

# Experiment

## Determination of partial molal volume



*Prepared By:*

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Date: .....

Room Temperature: 25 °C

**Objective: To determine partial molal volume of methanol solution in water.****Requirements:**

**(a) Apparatus and Glassware:** Analytical electronic balance, Thermostat bath, Pycnometer (Weld type), Volumetric flask, Beaker, Pipette, Tissue paper.

**(b) Chemicals:**

- Methanol (Molecular Weight = 32.040 g)
- Distilled water (Molecular Weight = 18.016 g)

### 1. Principle

The partial molal property is a thermodynamic quantity which indicates how an extensive property of a solution or mixture varies with changes in the molal composition of the mixture at constant temperature,  $T$  and pressure,  $P$ . Thus, any extensive property,  $X$  of a mixture or solution may be expressed in terms of partial molal properties and is given by

$$X = n_1 \bar{X}_1 + n_2 \bar{X}_2 + \dots + n_i \bar{X}_i + \dots \quad \text{at constant } T \text{ and } P \quad (1)$$

where  $n_i$  is number of mole of constituent  $i$ , and  $\bar{X}_i$  is the partial molal quantity of a constituent  $i$ . Therefore, this quantity is the contribution per mole of the constituent  $i$  to  $X$  in the system at constant  $T$  and  $P$ . Mathematically, it is the partial derivative of the extensive property with respect to the amount (number of moles) of the component of interest at  $T$  and  $P$  and is expressed as

$$\bar{X}_i = \left( \frac{\partial X}{\partial n_i} \right)_{T, P, n_{j \neq i}} \quad (2)$$

We are concern in this experiment with the partial molal volume,  $\bar{V}_i$ , which is the increase in volume of the system at a constant  $T$  and  $P$ , resulting from addition of 1 mole of  $i$  constituent to such a large quantity of the system that there is no appreciable change in the concentration. Hence, the property of the solution, e.g. the volume of solute and solvent changes continuously as the composition is changed. Let  $V$  represent total volume of a binary solution at constant  $T$  and  $P$ . Then,  $V$  will be a function of the two independent variables  $n_1$  and  $n_2$  (moles of the two components present) and can be represented as

$$V = n_1\bar{V}_1 + n_2\bar{V}_2 \quad \text{at constant } T \text{ and } P \quad (3)$$

where the partial molal volumes of component 1,  $\bar{V}_1$  and component 2,  $\bar{V}_2$  are defined by the relations

$$\bar{V}_1 = \left( \frac{\partial V}{\partial n_1} \right)_{T,P,n_2} \quad \text{and} \quad \bar{V}_2 = \left( \frac{\partial V}{\partial n_2} \right)_{T,P,n_1} \quad (4)$$

The partial molal volumes may be evaluated from density measurement. **Lewis** and **Randall** have given a procedure for finding the partial molal volumes by defining another quantity, the *apparent molal volume*,  $\phi$  is defined by following equation for component 2

$$\phi = \frac{1}{n_2} \left( V - n_1\bar{V}_1^0 \right) \quad \text{at constant } T \text{ and } P \quad (5)$$

Rearranging this equation

$$V = n_1\bar{V}_1^0 + n_2\phi \quad (6)$$

where,  $V$  is the volume of solution containing  $n_1$  moles of component 1 and  $n_2$  moles of component 2.  $\bar{V}_1^0$  is the molar volume of the pure component 1 at given  $T$  and  $P$ . Now by the definition of partial molal volumes [(Eq. (6)] and using Eq. (3)

$$\bar{V}_2 = \left( \frac{\partial V}{\partial n_2} \right)_{T,P,n_1} = \phi + n_2 \left( \frac{\partial \phi}{\partial n_2} \right)_{T,P,n_1} \quad (7)$$

$$\text{and} \quad \bar{V}_1 = \frac{V - n_2\bar{V}_2}{n_1} = \frac{1}{n_1} \left[ n_1\bar{V}_1^0 - n_2^2 \left( \frac{\partial \phi}{\partial n_2} \right)_{T,P,n_1} \right] \quad (8)$$

