CHE392
3a - LIQUID-LIQUID PHASE EQUILIBRIUM

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Content

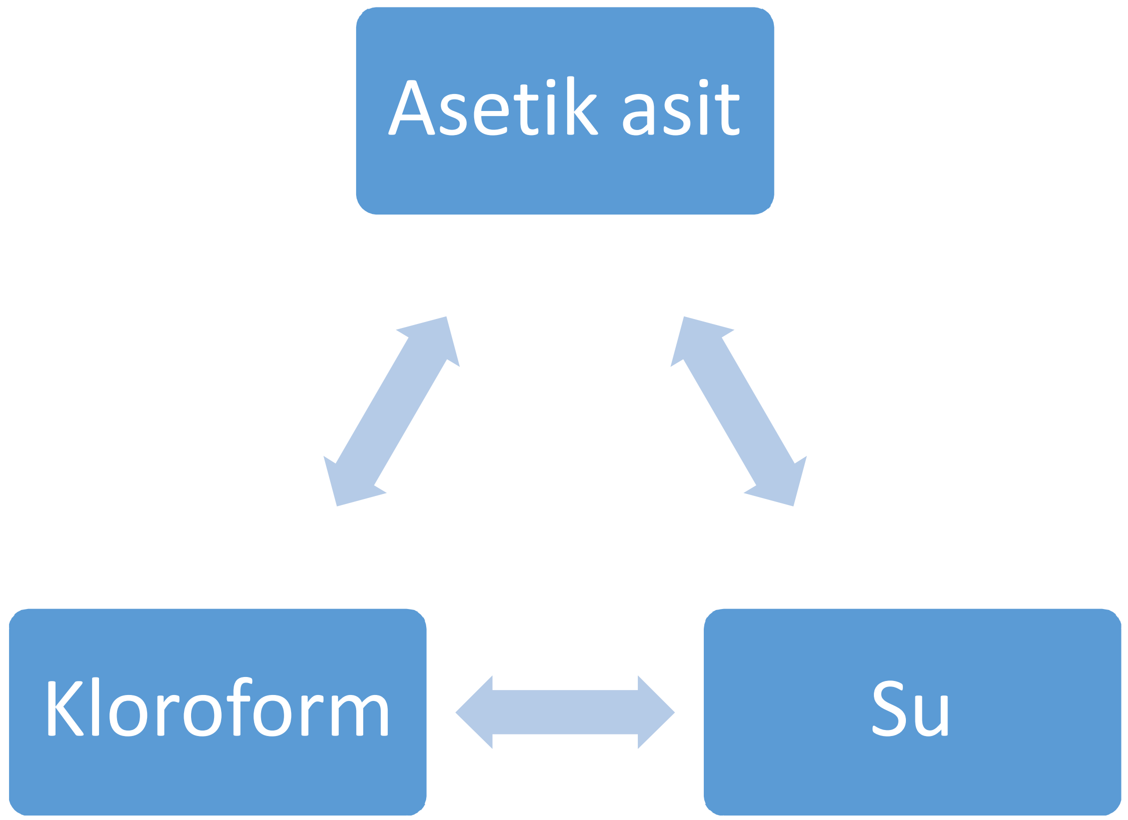
Purpose

The purpose of the study is to examine the three-component systems and to create a liquid-liquid phase diagram for these systems.

In this experiment, phase equilibrium of the three-component liquid systems which are partially miscible with each other (two of which do not mix with each other or partially miscible and the third one is completely miscible in the other two) will be studied.

Purpose

In this experiment, the three component system consisting of acetic acid, water and chloroform is used. While chloroform and water are partially miscible, acetic acid is completely miscible in both chloroform and water.

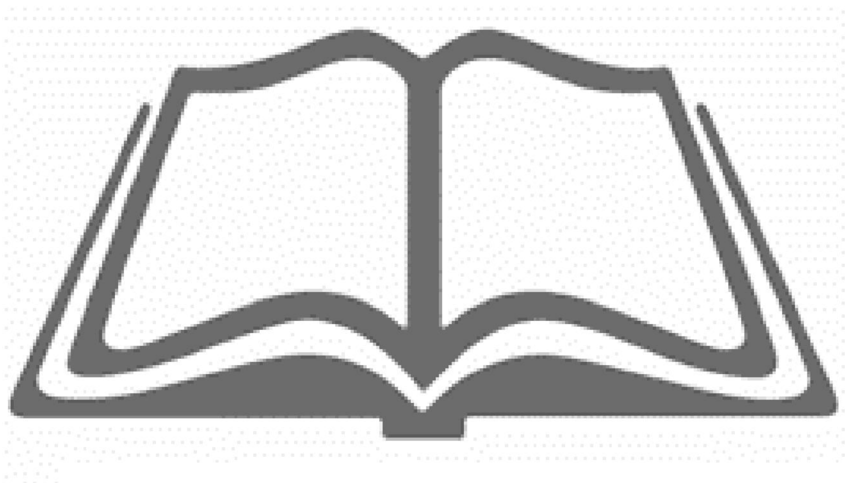


Chemicals

- Acetic acid
- Chloroform

MSDS

Theoretical Basis



What is Gibbs Phase Rule?

In order to define a system which is in equilibrium, the number of independent variables that define the system must be known. The number of these independent variables determines the degree of freedom of the system.

The Gibbs phase rule is used to find the degree of freedom, and the degree of freedom implies how many of the independent variables that define an equilibrium system can be changed independently.

What is Gibbs Phase Rule?

Gibbs phase rule is expressed with the following equation.

$F=C+2-P$

Here;

