Partial molar volumes (Item No.: P3020501)

Curricular Relevance
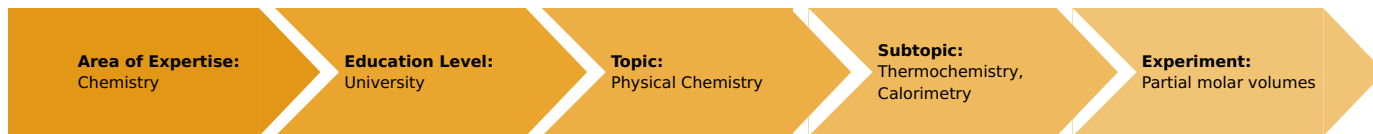
Area of Expertise: Chemistry	Education Level: University	Topic: Physical Chemistry	Subtopic: Thermochemistry, Calorimetry	Experiment: Partial molar volumes

Difficulty	**Preparation Time**	**Execution Time**	**Recommended Group Size**
Difficult	10 Minutes	20 Minutes	2 Students

Additional Requirements:

- Precision balance, 620 g / 0.001 g

Experiment Variations:

Keywords:

principles of thermodynamics, ideal and non-ideal behaviour of gases and liquids, volume contraction, molar and partial molar quantities

Overview

Short description

Principle

Due to intermolecular interactions, the total volume measured when two real liquids (e.g. ethanol and water) are mixed deviates from the total volume calculated from the individual volumes of the two liquids (volume contraction). To describe this non-ideal behaviour in the mixing phase, one defines partial molar quantities which are dependent on the composition of the system. The values of these can be experimentally determined.

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Figure 1: Experimental set-up.

Safety instructions

Ethanol
H225: Highly flammable liquid and vapour
H319: Causes serious eye irritation
P210: Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.

Equipment

Position No.	Material	Order No.	Quantity
1	Immersion thermostat Alpha A, 230 V	08493-93	1
2	Bath for thermostat, makrolon	08487-02	1
3	External circulation set for thermostat Alpha A	08493-02	1
4	Support base DEMO	02007-55	1
5	Support rod, stainless steel, 500 mm	02032-00	2
6	Right angle boss-head clamp	37697-00	5
7	Universal clamp	37715-00	4
8	Pycnometer, calibrated, 25 ml	03023-00	9
9	Bottle,nar.mouth,100ml,clear,p.st	41101-01	9
10	Funnel, glass, top dia. 55 mm	34457-00	9
11	Beaker, high, BORO 3.3, 50 ml	46025-00	2
12	Pasteur pipettes, 250 pcs	36590-00	1
13	Rubber caps, 10 pcs	39275-03	1
14	Rubber tubing, i.d. 6 mm	39282-00	3
15	Hose clip, diam. 8-16 mm, 1 pc.	40996-02	4
16	Wash bottle, plastic, 500 ml	33931-00	1
17	Ethyl alcohol, absolute 500 ml	30008-50	1
18	Water, distilled 5 l	31246-81	1
19	Tubing connector, ID 6-10mm	47516-01	2

Task

Measure the densities of different ethanol-water mixtures of specified composition at 20 °C with pycnometers. Calculate the real volumes and the mean molar mixing volumes of the investigated ethanol-water mixtures and also the partial molar volumes of each liquid for selected compositions. Compare them with the molar volumes of the pure substances at 20 °C.

Set-up and procedure

Set up the experiment as shown in Fig. 1. Prepare the ethanol-water mixtures in the narrow neck bottles on the laboratory balance in the approximate mass composition specified in Table 1, weighing ethanol into the predetermined mass of water (weighing accuracy 0.001 g). Close the bottles immediately when the desired mass has been reached. Fill dry pycnometers of known empty mass completely with the mixtures. Cover them with aluminium foil and position them in the temperature-controlled bath for about 30 min at 20 °C for temperature equilibration. Subsequently, remove the pycnometers and weigh them after meticulous drying.

Calculate the masses of 25 ml of the respective mixtures as the difference of the two weights.

