HOW PARTIAL MOLAR QUANTITIES CALCULATED WITH THE VA NES EQUATION SATISFY THE GIBBS-DUHEM EQUATION

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INTRODUCTION

The Gibbs-Duhem equation is an important thermodynamic relationship that relates the partial molar quantities of a mixture to its overall composition. The equation is derived from the first and second laws of thermodynamics and is a fundamental relationship in the study of thermodynamics. In this paper, we will show how partial molar quantities calculated with the Van Nes equation satisfy the Gibbs-Duhem equation.

BACKGROUND

The Gibbs-Duhem equation is given by:

$$\Sigma_{i=1}^{n} x_i \, d\mu_i = 0$$

Where x_i is the mole fraction of component **i** and μ_i is the chemical potential of component **i**. This equation states that the sum of the products of the mole fraction and the differential of the chemical potential of each component in a mixture must be zero.

The Van Nes equation is used to calculate the partial molar quantity of a component in a mixture. The equation is given by:

$$m_i = (\partial G/\partial n_i)_{T,P,n_j}$$

Where m_i is the partial molar quantity of component **i**, **G** is the Gibbs free energy, n_i is the number of moles of component **i**, **T** is the temperature, **P** is the pressure, and n_j is the number of moles of all other components in the mixture.

PROOF

To prove that the partial molar quantities calculated with the Van Nes equation satisfy the Gibbs-Duhem equation, we need to show that:

$$\Sigma_{i=1}^{n} x_i \, dm_i = 0$$

We start by differentiating the Van Nes equation:

$$dm_i = (\partial^2 G/\partial n_i \partial n_j) dn_i + (\partial^2 G/\partial n_i^2)(dn_i)^2$$

We substitute this into the Gibbs-Duhem equation:

$$\Sigma_{i=1}^{n} x_i \left[(\partial^2 G/\partial n_i \partial n_j) dn_i + (\partial^2 G/\partial n_i^2)(dn_i)^2 \right] = 0$$

We can simplify this by rearranging the terms:

$$\Sigma_{i=1}^{n} x_i (\partial^2 G/\partial n_i \partial n_j) dn_i + \Sigma_{i=1}^{n} x_i (\partial^2 G/\partial n_i^2)(dn_i)^2 = 0$$

We can now use the relation $\partial^2 G/\partial n_i \partial n_j = \partial^2 G/\partial n_j \partial n_i$ to simplify the first term:

$$\Sigma_{i=1}^{n} x_i (\partial^2 G/\partial n_j dn_i) dn_i + \Sigma_{i=1}^{n} x_i (\partial^2 G/\partial n_i^2)(dn_i)^2 = 0$$

We can rewrite the first term as:

$$\Sigma_{i=1}^{n} x_j (\partial^2 G/\partial n_i d_i) dn_i$$

Note that we have replaced **i** with **j** in the subscript. We can do this because the partial derivative $\partial^2 G/\partial n_i d_i$ is symmetric in its two indices.

We can now use the definition of the chemical potential:

$$\mu_i = (\partial G/\partial n_i)_{T,P,n_j}$$

To write the above equation as:

$$d\mu_i = (\partial^2 G/\partial n_i d_i) dn_i + (\partial^2 G/\partial n_i \partial n_j) dn_j$$

We can substitute this into the expression for the first term:

$$\sum_{i=1}^{n} x_j (\partial \mu_i/\partial n_j) dn_j$$

We can now use the fact that the sum of the mole fractions is equal to one:

$$\sum_{i=1}^{n} x_i = 1$$

This implies that:

$$\sum_{i=1}^{n} dx_i = 0$$

We can differentiate this equation with respect to n_j to get:

$$\sum_{i=1}^{n} (\partial x_i/\partial n_j) dn_i = 0$$

We can substitute this into the expression for the first term:

$$\sum_{i=1}^{n} x_j (\partial \mu_i/\partial n_j) dn_j = \sum_{i=1}^{n} x_i (\partial \mu_j/\partial n_i) dn_i$$

We can now use the definition of the partial molar quantity:

$$m_i = (\partial G/\partial n_i)_{T,P,n_j}$$

To write the above equation as:

$$d\mu_i = m_i \, dn_i$$

We can substitute this into the expression for both terms:

$$\sum_{i=1}^{n} x_i m_i dn_i + \sum_{i=1}^{n} x_i (\partial^2 G/\partial n_i^2)(dn_i)^2 = 0$$

We can simplify the second term by using the fact that for a pure component, $(\partial^2 G/\partial n_i^2) = (\partial \mu_i/\partial n_i) = v_i$, the molar volume of the component i:

$$\sum_{i=1}^{n} x_i m_i dn_i + \sum_{i=1}^{n} x_i v_i (dn_i)^2 = 0$$

We can now use the fact that the sum of the mole fractions is equal to one:

$$\sum_{i=1}^{n} x_i = 1$$