-69) also applies to the mixing of two ideal gases, although the basis of obtaining it is through the Sackur–Tetrode equation [Eq. (6-83)], which gives the volume dependence of the entropy of an ideal gas to be $R \ln V$. Then $\Delta S$ for the mixing process of Eq. (9-52) is, per mole,

$$\Delta S_M = x_1 R \ln \frac{V}{V_1} + x_2 R \ln \frac{V}{V_2}, \quad (9-115)$$

where $V_1$ and $V_2$ are the initial volumes of the two gases and $V$ is their common final volume. Since $V_1 = x_1 V$ and $V_2 = x_2 V$, Eq. (9-69) again results.

Thus two very different pictures have produced the same conclusion. One must be cautious in assuming that, simply because a particular model yields a correct equation, the model itself is therefore correct.

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**SPECIAL TOPICS**

**9-ST-1 Partial Molal Quantities**

The derivations of the Gibbs–Duhem equation [Eq. (9-49)] and of Eq. (9-104) for volumes are specific examples of a more general procedure. If the independent variables of some function $y = f(u, v, w, \ldots)$ are extensive quantities, that is, ones which increase in proportion to the amount of the system, then by a theorem due to Euler, it must be true that

$$u \left( \frac{\partial f}{\partial u} \right)_{v,w,\ldots} + v \left( \frac{\partial f}{\partial v} \right)_{u,w,\ldots} + w \left( \frac{\partial f}{\partial w} \right)_{u,v,\ldots} + \cdots = f. \quad (9-116)$$
This theorem was invoked implicitly in integrating Eq. (9-28), with \( E = f(S, v, n) \), to obtain Eq. (9-45).

In the case of partial molal quantities we restrict ourselves to a system at constant temperature and pressure, so that the amounts \( n_i \) of the various components are the only variables. Thus in the case of a two-component system, for some property \( P \), we have

\[
dP = \left( \frac{\partial P}{\partial n_1} \right)_{n_2} dn_1 + \left( \frac{\partial P}{\partial n_2} \right)_{n_1} dn_2 = P_1 dn_1 + P_2 dn_2. \tag{9-117}\]

where \( P_1 \) and \( P_2 \) are the partial molal values. Then, by Euler's theorem,

\[
P = n_1 P_1 + n_2 P_2. \tag{9-118}\]

Differentiation and comparison with Eq. (9-117) gives

\[
n_1 dP_1 + n_2 dP_2 = 0. \tag{9-119}\]

Equation (9-48) corresponded to the case of \( P = G \) and Eq. (9-104) to that of \( P = v \). For \( P = H \) we have

\[
H = n_1 H_1 + n_2 H_2 \tag{9-120}\]

and

\[
n_1 dH_1 + n_2 dH_2 = 0. \tag{9-121}\]

There are some useful special procedures for obtaining partial molal quantities from experimental data, which can be illustrated easily for volume. We define the average molar volume as

\[
V_{av} = \frac{v}{n_1 + n_2}. \tag{9-122}\]

Then

\[
V_1 = \left( \frac{\partial v}{\partial n_1} \right)_{n_2} = V_{av} + (n_1 + n_2) \left( \frac{\partial V_{av}}{\partial x_2} \right)_{n_2} \left( \frac{\partial x_2}{\partial n_1} \right)_{n_2}, \]

Since

\[
\left( \frac{\partial x_2}{\partial n_1} \right)_{n_2} = -\frac{n_2}{(n_1 + n_2)^2}, \]

it follows that (note Problem 9-18)

\[
V_1 = V_{av} - x_2 \frac{dV_{av}}{dx_2}. \tag{9-123}\]

Equation (9-123) has a simple geometric meaning. If \( V_{av} \) is plotted against mole fraction, then \( dV_{av}/dx_2 \) is the slope of the tangent at composition \( x_2 \), and the intercept of the tangent at \( x_2 = 0 \) then gives \( V_1 \). Since the equation is symmetric, the intercept at \( x_2 = 1 \) gives \( V_2 \). The situation is illustrated in Fig. 9-22 for the acetone–chloroform system. Also, of course, Eq. (9-105) may be used for the calculation of \( V_2 \) if \( V_1 \) is known as a function of composition.

The volume change when the pure components are mixed is

\[
\Delta V_M = V_{av} - x_1 V_1^0 - x_2 V_2^0, \tag{9-124}\]
where $V_1^\circ$ and $V_2^\circ$ are the molar volumes of the pure species. Alternatively, using Eq. (9-103), we obtain

$$\Delta V_M = x_1(V_1^\circ) + x_2(V_2^\circ). \quad (9-125)$$

Enthalpies are treated somewhat similarly, but a complication is that, unlike volumes, absolute enthalpies are not known. It is necessary, then, to deal entirely with heats of mixing. The enthalpy change for the process

$$n_1 \text{ (component 1)} + n_2 \text{ (component 2)} = \text{ solution}$$

is called the integral heat of solution, as an alternative expression to the heat of mixing $\Delta H_M$. For this process

$$\Delta H_M = H_{\text{soln}} - n_1H_1^\circ - n_2H_2^\circ, \quad (9-126)$$

where $H_1^\circ$ and $H_2^\circ$ are the enthalpies of the pure components. Alternatively, using Eq. (9-120), we obtain

