Introduction

The purpose of this experiment is to measure and calculate the partial molar volumes of sodium chloride solutions as a function of concentration from densities measured with a pycnometer, as well as to calculate three types of density measurements of CaCO3, a powder.

The partial molar volume is defined as, the increase in the volume of an infinite amount of solution (or any amount so large that insignificant concentration change will result.), when one mole of component **i** is added. The partial molar volume is not necessarily equal to the volume of one mole of pure **i.**

This quantity is of interest because of its thermodynamic relationships with other partial molar quantities such as chemical potential (Gibbs free energy). The deviations from values expected for ideal solutions of partial molar volumes are also of interest in connection with the theory of solutions especially as applied to binary mixtures of liquid components.

The volume of the pycnometer is determined using the equation:

$$V = \frac{W_o - W_e}{d_o} \qquad \text{(Equation 1)}$$

in which W_o is the weight of the pycnometer filled with deionized water, W_e is the weight of the dry pycnometer, and d_o is the density of pure water at 25 degrees Celsius. The calculation of the density of the solution is found by:

$$D = \frac{W_{solution}}{V} \qquad \text{(Equation 2)}$$

The calculation for the molality of the solution is found by:

$$m = \frac{1}{(d / M) - (M_2 / 1000 mol/kg)} \qquad \text{(Equation 3)}$$

where d is the density of the solution and M is the molarity of the solution, and M_2 is the solute molar mass.

The calculation for the apparent molar volume is found using the equation:

$$\phi = \frac{1}{d}\left(M_2 - \frac{1000\text{mol/kg}}{M}\,\frac{W-W_o}{W_o-W_e}\right) \quad \text{(Equation 4).}$$

The partial molar volume of solvent and solute is then calculated using equations:

$$\textbf{Solvent} \qquad \tilde{V}_1 = V_1^0 - \frac{m}{55.51}\,\frac{m^{1/2}}{2}\,\frac{d\phi}{dm^{1/2}}$$

$$\textbf{Solute} \qquad V_2 = \phi^0 + \frac{3m^{1/2}}{2}\,\frac{d\phi}{dm^{1/2}} \quad \text{(Equations 5\&6).}$$

There are three types of density of powder measurement made, each one is given the symbol ρ and a corresponding subscript. The First being the bulk density. This is defined as the density of an uncompacted powder including the air spaces between particles. This is also calculated using the equation:

$$\rho_B = \frac{W_p}{V_B} \quad \text{(Equation 7).}$$

Where Wp is the weight of the powder, and the VB is the volume of the bulk powder observed using a 10ml graduated cylinder.

The tapped density is defined as the density of a compacted powder including any residual air spaces between the particles. The tapped density measurement is found by using the equation:

$$\rho_T = \frac{W_p}{V_T} \quad \text{(Equation 8).}$$

where V_T is the tapped volume observed using a 10ml graduated cylinder. The apparent density is defined as the density of the powder particles themselves and is determined using the equation:

$$\rho A = \frac{Ms}{Vs} \qquad \text{(Equation 9).}$$

where Vs is the volume of the solid, and Ms is the mass of the solid.

These three measures of density differ in that the bulk density measures uncompacted particles, meaning the particle themselves and the air spaces that exist between them, whereas the tapped density is a measurement of the compacted particles and air spaces, while the apparent density is a measurement of the density of the particles only.

Procedure

The experimental method was similar to that described in the textbook (Garland, Nibler, and Shoemaker, 3rd ed., Exp. 9). The design of the pycnometer that was used differs from that of the pycnometers in the text and was shown below in Fig 1.

