

Fakulteta za kemijo in kemijsko tehnologijo

# Laboratory manual for Thermodynamics

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# 1. Vapour-liquid equilibrium

#### **Theoretical background**

Equilibrium represents a static condition in which no change occurs in the macroscopic properties of a system with time. This implies a balance of all potentials that may cause change. In engineering practice, the assumption of equilibrium is justified when it leads to results of satisfactory accuracy. For example, in a distillation column, equilibrium between vapour and reboiler (between gas and liquid phases) is commonly assumed. For finite vaporization rates this is an approximation, but it does not introduce a significant error into engineering calculations. An isolated system consisting of liquid and vapour phases in intimate contact eventually reaches a final state where no tendency exists for a change to occur within the system. The temperature, pressure, and phase compositions reach final values which thereafter remain fixed. The system is in equilibrium. Nevertheless, at the microscopic level, conditions are not static. The molecules comprising a phase at a given time are not the same molecules that later occupy the same phase. Molecules with sufficiently high velocities near the interface overcome surface forces and pass into the other phase. However, the average rate of passage of molecules is the same in both directions, and no net interphase transfer of matter occurs.

#### Vapour liquid equilibrium - VLE

VLE is the state of coexistence of liquid and vapour phases. When a liquid mixture of two components of different volatility is heated up in a closed vessel, vaporisation of both components will occur until the pressure of the vapour attains a steady state corresponding to the boiling point temperature of the mixture. If the temperature of this mixture is maintained constant, vaporisation and condensation of the two components will proceed until equilibrium between the vapour and the liquid is attained. The equilibrium concentration of each component in the liquid phase is often different from its concentration in the vapour phase, but there is a correlation. Such VLE concentration data is often known or can be determined experimentally for vapour-liquid mixtures with various components. In certain cases such VLE data can be determined or approximated with the help of certain theories such as Raoult's Law, Dalton's Law, and/or Henry's Law. It is well-known that equilibria described above are dependent on the total pressure in the vessel.

The most common VLE problem is to calculate the temperature and vapour composition  $y_i$  that is in equilibrium with a liquid at a known total pressure of the system *P* and with a known liquid composition (all the  $x_i$  values). At phase equilibrium the "chemical potential"  $\mu_i$  of each component in the liquid  $\mu_i^l$  and vapour phases  $\mu_i^g$  must be equal:

$$\boldsymbol{\mu}_i^l = \boldsymbol{\mu}_i^g \,, \tag{1.1}$$

The liquid-phase chemical potential of component *i* can be expressed in terms of liquid mole fraction  $x_i$  vapour pressure  $P_i^{sat}$ , and activity coefficient  $\gamma_i$ :

$$\boldsymbol{\mu}_{i}^{l} = \boldsymbol{\gamma}_{i} \cdot \boldsymbol{x}_{i} \cdot \boldsymbol{P}_{i}^{sat} \tag{1.2}$$

The vapour-phase chemical potential of component *i* can be expressed in terms of vapour mole fraction  $y_i$ , the total system pressure *P*, and fugacity coefficient  $\Phi_i$ .

$$\boldsymbol{\mu}_i^g = \boldsymbol{\Phi}_i \cdot \boldsymbol{y}_i \cdot \boldsymbol{P} \tag{1.3}$$

Therefore the general relationship between vapour and liquid phases is

$$\Phi_i \cdot \mathbf{y}_i \cdot \mathbf{P} = \boldsymbol{\gamma}_i \cdot \mathbf{x}_i \cdot \mathbf{P}_i^{sat} \tag{1.4}$$

If the pressure of the system is not high, the fugacity coefficient is unity. If the liquid phase is ideal i.e., there is no interaction between the molecules, the activity coefficient is unity. The latter situation is much less common than the former because components interact in liquid mixtures. They can either attract or repulse. Actually, the activity coefficient expresses the extent of the non-ideality, modifying the activity of the molecules of each component in the mixture in exerting its partial pressure. This is the simplest explanation of the activity and the activity coefficient. The activity coefficient of a component in mixture varies with pressure, temperature and composition of the mixture. Therefore it has to be determined experimentally. It is most frequently calculated from the vapour-liquid equilibrium data for specified conditions.

#### **Experimental apparatus**

Equilibrium apparatus used for measuring vapour-liquid equilibrium data was developed by Ellis. The still is classed as a circulating still. Circulation method was used to find VLE data for binary mixture composed from ethanol and water. The main parts of the still are boiling chamber/section, condensation section, reflux section, heating media. Heating coils are provided inside the boiling section. The schematic diagram of the apparatus assembly is shown in Figure 1. In the boiling chamber A, the mixture vigorously ebullates to produce a vapour liquid mixture that passes through the glass spiral tube B. The vapour entrains drops of the liquid which equilibrate with the vapour and this mixture emerges from the tube at equilibrium, pouring the thermocouple pocket C which contains a thermocouple to measure the boiling temperatures. The vapour then rises through the central tube E, while the liquid drops fall back into the chamber F. The vapour emerging from the tube E passes through the annulus G which is heated electrically in order to prevent condensation. Therefore all the vapour phase passes to the water cooled condenser H. At this place the vapour phase is totally condensed and accumulates in the receiver J. When the receiver J is full of condensate, it overflows and passes through the tube P to mix with the liquid flowing down the tube K from the chamber F. This mixture enters into the heater A to be vaporized again. After thermal equilibrium is reached i.e. when the temperature of vapour and liquid are same, sample of vapour and liquid are withdrawn from the respective ports and analysed with a help of refractometer. The contents of the still are circulated in this way for several hours to ensure that equilibrium is attained. A sample of the vapour phase is taken from the tap M, and a sample of the liquid phase from the tap N.

#### **Experimental procedure and analysis**

Pour the prepared mixture of ethanol and water pour the still until the liquid reaches 'the full level mark'. Turn on the cooling water, and ensure its rapid flow through the condenser. Switch on the electricity to the heating jacket. Turn on the controller of the still to the maximum, and the controller for jacket heater just to one half. When boiling commences, control that 20 drops per minute fall from the base of the condenser into the receiver J. Note the temperature of the boiling liquid recorded by the thermocouple in the pocket C and continue boiling the mixture at this constant rate until the temperature becomes constant. Moreover, the jacket heater has to

be adjusted so that the temperature recorded by thermometer in the pocket R registers  $1^{\circ}C$ 



higher, than the boiling temperature recorded at the site C.

Figure 1.1. : Dynamic recirculating apparatus (Modified Ellis device)

Prepare four clean dry sample bottles – two of them for the liquid sample and the other two for the condensed vapour sample. Draw off about 2 ml of liquid through the tap N into the one bottle, but this liquid is still **not a sample.** Then, immediately withdraw around 10 ml of the

sample into the second bottle from tab N and replace the stopper of the sample bottle as quickly as possible. Moreover, immediately cool the bottle and its content by immersing it in cold water. Repeat this procedure with the sample of the condensed vapour phase from tap M. Determination of the refractive index at 20°C for the cooled samples of both phases followes.

#### Measurements and results

The vapour pressure of the pure substance is calculated with an Antoine-type equation as following (*T*-temperature in  $^{\circ}$ C)

$$\log P_i^{sat} = A - \frac{B}{C+T} \tag{1.5}$$

	Α	В	С	$T_{\min}$ °C	T <sub>max</sub> °C
Water	8.07131	1730.63	233.426	1	100
Water	8.14019	1810.94	244.485	99	374
Ethanol	8.20417	1642.89	230.300	-57	80
Ethanol	7.68117	1332.04	199.200	77	243

**Table 1.1:** The <u>Antoine's constants</u> are given in °C and mmHg. (760 mmHg = 101.325 kPa = 1.000 atm = normal pressure)

$\ln P_i^{sat} = A - \frac{B}{C+T}$					
	Α	В	С		
Water	16.67583	3674.491	226.448		
Ethanol	16.26205	3799.887	226.346		

Table 1.2: The <u>Antoine's constants</u> are given in °C and kPa.

