

2.2: The Gibbs-Duhem Equation Relates Chemical Potential and Composition at Equilibrium

At **equilibrium**, there is no change in chemical potential for the system:

$$\sum_i n_i d\mu_i = 0 \quad (2.2.1)$$

This is the Gibbs-Duhem relationship and it places a compositional constraint upon any changes in the chemical potential in a mixture at constant temperature and pressure for a given composition. This result is easily derived when one considers that μ_i represents the partial molar Gibbs function for component i . And as with other partial molar quantities:

$$G_{\text{tot}} = \sum_i n_i \mu_i \quad (2.2.2)$$

Taking the derivative of both sides yields:

$$dG_{\text{tot}} = \sum_i n_i d\mu_i + \sum_i \mu_i dn_i \quad (2.2.3)$$

But dG can also be expressed as:

$$dG = V dp - s dT + \sum_i \mu_i dn_i \quad (2.2.4)$$

Setting these two expressions equal to one another:

$$\sum_i n_i d\mu_i + \sum_i \mu_i dn_i = V dp - s dT + \sum_i \mu_i dn_i \quad (2.2.5)$$

And after canceling terms, one gets:

$$\sum_i n_i d\mu_i = V dp - s dT \quad (2.2.6)$$

For a system at constant temperature and pressure:

$$V dp - s dT = 0 \quad (2.2.7)$$

Substituting Equation 2.2.7 into 2.2.6 results in the **Gibbs-Duhem equation** (Equation 2.2.1). This expression relates how the chemical potential can change for a given composition while the system maintains equilibrium.

2.2.1: Gibbs-Duhem for Binary Systems

For a binary system consisting of components two components, A and B :

$$n_B d\mu_B + n_A d\mu_A = 0 \quad (2.2.8)$$

Rearranging:

$$d\mu_B = -\frac{n_A}{n_B} d\mu_A \quad (2.2.9)$$

Consider a Gibbs free energy that only includes μ_n conjugate variables as we obtained it from our scaling experiment at T and P constant:

$$G = \mu_A n_A + \mu_B n_B$$

Consider a change in G :

$$\begin{aligned} dG &= d(\mu_A n_A) + d(\mu_B n_B) \\ dG &= n_A d\mu_A + \mu_A dn_A + n_B d\mu_B + \mu_B dn_B \end{aligned}$$

However, if we simply write out a change in G due to the number of moles we have:

$$dG = \mu_A dn_A + \mu_B dn_B$$

Consequently the other terms must add up to zero:

$$0 = n_A d\mu_A + n_B d\mu_B$$

$$d\mu_A = -\frac{n_B}{n_A} d\mu_B$$

$$d\mu_A = -\frac{x_B}{x_A} d\mu_B$$

In the last step we have simply divided both denominator and numerator by the total number of moles. This expression is the Gibbs-Duhem equation for a 2-component system. It relates the change in one thermodynamic potential ($d\mu_A$) to the other ($d\mu_B$).

The Gibbs-Duhem equation relates the change in one thermodynamic potential ($d\mu_A$) to the other ($d\mu_B$).

2.2.2: Gibbs-Duhem in the Ideal Case

In the ideal case we have:

$$\mu_B = \mu_B^* + RT \ln x_B$$

Gibbs-Duhem gives:

$$d\mu_A = -\frac{x_B}{x_A} d\mu_B$$

As:

$$d\mu_B = 0 + \frac{RT}{x_B}$$

with x_B being the only active variable at constant temperature, we get:

$$d\mu_A = -\frac{x_B}{x_A} \frac{RT}{x_B} = -\frac{RT}{x_A}$$

If we now wish to find μ_A we need to integrate $d\mu_A$, e.g. from pure 1 to x_A . This produces:

$$\mu_A = \mu_A^* + RT \ln x_A$$

This demonstrates that Raoult's law can only hold over the whole range for one component **if** it also holds for the other over the whole range.

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