F: Degrees of freedom

C: Number of components

P: Number of phases

Degrees of Freedom for Three Component Systems

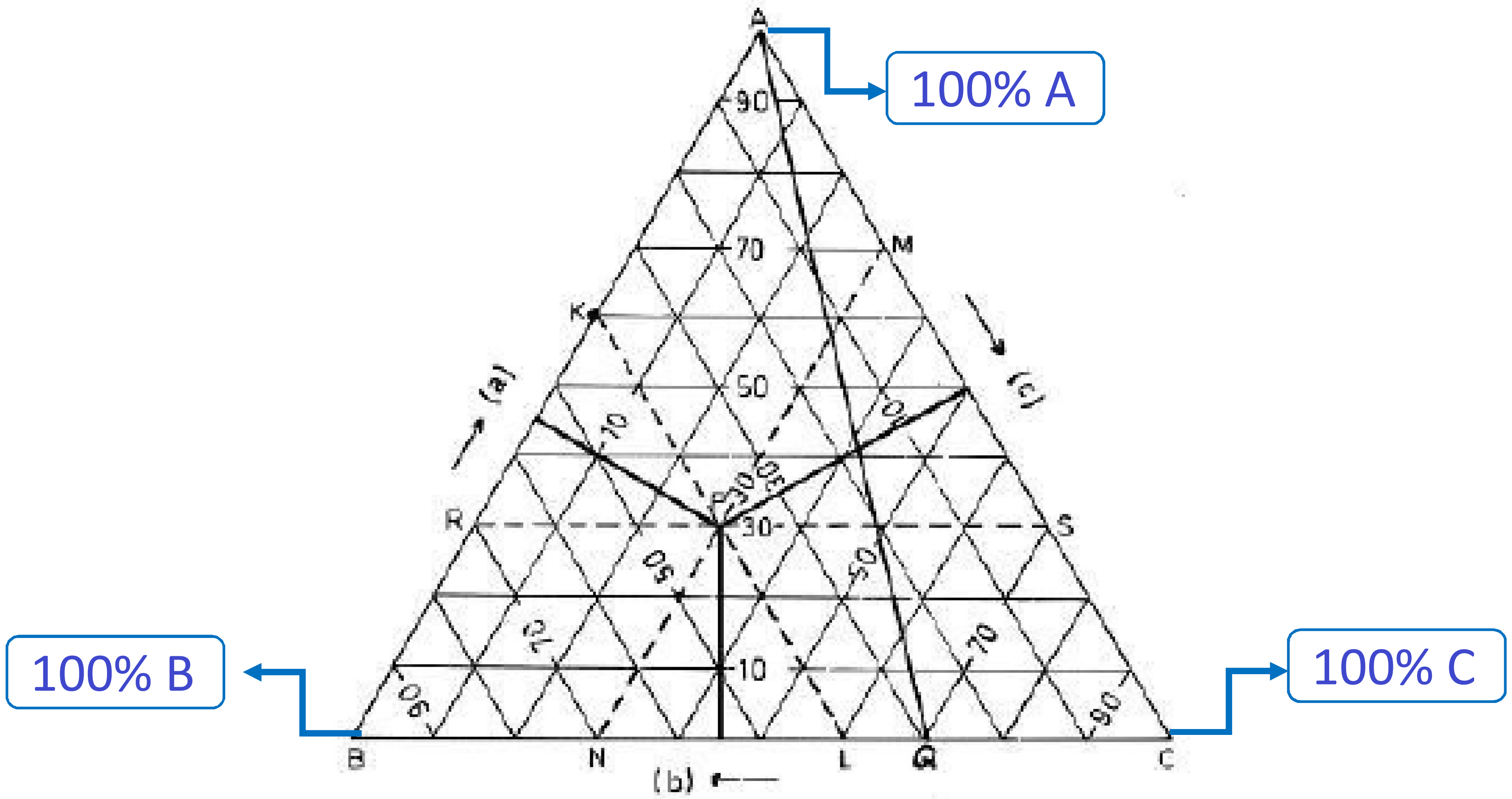
When the Gibbs phase rule is applied to the acetic acid, water and chloroform system under constant temperature and pressure conditions, the degree of freedom is found as 2. This means that the mixture in question can be identified by giving the concentration of any two of the independent variables.

P=1, F=4	**Constant temperature and pressure** →	P=1, F=2
P=2, F=3		P=2, F=1
P=3, F=2		P=3, F=0

Equilateral Triangle Drawings for Three Component Systems

In the case where the triple system consists of A, B and C, these three components are placed in each corner of the equilateral triangle.

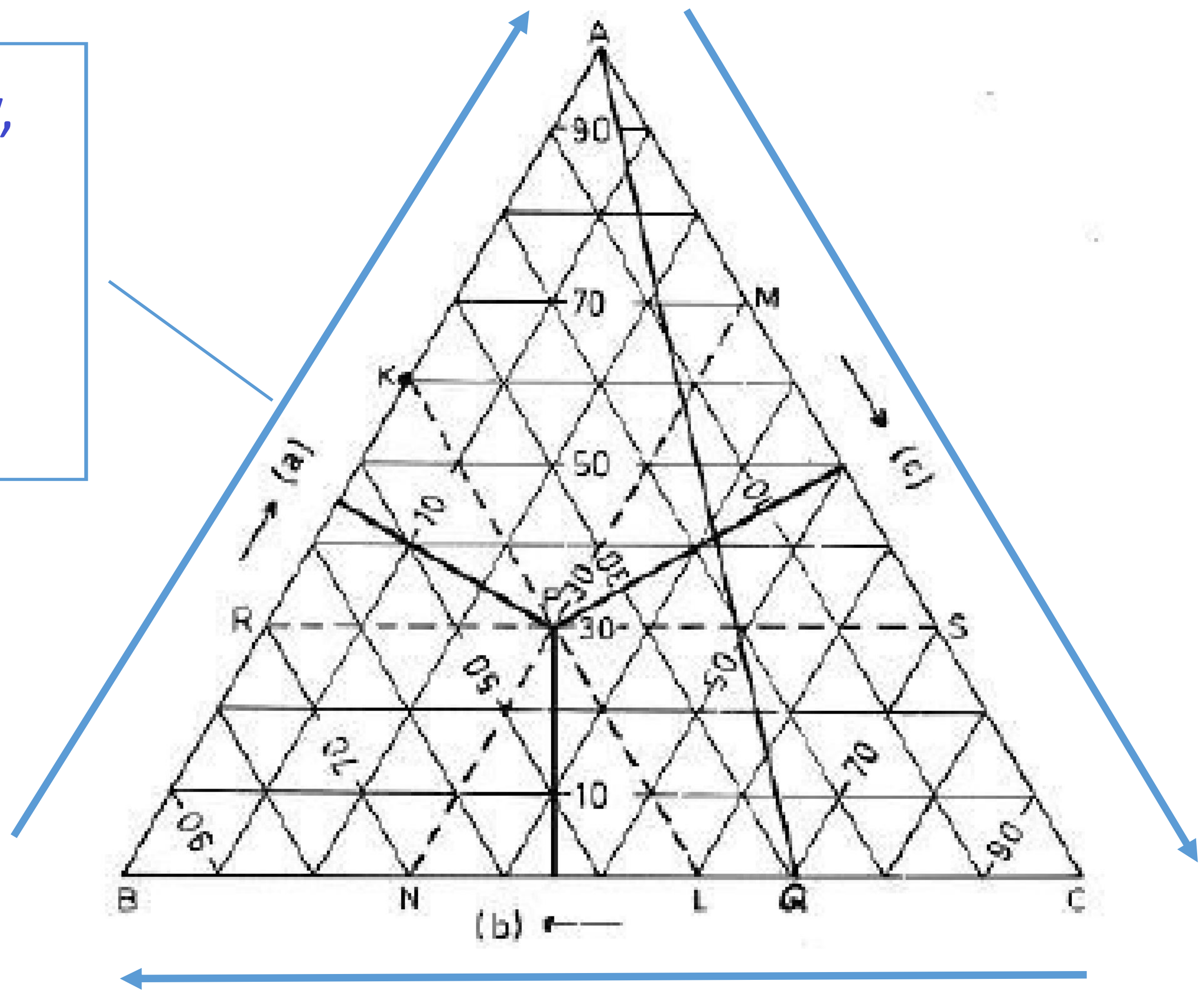
Corners of the triangles symbolized as A, B and C show pure (100%) A, B and C respectively.



