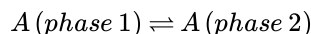


6.4: Distribution Equilibria

A system can contain more than one phase, and more than one chemical substance can be present in each phase. If one of the substances is present in two phases, we say that the substance is ***distributed*** between the two phases. We can describe the equilibrium distribution quantitatively by specifying the concentration of the substance in each phase. At constant temperature, we find experimentally that the ratio of these concentrations is approximately constant. Letting A be the substance that is distributed, we find for the *distribution equilibrium*



the ***equilibrium constant***

$$K = \frac{[A]_{\text{phase 2}}}{[A]_{\text{phase 1}}}$$

where K varies with temperature and pressure.

For example, iodine is slightly soluble in water and much more soluble in chloroform. Since water and chloroform are essentially immiscible, a system containing water, chloroform, and iodine will contain two liquid phases. If there is not enough iodine present to make a saturated solution with both liquids, the system will reach equilibrium with all of the iodine dissolved in the two immiscible solvents. Experimentally, the equilibrium concentration ratio

$$K = \frac{[I_2]_{\text{water}}}{[I_2]_{\text{chloroform}}}$$

is approximately constant, whatever amounts of the three substances are mixed.

We begin our development of physical chemistry by reasoning about the effects of concentrations on the properties of chemical systems. In Chapter 5, we find that rate laws expressed using concentration variables are adequate for the analysis of reaction mechanisms. Consideration of these rate laws leads us to the equilibrium constant for a chemical reaction expressed as a function of concentrations. Eventually, however, we discover that an adequately accurate theory of chemical equilibrium must be expressed using new quantities, which we call ***chemical activities***². We can think of a chemical activity as an “effective concentration” or a “corrected concentration,” where the correction is for the effects of intermolecular interactions. When we allow for the effects of intermolecular interactions, we find that we must replace the concentration terms by chemical activities. For the distribution equilibrium constant, we have

$$K = \frac{\tilde{a}_{A,\text{phase 2}}}{\tilde{a}_{A,\text{phase 1}}}$$

where $\tilde{a}_{A,\text{phase 1}}$ denotes the chemical activity of species A , in phase 1, at equilibrium.

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