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State Behaviour of Liquids

Instructions for laboratory exercises

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1. Theoretical Introduction

1.1. Equation of state

The state behaviour of systems can be expressed in a general form of an equation of state

$$V = \frac{m}{\rho} = g(T, p, n) \quad \text{or} \quad V_m = \frac{M}{\rho} = \frac{V}{n} = f(T, p) \quad (1.1)$$

for a pure substance, and

$$V = \frac{m}{\rho} = g(T, p, n_1, n_2, \dots, n_N) \quad \text{or} \quad V_m = \frac{M}{\rho} = \frac{V}{n} = f(T, p, x_1, \dots, x_{N-1}) \quad (1.2)$$

for a mixture of N components. In Eqs. (1.1) and (1.2) V is the total volume of the system (extensive quantity), m the total mass of the system, ρ the density (mass density), V_m the molar volume (intensive quantity), M the molar mass (of either pure substance or a mixture), n, n_1, n_2, \dots, n_N the amounts of substance of components ($n = n_1 + n_2 + \dots + n_N$) and x_1, x_2, \dots mole fractions.

Besides of the theoretical significance of state behaviour for a study and understanding of microstructure of systems, the knowledge of state behaviour is of basic importance in obtaining data on thermodynamic properties of systems. As an example the well-known relations for pressure dependences of enthalpy (H), Gibbs energy (G) and thermal capacity (C_p)

$$\left(\frac{\partial H}{\partial p}\right)_{T,n} = V - T\left(\frac{\partial V}{\partial T}\right)_{p,n}, \quad \left(\frac{\partial G}{\partial p}\right)_{T,n} = V, \quad \left(\frac{\partial C_p}{\partial p}\right)_{T,n} = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_{p,n} \quad (1.3)$$

can be presented.

1.2. Dependence of volume (density) on temperature and pressure

As follows from the above equations, the volume (density) of a system depends on temperature, pressure, and, in the case of mixture, on composition. Volume changes related to the changes of these variables are expressed using defined quantities.

Relative change of volume (density) related to the unit change of temperature at constant pressure and composition is usually expressed using the coefficient of isobaric thermal expansion (shortly isobaric thermal expansivity)

$$\alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{p,n_1,n_2,\dots} = \frac{1}{V_m}\left(\frac{\partial V_m}{\partial T}\right)_{p,x_1,x_2,\dots} = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_{p,x_1,x_2,\dots} \quad (1.4)$$

Similarly a relative change of volume (density) related to the unit change of pressure at constant temperature and composition is characterized by the coefficient of isothermal compressibility (shortly isothermal compressibility)

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{T, n_1, n_2, \dots} = -\frac{1}{V_m} \left(\frac{\partial V_m}{\partial p} \right)_{T, x_1, x_2, \dots} = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial p} \right)_{T, x_1, x_2, \dots} . \quad (1.5)$$

Thermal pressure coefficient

$$\beta_V = \left(\frac{\partial p}{\partial T} \right)_{V_m, x_1, x_2, \dots} \quad (1.6)$$

is the complementary coefficient to α_p a κ_T . It can be easily derived that

$$\beta_V = \frac{\alpha_p}{\kappa_T} . \quad (1.7)$$

Adiabatic reversible compression or expansion of the system (*i.e.*, the process at constant entropy) can be characterized using the coefficient of isentropic compressibility (alternatively named isentropic or adiabatic compressibility)

$$\kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{S, n_1, n_2, \dots} = -\frac{1}{V_m} \left(\frac{\partial V_m}{\partial p} \right)_{S, x_1, x_2, \dots} = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial p} \right)_{S, x_1, x_2, \dots} . \quad (1.8)$$

Isothermal and adiabatic properties are mutually linked through thermal (caloric) properties. In the case of the above compressibilities the thermal capacity (heat capacity at constant pressure C_p and that at constant volume C_V) is the link

$$\kappa_T - \kappa_S = \frac{TV\alpha_p^2}{C_p} = \frac{TV_m\alpha_p^2}{C_{p,m}} = \frac{TM\alpha_p^2}{\rho C_{p,m}} , \quad \frac{\kappa_T}{\kappa_S} = \frac{C_{p,m}}{C_{V,m}} . \quad (1.9)$$

Speed of sound does not incorporate volume or density directly but is closely related to the state behaviour. Speed of sound wave travelling through an elastic medium is the mechanical process when the system at particular location is periodically compressed and expanded (pressure at that place is periodically changing). At low frequencies (of the order of MHz) the measured speed of sound is equal to the thermodynamic speed of sound u , which is related to the isentropic compressibility *via* the Newton – Laplace equation

$$\kappa_S = \frac{1}{\rho u^2} . \quad (1.10)$$

Using this equation it is feasible to obtain experimental data on the isentropic compressibility and employ them for evaluation of data for thermodynamic properties of systems (see Eq. (1.9)).

1.3. Dependence of volume (density) on composition

1.3.1. Ideal mixture

Properties of real mixtures are usually compared to the properties of the thermodynamic model mixture called an ideal mixture. From the point of view of state behaviour the ideal mixture is defined as a mixture that obeys the Amagat's law that expresses the additivity of volumes (for the sake of simplicity two-component mixtures will be considered in the following text)

$$\begin{aligned} V^{\text{ideal}}(T, p, n_1, n_2) &= V_1^{\circ}(T, p, n_1) + V_2^{\circ}(T, p, n_2) = n_1 V_{m,1}^{\circ}(T, p) + n_2 V_{m,2}^{\circ}(T, p) \quad , \\ V_m^{\text{ideal}}(T, p, x_1) &= x_1 V_{m,1}^{\circ}(T, p) + x_2 V_{m,2}^{\circ}(T, p) = x_1 \{V_{m,1}^{\circ}(T, p) - V_{m,2}^{\circ}(T, p)\} + V_{m,2}^{\circ}(T, p) \quad , \end{aligned} \quad (1.11)$$

where $V_{m,1}^{\circ}$ a $V_{m,2}^{\circ}$ are the molar volumes of pure components at given temperature and pressure. Density of the ideal binary mixture is then given by the formula

$$\frac{1}{\rho^{\text{ideal}}} = v^{\text{ideal}} = \frac{w_1}{\rho_1} + \frac{w_2}{\rho_2} = w_1 v_1 + w_2 v_2 \quad (1.12)$$

where v , v_1 , a v_2 are specific volumes ($v = 1/\rho$) of mixture and pure components 1 and 2, resp., ρ_1 and ρ_2 the densities of pure components 1 and 2, and w_1 and $w_2 = 1 - w_1$ their mass fractions.

The Amagat's law applied to the above defined coefficients (Eqs. (1.4), (1.5)) results in relations for α_p^{ideal} a κ_T^{ideal} of the ideal mixture

$$\alpha_p^{\text{ideal}} = \phi_1 \alpha_{p,1}^{\circ} + \phi_2 \alpha_{p,2}^{\circ} \quad (1.13)$$

$$\kappa_T^{\text{ideal}} = \phi_1 \kappa_{T,1}^{\circ} + \phi_2 \kappa_{T,2}^{\circ} \quad (1.14)$$

where ϕ_1 a ϕ_2 are the volume fractions of components ($\phi_i = x_i V_{m,i}^{\circ} / V_m^{\text{ideal}}$, $i = 1, 2$).

In the case of isentropic compressibility the situation is rather different. Here the derivatives with respect to pressure are performed at constant entropy of the mixture (isentropic compressibility of mixture) and at constant entropy of pure components (isentropic compressibilities of pure components). Eq. (1.9) combined with Eq. (1.14) leads to the expression

$$\kappa_S^{\text{ideal}} = \kappa_T^{\text{ideal}} - \frac{TV_m^{\text{ideal}} (\alpha_p^{\text{ideal}})^2}{C_{p,m}^{\text{ideal}}} = \phi_1 \kappa_{S,1}^{\circ} + \phi_2 \kappa_{S,2}^{\circ} + T \left[\phi_1 \frac{V_{m,1}^{\circ} (\alpha_{p,1}^{\circ})^2}{C_{p,m,1}^{\circ}} + \phi_2 \frac{V_{m,2}^{\circ} (\alpha_{p,2}^{\circ})^2}{C_{p,m,2}^{\circ}} - \frac{V_m^{\text{ideal}} (\alpha_p^{\text{ideal}})^2}{C_{p,m}^{\text{ideal}}} \right] \quad (1.15)$$

Heat capacity of the ideal mixture is given by the relation

$$C_{p,m}^{\text{ideal}} = x_1 C_{p,m,1}^{\circ} + x_2 C_{p,m,2}^{\circ} \quad (1.16)$$

and thus the combination of the Newton – Laplace equation (1.10) with Eqs. (1.12) and (1.15) gives a tool for evaluation of the speed of sound in the ideal mixture

$$u^{\text{ideal}} = \frac{1}{\left(\rho^{\text{ideal}} \kappa_S^{\text{ideal}}\right)^{1/2}} . \quad (1.17)$$

1.3.2. Real mixtures

Two concepts are applied for description of the dependence of volume (density) on composition:

- a) description using partial or apparent molar volumes of the components in a mixture,
- b) description of deviations from the ideal mixture using the excess volume.

a) Partial molar volume of the component in a mixture is defined as a volume change on adding one mole of the component into the mixture at constant temperature, pressure and amount of other components, *i.e.*

$$\bar{V}_1 = \left(\frac{\partial V}{\partial n_1} \right)_{T,p,n_2} = V_m + x_2 \left(\frac{\partial V_m}{\partial x_1} \right)_{T,p} , \quad \bar{V}_2 = \left(\frac{\partial V}{\partial n_2} \right)_{T,p,n_1} = V_m - x_1 \left(\frac{\partial V_m}{\partial x_1} \right)_{T,p} . \quad (1.18)$$

Partial molar volumes are additive, *i.e.* the total volume of the system and the molar volume are given by the expressions

$$V = n_1 \bar{V}_1 + n_2 \bar{V}_2 \quad , \quad \text{resp.} \quad V_m = x_1 \bar{V}_1 + x_2 \bar{V}_2 = x_1 (\bar{V}_1 - \bar{V}_2) + \bar{V}_2 . \quad (1.19)$$

If the volume of the ideal mixture (Amagat's law (1.11)) is substituted into Eq. (1.18) the equalities (1.20) result

$$\bar{V}_1^{\text{ideal}} = V_{m,1}^{\circ} \quad , \quad \bar{V}_2^{\text{ideal}} = V_{m,2}^{\circ} \quad , \quad (1.20)$$

i.e., partial molar volumes of components in the ideal mixture are equal to molar volumes of pure components.