The  $\phi$  of the solution can be calculated from the density of the solution. If  $M_1$  and  $M_2$  are the molecular weight of solvent and solute, respectively, and  $d$  is the density of solution then  $\phi$  as defined by Eq. (5) is given by

$$\phi = \frac{1}{n_2} \left( \frac{n_1M_1 + n_2M_2}{d} - n_1\bar{V}_1^0 \right) \quad (9)$$

If  $n_1$  is equal to the number of moles of solvent and  $n_2$  is the number of moles of solute in 1000 g of solvent, then  $n_2 = m_2$  the molality, therefore,

$$V = \frac{n_1 M_1 + n_2 M_2}{d} = \frac{1000 + m_2 M_2}{d} \quad (10)$$

and  $n_1 \bar{V}_1^0 = \frac{1000}{d_0}$  (11)

Thus, Eq. (9) is set by

$$\phi = \frac{1}{d} \left[ M_2 - \frac{1000}{m_2} \frac{(d - d_0)}{d_0} \right] \quad (12)$$

$$= \frac{1}{d} \left[ M_2 - \frac{1000}{m_2} \frac{(W - W_0)}{(W_0 - W_e)} \right] \quad (13)$$

where  $d_0$  is the density of the pure solvent. In Eq (13), the directly measured weights of the pycnometer— $W_e$  when empty,  $W_0$  when filled to the mark with pure solvent, and  $W$  when filled to the mark with solution—are used. This equation is preferable to Eq. (12) for calculation of  $\phi$ , as it avoid the necessity of computing the densities to the high precision that would otherwise be necessary in obtaining the small difference  $d - d_0$ . In this way, the value of  $\phi$  for the solute can be determined for a molality  $m_2$ .

When component 1 (solvent) is water the equation (7) and (8) can be rewritten as

$$\bar{V}_2 = \left( \frac{\partial V}{\partial n_2} \right)_{T,P,n_1} = \phi + n_2 \left( \frac{\partial \phi}{\partial n_2} \right)_{T,P,n_1} = \phi + m_2 \frac{d\phi}{dm_2} \quad (14)$$

and  $\bar{V}_1 = \frac{1}{n_1} \left[ n_1 \bar{V}_1^0 - n_2^2 \left( \frac{\partial \phi}{\partial n_2} \right)_{T,P,n_1} \right] = \bar{V}_1^0 - \frac{m_2^2}{55.51} \left( \frac{d\phi}{dm_2} \right)$  (15)

where 1000 g of water (= 55.51 moles) and  $\bar{V}_1^0$  is the molar volume of pure water (= 18.016/0.997044 = 18.069 mL at 25 °C). We might proceed by plotting  $\phi$  vs.  $m_2$  and drawing a smooth curve through the points. Slope,  $\left( \frac{d\phi}{dm_2} \right)$  can be calculated by constructing a tangent at desired concentration. Calculate  $\bar{V}_2$  and  $\bar{V}_1$  from Eqs. (14) and (15), respectively.

## 2. Solution Preparation:

Prepare mixture of 25 mL each as given in the following table, containing methanol and water in concentration varying between 0.01 to 0.9 mole fractions of methanol. Keep these solutions in a thermostat.

Density of Water = 0.997044 g/mL at 25 °C

Density of Methanol = 0.791 g/mL at 25 °C

S. No.	% (v/v) of Methanol	Methanol		Water		Mole Fraction	Molality ( $m_2$ ) mol/kg
		mL	g	mL	g		
1	90	22.5	17.798	2.5	2.493	0.8006	222.8498
2	80	20.0	15.820	5.0	4.985	0.6409	99.0443
3	70	17.5	13.843	7.5	7.478	0.5100	57.7759
4	60	15.0	11.865	10.0	9.970	0.4009	37.1416
5	50	12.5	9.888	12.5	12.463	0.3085	24.7611
6	40	10.0	7.910	15.0	14.956	0.2292	16.5074
7	30	7.5	5.933	17.5	17.448	0.1605	10.6119
8	20	5.0	3.955	20.0	19.941	0.1003	6.1903
9	10	2.5	1.978	22.5	22.433	0.0472	2.7512

