

# Ternary phase diagrams

Theory: P.W. Atkins: *Physical Chemistry* (6th Ed.) Chapters 8.1–8.7.

Type of practice: Individual.

Purpose of practice: To study partially miscible ternary systems, practice the Gibbs' phase rule and use a triangular phase diagram.

## 1 Introduction

The Gibbs' phase rule describes the relation between the number of degrees of freedom ( $F$ ),<sup>1</sup> the number of phases ( $P$ ), and the number of components ( $C$ ):

$$F = C - P + 2.$$

According to this rule the maximum number of degrees of freedom for a three-component system is four, since the minimum number of the phases is one. Hence, the system can be described by four state variables, like temperature ( $T$ ), pressure ( $p$ ) and mole fractions of two components. The full representation is possible in four dimensions. If two of the state variables are kept constant (e.g.  $T$  and  $p$ ), then the system can be depicted in two dimensions (at a given  $T$  and  $p$ ). This illustration can also show the number of phases for a given composition.

The regular Descartes coordinate system can be used when the mole fraction of  $B$  (vertical axis) is plotted as a function of the mole fraction of  $A$  (horizontal axis). This method, however, hinders the equivalence of the three components as the composition of the third component  $C$  can be obtained indirectly from  $x_A + x_B + x_C = 1$  relation. Therefore the ternary systems are illustrated in the so-called triangular phase diagrams where the points are drawn in an equilateral triangle (all sides have the same length) as shown in Figure 1 applying the following rules:

- The length of each side of the triangle is one in mole fraction unit.
- The vertices of the triangles correspond to a one-component system, i.e., to single component  $A$ ,  $B$  and  $C$ .
- Along the edges of the triangles, the composition of two-component systems can be given. For example, the side connecting vertices  $A$  and  $B$  gives the composition of a system containing only  $A$  and  $B$ , and no  $C$ . When a point is farther from vertex  $A$ , the mole fraction of component  $A$  is smaller. The scaling is linear, e.g. point  $x_A = 0.8$ ,  $x_B = 0.2$  and  $x_C = 0.0$  is along the line (side) connecting vertices  $A$  and  $B$ , its distance is 0.2 unit from apex  $A$  and its distance is 0.8 from apex  $B$ .
- The interior points correspond to a three-component system. Figure 1 shows how a point can be represented in a triangular diagram. The most practical method is to mark the mole fractions of each component along the edges of the triangle, then connect these points with straight lines as shown with dashed lines in Figure 1. Points  $A_1$  and  $A_2$  give the mole fraction of component  $A$  along the two edges of the triangle. This points are connected with a dashed line. For point  $A_1$  a bold line and a bracket shows the mole fraction starting from apex  $B$ . Dashed lines illustrate the mole fractions of components  $B$  and  $C$  as well.
- The three dashed lines intersect in a single point. This intersection, point ( $P$ ) is the position of the system with the desired composition in the triangular diagram. The intersection can be determined from two lines, therefore the use of any two lines from the three is sufficient, i.e., in a three-component system, from the mole fraction of any two components the third can be calculated.

When we want to read the mole fractions of any points in the diagram, we have to draw a parallel line to the edges through the point (dashed lines in Figure 1). From the intersections of these lines with the edges of the triangle we can read the desired mole fractions.

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<sup>1</sup>The number of degrees of freedom is the number of freely variable intensive parameters.

