

**Table 14.2**  
Dependence of azeotropic temperature and composition on pressure

Pressure/mmHg	Mass % HCl	$t_b/^{\circ}\text{C}$
500	20.916	97.578
700	20.360	106.424
760	20.222	108.584
800	20.155	110.007

W. D. Bonner, R. E. Wallace, *J. Amer. Chem. Soc.* **52**:1747 (1930).

## 14.10 THE IDEAL DILUTE SOLUTION

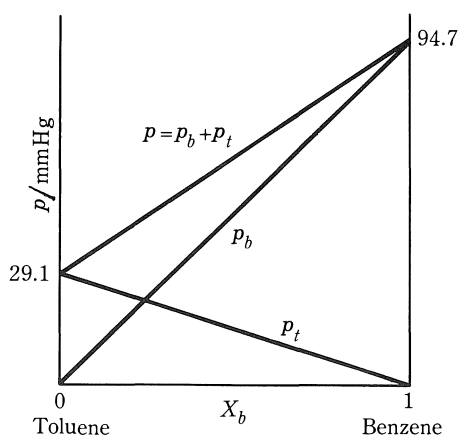
The rigid requirement of the ideal solution that every component obey Raoult's law over the entire range of composition is relaxed in the definition of the *ideal dilute solution*. To arrive at the laws governing dilute solutions, we must examine the experimental behavior of these solutions. The vapor-pressure curves for three systems are described below.

### 14.10.1 Benzene-Toluene

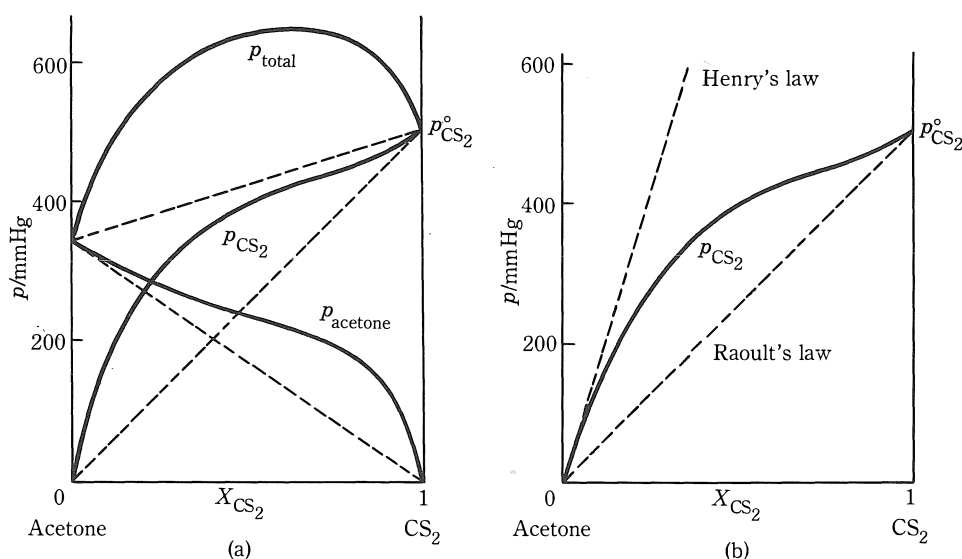
Figure 14.11 shows the vapor pressure versus mole fraction of benzene for the benzene-toluene system, which behaves ideally to a good degree of accuracy over the entire range of composition. The partial pressures of benzene and toluene, also shown in the figure, are linear functions of the mole fraction of benzene, since Raoult's law is obeyed.

### 14.10.2 Acetone-Carbon Disulfide

Figure 14.12(a) shows the partial-pressure curves and the total vapor pressure of mixtures of carbon disulfide and acetone. In this system the individual partial-pressure curves fall well above the Raoult's law predictions indicated by the dashed lines. The system exhibits positive deviations from Raoult's law. The total vapor pressure exhibits a maximum that lies above the vapor pressure of either component.



**Figure 14.11** Vapor pressures in the benzene-toluene system.



**Figure 14.12** Vapor pressure in the acetone-carbon disulfide system (35.17 °C).  
[J. v. Zawidski, *Z. physik Chem.*, **35**:129 (1900).]

