

The mol fraction of water is given by the balance in each phase:

$$x_w = 0.999987, \quad y_w = 0.0313421.$$

Comments If the volatility of the solvent is neglected (this is equivalent to setting $P_w^{\text{sat}} = 0$ in the above equations), then $y_1 = y_1^*$, $y_2 = y_2^*$ and the solubility of gas component i is

$$x_i = \frac{y_i P}{k_i^H}.$$

In this approximation, the mol fraction of gas component i in the liquid is equal to the partial pressure of the component in the gas divided by its Henry's law constant.

Temperature and Pressure Effects on Henry's Law Constant

For a given system of solute/solvent, Henry's law constant is a function of temperature and total pressure. The effect of pressure is small and can be neglected because pressure has generally little effect on properties in the liquid phase. Temperature is a more sensitive variable and must be accounted for. Commonly, literature data on Henry's law constant are presented in the form of a temperature dependent equation of the form,

$$\ln \frac{k_i^H(T)}{k_i^H(T_0)} = A \left(\frac{1}{T} - \frac{1}{T_0} \right), \quad (13.21)$$

where H_0 is the value of Henry's law constant at some known temperature T_0 , often chosen as $T_0 = 298.15$ K. The parameter A (with units of 1/K) is obtained through trough numerical fitting of data and depends on the nature of the solute and solvent. Occasionally, more complex equations are used to capture more accurately the effect of temperature.³ For many gases at low pressures, increasing temperature increases solubility. This trend is often reversed at higher temperatures.

NOTE

Henry's Law and Formal Thermodynamics

Henry's law owes its name to William Henry, the British chemist who reported the linearity between solubility and partial pressure in the early 1800s. The empirical observation of linearity was made independently of thermodynamics and took the force of a "physical law." It is not a new physical principle, however, and the constant it introduces is fully accounted for by thermodynamics. To establish the relationship between formal quantities introduced earlier and Henry's law constant, we return to the general expression for the fugacity of a species in a mixture in eq. (10.15). Applying this equation to the infinite dilution limit, we have

$$f_i = x_i \phi_i^\infty P, \quad (13.22)$$

3. See, for example, Sandler [3].