Alternative method of the description of the composition dependence of volume employs apparent molar volume. In this case the mixture is defined non-symmetrically, *i.e.*, one of the components is defined as a solvent (1) and the other one (in the case of binary mixture) as a solute (2). In this concept the mixture is usually called “solution” (of the solute in the solvent). Apparent molar volume of the solute V_2^{app} is defined by the expression

$$V = n_1 V_{m,1}^{\circ} + n_2 V_2^{\text{app}} \quad , \quad V_2^{\text{app}} = \frac{V - n_1 V_{m,1}^{\circ}}{n_2} , \quad (1.21)$$

where $V_{m,1}^{\circ}$ is the molar volume of pure solvent. Apparent molar volume can be evaluated from data on the density of the solution with the molality of the solute $\underline{m}_2 = n_2 / m_1$ (amount of solute (2) per unit mass of the solvent (1)) using the formula

$$V_2^{\text{app}} = \frac{M_2}{\rho} - \frac{\rho - \rho_1}{\underline{m}_2 \rho \rho_1} = \frac{M_2}{\rho} - \frac{\Delta \rho}{\underline{m}_2 \rho \rho_1} , \quad (1.22)$$

where ρ and ρ_1 are densities of solution and pure solvent, resp. It can be easily verified that at infinite dilution (zero concentration of the solute) the equality

$$\lim_{n_2 \rightarrow 0} (V_2^{\text{app}}) = \lim_{n_2 \rightarrow 0} (\bar{V}_2) = \bar{V}_2^0 \quad (1.23)$$

holds. The quantity \bar{V}_2^0 is the partial molar volume at infinite dilution. It is often called standard partial molar (for the standard state of infinite dilution) and represents a volume change on adding one mole of the solute into the infinite amount of the solvent. From the point of view of theoretical considerations concerning the structure of liquids this quantity is particularly significant because it represents the situation when the molecules of the solute are surrounded by the molecules of the solvent and mutual interactions of molecules of the solute are excluded (compared to mixtures with non-zero concentrations).

b) The concept of the description using deviations from the ideal mixture is based on the definition of the excess volume (excess quantities are always assumed to be molar, therefore we omit both the term molar and the subscript m)

$$V^E = V_m - V_m^{\text{ideal}} , \quad V_m^{\text{ideal}} = x_1 V_{m,1}^o + x_2 V_{m,2}^o = x_1 (V_{m,1}^o - V_{m,2}^o) + V_{m,2}^o \quad (1.24)$$

and then the volume of the mixture (total or molar one) is

$$V = n V_m^{\text{ideal}} + n V^E , \quad V_m = V_m^{\text{ideal}} + V^E . \quad (1.25)$$

It can be easily derived that

$$\bar{V}_1 = V_{m,1}^o + V^E + x_2 \left(\frac{\partial V^E}{\partial x_1} \right)_{T,p} , \quad \bar{V}_2 = V_{m,2}^o + V^E - x_1 \left(\frac{\partial V^E}{\partial x_1} \right)_{T,p} , \quad (1.26)$$

hold for the binary mixture where the excess volume is expressed as a function of one variable x_1 .

Using experimental data on density of the mixture ρ and pure components ρ_1, ρ_2 the excess volume is calculated from the definition (1.24) which, after the substitution $V_m = M / \rho$, leads to the expression

$$V^E = V_m - (x_1 V_{m,1}^o + x_2 V_{m,2}^o) = \frac{x_1 M_1 + x_2 M_2}{\rho} - \left(\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2} \right) . \quad (1.27)$$

It is worth mentioning that highly accurate data on both the densities of mixture and pure components and the mixture composition are necessary to get sufficiently accurate values of excess volume. Relation (1.27) represents subtraction of two large and nearly the same numbers (molar volume of real mixture and molar volume of the ideal mixture). Molar volumes are of the order of several tens or hundreds of cm^3/mol while magnitudes of the excess volume are of the order of tenths or units of cm^3/mol .

Following the general definitions of the excess quantity $Y^E = Y_m - Y_m^{\text{ideal}}$ the excess coefficients

$$\alpha_p^E = \alpha_p - \alpha_p^{\text{ideal}} = \alpha_p - (\phi_1 \alpha_{p,1}^o + \phi_2 \alpha_{p,2}^o) \quad (1.28)$$

$$\kappa_T^E = \kappa_T - \kappa_T^{\text{ideal}} = \kappa_T - (\phi_1 \kappa_{T,1}^o + \phi_2 \kappa_{T,2}^o) \quad (1.29)$$

$$\kappa_S^E = \kappa_S - \kappa_S^{\text{ideal}} = \kappa_S - \left\{ \phi_1 \kappa_{S,1}^o + \phi_2 \kappa_{S,2}^o + T \left[\phi_1 \frac{V_{m,1}^o (\alpha_{p,1}^o)^2}{C_{p,m,1}^o} + \phi_2 \frac{V_{m,2}^o (\alpha_{p,2}^o)^2}{C_{p,m,2}^o} - \frac{V_m^{\text{ideal}} (\alpha_p^{\text{ideal}})^2}{C_{p,m}^{\text{ideal}}} \right] \right\} \quad (1.30)$$

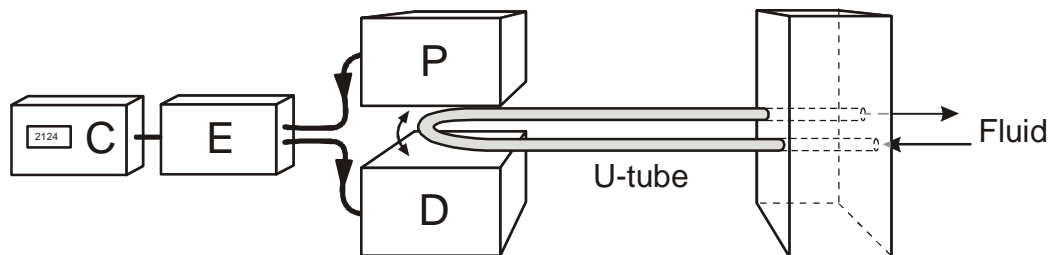
can be defined.

2. Experimental

2.1. Principle of vibrating-tube densimeter

All measurements in the laboratory practicum will be performed by the Density and Sound Velocity Analyzer DSA 5000 (manufacturer Anton Paar, Graz, Austria). A vibrating-tube densimeter with glass U-shaped tube and an additional cell for measurements of speed of sound are main parts of the instrument. The apparatus is equipped with a built-in thermostat allowing measurement in the temperature range from 0 to 70 °C, and with a sample changer which allows automatic loading up to 24 samples.

The principle of measurement by a vibrating-tube densimeter is based on the fact that the frequency (period) of oscillations of a U-shaped tube fixed in a heavy base depends on the total mass of the tube. It means that the frequency is a function of density of the fluid inside the tube.



Continuous oscillations of the tube are maintained by means of a driver D which electromagnetically forces the tube to oscillate and which is controlled by an electronics E. At the same time the electronics reprocesses the alternated electric signal which is produced by the moving tube in a pick-up device P operating on either photoelectric or electromagnetic principle. In other words, the vibrating-tube densimeter is the oscillator the frequency (period) of which is determined by the mechanical element – the U-tube. The oscillation period is measured by an electronic counter C.

Assuming the harmonic oscillator model, a simple relation between density ρ and oscillation period τ can be derived

$$\rho = A\tau^2 + B$$

where A and B are coefficients (constants for given temperature and pressure), which are related to the mechanical and geometrical properties of the U-tube. The values of these coefficients must be determined by a calibration procedure. The calibration of the DSA 5000 instrument is described in the following paragraph.

2.2. Calibration of the DSA 5000 instrument.

The calibration of the instrument is based on the measurement of oscillation periods for two fluids with known densities. Most frequently, the fluids are water and air. Density of liquid water (as a function of temperature), density of dry air (as a function of temperature and pressure) and speed of sound in liquid water (as a function of temperature) are stored in an internal memory of the instrument. All values required for the calibration are automatically loaded from the memory according to the set temperature and atmospheric pressure. Calibration is always performed at 20 °C. As described below, the U-tube is cleaned, dried and filled with air and then with water. During this procedure all necessary data are acquired

and results of the calibration (coefficients *A* and *B*, and data for speed of sound calibration) are stored in the instrument internal memory until the next calibration is performed. For measurement at other temperatures, all calibration parameters are automatically recalculated.

Calibration procedure

1. Fill a glass vial with acetone (approximately half of its volume) and put it into the sample changer (carousel).
2. On the sample changer, press the <START> button. The feeder will start filling the measuring cell.
3. When the filling is finished, press the <STOP> and then <0> button, and remove the vial from the sample changer.
4. Attach the hose leading from the air pump to the lower end of the filling needle.
5. By turning in a counterclockwise direction, release the handle of the peristaltic pump.
6. Press the <PUMP> button on the front panel of the DSA 5000. The air pump will blow air through the measuring cell and after 15 min will stop automatically. During pumping “Pump” flashes on the instrument display.
7. After the cell is dry, wait until the display shows current density of air (its value should be close to 0.0011 g/cm³).
8. Activate the calibration procedure using keys and menus
{Menu} [↵]
{adjustment} [↵]
{adjust} [↵]
{d+vos(air,water)} [↵]
{OK}.
9. Enter current atmospheric pressure in hPa/mbar (you can find its value in the lab B).
10. Wait until temperature is stabilized (“valid“ is displayed as the condition) and then press the {OK} soft key.
11. Put a vial with demineralised water into the sample changer. Disconnect the air hose from the filling needle, return back the handle of the peristaltic pump and press the <START> button on the filling unit. The measuring cell will be filled with water. Caution: Leave the air hose on the left side of the instrument; otherwise it could get into the mechanical gear of the sample changer.
12. Wait until temperature is reached and then press the {OK} key for measurement of the oscillation period.
13. Save the result of calibration by the {Save} soft key. Choose {NO} as response to **Print?**
14. Finish the calibration procedure by the {OK} soft key.

Check the validity of the calibration by the “water check” function

1. Put a vial with demineralised water into the sample changer.
2. Activate the “water check” procedure using {Menu} and keys
{adjustment} [↵]
{watercheck} [↵]
{start watercheck}[↵].
3. Press the <START> button on the filling unit. After filling the cell wait until temperature is reached.
4. If the measurement of density and speed of sound is within the permitted range the display shows “water check: OK”. Save the result by the [Save] soft key. Choose [NO] as response to **Print?**
5. Terminate the procedure by pressing the <STOP> and <0> buttons on the filling unit.

3. Laboratory exercises

The text below gives instructions for laboratory exercises. Basic directions for preparation of samples, measurements and processing of experimental data are given. Representation of experimental data and their processing is shown in the Appendices. The examples are in the form of MS Excel spreadsheets and may serve as a guide for reporting of experimental data and calculated results.

3.1. Partial molar volumes in two component system

Instructions are included in the exercise no. 9 of **Laboratory of Physical Chemistry I**. (“Návody pro laboratorní cvičení z fyzikální chemie”, skripta VŠCHT, pp. 67 – 71, available in the English translation).

3.2. Thermal expansivity of liquids

Name of the exercise:

3.2. Determination of the coefficient of isobaric thermal expansion for pure liquid

Aim of the exercise:

Measurement of density of a pure liquid at several temperatures and evaluation of the coefficient of isobaric thermal expansion.

Definition of the coefficient of isobaric thermal expansion (often shortened to isobaric thermal expansivity) is given by Eq. (1.4). Its value gives a relative volume (density) change per unit change of temperature. Multiplied by 100 it gives the relative change in percent. It is evident, that for evaluation of this coefficient a dependence of total volume, molar volume or density on temperature at constant pressure must be known. From the experimental point of view, it requires a measurement of density at several temperatures.

Experimental

Sample preparation

Sample is an organic liquid. It must be (at least partially) degassed, otherwise bubbles of air can form in the liquid at elevated temperatures. Partial degassing can be reached by decreasing of pressure (by a water pump) in a degassing vessel. After this operation, the liquid must be quickly transferred into a vial. If the measured liquid is immiscible with water and the measuring unit (tube and the sound cell of DSA 5000) is filled with water then water should be washed out with acetone and the unit dried using a built-in pump (the procedure is that described in “Calibration” section). Density of the liquid is then measured by means of the DSA 5000 instrument at given temperatures (in the Appendix, temperature range is from 25 to 65 °C by steps of 5 K). Primary experimental data (temperature and density) are collected in a table.

