2.06   Liquid phase equilibria   (5 points)

1   Outline

Multiphase systems are common in industrial processes, in which many valuable reactions are heterogeneous. In addition, some important types of polymerization are performed in mixed-phase systems, in which growth of the polymer chain occurs at the interface between two immiscible phases. (You may have come across an example of this in school chemistry - the generation of 6,10-nylon is often demonstrated by a condensation reaction which occurs between two species dissolved in different, immiscible solvents; reaction only occurs where the solvents meet, at the interface.) The properties of multiphase multicomponent systems are therefore of some practical importance; it is this type of system you will study in this experiment.

2   Safety

The chemicals used in this experiment present little risk to health; however, hexane is extremely flammable, and is a fire risk. Do not keep hexane on the bench on an open beaker and be sure to safely dispose of chemicals at the end of your work. If you are unsure about using the high pressure gas regulators, ask for advice from the technician or a demonstrator.

3   Theory

The conditions of equilibrium between phases can be summarized in the Phase Rule, deduced thermodynamically by Gibbs. The phase rule is one of the simplest relations in science:

$$F + P = C + 2$$

In this expression:

C is the number of components in a system (broadly speaking, this is the number of different chemicals present, though minor complications arise if some of the chemicals are in equilibrium with one another)

P is the number of phases (liquid, solid and gas - note that there may be more than one liquid or solid phase, though only a single gas phase is possible, so the total number of phases could be more than three), and

F is the number of degrees of freedom (in other, words, the physical variables which we can control, such as temperature, pressure or mole fraction of the components).

You will apply the phase rule to a ternary (three-component) system in this experiment, using mixtures of hexane, 1-propanol and water. To fully investigate fully this system, including the establishment of the positions of the "tie lines" and the composition at the "Plait Point" (see below) will require analysis of samples over a range of compositions.

Before starting ensure that you understand and can use triangular phase diagrams; these are discussed in Atkins and in other textbooks on Physical Chemistry. An outline of their use follows.

2.1 Triangular phase diagrams

The figure on the next page shows the unusual-looking graph paper on which a phase diagram is plotted; suitable graph paper can be obtained from the technician. The purpose of a triangular diagram is to show the regions of composition over which a three-component system forms one or two liquid phases (just as the P/T phase diagram for a single material shows the regions in which gas, liquid and solid are stable). From such a diagram, it is simple to determine whether a given mixture of three components will form a single phase, or separate into two phases, (or even three) as we shall now see.

The difficulty of drawing a function of three variables in two dimensions is neatly dealt with by using triangular graph paper, in which the amount of each species is related to the distance from a corner.

Every point on or within the triangle represents the composition of a particular mixture of A, B and C. (Note that the distances to the three corners add up to 100% from every point within the triangle.) Let's start at a corner. The corners of the triangle represent a system containing 100% of one particular component (by weight or by volume, either one may be used, provided that one is consistent throughout). Thus, the top corner of the triangle shown in Fig. 1 corresponds to a sample which consists of pure C, and the bottom left corner corresponds to a sample containing only A.

As we move away from a corner towards the opposite side, the amount of that species diminishes, until every point along the edge opposite a corner denotes a sample containing none of the material. Point x in Fig. 1. therefore corresponds to a sample containing no B. Its composition is 40% A, 0% B, 60% C. Check now that you understand how to calculate the composition of each point by determining the compositions of the points shown as y and z in Fig. 1 - their compositions are shown in the footnote below[1].
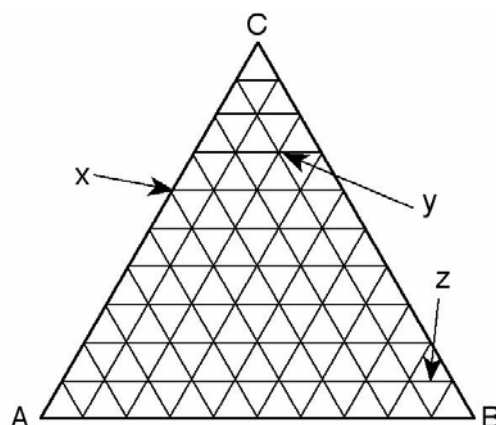
So what points do we actually plot on the graph? The role of the figure is to show the compositions of mixtures which separate into two phases, so the figure consists of a curved line which divides the plot into two regions. If you prepare a sample whose composition lies within a "two-phase" region, it will separate into two layers whose compositions lie at the end of a "tie-line" as shown in Fig. 2. If your sample has a composition in the one-phase region, only a single layer will be formed. Further, the amounts of the two phases formed by a sample whose composition places it in the two-phase region are given by the Lever rule, the ratio of the amount of layer x in Fig 2 to the amount of layer y being inversely proportional to the distances of point x and point y from the point marking the composition of the sample as a whole.
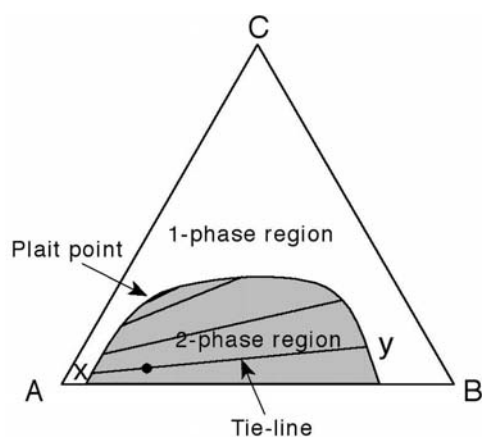
The lengths of the tie-lines gradually diminish as one moves toward corner C. The point at which the tie-line is of negligible length is called the Plait point, and is one of the pieces of data to be found in this experiment.