Table 1: Ethanol-water mixtures to be investigated

m (C_2H_5OH) / g	m (H_2O) / g
30.60	1.35
29.25	2.85
27.90	4.70
26.20	6.85
24.15	9.45
21.60	12.65
18.35	16.75
14.15	22.10
8.35	29.40

Theory and evaluation

The volume v_{id} and the mean molar volume V_{id} of an ideal mixture of the components A and B can be calculated if the quantitative composition is known.

$$x_A = \frac{n_A}{n_A + n_B} \tag{1.1}$$

$$x_B = \frac{n_B}{n_A + n_B} \tag{1.2}$$

$x_A ; x_B$ mole fraction of the components A and B, respectively

$n_A ; n_B$ amounts of A and B respectively

$$V_{id} = \frac{v_{id}}{n_A + n_B} = V_A x_A + V_B x_B \tag{2}$$

However, the assumed additivity in equation (2) loses its validity in cases of real mixtures (e.g. ethanol / water). The real volumes v_r and V_r deviate more or less strongly from the ideal volumes due to volume contraction but can still be calculated if the molar volumes of the pure components A and B are replaced by the partial molar volumes V_A and V_B which are independent of the composition.

$$\bar{V}_A = \left(\frac{\delta v_r}{\delta n_A}\right)_{T.p.n_B} \tag{3.1}$$

$$\bar{V}_B = \left(\frac{\delta v_r}{\delta n_B}\right)_{T.p.n_A} \tag{3.2}$$

$$V_r = \frac{v_r}{n_A + n_B} = \bar{V}_A x_A + \bar{V}_B x_B \tag{4}$$

The difference between the mean molar volumes defined according to equations (2) and (4) is designated as the mean molar mixing volume $\Delta_M V$ and is an intensive measure of the deviation of the mixture from ideal behaviour.

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$$\Delta_M V = V_r - V_{id} = [(V_A - V_B) - (V_A - V_B)]x_A + (V_B - V_B) \tag{5}$$

The dependence of it on the composition is described by the relationship

$$\frac{d(\Delta_M V)}{dx_A} = \frac{dV_r}{dx_A} = \frac{dV_{id}}{dx_A} = (\bar{V}_A - \bar{V}_B) - (V_A - V_B) \tag{6}$$

under consideration of the Gibbs-Duhem equation.

Analogous correlations can be formulated for x_B due to the fact that $x_A = 1 - x_B$.

After substituting (6) in (5), the following relationships are obtained:

$$\bar{V}_B = \Delta_M V - \frac{d(\Delta_M V)}{dx_A} x_A + V_B \tag{7.1}$$

$$\bar{V}_A = \Delta_M V - \frac{d(\Delta_M V)}{dx_A} x_B + V_A \tag{7.2}$$

According to this, the partial molar volumes of the components A and B for the specific compositions (x_A , x_B) can be determined if the molar volumes of the pure substances (V_A , V_B) and their differential quotients d ($\Delta_M V$) / d x_A are known. These can be obtained as the tangent to the graphical plot of $\Delta_M V$ versus x_A (Fig. 2). This is, however, better calculated by deriving the functional correlation $\Delta_M V = f(x_A)$ for selected values of x_A .

The following procedure is recommended for this: First, calculate the exact mole fractional compositions from the weighedout masses of ethanol (A) and water (B) using equation (1.1) or (1.2). With the pycnometer data (m = mass of the liquid in the pycnometer; v = 25 ml = pycnometer volume), the densities ($p = m/v$) of the mixtures and the volumes v_r corresponding to the total masses ($m_A + m_B$) can be determined. These values can be converted into the mean molar volume v_r using equation (4) and then into the mean molar mixing volume $\Delta_M V$ in accordance with equations (2) and (5).

The molar volumes of the pure liquids required for these conversions are v_A = 58.277 ml / mol (ethanol) and v_A = 18.073 ml / mol (water) at T = 293.15 K.

Plot the dependence of the mean molar mixing volume $\Delta_M V$ on the composition x_A analogous to Fig. 2, and determine the differential quotients d($\Delta_M V$ / d x_A from the slope of the tangents for selected mole fractions x_A and the corresponding estimated values for $\Delta_M V$ from the curve itself.

[Note: The correlation between the variables can also be approximated by a polynomial of the second or higher degree using a computer-assisted method. By substituting arbitrary mole fractions x_A in the polynomial or its first derivative, the corresponding estimated value for $\Delta_M V$ and the differential quotients d($\Delta_M V$) / d x_A can be calculated.]

The partial molar volumes of both components are now accessible via equations (7.1) and (7.2).

Finally, calculate the mean molar volume V_r for a selected mixture which corresponds well to the experimental conditions from the partial molar volumes determined according to equation (4) and compare it with your experimental results.

