

MASS TRANSFER

- 7.3. Batch Distillation of Ethanol-Water Mixture in a Sieve Tray Column
- 7.5. Solid-Liquid Extraction by Soxhlet Apparatus from Oil-containing Substances
- 7.6. Measurement of Gas Diffusion Coefficient
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### 7.3. BATCH DISTILLATION OF ETHANOL-WATER MIXTURE IN A SIEVE TRAY COLUMN

**Keywords:** *Distillation, batch distillation, reflux, total reflux, rectification, efficiency, overall efficiency, sieve tray, McCabe-Thiele graphical method.*

**Before the experiment:** *Read the booklet carefully. Be aware of the safety precautions.*

#### 7.3.1. Aim

To investigate the basic principles and calculation techniques of Sieve Tray Batch Distillation, to determine the number of theoretical plates, variation of top and bottom composition with time and the column efficiency via the McCabe-Thiele Method and Fenske equation.

#### 7.3.2. Theory

A group of operations for separating the components of mixtures is based on the transfer of material from one homogeneous phase to another. Unlike purely mechanical separations these methods utilize differences in vapor pressure or solubility, not density or particle size.

Distillation is used to separate the components of a liquid solution, which depends upon the distribution of these various components between a vapor and a liquid phase. All components are present in both phases in accordance with their vapor-liquid equilibrium (VLE). The vapor phase is created from the liquid phase by vaporization at the boiling point. The separation of crude petroleum into gasoline, kerosene, fuel oil and lubricating stock; of a mixture of alcohol and water into its components are examples of distillation.

Distillation may be carried out by either of two principal methods. The first method is based on the production of a vapor by boiling the liquid mixture to be separated and condensing the vapors without allowing any liquid to return to the still in contact with the vapors. The second method is based on the return of part of the condensate to the still under such conditions that this returning liquid is brought into intimate contact with the vapors on their way to the condenser. Either of these methods may be conducted as a continuous process or as a batch process.

### 7.3.2.1. Batch Distillation

Batch distillation, which is the process of separating a specific quantity of a liquid mixture into products, is used extensively in the laboratory and in small production units that may have to serve for many mixtures. In batch distillation, a batch of liquid is charged to the reboiler and the system is first brought to uniform operation under total reflux. Then a portion of the overhead product is continuously withdrawn in accordance with the established reflux policy. The column operates as an enriching section. The progress of batch distillation can be controlled in several ways [1]:

1. Constant reflux, varying overhead composition. The reflux is set at a predetermined value where it is maintained for the run. Since the composition of the pot is changing the composition of the distillate also changes.
2. Constant overhead composition, varying reflux. If it is desired to maintain a constant overhead composition, the amount of reflux returned to the column must be increased. As time proceeds, the reboiler is gradually depleted of the lighter component. Finally a point is reached where the reflux ratio attains a very high value. The receivers are then changed, the reflux is reduced, and an intermediate cut is taken.

If we represent the moles of vapor by  $V$ , moles of liquid by in the pot by  $M$ , the mole fraction of the more volatile component in this liquid by  $x$ , and the mole fraction of the same component in the vapor by  $y$ , a material balance yields:

$$-y dV = d(Mx) \quad (7.3.1)$$

since  $dV = -dM$ , substitution and expansion gives:

$$y dM = M dx + x dM \quad (7.3.2)$$

Rearranging and integrating give

$$\ln \left( \frac{M_i}{M_f} \right) = \int_{x_f}^{x_i} \frac{dx}{(y-x)} \quad (7.3.3)$$

where subscript i represents the initial condition and f the final condition of the liquid in the still pot. An overall component balance gives the average distillate composition  $x_{d,avg}$

$$x_{d,avg} = \frac{(M_i x_i - M_f x_f)}{M_i - M_f} \quad (7.3.4)$$

Equations (7.3) and (7.4) hold for constant reflux policy. Fenske equation for calculating number of theoretical plates [2]:

$$n + 1 = \frac{\log \left[ \left( \frac{x_A}{x_B} \right)_D \left( \frac{x_B}{x_A} \right)_B \right]}{\log(\alpha_{avg})} \quad (7.3.5)$$

where A is the more volatile and B is the less volatile components in the mixture.  $\alpha_{avg}$  is calculated through geometric average of relative volatilities of overhead vapor and bottoms liquid:

$$\alpha_{avg} = \sqrt{\alpha_D \alpha_B} \quad (7.3.6)$$

$\alpha_i$  is the relative volatility of distillate and bottoms streams and can be calculated as the ratio of vapor pressures:

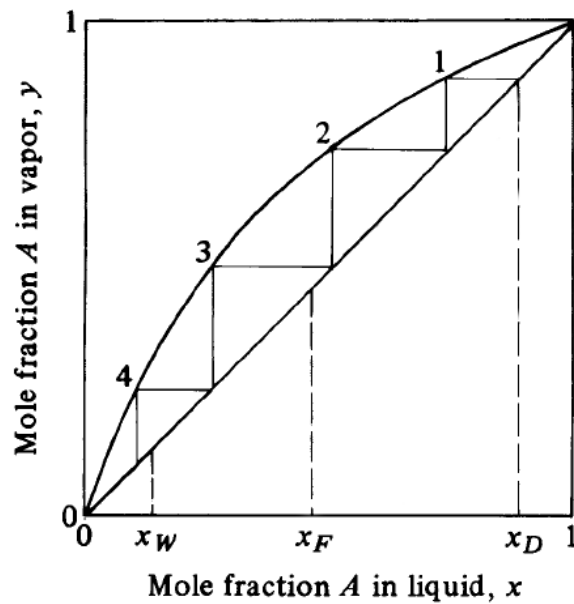
$$\alpha_i = \frac{P_{A,i}}{P_{B,i}} \quad (7.3.7)$$

Vapor pressures can be calculated through Antoine equation [3]:

$$\ln P_{sat}(kPa) = A - \frac{B}{T(^{\circ}C) + C} \quad (7.3.8)$$

### 7.3.2.2. McCabe Thiele Graphical Method

Since the composition within the column is continuously changing, rigorous calculation methods are extremely complex. The McCabe-Thiele graphical method gives a fast and easy but an approximate solution of binary distillation problems. The McCabe-Thiele method is based upon representation of the material balance equations as operating lines on the vapor vs. liquid equilibrium composition diagram [2].