Fig. 2. A typical completed triangular diagram.

3   Procedure

Detergent left on glassware after washing can disrupt an experiment of this kind. The grease-free burettes used in the experiment are left in place and should be free from contamination.

---

[1] The compositions are y: 10% A, 20% B, 70% C, z: 5% A, 85% B, 10% C.

3.1 Physical Titrations

First you will establish the general position and shape of the binodal curve (which separates the two-phase and one-phase regions of the phase diagram). You will do this by performing a series of titrations to find the composition at which a two-phase system changes into a one-phase system.

Measure out 5 cm^3 hexane and 1 cm^3 of water into a 100 cm^3 Erlenmeyer flask; since hexane is almost insoluble in water this will separate into two layers. You will now titrate this mixture with 1-propanol, gradually changing the composition of the system until it passes from the two-phase into the one-phase region.

Add a small portion of 1-propanol from the burette (say, 1 cm^3), then shake the mixture fairly vigorously to ensure equilibrium. Add another portion of propanol and repeat the process until the system passes from the two phase region (mixture is slightly milky when shaken) to the one phase region (mixture is clear when shaken). You need to exercise a little judgment when shaking the mixtures: shake too enthusiastically and some of the hexane will evaporate, leading to poor results; shake too gingerly and you will not succeed in dispersing one phase in the second. You may find it helpful to have a couple of "reference" samples for comparison, one of which forms a single layer and the other two layers, so that you can check what the shaken sample should look like.

Now that you've found the first point for your figure (don't forget to add it to the graph paper!) add a further 1 cm^3 of water to the mixture; this should bring the mixture back into the two-phase region. Now return to adding propanol to give another point, and so on. This procedure of determining the "end-point" by noting when a mixture loses its milkiness is a form of physical titration - the end-point is found not through the use of a chemical indicator, but from a physical change in the solution.

At this stage you are trying to establish the *general shape* of the phase boundary, so while you should perform the titrations carefully, they do not need to be duplicated. At each point, immediately calculate percentage by volume of the three components, and plot the point on the graph paper. Do this *as you work*, not after the titrations are over, otherwise you may find all your points crowded into one corner. Extra triangular graph paper is available from the service room if needed.

When the volume of liquid gets inconveniently large, discard the sample and start again from another point on the base line. Liquid phase behaviour is, of course, temperature dependent and your measurements will relate to a definite temperature; clearly it is most convenient to use room temperature.

3.2 Gas Chromatography

Instructions for the gas chromatograph are given below. Read them through before starting to use the apparatus. The microlitre syringe used for taking and injecting samples is a delicate and costly item; please handle it carefully. Injecting samples

through the injection port of the instrument without bending the needle requires care and skill - advice about doing this is given below.

You will determine by gas chromatography the compositions of pairs of ternary liquids in equilibrium with one another - in other words, the compositions of the two liquids joined by a tie-line. These compositions will be plotted on the same triangular diagram you prepared above, and will be shown with their tie-lines; you can then make an estimate of the composition at the Plait point.

Using the results of step 3.1, make up in stoppered boiling tubes or conical flasks five mixtures in the two phase region. As you prepare the sample, measure the volumes of the constituents carefully using the burettes, so that you know the overall composition of each sample precisely. Shake each sample well, then let them settle so that the layers separate. Each chromatogram will take 8-10 minutes so analysis of both layers of five systems plus the necessary calibrations will take about 90 minutes.