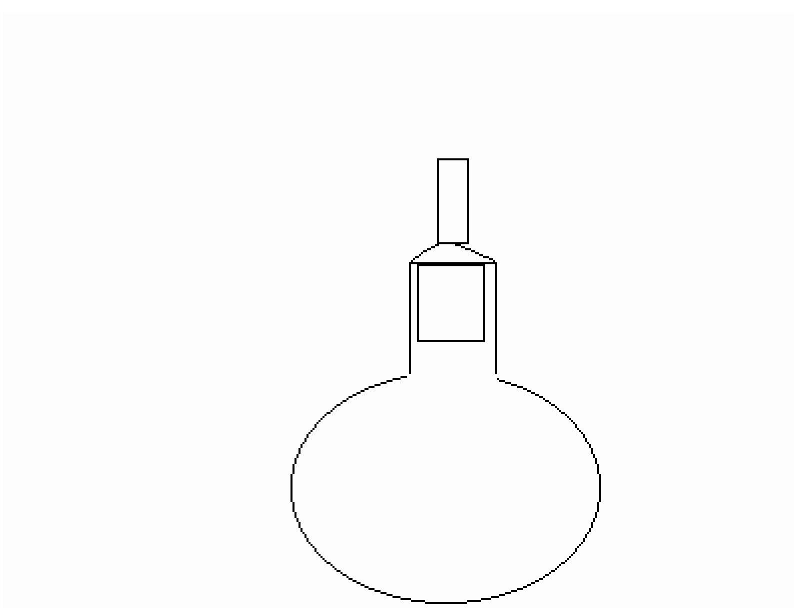

Fig 1. Pycnometer design

The procedure was modified in that only 100 mL of the dilute solutions are prepared. The first solution was made by abstracting 50 mL of 3.002 M NaCl solution into a volumetric flask which was then filled to the calibration mark, this solution is of 1:2 dilution. The next solution was produced using 50 mL of the 1:2 solution and 50mL of deionized water, this solution is of 1:4 dilution. This process was then repeated using the 1:4 dilution to create the 1:8 dilution, and subsequently the 1:8 dilution was used to create the 1:16 dilution. The procedure is also modified so that the solutions prepared were not pipeted by mouth, which is a safety violation in the laboratory.

The pycnometer is then cleaned and dried thoroughly. Once it was dried, it was then weighed empty and this weight was recorded as the W_E. This procedure was done twice at both the beginning and end of the lab period. Then the pycnometer was filled with deionized water, and allowed to equilibrate in a 25 degree Celsius thermostated bath for fifteen minutes. The sample was then weighed, this weight is recorded as the Wo. This procedure was done twice at both the beginning and end of the lab period.

The pycnometer was then emptied and allowed to dry. It was then filled with a sample from the 1:2 solution. The pycnometer was allowed to equilibrate for fifteen minutes in the water bath, and then weighed . This weight was recorded as $W_{1:2}$. This procedure was then repeated for every sample from the 1:4, 1:8, and 1:16 solutions, and the weights were recorded as $W_{1:4}$, $W_{1:8}$, and $W_{1:16}$ respectively.

In order to measure the bulk density of the powder, a clean, dry 10 mL graduated cylinder was weighed, this weight was recorded to the .0001 g using an analytical balance. The powder, CaCO3, was then placed uniformly, into the graduated cylinder until the cylinder was filled to the 10 mL mark. The filled cylinder was then weighed, and this weight was recorded as the Wp.

In order to measure the tapped density, the cylinder was covered with parafilm and firmly tapped against the laboratory notebook 500 times, the volume was then observed and recorded as the VT.

The apparent density was determined using the pycnometer. The CaCO3 was transferred form the graduated cylinder carefully and quantitatively. The pycnometer was then weighed, with this weight recorded as the Ws. Next , 10 mL of deionized water was added to the pycnometer, which was then shaken to insure that the powder was thoroughly moistened. The powder was then allowed to settle, then the pycnometer was filled with deionized water, completely submerged in a large beaker of deionized water, and then placed in a vacuum desiccator. A vacuum was carefully drawn on the system, removing air that may had got trapped by the powder. The mixture is then allowed to (boil) remain in the vacuum for 10 minutes. The apparatus was carefully observed to insure that large amounts of the powder did not escape from the system. After 10 minutes within the vacuum, the pycnometer was placed in the water bath (25 degrees Celsius) for 30 minutes. After the system was allowed to reach equilibration, the pycnometer was dried thoroughly and weighed. This weight was also recorded.