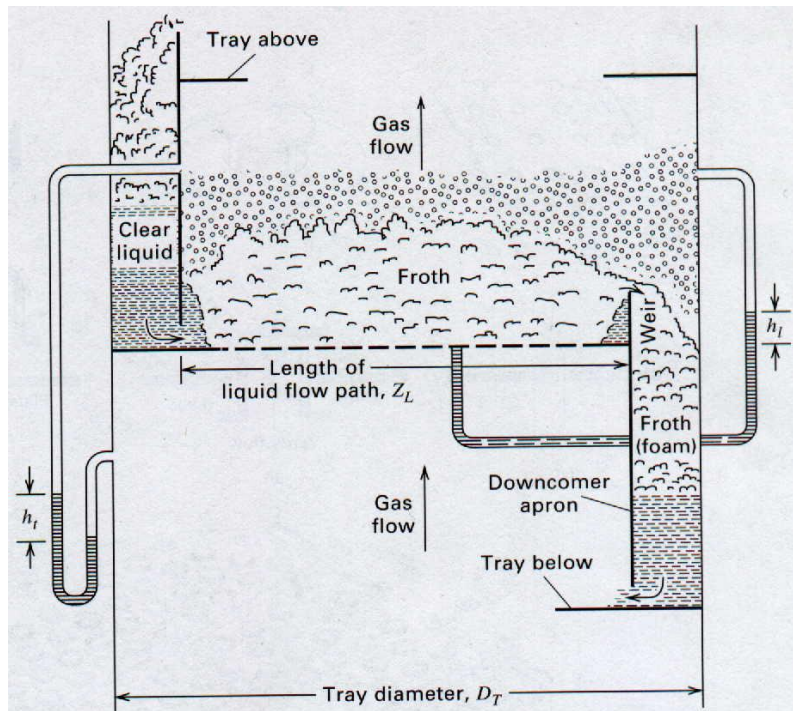


**Figure 7.3.1.** McCabe Thiele Method under total reflux [2].

The operating lines relate the composition of liquid leaving a plate to the composition of vapor beneath the plate, and are determined by material balances. The equilibrium data relate the composition of liquid leaving the plate to the composition of vapor over the plate. McCabe-Thiele suggested that the operating line be plotted on the same graph as the equilibrium curve of  $y$  versus  $x$ , so that the number of equilibrium stages can be determined by a graphical construction [2].

### 7.3.2.3. Sieve Plates

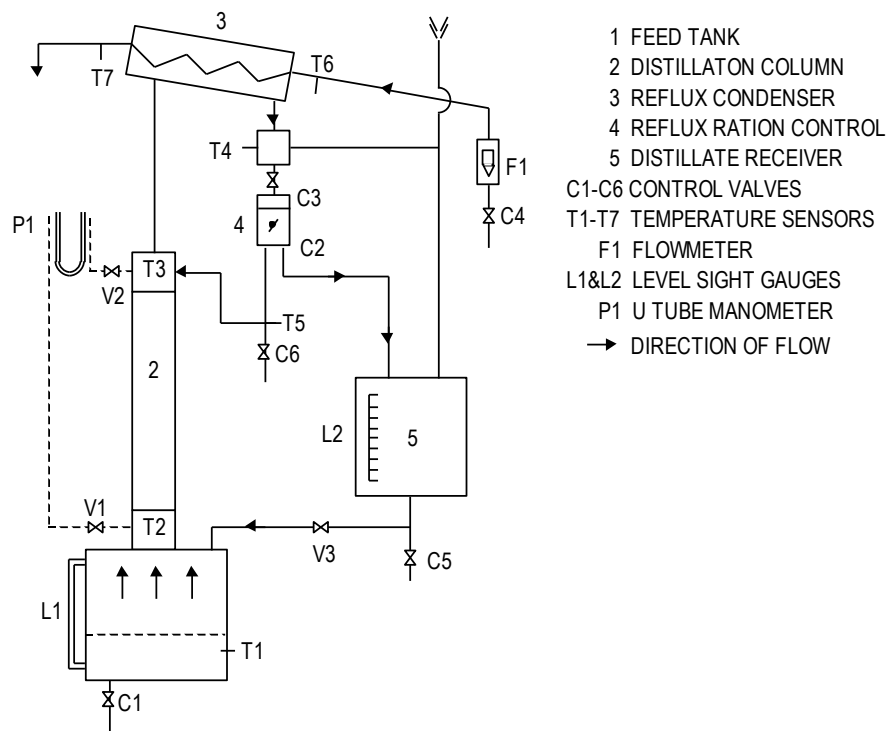
A sieve plate is designed to bring a rising stream of vapor into intimate contact with a descending stream of liquid. The liquid flows across the plate and passes over a weir to a downcomer leading to the plate below. The flow pattern on each plate is therefore cross-flow rather than countercurrent flow, but the column as a whole is still considered to have countercurrent flow of liquid and vapor. The fact that there is cross-flow of liquid on the plate is important in analyzing the hydraulic behavior of the column and in predicting the plate efficiency. Under normal conditions, the vapor velocity is high enough to create a frothy mixture of liquid and vapor that has a large surface area for mass transfer. The flow of vapor through the holes and the liquid on the plate requires a difference in pressure. The pressure drop across a single plate is usually 50 to 70 mm H<sub>2</sub>O [4].



**Figure 7.3.2.** Schematic representation of a sieve tray plate [4].

### 7.3.3. Experimental Setup

The Experimental Setup used in this experiment is shown in Figure 7.3.3.



**Figure 7.3.3.** Sieve Tray distillation column.

### 7.3.4. Procedure

1. Check that all vent lines are open and all drain valves are closed.
2. Turn on the overhead condenser cooling water supply.
3. Adjust the valves such that the column operates with 12 trays.
4. Turn on the computer and set heat duty to 5000 W.
5. Throughout the experiment at regular time intervals of 3 minutes, record the temperatures of trays 2, 6, 10 and the reboiler.
6. After temperature of tray 12 begins increasing, which means the vapor has reached to the condenser, take 5 distillate samples from the product-sampling valve in the interval of 3 minutes and record refractive indices of samples using the refractometer.
7. Turn off the system.
8. Turn off cooling water of the condenser after two hours.

**Safety Issues:** Hot distillate samples will be collected from the system, therefore safety glasses, oven mitts and lab coats are absolutely mandatory. Ethanol is used in the experiment. Follow the instructions below in case of exposure [5]. In case of eye contact, check for and remove any contact lenses. Immediately flush eyes with running water for at least 15 minutes, keeping eyelids open. In case of skin contact, wash with a disinfectant soap and cover the contaminated skin with an anti-bacterial cream. If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen.