Gas chromatography is a simple and elegant technique for the quantitative analysis of mixtures of volatile components. A metal or glass column is filled with a granular packing on which an oil is adsorbed (though "capillary columns" are also used, which are so narrow that the wall of the column itself provides the support for the oil and no packing is needed). A stream of inert gas (generally helium) is passed through the column and carries gaseous components over the packing. Column packings usually consist of a support phase, which is a porous, inert granular powder, such as powdered pumice, coated with an involatile liquid such as silicone oil, a high boiling ester, polyethylene glycol etc. This type of packing gives rise to the term gas-liquid chromatography or GLC.

A packing is required which gives good separation of each mixture to be analyzed. There are guidelines for this - polar columns hold back polar constituents and will separate them from otherwise similar non-polar materials, but a very polar column would give an unacceptably long retention time for alcohols.

At the entrance to the column is a port, closed by a rubber septum, through which a sample (typically 1-5 μl liquid or 0.1 cm^3 vapour) can be injected by syringe. At the end of the column a detector gives an electrical signal when something other than pure helium emerges. There are many types of detector. The present instrument contains a pair of flame ionization detectors. Each contains a minute hydrogen/air flame through which the output of the column flows. When a chemical emerges from the column it momentarily changes the electrical conductivity of the flame and the magnitude of a tiny current which is measured continuously across the flame changes. This change in current is used to indicate the presence of the sample.

Perhaps surprisingly, this eccentric-sounding method of detection is extremely sensitive. The injection block, columns and detectors can be heated individually to a temperature at which all the mixture constituents are in the vapour state.

When a sample is injected it is immediately vaporized and carried into the column by the flow of helium carrier gas. Within the column adsorption onto the oil which coats the packing, and subsequent desorption into the carrier gas, take place repeatedly as the sample is swept along. Substances more strongly adsorbed, more soluble in the liquid phase or less volatile will move less rapidly along the column than components with the opposite properties, so the original mixture separates into its constituents. This behaviour is similar to that occurring in a fractional distillation column. In fact, gas chromatograph column performance is often expressed in terms of "theoretical plates", but chromatography columns are far more efficient than distillation columns and 10^3 to 10^4 theoretical plates per metre are quite usual.

As each component emerges from the column and enters the detector, its presence is indicated as a peak on the recorder. The time between injection and detection of a particular constituent is called its retention time and serves to identify it; the magnitude of the recorder response gives the amount.

For the present application we use a simple adsorptive packing without a liquid phase, a granular porous styrene - divinyl benzene copolymer (Chromosorb 102) which is non-polar. It desorbs water, alcohols and low molecular weight hydrocarbons in order of their molecular weights.

3.3 Use of the gas chromatograph

a)   Check that the needle valve of the helium cylinder regulator is closed and that the pressure-regulating valve (the large two-winged handle on the front of the regulator) is turned fully anti-clockwise, which is the closed position (do not force this handle; turn it gently until a *slight resistance* is felt). Open the main connection from cylinder to regulator and check that the gauge shows a positive reading. Turn the winged handle clockwise to give a reading of 1.5 bar (which equals 1.5 atmospheres) on the regulator dial. Open the needle valve one turn.

b)   The GC contains two columns with different characteristics; you will use the right-hand column for this experiment. The column inlet (zone 1) the detector (zone 2) and the chart recorder for this column are all marked with a large yellow blob.

c)   Open the vertical flap on the left hand front face of the instrument and turn the right topmost knob, which controls the flow of helium through the column, until the pressure reads 150 kPa. If that pressure cannot be obtained, cautiously turn the winged handle on the regulator clockwise to allow a higher pressure into the gas supply line.

d)   Close and latch the oven door if it is open. Turn on the power (the on/off switch is located at the bottom front right of the instrument; you will have to bend down to see it.) Turn on the upper amplifier (top right) if it is not already on; the switch is at the rear of the unit. The instrument will start to warm up to its operating temperature (it should be already set at 210°C for this experiment). You should not need to touch any of

the set of buttons on the keypad at the bottom right of the instrument, which are mainly concerned with temperature programming.

e)   Turn on the air cylinder, observing the same precautions as you used with the helium cylinder. Set the pressure at the regulator to 1.2 bar. Turn the knurled knob at the bottom right below the dial labeled "air" on the GC to give a pressure of 100 kPa.

f)   Turn on the hydrogen cylinder, observing the same precautions as before. Set the hydrogen regulator pressure to 0.8 bar. In the flame ionization detector the effluent of the column is fed through a minute hydrogen/air flame situated at the end of the column in zone 2. The tiny changes in conductivity across the flame caused by changes in composition of the gas exiting the column are picked up by the EL980 detector and amplified before being sent to the chart recorder. Use the knurled knob to set the hydrogen pressure to 65 kPa.

