

## 16.3: Expressing the Activity Coefficient as a Deviation from Raoult's Law

If the components behave ideally in the gas phase and if pure liquid  $A$  at its equilibrium vapor pressure,  $P_A^\bullet$ , is the standard state for the activity of  $A$  in solution, we find in [Section 16.2](#) that the activity of component  $A$  is  $\tilde{a}_A(P, y_A, y_B) = x_A P / P_A^\bullet$ . Experimentally, we determine a relationship between the mole fractions of  $A$  in the gas and liquid phases. By expressing this relationship as the function  $x_A = x_A(y_A)$ , we can express the activity as a function of  $y_A$ . If Raoult's law is obeyed, we have seen that this function is  $x_A(y_A) = y_A P_A^\bullet / P$ , and the activity is  $\tilde{a}_A(P, y_A, y_B) = y_A$ .

If Raoult's law is not obeyed, we must find an alternative function that adequately describes the experimentally observed relationship between  $x_A$  and  $y_A$ . As we note in [Section 14.10](#), we want to construct this function so that it approaches  $y_A$  whenever the behavior of the solution approaches the behavior of an ideal solution. We can accomplish this by defining the activity coefficient for component  $A$ ,  $\gamma_A = \gamma_A(P, y_A, y_B)$ , by the equation

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

(Raoult's law activity)

where the argument lists serve to emphasize that the activity and the activity coefficient are functions of the same thermodynamic variables.

Dropping the argument lists and equating the two activity relationships, we have

$$\frac{x_A P}{P_A^\bullet} = y_A \gamma_A$$

so that the activity coefficient is

$$\gamma_A = \frac{x_A P}{y_A P_A^\bullet}$$

(Raoult's Law activity coefficient)

Since we are using pure liquid  $A$  at its equilibrium vapor pressure as the standard state for component  $A$ , the chemical potential can be expressed as

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

Introduction of the activity coefficient adds nothing to our store of information about the system. It merely provides a convenient way to recast the available information, so that the solute mole fraction,  $y_A$ , becomes the independent variable in the chemical-potential equation. (For a one-phase two-component system,  $\gamma_A$  is completely determined by the temperature, system pressure, and  $y_A$ . Then  $y_A$  is the concentration variable in the chemical-potential equation. If there are more than two components, additional concentration variables are required to specify the composition of the system and the values of  $\tilde{a}_A$  and  $\gamma_A$ .)

In summary, since the gas is ideal, the partial pressure of  $A$  above the solution is  $P_A = x_A P$ , whether the solution is ideal or not. If the solution is ideal, we have  $y_A P_A^\bullet = x_A P$ , so that  $y_A P_A^\bullet / P^\circ = x_A P / P^\circ$ . If the solution is not ideal, we introduce the activity coefficient,  $\gamma_A$ , as the "fudge factor" that makes  $\gamma_A y_A P_A^\bullet = x_A P$  true. That is, the activity coefficient is just the actual value of the partial pressure of ideal gas  $A$ ,  $x_A P$ , divided by the value it would have if the solution were ideal,  $y_A P_A^\bullet$ . The activity coefficient corrects for the departure of the real solution from the behavior that Raoult's law predicts for the ideal solution. When we define the activity coefficient so that  $\tilde{a}_A = y_A \gamma_A$ , we have  $\tilde{a}_A P_A^\bullet = x_A P$ , so that

$$\tilde{a}_A P_A^\bullet / P^\circ = \frac{x_A P}{P^\circ}$$

thus preserving the form of the ideal solution result—with  $\tilde{a}_A$  replacing  $y_A$ . For an ideal solution,  $\gamma_A = 1$ , and our result for the real solution activity reduces to the ideal solution activity.

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