## 3. Experimental Procedure

- (i) Clean pycnometer of approximately capacity 10 mL by washing with cleaning solution and rinsing 5 to 6 time with distilled water. Dry it in a 120 °C oven then cool it in a room temperature.
- (ii) Find the weight of empty Pycnometer ( $W_e$ ).
- (iii) Fill the pycnometer with distilled water and ensure that water is filled upto the top of the capillary and it free from air bubbles.
- (iv) Determine the weight of the pycnometer which is filled with water ( $W_0$ ). When doing this, make sure that the outside of the pycnometer is completely dry.
- (v) Similarly, weigh the pycnometer which is filled with different mixtures of methanol and water ( $W$ ).
- (vi) In your report, present in tabular form the quantities  $d$ ,  $m_2$ , and  $\phi$  for each solution studied.
- (vii) Also make the curves ( $\phi$  vs.  $m_2$ ) and ( $\bar{V}_1$  and  $\bar{V}_2$  vs.  $m_2$ ).
- (viii) Explain your results.

#### 4. Observation Table

$$d_0 = \text{Density of Water (25 }^\circ\text{C)} \text{ (g/mL)} \quad 0.997044$$

$$W_e = \text{Weight of Empty Pycnometer (g)} \quad 26.128$$

$$W_0 = \text{Weight of Pycnometer + Water (g)} \quad 38.718$$

$$V_p = \left( \frac{W_0 - W_e}{d_0} \right) = \text{Volume of Pycnometer (mL)} \quad 12.631338$$

$$\bar{V}_1^0 = \text{Molar volume of pure water (= } 18.016/0.997044 \text{)} \text{ (mL/mol)} \quad 18.069000$$

S. No.	Molality ( $m_2$ )	Weight of Pycnometer + Solution ( $W$ )	Density of Solution $d = \frac{W - W_e}{V_p}$	$\phi = \frac{1}{d} \left[ M_2 - \frac{1000}{m_2} \frac{(W - W_0)}{(W_0 - W_e)} \right]$	Slope $\frac{d\phi}{dm_2}$	$\bar{V}_1 = \bar{V}_1^0 - \frac{m_2^2}{55.51} \left( \frac{d\phi}{dm_2} \right)$	$\bar{V}_2 = \phi + m_2 \frac{d\phi}{dm_2}$
	mol/kg	G	g/mL	mL/mol		mL/mol	mL/mol
1	222.8498	36.494	0.820974	39.9920	0.00221	16.091823	40.484541
2	99.0443	36.885	0.851929	39.3337	0.00854	16.559804	40.179526
3	57.7759	37.208	0.877500	38.8778	0.01612	17.099635	39.809102
4	37.1416	37.470	0.898242	38.6399	0.02339	17.487727	39.508689
5	24.7611	37.759	0.921122	38.1223	0.03031	17.734224	38.872813
6	16.5074	37.984	0.938935	37.8840	0.03612	17.891690	38.480296
7	10.6119	38.180	0.954452	37.7867	0.04138	17.985053	38.225798
8	6.1903	38.380	0.970285	37.4895	0.04598	18.037259	37.774146
9	2.7512	38.557	0.984298	37.2719	0.04990	18.062196	37.409182

## 5. Calculation

- (i) The concentration ( $m_2$ ) of each solution of methanol and water is expressed in the terms of the molal concentration as given below

$$\text{Molality} = \frac{\text{No. of moles of solute}}{\text{Amount of solvent in gram}} \times 1000$$