$$\Delta H_M = n_1(H_1^\circ - H_1^\circ) + n_2(H_2^\circ - H_2^\circ) \quad (9-127)$$

or

$$\Delta H_M = n_1\bar{Q}_1 + n_2\bar{Q}_2, \quad (9-128)$$

where $\bar{Q}$ denotes the enthalpy relative to the pure component. According to Eq. (9-128), $\bar{Q}_2$ is given by

$$\bar{Q}_2 = \left[ \frac{\partial (\Delta H_M)}{\partial n_2} \right]_{n_1} \quad (9-129)$$

and could be obtained experimentally from the slope of a plot of $\Delta H_M$ versus $n_2$, from data on the heats of dissolution of various amounts of solute in a fixed amount of solvent. Therefore $\bar{Q}_2$ is called the differential enthalpy of solution.
Equation (9-128) may alternatively be written in the form

$$\Delta H_M = \frac{\Delta H_M}{n_1 + n_2} = x_1 \bar{Q}_1 + x_2 \bar{Q}_2. \quad (9-130)$$

The same graphical procedure may now be applied as was used for obtaining partial molal volumes. Thus if a plot of $\Delta H_M$ versus mole fraction is constructed, then the tangent at a given composition will have intercepts at $x_1 = 1$ and $x_2 = 1$ of $\bar{Q}_1$ and $\bar{Q}_2$, respectively, as illustrated in Fig. 9-23.

Many of the results on heats of solution are for electrolytes or other solid solutes, and for such systems it is customary to polarize the treatment around the solute species, component 2. One refers heats of solution of solutes to the value $\bar{Q}_2^o$ for an infinitely dilute solution by introducing a quantity called the relative enthalpy of solution $L$:

$$L = \bar{Q}_2 - \bar{Q}_2^0 = \bar{H}_2 - \bar{H}_2^0, \quad (9-131)$$

where $\bar{H}_2^0$ is the partial molal enthalpy of the solute at infinite dilution and $\bar{Q}_2^0 = \bar{H}_2^0 - \bar{H}_2^o$. By definition $L_2^o = 0$. Usually the pure liquid solvent is kept as the reference state for component 1, so we have

$$L_1 = \bar{Q}_1 = \bar{H}_1 - \bar{H}_1^o. \quad (9-132)$$

Since $\bar{H}_2^o$ and $\bar{H}_1^o$ are constants, insertion of the definitions for $L_1$ and $L_2$ into Eq. (9-121) gives

$$n_1 dL_1 + n_2 dL_2 = 0. \quad (9-133)$$

The $L$ quantities may thus be used in the same way as the $Q$ quantities, or in general as ordinary partial molal quantities. We also have

$$\Delta H_{M,x_2} - \Delta H_M^o = L = n_1 L_1 + n_2 L_2, \quad (9-134)$$

where $\Delta H_{M,x_2}$ is the enthalpy of mixing of $n_1$ moles of solvent and $n_2$ moles of solute to give a solution of composition $x_2$, and $\Delta H_M^o$ is the heat of solution of $n_2$ moles of solute to give an infinitely dilute solution.

One may obtain $L_1$ or $\bar{Q}_1$ experimentally as suggested by the equation analogous to Eq. (9-129), that is, from the variation of $\Delta H_M$ with $n_1$, as solvent is added to a
fixed amount of solute. The alternative, and equivalent, measurement is that of
the heat evolved on the addition of a small amount of solvent to a solution of
a given composition. This last is known as a heat of dilution. One may also obtain
$L_1$ by the graphical method of Fig. 9-23 or indirectly from $L_2$ values by the
integration of Eq. (9-133).

As a numerical illustration, for a 1.11 m solution of sodium chloride $L_1 = 4.0$ cal mole$^{-1}$ and
$L_2 = -248$ cal mole$^{-1}$. The heat of solution at infinite dilution is, from Tables 5-2 and 5-3,

$$
\text{NaCl}(s) + H_2O = \text{NaCl}(\text{infinitely dilute solution})
\Delta H = -97,302 - (-98,232) = 930 \text{ cal mole}^{-1}.
$$

The heat of solution to give a 1.11 m solution differs from this value by

$$
L = n_1L_1 + n_2L_2 \quad \text{[Eq. (9-134)]},
$$
or by $(55.5)(4.0) + (1.11)(-248) = 222 - 275 = -53$ cal per 1.11 mole or by $-48$ cal mole$^{-1}$.
The actual heat of solution is then $930 - 48 = 882$ cal mole$^{-1}$.

