

13.9: Equilibrium When An Ideal Gas Component is Also Present as A solute

Finally, let us consider a very large equilibrium system that contains ideal gas components A , B , C , and D , at pressures P_A , P_B , P_C , and P_D . We suppose that this system also contains a very large quantity of an inert solvent. This solvent is a liquid in which components A , B , C , and D are soluble. Let the concentrations of components A , B , C , and D in this solvent be $[A]$, $[B]$, $[C]$, and $[D]$. Since this solvent-containing system is at equilibrium, we know that A dissolved in the solvent at concentration $[A]$ is in equilibrium with ideal gas A at pressure P_A . Since we assume that both the gas and the solution phases are very large, the transport of a moles of A from one to the other does not significantly change any concentration in either phase. The Gibbs free energy change is zero for this phase-transfer process. The Gibbs free energy change for the ideal-gas reaction and its equilibrium position are unaffected by the presence of the solution.

In Chapter 6, we observe that a distribution equilibrium is characterized by an equilibrium constant; the ratio of the concentration of a given chemical species in one phase to its concentration in a second phase is (approximately) a constant. In the present instance, the partial pressure of component A is a measure of its gas-phase concentration and $[A]$ is a measure of its solution-phase concentration. Letting

$$\kappa_A = \left(\frac{P_A/P^\circ}{[A]} \right) = \frac{p_A}{[A]}$$

be the distribution constant for component A , we have $p_A = \kappa_A [A]$, and parallel relationships for components B , C , and D . Substituting the distribution equilibrium relationships into the equilibrium constant equation, we have

$$\Delta_r G^\circ = -RT \ln \frac{p_C^c p_D^d}{p_A^a p_B^b} = -RT \ln \frac{\kappa_C^c \kappa_D^d}{\kappa_A^a \kappa_B^b} - RT \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Evidently, we can characterize the position of equilibrium in this system using either the pressure-based constant,

$$K_P = \frac{p_C^c p_D^d}{p_A^a p_B^b}$$

or the concentration based constant,

$$K_C = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

The relationship between the pressure-based and the concentration-based constants is

$$K_C = \left(\frac{\kappa_C^c \kappa_D^d}{\kappa_A^a \kappa_B^b} \right) K_P$$

In our present discussion, the concentrations can be expressed in any convenient units. The numerical value of the concentration-based constant depends on the units of concentration and the values of the distribution-equilibrium constants as well as the standard Gibbs free energy change for the reaction of the ideal gases.

When all of the reacting species are non-volatile, all of the reacting substances are present in the solution. The partial pressures of these species in any gas phase above the solution is immeasurably small, and the Gibbs free energies of formation of the ideal gases are not accessible by thermal measurements. Since $\Delta_r G^\circ$ for the ideal-gas reaction is not available, it cannot be used to find K_P . Nevertheless, our thermodynamic model presumes that these parameters have finite—albeit immeasurable—values. The concentration-based constant

$$K_C = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

characterizes the position of equilibrium in solution even when the data to characterize the gas-phase equilibrium process are immeasurable.

We have again arrived at the same function of concentrations to characterize the position of equilibrium. It is the same whether the equilibrating species are present in the gas phase or in an inert-liquid solvent. To obtain this result, we have used our general

thermodynamic model for equilibrium, but we have made special assumptions about the properties of the reacting species. We have assumed that the gases behave ideally and that the distribution-equilibrium constants can be expressed using the species' concentrations. In [Chapter 15](#), we return to this subject and develop a rigorous model for chemical equilibrium that does not require these special assumptions.

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