(1.6)

vapour phase:  $\eta_{D}^{20} = 1.3635 \implies w\%$  of ethanol obtained from the calibration curve

$$n_1 = \frac{w\%}{M_{EOH}} = \frac{59}{46} = 1.2826$$
  $n_2 = \frac{w\%}{M_{H_2O}} = \frac{41.0}{18} = 2.2777$ 

*liquid phase:*  $\eta_D^{20} = 1.3560 \implies w\%$  of ethanol obtained from the calibration curve

$$n_1 = \frac{w\%}{M_{EOH}} = \frac{36.3}{46} = 0.7891$$
  $n_2 = \frac{w\%}{M_{H_2O}} = \frac{64.5}{18} = 3.5389$ 

mole fraction of the vapour phase

$$\boldsymbol{y}_1 = \frac{\boldsymbol{n}_1}{\boldsymbol{n}_1 + \boldsymbol{n}_2} \qquad \qquad \boldsymbol{y}_2 = 1 - \boldsymbol{y}_1$$

mole fraction of the liquid phase

$$\boldsymbol{x}_1 = \frac{\boldsymbol{n}_1}{\boldsymbol{n}_1 + \boldsymbol{n}_2} \qquad \qquad \boldsymbol{x}_2 = 1 - \boldsymbol{x}_1$$

Calculation of the activity coefficients of both components

$$\boldsymbol{\gamma}_1 = \frac{\boldsymbol{y}_1 \cdot \boldsymbol{P}}{\boldsymbol{x}_1 \cdot \boldsymbol{P}_1^{sat}} \qquad \qquad \boldsymbol{\gamma}_2 = \frac{\boldsymbol{y}_2 \cdot \boldsymbol{P}}{\boldsymbol{x}_2 \cdot \boldsymbol{P}_2^{sat}}$$

#### **Thermodynamic Consistency Tests - Integral Test**

The Gibbs-Duhem equation imposes a general coupling among the partial molar properties of the components in a mixture and generally represents the basis of most methods to test their thermodynamic consistency. Its general form is;

$$\sum x_i d \ln \gamma_i = -\frac{\Delta V}{RT} dP + \frac{\Delta H}{RT^2} dT$$
(1.7)

At constant temperature and pressure Eq.1.7 may be written for a binary system

$$\boldsymbol{x}_1 \frac{\boldsymbol{d} \ln \boldsymbol{\gamma}_1}{\boldsymbol{d} \boldsymbol{x}_1} + \boldsymbol{x}_2 \frac{\boldsymbol{d} \ln \boldsymbol{\gamma}_2}{\boldsymbol{d} \boldsymbol{x}_2} = 0 \tag{1.8}$$

Equation 1.8 represents the basis of the so-called point-to-point test for thermodynamic consistency, but it is of little use, since VLE data are normally measured at either constant temperature or constant pressure. In its integrated form it becomes

$$\int_{0}^{1} \ln \frac{\gamma_1}{\gamma_2} dx_1 = 0 \tag{1.9}$$

Equation 9 – applicable to the case of only isothermal vapour-liquid equilibrium –means that if we plot  $\ln \frac{\gamma_1}{\gamma_2}$  versus  $x_1$ , the areas above (A) and below (B) the *x*-axis must be equal (Fig. 1.2).

This is the so-called area of Redlich-Kister test in which it is assumed that the volume and heat effects of mixing are negligible. In most isothermal cases, the volume of mixing can be safely neglected and a thermodynamic consistency test can be performed according to the Redlich-Kister method. This is however not the case for isobaric nonisothermal data for which

$$\int_{0}^{1} \ln \frac{\gamma_1}{\gamma_2} dx_1 = \int_{T_2^0}^{T_1^0} \frac{\Delta H}{RT^2} dT = I$$
(1.10)

The right-hand side integral of Equation 1.10 cannot be neglected, and its evaluation requires data on the variation of the heat of mixing with temperature and composition. For consistent data, the value of *I* represents the difference between areas A and B caused by heat of mixing effects, as well as experimental error. Experimental information on the variation of heat of mixing with temperature and composition is rarely available, and to overcome this difficulty Herington proposed an empirical test that estimated the value of the right-hand side integral in Eq.1.10 by using the total boiling point range of a mixture as the only parameter. According to Herington, some deviations from the expected behaviour will result from small experimental errors, and in the light of experience gained in the application of the test to isothermal data, an uncertainty of 10 units in *D* may be arbitrarily assigned to this source. Allowance may be made for the effect of these small deviations in the test by postulating that |D - J| must exceed 10 units before the data can be considered inconsistent. The Herington criteria then become |D - J| < 10 for consistent data and |D - J| > 10 for inconsistent data.

$$\boldsymbol{D} = \frac{|\mathbf{A} + \mathbf{B}|}{|\mathbf{A} - \mathbf{B}|} \cdot 100 < 150 \left| \frac{\boldsymbol{T}_{\max} - \boldsymbol{T}_{\min}}{\boldsymbol{T}_{\min}} \right| = \boldsymbol{J}$$



Where total area A and B of the plot are presented in Figure 1.2

Figure 1.2: An example of an integral test for binary mixtures.

The areas A and B are obtained from integral of  $\ln \frac{\gamma_1}{\gamma_2}$  by assistance of the solver program in Excel to find an interpolation line. An example of integral test is shown in Figure 1.2.

$$\boldsymbol{D} = \frac{|\mathbf{A} + \mathbf{B}|}{|\mathbf{A} - \mathbf{B}|} \cdot 100 = 100 \frac{\int_{0}^{1} \ln \frac{\gamma_{1}}{\gamma_{2}} dx_{1}}{|\mathbf{A} - \mathbf{B}|} = \dots$$
$$J = 150 \left| \frac{T_{\text{max}} - T_{\text{min}}}{T_{\text{min}}} \right| = \dots$$
$$|\boldsymbol{D} - \boldsymbol{J}| = \dots$$

# The excess Gibbs energy $(G^{E})$ and an activity coefficient

Central to the correlation of VLE data are the thermodynamic *excess properties*, which describe the behaviour of the liquid phase. These properties express the differences between actual property values of a solution and the values which would be exhibited by an ideal solution at the same temperature, pressure, and composition. With other words, they represent any kind of deviation from the ideal solution. Usually, they are a strong function of composition and also of temperature, but for liquids they are a weak function of pressure. The excess Gibbs energy cannot be measured directly, but must be calculated from VLE measurements. The excess

Gibbs energy for 1 mole of a binary solution can be expressed as follows:

$$\frac{\boldsymbol{G}^{E}}{\boldsymbol{R}\boldsymbol{T}} = \boldsymbol{x}_{1} \ln \boldsymbol{\gamma}_{1} + \boldsymbol{x}_{2} \ln \boldsymbol{\gamma}_{2}$$
(1.11)