### 7.3.5. Report Objectives

1. Plot the time dependent temperature data to observe the heating curve.
2. Calculate the number of theoretical plates using Fenske equation.
  - Use average tray temperature (exc. reboiler) to find distillate compositions.
  - Use reboiler temperature to find bottoms compositions from literature VLE data.
3. Make an analysis of the operation based on the McCabe-Thiele graphical method.
  - Use Table A.1 to find distillate composition using refractive indices obtained through samples.
  - Use reboiler temperature to find bottoms compositions from literature VLE data
4. Find Column efficiency via both methods and discuss the performance of the column.
5. State and discuss the assumptions made in your calculations.

## References

1. Perry, R. H. and D. Green, *Perry's Chemical Engineers' Handbook*, 6<sup>th</sup> edition, McGraw-Hill, 1988.
2. Geankoplis, C. J., *Transport Processes and Separation Process Principles*, 4<sup>th</sup> edition, Prentice Hall, 2009.
3. Smith, J. M., H. C. Van Ness and M. M. Abbott, *Introduction to Chemical Engineering Thermodynamics*, 7<sup>th</sup> edition, McGraw-Hill, 2005.
4. McCabe, W. L., J. J. Smith and P. Harriott, *Unit Operations of Chemical Engineering*, McGraw Hill, 1993.
5. Ethanol MSDS, <http://www.sciencelab.com/msds.php?msdsId=9923955> (Last Update May 2013. Retrieved February 2014)

## Appendix: Refractive Index Data

**Table A.1.** Volume vs. refractive indices for ethanol-water mixture.

<b>V<sub>EtOH</sub></b> <b>(ml)</b>	<b>V<sub>water</sub></b> <b>(ml)</b>	<b>Refractive</b> <b>Index</b>
0	100	33.2
10	90	33.5
20	80	34.1
30	70	34.7
40	60	35.2
50	50	35.6
60	40	35.9
70	30	36.1
80	20	36.3
90	10	36.4
100	0	36.5



## 7.5. SOLID-LIQUID EXTRACTION BY SOXHLET APPARATUS FROM OIL CONTAINING SUBSTANCES

**Keywords:** *Mass transfer, leaching, soxhlet apparatus, distillation, triangular diagram.*

**Before the experiment:** *See your TA before the experiment! Read the booklet carefully. Be aware of the safety precautions. Bring data sheet provided in Appendix A.*

### 7.5.1. Aim

To perform mass balance to measure the moisture and oil content of potato chips by solid-liquid extraction (leaching).

### 7.5.2. Theory

Extraction is used to transfer a constituent of a liquid to another liquid (solvent). The term solid-liquid extraction is restricted to those situations in which a solid phase is present and includes those operations frequently referred to as leaching, lixiviation and washing [1].

Extraction always involves two steps:

1. Contact of the solvent with the solid to be treated so as to transfer the soluble constituent (solute) to the solvent;
2. Separation or washing of the solution from the residual solid.

These two steps may be conducted in separate equipment or in the same piece of equipment.

Liquid always adheres to the solid which must be washed to prevent either the loss of solution if the soluble constituent is the desired material or the contamination loss of the solids if these are the desired material. The complete process also includes the separate recovery of the solute and solvent. This is done by another operation such as evaporation or distillation [2].

The equipment used for solid-liquid extraction is classified according to the manner in which the first step is done. The term *solid bed* or *fixed bed* refers to any operation in which the solid particles are kept in relatively fixed positions with respect to each other while the solvent flows through the bed of solid particles. The opposite of this situation, called *dispersed contact*, refers to any operation in

which the solid particles, suspended in the fluid, are in motion relative to each other and to the solvent during the time of contact [3, 4].

### 7.5.2.1. Solid-liquid Extraction

Solid-liquid extraction (leaching) is the process of removing a solute or solutes from a solid by use of liquid solvent. Leaching is widely used in chemical industries where mechanical and thermal methods of separations are not possible or practical. Extraction of sugar from sugar beets, oil from oil bearing seeds, production of a concentrated solution of a valuable solid material are typical industrial examples of leaching. Leaching process can be considered in three parts:

1. Diffusion of the solvent through the pores of the solid
2. The diffused solvent dissolves the solutes (i.e. transfer the solute to the liquid phase).
3. Transfer of the solution from porous solid to the main bulk of the solution.

In a fixed-bed system, the solid particles are stationary in a tank, while solvent is allowed to percolate through the bed of undissolved solids. In leaching by the Soxhlet apparatus multiple contacts of solids with the fresh solvent is performed at each stage of operation [4].

Leaching process divides the flow into two parts: overflow and underflow. Overflow consists of solvent and solute, whereas underflow contains solvent and inert.

During the leaching process two material balances can be written. One is overall material balance;

$$M_{solid\ feed} + M_{hexane} = M_{underflow} + M_{overflow} \quad (7.5.1)$$

The other is the component balance;

$$M_{solid\ feed} \times x_{oil\ in\ feed} = M_{overflow} \times x_{oil\ in\ overflow} \quad (7.5.2)$$

The solid feed contains some moisture. Before the extraction process, the solid must be dry. Water content of the solid feed can be calculated as;

$$\text{moisture \%} = \frac{\text{mass}_{\text{wet solid}} - \text{mass}_{\text{dry solid}}}{\text{mass}_{\text{wet solid}}} \times 100 \quad (7.5.3)$$

Leaching process can be evaluated with the calculations of solute recovery and yield. Solute recovery is the ratio of mass of extracted solute to the mass of total solute in the solid. Solute yield, on the other hand, is the ratio of mass of extracted solute to the mass of dry based solid.