Procedure of operation the DSA 5000

The first step is the calibration of the instrument. Follow the procedure that has been described above (see paragraph 2.2.). Then, if necessary, dry the measuring unit.

The next step is the measurement.

1. Put the empty sample changer into its initial position – press the <STOP> and <0> buttons.
2. Place the glass vial filled with a sample into the sample changer.
3. From the instrument {Menu} on its display, select the following
 {measurements settings} [↵]
 {general settings} [↵]
 {temp scan} [↵]
 {on} [↵].
4. Set the temperature step and temperature range (enter the values provided by the assistant).
 {temp step} [↵] 5.00 [↵]
 {temp start} [↵] +25.00 [↵]
 {temp stop} [↵] +65.00 [↵].
5. Terminate the selection by the {Esc} soft key.
6. Response {Yes} to the question *Save changes?*
7. Terminate the temperature settings by the {Esc} soft key.
8. Press the <START> button on the sample changer to start measurements.
9. When the measurement cycle is finished and the sample changer returns to the initial position, press the <STOP> button.

Transfer the collected experimental data stored in the instrument memory into the PC by activating the *memory read-out* program installed on the PC.

Processing of experimental data

For evaluation of the coefficient of isobaric thermal expansivity two methods will be applied. The obtained results can be then compared. The evaluation is performed by means of the MS Excel spreadsheets (their examples are given in the Appendix).

A) Analytical derivative method

The analytical derivative method utilises Eq. (1.4)

$$\alpha_p = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_p = \frac{1}{V_m} \left(\frac{\partial V_m}{\partial T} \right)_p ,$$

where the required derivatives are obtained from analytically expressed functions $\rho(t)$ and $V_m(t)$. (Note: Think about the following: The derivative with respect to T in Kelvins is equal to the derivative with respect to t in degree Centigrade.) Generally, if experimental data are well represented, results for α_p evaluated from the both $\rho(t)$ and $V_m(t)$ should not differ too much.

Procedure of experimental data processing.

1. Collect experimental data into an Excel spreadsheet (see the columns A and B in the Appendix)
2. Calculate molar volume (column C). Use the molar mass provided by an assistant.
3. Plot the obtained data on $\rho(t)$ and $V_m(t)$ in graphs and fit them by appropriate functions. The most suitable functions are polynomials (in the Appendix the polynomial of the third degree is fitted to data). Display fitting functions with their parameters and set the number format to at least 7 non-zero digits (it is necessary for sufficient precision of calculations).

Use the displayed parameters and calculate density (column D) and molar volume (column H).

4. Calculate the deviations between the experimental and calculated data (columns E and I). The smaller they are the better fit of the data is obtained. The deviations should be randomly distributed to positive and negative values. If they are too high (more than estimated uncertainty of measurement) or if they exhibit an obvious trend, the chosen fitting function is not capable to describe the data. In this case, it is necessary, for instance, to increase degree of polynomial. The standard deviation can be calculated employing the SMODCH.VÝBĚR function.
5. Using the obtained fitting functions the derivatives $\partial\rho/\partial t$ and $\partial V_m/\partial t$ can be derived and their values calculated (columns F and J).
6. The coefficient of isobaric thermal expansion is evaluated from Eq (1.4) (columns G and K; in the Appendix the values of the coefficient are very small so that they are multiplied by 1000.)
7. The column L shows a comparison of the coefficients calculated from $\partial\rho/\partial t$ and $\partial V_m/\partial t$. If experimental data are precise and are correctly fitted, the good agreement is achieved.

B) Secant evaluation method (method of differences)

This method utilises also the definition of the coefficient of isobaric thermal expansion (1.4). The following procedure will employ only density ρ not molar volume V_m . The derivative $\partial\rho/\partial t$ is substituted by the ratio of differences, *i.e.*

$$\alpha_p = -\frac{1}{\rho} \left(\frac{\partial\rho}{\partial T} \right)_p \approx -\frac{1}{\rho} \left(\frac{\Delta\rho}{\Delta T} \right) .$$

Procedure of experimental data processing.

1. Collect experimental data into an Excel spreadsheet (see the columns A and B in the Appendix)
2. Choose a proper temperature increment (*e.g.*, 5 K, as it is in the Appendix).
3. Calculate mean values (averages) of temperature and density in each temperature interval (columns C and D).
4. Calculate differences in density for each temperature interval (*i.e.* subtract density at lower temperature from that at higher temperature). (Column E).
5. Calculate the coefficient of isobaric thermal expansion for each temperature interval (column F, the coefficient is multiplied by 1000).
6. Compare the results with those obtained by the method A. For this purpose calculate the coefficient for the mean temperatures of each interval. Use the evaluated (by the method A above) function $\rho(T)$. In the example, the calculated values of the coefficient are in the column H and deviations (*i.e.* the comparison of the both methods) in the column I. The agreement is excellent. With increasing temperature increment the agreement will become worse. Try it for the temperature increment of 40 K. Realise that results obtained by this method are the mean values for particular temperature intervals so that the agreement with the method A in the middle of intervals is very good. The method B however does not provide results for other temperatures. Such values can be estimated for example by interpolation. On the contrary, the method A can be applied for obtaining the coefficients at any temperature within the experimental temperature range.

3.3. Standard partial molar volumes of organic substances in water

a) Basic version

Name of the exercise:

3.3a. Determination of the standard partial molar volume of an organic substance in water at several temperatures

Aim of the exercise:

Measurement of density of dilute solutions of an organic substance in water. Evaluation of apparent molar volumes and standard partial molar volumes at several temperatures.

A standard partial molar volume is the partial molar volume of a solute (index 2) in a solvent (here it is water, index 1) at the infinite dilution, *i.e.* at zero concentration of the solute. The standard partial molar volume is usually evaluated by an extrapolation of data experimentally determined for solutions with non-zero compositions to the infinite dilution.

Experimental

Sample preparation

Seven mixtures with molality up to about 1.2 mol/kg are prepared into 250-ml Erlenmeyer flasks with stoppers. In the case of less soluble organic solutes the number of solutions and maximum concentration will be assigned by an assistant. About 200 ml of demineralised water is weighted (with resolution of 0.01 g) into each flask. Mass of water is recorded in the column A (see the Appendix). Pre-calculated amounts of the sample (organic substance) are then differentially weighted (on an analytical balance) from a syringe into the flasks (column B). After weighing the mixtures are homogenized by using a magnetic stirrer. Using molar mass provided by the assistant, molality of each solution is then calculated (column C).

The prepared mixtures are filled into glass vials equipped with caps and silicone septa. The vials are inserted into the 2nd to 8th position of the sample changer. Vials filled with pure water are inserted into positions 1 and 9. Values measured for water from vials 1 and 9 should not differ significantly (within few units of the order 10^{-6} g/cm³), average values at each experimental temperature are then used as density of water for data treatment. Densities are then measured by the instrument DSA 5000 at several temperatures (given by the assistant). The acquired data are collected in tables of the Excel spreadsheet (see the columns A–E).

Procedure of operation the DSA 5000

At first, perform the calibration of the instrument. See the calibration procedure described above (paragraph 2.2).

The measurement:

1. Put the empty sample changer to its initial position by pressing the <STOP> and <0> buttons.
2. Insert the vials with samples into the sample changer.
3. Use soft keys and the Enter key [↵] and from the instrument {Menu} on its display select the following
 {measurements settings} [↵]
 {general settings} [↵]
 {temp scan} [↵]
 {on} [↵].
4. Set the temperature step and temperature range (enter the values provided by the assistant).

{temp step} [←] 20.00 [←]
 {temp start} [←] +25.00 [←]
 {temp stop} [←] +65.00 [←].

5. Terminate the selection by the {Esc} soft key.
6. Response {Yes} to the question *Save changes?*
7. Terminate the temperature settings by the {Esc} soft key.
8. Press the <START> button on the sample changer to start measurements.
9. When the measurement cycle is finished and the sample changer returns to the initial position, press the <STOP> button.

Transfer the collected experimental data stored in the instrument memory into the PC by activating the *memory read-out* program installed on the PC.

Processing of experimental data

Use the MS Excel and its functions for processing of the obtained experimental data. Examples of the Excel spreadsheets are given in the Appendix.

Collect your experimental data into the Excel spreadsheet (see the columns A–E in the Appendix). Fill the column F with density of water and calculate differences between density of the mixture and that of water (column G). Evaluation of the standard partial molar volume can be performed by two methods.

A) Extrapolation of apparent molar volumes

Calculate apparent molar volumes at each composition from Eq. (1.22) into the column H (use correct units). Plot the obtained values for each experimental temperature as a function of molality. Fit these plots by appropriate functions (e.g. polynomials) and display them in the graphs. The absolute term of the used polynomial is equal to the apparent molar volume extrapolated to zero concentration of the solute. This value is also equal to the standard partial molar volume (see Eq. (1.23)).

B) Extrapolation of $\Delta\rho/\underline{m}_2$

Evaluation of the standard partial molar volume is based on the relation giving volume of a mixture which contains 1 kg of a solvent

$$V = (1 + M_2 \underline{m}_2) / \rho = (1 + M_2 \underline{m}_2) / (\rho_1 + a \underline{m}_2 + b \underline{m}_2^2 + c \underline{m}_2^3)$$

The density ρ in this equation is expressed by the polynomial which can be rearranged into

$$\Delta\rho / \underline{m}_2 = (\rho - \rho_1) / \underline{m}_2 = a + b \underline{m}_2 + c \underline{m}_2^2$$

where ρ_1 is density of pure solvent (i.e. water).

The partial molar volume is the derivative of the total volume with respect to molality of the solute, therefore

$$\bar{V}_2 = (\partial V / \partial \underline{m}_2)_{T,p,n_1} = \{M_2 \rho_1 - a - 2b \underline{m}_2 - (M_2 b + 3c) \underline{m}_2^2 - 2M_2 c \underline{m}_2^3\} / (\rho_1 + a \underline{m}_2 + b \underline{m}_2^2 + c \underline{m}_2^3)^2$$

The standard partial molar volume is then obtained as the limit ($\underline{m}_2 \rightarrow 0$)

$$\bar{V}_2^0 = (1 / \rho_1) [M_2 - (a / \rho_1)]$$

where M_2 is molar mass of the solute and a is the limiting value of the ratio $\Delta\rho/\underline{m}_2$. This value is evaluated from experimental data.

Calculate the ratios $\Delta\rho/m_2$ (column H). Plot the obtained values for each experimental temperature as a function of molality. Fit these plots by polynomial functions and display them in the graphs. The limiting value ($m_2 \rightarrow 0$) of $\Delta\rho/m_2$ is equal to the absolute term (a) of the polynomial. The standard partial molar volume of the solute can be then calculated according to the equation derived above. Average value for density of water at each temperature (column F) is used for the calculations.

Note: The example in the Appendix shows an evaluation of measurements of a real system. The both methods resulted in almost the same values.

b) Extended version

Name of the exercise:

3.3b. Determination of the standard partial molar volumes of selected organic substances in water and evaluation of structural-group contributions.