There are several models based on different concepts, but their general feature is that the capability to predict the vapour-liquid or liquid-liquid equilibrium is based on the use of experimental data to fit the model parameters for each binary pair. The model parameters are sometimes called interaction energies due to the fact that the formulation of the models requires these parameters to have the units of energy (for example, kJ/mol). Liquid activity models such as Margules, Wilson, NRTL or UNIQUAC have a set of parameters for each binary component pair. In Wilson model, there are two interaction parameters for a composition pair. In addition, for each pure component the molar volume must be known. UNIQUAC also has two interaction parameters for each component pair. In NRTL there are, in principle, three parameters for a component pairs. In our case the data will be modelled with Margules (two interaction parameters for a composition pair) liquid activity coefficient model. Margules presented the following expression for the excess Gibbs energy of a binary solution:

$$\frac{G^{E}}{x_{1} \cdot x_{2}RT} = A_{21}x_{1} + A_{12}x_{2}, \qquad (1.12)$$

where  $A_{12}$  and  $A_{21}$  present Margules constants which are independent of temperature and composition. The activity coefficients derived from the equation with the application of the relation

$$\ln \gamma_i = \left[\frac{\partial \left(nG^E/RT\right)}{\partial n_i}\right]_{P,T,n_j}$$
(1.13)

are given by

$$\ln \gamma_1 = x_2^2 \Big[ A_{12} + 2 \Big( A_{21} - A_{12} \Big) x_1 \Big]$$
(1.14)

$$\ln \gamma_2 = x_1^2 \Big[ A_{21} + 2 \big( A_{12} - A_{21} \big) x_2 \Big]$$
(1.15)

For the limiting condition of infinite dilution, they show, that  $x_1=0$ ,  $\gamma_1^{\infty}=A_{12}$ , and when  $x_2=0$  (x<sub>1</sub>=1),  $\gamma_2^{\infty}=A_{21}$ . The intercepts at  $x_1=0$  and  $x_1=1$  of the strait line drawn to represent  $G^E/x_1x_2RT$  data points (see Fig 1.3)

T°(C)	<b>X</b> 1	<b>y</b> 1
99.00	0.00	0.0000
89.75	0.05	0.3240
85.25	0.10	0.4390
82.10	0.20	0.5340
80.70	0.30	0.5770
79.75	0.40	0.6130
78.90	0.50	0.6520
78.25	0.60	0.7000
77.60	0.70	0.7500
77.10	0.80	0.8200
76.90	0.90	0.8998
76.90	0.95	0.9470
76.20	1.00	1.0000

Table 1.3.: Consistent data for ethanol (1)-water (2) system at P = 98.65kPa.



Figure 1.3.: Liquid-phase properties from VLR data for ethanol (1)-water (2) at 20°C.



Figure 1.4: Calibration curve of refractive index for ethanol/water, vs. mass fraction

#### Correlation between measured and calculated values for the T-x1-y1

#### **BUBLE T- calculation**

For purpose of finding an initial temperature to start an iteration procedure, you have to need values of saturation temperatures of the pure species (for EtOH and H<sub>2</sub>O) at pressure P.

$$T_{i}^{sat} = \frac{B_{i}}{C_{i} - \ln P} - A_{i}$$

$$i = \text{EtOH, H}_{2}\text{O}$$

$$A_{i}, B_{i}, C_{i} \dots \text{Antoine's constants}$$
(1.16)

For the given P (the ambient pressure) and  $x_1$  (both of them are data from the experimental exercise-VLE) the first value of BUBLE T is calculated on the basis of the following equation.

$$\boldsymbol{T} = \boldsymbol{x}_1 \cdot \boldsymbol{T}_1^{sat} + \boldsymbol{x}_2 \cdot \boldsymbol{T}_2^{sat}$$
(1.17)

In the next step the vapour pressures are given by the Antoine equation,

$$\ln P_i^{sat} = A_i - \frac{B_i}{C_i + T} \tag{1.6}$$

Activity coefficient of EtOH (1) and  $H_2O$  (2) are calculated according to the Margules equation, as follows,

$$\ln \gamma_1 = x_2^2 \Big[ A_{12} + 2 \big( A_{21} - A_{12} \big) x_1 \Big]$$
(1.14)

$$\ln \gamma_2 = x_1^2 \Big[ A_{21} + 2 \Big( A_{12} - A_{21} \Big) x_2 \Big]$$
(1.15)

The new value of  $P_1^{\text{sat}}$ , is calculated by equation (1.18)

$$P_1^{sat^*} = \frac{P}{x_1 \cdot \gamma_1 + x_2 \cdot \gamma_2 \left(\frac{P_2^{sat}}{P_1^{sat}}\right)}$$
 Values obtained  
from Antoine eq (1.18)

With these new values for  $P_1^{sat^*}$  from (Eq.1.16) we cancalculate new  $T_1^{sat}$  and  $T_2^{sat}$  and in continuation also the new boiling temperature *T* (Eq. 1.17).

Repeat the whole procedure until the difference between T and  $T_{n-1}$  is negligible. Moreover, at the last obtainable temperature calculate the composition of the vapour phase as follows:

$$\boldsymbol{y}_1 = \frac{\boldsymbol{x}_1 \cdot \boldsymbol{\gamma}_1 \cdot \boldsymbol{P}_1^{sat}}{\boldsymbol{P}}$$
(1.19)

#### Data analysis and reporting:

- Summary of the experimental work (report in table)

- VLE- data (T<sub>boiling</sub>, *P*, η- refractive index (vapour and liquid phase), w%, weight fraction from the calibration curve (for vapour and liquid phase),
- Temperature and mole fraction of ethanol (vapour and liquid phase)
- $P_1^{\text{sat}}$ ,  $P_2^{\text{sat}}$ ,  $\gamma_1$ ,  $\gamma_2$  (Roult law),  $\ln \frac{\gamma_1}{\gamma_2}$ ,  $\frac{G^E}{RT}$  and  $\frac{G^E}{x_1 x_2 RT}$  for ethanol and water (separate table for consistent data and experimental data).

-Compute and plot the following:

- T-x-y diagram (consistent data + experimental point)
- X-Y equilibrium graph

-Thermodynamic consistency test:

• Plote graph for the consistency test;  $\ln \frac{\gamma_1}{\gamma_2} = f(x_i)$ , versus  $x_i$ , over the complete composition range;  $x_1 = 0.0 \, x_1 = 1.0$  (just for consistent data) and integrate the area under the curve (the areas under the curve on the either side should be equal).

-Calculate and plot activity coefficient-composition diagram for consistent data on the same graph  $\ln \gamma_1, \ln \gamma_2$ , and also  $\frac{G^E}{RT}$  and  $\frac{G^E}{x_1 x_2 RT}$ 

- graphically determine the Margules constants  $A_{12}$ ,  $A_{21}$
- Make the same calculation for experimental data and include point in the same graph

-Correlation of the measured T-x-y data with the calculated ones.

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# 2. Liquid-Liquid equilibria

# **Theoretical background**

While distillation works on the principle of boiling point difference, liquid-liquid extraction works on the principle of chemical structure difference. This makes extraction ideally suited for separation problems such as these listed below by industry;

Chemical	-Washing of acids/bases, polar compounds from organics		
Pharmaceuticals	-Recovery of active materials from fermentation broths		
	-Purification of vitamin products		
Effluent Treatment	-Recovery of phenol		
	-Recovery of acetic acid from dilute solutions		
Polymer Processing	-Recovery of caprolactam for nylon manufacture		
	-Separation of catalyst from reaction products		
Petroleum	-Lube oil quality improvement		
	-Separation of aromatics/aliphatics		
Petrochemicals	-Separation of olefins/parafins		
	-Separation of structural isomers		
Food Industry	-Decaffeination of coffee and tea		
	-Separation of essential oils (flavors and fragrances)		
Metals Industry	-Copper production		
	-Recovery of rare earth elements		
Inorganic Chemicals	-Purification of phosphoric acid		

Extraction is driven by chemical differences, not by vapour pressure differences, and thus can be used in situations when distillation is impractical. For instance, it can be used to separate materials with similar boiling points (so that distillation is impractical) or mixtures containing temperature sensitive compounds.