Equilateral Triangle Drawings for Three Component Systems

- As it moves clockwise around the equilateral triangle, the concentration of the component behind the arrow decreases, and the concentration of the component opposite the arrow increases.

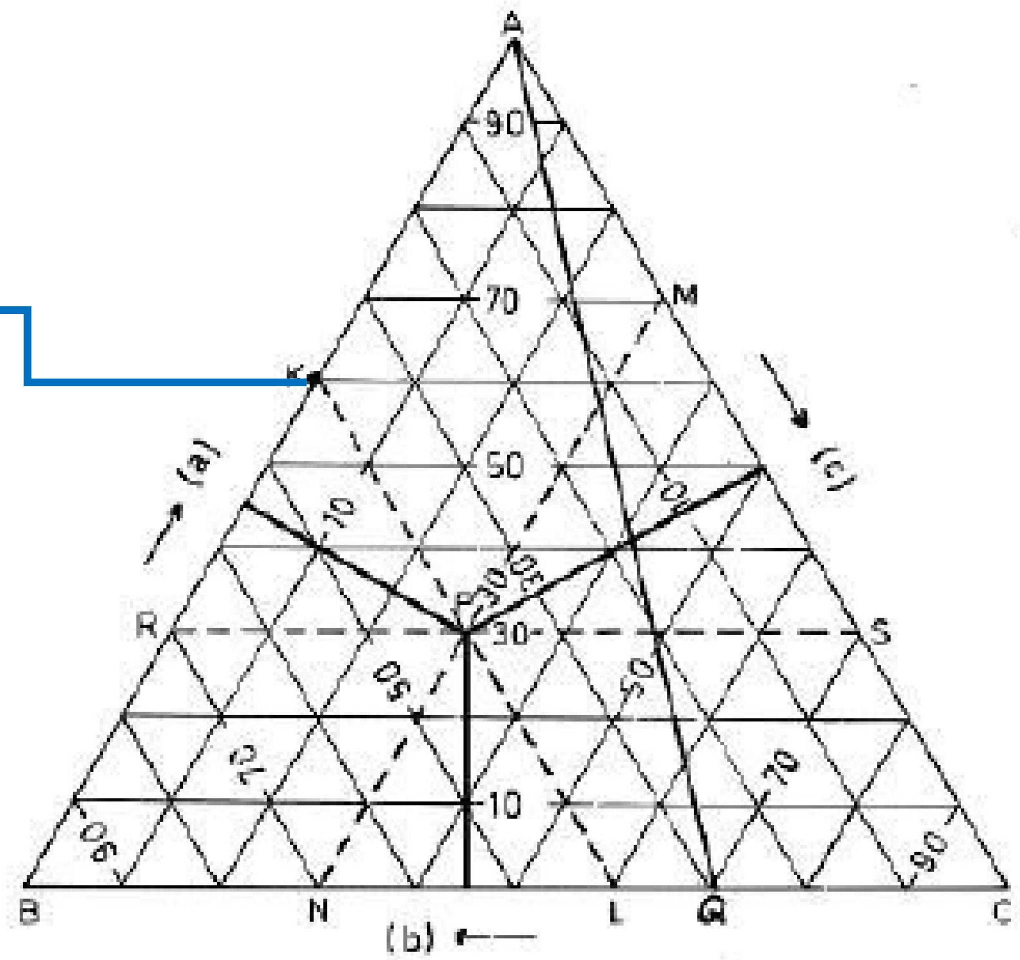
In the direction of the arrow, the concentration of the A component increases, while the concentration of the B component decreases.



Equilateral Triangle Drawings for Three Component Systems

The point on either side of the equilateral triangle represents a two-component system.

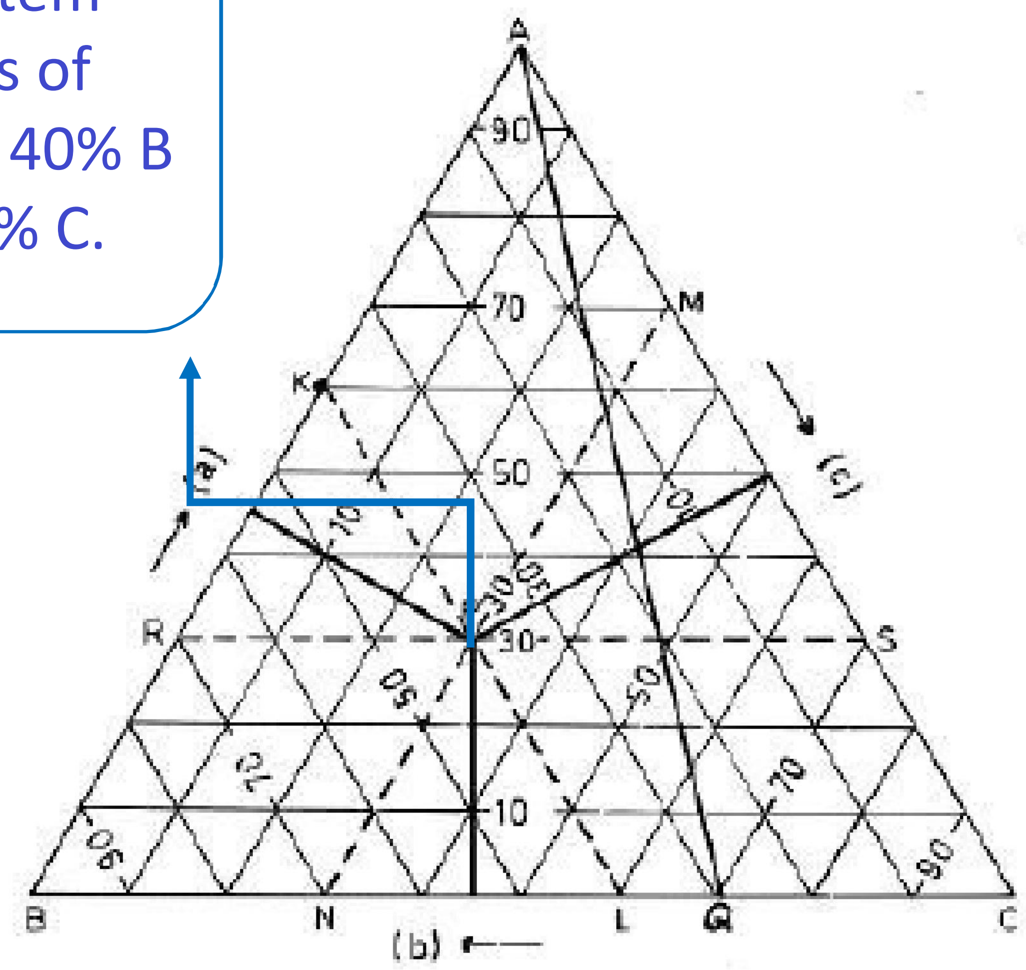
Point K on the line AB shows a two component system with 60% A and 40% B