g)   Wait for two minutes to allow hydrogen to reach the detector unit, then press the green "Ignite" button at the left of the EL980 unit. There may be a very faint pop as the flame is lit. DO NOT PRESS THE IGNITE BUTTON FOR THAN THREE SECONDS OR YOU MAY DAMAGE THE INSTRUMENT.

h)   Check that the flame is lit by holding for a moment the chunky mirror (kept on the shelf behind the instrument) at an angle just to the side of one of the holes at the top of the detector mounting. If the flame is lit, a small patch of condensation will appear on the mirror, showing that water vapour is being formed. If the flame will not light, seek help.

i)   The **range** and **attenuation** buttons on the detector unit control the detector sensitivity. Set the **range** initially at 3 and **attenuation** at 9. You can vary these by pressing the keys below the display. Raising the attenuation cuts down ("attenuates") the sensitivity; each change of one unit in attenuation changes the output signal by a factor of two.

j)   Samples are injected into the column using a very delicate syringe. This is easily damaged, so must be handled with great care. To inject a sample, immerse the needle tip in the liquid, then gently raise and lower the needle plunger several times. Do not pull the plunger right to the top of the barrel or it may come out. Now slowly draw in more sample than you need and expel the excess until you have the correct amount in the syringe. Check that the expelled liquid has appeared at the tip of the needle - if no liquid appears the syringe may not be sucking up any liquid. Momentarily touch the tip with a piece of tissue to remove the expelled liquid.

k)   Hold the syringe vertically over the column inlet. The needle must be pushed centrally through the septum. Lower the end of the needle onto the septum then, holding the syringe vertically, carefully slide the needle through the septum. Little force should be required - do not try to force the needle through, or you will bend it and ruin the

(expensive!) syringe. If the needle seems reluctant to penetrate the septum, move to a slightly different place on the septum and try again.

l)   When the syringe has been inserted as far as it will go push the plunger down gently (remember it is fragile) but fairly quickly. Do not wait after the syringe has been inserted before pushing down the plunger, since material will be evaporating rapidly as soon as the needle meets the hot gases within. Mark the injection time on the chart recorder. Leave the syringe in position for twenty seconds, then carefully withdraw it. Return it to a safe place; do not leave it lying on the bench from where it may roll onto the floor and break.

m)   Under the conditions of the experiment a peak corresponding to elution of the propanol should appear after about 120 seconds, while one due to the hexane should appear after about 290 seconds.

n)   The chromatograph column packing has a finite life at the operating temperature; do not leave the chromatograph turned on for long periods if you are not performing analyses. At the end of the experiment (unless the second column is being used for another experiment) turn off power to all the components, and close all valves and regulators.

3.4 Calibration

Make up a solution containing equal volumes of 1-propanol and hexane in a stoppered flask. You will use this mixture to establish the retention times of the constituents and the sensitivity - the relationship between the amount of a constituent and the recorder response (which will not be the same for all components). You may like to make up a second mixture with different amounts of the constituents to check that your analyses are reasonably quantitative. Inject a $5\mu l$ sample of the mixture. If the peaks are too small, or go off the top of the chart paper, adjust the injection volumes and/or the attenuation and range controls, and repeat.

Water is not detected by the flame ionization detector, so you do not need to include water in your calibration sample.

3.5 Analysis of the liquid layers

When the pairs of equilibrium liquids have stood for a while the phase boundaries will be sharp and clear. Samples can be withdrawn from the upper layer without disturbing the boundary by making sure the point of the micro syringe is near the surface of the liquid. To make sure you have a representative sample and, to eliminate any possibility of contamination by traces of the previous sample left in the syringe, slowly draw in and expel $5\mu l$ of the liquid several times. Then draw in rather more than $5\mu l$, remove the syringe, wipe the needle, push the plunger gently in until exactly $5\mu l$ of liquid are left and inject this into the chromatograph.

Sample the lower layer by passing the syringe carefully through the upper layer until the tip of the needle is close to the bottom of the tube. To make sure none of the upper layer gets entrained in the needle it is a good idea to draw in a little air; when the needle has reached the bottom of the tube you can expel this air, together with any traces of the upper layer, by pushing the plunger down. Slowly rinse out the syringe as before, fill beyond the $5\mu l$ mark, withdraw the syringe through the upper layer, wipe the needle, adjust to exactly $5\mu l$, and carry on with the analysis.

4   Calculations

From the percentage composition of your calibration mixture and the relative peak heights given by GC for each constituent, calculate factors which convert peak heights into relative volumes and hence into volume percentages. (Alternatively, and more accurately, use peak areas.)

Calculate the compositions of the pairs of equilibrium liquids for each of your mixtures. Plot on your triangular diagram the compositions determined above. Estimate the composition at the plait point. Discuss the sources and magnitude of errors in your results.