Aim of the exercise:

Measurement of density of dilute aqueous solutions of several compounds from a homological series. Evaluation of apparent molar volume and standard partial molar volume at a defined temperature. Evaluation of group contributions.

A standard partial molar volume is the partial molar volume of a solute (index 2) in a solvent (here it is water, index 1) at the infinite dilution, *i.e.* at zero concentration of the solute. The standard partial molar volume is usually evaluated by an extrapolation of experimentally determined data for non-zero compositions to the infinite dilution.

If experimental data on the standard partial molar volumes are acquired for several compounds differing in number of a particular structural group, the standard partial molar volume of that group can be evaluated. This quantity then represents so called “group contribution” of the structural group. Knowing group contributions for all structural groups that form a molecule, its standard partial molar volume can be calculated (*i.e.* estimated or predicted).

Experimental

Sample preparation

Several organic compounds (usually three) will be measured. Their structures will be specified by an assistant so that molar masses of the compounds can be calculated.

Several mixtures specified by the assistant (usually from 4 to 6 mixtures differing in concentration) are prepared for each compound. About 200 ml of demineralised water is weighted (with resolution of 0.01 g) into a 250-ml Erlenmeyer flask (column A in the Appendix). Pre-calculated amounts of the sample (organic substance) are then differentially weighted (on an analytical balance) from a syringe into the flasks (column B). Maximum concentration is about 1 mol/kg. Using the molar masses, molalities are calculated (column C). Before the measurements, the organic substances must be completely dissolved in water. If necessary, use a magnetic stirrer.

The prepared mixtures are filled into glass vials equipped with caps and silicone septa. These vials together with vials containing pure water are inserted into the sample changer in series displayed in the following figure.

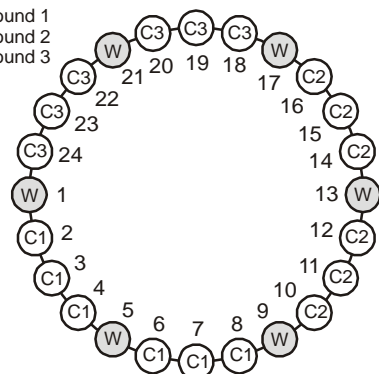
Measurement of 3 compounds

W – water

C1 – mixture of compound 1

C2 – mixture of compound 2

C3 – mixture of compound 3



Measurement of 4 compounds

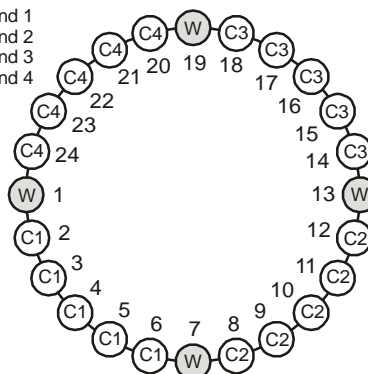
W – water

C1 – mixture of compound 1

C2 – mixture of compound 2

C3 – mixture of compound 3

C4 – mixture of compound 4



Densities of the mixtures are then measured by the instrument DSA 5000 at given temperature. The measurements of pure water (solvent) serve for the check of a possible instrument drift. Values measured for water should not differ significantly (within few units of the order 10^{-6} g/cm³), average values are then used as density of water for data treatment. The acquired data are collected in tables of the Excel spreadsheet (see the columns A–E).

Procedure of operation the DSA 5000

At first, perform the calibration of the instrument. See the calibration procedure described above (paragraph 2.2).

The measurement:

1. Put the empty sample changer to its initial position by pressing the <STOP> and <0> buttons.
2. Insert the vials with samples into the sample changer.
3. Use soft keys and the Enter key [↵] and from the instrument {Menu} on its display select the following
{measurements settings} [↵]
{general settings} [↵]
{temp scan} [↵]
{off} [↵].
Terminate the setting by the {Esc} soft key.
Response {Yes} to the question *Save changes?*
4. Return to the primary menu and set the experimental temperature
{Menu} [↵]
{temperature setting} [↵]
{set temperature °C} [↵]
[↵].
Using the soft keys {Left, Right} and arrows {Up, Down} set the desired temperature.
Terminate the setting by the {Esc} soft key.
Response {Yes} to the question *Save changes?*
5. Finish the selection by the {Esc} soft key.
6. Press the <START> button on the sample changer to start measurements.
7. When the measurement cycle is finished and the sample changer returns to the initial position, press the <STOP> button.

Transfer the collected experimental data stored in the instrument memory into the PC by activating the *memory read-out* program installed on the PC.

Processing of experimental data

Use the MS Excel and its functions for processing of the obtained experimental data. Examples of the Excel spreadsheets are given in the Appendix.

Evaluation of the standard partial molar volumes

Collect your experimental data into the Excel spreadsheet (see the columns A–E in the Appendix). Fill the column F with proper value of the density of water and calculate differences between density of the mixture and that of water (column G).

The evaluation of the standard partial molar volumes as described below is performed using the method of extrapolation of the apparent molar volumes, *i.e.* the method A of the

exercise 3.3a. “Determination of the standard partial molar volume of an organic substance in water at several temperatures”. Alternatively it is possible to employ the method B of the exercise 3.3a. (extrapolation of the ratio $\Delta\rho/m_2$).

For each composition the apparent molar volume (column H) is calculated from Eq. (1.22). The average values are used for density of water (column F). The calculated apparent molar volumes for each compound are plotted in graphs as functions of molality, fitted by proper functions (*e.g.* polynomials) and the resulting fitting functions displayed. If a polynomial is used, the polynomial’s absolute term is equal to the extrapolated apparent molar volume. Extrapolated apparent molar volumes are equal to the standard partial molar volumes (see Eq. (1.23)).

Evaluation of group contributions to the standard partial molar volume.

At first, a structure of the measured compounds must be examined and the group, a contribution of which can be evaluated from the acquired data, must be selected. In the Appendix, it is the $-\text{CH}_2-$ group. A dependence of standard partial molar volume on number of the selected group in each molecule is plotted. If the value of the group contribution is independent on the size of molecule, the linear dependence is obtained. The resulting group contribution is a slope of the corresponding straight line. Its intercept is then the standard partial molar volume of the rest of the molecule (*i.e.* the compound with zero number of the group).

If a limited number of compounds is measured, group contributions can be evaluated by subsequent subtractions of the partial molar volumes. A particular procedure depends on the structure of the measured compounds.

In the example given in the Appendix, the contribution of the $-\text{CH}_2-$ group is $15.756 \text{ cm}^3/\text{mol}$ so the contribution of the rest of the molecule (*i.e.* CH_3OH) is $39.478 \text{ cm}^3/\text{mol}$. This value represents the predicted standard partial molar volume of methanol. It differs significantly from the experimental value published in the literature $38.22 \text{ cm}^3/\text{mol}$. This fact confirms the experience that the first members of homological series are usually out of the trends exhibited by the higher members.

If the CH_3- group is considered to be the a combination of the H atom and the $-\text{CH}_2-$ group, the partial molar volume of water (in water) can be predicted as well. The value $23.722 \text{ cm}^3/\text{mol}$ ($= 39.478 - 15.756$) is for the mentioned reason also substantially different from the molar volume of water ($18.069 \text{ cm}^3/\text{mol}$) at $25 \text{ }^\circ\text{C}$.

The value of the group contribution can be used for prediction (by interpolation or extrapolation) of the standard partial molar volumes for other members of homological series. The example in the Appendix shows the values predicted for 1-pentanol, 1-hexanol and 1-heptanol. You may try to perform similar predictions for other compounds. The prediction can then be compared with experimental data from the literature. Data sources for a comparison with published experimental values will be provided by an assistant.

3.4. Isentropic compressibility of liquid systems

a) Basic version

Name of the exercise:

3.4a. Excess volume and isentropic compressibility of binary liquid mixture

Aim of the exercise:

Measurement of density and speed of sound of binary liquid mixtures and evaluation of the excess volume and isentropic compressibility.

Experimental

Sample preparation

Nine binary mixtures with mole fractions 0.1, 0.2, ..0.9 are prepared by weighing into 100 ml Erlenmeyer flasks with stoppers. Approximate amounts of pure components to be weighted should be calculated in advance to cover evenly the entire concentration range. Molar masses of the pure compounds will be provided by an assistant. The data are recorded in the columns A and B and molar fractions of component 1 (x_1 , column C) in each mixture are calculated (see the Appendix). Immediately after weighing the flasks are closed and placed on a magnetic stirrer.

The prepared mixtures are filled into glass vials equipped with caps and silicone septa. The vials are inserted into the 2nd to 10th position of the sample changer. Vials with pure components are inserted into the first and the 11th positions. If the measured liquids (pure components and mixtures) are immiscible with water and the measuring unit (tube and the sound cell of DSA 5000) is filled with water then water should be washed out with acetone and the unit dried using a built-in pump (the procedure is that described in "Calibration" section). Water can be also removed from the unit by acetone from a vial inserted into the first position of the sample changer (then the vials with measured samples are inserted into positions 2 to 12). Densities and speed of sound data of the mixtures and pure components are then measured by the instrument DSA 5000 at temperature specified by an assistant. The acquired data are collected in tables of the Excel spreadsheets (see the columns D and E).

Procedure of operation the DSA 5000

At first, perform the calibration of the instrument. See the calibration procedure described above (paragraph 2.2). Then, if necessary, dry the measuring unit.

The measurement:

1. Put the empty sample changer to its initial position by pressing the <STOP> and <0> buttons.
2. Insert the vials with samples into the sample changer.
3. Use soft keys and the Enter key [↵] and from the instrument {Menu} on its display select the following
{measurements settings} [↵]
{general settings} [↵]
{temp scan} [↵]
{off} [↵].
Terminate the setting by the {Esc} soft key.
Response {Yes} to the question *Save changes?*
4. Return to the primary menu and set the experimental temperature

{Menu} [↵]
{temperature setting} [↵]
{set temperature °C} [↵]
[↵].

Using the soft keys {Left, Right} and arrows {Up, Down} set the desired temperature.
Terminate the setting by the {Esc} soft key.

Response {Yes} to the question *Save changes?*

5. Terminate the selection by the {Esc} soft key.
6. Press the <START> button on the sample changer to start measurements.
7. When the measurement cycle is finished and the sample changer returns to the initial position, press the <STOP> button.

Transfer the collected experimental data stored in the instrument memory into the PC by activating the *memory read-out* program installed on the PC.

Processing of experimental data

Use the MS Excel and its functions for processing of the obtained experimental data. Examples of the Excel spreadsheets are given in the Appendix.

Experimental data (column A–E) are used for evaluation of the following quantities

- the excess volume using Eq. (1.27) – column F
- the isentropic compressibility using Eq. (1.10) – column G, and deviations from molar average (column H), *i.e.* $\Delta\kappa_S = \kappa_S - (x_1\kappa_{S,1} + x_2\kappa_{S,2})$. Note: These deviations are not differences between behaviours in the real and ideal systems, because the ideal isentropic compressibility is given by the more complicated expression (see Eqs. (1.15) and (1.30)). Plot the both quantities in graphs as functions of mole fraction x_1 .