Equilateral Triangle Drawings for Three Component Systems

- Any mixture within the equilateral triangle contains three components.
- The percentage of the components in the mixture is determined by reading the edges of the parallel lines drawn at the edges of the triangle from this point.
- A line parallel to the edge opposite to the corner and passing through the point is drawn to the edge corresponding to that corner. The percentage of the component is read from where the parallel crosses the change edge of the component.

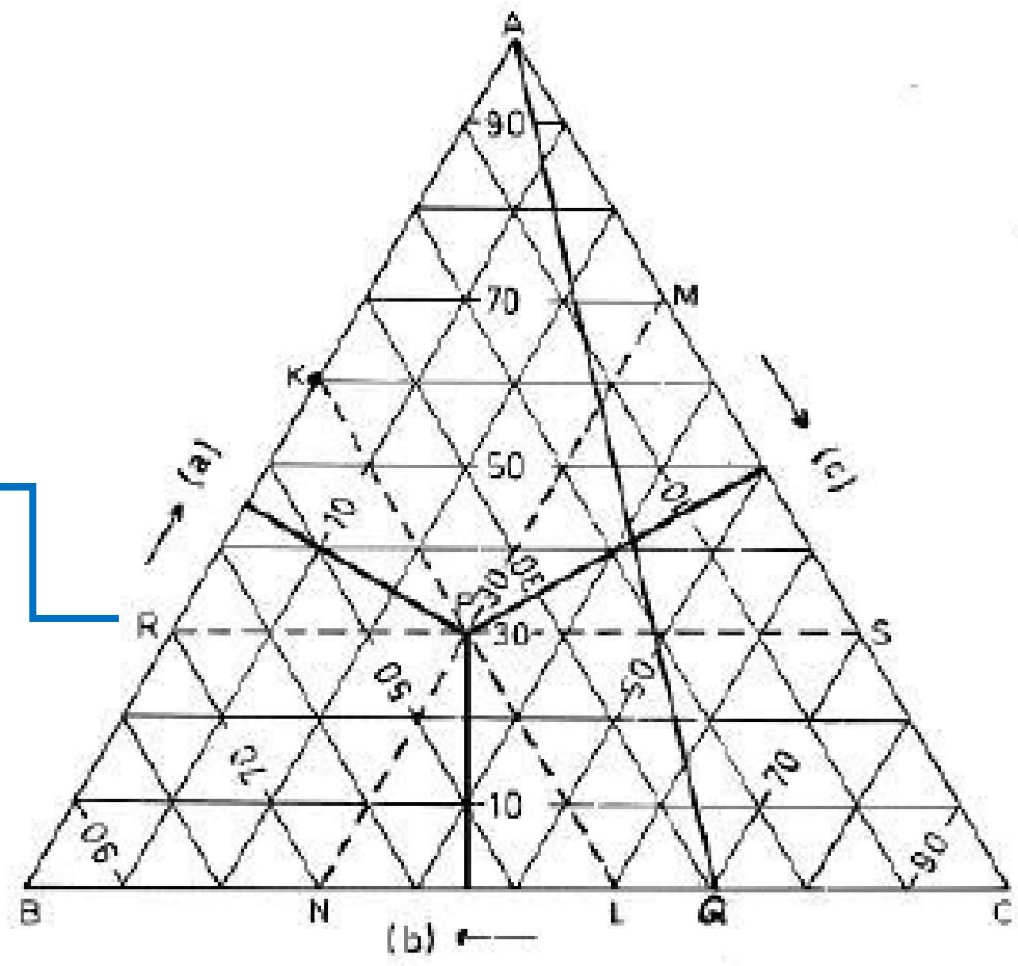
"P" system consists of 30% A, 40% B and 30% C.



Equilateral Triangle Drawings for Three Component Systems

- On the line drawn parallel to the edge of the triangle and connecting the other edges, the percentage of the component located at the opposite corner of the parallel line is constant.

For example, the amount of component A is 30% in all mixtures on the RPS line.



Example: Showing the given points on a triangle diagram

Show the points P1, P2 and P3 given below on the triangle diagram.

