A First Course on Kinetics and Reaction Engineering
Unit 3. Reaction Equilibrium

Definitions

chemical reaction equilibrium - state of a reacting system where the net rates of all reactions is equal to zero, and consequently the composition is constant

equilibrium composition - the composition of a system that has reached chemical reaction equilibrium

Nomenclature

$\Delta G^0_j(T)$ standard Gibbs free energy change for reaction j at temperature T

$\Delta H_j(T)$ heat of reaction j at temperature T; a superscripted 0 indicates all species are in their standard states

γ_i activity coefficient of species i

φ_i fugacity coefficient of species i

$\nu_{i,j}$ stoichiometric coefficient of species i in reaction j; value is positive for products and negative for reactants

$K_j(T)$ equilibrium constant for reaction j at temperature T

N_{ind} the number of mathematically independent chemical reactions taking place in a system

P pressure

R ideal gas constant

T temperature

a_i thermodynamic activity of species i

f_i fugacity of species i, a carat (^) over the symbol indicates the species as it exists in the mixture, a subscripted *(ss)* indicates the pure species in its standard state

h_i Henry's law constant for species i

n_i moles of species i; a superscripted 0 denotes an initial or starting value; $i = total$ signifies the total number of moles

x_i liquid phase mole fraction of species i

y_i gas phase mole fraction of species i

Equations

$$K_j\left(298\text{ K}\right) = \exp\left\{\frac{-\Delta G_j^0\left(298\text{ K}\right)}{R\left(298K\right)}\right\} \tag{3.1}$$

$$K_j\left(T\right) = \exp\left\{\frac{-\Delta G_j^0\left(T\right)}{RT}\right\} \tag{3.2}$$

$$\frac{d\left(\ln\left(K_j(T)\right)\right)}{dT} = \frac{\Delta H_j^0(T)}{RT^2} \tag{3.3}$$

$$d\left(\ln\left(K_j(T)\right)\right) = \frac{\Delta H_j^0(T)}{RT^2}dT \tag{3.4}$$

$$\int_{\ln\left(K_j(298\text{ K})\right)}^{\ln\left(K_j(T)\right)} d\left(\ln\left(K_j(T)\right)\right) = \int_{298\,K}^{T} \frac{\Delta H_j^0(T)}{RT^2}dT \tag{3.5}$$

$$K_j(T) = K_j(298\text{ K})\exp\left\{\int_{298\text{ K}}^{T} \frac{\Delta H_j^0(T)}{RT^2}dT\right\} \tag{3.6}$$

$$K_j(T) = \prod_{\substack{i=\text{all}\\ \text{species}}} a_i^{\nu_{i,j}} \tag{3.7}$$

$$a_i = \frac{\hat{f}_i}{f_{i(ss)}} \tag{3.8}$$

$\hat{f}_i = y_i P$ (ideal gases) (3.9)

$\hat{f}_i = y_i \varphi_i P$ (ideal gases) (3.10)

$a_i = \dfrac{y_i P}{1\text{ atm}}$ (ideal gases) (3.11)

$a_i = \dfrac{y_i \varphi_i P}{1\text{ atm}}$ (non-ideal gases) (3.12)

$a_i = x_i$ (ideal solutions) (3.13)

$a_i = h_i x_i$ (non-ideal solutions where i obeys Henry's law) (3.14)

$a_i = \gamma_i x_i$ (non-ideal solutions in general) (3.15)

$$y_i\ (\text{or } x_i) = \frac{n_i}{n_{total}} \tag{3.16}$$