PARTIAL MOLAR VOLUME

1. PURPOSE OF THE WORK

Determination of partial molar volumes of components in the water-ethanol system.

2. THEORETICAL NOTIONS

The partial molar volume of a component in a mixture is the volume variation that accompanies a unit variation in the number of moles in that component.

$$\bar{V}_i = \frac{\partial v}{\partial n_i}, i = \overline{1, N} \tag{1}$$

N being the number of components. The connection between the molar volume of the mixture and the partial molar volume of a component is given by the *van Ness* equation

$$\bar{V}_i = V + \frac{\partial V}{\partial x_i} - \sum_{j=1}^{N} x_j \frac{\partial V}{\partial x_j} \tag{2}$$

which, for a binary mixture, generates the system

$$\begin{aligned} \bar{V}_1 &= V + (1 - x_1)\frac{\mathrm{d}V}{\mathrm{d}x_1} \\ \bar{V}_2 &= V - x_1 \frac{\mathrm{d}V}{\mathrm{d}x_1} \end{aligned} \tag{3}$$

Using these equations, the partially molar volumes of the components in a binary mixture can be determined from experimental data in several ways, three of which are described below. In all cases, the experimental data represent the dependence of the molar volume of the composition mixture (volumetric curve).

1.1. Determination of partial molar volumes with the volumetric curve

Note with $V(x)$ the function that generates the volumetric curve and with x_0 an arbitrary value of the molar fraction of the component in the mixture. The equation of the tangent $x_1 = x_0$ to the volumetric curve will be:

$$\tau_{x_0} : y = V_0 + (x_1 - x_0) \cdot \left. \frac{\mathrm{d}V}{\mathrm{d}x_1} \right|_{x_1 = x_0}$$

in which $V_0 = V(x_0)$. The intersections of this line with the axes of the graph ($x_1 = 0$, respectively $x_1 = 1$) will be

$$y = V_0 + (1 - x_0) \cdot \left.\frac{\mathrm{d}V}{\mathrm{d}x_1}\right|_{x_1 = x_0},$$

respectively

$$y = V_0 - x_0 \cdot \left.\frac{\mathrm{d}V}{\mathrm{d}x_1}\right|_{x_1 = x_0}$$

that is, exactly the values given by equations (3). Therefore, the partially molar volumes can be determined by plotting the graph of the volumetric curve, constructing the tangent to the curve at the desired composition and determining the ordinates of the points of intersection with the axes of the graph (figure 1):

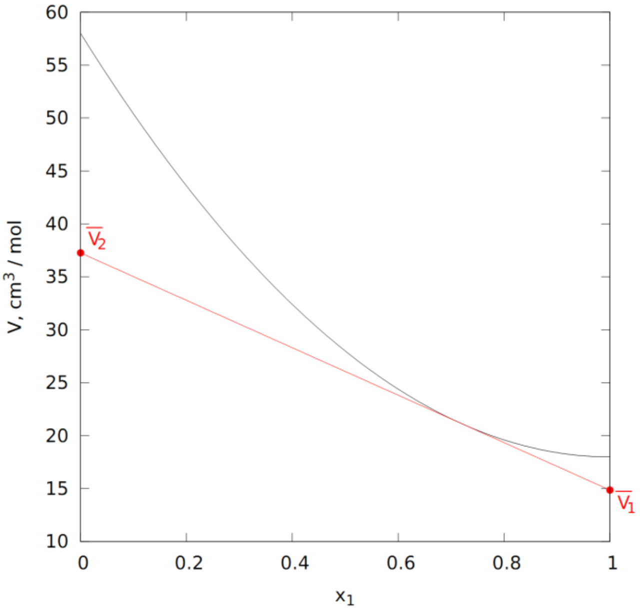

Fig. 1. Determination of the partial molar volume of the volumetric curve.

Although extremely simple, this method has the disadvantage of being inaccurate for systems whose volumetric curve is almost linear, in which case its graph is confused with tangents.