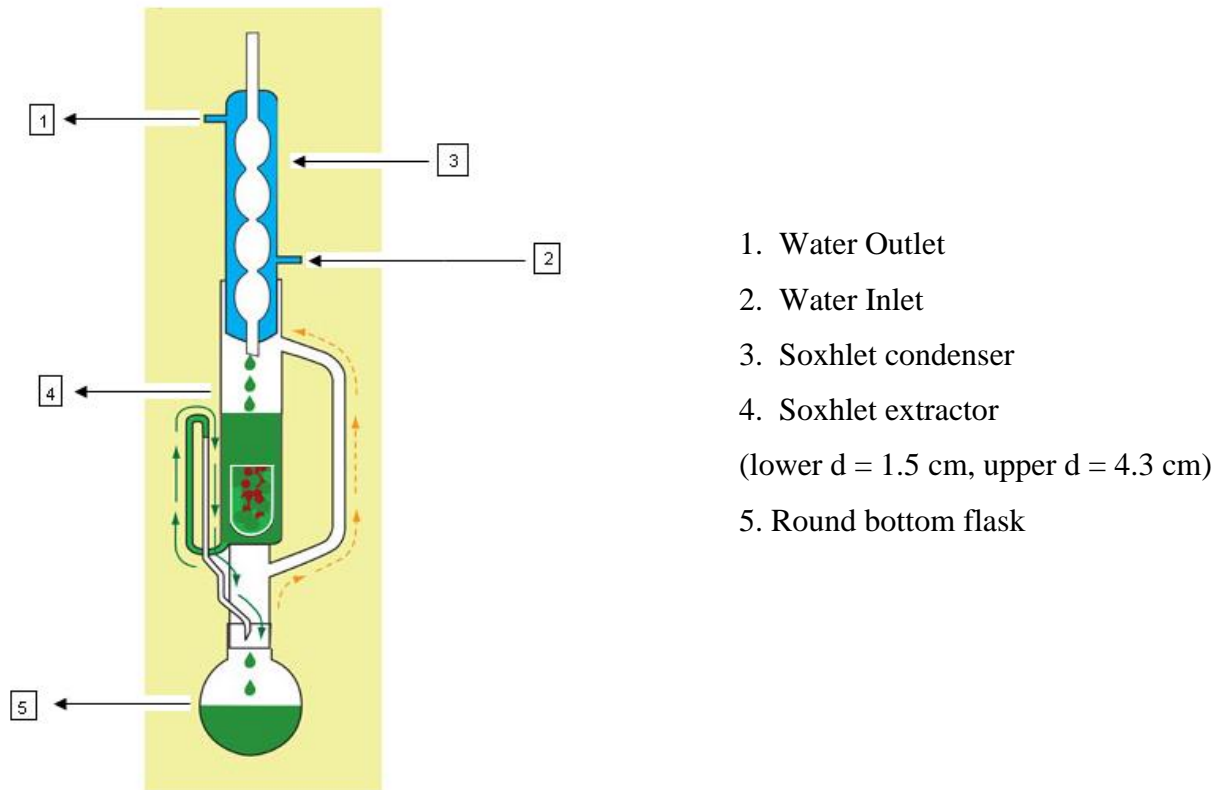
### 7.5.2.2. Soxhlet Apparatus

The apparatus is composed of a distilling pot, a porous container which contains the solid, and a condenser. It was first described in 1879. Basically, the solvent vapor coming from the distilled pot goes up by-passing the solid particles to the condenser and then condenses here. The condensed solvent is allowed to drip back onto the porous container where it meets with the solid. This liquid condensate performs the extraction by passing through the container and then back to the reservoir. This cycle can be repeated continuously, and sustained as long as to reach any desired concentration. The most important feature of this apparatus is that, when the solvent is boiled for the second time, it left the oil extracted from the solid in the reservoir, and the solid meets with fresh solute at each repetitive runs. In this apparatus, the low vapor pressure solvents such as methanol, acetone, hexane etc. are preferred to achieve a fast condensation [5].

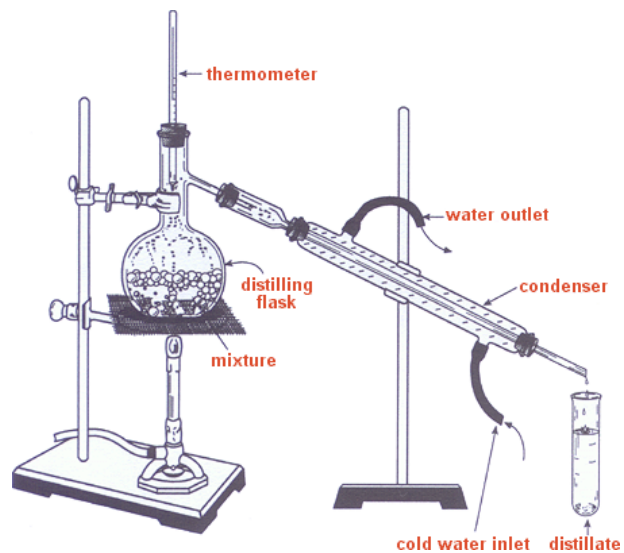
This experiment aims to study the basic principles of leaching by extraction of oil from potato chips using hexane as a solvent. Soxhlet apparatus will be used to perform extraction; whereas distillation setup will be utilized to separate oil from hexane. Mass balance will be done for moisture content, oil recovery and yield.

### 7.5.3. Experimental Setup

The experimental setup used in this experiment is shown in Figure 7.5.1.



**Figure 7.5.1.** Soxhlet apparatus.



**Figure 7.5.2.** Simple distillation apparatus.

#### 7.5.4. Procedure

Use data sheet provided in Appendix A to collect all your data.

1. Weigh approximately 9 grams of potato chips containing oil.
2. Crush and dry them in an oven for 30 minutes at 200°C and determine the moisture content.
3. Add the sample into the thimble.
4. Place several boiling chips into a clean, dry round bottom flask. Weigh the container with boiling chips and record as the tare weight of the container.
5. Pour 325 ml hexane into the round bottom flask as a solvent.
6. Insert thimble and sample into the extractor, assemble the Soxhlet apparatus and start leaching and continue the process up to the end of the third siphon.
7. When the extraction time is complete, remove the thimble and sample. Transfer it into an evaporating dish. Weigh the sample. Dry it in an oven. Weigh the sample the next day again.
8. Weigh the round bottom flask with hexane and extracted oil before distillation.
9. Assemble distillation apparatus and distill the extract in order to separate the oil and solvent.
10. Weigh the recovered hexane.
11. Let the round bottom flask with recovered oil dry overnight in oven. Weigh the container the next day again.