Molar volume of the ideal mixture (column I) is calculated from the Amagat's law (Eq. 1.11). From these data, densities of ideal mixture of the measured components are calculated (column J). For this purpose, the Eq. (1.12) utilizing weight fractions can be used as well. The densities of the real mixture (column D) and those of the ideal mixture (column J) are plotted in the same graph as functions of x_1 . The differences between these densities (column K) are then plotted in the next graph. Compare and discuss a sign of the obtained results and that of the excess volume.

b) Extended version

Name of the exercise:

3.4b. Isentropic and isothermal compressibility of pure liquid

Aim of the exercise:

Measurements of density and speed of sound of a pure liquid at several temperatures and evaluation of the isentropic compressibility and isobaric thermal expansivity. Evaluation of the isothermal compressibility using the data for heat capacity. Estimation of state behaviour (density) of a liquid at moderate pressures.

Sample preparation

The sample is an organic liquid. It should be (at least partially) degassed, otherwise bubbles of air can form in the liquid at elevated temperatures. Partial degassing can be reached by decreasing of pressure (by a water pump) in a degassing vessel. After this operation, the liquid must be quickly transferred into a vial. If the measured liquid is immiscible with water and the measuring unit (tube and the sound cell of DSA 5000) is filled with water then water should be washed out with acetone and the unit dried using a built-in pump (the procedure is that described in “Calibration” section). Density of the liquid and speed of sound are then measured by means of the DSA 5000 instrument at given temperatures (in the Appendix, temperature range is from 25 to 60 °C by steps of 5 K). Primary experimental data (temperature, density, speed of sound) are collected into a MS Excel spreadsheet (columns A–C).

Procedure of operation the DSA 5000

The first step is the calibration of the instrument. Follow the procedure that has been described above (paragraph 2.2). Then, if necessary, dry the measuring unit.

The next step is the measurement.

1. Put the empty sample changer into its initial position – press the <STOP> and <0> buttons.
2. Place the glass vial filled with a sample into the sample changer.
3. From the instrument {Menu} on its display select the following
{measurements settings} [←]
{general settings} [←]
{temp scan} [←]
{on} [←].
4. Set the temperature step and temperature range (enter the values provided by the assistant).
{temp step} [←] 5.00 [←]
{temp start} [←] +25.00 [←]
{temp stop} [←] +60.00 [←].
5. Terminate the selection by the {Esc} soft key.
6. Response {Yes} to the question *Save changes?*
7. Terminate the temperature settings by the {Esc} soft key.
8. Press the <START> button on the sample changer to start measurements.
9. When the measurement cycle is finished and the sample changer returns to the initial position, press the <STOP> button.

Transfer the collected experimental data stored in the instrument memory into the PC by activating the *memory read-out* program installed on the PC.

Processing of experimental data

Use the MS Excel and its functions for processing of the obtained experimental data. Examples of the Excel spreadsheets are given in the Appendix.

- The isothermal compressibility can be calculated from Eq. (1.9) (the equation on the left side). The isentropic compressibility, density, isobaric thermal expansivity and heat capacity of the measured sample must be known for the calculation. The isentropic compressibility is calculated from Eq. (1.10) (column D).
- The isobaric thermal expansivity is obtained from the definition (1.4). The derivative of density with respect to temperature is evaluated from experimental data. The data on density are regressed by a suitable function of temperature (*e.g.* polynomial) and the derivative needed can be then obtained analytically (column E). For details see the exercise 3.2. “Determination of the coefficient of isobaric thermal expansivity for pure liquid“.
- Necessary data for the isobaric heat capacity for the measured liquid will be provided by an assistant. The values (in appropriate units) are recorded in the column F.

The isothermal compressibility of the sample (column G) is calculated from Eq. (1.9) using the prepared data (columns B, D, E, F).

Knowledge of the isothermal compressibility and isobaric thermal expansivity allows the evaluation of the isochoric thermal pressure coefficient (see Eq. (1.7)). The meaning of this quantity is a pressure change caused by the temperature change of 1 K at constant volume of the system. Values are given in the column H.

Note: In the Appendix there are also data on the isothermal compressibility and isobaric thermal expansivity published for water by NIST (National Institute of Standards and Technology, USA) – columns I and K. The comparison with the experimental data obtained is very good (columns J and L). You will not make such a comparison for your sample liquid, of course.

Estimation of state behaviour of a liquid (its density) at moderate pressures

If the isothermal compressibility κ_T is known, an influence of pressure on density or volume can be estimated. At constant temperature, the definition (1.5) can be rearranged to the form

$$\frac{d\rho}{\rho} = \kappa_T dp$$

Assuming that κ_T does not depend on pressure (this assumption is acceptable if the conditions are far enough from the critical point and the pressure interval is not too wide), the equation can be integrated from p_1 to p_2

$$\rho(p_2) = \rho(p_1) \cdot \exp[\kappa_T (p_2 - p_1)]$$

The expression allows the estimation of density at pressure p_2 using a known value of density at pressure p_1 .

The example in the Appendix shows the calculated values of density at four pressures (column DA–GA) which utilises the measured densities at the atmospheric pressure (0.101 MPa) (column CA) and the obtained values of the isothermal compressibility κ_T (column BA). The differences $\rho(p_2) - \rho(p_1 = 0.101 \text{ MPa})$ at 25 and 60 °C are plotted in the graph as a function of pressure. The curve for 60 °C is a bit lower than that at 25 °C. It is due to the value of κ_T which is smaller at 60 °C than that at 25 °C (see column BA).

Note: Water exhibits many anomalies and thus the results obtained for organic compounds can differ significantly from those shown for water in the Appendix.

4. Appendices

Appendix: Example of the data treatment for the exercise

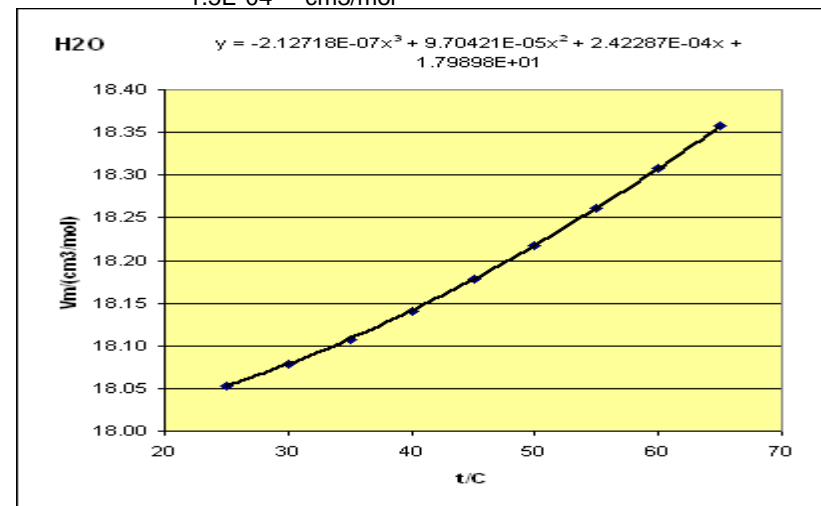
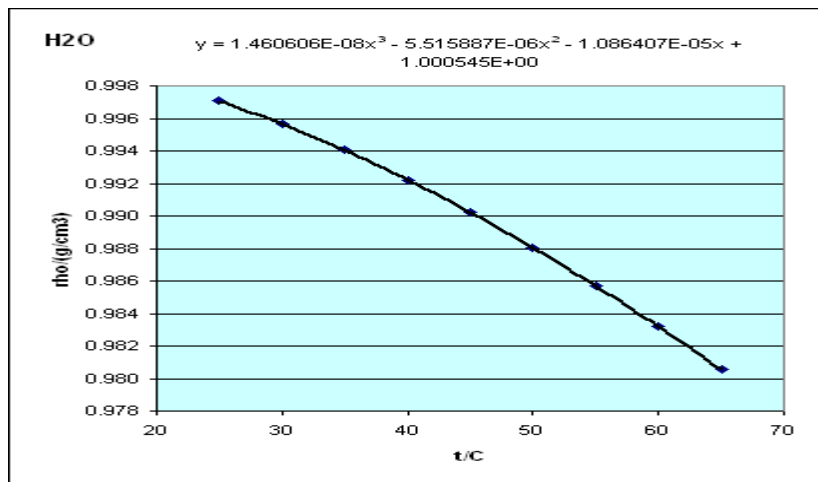
3.2. " Determination of the coefficient of isobaric thermal expansion of pure liquid "

A) Method using an analytical function

EXPERIMENT			Calculation from the dependence $\rho(t)$				Calculation from the dependence $V_m(t)$				
A	B	C	D	E	F	G	H	I	J	K	L
t	$\rho(\text{exp})$	V_m	$\rho(\text{calc})$	dev.(c-e)	$d(\rho)/dt$	$1000 \cdot \alpha$	$V_m(\text{calc})$	dev(c-e)	dV_m/dt	$1000 \cdot \alpha$	dev(ρ, V_m)
C	g/cm ³	cm ³ /mol	g/cm ³	g/cm ³	g/cm ³ /K	1/K	cm ³ /mol	cm ³ /mol	cm ³ /mol/K	1/K	1/K
25.00	0.997057	18.05313	0.997054	-2.8E-06	-2.593E-04	0.260	18.05318	5.4E-05	4.696E-03	0.260	0.000
30.00	0.995642	18.07879	0.995649	7.1E-06	-3.024E-04	0.304	18.07866	-1.2E-04	5.490E-03	0.304	0.000
35.00	0.994041	18.10791	0.994034	-7.0E-06	-3.433E-04	0.345	18.10804	1.3E-04	6.253E-03	0.345	0.000
40.00	0.992226	18.14103	0.992220	-6.2E-06	-3.820E-04	0.385	18.14114	1.2E-04	6.985E-03	0.385	0.000
45.00	0.990202	18.17811	0.990217	1.5E-05	-4.186E-04	0.423	18.17783	-2.8E-04	7.684E-03	0.423	0.000
50.00	0.988051	18.21768	0.988038	-1.3E-05	-4.529E-04	0.458	18.21793	2.5E-04	8.351E-03	0.458	0.000
55.00	0.985690	18.26132	0.985692	2.0E-06	-4.851E-04	0.492	18.26129	-3.2E-05	8.987E-03	0.492	0.000
60.00	0.983189	18.30777	0.983191	1.9E-06	-5.150E-04	0.524	18.30774	-3.0E-05	9.590E-03	0.524	0.000
65.00	0.980547	18.35710	0.980545	-1.6E-06	-5.428E-04	0.554	18.35713	3.3E-05	1.016E-02	0.554	0.000

std.dev.= 8.4E-06 g/cm³

std.dev.= 1.5E-04 cm³/mol



B) Method using secants (differences)

EXPERIMENT

Intervals by 5 K

A	B	C	D	E	F
t	rho(exp)	t(average)	rho(average)	delta(rho)	1000*alpha
C	g/cm3	C	g/cm3	g/cm3	1/K
25.00	0.997048				
		27.50	0.996349	-0.001399	0.281
30.00	0.995649				
		32.50	0.994841	-0.001616	0.325
35.00	0.994033				
		37.50	0.993125	-0.001817	0.366
40.00	0.992216				
		42.50	0.991215	-0.002003	0.404
45.00	0.990213				
		47.50	0.989124	-0.002178	0.440
50.00	0.988035				
		52.50	0.986864	-0.002342	0.475
55.00	0.985693				
		57.50	0.984445	-0.002497	0.507
60.00	0.983196				
		62.50	0.981874	-0.002645	0.539
65.00	0.980551				

