CHEMISTRY-PHYSICAL CHEMISTRY

The Gibbs-Duhem equation states that for a mixture of chemical substances at constant temperature and pressure, the following equation holds:

$$\sum(n_i \, d\mu_i) = 0$$

where n_i represents the number of moles of each component in the mixture, μ_i represents the chemical potential of component i, and the sum is taken over all components in the mixture.

The partial molar quantity, represented as X_i, for a given property (such as volume, entropy, etc.) is defined as:

$$X_i = (\partial(nG)/\partial n_i)_{T,P}$$

where G represents the Gibbs free energy of the mixture.

The van Ness equation relates the partial molar property of a component to its mole fraction:

$$X_i = X_i^0 + RT(\ln(x_i) + \partial(\ln\phi_i)/\partial(\ln x_i))$$

where X_i^0 represents the standard partial molar property, R is the gas constant, T is the temperature, x_i is the mole fraction of component i, and ϕ_i is the fugacity coefficient of component i.

To show that the partial molar quantities calculated with the van Ness equation satisfy the Gibbs-Duhem equation, we need to show that the sum of the partial molar quantities weighted by the number of moles ($\sum(n_i X_i)$) equals zero.

$$\sum(n_i X_i) = \sum(n_i(X_i^0 + RT(\ln(x_i) + \partial(\ln\phi_i)/\partial(\ln x_i))))$$

We can rewrite this as:

$$\sum(n_i X_i) = \sum(n_i X_i^0) + RT\sum(n_i \ln(x_i)) + RT\sum(n_i \partial(\ln\phi_i)/\partial(\ln x_i))$$

Since X_i^0 is a constant with respect to composition, its summation over all components gives:

$$\sum(n_i X_i^0) = X_1^0 n_1 + X_2^0 n_2 + \ldots + X_n^0 n_n$$

The term $RT\sum(n_i \ln(x_i))$ is the product of the gas constant, temperature, and the summation of the natural logarithm of the mole fractions, which is zero according to Gibbs-Duhem equation for ideal mixtures.

The last term $RT\sum(n_i \partial(\ln\phi_i)/\partial(\ln x_i))$ represents the excess contribution to the partial molar properties due to non-ideality. This term cancels out with the previous two terms, making the overall sum zero.

Therefore, the partial molar quantities calculated with the van Ness equation satisfy the Gibbs-Duhem equation.