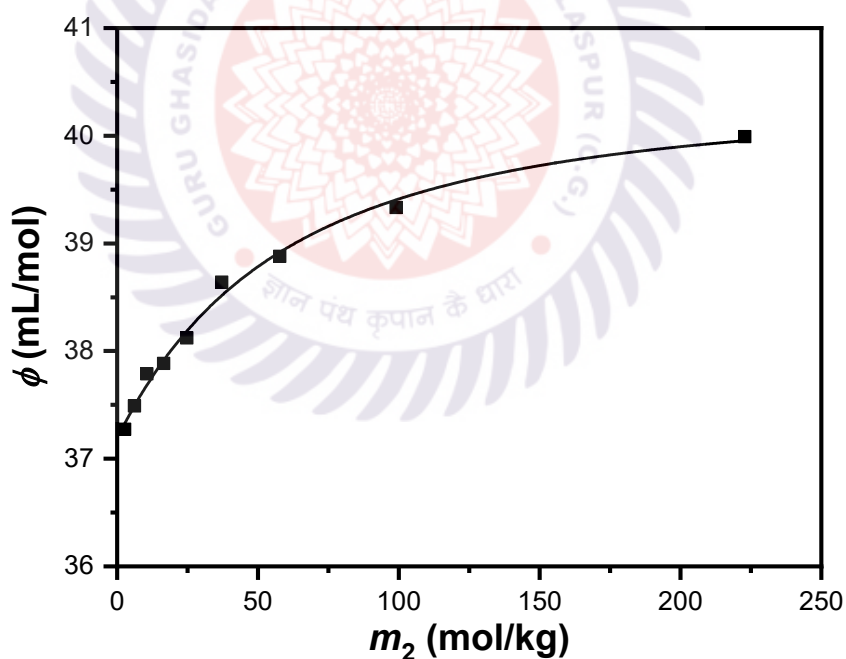
- (ii) The volume of pycnometer,  $V_p$  is calculated as following

$$= \left( \frac{\text{Weight of pycnometer filled with water, } W_0 - \text{Weight of empty pycnometer, } W_e}{\text{Density of pure water, } d_0} \right)$$

- (iii) The density of each solution ( $d$ ) of methanol and water is calculated as following

$$= \left( \frac{\text{Weight of pycnometer filled with solution, } W - \text{Weight of empty pycnometer, } W_e}{\text{Volume of pycnometer, } V_p} \right)$$

- (iv) The values of  $\phi$  are calculated at various concentrations from Eq. (13). **Fig. 1** shows graph between  $\phi$  and ( $m_2$ ).



**Fig. 1.** Plot between  $\phi$  and  $m_2$

The slope  $\frac{\partial \phi}{\partial m_2}$  of the smooth curve is obtained by drawing a tangent at each point of the concentration.

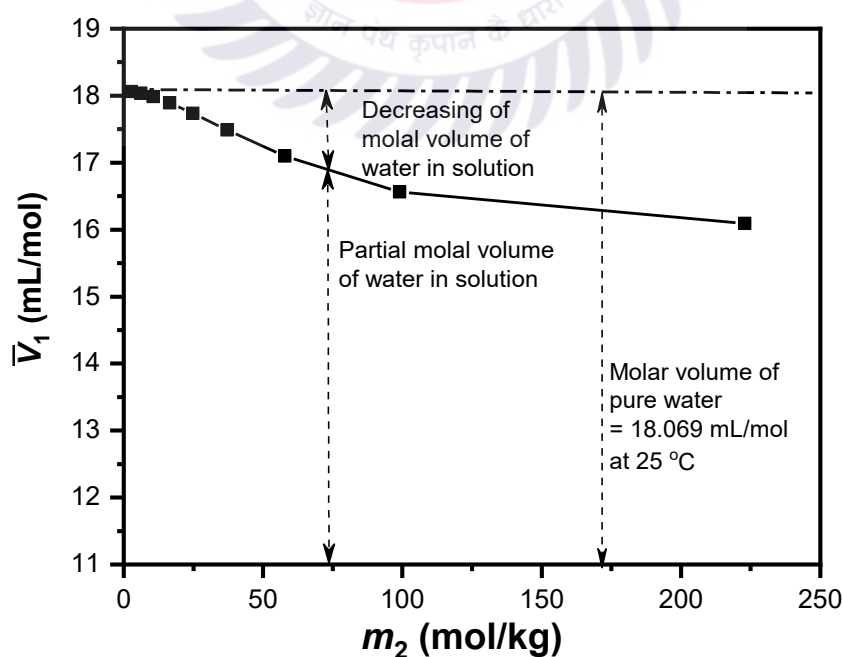
- (v) Finally,  $\bar{V}_2$  and  $\bar{V}_1$  at above concentrations are evaluated by using Eqs. (14) and (15), respectively.