EXPERIMENT

One interval 40 K wide

A	B	C	D	E	F
t	rho(exp)	t(average)	rho(average)	delta(rho)	1000*alpha
C	g/cm3	C	g/cm3	g/cm3	1/K
25.00	0.997048				
		45.00	0.988800	-0.016497	0.417
65.00	0.980551				

Comparison with the evaluation from analytical function

G	H	I
	1000*alpha	deviation
	1/K	1/K
	0.282	-0.001
	0.325	0.000
	0.365	0.000
	0.404	0.000
	0.441	0.000
	0.475	-0.001
	0.508	-0.001
	0.539	0.000

Comparison with the evaluation from analytical function

G	H	I
	1000*alpha	deviation
	1/K	1/K
	0.423	-0.006

Appendix: Example of the data treatment for the exercise

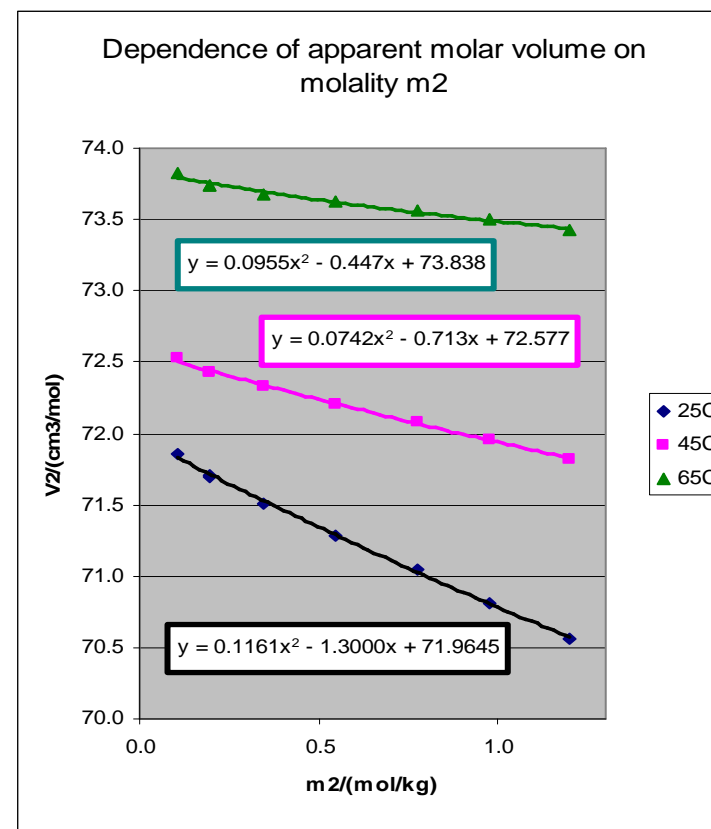
3.3a. "Determination of the standard partial molar volume of an organic substance in water at several temperatures"

EXPERIMENT organic subst. (2) in water (1) Method A: Evaluation using apparent molar volumes

M2 = 60.11419 g/mol

A	B	C	D	E	F	G	H
mass of 1	mass of 2	m ₂	t	rho(solution)	rho(H ₂ O)	del(rho)	V ₂ (apparent)
g	g	mol/kg	C	g/cm ³	g/cm ³	g/cm ³	cm ³ /mol
185.26	1.1770	0.10569	25.008	0.995841	0.997047	-0.001206	71.859
190.24	2.2350	0.19543	25.012	0.994860	0.997047	-0.002187	71.705
189.56	3.9465	0.34633	25.005	0.993278	0.997047	-0.003769	71.509
195.74	6.4101	0.54476	24.997	0.991314	0.997047	-0.005733	71.288
198.71	9.2570	0.77495	25.003	0.989194	0.997047	-0.007853	71.045
197.68	11.6309	0.97875	25.010	0.987473	0.997047	-0.009574	70.812
201.83	14.5770	1.20145	25.008	0.985740	0.997047	-0.011307	70.559
mean t/C			25.005	extrapolation m ₂ =0			71.965

m ₂	t	rho(solution)	rho(H ₂ O)	del(rho)	V ₂ (apparent)	
mol/kg	C	g/cm ³	g/cm ³	g/cm ³	cm ³ /mol	
0.10569	45.002	0.988996	0.990212	-0.001216	72.531	
0.19543	45.010	0.987997	0.990212	-0.002215	72.428	
0.34633	45.008	0.986363	0.990212	-0.003849	72.325	
0.54476	44.997	0.984298	0.990212	-0.005914	72.212	
0.77495	45.002	0.982024	0.990212	-0.008188	72.081	
0.97875	45.006	0.980119	0.990212	-0.010093	71.959	
1.20145	44.993	0.978154	0.990212	-0.012058	71.819	
mean t/C		45.002	extrapolation m ₂ =0			72.577



<u>m2</u>	t	rho(solution)	rho(H2O)	del(rho)	V2(apparent)
mol/kg	C	g/cm3	g/cm3	g/cm3	cm3/mol
0.10569	65.003	0.979287	0.980549	-0.001262	73.820
0.19543	64.997	0.978245	0.980549	-0.002304	73.741
0.34633	65.012	0.976529	0.980549	-0.004020	73.681
0.54476	65.008	0.974342	0.980549	-0.006207	73.624
0.77495	64.994	0.971902	0.980549	-0.008647	73.560
0.97875	65.002	0.969830	0.980549	-0.010719	73.500
1.20145	65.006	0.967660	0.980549	-0.012889	73.429
mean t/C	65.001		extrapolation m2=0		73.838

EXPERIMENT

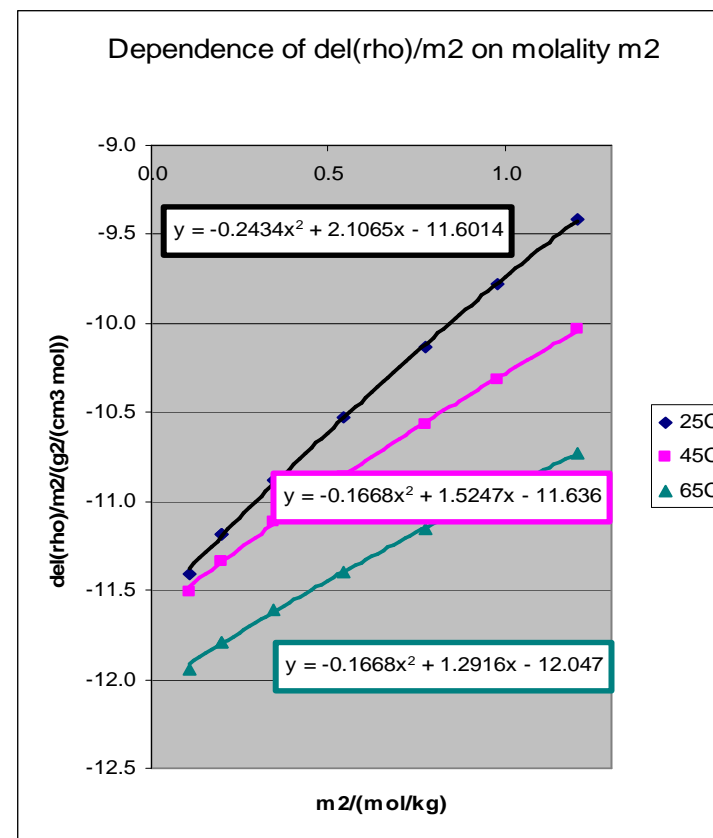
organic subst.(2) in water (1)

Method B: Evaluation using extrapolation of del(rho)/m2

C	D	E	F	G	H
<u>m2</u>	t	rho(solution)	rho(H2O)	del(rho)	del(rho)/m2
mol/kg	C	g/cm3	g/cm3	g/cm3	g2/(cm3 mol)
0.10569	25.008	0.995841	0.997047	-0.001206	-11.412
0.19543	25.012	0.994860	0.997047	-0.002187	-11.188
0.34633	25.005	0.993278	0.997047	-0.003769	-10.882
0.54476	24.997	0.991314	0.997047	-0.005733	-10.524
0.77495	25.003	0.989194	0.997047	-0.007853	-10.133
0.97875	25.010	0.987473	0.997047	-0.009574	-9.782
1.20145	25.008	0.985740	0.997047	-0.011307	-9.411
			extrapolation m2=0		-11.6014
mean t/C	25.005	mean rho	0.997047	V2 =	71.962

m2	t	rho(solution)	rho(H2O)	del(rho)	del(rho)/m2
mol/kg	C	g/cm3	g/cm3	g/cm3	g2/(cm3 mol)
0.10569	45.002	0.988996	0.990212	-0.001216	-11.505
0.19543	45.010	0.987997	0.990212	-0.002215	-11.332
0.34633	45.008	0.986363	0.990212	-0.003849	-11.115
0.54476	44.997	0.984298	0.990212	-0.005914	-10.856
0.77495	45.002	0.982024	0.990212	-0.008188	-10.566
0.97875	45.006	0.980119	0.990212	-0.010093	-10.312
1.20145	44.993	0.978154	0.990212	-0.012058	-10.037
extrapolation m2=0					-11.636
mean t/C	45.002	mean rho	0.990212	V2 =	72.576

m2	t	rho(solution)	rho(H2O)	del(rho)	del(rho)/m2
mol/kg	C	g/cm3	g/cm3	g/cm3	g2/(cm3 mol)
0.10569	65.003	0.979287	0.980549	-0.001262	-11.940
0.19543	64.997	0.978245	0.980549	-0.002304	-11.789
0.34633	65.012	0.976529	0.980549	-0.004020	-11.607
0.54476	65.008	0.974342	0.980549	-0.006207	-11.394
0.77495	64.994	0.971902	0.980549	-0.008647	-11.158
0.97875	65.002	0.969830	0.980549	-0.010719	-10.952
1.20145	65.006	0.967660	0.980549	-0.012889	-10.728
extrapolation m2=0					-12.047
mean t/C	65.001	mean rho	0.980549	V2 =	73.836



Appendix: Example of the data treatment for the exercise

3.3b. " Determination of standard partial molar volume of selected organic substances in water and evaluation of group contributions "

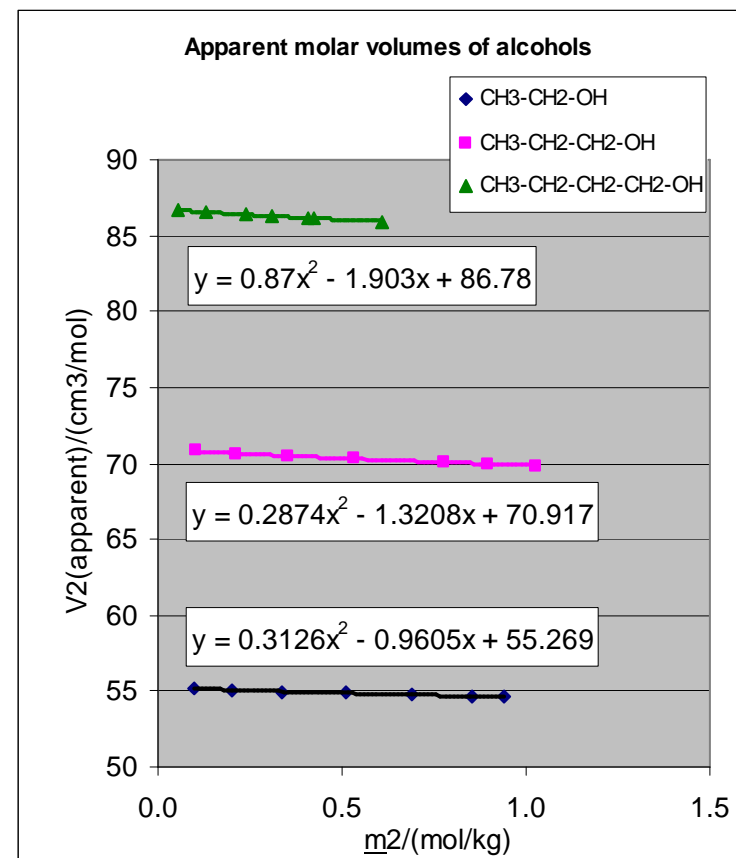
EXPERIMENT organic subst. (2) in water (1) Evaluation using apparent molar volumes