*Liquid-Liquid extraction* or solvent extraction is actually a mass transfer operation in which a liquid solution (feed) is contacted with an immiscible or nearly immiscible liquid (solvent) that exhibits preferential affinity or selectivity towards one or more of the components in the feed. Thus, if a solution consists of two component A and C, where A is the substance which is desired to recover and C is the liquid, in which the component A is dissolved; A is the 'solute' to be extracted, C is the 'carrier liquid', and the initial solution of A in C is the feed to the extraction process. There it is treated with the solvent B and in this process a large amount of

A will be transferred to B. Therefore a prerequisite is that the liquids B and C do not dissolve in one another to any great extent, but A will be soluble in both.



#### Phase-equilibria – Partially Miscible System

Generally the liquids of B and C are not absolutely insoluble in one another and the three components usually comprise a 'partially miscible system' in which a small amount of B dissolves in C and a small amount of C dissolves in B and this solubility varies with the amount of the solute A that is present. The solubility of such system can be represented as *'Triangular ternary diagram'*. It represents the equilibrium between the various phases that are formed between the three components, as a function of temperature. Normally, pressure is not a viable variable in ternary phase diagram construction, and is therefore held constant at 1 atm. As is depicted on the Figure 2.1 the pure components (A, B,C) are located in the respective corners of the triangle. The side AB represents mixture of A and B. For example the mid-point of the side AB corresponds to a mixture of 50% of A and 50% of B by weight (Fig.2.1.). The concentration of each of the three components can be expressed as either 'wt. %' or 'mol-fraction'. Sum of the concentration of the three components must add up to 100% or 1.



Figure 2.1: Reading a ternary diagram

The point A is at the top of the heavy vertical red line (arrow). Along this line is indicated percent of A. The A point plotted at the top of the vertical line nearest A indicates 100% of A and the horizontal bar at the bottom of the line (farthest from A) represents 0% of A. The point B is at the lower left apex of the triangle. We construct a percent abundance scale for B by rotating the heavy red scale line 120 degrees' counter clock wise so that it runs from the right side of the triangle to the lower left corner. The right side of the triangle now becomes the base line for the percent scale for B, and a series of red lines have been drawn parallel to the triangle's right side to mark off the percentages. These lines are projected out to the left and bottom sides of the triangle, and the percent scale for B laid out along the left side. The point C is at the lower right apex of the triangle. We construct the percent abundance scale for C by rotating the heavy

red scale line another 120 degrees so that it runs from the left side of the triangle to the lower right corner, and the percent scale lines and percent abundance numbers rotate with it.



Figure 2.2.: Liquid-Liquid phase diagram where components A and B are partially miscible.

Thus consider the point 'q' representing a 50% of solution A in C (see Fig.2.2). This is homogenous since A and C are completely miscible. Now, let a small amount of B be added to this solution to form a three component mixture whose composition will be represented inside the triangle. Since the scales are liner this mixture will be represented by a point on the line qB; say at 'r' such that the ratio of:-

$$\frac{\text{Amount of B in mixture}}{\text{Amount of q in mixture}} = \frac{\text{Length of Line qr}}{\text{Length of Line Br}}$$
(2.1)

Point 'r' will represent a mixture made up of one part of pure B and nine parts of a solution of 50 % A in C, and will result in a solution containing 0.45 mass fraction of A, 0.45 mass fraction of C and 0.1 mass fraction of B as can be read from Figure 2.2. Equation 2.1 is known as the 'Lever Rule' and applies to all analyses involving triangular diagrams.

When a small amount of component B is added to the solution 'q' it will dissolve to from a three component solution and its composition will be represented by a point on the line qB. As the amount of B added is increased, this point will move away from 'q' to 'B', but because of the limited solubility of component B a point will be reached where the solution becomes saturated in B. Further additions of B will yield a turbid mixture if the liquids are agitated and two liquid layers will separate when the mixture is allowed to stand. Let this point be 's' on Fig.2.2. It represents the mutual solubility of the three components, and if the above procedure is repeated, starting with different binary mixtures of A and C, the "mutual solubility curve binodal curve" (or mutual saturation curve) will be obtained. From the above, it is evident that the area within the triangle and above the curve correspond to homogeneous mixtures of A, B and C completely miscible in one another. Below the curve the limits of solubility will have been exceeded and two phases will be formed. In fact, if the solution 'q' is agitated with a known quantity of the solvent B such that the heterogeneous mixture formed will be of composition 't', two liquid layers will be formed when the agitator is stopped; one composition 'y' and another composition 'x'. Both 'x' and 'y' will be clear saturated solutions and the straight line joining their compositions on Fig.2.2 will pass through point 't'. This line is known as "tie line", and is by definition the straight line joining an extract and raffinate in equilibrium with one another. There will be an infinite number of tie lines describing the equilibrium of a partially miscible three component system and it is impossible to determine all experimentally. Therefore in practice a small number, never less than five, are determined experimentally and these are correlated by constructing a "tie line correlation curve" as shown for two tie lines in Fig.2.2. That is, a horizontal line is drawn from extract composition point to intersect an inclined line, parallel to side AB of the triangle, from the corresponding raffinate composition point to give the coordinates is obviously the tie line correlation curve and its intersection with the saturation curve gives the "*plait point*". At this point, the last of the tie lines, the mass fraction of A in C in the raffinate is identical with the mass fraction of A and B in the extract.

#### **Determination of Phase Equilibria of a Three Component System**

There are several methods of determining the mutual solubility and tie line data of an immiscible liquid system, but the most convenient and reliable method is to utilise the Smith-Bonner cell. (Fig 2.3) This cell can be used to determine the mutual saturation curve by *cloud point titration* and also to equilibrate a two phase mixture to obtain *tie-line* data.

The apparatus, illustrated in Figure 2.3 consists of three glass vessels each of 100 ml capacity surrounded by glass jacket welded to the cell through which water is circulated to maintain the contests of the cell at any desired temperature. The cell is provided with an agitator whose speed can be controlled, and a side arm near the top as shown for charging the liquid components. The water jacket is connected to a thermostatic bath containing a circulating pump and temperature controller capable of maintaining the temperature at any desired level up to 80 °C. The binodal curve for the water (1)-acetic acid (2)-chloroform (3) ternary system was determined by the cloud-point method. Binary mixtures of known compositions were shaken in a glass stoppered cell (Fig.2.3) equipped with a stirrer and jacketed for circulating water from a constant temperature bath at 25 °C and then titrating with the third component to detect the cloud point. The line data are obtained by agitating heterogeneous mixtures of three components in the cell for at least two hours at the constant desired temperature; then allowing the phase to separate and determining the composition of each phase, preferably by refractive index measurement. Because of the time required to attain phase equilibrium and sufficient tie line data it is more convenient to operate three cells simultaneously. Generally an Abbe Refractometer is the most convenient for refractive index measurement and is sufficiently accurate for these determinations since its temperature can be controlled by connecting to the same thermostatic bath.



Scheme of the Smith-Boner-apparatus

Figure 2.3: Smith-Bonner apparatus

## **Determination of the tie lines**

### The calibration curve

Prepare calibration curves of Refractive Index vs. Composition as follows:

a) Saturate 50 ml of water with chloroform in the Smith-Bonner cell maintained at a temperature of 25 °C and then add 2.5 ml of acetic acid and continue agitating for further 15 minutes. Stop the agitator and then withdraw a few drops of the solution so formed with clean, dry, glass rod and transfer immediately to the rest section of the Abbe Refractomer and measure the refractive index.

