

High-Pressure Vapor-Liquid Equilibria in Ammonia-Water-Nitrogen-Hydrogen System

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The results of ideal and nonideal vapor-liquid equilibria of ammonia-water-nitrogen-hydrogen, a system of industrial importance, have been examined. Redlich-Kwong equation of state and the Gompertz equation have been used to determine the fugacities and activity coefficients in the vapor and liquid phases, respectively. The standard fugacity in the liquid phase is found by integrating the fundamental thermodynamic equation by using the Gamson-Watson expression.

A trial and error procedure for the determination of a nonideal equilibrium system has been suggested. A comparison has been made between the available experimental values and the calculated ones. The importance of the use of fugacities which include deviations from ideality in calculating thermodynamic equilibria has been pointed out.

In ammonia production process, ammonia is separated from the effluent gas of the reactor by high-pressure liquid absorption in dilute ammonia solution. The components of this gas are mainly nitrogen and hydrogen. For the proper design of the absorber and of any other apparatus in which the four compounds—ammonia, water, nitrogen, and hydrogen—are simultaneously present in the liquid and vapor phases, it is necessary to know the relationships of their thermodynamic equilibrium.

The physical equilibrium between a vapor and a liquid is represented by constant K which is the ratio between the mole fraction y of a component in the vapor phase and the mole fraction x of the same component in the liquid phase.

In the present case we have four values of K , respectively, for the four components but, in order to simplify the solution of the problem, only K values of ammonia and water will be determined, with the assumption that nitrogen and hydrogen are present only in the vapor phase. This assumption seems to be reasonable for the particular circumstances of the case and for the limits in which the problem has to be solved. That is, large quantities of incompressible gases are present in the vapor phase and the mole fraction of ammonia and water in vapor will not be substantially different if small quantities will be absorbed in the liquid phase. On the other hand, small quantities of gas absorbed in the liquid phase will not change the mole fraction of water and ammonia or their molecular attraction.

THERMODYNAMIC BASIS

The general criterion of thermodynamic equilibrium in any heterogeneous system is that the chemical potential of any component be the same in every phase. For the treatment of the problem it is convenient to define a thermodynamic property directly related to fugacity and then also to chemical potential. This is activity a , defined as the ratio of the fugacity of a component in a given state to its fugacity in its standard state at the same temperature.

$$a_i = \left(\frac{f_i}{f_i^\circ} \right)_t \quad (1)$$

For the system at constant temperature, the fugacity of each component has to be equal in every phase:

$$f_{i,v}^\circ \cdot a_{i,v} = f_{i,L}^\circ \cdot a_{i,L} \quad (2)$$

$$\frac{a_{i,v}}{a_{i,L}} = \frac{f_{i,L}^\circ}{f_{i,v}^\circ} = K'_i \text{ (vaporization constant)} \quad (3)$$

It is convenient to choose the pure component in the

gaseous state at the temperature and pressure of the system as the standard state of the components in the vapor phase and the pure component in the liquid state at the temperature and pressure of the system for the standard state of the components in the liquid phase.

Before using Equation (3) it is necessary to place activity as a function of mole fraction and activity coefficients. This is another term equal to the ratio between activity and mole fraction.

For the vapor phase

$$a_{i,v} = \frac{f_{i,v}}{f_{i,v}^\circ} = \phi_{i,v} \cdot y_i \quad (4)$$

For the liquid phase

$$a_{i,L} = \frac{f_{i,L}}{f_{i,L}^\circ} = \gamma_{i,L} \cdot x_i \quad (5)$$

Substituting (4) and (5) into (3), one obtains

$$\frac{a_{i,v}}{a_{i,L}} = \frac{\phi_{i,v} \cdot y_i}{\gamma_{i,L} \cdot x_i} = K'_i \quad (6)$$

and then

$$\frac{y_i}{x_i} = K'_i \frac{\gamma_{i,L}}{\phi_{i,v}} = K_i \text{ (equilibrium constant)} \quad (7)$$

This is the final thermodynamic expression which has been used in the present work.

Equation (7), which relates to phase equilibria of component i , can be applied in two different ways if one considers an ideal solution of the components or a nonideal solution. The idea of an ideal solution was first introduced by G. M. Lewis, who defined it as a solution in which the fugacity of every component is proportional to its mole fraction for all the values of temperature and pressure.

Assuming ideal solution with the chosen standard states, we have $f_{i,v}^\circ = P$ and $f_{i,L}^\circ = p_i$. Applying the Lewis rule to the vapor phase $f_{i,v} = y_i \cdot P$, from Equation (4) $f_{i,v}/f_{i,v}^\circ = y_i P/P = \phi_{i,v} y_i$, then the activity coefficient $\phi_{i,v}$ equals to unity. For the liquid phase of our system, it is not possible to assume an ideal solution for which $\gamma_{i,L}$ would become equal to one because of the differences in molecular structure between water and ammonia.

Then from Equation (5) $f_{i,L} = p_i \cdot \gamma_{i,L} \cdot x_i$. Applying then Equation (7) to the ideal solution, we obtain Equation (8):

$$\frac{y_i}{x_i} = \frac{f_{i,L}^\circ \gamma_{i,L}}{f_{i,v}^\circ \phi_{i,v}} = \frac{p_i \gamma_{i,L}}{P} = K_i \quad (8)$$

If one considers a nonideal solution, by choosing the same standard states, Equation (7) has to be transformed