**Pycnometric Method. Calculation of Parcial Molar Volume of Molecules.**

Increasing of volume, caused by the addition to the solution of a unit of mass of dissolved substance (partial specific volume) is **∂v/∂m=[v]**. Partial specific volume is sometimes assumed to be equal to the reciprocal density of soluted substance what is not exactly right, but often gives a good coincidence. Practice shows that increasing of solution volume does not correspond to the volume of solid substance; for instance, dissolution of a glass of sugar in a glass of water gives solution, the volume of which is far less than two glasses (a little more than one). It is important also to remember that **[v]** of a given macromolecule is not an invariant parameter, but depends on the composition of a solvent, i.e. from concentration of salt, **ðÍ**, the presence or absence of other soluted substances etc. Picnometry is the most direct way of !!! measurement, however, the greate amounts of solution with the high concentration are required for the achievement of sufficient accuracy.

The volume of a solution is dependent on its temperature (***T***) and pressure (***P***) and the amount of each component ($n_1, n_2, ...$) used to form the mixture; $V(T, P, n_1, n_2, ...)$. For a binary system held at constant temperature and pressure, we can write its differential volume upon addition of removal or either component as:

$$dV = (dV/dn_1)_{T,P,\, n2} + (dV/dn_2)_{T,P,\, n1}$$

If we define the Partial Molar Volume of each component as:

$$\tilde{V} = (dV/dn_i)_{T,P,\, n(i=j)}$$

then we can write the differential volume change as:

$$dV = \tilde{V}_1 dn_1 + \tilde{V}_2 dn_2$$

Integration of the differential volume yields an expression which allows us to determine the solution’s volume from the partial molar volumes of its components:

$$V = n_1 \tilde{V} + n_2 \tilde{V}_2$$

Beyond being useful in its own right, this determination is useful because many other thermodynamicquantities depend on system volume measurements

## *Details Concerning Partial Molar Volumes*

It must be emphasized, the partial molar volume of a substance is not equal to the Molar Volume of the substance when pure; .

Example

The molar volumes of Water and Ethanol at 20$_o$C are:

$\tilde{V}_{H2O}$**= 18.0 ml/mole**

$\tilde{V}_{Eth}$**= 58.0 ml/mole**

Parenthetically, the molar volume of a pure substance is related to its density via its molar mass **($M_i$)** $\tilde{V}_i = M_i / \rho_i$.

For Water, we have:

$\tilde{V}_{H2O}$ **.= (18.0 g/mole) / (1.0 g/ml) = 18.0 ml/mole**

If the molar volumes of Ethanol and Water did not change upon mixing, we would predict an Aqueous Ethanol solution prepared from 2 moles of each of these components would have a total volume of:

**V = (2 mole) (18.0 ml/mole) + (2 mole) (58.0 ml/mole) = 152 ml**

But these molar volumes do change. At a mole fraction of $x_{EtOH}$ = 0.5, the partial molar volumes of Ethanol and Water are:

$\tilde{V}_{H2O}$ **= 16.9 ml/mole**

$\tilde{V}_{Eth}$**= 57.4 ml/mole**

Thus, for our example solution, we have total volume of:

**V = (2 mole) (16.9 ml/mole) + (2 mole) (57.4 ml/mole) = 148.6 ml**

In other words, the system experiences a **3.4 mL** contraction when the components are mixed. This situation should not be unexpected. Liquid Water has a fairly open structure; being not too different from that of Ice. The voids in its structure can be "filled" with the non-polar hydrocarbon portion of the Ethanol molecule **($CH_3CH_2OH$). P**

## *How to Measure Partial Molar Volumes*

It is relatively easy to show that solution density ($\rho$) measurements are sufficient to determine the partial molar volumes of the components in a binary liquid solution.

$$\rho = 1/ \tilde{V}_{NaCl}$$

For the Aqueous NaCl solutions we wish to examine, we can write the total solution volume in terms of the partial molar volumes as:

$$V = n_{H2O}\, \tilde{V}_{H2O} + n_{NaCl}\, \tilde{V}_{NaCl}$$

This quantity represents the "apparent" volume of NaCl required to bring the Water's volume up to the solution volume.