Start up the agitator and then add a further 2.5 ml of acetic acid. Allow 15 minutes for the solution to homogenise and then withdraw the sample as above and determine the refractive index. Repeat the above procedure until 25 ml of acetic acid has been added there by giving sufficient points to construct the calibration curve of w% acetic acid in the water saturated with chloroform.

b) Saturate 50 ml of chloroform with water and repeat the above procedure to obtain the calibration curve of w% acetic acid in the chloroform saturated with water.

Refractive index

#### HAc in water saturated with chloroform

HAc in chloroform saturated with water

$V_{\rm CH3COOH}/{ m ml}$	Refractive index
2.5	
5.0	
7.5	
10.0	
12.5	
15.0	
17.5	
20.0	

Illustrative curves are presented in Figs.2.4 and 2.5. However, it should be emphasised that the experimentalist should always prepare his own celebration curves using the same solutions as those to be utilised in the tie-line determinations.



Figure 2.4.: Calibration curve - *water saturated with chloroform* (Refractive index vs. w% of acetic acid).



Figure 2.5: Calibration curve - *chloroform saturated with water* (Refractive index vs. w% of acetic acid).

#### **Tie – Line Determination**

Fill the cell with a heterogeneous mixture consisting of X ml of distilled water, Y ml of acetic acid and Z ml of chloroform. Maintain a constant temperature of 25° C in the cell as before. Agitate the mixture using the mid-speed for at least two hours at this temperature. Stop the

agitator (but leave the constant temperature water circulating) and leave the mixture for about 1 hour to settle into two distinct, clear layers with a sharp interface. Withdraw a sample of each phase, using a glass rod, and measure the refractive index of each sample at 25°C. For this purpose four consecutive drops should be observed in the refractometer and, unless exactly reproducible readings are obtained, an average value of refractive index recorded. The precise amount of acetic acid present can be determined from the calibration curves similar to Figs 2.4 and 2.5 and since the composition of these solutions will be on the saturated mutual solubility curve which can be performed on the ternary diagram. A test of accuracy of the experiment work can be made since the tie-line of the compositions of the extract and raffinate in equilibrium with one another must pass through the total mixture point based on the amounts added to the Smith-Bonner cell.

Repeat the above experimental procedure with total mixtures containing the following quantities of different liquids in order to determine the composition of five tie-lines.

V <sub>H2O</sub> (ml)	V <sub>HAc</sub> (ml)	V <sub>CHCl3</sub> (ml)	$\eta_{{}_{H\!AcvH_2O}}$	$\eta_{{}_{H\!A\!cvC\!H\!C\!l_3}}$	$W\%_{HAcvH_2O}$	W% HACVCHCl 3
20	8	22	1.3510	1.4361	25.14	3.55
12	15	23	1.3655	1.4215	45.86	16.82
15	10	25	1.3571	1.4319	33.86	7.36

Table 2.1 Example of experimental values of three tie-lines.

#### Determination of the "mutual solubility curve- binodal curve"

Fill the cell with a homogeneous mixture consisting of *X* ml distilled water and *Y* ml of acetic acid. Switch on the thermostat unit and check that water is circulating through the jacket of the cell. Set the temperature control to the temperature desired for the equilibrium determination; in this experiment the temperature is  $25 \,^{\circ}$  C. Switch on the stirrer and adjust the speed control to the mid-point of the range. Allow 10 minutes for the contents of the cell to reach the set temperature. Slowly titrate chloroform into the mixture in the cell so that the temperature remains constant at  $25^{\circ}$ C and continue the titration until **'cloudiness'** appears and persists, in the mixture; at this point record the exact quantity of chloroform that has been added. This is

the cloud point at which chloroform added saturates the ternary mixture so that the amounts of water, acetic acid and chloroform are in the equilibrium. It represents one point on the ternary solubility curve.

Empty the cell and wash using about 5 ml acetone directed into the top of the interior walls using a wash bottle and collect in a beaker for disposal. Repeat the experiment with other homogeneous mixtures of distilled water and acetic acid to obtain further points on the solubility curve. Not less than six points are required to construct one side of the curve.

## Chloroform Rich Phase

Repeat the procedure using homogenous chloroform-acetic acid solutions and titrating with water. At least a further six points are required.

For the conversion of volume to weight - the volumes were measured at ambient (25°C), and use the following liquid densities determined at 25°C

Component	ho /gml <sup>-1</sup>
water	0.9982
Acetic acid	1.0500
Chloroform	1.4750

V / ml	V / ml	Titration values V / ml
38 ml H <sub>2</sub> 0	10 ml HAc	* 1.8 ml CHCl <sub>3</sub>
15 ml H <sub>2</sub> 0	10 ml HAc	* 1.5 ml CHCl <sub>3</sub>

Example (two points for binodale)

$$ut\% = \frac{m}{\sum m}$$

<b>m</b> н20 (g)	m <sub>HAc</sub> (g)	<b>m</b> <sub>снсв</sub> ( <b>g</b> )	W% H2O	W% HAc	W% CHCl <sub>3</sub>
37.93	10.5	2.66	74.25	20.55	5.20
14.97	10.5	2.21	54.08	37.93	7.99

#### **Correlations - Tests of Reliability of Results**

The reliability of the equilibrium data may be tested by applying the Othmer-Tobias correlation producer. This correlation indicates that there is a liner relation between the values of

$$\ln\left(\frac{1 - w_{11}}{w_{11}}\right) = a + b \cdot \ln\left(\frac{1 - w_{33}}{w_{33}}\right) \quad \text{where,}$$
(2)

 $w_{33}$  = solvent fraction in the extract phase

 $w_{11}$  = fraction by weight of the carrier liquid in the raffinate phase.

From the Fig.2.6 it can be seen that the tie lines determined experimentally fall onto a very good straight line. The point that is slightly off the line could be repeated. Nevertheless all the other tie lines lie on a good straight line and therefore one must reevaluate that particular experimental result.



Figure 2.6: The Othmer-Tobias correlation test

#### **Distribution ratio**

In solvent extraction, a distribution ratio is often quoted as a measure of how well-extracted a species is. The distribution ratio (D) is equal to the <u>concentration</u> of a <u>solute</u> in the organic phase divided by its concentration or mole fraction in the aqueous phase. Depending on the system, the distribution ratio can be a function of temperature, the concentration of chemical species in the system, and a large number of other parameters.

$$\boldsymbol{D}_1 = \frac{\boldsymbol{w}_{13}}{\boldsymbol{w}_{11}},$$

 $w_{13}$  - weight fraction of water in the chloroform rich phase  $w_{11}$  - weight fraction of water in the water rich phase

$$D_2 = \frac{w_{23}}{w_{33}},$$

 $w_{23}$  - weight fraction of acetic acid in the chloroform rich phase  $w_{33}$  - weight fraction of acetic acid in the water rich phase

#### **Separation factor**

The separation factor is one distribution ratio divided by another; it is a measure of the ability of the system to separate two solutes.

$$S = \frac{D_2}{D_1}$$

The effectiveness of extraction is given by its separation factor (S), which is an indication of the ability of chloroform to separate acetic acid from water. This quantity has to be greater than one, which means that extraction of acetic acid by chloroform is possible. It is, however, not constant over the whole two-phase region.

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# 3. Heat of Solution

## **Theoretical background**

The molecules or ions making up a solid solute exist in a highly ordered state which is referred to as a lattice. When this solute dissolves in solvent, particles such as ions must be removed from the lattice and each solute particle must then be completely surrounded by solvent molecules. The process of dissolving a solid solute in a liquid solvent can therefore be thought of as occurring in two steps:

Step 1: A particle of solute, such as an ion or a molecule, breaks away from the lattice.

Step 2: The solute particle is surrounded by solvent molecules.