**Safety Issues:** In this experiment, hexane will be used as a solvent. It is hazardous in case of skin contact (permeator), ingestion and inhalation; and slightly hazardous in case of skin contact (irritant) and eye contact (irritant) [6]. The experiment will be performed under the hood. Beware of heater. Apparatus for both extraction and distillation requires gentle handling. Make sure to turn off the cooling water at the end of the experiment. In case of eye contact, check for and remove any contact lenses. Immediately flush eyes with running water for at least 15 minutes, keeping eyelids open. Get medical attention if irritation occurs. If there is any skin contact, wash with soap and water. Cover the irritated skin with an emollient. Get medical attention if irritation develops. In case of inhalation, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention if symptoms appear [6].

### 7.5.5. Report Objectives

1. Perform the necessary mass balance for hexane in order to calculate the amount of lost hexane.
2. Perform overall mass balance considering input values are feed and solvent (hexane) and output values are overflow and underflow.
3. Calculate the moisture content, oil yield and percent oil recovery.
4. Prepare a triangular phase diagram to indicate mass compositions of each stream.

### References

1. McCabe, W. L. and J. C. Smith, *Unit Operations of Chemical Engineering*, 5<sup>th</sup> edition, McGraw-Hill, 1993.
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4. Brown, G. G., *Unit Operations*, John Wiley & Sons, 1956.
5. Jensen W. B., The Origin of the Soxhlet Extractor, *Journal of Chemical Education*, Vol. 84, No. 12, pp:1913, 2007.
6. Hexane MSDS, <http://www.sciencelab.com/msds.php?msdsId=9927187> (Last Update May 2013. Retrieved February 2014.)

## Appendix

Table A.1. Experimental Data Sheet

Step	Measured Object	Weight (g)
1	Evaporating Dish 1	
2	Evaporating Dish 1 + Potato Chips (Inert + Oil + Water)	
3	Evaporating Dish 1 + Crashed Potato Chips (Before Evaporation) (Inert + Oil + Water)	
4	Evaporating Dish 1 + Crashed Potato Chips (After Evaporation) (Inert + Oil)	
5	Balloon	
6	Folio 0 (For balloon)	
7	Balloon + Boiling Chip	
8	325 ml hexane	
9	Thimble	
10	Soxhlet Extractor	
11	Folio 1 + Folio 2 (For Soxhlet Extractor)	
12	Erlenmeyer + Folio 3	
13	Evaporating Dish 2	
14	Soxhlet Extractor + Folio 1 + Folio 2 + Thimble + Crashed Potato Chips (Inert) + Hexane 1 (After Extraction)	
15	Evaporating Dish 2 + Thimble + Crashed Potato Chips (Inert) + Hexane 2 (After Extraction, Before Evaporation)	
16	Balloon + Boiling Chip + Folio 0 + Oil + Hexane 3 (After Extraction, Before Distillation)	
17	Erlenmeyer + Folio 3 + Hexane 4 (After Distillation)	
18	Balloon + Boiling Chip + Oil (After Distillation)	
19	Balloon + Boiling Chip + Oil (After 1 Day)	
20	Evaporating Dish 2 + Thimble + Crashed Potato Chips (Inert) (After 1 Day)	

## 7.6 MEASUREMENT OF GAS DIFFUSION COEFFICIENT

**Keywords:** *Gas diffusion coefficient, diffusion flux, mass transfer, Winkelmann method, Stefan's law.*

**Before the experiment:** *Read the booklet carefully.*

### 7.6.1. Aim

To determine the diffusion coefficient of acetone in air at different temperatures.

### 7.6.2. Theory

In chemical engineering, especially in separation processes, mass transfer phenomenon has a crucial role in understanding the nature of a system. The particular mass transfer mechanism, which will be investigated in this experiment, is the molecular diffusion. Molecular diffusion is caused by random movements of molecules due to their kinetic energy. The molecules (or macroscopically the mass) are transferred to all directions, i.e. mass fluxes are in all directions, and the transfer in each direction is driven by the concentration gradient in the corresponding direction. This concept is employed in analyses in a variety of classical branches in chemical engineering, such as chemical reactor and catalyst design. Besides, diffusion through semipermeable boundaries plays an important role in study areas of bio-chemical engineering and membrane technology [1].

Main characteristic of molecular mass transfer is explained by Fick's law. For steady-state diffusion [2]:

$$J_{Az}^* = -D_{AB} \frac{dc_A}{dz} \quad (7.6.1)$$

where  $J_{Az}^*$  is the molar flux of A due to molecular diffusion in the z direction in mol A/(s.cm<sup>2</sup>),  $D_{AB}$  is the molecular diffusivity of the molecule A in B in cm<sup>2</sup>/s, and  $c_A$  is the concentration of A in mol A/cm<sup>3</sup>.

In general case, superposition of diffusion of A into B and convection is [1]:

$$N_A = -cD_{AB} \frac{dx_A}{dz} + \frac{c_A}{c} (N_A + N_B) \quad (7.6.2)$$



where  $N_A$  is the molar flux of A in the z direction in mol A/(s.cm<sup>2</sup>),  $N_B$  is the molar flux of B in mol B/(s.cm<sup>2</sup>),  $D_{AB}$  is the molecular diffusivity of the molecule A in B in cm<sup>2</sup>/s,  $c_A$  is the concentration of A in mol A/cm<sup>3</sup> and  $c$  is the total concentration of A and B in mol/cm<sup>3</sup>.

In this experiment, the molecular diffusion of gases is examined for a particular case, in which, gas A diffuses through a stagnant and non-diffusing gas B, meaning that the molar flux of B,  $N_B$ , is zero. This special case can be used to model some certain chemical engineering units, e.g. evaporators. The molar flux of A in this case can be determined by:

$$N_A = - \frac{cD_{AB}}{1 - x_A} \frac{dx_A}{dz} \quad (7.6.3)$$

A widely employed method in determination of the gas diffusion coefficient is the Winkelmann's method (or Stefan's law), in which substance A (acetone in this experiment) is contained in a narrow tube in its liquid form, and a stream of gas B (air in this experiment) is present at the top of the tube [2, 3]. The described setup suggests two consecutive transfer steps: the evaporation of the liquid A at the interface and the diffusion of the gas A from the liquid-gas interface to the top of the tube, where it is swept by the air stream. The rate of mass transfer for the second step can be written in an alternative form as:

$$N_A = D_{AB} \frac{c_A (c_A + c_{Bm})}{L c_{Bm}} \quad (7.6.4)$$

where,  $c_A$  is the saturation concentration at the gas-liquid interface,  $L$  is the effective distance of mass transfer and  $c_{Bm}$  is the logarithmic mean vapor concentration. The transfer rate representing the first mechanism (evaporation) is given by:

$$N_A = \frac{\rho}{M_w} \frac{dL}{dt} \quad (7.6.5)$$

where,  $\rho$  and  $M_w$  are the density (in liquid form) and the molecular weight of A, respectively. By equating those two expressions for the transfer rate and solving the resulting differential equation, the following relation is obtained:

$$\frac{t}{L - L_0} = \frac{\rho}{2M_w D_{AB} c_A (c_A + c_{Bm})} (L - L_0) + \frac{\rho c_{Bm}}{M_w D_{AB} c_A (c_A + c_{Bm})} L_0 \quad (7.6.6)$$

$L_0$  here, stands for the initial distance between the top of the tube and the gas-liquid interface.