Substance 1: ethanol

A	B	C	D	E	F	G	H
M2 =	46.08122	g/mol	formula	CH3-CH2-OH			
mass of 1	mass of 2	m2	t	rho(solution)	rho(H2O)	del(rho)	V2(apparent)
g	g	mol/kg	C	g/cm3	g/cm3	g/cm3	cm3/mol
194.78	0.8659	0.09647	25.008	0.996190	0.997047	-0.000857	55.200
190.24	1.7585	0.20059	25.012	0.995302	0.997047	-0.001745	55.067
200.21	3.0963	0.33561	24.996	0.994180	0.997047	-0.002867	54.969
189.56	4.4645	0.51109	25.005	0.992773	0.997047	-0.004274	54.865
195.74	6.2292	0.69060	24.997	0.991389	0.997047	-0.005658	54.770
198.71	7.8262	0.85469	25.003	0.990177	0.997047	-0.006870	54.680
197.68	8.5878	0.94275	25.010	0.989547	0.997047	-0.007500	54.631
mean t/C			25.004	extrapolation m2=0			55.27

Substance 2: 1-propanol

A	B	C	D	E	F	G	H
M2 =	60.11419	g/mol	formula	CH3-CH2-CH2-OH			
mass of 1	mass of 2	m2	t	rho(solution)	rho(H2O)	del(rho)	V2(apparent)
g	g	mol/kg	C	g/cm3	g/cm3	g/cm3	cm3/mol
191.25	1.1585	0.10076	25.008	0.996000	0.997046	-0.001046	70.805
196.84	2.5112	0.21222	25.012	0.994897	0.997046	-0.002149	70.631
200.87	4.2751	0.35404	24.996	0.993548	0.997046	-0.003498	70.479
186.76	5.9612	0.53097	25.005	0.991958	0.997046	-0.005089	70.291
199.84	9.3387	0.77737	24.997	0.989870	0.997046	-0.007176	70.083
205.78	11.0683	0.89475	25.003	0.988941	0.997046	-0.008105	69.973
199.74	12.3045	1.02476	25.010	0.987956	0.997046	-0.009090	69.852
mean t/C			25.004	extrapolation m2=0			70.92



Substance 3: 1-butanol

M2 = 74.14715 g/mol formula CH₃-CH₂-CH₂-CH₂-OH

mass of 1	mass of 2	m2	t	rho(solution)	rho(H2O)	del(rho)	V2(apparent)
g	g	mol/kg	C	g/cm3	g/cm3	g/cm3	cm3/mol
185.26	0.7624	0.05551	25.008	0.996370	0.997047	-0.000677	86.701
198.67	1.9286	0.13092	25.012	0.995484	0.997047	-0.001563	86.514
200.69	3.5660	0.23964	24.996	0.994246	0.997047	-0.002801	86.366
214.68	4.9672	0.31205	25.005	0.993449	0.997047	-0.003598	86.278
199.87	6.0646	0.40923	24.997	0.992414	0.997047	-0.004633	86.155
196.47	6.1456	0.42187	25.003	0.992282	0.997047	-0.004765	86.141
208.69	9.4328	0.60960	25.010	0.990384	0.997047	-0.006663	85.936
mean t/C			25.004	extrapolation m2=0			86.78

Evaluation of group contribution of the group -CH₂-

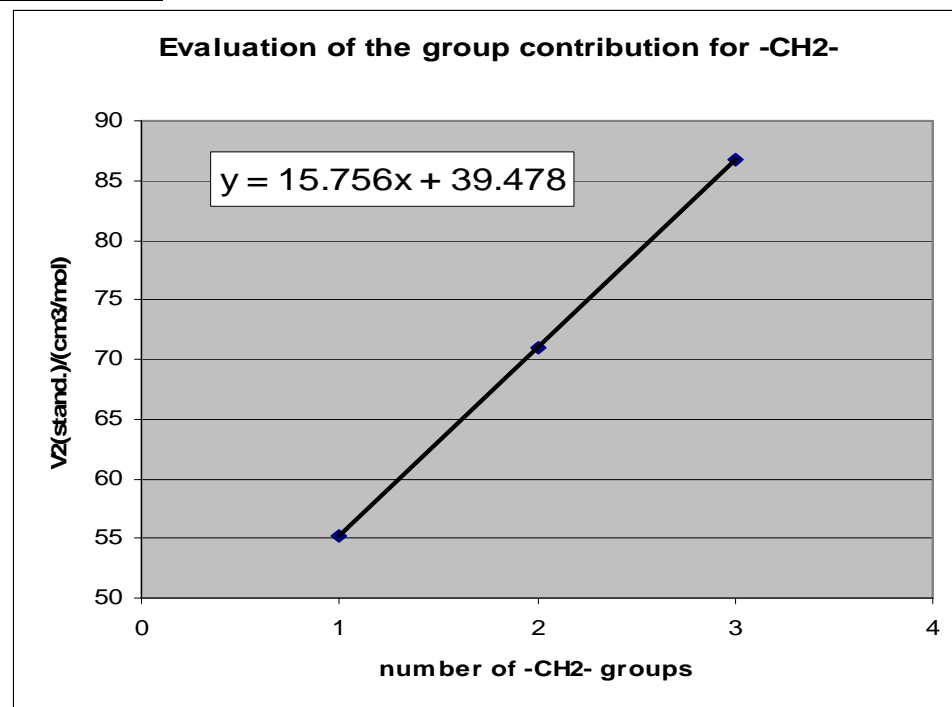
Formula	No. of groups -CH ₂ -	Std. partial mol. volume
		cm ³ /mol
CH ₃ -CH ₂ -OH	1	55.27
CH ₃ -CH ₂ -CH ₂ -OH	2	70.92
CH ₃ -CH ₂ -CH ₂ -CH ₂ -OH	3	86.78

Group contribution -CH₂- 15.756 cm³/mol the slope of the straight line
 Rest of molecule (CH₃-OH) 39.478 cm³/mol the intercept

Std. partial molar volume CH₃OH at 25 C from the literature
 38.22 cm³/mol

Prediction of standard partial molar volumes of higher 1-alkanols

Substance	No of groups -CH ₂ -	Std. partial mol. volume
		cm ³ /mol
1-pentanol	4	102.50
1-hexanol	5	118.26
1-heptanol	6	134.01



Appendix: Example of the data treatment for the exercise

3.4a. " Excess volume and isentropic compressibility of binary liquid mixture"

Component 1: 1-butanol M1 = 74.14715 g/mol formula CH₃-(CH₂)₃-OH

Component 2: n-decane M2 = 142.34553 g/mol formula CH₃-(CH₂)₈-CH₃

EXPERIMENT Mixture of (1) and (2) Calculation

A B C D E F G H

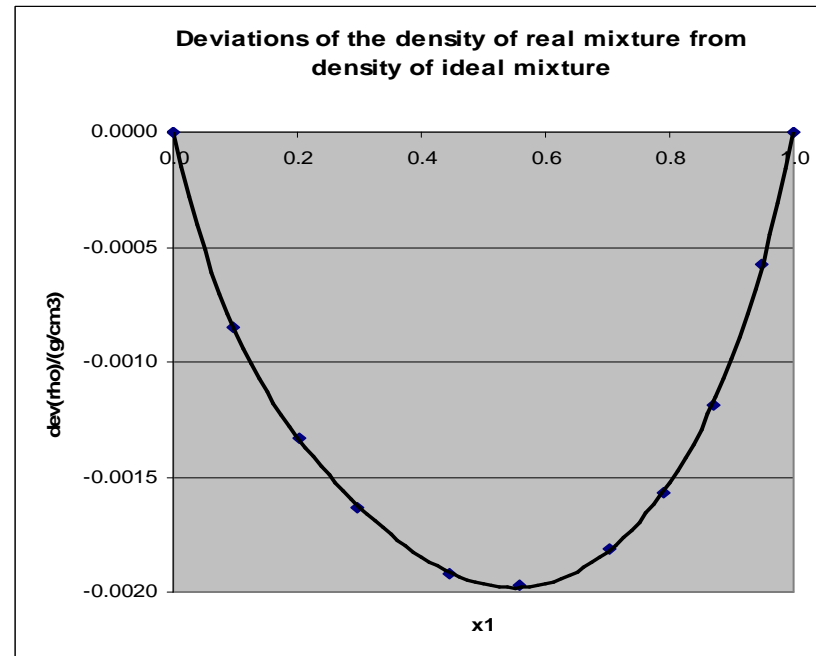
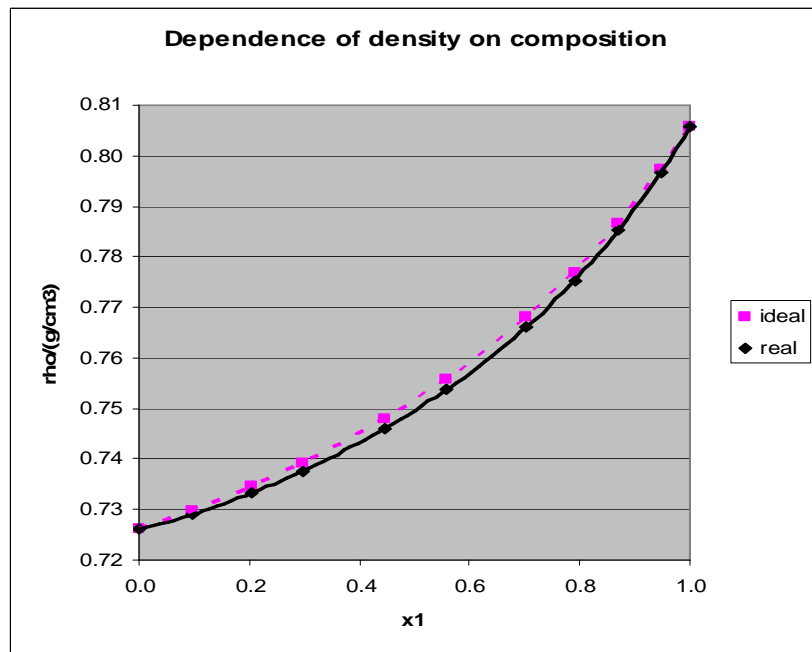
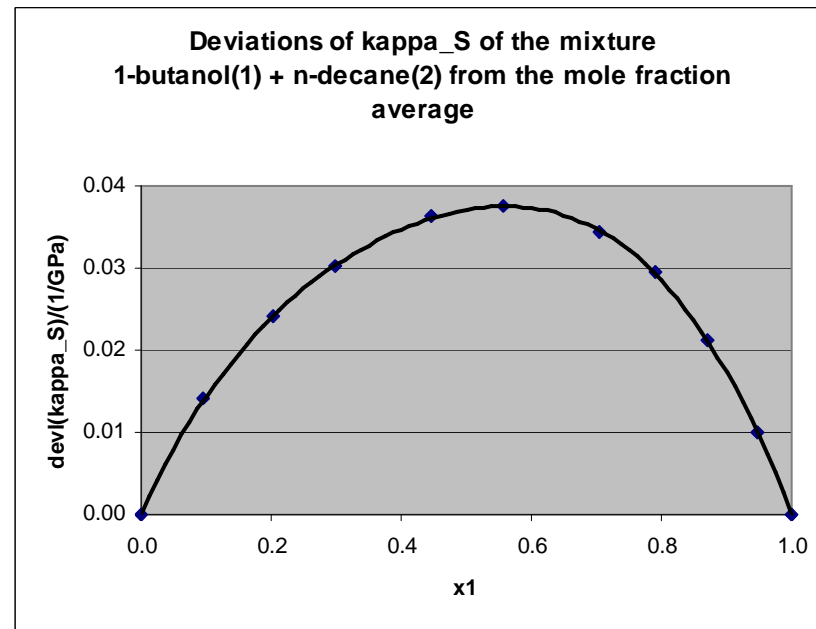
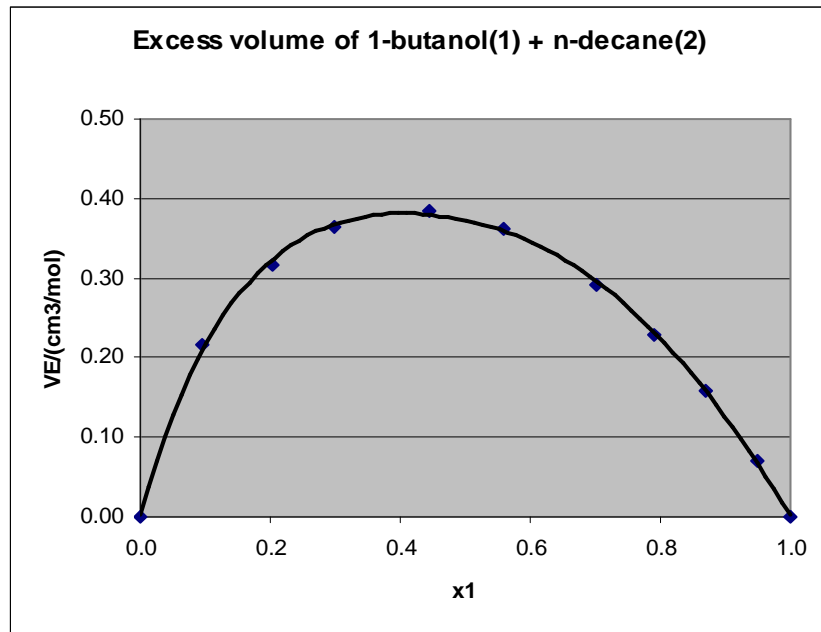
t = 25 C