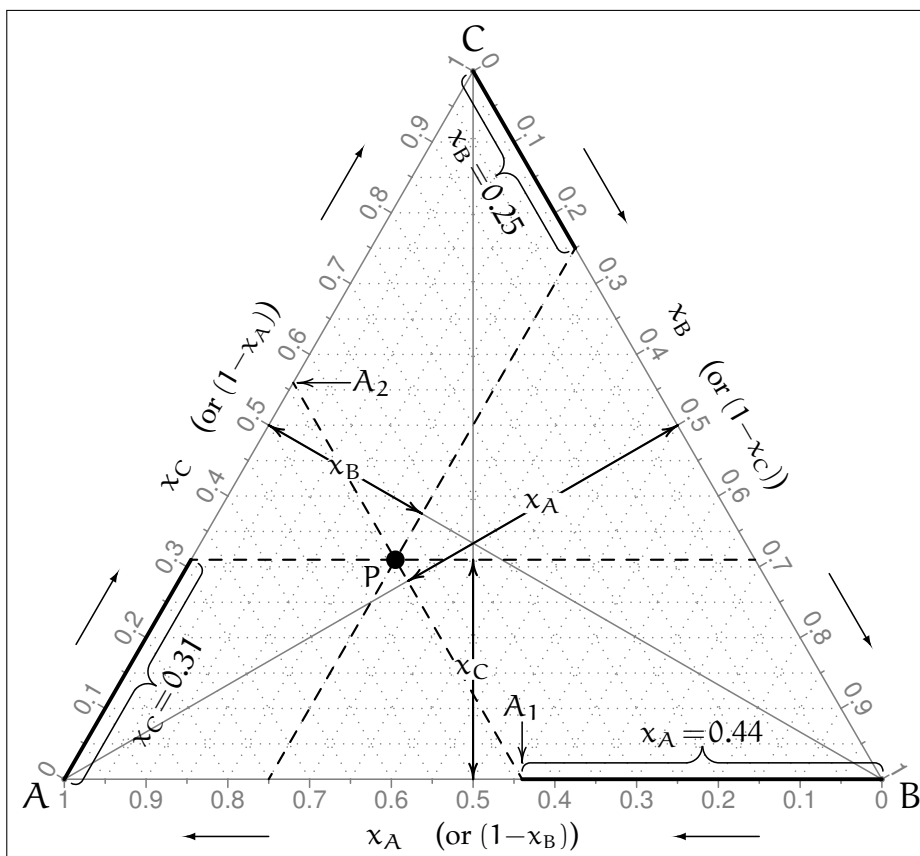


Figure 1: The use of the triangular diagram to represent the composition of a three-component system ( $A$ ,  $B$  and  $C$ ). The example case is point  $P$  with composition  $x_A = 0.44$ ,  $x_B = 0.25$  and  $x_C = 1 - x_A - x_B = 0.31$ . Detailed explanation in the text.

## 2 Construction and interpretation of a triangular phase diagram

One of the most significant ternary systems is that of the partially miscible liquids which, depending on their composition, can be one-, two- and three-phase system. Phase curves (so-called binodal curves) separating the one- and two-phase systems are presented in triangular phase diagrams. There are several possibilities to obtain partially miscible systems. In the practice we will consider one where from the three liquids, liquid  $A$  and  $B$  are partially miscible, while liquid  $C$  is fully miscible with both  $A$  and  $B$  as illustrated in Figure 2. The phase curve divides the diagram into two:

1. At certain compositions the system has a single phase (e.g. point  $P$ ). The exact composition of the mixture can be read from the triangular phase diagram.
2. At other compositions, like point  $Q$ , the system exhibits two phases: one phase rich in component  $A$  (namely water), the other is rich in component  $B$  (propyl acetate). Component  $C$  is partitioned between the two phase. In such heterogeneous systems the mole fraction in point  $Q$  describes the average mole fraction of the two phases. The composition of each phases is given by the composition of points  $Q_A$  and  $Q_B$ : from composition  $Q_A$  the acetone content in a water saturated with propyl acetate, while from composition  $Q_B$  the acetone content in a propyl acetate saturated with water can be determined along with the overall composition of  $Q$ .

Straight lines in infinite number can be drawn through point  $Q$  and intersecting the binodal curve in two points. There is only one line, the tie line, which gives the real composition ( $Q_A$  and  $Q_B$ ). This line can be determined experimentally by extracting the two phases and analyze their composition separately. There exists a simple, Tarasenkov's rule which states that the tie lines intersect in a single point  $T$  outside of the triangular diagram (more precisely the point lies in the extension of the appropriate side