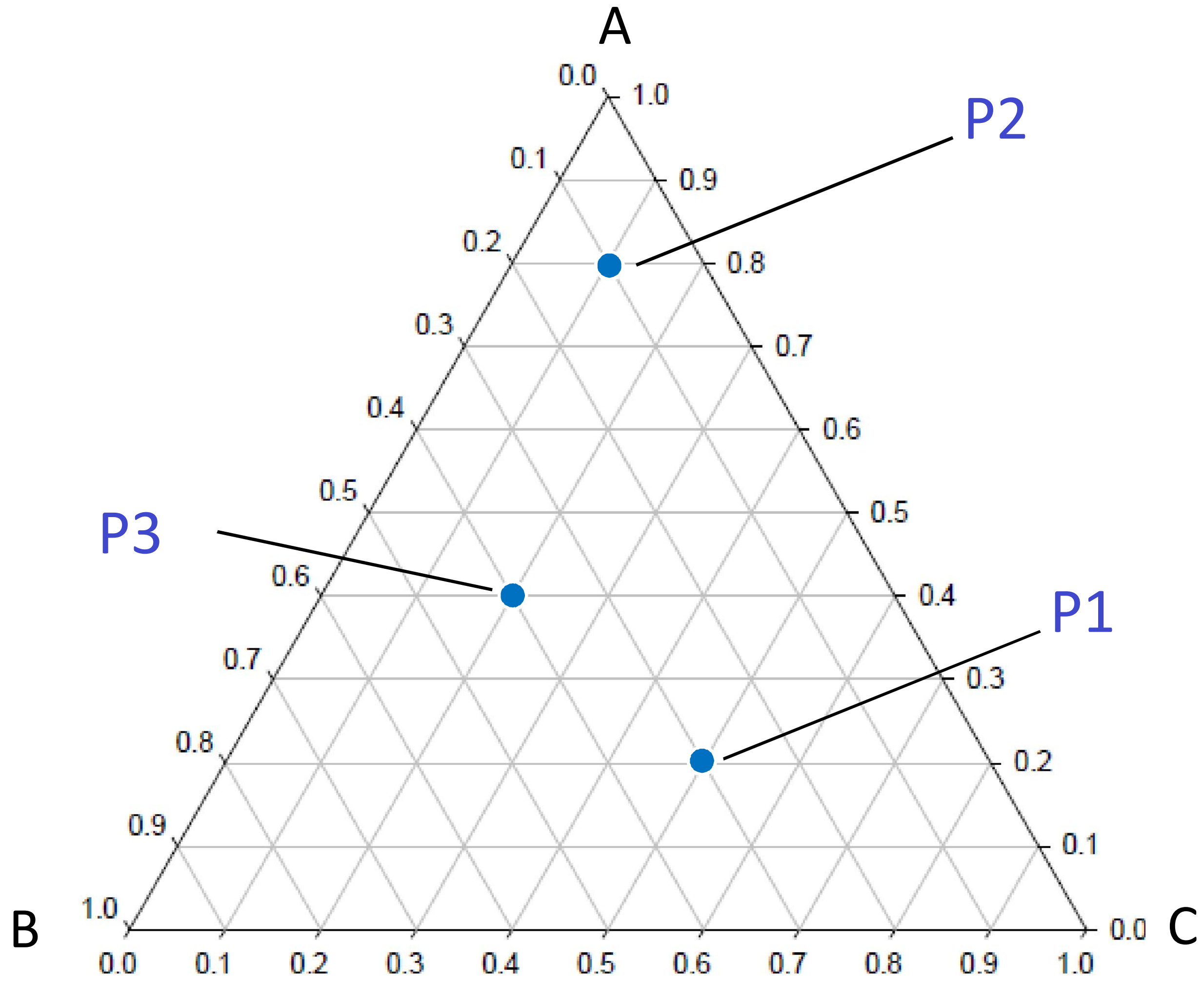
P1: 20% A
40% B
40% C

P2: 70% A
15% B
15% C

P3: 45% A
45% B
10% C

Example: Determination of the composition of the points given on the triangle diagram

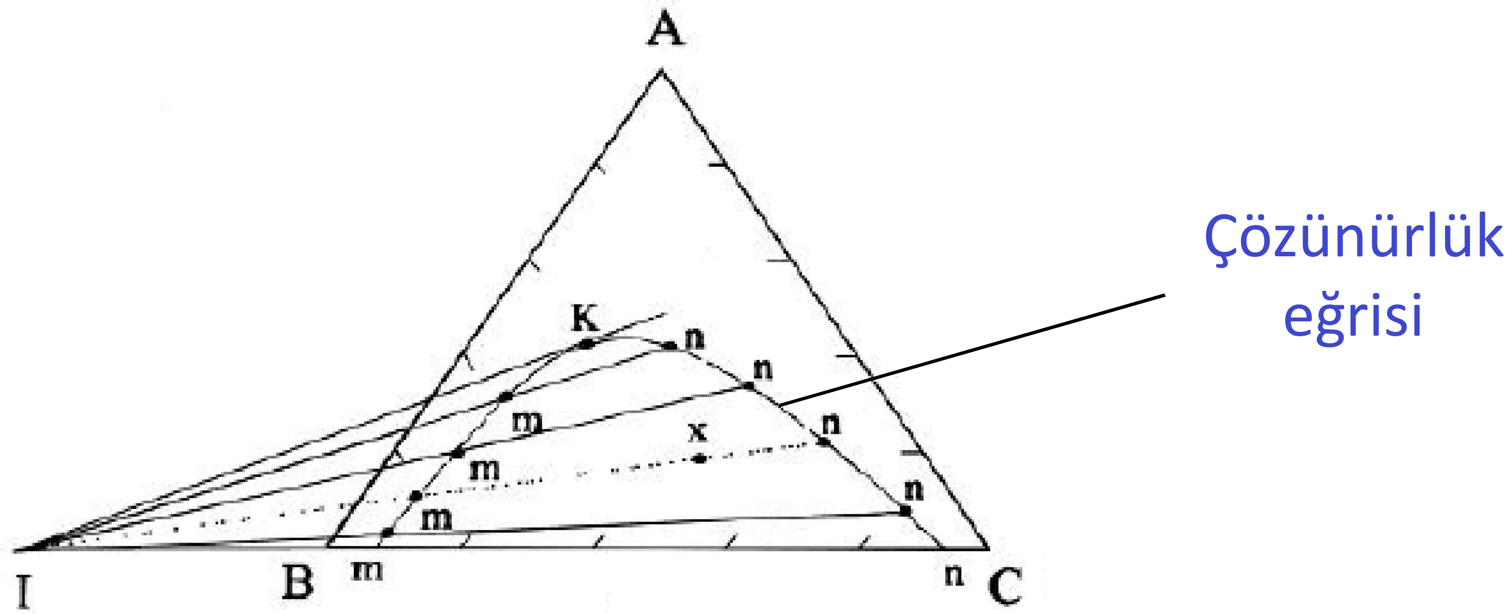
Determine the compositions of the points P1, P2 and P3 given on the triangle diagram below.



What is the Solubility Curve?