To form solution energy is required to break the bonds between the particles within the solid/liquid. Heat is also required to break the bonds in a solvent to insert one of the solute molecules into solution. Hence these processes are endothermic. Heat is released when the solute molecules form bonds with the solvent molecules i.e. this process is exothermic.

Depending on whether more energy is used to break the bonds within the solute and solvent or is released when new bonds are formed between the solute and solvent, the process overall can be exothermic or endothermic.

- If more energy is required to break the bonds within the solute and solvent than the energy released when new bonds are formed between the solute and solvent, then the process is endothermic.
- If more energy is released when new bonds are formed between the solute and solvent than the energy required to break the bonds within the solute and solvent, then the process is exothermic.

The heat effects that accompany the dissolution of the solute in the solvent or in the solution are quantitatively described by integral and differential heat of solution.

- <u>Integral enthalpy (or heat) of solution</u>,  $\Delta_{sol}H$  is the heat absorbed or released when a solute is dissolved in a definite amount of solvent. The heat of solution depends on the nature of the solute and on its concentration in the final solution. The integral heat of solution when one mole of solute is added to an infinite amount of solvent. The solution processes are conveniently represented by physical-change equation analogous to chemical-reaction equations as follows:

$$HCl(g)+5 H_2O(l) \rightarrow HCl (5 H_2O)$$
  $\Delta_{sol}H^{\bullet}(298K) = -63,467 kJmol^{-1}$ 

Often heat of solution is not reported directly and must be calculated from heats of formation, by the reverse of the calculation as is illustrated below:

$$\text{LiCl}(s) + 5\text{H}_2\text{O}(l) \rightarrow \text{LiCl}(5\text{H}_2\text{O})$$
  $\Delta_{sol}H^{\bullet}(298K) = -28,194 \, kJ$ 

Integral heat of solution for dissolving 1 mol of LiCl into the 5 moles of water is -28,194 kJ.

- <u>Differential heat of solution</u>,  $\Delta_{dif}H$  is the partial derivative of the total heat of solution with respect to the molal concentration of one component of the solution, when the concentration of the other component or components, the pressure, and the temperature are held constant.

The differential heat of solution cannot be measured; it can be calculated according to equation 3.1

$$\Delta_{dif}H\left(T,p,\frac{n_2}{n_1}\right) = \left(\frac{\partial(n_2\Delta_{sol}H)}{\partial n_2}\right)_{n_{1,T,p}}$$
(3.1)

At a constant amount of water,  $\frac{1000}{18gmol^{-1}} = 55,56 mol = n_1$ , the expression  $n_2$  can be changed by b – molality of the solution, therefore the differential heat of solution (3.1) is expressed as follows:

$$\Delta_{dif}H\left(T,p,\frac{n_2}{n_1}\right) = \Delta_{sol}H(T,p,b) + b\left(\frac{\partial(\Delta_{sol}H)}{\partial b}\right)_{T,p}$$
(3.2)

<u>The integral heat of dilution</u>  $\Delta_{dil}H$  between molalities  $\boldsymbol{b}_1$  and  $\boldsymbol{b}_2$  is defined as the heat effect, at constant temperature and pressure, accompanying the addition of enough solvent to a quantity of solution of molality  $\boldsymbol{b}_1$  containing one mole of solute to reduce its molality to the lower value  $\boldsymbol{b}_2$ . The integral heat of dilution is thus equal to the difference of the integral heats of solution at the two molalities involved:

$$\Delta_{dil}H = \Delta_{sol}H(b_2) - \Delta_{sol}H(b_1) \tag{3.3}$$

#### Procedure

#### Standardizing the calorimeter

In order to calculate the heat, Q, involved in a reaction, the heat capacity, C (energy equivalent) of the calorimeter and its contents must be known. Values of C are determined by running several calibration experiments in which the calorimeter is operated in the usual manner but with reactants which release (or absorb) a known amount of heat.

$$C = \frac{Q_E}{\Delta T_C} \tag{3.4}$$

#### Standardization with TRIS.

For standardizing the **1451 calorimeter**, solid TRIS can be dissolved in dilute hydrochloric acid in a controlled reaction for which the amount of heat evolved is well established. In the recommended standardization procedure described below, 0.5 g of TRIS is dissolved in 100 *ml* of 0.1 *N* HC1 to evolve 245.76 J/(g of TRIS) at 25°C. For the selected mass of TRIS, the heat  $Q_E$  at the reaction temperature of the  $T_{0.63}$  is expressed according to equation (3.5)

$$Q_E/J = m(245.76 + 1.4364(25 - T_{0.63}))$$
(3.5)

The term  $1.4364(25 - T_{0.63})$  adjusts the heat of reaction to any temperature above or below the 25 °C (reference temperature) m represents the mass of TRIS in g.

This is the procedure:

- 1. Initially, the Dewar flask is filled with 100.00 ml of 0.10 mol/ L HCl (take a pipette) and then placed into the calorimeter.
- 2. Weigh  $0.50 \pm 0.01$  g of TRIS into the teflon dish on an analytical balance to an accuracy of  $\pm 0.0001$  g.
- 3. Assemble the rotating cell; place it in the calorimeter and start the motor.
- Let the calorimeter reach to equilibrium; set the recorder at 0.1 V (1.0°C) full scale; set the baseline at the bottom of the chart for an exothermic reaction and trace a thermogram as previously described.
- 5. Analyse the thermogram to determine the net corrected temperature rise,  $\Delta T_C$  and  $T_{0.63}$ . (see Figure 3.1)
- 6. Calculate the known energy  $Q_E$  input by substituting in the equation (3.5):

7. Calculate the heat capacity of the calorimeter C(3.4)

#### Calculating the Energy change

Determination of *integral heat of solution* for LiCl in *n* moles of water

- The whole procedure is the same as was at standardization of calorimeter with one difference, instead of HCl, take now 100.0 ml of distilled water. Use four weighed samples of LiCl(s) of such size as to prepare solutions of about 0.15, 0.3, 0.5, 1.0 molalities [ set the recorder at 0.1 V (1.0°C full scale) or 1.0 V (10.0°C full scale), which is depends on the concentration of the solution].
- Analyse the thermogram for dissolution of LiCl and determine  $\Delta T_C = T_2 T_1$
- Calculate the heat, Q, according to equation (3.6)  $Q = \Delta T_C \cdot C$ (3.6)
- Calculate the  $\Delta_{sol}H$  for each solution in J/g

$$\Delta_{sol}H = -\frac{Q}{m} , \qquad (3.7)$$

where *m* is the mass of LiCl. By multiplying with molar mass *M* (LiCl) the  $\Delta_{sol}H$  for one mole of LiCl at  $T_{0.63}$  is obtained.



Figure 3.1: Graphic Procedure for Determining  $\Delta T_{c}$ 

Integral heat of solution depends on the concentration, so we have to give in what amount of water we have dissolved 1 mol of LiCl.



Figure 3.2 Liquid calorimeter

## The measurement protocol

The temperature measuring system in this calorimeter consists of a thermistor probe and a special bridge designed for use within the ten-degree span from 20° to 30° C. The following values will apply when equating changes in thermometer output to temperature changes.

 $0.1 V = 1.0^{\circ}C$  $1 V = 10.0^{\circ}C$ 

There are five switch positions on the selector switch in the centre of thermometer panel,

OFF, ZERO, NULL, CAL and READ.

- 1. Turn the recorder on and turn the thermometer selector switch to ZERO (calorimeter) for a warm up period before making any adjustments. Although the thermometer will usually warm up in ten minutes, a longer time period up to thirty minutes may be required to reach maximum stability.
- 2. Start the chart drive (recorder) at a speed of 3 cm/s.
- 3. Set the range switch on the recorder to 1.0 V (Volt) full scale. In this position the full scale of the chart represents a span of 10°C.
- 4. Turn the selector switch to NULL and bring the pen to its zero base-line with the null adjustment.