Figure 14.12(b) displays another interesting feature of this system. In this figure only the partial pressure of carbon disulfide is shown; in the region near  $X_{CS_2} = 1$ , when CS<sub>2</sub> is the solvent, the partial-pressure curve is tangent to the Raoult's law line. However, in the region near  $X_{CS_2} = 0$ , when CS<sub>2</sub> is the solute present in low concentration, the partial-pressure curve is linear.

$$p_{CS_2} = K_{CS_2} X_{CS_2}, \quad (14.14)$$

where  $K_{CS_2}$  is a constant. The slope of the line in this region is different from the Raoult's law slope. The solute obeys *Henry's law*, Eq. (14.14), where  $K_{CS_2}$  is the Henry's law constant. Inspection of the partial-pressure curve of the acetone discloses the same type of behavior:

$$\begin{aligned} p_{acetone} &= X_{acetone} p_{acetone}^\circ && \text{near } X_{acetone} = 1; \\ p_{acetone} &= K_{acetone} X_{acetone} && \text{near } X_{acetone} = 0. \end{aligned}$$

Note that if the solution were ideal, then  $K$  would equal  $p^\circ$  and both Henry's law and Raoult's law would convey the same information.

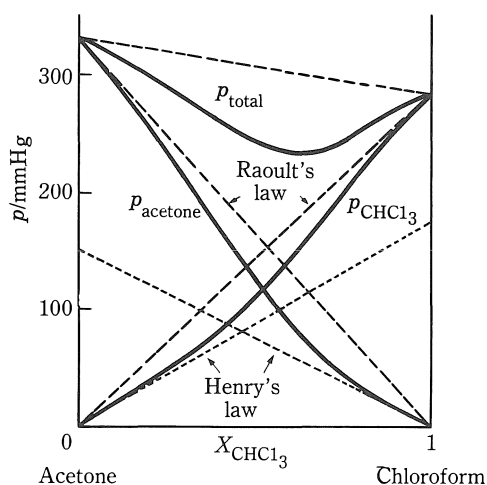
### 14.10.3 Acetone-Chloroform

In the acetone-chloroform system shown in Fig. 14.13, the vapor pressure curves fall below the Raoult's law predictions. This system exhibits *negative* deviations from Raoult's law. The total vapor pressure has a minimum value that lies below the vapor pressure of either of the pure components. The Henry's law lines, the fine dashed lines in the figure, also lie below the Raoult's law lines for this system.

Algebraically, we can express the properties of the ideal dilute solution by the following equations:

$$\text{Solvent (Raoult's law):} \quad p_1 = x_1 p_1^\circ, \quad (14.15)$$

$$\text{Solutes (Henry's law):} \quad p_j = K_j x_j, \quad (14.16)$$



**Figure 14.13** Vapor pressure in the acetone–chloroform system (35.17°C). [J. v. Zawidski, *Z. physik Chem.*, **35**:129 (1900).]

where the subscript  $j$  denotes any of the solutes, and the subscript 1 denotes the solvent. All real solutions approach the behavior described by Eqs. (14.15) and (14.16), provided that the solution is sufficiently dilute. The same is true if several solutes are present, but the solution must be dilute in all solutes; each solute has a different value of  $K_j$ .

#### 14.11 THE CHEMICAL POTENTIALS IN THE IDEAL DILUTE SOLUTION

Since the solvent follows Raoult's law, the chemical potential of the solvent is given by Eq. (14.3), repeated here for easy comparison:

$$\mu_1 = \mu_1^\circ(T, p) + RT \ln x_1.$$

For the solutes we require, as usual, equality of the chemical potential in the liquid,  $\mu_j(l)$ , with that in the gas phase,  $\mu_j(g)$ :

$$\mu_j(l) = \mu_j(g) = \mu_j^\circ(g) + RT \ln p_j.$$

Using Henry's law, Eq. (14.16), for  $p_j$ , this becomes

$$\mu_j(l) = \mu_j^\circ(g) + RT \ln K_j + RT \ln x_j$$

We define a standard free energy,  $\mu_j^*(l)$ , by

$$\mu_j^*(l) = \mu_j^\circ(g) + RT \ln K_j \quad (14.17)$$

where  $\mu_j^*$  is a function of temperature and pressure but not of composition. The final expression for  $\mu_j$  in the liquid is

$$\mu_j = \mu_j^* + RT \ln x_j \quad (14.18)$$

According to Eq. (14.18),  $\mu_j^*$  is the chemical potential the solute  $j$  would have in the hypothetical state in which  $x_j = 1$  if Henry's law were obeyed over the entire range,  $0 \leq x_j \leq 1$ .

