3. DENSITY, EXPANSION COEFFICIENT AND ENTHALPY CHANGE IN LIQUID TRANSFORMATION

GOALS

● Measure the density variation of a liquid within a temperature interval.

● Obtain the expansion coefficient of a liquid in the aforementioned interval.

● Analyse the enthalpy change of the liquid when the volume changes with the temperature at the same temperature range.

THEORETICAL BACKGROUND

The density, or quotient between the mass (in grams or Kg) and the volume occupied by this mass (in cm^3 or litres), is a characteristic magnitude of different substances or materials. To give just one example, plastic materials, with densities that rarely exceed 1 g/cm^3 have replaced metallic parts in automobiles which used to be made of metals like iron, steel or copper with densities up to eight times higher. As a consequence, car weights have been substantially lowered, thereby their fuel consumption has been also reduced.

The inverse of density (its symbol is ρ) is known as its ***specific volume*** *v or V_s* (in cm^3/g or l/Kg), or volume occupied by one gram of a certain substance.

$$V_s = v = \frac{1}{\rho}$$

When the temperature of a material (solid, liquid or gas) increases, its volume increases too, and therefore, its density drops. There are rare exceptions to this rule. The measurement of how the volume changes over temperature is known as the *thermal expansion coefficient*:

$$\boxed{\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p}$$

where V is the volume occupied by a certain quantity of a substance. The partial derivative appearing in brackets expresses how the volume changes due to the effect of temperature at constant pressure (usually atmospheric pressure). If you take the volume occupied by one gram of this substance (or specific volume), you can obtain an equivalent definition:

$$\boxed{\alpha = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p}$$

the first expressed as a function of the specific volume and the second of the density. The second equation is obtained from the first using knowledge regarding derivation.

The experiments that you are going to perform involve determining the density of a pure liquid at several temperatures. From this, you will determine the $\left(\frac{\partial \rho}{\partial T}\right)_p$ coefficient, from which, using the last expression, the expansion coefficient (α) can be obtained at each temperature at which the density has been measured.

In *Physical Chemistry I*, it is proved the importance of the expansion coefficient when determining many changes in the properties of pure substances. For example, the changes of enthalpy after a volume change and constant pressure can be written as:

$$\left(\frac{\partial H}{\partial V}\right)_p = \frac{C_p}{\alpha V}$$

where the expansion coefficient (α) and the heat capacity of a body at constant pressure (C_p) appear. If the pressure does not vary, as is the case of measurements taken in the lab at atmospheric pressure, the former expression can be written as:

$$\frac{dH}{dV} = \frac{C_p}{\alpha V} \rightarrow dH = \frac{C_p}{\alpha V} dV$$

If a liquid, as used in this experiment, undergoes a volume change as a consequence of increased temperature, the change of enthalpy can be written, after integrating the previous equation, as:

$$\Delta H = \frac{C_p}{\alpha} \ln \frac{V_2}{V_1}$$

as long as you suppose that α and the heat capacity are kept constant during the volume change (not too risky if the volume change is relatively small). If you used the molar heat capacity in this formula, the corresponding change of enthalpy would be expressed in units of energy per mol.

EXPERIMENTAL PROCEDURE

Material	Reactants
10 mL volumetric Flask	Deionised water
Thermostatic bath	Butanol
A syringe	
Digital thermometer (with decimal precision)	

In this experiment, measuring the density of a liquid, you will have to determine the expansion coefficient (α) of the liquid at five different temperatures. A thermostatic bath is going to be used to maintain the temperature constant. The Teachers will explain how it works.

The first step will be to calibrate a volumetric flask. The provided volumetric flask has a volume (certified by the manufacturer) of 10.0 (±0.1) cm^3, but we will try to measure it with a little more accuracy. To do this, you have to use distilled water whose density is very accurately known at a wide interval of temperatures (see tables provided at the work station). The flask volume will be measured at 25ºC or around that temperature, which will be achieved by putting it in a thermostatic bath. The temperature will be accurately measured with a thermometer made up of a thermometric probe and a measurement unit. Note down this temperature in your laboratory book. Then, close the dry flask with its lid and weigh it all on the laboratory balance that reaches up to 0.0001g.

Volumetric flask

Fill it with distilled water and put it in the thermostatic bath. After appropriate thermostating time, during which the level might fluctuate because the bath and laboratory temperatures are different but close, adjust the liquid level up to the marker using a syringe. After checking that this marker level is holding steady, indicating that it is properly thermostated by the bath, remove the flask from the bath, dry the outside carefully with filter paper or toilet paper and weigh it again. The weight difference, divided by the density of the water at the bath temperature will give you the flask volume. Remember that when taking the full flask to the scales for weighing, the level can vary as it is adjusting from the bath temperature to room temperature. However, the mass of water inside refers to the amount that came exactly to the marker at the bath temperature.

To check the reliability of the results, the same experiment will be performed twice over. To do this, empty and dry the flask and start again from the beginning. You will thereby obtain an average volume for the flask that is a little more accurate than provided by the manufacturer.

Supposing that the flask volume remains constant with temperature (glass expands very little as its expansion coefficient is very small compared to the liquids that you are using), by performing the same experiment with a liquid such as n-butanol, you can use this volume to measure the aforementioned density at several temperatures close to 25, 30, 35, 40 and 45ºC. The experiments will be performed just once at each T. Once again, it is not so important that the temperature is 25.0 but the temperature that is used (such as 25.2 or 44.7) should be noted down carefully.

Representing ρ vs *T*, will give us $\left(\frac{\partial \rho}{\partial T}\right)_p$, and having that value, will allow us to evaluate α at each temperature.

Points to consider for a successful experiment

Before each weighing, check the zero on the scales, as it can fluctuate with use in the lab.

To dry the flask properly, clean it with a little acetone and dry it with a hair dryer but not too much or it might become deformed, changing its volume.

Do not weigh the flask if it is hot. As it gets cooler, the water vapour from the atmosphere condenses on its walls and the weight of the flask on the scales will increase.

The marker level criterion can be subjective but it should always be read the same way.

There should be no liquid, not even in the form of droplets above the marker. To remove it, dry it with a little rolled up filter paper inserted in the flask or suck it up using the syringe and needle provided for the marker level.

When taking measurements with water, air bubbles might appear in the liquid. If this happens, try to remove them with the needle and syringe used for levelling or change the water. It is best to use water that has been resting for a while and not recently taken from the general container of deionised water.

Questions to be resolved

1. Using their knowledge on derivation, students should demonstrate the equation that implies expressing α in terms of the density, working from the equation that expresses it in terms of specific volume.
2. Once density measurements have been taken at several temperatures as described, how is the partial derivative $\left(\frac{\partial \rho}{\partial T}\right)_p$ calculated?
3. Give an example of how the density might vary with temperature so that $\left(\frac{\partial \rho}{\partial T}\right)_p$ is not constant. How would this derivative then be determined?
4. Why do we write $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p$? Where V is any volume and v the specific volume or volume per unit of mass (in cm^3/g or litres/Kg).

5. What units does α have?

6. Use the specific heat value for butanol that you obtained last year in MEQ/MEK, or look for it in bibliographic resources, or on the internet, to determine the change of molar enthalpy when the volume changes between the extreme temperature values used in this experiment.

7. This actual change of enthalpy can be calculated using the T as a variable instead of the volume. Check that the results obtained are consistent and explain any possible differences.