### 7.6.3. Experimental Setup



- 1) T-tube (Stefan tube)
- 2) Aluminum block with Vernier scale
- 3) Heater
- 4) Microscope
- 5) Fan
- 6) Controller

#### 7.6.4. Procedure

1. Set the temperature to 40 °C and wait until it is reached.
2. Inject a suitable amount of liquid acetone in the T-tube and plug it into the heated metal block.
3. Start E-scope program in the computer.
4. Take 15 screenshots and, measure and record the distance between the interface and a reference point with an interval 7 minutes.
5. Repeat the procedure for 50 °C, but take the screenshots with an interval of 1 minute.

**Safety Issues:** This experiment does not involve use of any hazardous or corrosive chemicals. At all times wear lab coats, eyewear and gloves.

#### 7.6.5. Report Objectives

1. Derive Eq. 7.6.6 starting from Eqs. 7.6.4 and 7.6.5.
2. Determine  $(L-L_0)$  and  $t/(L-L_0)$  for each measurement.
3. Plot  $t/(L-L_0)$  vs.  $(L-L_0)$  and fit a line.
4. Use the resulting slope of that line to determine the diffusion coefficient.
5. Compare the experimental result with literature values.

#### References

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## 7.7 MEASUREMENT OF LIQUID DIFFUSION COEFFICIENT

**Keywords:** *Liquid diffusion coefficient, diffusion flux, mass transfer.*

**Before the experiment:** *Read the booklet carefully. Review ionic conductivity in solutions, and methods of measuring electrical conductivity.*

### 7.71. Aim

To determine the liquid diffusion coefficient of different salt solutions in distilled water.

### 7.7.2. Theory

Mass transfer is the transportation of mass from one point to another. Mass transfer may take place in a single phase or over phase boundaries in multiphase systems. When two solutions of different concentrations, originally at equilibrium with their surroundings, are contacted, a concentration gradient is created and mass transfer occurs until a new equilibrium is reached. When the concentration gradient is zero, the system stays at equilibrium, since there is not any driving force [1].

There are two different types of mass transfer mechanism, which are convective mass transfer and diffusional mass transfer. Convective mass transfer occurs due to bulk motion, while there is no bulk motion in the diffusion mass transfer. Due to lack of bulk motion, diffusion is a slow process and occurs only from high concentration to low concentration [2].

#### 7.7.2.1. Fick's Law of Diffusion

Fick's law of diffusion describes diffusion and can be used to determine the diffusion coefficient (D). Fick's law relates the diffusive flux to the concentration field, by postulating that the flux goes from regions of high concentration to regions of low concentration, with a magnitude that is proportional to the concentration gradient [3].

Fick's law can be written with mass transfer rate instead of concentration gradient;

$$J = -D_{AB} \times \frac{\partial C}{\partial X} = -\frac{1}{A} \times \frac{dm}{dt} \quad (7.7.1)$$

Where,

$J =$	Diffusion flux	$mole \times cm^{-1} \times s^{-1}$
$D_{AB} =$	Diffusion coefficient	$cm^2 \times s^{-1}$
$\frac{\partial C}{\partial X} =$	Concentration gradient	$mole \times cm^{-4}$
$A =$	Cross sectional area which is perpendicular to flow	$cm^2$
$\frac{dm}{dt} =$	Mass transfer rate	$mole \times s^{-1}$

Liquid diffusion coefficient is determined via this experiment in the setup shown as Figure 1. In this setup, concentrated solution is placed in the J-tube and diffusion vessel is filled with distilled water. Diffusion occurs from bottom to top, i.e. from the diffusion cell which is a J-tube to the diffusion vessel, through capillaries shown in Figure 1.

Concentration gradient inside capillaries is assumed constant. Therefore, we can rewrite the Fick's law as following;

$$J = -D_{AB} \times \frac{\Delta C}{\Delta x} \quad (7.7.2)$$

Also concentration at the bottom and the top of the capillaries is assumed constant while the bottom concentration is the same with salt solution, the top concentration is zero because of large amount of distilled water in big vessel. Therefore;

$$J = -D_{AB} \times \frac{M_{in}}{x} \quad (7.7.3)$$

Where,  $M_{in}$  [mol/L] is molarity of salt solution and  $x$  [cm] is capillaries' length.

Mass transfer rate can be expressed by rate of conductivity change of distilled water in the diffusion vessel (Figure 1);

$$\frac{dm}{dt} = \frac{dk}{dt} \times \frac{V}{C_M} \quad (7.7.4)$$

Where,  $\frac{dk}{dt}$  [ $\Omega^{-1} \times s^{-1}$ ] is rate of conductivity change and  $C_M$  [ $\Omega^{-1} \times L \times mol^{-1}$ ] is the change in conductivity with respect to molarity change.  $C_M$  value can be calculated by calibration curve method.