Heats of mixing or of solution are direct, calorimetrically determined quantities,
and the preceding framework of relationships and definitions has been developed
with this in mind. Free energies of mixing are determined indirectly, through vapor
pressure measurements, but may still be treated in just the same way. The equation
analogous to Eq. (9-130) is

$$
\Delta G_M = x_1\mu_1^{\text{(rel)}} + x_2\mu_2^{\text{(rel)}},
$$

where $\mu_1^{\text{(rel)}} = \mu_1 - \mu_1^\circ$ and $\mu_2^{\text{(rel)}} = \mu_2 - \mu_2^\circ$. Equation (9-135) is the same as
Eq. (9-75). Again, if $\Delta G_M$ is plotted against mole fraction, the tangent line at a
given composition has intercepts at $x_1 = 1$ and $x_2 = 1$ corresponding to $\mu_1^{\text{(rel)}}$ and
$\mu_2^{\text{(rel)}}$, that is, to $RT\ln \gamma_1$ and $RT\ln \gamma_2$, respectively. If the plot is of $\Delta G_E$, the
intercepts give $RT\ln \gamma_1$ and $RT\ln \gamma_2$, as indicated in Fig. 9-13 for $x_c = 0.4$.

Figure 9-24 is calculated from the Margules equations using an $\alpha$ of 2.5, and

FIG. 9-24. Free energy of mixing for a system obeying the Margules equations with an $\alpha$ of 2.5.
illustrates an important further point. Since there are two minima, there are two compositions, \( x^a \) and \( x^\beta \), for which the \( a_1 \) and \( a_2 \) values are the same. The situation is one of partial miscibility and a system of overall composition lying between \( x^a \) and \( x^\beta \) will spontaneously separate into phases of those two compositions. The figure is symmetric because of the simplicity of the model; in most actual cases of two partially miscible liquids the two minima would not be symmetrically disposed.

9-ST-2 The Surface Tension of Solutions. The Gibbs Equation

An important application of thermodynamics is to the variation of surface tension of a solution with its composition. The following derivation is essentially that of J. W. Gibbs, and the result is known as the Gibbs adsorption equation. We wish to deal with surface thermodynamic quantities and we must somehow separate their contribution from those of the bulk phases that form the interface. We do this by locating an arbitrary dividing plane \( S-S \) roughly in the interfacial region as shown in Fig. 9-25. We then assign a total energy and entropy to bulk phase \( \alpha \) assuming it to continue unchanged up to this dividing plane, and similarly for bulk phase \( \beta \). The actual total energy and enthalpy of the system are then written as

\[
\mathcal{E} = \mathcal{E}^\alpha + \mathcal{E}^\beta + \mathcal{E}_S, \quad \mathcal{S} = \mathcal{S}^\alpha + \mathcal{S}^\beta + \mathcal{S}_S, \tag{9-136}
\]

where \( \mathcal{E}^S \) and \( \mathcal{S}^S \) are now called the surface excess energy and entropy. Similarly, we have

\[
n_i = n_i^\alpha + n_i^\beta + n_i^S. \tag{9-137}
\]

For a small, reversible change \( d\mathcal{E} \) in the energy of the whole system,

\[
d\mathcal{E} = d\mathcal{E}^\alpha + d\mathcal{E}^\beta + d\mathcal{E}^S = T\, d\mathcal{S}^\alpha - P\, dv + \sum \mu_i \, d\eta_i^\alpha + T\, d\mathcal{S}^\beta - P\, dv^\beta
\]

\[
+ \sum \mu_i \, d\eta_i^\beta + T\, d\mathcal{S}^S + \sum \mu_i \, d\eta_i^S + \gamma \, d\mathcal{A}
\]

(9-138)

(the volume is entirely taken care of by \( v^\alpha + v^\beta \)). Equation (9-28) applies separately
to phases $\alpha$ and $\beta$, so these terms all drop out, to leave

$$dE^s = T dS^s + \sum_i \mu_i dn_i^s + \gamma d\mathcal{A}. \quad (9-139)$$

The Euler theorem (preceding section) may now be applied; that is, Eq. (9-139) may be integrated, with $T, \mu_i$, and $\gamma$ kept constant, to give

$$E^s = TS^s + \sum_i \mu_i n_i^s + \gamma \mathcal{A}. \quad (9-140)$$

Differentiation and comparison with the preceding equation gives

$$0 = S^s dT + \sum_i n_i^s d\mu_i + \mathcal{A} d\gamma. \quad (9-141)$$

For a two-component system at constant temperature,

$$n_1^s d\mu_1 + n_2^s d\mu_2 + \mathcal{A} d\gamma = 0. \quad (9-142)$$

It is convenient for us to divide through by the area $\mathcal{A}$ to obtain

$$d\gamma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2, \quad (9-143)$$

where $\Gamma_1$ and $\Gamma_2$ are the excess quantities per unit area.

The exact position of the dividing surface shown in Fig. 9-25 is not specified; clearly the values of $\Gamma$ will depend on this. We now specify the location to be such that $\Gamma_1 = 0$, so that Eq. (9-143) reduces to

$$\Gamma_2 = -\left( \frac{\partial \gamma}{\partial \mu_2} \right)_T, \quad (9-144)$$

where the superscript is a reminder of the choice that has been made. The chemical potential may be expressed in terms of activity,

$$\Gamma_2 = - \frac{1}{RT} \frac{d\gamma}{d(\ln a_2)}. \quad (9-145)$$

Finally, in dilute solution the activity will be proportional to concentration, so that an approximate form is

$$\Gamma_2 = - \frac{C}{RT} \frac{d\gamma}{dC}. \quad (9-146)$$

The preceding are various forms of the Gibbs equation.