- 5. Turn the selector switch to CAL and adjust to 100% (a pen to the 100% position on the chart.
- 6. Turn the selector switch to READ. The position 1.0 V full scale on the chart represents a span of 10°C. Each major unit on the chart represents 1°C. Therefore a reading of 4.52 units on the chart indicates a temperature of 24.52°C in the calorimeter (20°C baseline + 4.52°C on the chart scale). At the beginning the calorimeter is set to 20 °C. Then change the range selector on the recorder to 0.1 V (1.0 °C) full scale. If the pen then moves to 5.23 major divisions on the chart, the temperature in the calorimeter is 24.523°C (24°C baseline + 0.523°C on the chart).
- 7. Beginning the Trace. The liquid in the Dewar and the sample in the rotating cell must reach thermal equilibrium, and the recorder must trace a straight line for at least 3 or 4 minutes before starting the reaction

# Reading the thermogram (Fig. 3.1.)

In order to determine the net temperature change produced by the reaction it is necessary to locate a point on the thermogram at which the temperature reached 63% of its total rise (or fall). This can be done easily using the graphic procedure which is described below, although other variations of this method can be used as well.

- 1. Place a straight edge over the pre period drift line and extend this line well past the point at which the cell was opened to start the reaction.
- 2. Move the straight edge to the post period drift line and extrapolate this line backward to the time when the cell was opened. If there are fluctuations in the drift lines due to noise or other variations in the signal, use the best average when drawing these extrapolations.
- 3. Using a centimeter scale, measure the vertical distance, R, between the two extrapolated lines at a point near the middle of the reaction period.
- 4. Multiply the distance, R, by 0.63, then
- 5. Set the zero end of the centimeter scale on the extrapolated preperiod drift line and movethe scale along this line to locate a vertical intercept with the thermogram which is exactly 0.63R above the preperiod drift line. Draw a vertical line through this point to intercept both draft lines.
- 6. Read the initial temperature,  $T_1$ , and the final temperature,  $T_2$ , at the points of intersection with the drift lines and subtract to determine the corrected temperature.

$$\Delta T_C = T_2 - T_1 T_{0.63} = T_1 + (\Delta T_C \cdot 0.63)$$

#### **Measurements and calculations**

- In the table all the weighted mass of TRIS and LiCl, volume of solvents and all the temperatures obtained from thermograms ( $T_1, T_2, \Delta T_C, T_{0.63}$ ) have to be presented.
- The next table should contained calculated values of  $Q_E$ , C, Q,  $\Delta_{sol}H$  and integral heat of solution within different amounts of water.
- Compare your results (values of integral heat of solution for LiCl) with those of the literature: *Introduction to chemical engineering thermodynamics / J.M. Smith, H.C. Van Ness, McGraw-Hill, 1987, fourth edition, page. 436.*
- The integral heat of solution, should be plotted as a function of molality, and the differential heat of solution should be evaluated at given molality (assistant) by use of Eq. (3.2).
- Calculate the integral heat of dilution at molality of 0.5 and 1.0.



- All the thermograms should be added.

 $\widetilde{n}$ , moles of H<sub>2</sub>O per mole of solute

Figure 3A :Heat of solution at 25 °C (Based on data from "The NBS Tables of Chemical Thermodynamic Properties", "J. Phys. Chem. Ref. Data., Vol.11, suppl.2,1982.)

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# 4. Partial molar quantities

#### **Theoretical background**

Definition of partial molar quantity is as follows: Change in the considered extensive quantity when an infinitesimal amount of substance is added to the system at constant temperature, pressure and amounts of all other constituents of the system divided by the added amount.

A partial molar quantity is an intensive state function. Its value depends on the temperature, pressure, and composition of the mixture because of various types of molecular interactions. Imagine a huge volume of pure water at 25°C. When a further 1 mol H<sub>2</sub>O is added, the volume increases by 18 cm<sup>3</sup> and we can report that 18 cm<sup>3</sup> mol<sup>-1</sup> is the molar volume of pure water. However, when we add 1 mol H<sub>2</sub>O to a huge volume of pure ethanol, the volume increases by only 14 cm<sup>3</sup>. The reason for the different increase in volume is that the volume occupied by a given number of water molecules depends on the identity of the molecules that surround them. In the latter case there is so much ethanol present that each  $H_2O$  molecule is surrounded by ethanol molecules exclusively, and the tighter packing of the molecules results in H<sub>2</sub>O molecules increasing the volume by only 14 cm<sup>3</sup>. The quantity 14 cm<sup>3</sup> mol<sup>-1</sup> is the partial molar volume of water in pure ethanol. In general, the partial molar volume of a substance A in a mixture is the change in volume per mole of A added to a large volume of the mixture. The partial molar volumes of the components of a mixture vary with composition because the environment of each type of molecule changes as the composition shifts from pure A to pure B. It is this changing molecular environment, and the consequential modification of the interaction acting between molecules, that results in the variation of the thermodynamic properties of a mixture as its composition is changed.

The partial molar volume is the contribution that one component in a mixture makes to the total volume of a sample. The partial molar volume,  $V_J$ , of a substance J at some general composition is defined formally as follows:

$$\overline{V}_{J} = \left(\frac{\partial V}{\partial n_{J}}\right)_{p,T,n_{i}} \tag{4.1}$$

The **partial molar volume** is the slope of a plot of total volume as the amount of J in the sample is changed (volume vs. Composition, Figure 4.1) the pressure, temperature, and the amount of the other components being constant.



Figure 4.1: The partial molar volume of a substance is the slope of the variation of the total volume of the sample plotted against the composition. In general, partial molar quantities vary with the composition, as shown by the different slopes at the compositions *a* and *b*. Note that the partial molar volume at *b* is negative: the overall volume of the sample decreases as A is added (Atkins).

The definition in eqn 4.1 implies that, when the composition of the mixture is changed by the addition of  $dn_A$  of A and  $dn_B$  of component B, then the total volume of the mixture changes by:

$$dV = \left(\frac{\partial V}{\partial n_A}\right)_{p,T,n_B} dn_A + \left(\frac{\partial V}{\partial n_B}\right)_{p,T,n_A} dn_B = \overline{V_A} dn_A + \overline{V_B} dn_B$$
(4.2)

The integration of the equation is carried out with a constant composition, where the partial molar volumes are constant. The whole volume is then expressed as follows:

Provided the composition is held constant as the amounts of A and B are increased, the final volume of a mixture can be calculated by integration. Because the partial molar volumes are constant (provided the composition is held constant throughout the integration) the whole volume we can write as follows:

$$nV = \overline{V_A} n_A + \overline{V_B} n_B \tag{4.3}$$

Further, the above equation is divided by the amount of substance n, and the expression for the molar volume of the solution V is in accordance with the equation (4.4);

$$V = \overline{V_A} \cdot X_A + \overline{V_B} \cdot X_B \tag{4.4}$$

The partial molar volume of component A and B can be determined from the molar volume given by the mole fraction of  $X_A$  or  $X_B$ ,

$$V = (\overline{V_A} - \overline{V_B}) \cdot X_A + \overline{V_B} \qquad \text{or} \qquad V = \overline{V_A} - (\overline{V_A} - \overline{V_B}) \cdot X_B$$

Now we can express  $\overline{V_A}$  and  $\overline{V_B}$  as follows:

$$\overline{V_A} = V + (\overline{V_A} - \overline{V_B}) \cdot X_B \qquad \text{and} \qquad \overline{V_B} = V - (\overline{V_A} - \overline{V_B}) \cdot X_A \qquad (4.5)$$

The difference of the partial molar volumes of the components is equal to the derivative of the molar volume with respect to  $X_A$ ,  $(\overline{V_A} - \overline{V_B}) = \frac{dV}{dX_A}$ . By insertion of the previous expression into the equation (4.5) the partial molar volumes of components A and B could be expressed in accordance with equation (4.6):

$$\overline{V_A} = V + X_B \frac{dV}{dX_A}$$
 and  $\overline{V_B} = V - X_A \frac{dV}{dX_A}$  (4.6)

Partial molar volumes could be obtained through the determination of the molar volumes V of mixtures (at different molar fractions). In continuation a mathematical function that represents V as a function of molar fraction (of the added component) has to be determined e.g.

