

## 16.8: When the Solute Obeys Henry's Law, the Solvent Obeys Raoult's Law

In Section 16.4, we conclude that any sufficiently dilute solute obeys Henry's law, and define a hypothetical, pure-liquid standard state that makes the solute activity equal to its mole fraction,  $\tilde{a}_A(P, y_A, y_B) = y_A$ . In Section 16.7, we find that the mole fractions and activities of the components of any binary solution are related by

$$y_A d \ln \tilde{a}_A + y_B d \ln \tilde{a}_B = 0.$$

For a solute that obeys Henry's law, we have

$$\begin{aligned} d \ln \tilde{a}_B &= - \left( \frac{y_A}{y_B} \right) d \ln y_A \\ &= - \left( \frac{y_A}{y_B} \right) (d \ln y_B) \left( \frac{d \ln y_A}{d \ln y_B} \right) \\ &= - \left( \frac{y_A}{y_B} \right) (d \ln y_B) \left( \frac{dy_A/y_A}{dy_B/y_B} \right) \\ &= - \left( \frac{y_A}{y_B} \right) (d \ln y_B) \left( \frac{-dy_B/y_B}{dy_B/y_B} \right) \\ &= d \ln y_B \end{aligned}$$

This result follows for any choice of standard state for the activity of solvent  $B$ . It is satisfied by  $\tilde{a}_B = ky_B$ , where  $k$  is a constant. It is valid even if  $A$  is completely nonvolatile. When gas-phase  $B$  behaves as an ideal gas, and we choose the ideal gas at  $P^\circ$  as the standard state for both gas- and solution-phase  $B$ , we have

$$\tilde{a}_B(\text{gas}) = f_B = P_B/P^\circ = x_B P/P^\circ$$

Since the standard states are the same, the fugacity and activity of  $B$  in solution are the same as they are in the gas phase above it. We have  $\tilde{a}_B(\text{solution}) = ky_B = x_B P/P^\circ$ . To find  $k$ , we consider the system comprised of pure  $B$ , for which  $y_B = x_B = 1$  and  $P = P_B^\star$ . Substituting, we find  $k = P_B^\star/P^\circ$ . With this value for  $k$ ,

$$\tilde{a}_B(\text{solution}) = P_B^\star y_B/P^\circ = x_B P/P^\circ$$

so that

$$y_B P_B^\star = x_B P.$$

This is **Raoult's law**.

*Thus when the solute obeys Henry's law and the solvent behaves as an ideal gas in the gas phase above its solution, the solvent obeys Raoult's law.*

Evidently the converse is also true. If the solvent obeys Raoult's law,  $y_B P_B^\star = x_B P$ . With pure ideal gas  $B$  as the standard state for  $B$  in both the gas phase and the solution phase, we have

$$\tilde{a}_B(\text{solution}) = \tilde{a}_B(\text{gas}) = f_B = P_B/P^\circ = x_B P/P^\circ = y_B (P_B^\star/P^\circ)$$

so that

$$d \ln \tilde{a}_B(\text{solution}) = d \ln y_B$$

From  $y_A d \ln \tilde{a}_A + y_B d \ln \tilde{a}_B = 0$  and  $d \ln \tilde{a}_B = d \ln y_B$ , we have

$$d \ln \tilde{a}_A = - \left( \frac{y_B}{y_A} \right) d \ln y_B = - \left( \frac{y_B}{y_A} \right) \left( \frac{dy_B}{y_B} \right) = \frac{dy_A}{y_A} = d \ln y_A$$

so that  $\tilde{a}_A(\text{solution}) = ky_A$ , where  $k$  is a constant. When we choose the standard state such that  $\tilde{a}_A(\text{ss, solution}) = 1$  when  $y_A = 1$ , we find  $k = 1$  and  $\tilde{a}_A(\text{solution}) = y_A$ . The activity of the solute is related to its fugacity and the fugacity of its standard state by

$$\tilde{a}_A(\text{solution}) = y_A = \frac{f_A(\text{solution})}{f_A(ss, \text{solution})}$$

When  $y_A = 1$ , the fugacity is that of the standard state, which is a system of the hypothetical pure liquid in equilibrium with its own ideal gas. Letting the pressure of this ideal gas be  $\kappa_A$ , we have  $f_A(ss, \text{solution}) = \kappa_A$ , so that  $f_A(\text{solution}) = \kappa_A y_A$ , which is equal to the fugacity of the gas with which it is at equilibrium. The fugacity of the ideal gas is  $x_A P$ , so that

$$x_A P = \kappa_A y_A.$$

This is Henry's law. Thus, if solvent  $B$  obeys Raoult's law, solute  $A$  obeys Henry's law.

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