Data and results

Fig. 2 illustrates the volume contraction that occurs on mixing of ethanol and water. From the corresponding polynomial and its first derivative, e.g. for $x_A = x_B = 0.5$, one obtains the partial molar volumes V_A = 56.64 ml / mol (ethanol) and V_B = 16.82 ml / mol (water) by substitution in equations (7.1) and (7.2). These values are definitely less than the molar volumes of the pure substances at 273.15 K (V_A = 58.277 ml / mol, V_B = 18.073 ml / mol). Substituting these values in eqn. (4), one obtains a mean molar volume of V_r = 36.73 ml / mol. The perfect agreement with the experimentally determined value (V_r = 36.73 ml / mol) confirms the validity of the additivity shown in equation (4) and thus the utility of the partial molar volumes for the calculation of the volume of mixed phases of known composition.
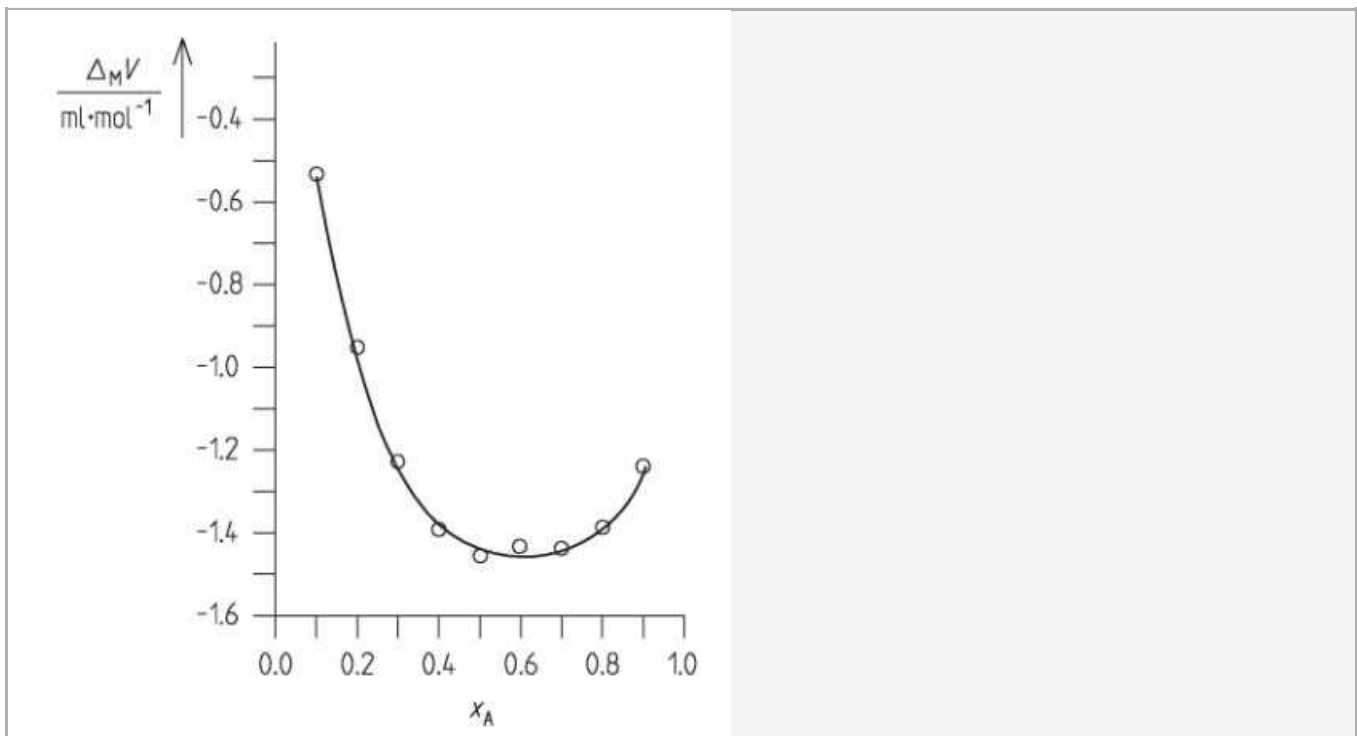
Figure 2: Dependence of the mean molar mixing volumes ΔMV on the composition of different ethanol-water mixtures described by the mole fraction xA of ethanol (T = 293.25 K)

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