Combining equations 7.7.3 and 7.7.4, the following equation is obtained.

$$D_{AB} \times N \times \frac{M_{in}}{x} = \frac{1}{A} \times \frac{dk}{dt} \times \frac{V}{C_M} \quad (7.7.5)$$

when we rearrange the equation and open the area term, we get;

$$D_{AB} = \frac{4 \times V \times x}{\pi \times d^2 \times N \times M_{in} \times C_m} \times \frac{dk}{dt} \times 10^3 \quad (7.7.6)$$

Where,

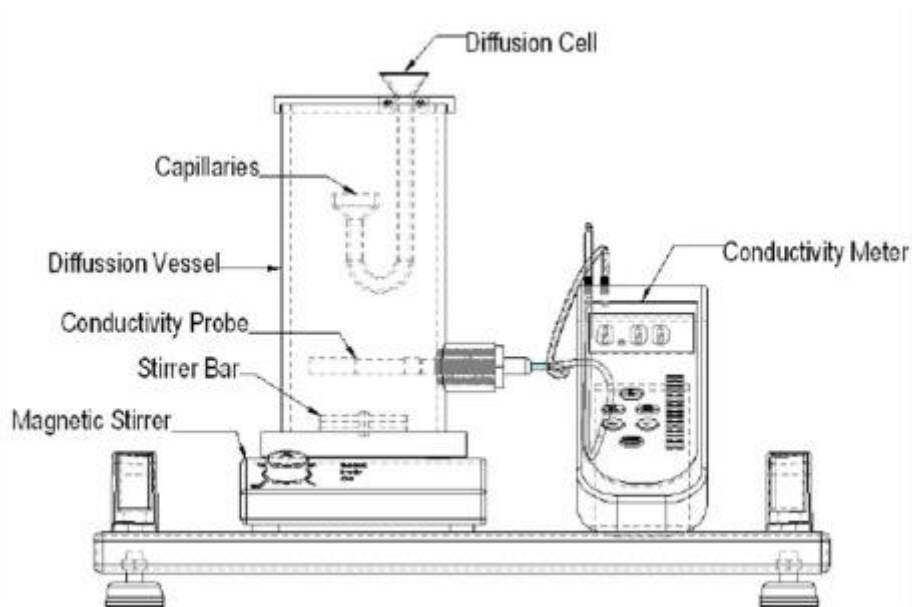
$D_{AB}$ =	Diffusion coefficient	$cm^2 \times s^{-1}$	
$V$ =	Volume of water in outer vessel	$L$	1.0
$x$ =	Length of capillaries	$cm$	0.45
$d$ =	Diameter of capillaries	$cm$	0.1
$N$ =	Number of capillaries		121
$M$ =	Molarity of salt solution in diffusion cell	$gmol/L$	
$C_M$ =	Change in conductivity per change in molarity	$\Omega^{-1} \times L \times mol^{-1}$	
$\frac{dk}{dt}$ =	Rate of change of conductivity (slope of graph)	$\Omega^{-1} \times s^{-1}$	

### 7.7.2.2. Calibration Curve

A calibration curve is a method which is used generally in analytical chemistry to examine the concentration of an unknown sample solution. The curve is generated using data from various concentrations of the solution: concentration data is on the x-axis, while the other variables are on the y-axis. Once the curve has been plotted, the concentration of the unknown solution can be determined by placing it on the curve based on its observable variable [4].

### 7.7.3. Experimental Setup

Liquid Diffusion Coefficient Apparatus consists of diffusion cell, diffusion vessel conductivity probe, conductivity meter, stirrer bar and magnetic stirrer will be used in the experiment.



**Figure 1.** Liquid Diffusion Coefficient Apparatus

#### 7.7.4. Procedure

6. Prepare 1 M NaCl and 1 M CaCl<sub>2</sub> solutions in different beakers.
  7. Fill the diffusion cell with 1 M NaCl solution.
  8. Plug the conductivity meter into the vessel.
  9. Fill the diffusion vessel with 1 L distilled water.
  10. Switch on the magnetic stirrer.
  11. When the diffusion cell was put into the vessel, start the stopwatch.
  12. Record the conductivity data appeared on the screen of the conductivity meter every 20 seconds for 40 minutes.
  13. Apply the same procedure for CaCl<sub>2</sub> solution for constructing calibration curve.
  14. Prepare 100 ml of 0.01 M NaCl solution in a 1000 ml beaker, record conductivity data.
  15. Add 100 ml distilled water to the beaker to dilute the NaCl solution, make sure it is perfectly mixed, and record conductivity data. Repeat this step eight more times to prepare a calibration curve.
  16. These data were transferred to excel and obtained a calibration curve.
- Same procedure was applied for 0.01 M NaCl and 0.01 M CaCl<sub>2</sub> solutions and data are recorded.

**Safety Issues:** This experiment does not involve use of any hazardous or corrosive chemicals. At all times wear lab coats, eyewear and gloves.

### 7.7.5. Report Objectives

1. Construct the calibration curve and determine the  $C_M$ , for both NaCl and CaCl<sub>2</sub>.
2. Draw the conductivity (k) vs. time (seconds) data and determine dk/dt for both solutions.
3. Determine the diffusion coefficient for NaCl and CaCl<sub>2</sub> using the equation 6.
4. Compare the experimental result with literature values.

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## 7.8. AERATION

**Keywords:** *Aeration, absorption, oxygen transfer.*

### 7.8.1. Aim

To study the oxygen transfer to water under non-steady state conditions and to determine the effects of mixing on the coefficient of absorption and the oxygenation capacity of a system

### 7.8.2. Theory

The transfer of gases into or out of water is of great importance in the management of water quality, whether the aim is to provide water suitable for domestic or industrial use, or to convert sewage or other effluents to a safe and inoffensive form for discharge to the environment.

Examples include;

- Removal of carbon dioxide and hydrogen sulphide from raw water from deep wells or the lower levels of a storage reservoir.
- Addition of atmospheric oxygen to waters to improve taste, and in some instances to convert soluble ferrous salts to insoluble ferric salts for subsequent removal.
- Addition of atmospheric oxygen (or sometimes pure oxygen) to sewage and organic wastes to permit biological breakdown and oxidation.
- Addition of chlorine or ozone for disinfection, or sulphur dioxide for de-chlorination.
- Removal of oxygen from industrial or boiler feed water to reduce corrosiveness.

Besides these processes of treatment, the natural solution of atmospheric oxygen in rivers and other bodies of water is essential for the maintenance of aquatic life, particularly fish, and for self purification brought about by bacteria and other organisms. Natural aeration is sometimes supplemented by artificial means. The solution of oxygen in water is the outstanding important form of gas transfer in the field of water quality management. "Aeration" implies bringing water and air into intimate contact, usually to facilitate oxygen transfer.