Figure 9-26 may help to explain the physical meaning of this conventional choice of location of the dividing surface. The figure shows schematically how the concentrations of solvent and of solute might vary across the interfacial region. The $\beta$ phase is assumed to be vapor, so the concentrations in it are negligible. The surface excess is the difference between the amount actually present and that which would be present were the bulk phase to continue unchanged up to S–S so that the phase boundary became a step. The net shaded area for the solvent is then its surface excess, and S–S has been located so that this is zero. The surface excess of the solute is also given by its net shaded area and is positive in this example. An alternative, operational definition is as follows. If a sample of interface is taken, of 1 cm$^2$ area, and deep enough to include at least some bulk phase on either side,
Solvent

S

C

x

Solute

FIG. 9-26. Illustration of the $\Gamma_2^1$ convention for the Gibbs equation. The dividing surface is located so that the shaded areas for the solvent curve balance. [From A. W. Adamson, "The Physical Chemistry of Surfaces," 3rd ed. Copyright 1976, Wiley (Interscience), New York. Used with permission of John Wiley & Sons, Inc.]

then $\Gamma_2^1$ is the (algebraic) excess of solute over the number of moles that would be present in a bulk region containing the same number of moles of solvent. The excess $\Gamma_2^1$ may be measured directly. In an experiment by J. W. McBain, a fast-moving knife blade (called a microtome) scooped a 3.2 g sample of solution at 20°C from the surface of a trough having a surface area of 310 cm$^2$. The solution contained 5 g of phenol ($M = 94$ g mole$^{-1}$) per 1000 g of water, that is, it was 0.053 $m$. It was found, by means of an interferometer, that the sample contained $2.52 \times 10^{-6}$ g more of phenol per gram of water than did the bulk solution. The value of $\Gamma_2^1$ is thus $(2.52 \times 10^{-6})(3.2)/(94)(310) = 2.77 \times 10^{-10}$ mole cm$^{-2}$.

The Gibbs equation allows an indirect calculation of $\Gamma_2^1$ from surface tension data. Continuing with the preceding example, the surface tensions of 0.05 $m$ and 0.127 $m$ solutions were 67.7 and 60.1 dyn cm$^{-1}$, respectively, at 20°C. A plot of $\gamma$ versus $C$ gives a slope, $-dy/dC$, of 100 dyn cm$^{-1}$ M$^{-1}$ and application of Eq. (9-146) yields

$$\Gamma_2^1 = \frac{(0.063)(100)}{(8.31 \times 10^7)(293)} = 2.2 \times 10^{-10} \text{ mole cm}^{-2}.$$

The two numbers agree fairly well—the microtome experiment is a very difficult one and was, in fact, a triumph of its day (1930's).

The value of $\Gamma_2^1$ obtained is, in one sense, a very small number. It corresponds, however, to about 80 Å$^2$ per molecule, or perhaps twice the value for a close-packed monolayer of molecules lying flat on the surface. The surface population is thus quite high.

As the example illustrates, if the surface tension of a solution decreases with increasing concentration, then $\Gamma_2^1$ is positive and the solute is concentrated at the interface. Conversely, as with electrolyte solutions, if $dy/dC$ is positive, then $\Gamma_2^1$ is negative, meaning that the surface concentration of electrolyte is less than it is in solution. In the case of 1 $M$ sodium chloride, the negative surface excess is equivalent to a surface layer of pure water about one molecule thick.

In sufficiently dilute solution, the surface tension will approach proportionality to concentration, that is,

$$\gamma = \gamma^0 - bC,$$  \hspace{1cm} (9-147)

where $\gamma^0$ is the surface tension of the pure solvent. The product $C dy/dC$ is now
just \(-(\gamma^o - \gamma)\), so Eq. (9-146) reduces to

\[ \Gamma_s^1 = \frac{\gamma^o - \gamma}{RT}. \]

It is now convenient to introduce the quantity \(\pi\), called the surface pressure, and defined as

\[ \pi = \frac{\gamma^o - \gamma}{\sigma}. \] (9-148)

Also \(\Gamma_s^1 = 1/\sigma\), where \(\sigma\) is the area per mole. With these substitutions Eq. (9-146) becomes

\[ \pi\sigma = RT. \] (9-149)

This is the equation of state of a two-dimensional ideal gas! The film pressure does in fact correspond to a two-dimensional pressure. As illustrated in Fig. 9-27, if a flexible membrane separates pure solvent from solution, the floating barrier will experience a force \(\pi l\), where \(l\) is its length. Returning to the numerical example, the film pressure of a 0.05 m solution of phenol was given as 5.2 dyn cm\(^{-1}\). Again, this seems like a small number. The force is being exerted by a monolayer, however, and so we obtain the equivalent three-dimensional pressure by dividing by the depth of a molecule. In this case, the result is about \(5.2/(4 \times 10^{-8})\) or \(1.3 \times 10^8\) dyn cm\(^{-2}\), which corresponds to 130 atm. Thus the lateral compression on the monolayer is quite appreciable at the molecular level.