The concept of the ideal dilute solution is extended to include nonvolatile solutes by requiring that the chemical potential of such solutes also have the form given by Eq. (14.18).

The mole fractions,  $x_j$ , often are not convenient measures for the concentration of solutes in dilute solution. Molalities,  $m_j$ , and molarities,  $c_j$ , are more commonly used. We can use Eq. (14.18) to obtain expressions for the chemical potential in terms of  $m_j$  or  $c_j$ . To do this we must write  $x_j$  in terms of  $m_j$  or  $c_j$ .

By definition,  $x_j = n_j/(n + \sum_j n_j)$ , where  $n$  is the number of moles of solvent. Also by definition, the molality of  $j$  is the number of moles of  $j$  per unit mass (1 kg) of solvent. Thus, if  $M$  is the molar mass (kg/mol) of the solvent, we have

$$m_j = \frac{n_j}{nM} \quad \text{or} \quad n_j = nMm_j. \quad (14.19)$$

Using this result for  $n_j$  in the expression for  $x_j$ , we obtain

$$x_j = \frac{Mm_j}{1 + Mm}, \quad (14.20)$$

where  $m = \sum_j m_j$ , the total molality of all the solutes. In dilute solution as  $m$  approaches zero, we have

$$\lim_{m \rightarrow 0} \left( \frac{x_j}{m_j} \right) = \lim_{m \rightarrow 0} \frac{M}{1 + mM} = M,$$

so that near  $m = 0$ ,

$$x_j = Mm_j. \quad (14.21)$$

This can be written in the form

$$x_j = Mm^\circ \left( \frac{m_j}{m^\circ} \right) \quad (14.22)$$

where  $m^\circ$  is the standard molal concentration,  $m^\circ = 1$  mol/kg. This value for  $x_j$  may be used in Eq. (14.18), which becomes

$$\mu_j = \mu_j^* + RT \ln Mm^\circ + RT \ln \left( \frac{m_j}{m^\circ} \right)$$

Defining  $\mu_j^{**} = \mu_j^* + RT \ln Mm^\circ$ , this becomes

$$\mu_j = \mu_j^{**} + RT \ln m_j \quad (14.23)$$

in which we understand  $m_j$  as an abbreviation for the pure number,  $m_j/(1 \text{ mol/kg})$ . Equation (14.23) expresses the  $\mu_j$  in a dilute solution as a convenient function of  $m_j$ . The standard value,  $\mu_j^{**}$ , is the value  $\mu_j$  would have in the hypothetical state of unit molality if the solution had the properties of the ideal dilute solution in the entire range,  $0 \leq m_j \leq 1$ .

To express  $\mu_j$  in terms of  $c_j$ , we first establish the relation between  $m_j$  and  $\tilde{c}_j$ , the concentration in SI units, mol/m<sup>3</sup>. By definition

$$\tilde{c}_j = \frac{n_j}{V} = \frac{nMm_j}{V}$$

If  $\rho_s$  is the density of the solution, then  $V = w/\rho_s$ , where the mass of the solution,  $w = nM + \sum_j n_j M_j = nM + \sum_j nMm_j M_j$ . Thus

$$V = \frac{nM}{\rho_s} \left( 1 + \sum_j m_j M_j \right)$$

and

$$\tilde{c}_j = \frac{\rho_s m_j}{1 + \sum_j m_j M_j}. \quad (14.24)$$

As all the  $m_j$  approach zero we have

$$\lim_{m_j \rightarrow 0} \left( \frac{\tilde{c}_j}{m_j} \right) = \lim_{m_j \rightarrow 0} \frac{\rho_s}{1 + \sum_j m_j M_j} = \rho,$$

where  $\rho$  is the density of the pure solvent. Thus, in dilute solution,

$$\tilde{c}_j = \rho m_j \quad \text{or} \quad m_j = \frac{\tilde{c}_j}{\rho} \quad (14.25)$$

