Chapter 13

Miscibility, Solubility, and Other Phase Equilibria

In the previous chapters we applied the theory of phase equilibrium to a very important and very common problem in chemical engineering: vapor-liquid equilibrium. This is not the only type of phase equilibrium that is encountered in practice. Some liquids have limited miscibility in each other. When mixed, they form two liquid phases and give rise to liquid-liquid equilibrium (LLE). When such is system is brought to boil, it forms a third phase, vapor, and the thermodynamic problem in one of vapor-liquid-liquid equilibrium (VLLE). Limited solubility is also encountered in mixtures of gases with liquids (oxygen in water, for example) and of solids in liquids (glucose in water). Another problem of industrial and biological relevance is osmosis. In this case partial equilibrium is established between two liquids via a semipermeable membrane that restricts the passage of one component. These problems may seem unrelated but they have a common thread: they are all governed by the basic principle that requires the chemical potential (or the fugacity) of a component distributed in various phases to be the same in all phases. In this chapter we apply the principles of thermodynamics to such problems. The objectives in this chapter are to:

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1. Apply the minimization of the Gibbs free energy as a criterion to determine the limits of mutual miscibility of liquids.
2. Use Henry's law to calculate the fugacity of a dissolved gas and calculate phase equilibrium in gas-liquid systems.
3. Calculate equilibrium through a semipermeable membrane and analyze separation processes that are based on osmotic effects.

13.1 Equilibrium between Partially Miscible Liquids

Liquids exhibit partial miscibility when their interactions show strong positive deviations from ideality. This indicates that cross interactions are unfavorable to such an extent that full miscibility is not possible. When a mixture of two liquids forms

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