More generally, the Gibbs equation allows surface tension–concentration data to be translated into values of \(\pi\) versus \(\sigma\) and such plots often look much like the ones of \(P\) versus \(V\) for a nonideal gas. A two-dimensional van der Waals equation may be used, for example,

\[ \left(\pi + \frac{a}{\sigma^2}\right)(\sigma - b) = RT. \] (9-150)

Such films are known as Gibbs monolayers, since they are normally studied through use of the Gibbs equation.

If the surfactant is quite insoluble, then, as mentioned in Section 9-CN-1, it may be spread directly onto the liquid surface, usually one of water. Now \(\Gamma_s^1\) is known directly, as the amount placed on a known area of surface, and hence \(\sigma\) also is known. The film pressure is usually obtained from surface tension measurements, by the Wilhelmy slide method, although the force on a floating barrier may also be measured directly. The data are again usually reported as \(\pi\) versus \(\sigma\) plots.

Such plots may resemble those for bulk phases. As illustrated in Fig. 9-28, a film or monolayer of stearic acid has a very low compressibility; the \(\pi\) versus \(\sigma\) plot extrapolates to an area of about 22 Å\(^2\) per molecule, corresponding to close-
packing, and in general the film behaves as though it were a two-dimensional solid. On the other hand, the bulky tri-\(p\)-cresyl phosphate molecule forms a highly compressible film and one whose properties are like those of a low-density but viscous fluid. Note that nonideal two-dimensional mixtures are possible! The mixed film shows a \(\pi-\sigma\) behavior that departs significantly from that expected for an ideal solution. At low film pressures the tri-\(p\)-cresyl phosphate seems to dominate, whereas at high film pressures the mixed film behaves more like stearic acid.

**General References**

General treatises cited in Chapter 1.


**Cited References**


EXERCISES

Take as exact numbers given to one significant figure.

9-1 Assume that benzene and toluene form ideal solutions; the normal boiling point of benzene is 80°C and at this temperature the vapor pressure of toluene is 350 Torr. Calculate the separate partial pressures and the total vapor pressure at 80°C of a solution of \( x_b = 0.2 \). What composition of solution would boil at 80°C under the reduced pressure of 500 Torr?

\[
\begin{align*}
A_n &\ s. \ P_b = 152 \text{ Torr}, P_t = 280 \text{ Torr}, P_{tot} = 432 \text{ Torr}; x_t = 0.634.
\end{align*}
\]

9-2 Calculate the composition of the vapor in equilibrium with each of the two solutions of Exercise 9-1.

\[
\begin{align*}
A_n &\ s. \ y_b = 0.352, y_b = 0.556.
\end{align*}
\]

9-3 The vapor pressure of propyl acetate (pa) is 21.5 Torr at 17°C. A mixture of 0.2 mole of pa with 0.5 mole of ipa (isopropyl acetate) has a total vapor pressure of 34.7 Torr at 17°C. Assuming ideal solution behavior, calculate the vapor pressure of ipa at this temperature and the composition of the vapor above the solution.

\[
\begin{align*}
A_n &\ s. \ P_{ipa}^{\circ} = 40.0 \text{ Torr}, y_{pa} = 0.177.
\end{align*}
\]

9-4 The molecular weight of substance B is 70 g mole\(^{-1}\) and dissolving 0.300 g in 2 mole of nonvolatile solvent A gives a solution of vapor pressure 2.50 Torr. Calculate the Henry's law constant for B dissolved in A.

\[
\begin{align*}
A_n &\ s. \ 1170 \text{ Torr}.
\end{align*}
\]

9-5 The Henry's law constant for Kr in water is 2.00 \( \times 10^4 \) atm at 20°C. How many grams of Kr should dissolve in 1000 g of water at this temperature under pressure of 30 atm?

\[
\begin{align*}
A_n &\ s. \ 6.99 \text{ g}.
\end{align*}
\]

9-6 The Henry's law constant for H\(_2\) in water is 5.51 \( \times 10^7 \) Torr at 30°C. How many cubic centimeters of H\(_2\), measured at 30°C and the pressure used, should dissolve in 1 cm\(^3\) of water?

\[
\begin{align*}
A_n &\ s. \ 0.0191 \text{ cm}^3 \text{ of H}_2 \text{ per cm}^3 \text{ of water}.
\end{align*}
\]

9-7 Two mole of toluene and 8 mole of benzene are introduced into a vessel at 20°C and the total vapor pressure is found to be 60 Torr. Using Fig. 9-2(b), estimate the number of moles of vapor formed and the compositions of the liquid and vapor phases present.

\[
\begin{align*}
A_n &\ s. \ x_t = 0.35, y_t = 0.18, n_v = 8.8.
\end{align*}
\]

9-8 Water and toluene are essentially immiscible. The vapor pressures of the pure liquids at 90°C are 525 and 400 Torr, respectively. Calculate the composition of the vapor above a mixture of the two liquids.

\[
\begin{align*}
A_n &\ s. \ x_t = 0.43.
\end{align*}
\]

9-9 Isopropyl alcohol (ipa) and benzene (b) form nonideal solutions. If \( x_{ipa} \) is 0.059, the partial pressure of ipa is 12.9 Torr at 25°C. The vapor pressures of the pure liquids are 44.0 and 94.4 Torr, respectively. Calculate \( k_{ipa} \) and \( \alpha \) and estimate \( k_b \).