mass of 1	mass of 2	x1	rho	u	VE	kappa_S	del(kappa)
g	g		g/cm3	m/s	cm3/mol	1/GPa	1/GPa
x	x	0.00000	0.726090	1234.7	0.0000	0.9034	0.0000
2.0125	36.6934	0.09526	0.728990	1228.9	0.2166	0.9083	0.0141
4.2154	31.4878	0.20446	0.733330	1225.6	0.3164	0.9078	0.0240
7.4896	33.9684	0.29740	0.737650	1223.9	0.3653	0.9050	0.0301
10.2145	24.4123	0.44545	0.745960	1222.5	0.3856	0.8970	0.0363
13.5468	20.6112	0.55787	0.753720	1222.7	0.3613	0.8875	0.0376
17.4896	14.1776	0.70311	0.766170	1224.6	0.2913	0.8703	0.0344
24.5478	12.5166	0.79014	0.775350	1226.7	0.2298	0.8571	0.0295
30.1445	8.5946	0.87069	0.785360	1230.4	0.1591	0.8411	0.0212
35.4579	3.7369	0.94796	0.796760	1235.3	0.0707	0.8225	0.0100
x	x	1.00000	0.805670	1239.8	0.0000	0.8075	0.0000

I J K

Ideal mixture

Vm	rho	del(rho)
cm3/mol	g/cm3	g/cm3
196.044	0.726090	0.000000
186.136	0.729838	-0.000848
174.778	0.734658	-0.001328
165.111	0.739282	-0.001632
149.712	0.747881	-0.001921
138.019	0.755693	-0.001973
122.912	0.767986	-0.001816
113.860	0.776915	-0.001565
105.481	0.786544	-0.001184
97.444	0.797338	-0.000578
92.032	0.805670	0.000000



Appendix: Example of the data treatment for the exercise

3.4b. " Isentropic and isothermal compressibility of pure liquid "

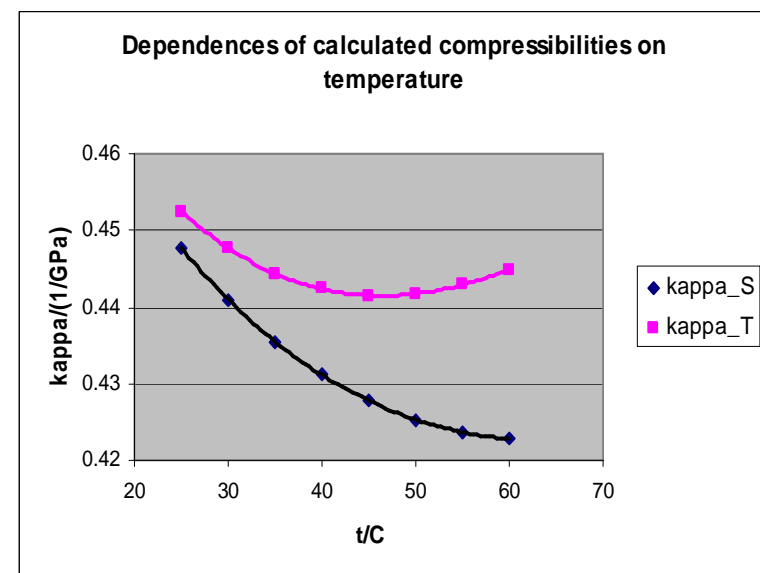
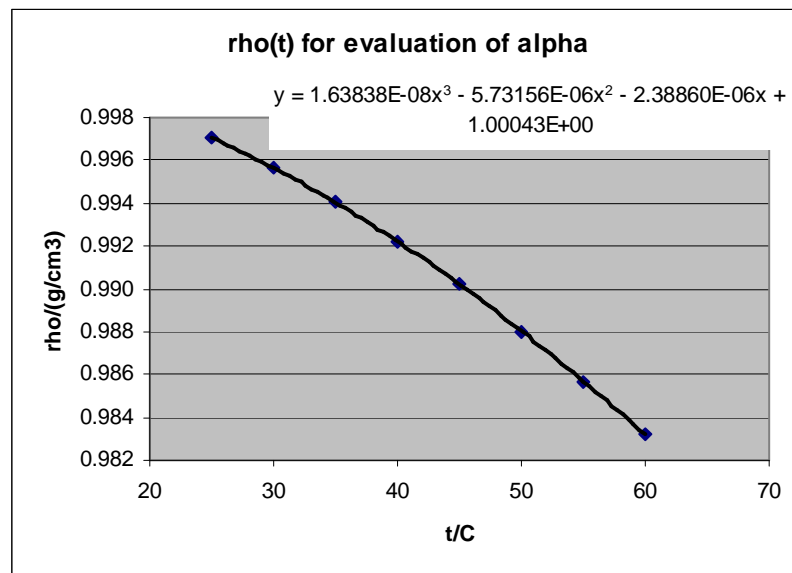
Water

Molar

mass = 18 g/mol

EXPERIMENT			Calculation		Ext. data	Calculation	
A	B	C	D	E	F	G	H
t	rho	u	kappa_S	alpha_P	Cp	kappa_T	beta_V
C	g/cm3	m/s	1/GPa	1/kK	kJ/(K g)	1/GPa	MPa/K
25.00	0.997048	1496.70	0.4477	0.2590	0.0041813	0.4525	0.5724
30.00	0.995649	1509.15	0.4410	0.3034	0.0041798	0.4477	0.6776
35.00	0.994033	1519.85	0.4355	0.3455	0.0041793	0.4444	0.7774
40.00	0.992216	1528.90	0.4312	0.3853	0.0041794	0.4424	0.8709
45.00	0.990213	1536.45	0.4278	0.4228	0.0041801	0.4415	0.9577
50.00	0.988035	1542.58	0.4253	0.4582	0.0041813	0.4418	1.0371
55.00	0.985693	1547.39	0.4237	0.4912	0.0041830	0.4429	1.1091
60.00	0.983196	1550.97	0.4228	0.5220	0.0041850	0.4449	1.1734

NIST		NIST	
I	J	K	L
kappa_T	del kappa T	alpha_P	del alpha P
1/MPa	1/GPa	1/K	1/kK
0.00045246	0.0001	0.00025729	0.0017
0.00044769	0.0000	0.00030338	0.0000
0.00044439	0.0000	0.00034589	-0.0004
0.00044238	0.0000	0.00038548	-0.0002
0.00044153	0.0000	0.00042264	0.0002
0.00044173	0.0000	0.00045778	0.0004
0.00044290	0.0000	0.00049122	0.0000
0.00044498	-0.0001	0.00052325	-0.0012



Estimation of density at elevated pressure using isothermal compressibility

	AA	BA	CA	DA	EA	FA	GA	HA	IA	JA	KA
								deviations rho(p) - rho(0.101 MPa)			
	p/MPa =	0.101	0.25	0.50	0.75	1.00	0.25	0.50	0.75	1.00	
t	kappa_T	rho	rho	rho	rho	rho	del(rho)	del(rho)	del(rho)	del(rho)	
C	1/GPa	g/cm3	g/cm3	g/cm3	g/cm3	g/cm3	g/cm3	g/cm3	g/cm3	g/cm3	g/cm3
25.00	0.4525	0.997048	0.997115	0.997228	0.997341	0.997454	0.000067	0.000180	0.000293	0.000406	
30.00	0.4477	0.995649	0.995715	0.995827	0.995938	0.996050	0.000066	0.000178	0.000289	0.000401	
35.00	0.4444	0.994033	0.994099	0.994209	0.994320	0.994430	0.000066	0.000176	0.000287	0.000397	
40.00	0.4424	0.992216	0.992281	0.992391	0.992501	0.992611	0.000065	0.000175	0.000285	0.000395	
45.00	0.4415	0.990213	0.990278	0.990387	0.990497	0.990606	0.000065	0.000174	0.000284	0.000393	
50.00	0.4418	0.988035	0.988100	0.988209	0.988318	0.988427	0.000065	0.000174	0.000283	0.000392	
55.00	0.4429	0.985693	0.985758	0.985867	0.985976	0.986086	0.000065	0.000174	0.000283	0.000393	
60.00	0.4449	0.983196	0.983261	0.983371	0.983480	0.983589	0.000065	0.000175	0.000284	0.000393	