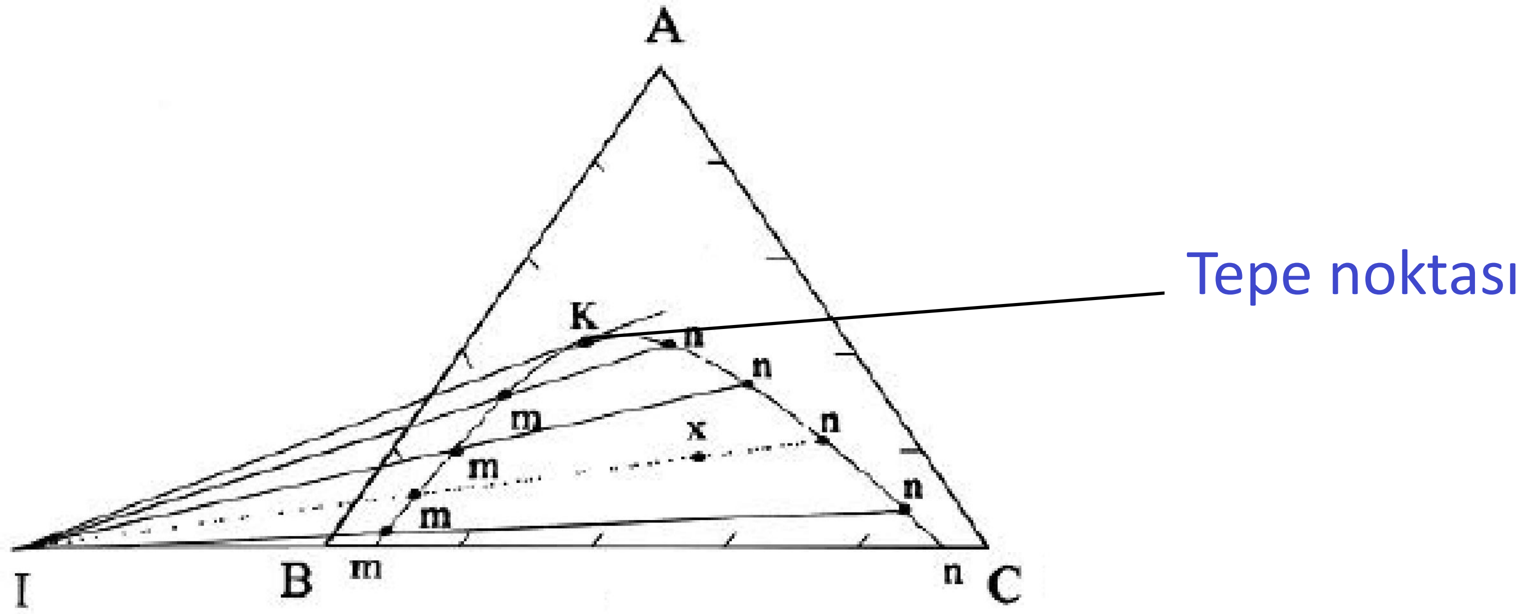
The m points shows the solubility of component C in component B, and n points shows the solubility of component B in component C.

With the addition of compound A, the composition of phase m, in which B is the solvent, is changed along the mK curve, while the composition of phase n, in which C is the solvent, is changed along the nK curve to reach the K point. The resulting mKn curve is called the solubility curve.



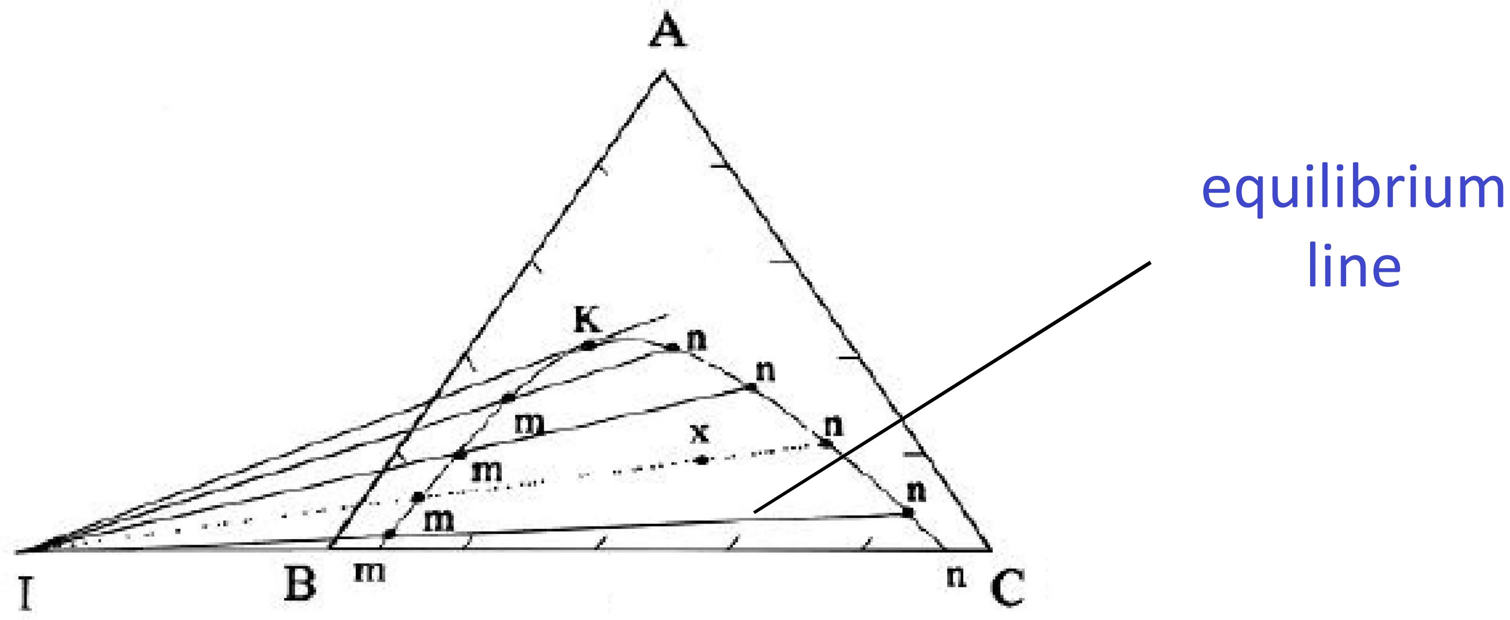
What is the Peak Point?

Point K is called the peak point or isothermal critical point. At this point, the composition of two phases thermodynamically in equilibrium with each other (m and n phases) are the same.



What is the Equilibrium Line?