 $V = a + b \cdot X_A + c \cdot X_A^2$ . Finally,  $\frac{dV}{X_A}$  is the derivative of the function  $V = f(X_A)$  (actually  $V = f(X_A)$  represents a quadratic function of  $X_A$  in the concentration ranges of measurements).

#### Change of the molar volume because of mixing

The change of the volume because of mixing  $\Delta V$  is the volume change that is observed if 1 mol of solution from pure liquid (A and B i.e. methanol-water) at constant p and T is generated:

$$\Delta V = V - (X_A \cdot V_A + X_B \cdot V_B), \text{ where}$$
(4.7)

 $V_A$  and  $V_B$  are molar volume of pure components. The volume of the solution V could be higher or lower as are the sum of individual volume of pure components. In case of higher volume of the solution V (positive change of the molar volume) indicates volume expansion upon mixing and thus repulsive interaction of mixing solvents or weaker interactions than the interactions of pure solvents. On the other hand, negative change of the molar volume shows stronger interactions of mixed molecules than individual molecules before mixing. When molecules within the mixture are approximately of the equal size, then the forces between them are almost indentical also after mixing. Therefore  $\Delta V=0$  meaning the solution is ideal.

Relation between  $\Delta V$  and partial molar volumes could be obtained if molar volume of solution *V* is expressed as follows  $V = \overline{V_A} \cdot X_A + \overline{V_B} \cdot X_B$  (Eq.4.4). When this expression is inserted into the equation 4.7 we obtain

$$\Delta V = (\overline{V_A} \cdot X_A + \overline{V_B} \cdot X_B) - (X_A \cdot V_A + X_B \cdot V_B) = X_A \cdot (\overline{V_A} - V_A) + X_B \cdot (\overline{V_B} - V_B)$$

The partial properties, exactly the partial molar volume changes of mixing are found by the application of equations (4.8):

$$\Delta \bar{V}_A = \bar{V}_A - V_A \qquad \text{and} \qquad \Delta \bar{V}_B = \bar{V}_B - V_B \qquad (4.8)$$

$$\Delta V = X_A \cdot \Delta \bar{V}_A + X_B \cdot \Delta \bar{V}_B \tag{4.9}$$

We can say that the  $\Delta \overline{V}_A$  represents the volume change of solution when 1 mol of A becomes a component of the solution at particular composition at constant pressure and temperature (the partial molar volumes are properties of the mixture, and not just of the individual components).

#### Procedure

Prepare five solutions of methanol in distilled water according to the instructions of the teaching assistant.

Weigh empty flasks, flasks with added methanol and finaly with added distilled water filled up to the mark. The densities of the solutions are measured with a Mettler density meter that has been calibrated by determining the density of water at the temperature 20°C (follow the instructions of the teaching assistant). First, rinse the meter with a few portions of reagent grade water using the following steps. Fill the meter by dipping the inlet tube into the liquid and pulling the liquid into the oscillator U-tube using the syringe. Carefully examine the U-tube to ensure that there are no bubbles. Exercise extreme care in filling, rinsing, cleaning, and handling the meter.

#### **Results and Calculations**

On the basis of the weights of flasks, a mass of methanol and water could be obtained, further regarding to the densities of the sample solutions calculate the partial molar quantities as follows

- Calculate the mole for each component and in continuation the number of moles of solute per 1 mole of water
- Methanol(2)-<sub>Water</sub>(1)

$$n_{MeOH} = \frac{m_{MeOH}}{M_{MeOH}} \qquad n_{M_{H_2O}} = \frac{m_{H_2O}}{M_{H_2O}}$$

$$n_{MeOH} = 3.199 \text{ g/ } (32 \frac{\text{g}}{\text{mol}}) \qquad n_{M_{H_2O}} = 0.3398 \text{ mol}$$

$$n_{MeOH} = 0.09998 \text{ mol}$$

$$0.09998 \text{mol MeOH.....0.33984 mol H_2O}$$

$$\underline{x \text{ mol.....1mol H_2O}}$$

 $x = 0.2942 \text{ mol MeOH per 1 mol H}_2\text{O}$ 

• Volume of solution V<sub>solution</sub>

$$V_{solution} = \frac{n_1 M_1 + n_2 M_2}{\rho_{solution}}$$

$$\rho_{\text{solution.}} = 945.38 \text{ g/dm}^3$$

 $V_{solution} = \frac{1mol \cdot \frac{18g}{mol} + 0.2942 \ mol \cdot \frac{32g}{mol}}{945.18g/dm^3} = 29.004 \ ml \ (0.029 \ dm^3)$ 

Molar volume

*Quantity symbol:*  $V_{\rm m}$  SI unit: cubic meter per mole (m<sup>3</sup>/mol).

*Definition*: volume of a substance divided by the amount of substance:  $V_{\rm m} = V/n$ .

Notes:

- 1. The word "molar" means "divided by amount of substance."
- 2. For a mixture, this term is often called "mean molar volume."
- mean molar volume  $V_m$

$$V_m = \frac{V_{solution}}{n_1 + n_2} = \frac{29.004 \ ml}{1 \ mol + 0.2942 \ mol} = 22.411 \ ml/mol$$

• mole fraction  $X_2$ 

$$X_2 = \frac{n_2}{n_1 + n_2}$$

• Draw a graph  $V_m$  vs.  $X_2$ , and with the help of the program EXCEL determine the equation of the curve (second degree polynomial)

$$V_m = aX_2^2 + bX + c$$

• determine the constants a, b, c and make the derivative curve

$$V_m' = 2aX_2 + b$$

$$\overline{V}_1 = V_m - \underbrace{\frac{n_2}{n_1 + n_2}}_{X_2} \cdot \underbrace{\frac{\partial V_m}{\partial X_2}}_{2aX_2 + b}$$

$$\overline{V_1} = V_m - 2aX_2^2 - bX_2 \qquad \qquad \overline{V_2} = \frac{V_m - X_I\overline{V_I}}{X_2}$$

• partial molar volume for pure components

$$V_{1} = \frac{M_{H_{2}O}}{\rho_{H_{2}O}} \qquad \qquad V_{2} = \frac{M_{MeOH}}{\rho_{MeOH}}$$

• calculate the excess volumes (partial molar change of mixing)

$$\Delta V_1 = V_1 - V_1$$
$$\overline{\Delta V_2} = \overline{V_2} - V_2$$

• excess volume (total) of binary system

$$\Delta V = x_1 \overline{\Delta V_1} + x_2 \overline{\Delta V_2}$$

• draw the following figures

$$-\mathbf{V}_{\mathrm{m}} = \mathbf{f} (\mathbf{X}_{2})$$
$$-\overline{V_{1}}, \overline{V_{2}} = \mathbf{f} (\mathbf{X}_{2})$$

$$-\Delta V, \overline{\Delta V_1}, \overline{\Delta V_2} = f(X_2)$$

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