1.2. Determination of partial molar volumes from the excess volumetric curve

Non-ideal systems are characterized by a set of functions called "excess", defined as differences between the function of the non-ideal mixture and the function of a hypothetical mixture with the same composition and ideal behavior. Thus, the excess volume has the expression

$$v^E = v - \sum_{i=1}^{N} n_i V_i^0$$

or, in terms of molar sizes,

$$V^E = V - \sum_{i=1}^{N} x_i V_i^0$$

Combining the first relation with the definition of the partial molar volume results

$$\overline{V}_i = V_i^0 + \frac{\partial v^E}{\partial n_i} = V_i^0 + \overline{V^E}_i$$

Wherein $\overline{V^E}_i$ is the partial molar volume of excess.

For a binary system, it turns out in the end:

$$\begin{aligned} \overline{V}_1 = V_1^0 + \overline{V^E}_1 &= V_1^0 + V^E + (1 - x_1)\frac{\mathrm{d}V^E}{\mathrm{d}x_1} \\ \overline{V}_2 = V_2^0 + \overline{V^E}_2 &= V_2^0 + V^E - x_1\frac{\mathrm{d}V^E}{\mathrm{d}x_1} \end{aligned} \tag{4}$$

These relations suggest a variant of the tangent method in which the tangents are constructed starting from the excess volumetric curve, resulting in partial molar excess volumes; the partially molar volumes are then calculated from them by adding with the molar volumes of the pure components (figure 2).

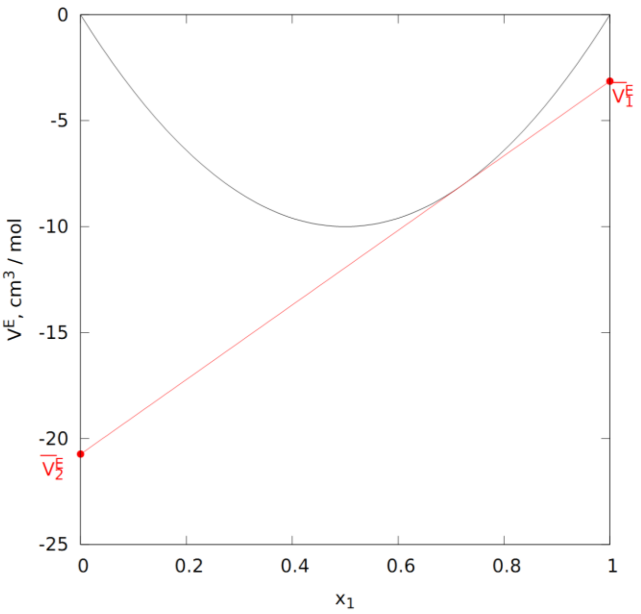

Fig. 2. Determination of the partial molar volume from the excess volumetric curve.

This method has the advantage of using a much steeper curve as a support for the construction of tangents, which significantly simplifies the drawing operation.

1.3. Analytical determination of partial molar volumes

The methods described above are graphical methods. Although simple, they contain a subjective component (dependent on the person applying them), which affects the reproducibility of the results. Analytical methods, although more complex, remove this shortcoming, providing identical results each time they are applied to the same set of experimental data.

Such a method involves identifying an expression for the function $V = V(x_1)$, which is then used in equations (3) to obtain the numerical values of the partial molar volumes. The simplest and most commonly used way to identify such a function is multiline regression with the *Redlich-Kister* model:

$$V = x_1V_1^0 + (1-x_1)V_2^0 + x_1(1-x_1)\left[a + b(1-2x_1) + c(1-2x_1)^2 + \cdots\right]$$

wherein $a, b, c, \ldots$ are adjustable parameters to be determined by regression. For its application, we will notice that the molar volumes of the pure components are constant (they are not adjustable), so we can build the multilinear model:

$$\begin{aligned} Y(x) &= V - x_1V_1^0 - (1-x_1)V_2^0 = \\ &= ax_1(1-x_1) + bx_1(1-x_1)(1-2x_1) + cx_1(1-x_1)(1-2x_1)^2 + \cdots \\ &= aX_1 + bX_2 + cX_3 + \cdots \end{aligned}$$

whose parameters ($a, b, c, \ldots$) can be calculated, for example, by solving the system of orthogonal equations.

After determining the parameters, the partial molar volumes are easily calculated, replacing the *Redlich – Kister* equation in the *van Ness* equations (3) and performing the necessary calculations.