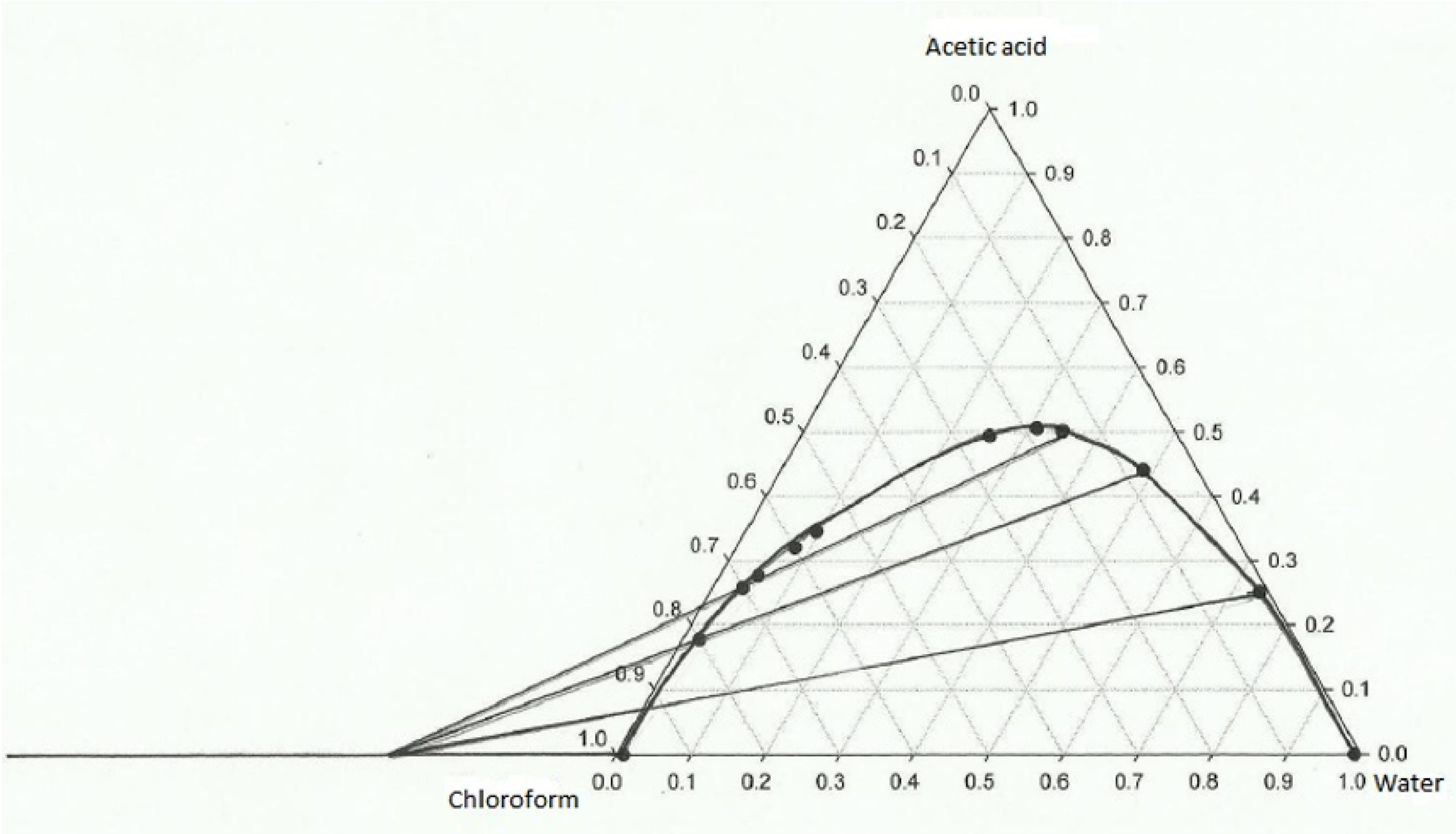
The mKn curve represents the equilibrium state of two phases and at each point on the curve, there are two liquid phases that are in equilibrium with each other. There are always two phases inside this curve and one phase outside. The mn line is called the equilibrium line, connecting the m and n phases which are in equilibrium with each other.



Experimental Study

Experimental Study

➢ Specify three points as P1, P2 and P3 on the equilibrium lines in the triple phase diagram given for acetic acid-chloroform-water system.



Experimental Study

- Determine the compositios of points P1, P2 and P3 and fill in Table 1 given in the "Experiment Data Sheet".

Table 1. Creation of compositions at selected points on equilibrium lines

	Component					
Point Name	A		B		C	
	Mass (%)	Volume(ml)	Mass (%)	Volume(ml)	Mass (%)	Volume(ml)
P1						
P2						
P3						

Experimental Study

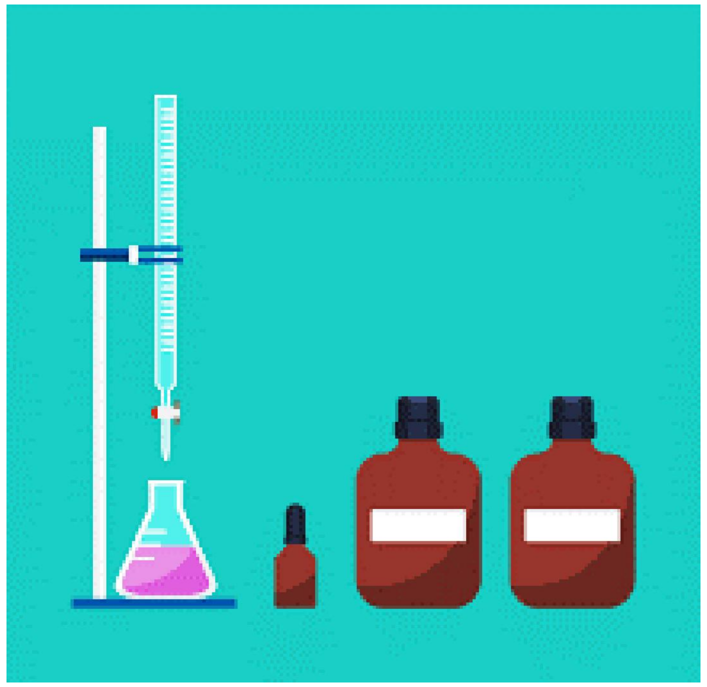
- Prepare the mixture of water-acetic acid-chloroform in the separation funnel as a total of 20 ml at the specified compositions (P1, P2 and P3).
- By thoroughly shaking the mixture, ensure that the distribution of the components between the phases reaches an equilibrium.
- Allow the mixture to stand in the separating funnel for sufficient time (10-15 minutes) to separate the two liquid phases from each other.