Rewriting to introduce the dimensionless ratios, Eq. (14.25) becomes

$$\frac{m_j}{m^\circ} = \frac{\tilde{c}^\circ}{\rho m^\circ} \left( \frac{\tilde{c}_j}{\tilde{c}^\circ} \right) \quad \text{or} \quad \frac{m_j}{m^\circ} = \frac{\tilde{c}^\circ}{\rho m^\circ} \left( \frac{c_j}{c^\circ} \right),$$

since  $\tilde{c}_j/\tilde{c}^\circ = c_j/c^\circ$ . Putting this value of  $m_j/m^\circ$  in Eq. (14.23) yields

$$\mu_j = \mu_j^{**} + RT \ln \left( \frac{\tilde{c}^\circ}{\rho m^\circ} \right) + RT \ln \frac{c_j}{c^\circ}.$$

This can be written

$$\mu_j = \mu_j^\square + RT \ln c_j, \quad (14.26)$$

in which we understand  $c_j$  as an abbreviation for the pure number,  $c_j/(1 \text{ mol/L})$ . In Eq. (14.26) we have set

$$\mu_j^\square = \mu_j^{**} + RT \ln \left( \frac{\tilde{c}^\circ}{\rho m^\circ} \right). \quad (14.27)$$

Equation (14.26) relates  $\mu_j$  in dilute solution to  $c_j$ , the concentration in mol/L. It is not as commonly used as Eq. (14.23);  $\mu_j^\square$  is the chemical potential the solute would have at a concentration of 1 mol/L if the solution behaved ideally up to that concentration.

The difference between  $\mu_j^\square$  and  $\mu_j^{**}$  is not very large. Since  $c^\circ = 1 \text{ mol/L}$ , the corresponding value of  $\tilde{c}^\circ = 10^3 \text{ mol/m}^3$ . Also,  $m^\circ = 1 \text{ mol/kg}$ , and for water at 25 °C,  $\rho = 997.044 \text{ kg/m}^3$ . Then

$$\frac{\tilde{c}^\circ}{\rho m^\circ} = \frac{10^3 \text{ mol/m}^3}{(997.044 \text{ kg/m}^3)(1 \text{ mol/kg})} = 1.002965.$$

The second term in Eq. (14.27) becomes  $(8.314 \text{ J/K mol})(298.15 \text{ K}) \ln(1.002965) = 7.339 \text{ J/mol}$ . In most cases, this is less than the uncertainties in the experimental values so that the difference between the  $m_j$  and  $c_j$  standard states can be ignored.

## 14.12 HENRY'S LAW AND THE SOLUBILITY OF GASES

Henry's law, Eq. (14.16), relates the partial pressure of the solute in the vapor phase to the mole fraction of the solute in the solution. Viewing the relation in another way, Henry's law relates the equilibrium mole fraction, the solubility of  $j$  in the solution, to the partial pressure of  $j$  in the vapor:

$$x_j = \frac{1}{K_j} p_j. \quad (14.28)$$

Equation (14.28) states that the solubility  $x_j$  of a volatile constituent is proportional to the partial pressure of that constituent in the gaseous phase in equilibrium with the liquid. Equation (14.28) is used to correlate the data on solubility of gases in liquids. If the solvent and gas do not react chemically, the solubility of gases in liquids is usually small and the condition of diluteness is fulfilled. Here we have another example of the physical significance of the partial pressure.

The solubility of gases is often expressed as the Bunsen absorption coefficient,  $\alpha$ , which is the volume of gas, measured at 0 °C and 1 atm, dissolved by unit volume of solvent if the partial pressure of the gas is 1 atm.

