

16.6: Henry's Law and the Hypothetical One-molal Standard State

When the solution is dilute, it is often convenient to use the molality of the solute rather than its mole fraction. We define the molality as the number of moles solute, A , per kilogram of solvent, B . We use \underline{m}_A to represent the molality of A and \overline{M}_B to represent the gram-molar mass of B . A solution that contains n_A and n_B moles of A and B , respectively, contains a mass of solvent given in kilograms by

$$m_B = \frac{n_B \overline{M}_B}{1000}$$

Then the molality of A is

$$\underline{m}_A = \frac{n_A}{m_B} = \frac{1000 n_A}{\overline{M}_B n_B}$$

so that

$$n_A = \frac{\underline{m}_A n_B \overline{M}_B}{1000}$$

The mole fraction of A is given by

$$y_A = \frac{n_A}{n_A + n_B} = \frac{\underline{m}_A \overline{M}_B}{\underline{m}_A \overline{M}_B + 1000}$$

In dilute solution, where $n_A \ll n_B$ and $\underline{m}_A \overline{M}_B \ll 1000$, the mole fraction and molality of the solute are related by

$$y_A \approx \left(\frac{\overline{M}_B}{1000} \right) \underline{m}_A$$

(dilute solution)

Using this approximation, assuming that solute A obeys Henry's law and that gas A behaves ideally, we have

$$\begin{aligned} \mu_A(P, \underline{m}_A) &= \mu_A(P, y_A, y_B) = \mu_A(g, P, x_A, x_B) = \Delta_f G^\circ(A, HIG^\circ) + RT \ln \left[\frac{x_A P}{P^\circ} \right] \\ &= \Delta_f G^\circ(A, HIG^\circ) + RT \ln \left[\frac{\kappa_A y_A}{P^\circ} \right] \\ &= \Delta_f G^\circ(A, HIG^\circ) + RT \ln \left[\frac{\kappa_A \overline{M}_B}{1000 P^\circ} \right] + RT \ln \underline{m}_A \end{aligned}$$

(solute A obeys Henry's law)

When Henry's law is not obeyed over the composition range of interest, it is often convenient to choose the standard state of the solute to be a one-molal solution of a hypothetical substance that obeys Henry's law with the Henry's law constant κ_A . Then the activity of this solution is unity, and its chemical potential is the chemical potential of A in this hypothetical standard state. Letting this standard-state chemical potential be $\tilde{\mu}_A^\circ(\text{Hyp 1 } \underline{m} \text{ solute}, P)$, we have

$$\tilde{\mu}_A^\circ(\text{Hyp 1 } \underline{m} \text{ solute}, P) = \Delta_f G^\circ(A, HIG^\circ) + RT \ln \left[\frac{\kappa_A \overline{M}_B}{1000 P^\circ} \right]$$

The chemical potential of a substance that satisfies Henry's law is

$$\mu_A(HL, P, \underline{m}_A) = \tilde{\mu}_A^\circ(\text{Hyp 1 } \underline{m} \text{ solute}, P) + RT \ln \underline{m}_A$$

If A behaves as an ideal gas and the solution is dilute ($\underline{m}_A \overline{M}_B \ll 1000$), but \underline{m}_A is above the range in which Henry's law is obeyed, we introduce the Henry's law activity coefficient, $\gamma_A = \tilde{a}_A / \underline{m}_A$, to measure the departure of the real solution behavior from that predicted by Henry's law. Then the chemical potential of A in any solution is

$$\begin{aligned}\mu_A(P, \underline{m}_A) &= \tilde{\mu}_A^o(\text{Hyp 1 } \underline{m} \text{ solute}, P) + RT \ln \tilde{a}_A = \tilde{\mu}_A^o(\text{Hyp 1 } \underline{m} \text{ solute}, P) + RT \ln \underline{m}_A \gamma_A \\ &= \tilde{\mu}_A^o(\text{Hyp 1 } \underline{m} \text{ solute}, P) + RT \ln \gamma_A + RT \ln \underline{m}_A\end{aligned}$$

and the logarithm of the activity coefficient measures the difference between the chemical potential of the real solute and that of a solute that obeys Henry's law over an extended concentration range:

$$\ln \gamma_A = \frac{\mu_A(P, \underline{m}_A) - \mu_A(HL, P, \underline{m}_A)}{RT}$$

In [Section 16.19](#), we consider the determination of Henry's law-based activity coefficients further.

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