\[
\begin{align*}
A_n &\ s. \ k_{ipa} = 269 \text{ Torr}, \alpha = 1.81, k_b = 577 \text{ Torr}.
\end{align*}
\]

9-10 Calculate the free energy, enthalpy, and entropy of mixing for the process 0.2 O\(_2\)(1 atm, 25°C) + 0.8 N\(_2\)(1 atm, 25°C) = air(1 atm, 25°C). Assume ideal gas behavior.

\[
\begin{align*}
A_n &\ s. \ \Delta G_M = -297 \text{ cal}, \Delta H_M = 0, \Delta S_M = 0.994 \text{ cal K}^{-1}.
\end{align*}
\]
9-11 Assuming ideal solution behavior, calculate the free energy, enthalpy, and entropy of mixing of 0.25 mole of benzene with 0.50 mole of toluene at 30°C.

\[ \Delta G_m = -288 \text{ cal} \]
\[ \Delta H_m = 0 \]
\[ \Delta S_m = 0.949 \text{ cal K}^{-1} \]

9-12 Determine the activity and the activity coefficient of ipa in the solution of Exercise 9-9 using pure ipa as the standard state.

\[ a_{ipa} = 0.293 \]
\[ \gamma_{ipa} = 4.97 \]

9-13 Using the data of Exercise 9-9, calculate the excess free energy of mixing one mole of ipa with sufficient benzene to form a solution of \( x_{ipa} = 0.059 \) at 25°C.

\[ \Delta G_m = 1009 \text{ cal} \]

9-14 A certain amount of an ethanol–benzene solution of \( x_b = 0.20 \) is introduced into a flask; some of it vaporizes and the residual solution has a total vapor pressure of 750 Torr at 72.5°C. Find the compositions of the final solution and of the vapor phase in equilibrium with it at 72.5°C, and the percent of original solution that vaporized.

\[ x_b(\text{final}) = 0.10, \gamma_b = 0.30, 50\% \]

9-15 The final solution as in Exercise 9-14 is boiled in an open flask until the boiling point (under 750 Torr pressure) rises from 72.5°C to 75°C. Estimate the number of moles of liquid remaining per mole originally present.

\[ \text{Ans.} \ 0.71 \]

9-16 In a steam distillation of an insoluble oil the boiling point of the mixture is found to be 95°C and the distillate is found to contain 80% by weight of the oil. Atmospheric pressure is 755 Torr, and the vapor pressure of water at 95°C is 634 Torr. Calculate the molecular weight of the oil.

\[ \text{Ans.} \ 377 \text{ g mole}^{-1} \]

9-17 One hundred grams of a 60 mole % solution of phenol in water \( x_p = 0.60 \) initially at 80°C is cooled. (a) At what temperature will the solution become turbid? (b) What are the amounts and compositions of the phases present at 40°C? (The abscissa scale of Fig. 9-20(a) is in mole fraction.)

\[ \text{Ans.} \ (a) \ 55°C; \ (b) \ 95 \text{ g of phenol-rich phase with } x_p = 0.67 \]
\[ \text{and 5 g of water-rich phase with } x_p = 0.10. \]

9-18 (a) Triethylamine is added to 0.2 mole of water at 30°C until the solution just becomes turbid. How many moles are added? (b) Water is added to 0.3 mole of triethylamine at 30°C until the solution just becomes turbid. How many moles are added? (c) The solutions of (a) and (b) are combined. Give the compositions and amounts of the phases present.

\[ \text{Ans.} \ (a) \ 0.013 \text{ mole}; \ (b) \ 0.013 \text{ mole}; \ (c) \ 0.31 \text{ mole of triethylamine-rich phase with } x_t = 0.96 \]
\[ \text{and 0.21 mole of water-rich phase with } x_t = 0.06. \]

**PROBLEMS**

9-1 Calculate the solubility of chloroform in water at 98.6°F and 0.1 atm pressure assuming that Raoult’s law is obeyed; the vapor pressure of chloroform is 320 mm Hg at this temperature.
9-2 The vapor pressures of ethylene bromide and propylene bromide are 172 and 127 Torr, respectively, at 80°C; the compounds form nearly ideal solutions. Thirty grams of ethylene bromide and 25 g of propylene bromide are equilibrated at 80°C and a total pressure of 150 Torr. Calculate the composition of the liquid phase and the moles of each compound in the vapor phase.

9-3 Calculate the minimum work to "unmix" air, that is, to obtain 80 liter of pure nitrogen and 20 liter of pure oxygen, each at 25°C and 1 atm pressure, from 100 liter of air at this pressure and temperature. The ∆H_M may be assumed to be zero.

9-4 Calculate the total vapor pressure of solutions of toluene and benzene of compositions 0.2, 0.4, 0.6, and 0.8 (mole fraction) for the temperatures 85, 95, 100, 105°C. Assume Raoult's law to hold, and look up the necessary data. Plot the results as P (in atm) versus mole fraction and also calculate and plot the composition of vapor in equilibrium with each of the solutions at each temperature. Construct from this information a plot of the normal boiling point versus composition. Give also the vapor composition line.