## 6. Result and Discussion

The obtained experiment values of  $\phi$ ,  $\bar{V}_1$ , and  $\bar{V}_2$  for water-methanol are summarized in the observation table.

As we know that, water (H<sub>2</sub>O) and methanol (CH<sub>3</sub>OH) are completely miscible liquids at room temperature and ambient pressure, as is to be expected from the polar character of these two molecules. The molecular dipole moments ( $\mu$ ) are almost similar [in the gas phase  $\mu(\text{H}_2\text{O}) = 1.86 \text{ D}$ ,  $\mu(\text{CH}_3\text{OH}) = 1.69 \text{ D}$ ].

The **Fig. 2** and **Fig. 3** represent the graph between partial molal volumes of solvent  $\bar{V}_1$  and solute  $\bar{V}_2$  versus molality of methanol, respectively in the solutions. In the above graphs, it is observed that partial molal volumes typically vary with concentration. And, also we can see that the systems experience contraction when methanol and water is mixed. This situation should not be unexpected. Liquid water has a fairly open structure; not being too different from that of ice. The voids in its structure can be “filled” with the non-polar hydrocarbon portion of the methanol molecule as shown in **Fig. 4**. Thus, the volume of the mixtures will be less than the volume of the components separately. Other solution systems may be also investigated, such as water-ethanol, benzene-CCl<sub>4</sub>, water-NaCl solution etc.



**Fig. 2** Partial molal volumes of water in their mixtures.



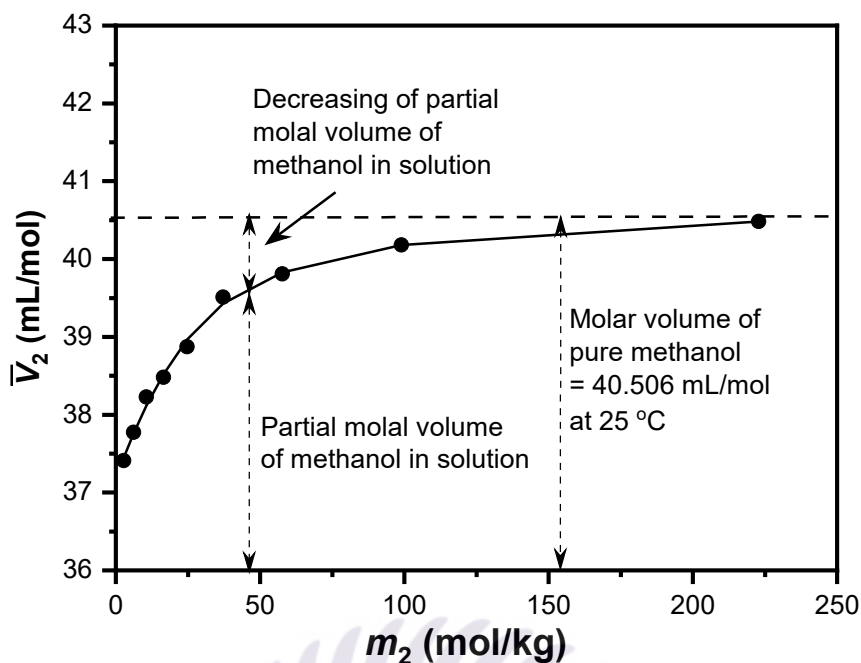


Fig. 3 Partial molal volumes of methanol in their mixtures.