$$\alpha_j = \frac{V_j^\circ(\text{g})}{V(\text{l})}, \quad (14.29)$$

but  $V_j^\circ(\text{g}) = n_j^\circ RT_0/p_0$ , while the volume of the solvent is  $V(\text{l}) = nM/\rho$ , where  $n$  is the number of moles of solvent,  $M$  its molar mass, and  $\rho$ , the density. Thus

$$\alpha_j = \frac{n_j^\circ RT_0/p_0}{nM/\rho}. \quad (14.30)$$

When the partial pressure of the gas,  $p_j = p^\circ = 1$  atm, the solubility by Henry's law is  $x_j^\circ$ ,

$$x_j^\circ = \frac{n_j^\circ}{n + n_j^\circ} = \frac{1}{K_j}$$

If the solution is dilute,  $n_j^\circ \ll n$  and we have

$$\frac{n_j^\circ}{n} = \frac{1}{K_j}. \quad (14.31)$$

Using this value of  $n_j^\circ/n$  in Eq. (14.30) brings it to

$$\alpha_j K_j = \left(\frac{RT_0}{p_0}\right) \left(\frac{\rho}{M}\right) = (0.022414 \text{ m}^3/\text{mol}) \frac{\rho}{M}, \quad (14.32)$$

which is the relation between the Henry's law constant  $K_j$  and the Bunsen absorption coefficient  $\alpha_j$ ; knowing one, we can calculate the other. The solubility of the gas in moles per unit volume of solvent,  $n_j^\circ/(nM/\rho)$ , is directly proportional to  $\alpha_j$ , Eq. (14.30); this makes  $\alpha_j$  more convenient than  $K_j$  for the discussion of solubility.

Some values of  $\alpha$  for various gases in water are given in Table 14.3. Note the increase in  $\alpha$  with increase in boiling point of the gas.

**Table 14.3**  
Bunsen absorption coefficients  
in water at 25°C

Gas	$t_b/^\circ\text{C}$	$\alpha$
Helium	−268.9	0.0087
Hydrogen	−252.8	0.0175
Nitrogen	−195.8	0.0143
Oxygen	−182.96	0.0283
Methane	−161.5	0.0300
Ethane	−88.3	0.0410

### 14.13 DISTRIBUTION OF A SOLUTE BETWEEN TWO SOLVENTS

If a dilute solution of iodine in water is shaken with carbon tetrachloride, the iodine is distributed between the two immiscible solvents. If  $\mu$  and  $\mu'$  are the chemical potentials of iodine in water and carbon tetrachloride, respectively, then at equilibrium  $\mu = \mu'$ . If both solutions are ideal dilute solutions, then, choosing Eq. (14.18) to express  $\mu$  and  $\mu'$ , the equilibrium condition becomes  $\mu^* + RT \ln x = \mu'^* + RT \ln x'$ , which can be rearranged to

$$RT \ln \frac{x'}{x} = -(\mu'^* - \mu). \quad (14.33)$$

Since both  $\mu'^*$  and  $\mu^*$  are independent of composition, it follows that

$$\frac{x'}{x} = K, \quad (14.34)$$

where  $K$ , the distribution coefficient or partition coefficient, is independent of the concentration of iodine in the two layers. The quantity  $\mu'^* - \mu^*$  is the standard Gibbs energy change  $\Delta G^*$  for the transformation



Equation (14.33) becomes

$$RT \ln K = -\Delta G^*, \quad (14.35)$$

which is the usual relation between the standard Gibbs energy change and the equilibrium constant of a chemical reaction.

If the solutions are quite dilute, then the mole fractions are proportional to the molalities or the molarities; so we have

$$K' = \frac{m'}{m} \quad \text{and} \quad K'' = \frac{c'}{c}, \quad (14.36)$$

where  $K'$  and  $K''$  are independent of the concentrations in the two layers. Equation (14.36) was originally proposed by W. Nernst and is called the Nernst distribution law.

### 14.14 CHEMICAL EQUILIBRIUM IN THE IDEAL SOLUTION

In Section 11.7 it was shown that the condition of chemical equilibrium is

$$\left( \sum_i v_i \mu_i \right)_{eq} = 0, \quad (14.37)$$

the  $v_i$  being the stoichiometric coefficients. To apply this condition to chemical equilibrium in the ideal solution, we simply insert the proper form of the  $\mu_i$  from Eq. (14.3). This yields directly

$$\sum_i v_i \mu_i^\circ + RT \sum_i \ln (x_i)_e^{v_i} = 0,$$

which can be written in the usual way

$$\Delta G^\circ = -RT \ln K, \quad (14.38)$$

where  $\Delta G^\circ$  is the standard Gibbs energy change for the reaction, and  $K$  is the equilibrium