A small amount of the vapor in equilibrium at 95°C with solution of x_t = 0.5 condenses. What is the vapor pressure of the condensate at 95°C? What is the boiling point of the original solution? Of the condensate? What is the composition of the vapor in equilibrium with the original solution at 95°C and with the condensate at 95°C? If the original solution were boiled in an open vessel until the boiling point rose 5°C, what would be the composition of the remaining solution and the number of moles of each component present in it, assuming that the original solution contained one mole of benzene?

9-5 Liquids A and B form an ideal solution. A solution of mole fraction x_A = 0.4 is treated as follows: (a) 0.30 mole is introduced into an evacuated vessel of volume such that, at 25°C, 15% of the liquid (mole %) evaporates. The final total pressure is 82.2 Torr at 25°C. (b) A portion of the equilibrium vapor is drawn off, condensed completely, and then found to have a total vapor pressure of 92.3 Torr at 25°C. Calculate the vapor pressures of pure liquids A and B at 25°C.

9-6 An aqueous solution of ammonia at 20°C has x_H = 0.0300 and the equilibrium water and ammonia vapor pressures are 17.5 and 18.2 Torr, respectively. A vessel of two liters capacity contains one liter of water, and 1.35 mole of ammonia is introduced. Calculate the total equilibrium pressure in the vessel.

9-7 Para-xylene and toluene form solutions which can be regarded as ideal. The vapor pressure of pure p-xylene is 34.0 mm and of pure toluene is 59.1 mm at 40°C. A liquid mixture of the two, containing 0.002 mole of each, is introduced in a previously evacuated 1-liter flask at 40°C. Neglecting the volume of the liquid phase in comparison with 1 liter, calculate the equilibrium composition of the liquid which remains after vaporization has occurred.

9-8 A solution of 1 mole of NaOH in 4.559 mole of water has a vapor pressure of 4.474 Torr at 15°C, whereas the vapor pressure of pure water is 12.788 Torr at 15°C. What is (a) the activity of water in the solution (that is, the effective mole fraction) and (b) the difference between the chemical potential (that is, molar free energy) of the water in the solution and in pure water (Fricke, 1929)?

9-9 The total vapor pressure of a 5 mole % solution of NH_4 in water at 20°C is 51.78 Torr and the vapor pressure of pure water at the same temperature is 17.36 Torr. Apply Henry's and Raoult's laws to calculate the partial pressures and total vapor pressure of a 2 mole % solution at the same temperature.

9-10 A solution containing 20 mole % of phenol in water is cooled to 50°C and the phenol-rich layer which separates out is drawn off. This phenol-rich layer is then cooled to 30°C, and of the two layers present, the one richest in phenol is again drawn off. If 100 g of original solution were used, how many grams of the final phenol-rich layer are obtained and what is the composition of this layer?
Suppose that a liquid A is miscible with a liquid B to the extent of 15 mole % and that B is miscible with A to the extent of 25 mole %. Construct the phase diagram analogous to Fig. 9-8 for this system and label each phase region.

The accompanying diagram shows the activity coefficients versus composition for carbon disulfide-acetone solutions. (a) Calculate and plot the corresponding vapor pressure diagram. (b) Calculate and plot the partial molal free energies and the total excess free energy as functions of solution composition. Assume 25°C; look up necessary $P^o$ values.

Construct an accurate diagram of the type of Fig. 9-8 for the water–toluene system at 90°C. (Use the data of Exercise 9-8.) Two-tenths mole of water and 0.3 mole of toluene are placed in a piston and cylinder arrangement kept at 90°C; the mixture is initially gaseous. The piston is gradually depressed so as to compress the mixture. At what pressure will liquid begin to condense? Which liquid? What will be the composition of the last vapor to condense as the pressure is further increased? What will this pressure be?

Demonstrate that the critical temperature for a system obeying the Margules equations is one for which $\alpha = 2$.

Complete Fig. 9-11 by adding the curves for $\gamma_a$ and $\gamma_c$ calculated from the Margules relationships. Assume the limiting activity coefficients to be 0.467 for both acetone and chloroform in obtaining your value for $\alpha$.

The International Critical Tables (1928) give the following data for the partial pressure of acetic acid above acetic acid–benzene solutions at 50°C:

<table>
<thead>
<tr>
<th>$x_a$ (%)</th>
<th>1.60</th>
<th>4.39</th>
<th>8.35</th>
<th>11.38</th>
<th>17.14</th>
<th>29.79</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P$ (Torr)</td>
<td>3.63</td>
<td>7.25</td>
<td>11.51</td>
<td>14.2</td>
<td>18.4</td>
<td>24.8</td>
</tr>
<tr>
<td>$x_a$ (%)</td>
<td>36.96</td>
<td>58.34</td>
<td>66.04</td>
<td>84.35</td>
<td>99.31</td>
<td></td>
</tr>
<tr>
<td>$P$ (Torr)</td>
<td>28.7</td>
<td>36.3</td>
<td>40.2</td>
<td>50.7</td>
<td>54.7</td>
<td></td>
</tr>
</tbody>
</table>

Calculate and plot the activities and activity coefficients of acetic acid as a function of composition. Apply the method of Fig. 9-12 to obtain the activities and activity coefficients of benzene for several concentrations and plot these results as well.

