Gibbs Duhem Equation (Lecture 31)

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Partial Molar Properties

$$\overline{M}_i \equiv \left[\frac{\partial(nM)}{\partial n_i}\right]_{P,T,n_j}$$

• A **partial molar property** is a thermodynamic quantity which indicates how an extensive property of a solution or mixture varies with changes in the molar composition of the mixture at constant temperature and pressure.

• When one mole of water is added to a large volume of water at 25 ℃, the volume increases by 18 cm^3. The molar volume of pure water would thus be reported as 18 $cm^3\ mol^{-1}$. However, addition of one mole of water to a large volume of pure ethanol results in an increase in volume of only 14 cm^3.

• The reason that the increase is different is that the volume occupied by a given number of water molecules depends upon the identity of the surrounding molecules. The value 14 cm^3 is said to be the partial molar volume of water in ethanol.

The Gibbs Duhem Equation

- Define the partial molar property of species i:

$$\overline{M}_i \equiv \left[\frac{\partial(nM)}{\partial n_i}\right]_{P,T,n_j}$$

  - the chemical potential and the particle molar Gibbs energy are identical:
  - for thermodynamic property *M*:

$$\mu_i \equiv \overline{G}_i$$

$$nM = M(P, T, n_1, n_2, \ldots, n_i, \ldots)$$

$$d(nM) = n\left[\frac{\partial M}{\partial P}\right]_{T,n} dP + n\left[\frac{\partial M}{\partial T}\right]_{P,n} dT + \sum_i \overline{M}_i dn_i$$

$$d(nM) = n\left[\frac{\partial M}{\partial P}\right]_{T,n} dP + n\left[\frac{\partial M}{\partial T}\right]_{P,n} dT + \sum_i \overline{M}_i dn_i$$

$$ndM + Mdn = n\left[\frac{\partial M}{\partial P}\right]_{T,n} dP + n\left[\frac{\partial M}{\partial T}\right]_{P,n} dT + \sum_i \overline{M}_i (x_i dn + n dx_i)$$

$$\left[dM - \left(\frac{\partial M}{\partial P}\right)_{T,n} dP - \left(\frac{\partial M}{\partial T}\right)_{P,n} dT - \sum_i \overline{M}_i dx_i\right] n + \left[M - \sum_i x_i \overline{M}_i\right] dn = 0$$

$$dM - \left(\frac{\partial M}{\partial P}\right)_{T,n} dP - \left(\frac{\partial M}{\partial T}\right)_{P,n} dT - \sum_i \overline{M}_i dx_i = 0$$

$$dM = \sum_i x_i d\overline{M}_i + \sum_i \overline{M}_i dx_i$$

$$\left(\frac{\partial M}{\partial P}\right)_{T,n} dP + \left(\frac{\partial M}{\partial T}\right)_{P,n} dT - \sum_i x_i d\overline{M}_i = 0$$

The Gibbs/Duhem equation

and

$$M - \sum_i x_i \overline{M}_i = 0$$

$$nM - \sum_i n_i \overline{M}_i = 0$$

Calculation of mixture properties from partial properties

THANK YOU