Experimental Study

➢ Measure the volumes and masses of the two phases you are separating from each other and determine the amount of acetic acid in phases with acid-base titration (NaOH, 1 M). Record your experimental data in the Table 2. (Use 1 ml of sample for acid-base titration.)

Table 2. Determination of lower and upper phase compositions at the selected point on the equilibrium line

Point Name	Upper Phase			Lower Phase		
	Volume(ml)	Mass(g)	Base consumed(ml)	Volume(ml)	Mass(g)	Base consumed(ml)
P1						
P2						
P3						



Calculations

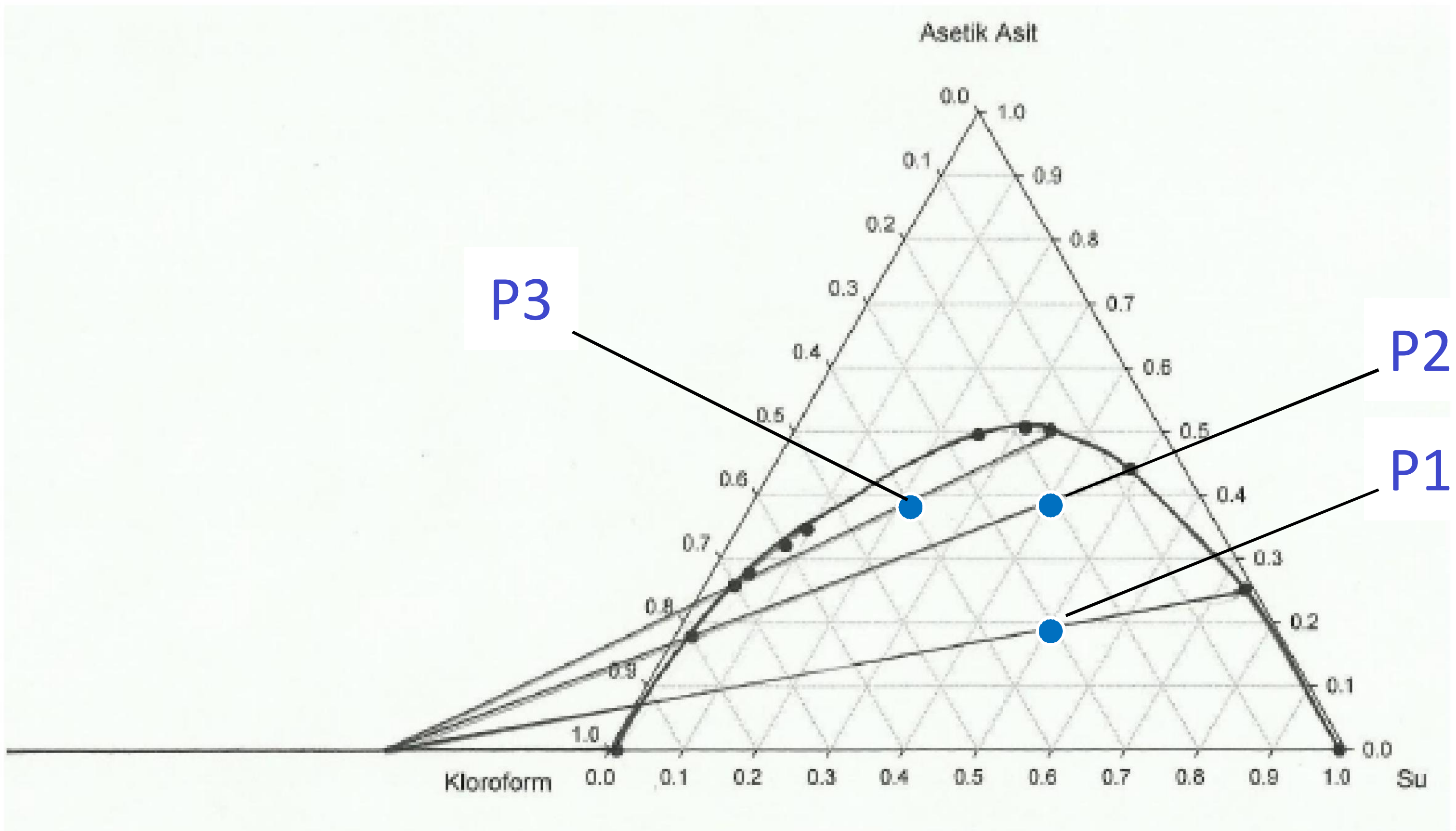
- Determine the acetic acid molarity of the lower and upper phases using the volumes of NaOH spent during titration of the lower and upper phases (Table 2) in the equation below ($M_{NaOH} = 1$ M, $V_{sample} = 1$ ml).

$$M_{sample} \times V_{sample} = M_{titrant} \times V_{titrant}$$

- Determine the percentages of acetic acid by mass in the lower and upper phase using the volume and mass data recorded for the lower and upper phase (Table 2). ($MA_{Acetic\ acid} = 60.5$ g/mole).
- Place the combinations of the phases found in the experimental studies in the triangle diagram given.
- Apply the lever arm rule and compare the experimental points with the theoretical points.

Experimental Data

➢Three points (P1, P2 and P3) are selected on the triangle diagram.



Experimental Data

- In the liquid-liquid phase equilibrium experiment, using P1, P2 and P3 mixtures, the following data were obtained. Calculate the acetic acid mass fraction in the upper and lower phases for each point and place the points in the triangle diagram with the help of the reverse arm rule. Compare the selected points with the experimentally determined points.

Not: Experiments were carried out by taking 1ml of sample.

Point name	Upper phase			Lower phase		
	Volume (ml)	Mass (g)	Base Consumed (ml)	Volume (ml)	Mass (g)	Base Consumed (ml)
P1	16,02	15,39	4,1	1,6	2,35	1,5
P2	17,5	16,05	7,2	3,8	2,55	3,8
P3	13	12,8	8,3	5,5	7,75	5,5

References

- Daniels, F., & R.A. Alberty, *“Physical Chemistry”*, 4th ed., John Wiley & Sons Co., New York, 1972.
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- Moore, W.J., *“Physical Chemistry”*, 5th ed., Prentice Hall, London, 1972.
- Chakrabarty, D.K., “An Introduction to Physical Chemistry”, Alpha Science International Ltd., 2001.
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Useful Links

- https://www.youtube.com/watch?v=z48Bo5bxqEM
- https://www.youtube.com/watch?v=gGYHXhcKM5s
- https://www.youtube.com/watch?v=h8tFnC4pNGc
- https://www.youtube.com/watch?v=7oqLUIHpqOc

Thank you for listening.