3. EXPERIMENTAL PART

The principle of the method

The volumetric curve is determined by density measurements, using the analytical balance, a calibrated pycnometer and solutions of known composition. Starting from these data, the molar volume of each solution is determined using the relation

$$V = \frac{M}{\rho} = \frac{x_1M_1 + x_2M_2}{\rho}$$

where $x_{1,2}$ are the molar fractions of the two components, $M_{1,2}$ are their molar masses and

ρ is the density of the solution. A molar volume - molar fraction data set is thus obtained from which the partial molar volumes can be determined by one of the methods described above.

3.1. APPARATUS AND SUBSTANCES

- 0.1 mg precision analytical balance, pycnometer, 5 Erlenmeyer flasks with 100 mL stopper, napkins, pure ethanol, distilled water.

3.2. PROCEDURE

3.2.1. Check that the vials with a ground-in stopper contain at least 5 mL of solution. If not, insufficient quantitative solutions are replaced with fresh solutions, prepared by mixing ethanol with water according to the table:

Solution	1	2	3	4	5
V_1 (water), mL	11,1	4,7	2,3	1,4	0,7
V_2 (alcohol), mL	8,9	15,3	17,7	18,6	19,3

3.2.2. Dry the pycnometer well (by wiping with a napkin) and weigh;

3.2.3. Determine the mass of the pycnometer filled with alcohol, the mass of the pycnometer filled with each of the 5 solutions in the order of increasing the amount of water (5 → 1), as well as the mass of the pycnometer filled with distilled water. To measure the solutions with a pycnometer, hold it with a napkin, fill it almost to the brim with liquid and place the stopper so that no air bubbles remain in the pycnometer or on the capillary of the stopper. The excess spilled liquid is wiped off with a napkin and then the pycnometer is weighed. Mass corresponding to the volume of the pycnometer in each solution is obtained by difference to the mass of the empty pycnometer.

4. EXPERIMENTAL DATA PROCESSING

4.1. The experimental data are entered in a form table:

Solution	**Empty**	**Alcool**	**Solution 5**	**Solution 4**	**Solution 3**	**Solution 2**	**Solution 1**	**Water**
Mass of the pycnometer with solution, g								

4.2. Using the measured data, complete the following table:

No.	**V_1 (mL water)**	**V_2 (mL alc.)**	**m_1, g**	**m_2, g**	**x_1**	**x_2**	**$\overline{M}$, g/mol**	**ρ, g/cm^3**	**V, mL**	**V^E, mL**	**$\overline{V}_1$, mL**	**$\overline{V}_2$, mL**
1.	20	0										
2.	11,1	8,9										
3.	4,7	15,3										
4.	2,3	17,7										
5.	1,4	18,6										
6.	0,7	19,3										
7.	0	20										

4.3. The densities of the working mixtures are determined on the basis of experimental weighing using the relation $\rho_{sol_i} = \frac{m_{pic,sol_i} - m_{pic,gol}}{m_{pic,H_2O} - m_{pic,gol}} \cdot \rho_{H_2O}$;

4.4. To calculate the mass of alcohol and water, the measured volumes for making the mixtures are multiplied by the densities of the pure components at working temperature $m_i = \rho_i \cdot V_i$;

4.5. The compositions of the solutions, expressed in molar fractions are given by the relations

$x_i = \frac{n_i}{\sum_i n_i} = \frac{\frac{m_i}{M_i}}{\sum_i \frac{m_i}{M_i}}$ (x_1 is calculated, and x_2 is obtained from the relation: $x_2 = 1 - x_1$);

4.6. The average molar mass of the solutions is calculated with the relation $\overline{M} = x_1 M_1 + x_2 M_2$;

4.7. The molar volume of the mixtures is calculated with the relation: $V_i = \frac{\overline{M_i}}{\rho_{sol_i}}$;

4.8. The excess molar volume is calculated: $V^E = V - \left(x_1 V_1^0 + x_2 V_2^0\right)$;

4.9. Using the above data, the partial molar volume is determined using one of the methods described in section 1.

5. QUESTIONS

5.1. Establish the connection between the general (2) and the particular (3) form of *van Ness*'s equation.

5.2. Check equation (4), starting from equation (3) and the definition of excess volume.

5.3. Calculate the expression of the derivative from equations (3) and obtain the expressions for the partial molar volumes starting from the *Redlich-Kister* equation.

5.4. Estimate the error in the graphical determination of the partial molar volume, if millimeter paper is used for the construction of the graph, knowing that the geometric representation accuracy is 1 mm.