Calculate $\Delta G_M$ for various compositions of the acetone-chloroform system at 35°C and plot the results.
9-18 Referring to Eq. (9-123), show that no error is introduced by writing \( \frac{\partial V_{av}}{\partial x_2} \) as \( dV_{av}/dx_2 \). State any assumptions explicitly.

9-19 An interesting relationship for ideal gas mixtures is

\[
\frac{\partial P}{\partial n_i}_{T,P,n_j} = \frac{RT}{v} (1 - x_i).
\]  

Derive this equation. [It may be used in an alternative derivation of Eq. (9-36).]

SPECIAL TOPICS PROBLEMS

9-1 The partial molal volumes for water and ethanol at 20°C are 17 and 57 cm\(^3\) mole\(^{-1}\), respectively, for a solution of \( x_e = 0.4 \). Calculate the volume change on mixing sufficient ethanol with two moles of water to give this final composition.

9-2 The apparent molar volume \( \phi_2 \) of a solute is defined as \( \phi_2 = (V - n_x V_1)/n_2 \), where \( V_1 \) is the molar volume of the pure solvent. It is found that for solutions of CaCl\(_2\), \( \phi_2 \) (in cm\(^3\)) is closely approximated by \( \phi_2 = 10.15 + 3.52 m - 1.62 m^2 \), where \( m \) is the molality, or number of moles of CaCl\(_2\) per 1000 g of water. Derive the expression for \( V \) as a function of \( m \) and thence an expression for \( \bar{V}_2 \) as a function of \( m \). Calculate \( \bar{V}_1 \) and \( \bar{V}_2 \) for an infinitely dilute solution and for a 0.7 \( m \) solution. Assume 25°C.

9-3 Mixtures of liquids A and B obey the Margules equations with an \( a \) of 2.2 at 25°C. Make an accurate plot analogous to Fig. 9-24. Construct the vapor pressure diagram (in the manner of Fig. 9-8) assuming that \( P_A^o = 200 \) Torr and \( P_B^o = 400 \) Torr, and label the phase regions. The constant \( a \) often varies inversely as \( T \). Calculate the consolute temperature for this system.

9-4 The density of aqueous acetic acid solutions varies with composition at 20°C as follows:

<table>
<thead>
<tr>
<th>wt % acetic acid</th>
<th>0</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>density (g cm(^{-3}))</td>
<td>0.9982</td>
<td>1.0125</td>
<td>1.0263</td>
<td>1.0384</td>
<td>1.0488</td>
<td>1.0575</td>
</tr>
<tr>
<td>density (g cm(^{-3}))</td>
<td>1.0642</td>
<td>1.0685</td>
<td>1.0700</td>
<td>1.0661</td>
<td>1.0498</td>
<td></td>
</tr>
<tr>
<td>wt % acetic acid:</td>
<td>60</td>
<td>70</td>
<td>80</td>
<td>90</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

Calculate \( V_{av} \) and plot it as a function of mole fraction of acetic acid. Determine the partial molar volumes of water and of acetic acid for nearly pure water, nearly pure acetic acid, and for several intermediate compositions. Plot these values against composition.

9-5 Show that \( \bar{Q}_2 = \phi - x_1 (d\phi/dx_1) \).

9-6 For the process

\[
\text{NaCl (solution, } m \text{) } \rightarrow \text{NaCl (infinite dilution)},
\]

\(-\Delta H \) has been found to vary as follows at 25°C:

<table>
<thead>
<tr>
<th>( m )</th>
<th>0.2</th>
<th>1.0</th>
<th>2.0</th>
<th>3.0</th>
<th>4.0</th>
<th>5.0</th>
<th>6.12</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-\Delta H ) (cal mole(^{-1}))</td>
<td>90</td>
<td>-23</td>
<td>-177</td>
<td>-304</td>
<td>-395</td>
<td>-453</td>
<td>-483</td>
</tr>
</tbody>
</table>

Calculate \( L_1 \) and \( L_2 \) for 2 \( m \) NaCl and for the saturated solution (6.12 \( m \)), and find the value for \( \Delta H \) for the process

\( \text{NaCl(s) + water } \rightarrow \text{saturated solution} \)

(remember Table 5-3).

9-7 Plot the data of Table 9-1 in the form of Fig. 9-24 and calculate \( \mu_{1(\text{soln})} \) and \( \mu_{2(\text{soln})} \) for solutions of \( x_1 = 0.2 \) and \( x_1 = 0.8 \) (species 1 being acetone).
9-8 The surface tension of an aqueous solution varies with concentration according to the equation \( \gamma = 72 - 500C \), provided that \( C \) is less than 0.05. Calculate the surface excess of solute for a 0.02 \( M \) solution. Assume 25°C.

9-9 Find the expression for \( \gamma \) as a function of \( C \) if \( \Gamma = \frac{aC}{1 + bC} \), where \( a \) and \( b \) are constants.

9-10 Find the expression for \( \Gamma \) as a function of \( C \) if Eq. (9-150) is obeyed.