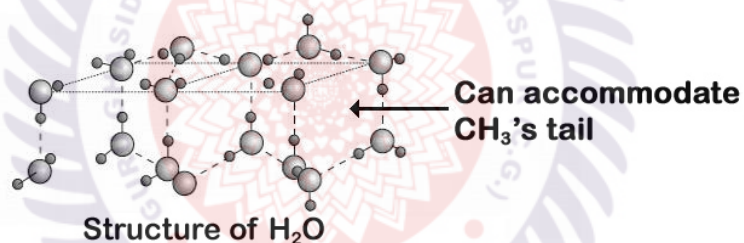


Fig. 4 Representation of CH<sub>3</sub>'s tails in voids of water.

Practical Application: The use of partial molal quantities is fundamental in the application of thermodynamics to solution systems. This is well illustrated in an article of unusual interest in which their application to the physical chemistry of solutions of substances of biological interest is described (E. F. Casassa and H. Eisenberg, Thermodynamic Analysis of Multicomponent Solutions, *Advan. Protein Chem* (1964) **19**, 287).

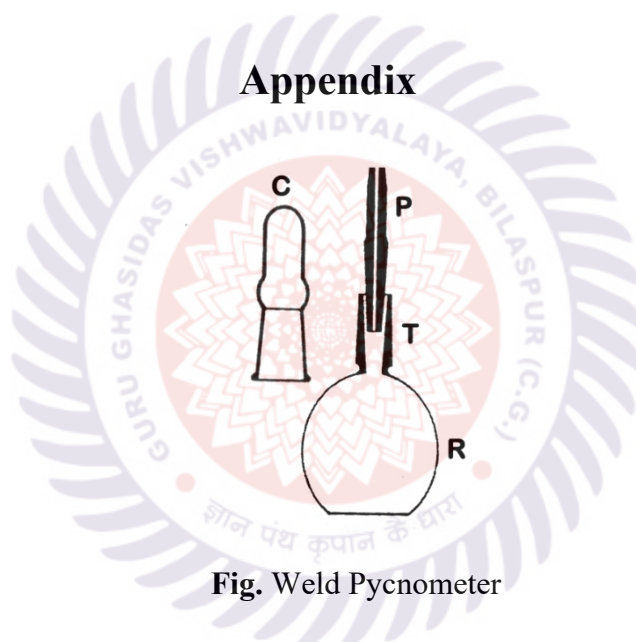
## 7. Precautions

- The weights of water and of the various solution held by pycnometer should be taken very carefully.
- The concentration of each solution is expressed in term of the molal concentration scale.

## 8. Further Reading

- (i) Read up details of the partial molal properties and its determinations.
- (ii) *Physical Chemistry*, P. W. Atkins and J. D. Paula, Eds: 7<sup>th</sup>, Oxford University Press.
- (iii) *Principle of Physical Chemistry*, B. R. Puri, L. R. Sharma, and Pathania, Vishal Publishing Co. Jalandhar.
- (iv) *Experiments in Physical Chemistry*, D. P. Shoemaker and C. W. Garland, McGraw-Hill, 1962.
- (v) *Experimental Physical Chemistry*, F Daniels, R. Alberty, J. W. Williams, C. D. Cornwell, P. Bender, and J. E. Harriman, McGraw-Hill, 1970.
- (vi) *Advanced Physico-Chemical Experiments*, J Rose, Sir Isaac Pitman & Sons Ltd, London.

## Appendix



**Fig. Weld Pycnometer**

The Weld pycnometer is initially filled to bring the liquid level about halfway up the throat **T** of the reservoir **R**. The pycnometer is placed in the thermostat with the cap **C** in position to prevent evaporation from the exposed liquid surface. When temperature equilibrium has been reached, the cap **C** is removed and the plug **P** is inserted. A moderate pressure is sufficient to seat the plug firmly. Any excess liquid on the tip of the plug is wiped off with a piece of filter paper, care being taken to avoid removing liquid from the plug capillary in this process. The pycnometer is then removed from the thermostat, wiped dry with a lineless cloth, and the dried cap put in the place. It is allowed to stand in the balance case for a few minutes before being weighed.