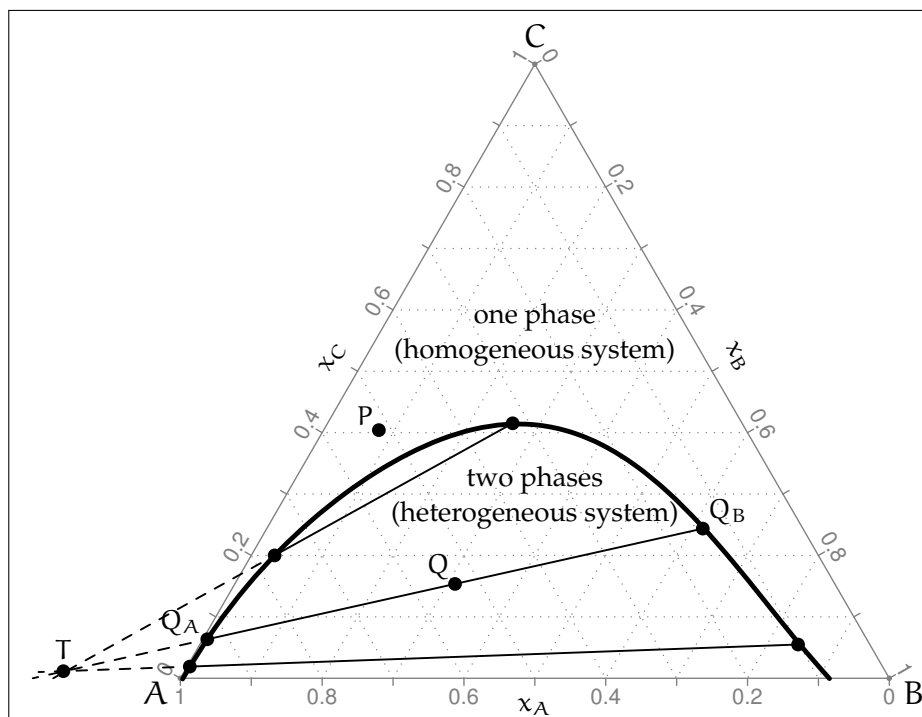


Figure 2: Representation of the liquid-liquid ternary phase diagram with components *A*: water, *B*: propyl acetate and *C*: acetone at atmospheric pressure and at 30°C. Component *A* and *B* are partially miscible, while component *C* is miscible with the other two.

of the triangle) and helps to locate the tie lines. The amount of the individual phases are given by the lever rule.

There are two practical applications for these type of ternary systems where the phase diagram is essential:

- For certain liquid-phase reactions, the reactants have no common solvents. Therefore, the reactants are dissolved in separate, partially miscible solvents and with a use of a third solvent single phase is created where the reaction can take place.
- Under certain conditions, the separation of fully miscible liquids is also possible by using an appropriate ternary system. For example Figure 2 shows that propyl acetate is an adequate solvent to remove acetone from water. It is clear from the graph that at composition *Q*, there are two phases: in *Q<sub>A</sub>* (water-rich phase) the acetone content is much lower than in *Q<sub>B</sub>* which is the propyl-acetate-rich phase.

### 3 Experimental construction of the phase diagram

The aim of the practice is to determine a ternary phase diagram with a series of titrations. Typically two-component systems are titrated with the third component and find the end point where the number of phases changes. A titration curve corresponds to straight line in the triangular diagram which connects a apex with a point lying in the opposite side of the triangle. For example in Figure 3a the line connecting apex *A* with the opposite side at point  $x_B = 0.4$  corresponds to a titration of solution *B* and *C* with mole fraction ratio of 0.4 : 0.6 with solution *A*. During the titration we recede from the  $\overline{BC}$  side approaching apex *A*. When the line intersects the binodal curve (as in our case), the number of phases changes. The titration lines will be presented with gray lines in the figures.

To determine the binodal curve, a series of titrations should be carried out using the following procedures:

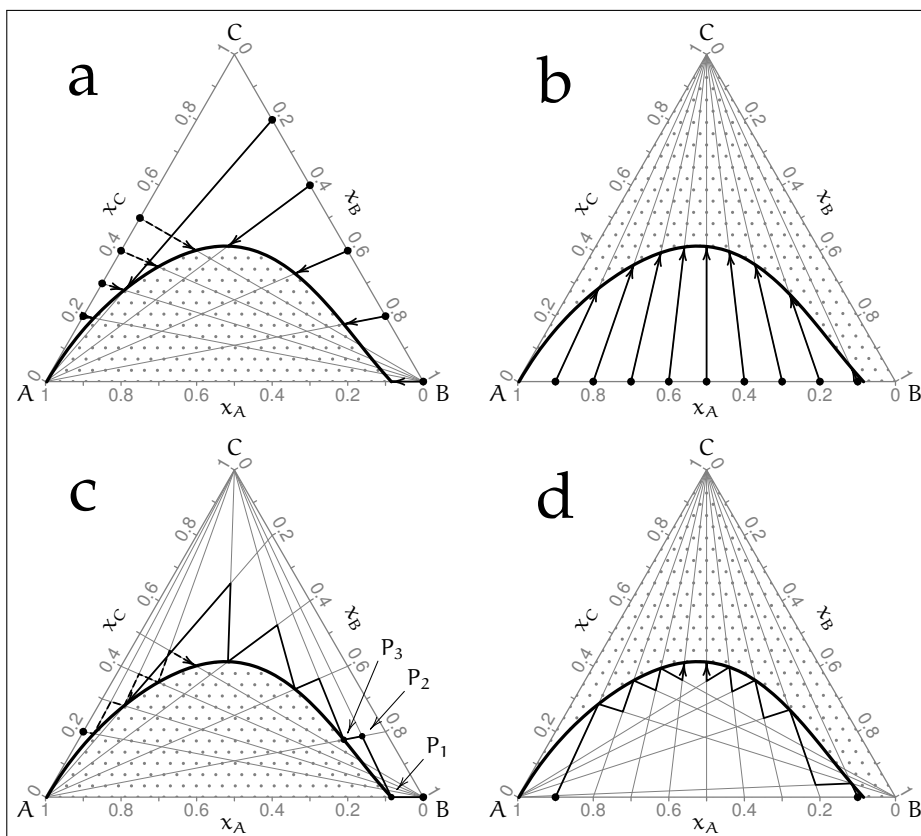


Figure 3: Titration curves for individual titrations (**a** and **b** diagrams), and for additive titrations (**c** and **d** diagrams). The arrows illustrate the titration started from compositions marked with bullets. The shaded areas are outside of the titration regions. Further explanation in the text.

1. Prepare several two-component system and titrate them individually with the third component until the number of phases changes. This method is the so-called *individual titration method*. See e.g. the solid arrows in Figure 3a where solutions of B and C are titrated with component A. The end point is the appearance of the second phase. Another example the dashed arrows in Figure 3a where solution of A and C are titrated with solution B. There is a third possibility when the partially miscible solution containing A and B is titrated with solution C (see arrows in Figure 3b). The end point is the disappearance of the second phase. All three cases and their combination can be used to locate the binodal line.

The disadvantage of the method is the excessive use of chemicals which may be expensive and contaminate the environment. Therefore another, more complicated procedure, the additive titration method is frequently used.

2. *Additive titration method* is illustrated in Figure 3c and d. To understand the method compare the titration series shown by solid arrows in Figures 3c and 3a.

First component B is titrated with component A reaching point  $P_1$  in the binodal curve in Figure 3c. Then appropriate amount of component C is added to the titrated sample to reach point  $P_2$  composition where the system has a single phase. Then the sample is further titrated with component A to reach composition ( $P_3$ ). (Going from point  $P_2$  to point  $P_3$  corresponds to the individual titration where a sample with composition  $x_B = 0.8$  and  $x_C = 0.2$  is titrated with component A.) Sufficient number of points can be determined along the binodal line by using only one sample without wasting chemicals.

## 4 Experimental

The system to be investigated consists of water (always component *A*) and components *B* and *C* as unknowns. Component *B* is the component which is *partially miscible with water*, while component *C* is fully miscible with it. *Always use the hood* as the unknowns are organic chemicals.

- At the beginning of the practice pick up the two unknowns and note their molar masses.
- Identify the unknowns as *B* and *C* by adding  $\sim 1\text{ cm}^3$ - $1\text{ cm}^3$  into two test tubes separately and add  $\sim 1\text{ cm}^3$ - $1\text{ cm}^3$  water to each test tube. Shake the solutions and look at the test tubes. One will have a single phase (component *C*), the other will be heterogeneous corresponding to component *B*.
- The density of the unknowns should be determined during the practice. Measure the mass of a dry Erlenmeyer flask of  $50\text{ cm}^3$  volume with stopper. Add into the flask  $5.00\text{ cm}^3$  unknown by an appropriate buret. Measure the mass of the flask with the solution. Calculate the solution density as the ratio of its mass to its volume.
- Determine the points of the binodal curve by titration. The instructor will identify the titration method (individual or additive) to be used and announce which titration series should be carried out. *If it is not specified otherwise*, solutions containing components *B* and *C* with compositions 95, 90, 80, ..., 10 V/V% for component *B* is titrated with solution *A*. For the first seven titration the additive titration method should be used (i.e., it is only 1 sample), while the last three titrations should be carried out with the individual titration method (3 samples!). The volume of the sample to be titrated is  $10\text{ cm}^3$  in all 4 cases and the titration should be stopped if the endpoint is greater than  $25\text{ cm}^3$ . The first sample (additive titration) is  $10\text{ cm}^3$  of component *B*. Before starting the titrations, calculate the required volume of solution *C* for the seven steps of titration given above considering the *volume of components B and C only*. The calculated volume for each step is the overall volume of the sample, i.e., you should add solution *C* to the sample to reach this volume in the sample.
- Determine the missing base point of the binodal line by individual titration. Measure out  $10.00\text{ cm}^3$  solution *A* into a clean and dry Erlenmeyer flask with stopper and titrate with solution *B*.

