

16.2: Raoult's Law and Ideal Solutions

An **ideal solution** is a homogeneous liquid solution that is at equilibrium with an ideal-gas solution in which the vapor pressure of each component satisfies Raoult's law¹. Since the gas is ideal, the partial pressure of A is $P_A = x_A P$. Raoult's law asserts a relationship among the gas- and solution-phase mole fractions of A , the vapor pressure of the pure liquid, and the pressure of the system:

$$P_A = x_A P = y_A P_A^*$$

(Raoult's law)

For a binary mixture of A and B that satisfies Raoult's law, we have also that $P_B = x_B P = y_B P_B^*$, and the total pressure becomes $P = P_A + P_B = y_A P_A^* + y_B P_B^*$. The lines sketched in Figure 4 show how P_A , P_B , and P vary with the solution-phase composition when the solution is ideal.

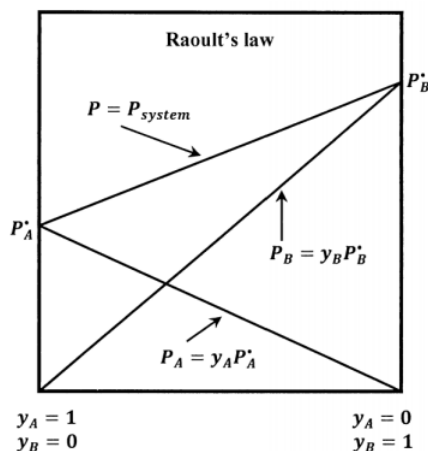


Figure 4. Equilibrium pressures over an ideal solution.

When the standard state for A in solution is taken to be pure liquid A at its equilibrium vapor pressure, substitution of Raoult's law into the results in Section 16.1 gives the activity of component A in an ideal solution as

$$\ln[\tilde{a}_A(P, y_A, y_B)] = \ln\left[\frac{x_A P}{P_A^*}\right] = \ln\left[\frac{y_A P_A^*}{P_A^*}\right] = \ln y_A$$

and

$$\tilde{a}_A(P, y_A, y_B) = y_A$$

(ideal solution, Raoult's law)

In general, the activity and chemical potential of a component depend on pressure. If the solution is ideal, we see that the system pressure is fixed by $P = y_A P_A^* + y_B P_B^*$, and the pure-component vapor pressures depend only on temperature. Since for the binary solution, $y_B = 1 - y_A$, we can write the chemical potential of component A as

$$\mu_A(P, y_A, y_B) = \mu_A(y_A) = \tilde{\mu}_A^o(\ell, P_A^*) + RT \ln y_A$$

(ideal solution)

We can also use relationships we develop earlier to find another representation for $\tilde{\mu}_A^o(\ell, P_A^*)$. The chemical potential of A in the liquid phase is the same as in the gas. Using the chemical potential for A in the gas phase that we find in Section 16.1, we have

$$\begin{aligned} \mu_A(P, y_A, y_B) &= \mu_A(g, P, x_A, x_B) = \Delta_f G^o(A, HIG^o) + RT \ln\left[\frac{x_A P}{P^o}\right] = \Delta_f G^o(A, HIG^o) + RT \ln\left[\frac{P_A^*}{P^o}\right] \\ &\quad + RT \ln y_A \end{aligned}$$

and hence,

$$\tilde{\mu}_A^o(\ell, P_A^*) = \Delta_f G^o(A, HIG^o) + RT \ln \left[\frac{P_A^*}{P^o} \right]$$

In [Section 15.4](#), we find, for an ideal gas,

$$\Delta_f G^o(A, HIG^o) + RT \ln \left[\frac{P_A^*}{P^o} \right] = \Delta_f G^o(A, \ell) + \int_{P^o}^{P_A^*} \bar{V}_A(\ell) dP$$

so that the chemical potential of the pure liquid at its vapor pressure is also given by

$$\tilde{\mu}_A^o(\ell, P_A^*) = \Delta_f G^o(A, \ell) + \int_{P^o}^{P_A^*} \bar{V}_A(\ell) dP$$

The integral is the difference between the Gibbs free energy of the pure liquid at its vapor pressure and that of the pure liquid at $P^o = 1 \text{ bar}$. Note that we can obtain the same result much more simply by integrating $(dG_A^*)_T = \bar{V}_A dP$ between the same two states. In [Section 15.3](#), we see that the value of the integral is usually negligible. To a good approximation, we have

$$\tilde{\mu}_A^o(\ell, P_A^*) \approx \Delta_f G^o(A, \ell)$$

(ideal solution)

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