Difficulties during the titrations:

1. When the appropriate solution aliquots are added, close the flask with the stopper and shake it *efficiently*.
2. The end point is difficult to identify. Any of the following observations indicate the appearance of a new phase:
  - the mixture becomes opaque and this turbidity stays even after shaking it;
  - tiny drops appear in the sample
  - drops stay in the inner wall of the titration flask

If the end point is not the appearance of a new phase but the *disappearance of an existing phase* then none of the above should be observed.

Do not be afraid to call your instructor in case of difficulties to identify the end point

3. Be patient. The titration volumes can differ by several magnitudes.
4. When there is no information about the endpoint of the titration, titrate dropwise not to overtitrate the solution.
5. If the Erlenmeyer flasks have to be dried, rinse the flasks 3–4 times with technical quality acetone and dry it with a water pump. Do not use dryers as the flasks with thick walls cool down slowly.

After finishing the experiments, show the results to the instructor because further titration may be needed. *Collect the used chemicals in the appropriate waste container. It is forbidden to pour them into the sink.*

## 5 Evaluation

1. Summarize the experimental data and the results of the calculations according to the table below:

$A = \text{H}_2\text{O}$ ,  $B = \dots$  unknown,  $C = \dots$  unknown

$M_r(A) = \dots$ ,  $M_r(B) = \dots$ ,  $M_r(C) = \dots$

$\rho(A) = \dots \text{ g/cm}^3$ ,  $\rho(B) = \dots \text{ g/cm}^3$ ,  $\rho(C) = \dots \text{ g/cm}^3$

| $V_A$<br>( $\text{cm}^3$ ) | $V_B$<br>( $\text{cm}^3$ ) | $V_C$<br>( $\text{cm}^3$ ) | $n_A$<br>(mol) | $n_B$<br>(mol) | $n_C$<br>(mol) | $n_{\text{total}}$<br>(mol) | $x_A$ | $x_B$ | $x_C$ |
|----------------------------|----------------------------|----------------------------|----------------|----------------|----------------|-----------------------------|-------|-------|-------|
|                            |                            |                            |                |                |                |                             |       |       |       |

2. Ask for a triangular diagram from the instructor.  
Plot the phase diagram of the ( $A$ ,  $B$ ,  $C$ ) ternary system using the calculated mole fractions. Discuss the diagram in 4–5 sentences.

## Control questions

1. Give the Gibbs phase rule. Define each symbol.
2. Give the maximum number of phases at equilibrium for a three-component system. Explain.
3. Mark the places of one-, two-, and three-component systems in a triangular phase diagram.
4. Describe in 4–5 sentences how to draw a point in a triangular diagram (any method can be used).
5. What is a phase curve?
6. Draw schematically a phase curve in a triangular phase diagram for a ternary system where two components are partially miscible and the third one is miscible with the two. Give the number of phases in each area.
7. Give the Taraszenkov rule. Define each symbol.
8. What practical application is possible for the ternary system given in 6. question?
9. Describe the individual titration method in 4–5 sentences.
10. Describe the additive titration method in 4–5 sentences.
11. Draw in a triangular phase diagram the changes in the composition of a three-component system with components  $A$ ,  $B$  and  $C$  when component  $A$  is added.
12. How the densities of the unknowns are determined?
13. A solution mixture of  $B$  and  $C$  is titrated with component  $A$ . At the endpoint the mixture contains  $4.3 \text{ cm}^3$   $A$ ,  $10.0 \text{ cm}^3$   $B$ , and  $7.3 \text{ cm}^3$   $C$ . How many  $\text{cm}^3$  of component  $C$  has to be added in order to have 40 V/V% of component  $B$  in the mixture considering only components  $B$  and  $C$ ?