**Table 7.8.1.** Solubility of Oxygen in Pure Water.

Temperature (°C)	Saturation Concentration $C_s$ (mg/l)	Temperature Correction Factor F
0	14.6	1.2920
2	13.8	1.2212
4	13.1	1.1593
6	12.5	1.1062
8	11.9	1.0531
10	11.3	1.0000
12	10.8	0.9558
14	10.4	0.9204
16	10.0	0.8850
18	9.5	0.8407
20	9.2	0.8142
22	8.8	0.7788
24	8.5	0.7522
26	8.2	0.7257
28	7.9	0.6991
30	7.6	0.6726

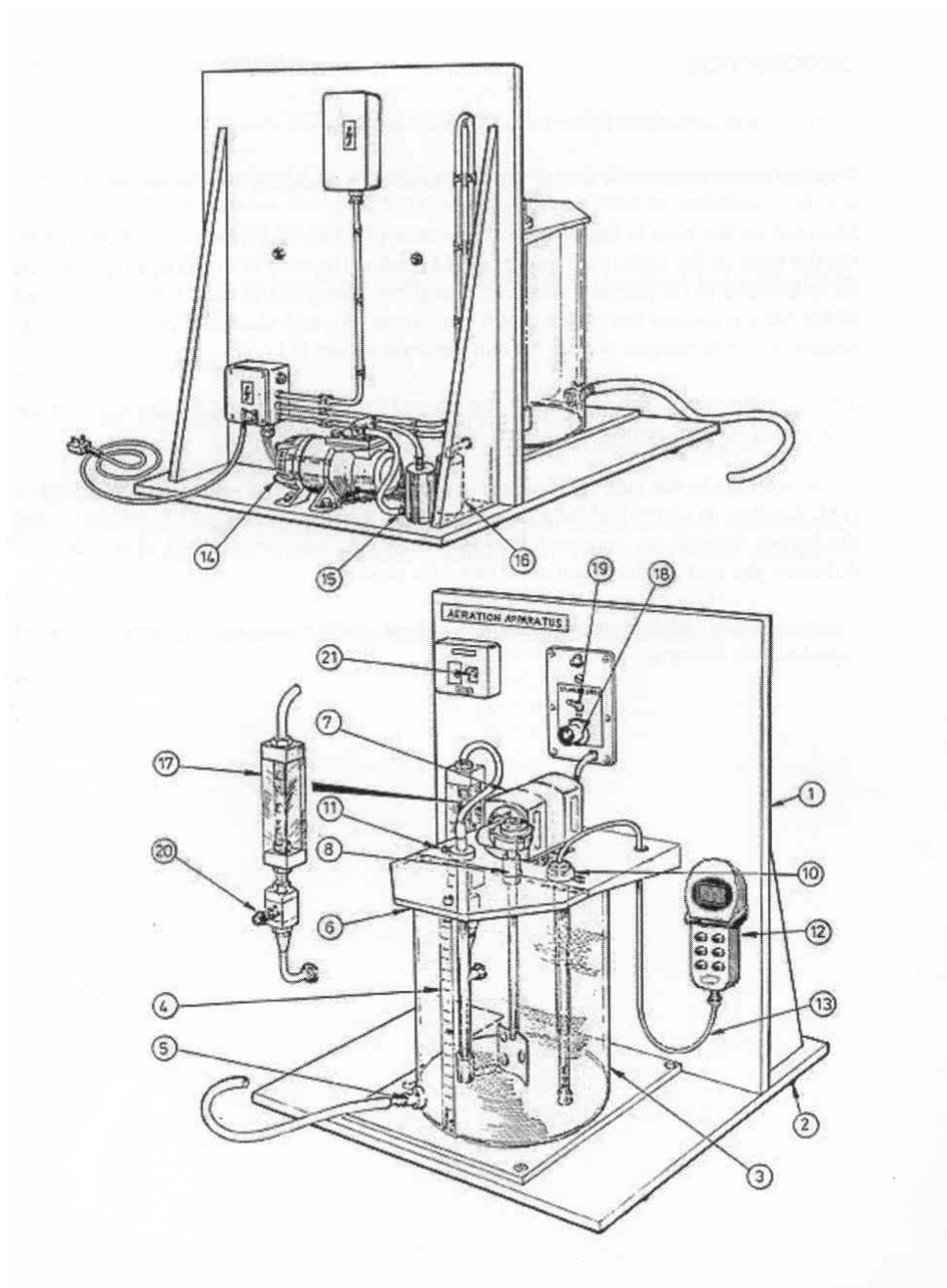
The table above gives the solubility of oxygen in mg/l in pure water at equilibrium with water vapor saturated air at the standard atmospheric pressure. A gas forming part of an atmosphere in contact with a liquid in which it is soluble will pass into solution up to the point at which the concentration of the gas in the liquid is in equilibrium with the concentration of the gas in the atmosphere. This equilibrium point is determined by the “coefficient of absorption  $K_s$ ”, which is the value of the concentration of the gas in the liquid, when the atmosphere is composed entirely of the gas under consideration.

$$K_s = \frac{\ln D_{t_1} - \ln D_{t_2}}{t_2 - t_1} = \frac{2.303(\log D_{t_1} - \log D_{t_2})}{t_2 - t_1} \quad (7.8.1)$$

$D_{t_1}$  and  $D_{t_2}$  are selected readings of oxygen concentrations in mg/l,  $t_1$  and  $t_2$  are the corresponding values of time. The oxygenation capacity of a system is defined as the rate of absorption of oxygen during the aeration of completely deoxygenated water at 10°C, where F is a temperature correction factor,  $C_{(10)}$  is the saturation concentration and V is the volume of water.

$$R_{(10)} = K_s F C_{(10)} V \quad (7.8.2)$$

### 7.8.3. Experimental Setup



- |                       |                               |
|-----------------------|-------------------------------|
| 1) base and backboard | 8) stirrer                    |
| 2) rubber feet        | 11) aerator tube              |
| 3) water tank         | 12) oxygen/temperature meter  |
| 4) depth gauge        | 13) filter                    |
| 5) drainage tap       | 14) pump                      |
| 6) lid of the tank    | 17) flowmeter                 |
| 7) stirrer motor      | 18) variable speed adjustment |

#### 7.8.4. Experimental Procedure

1. 10% solution of sodium sulphite,  $\text{Na}_2\text{SO}_3$ , and 1% solution of cobaltous chloride,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  are prepared.
2. The vessel is filled with 20 liters of tap water.
3. The diffuser and the oxygen electrode are located in the desired positions.
4. The stirrer is run at a moderate rate and 1.5 ml of the  $\text{Na}_2\text{SO}_3$  solution plus 0.5 ml of the  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  solution are added per liter of tap water present in the vessel. These quantities should be sufficient to de-oxygenate the water. The dissolved oxygen level is measured to ensure that it is less than 10% of the saturation value and, if necessary, a little more of each solution is added to bring the level to near zero.
5. The air flow is started and adjusted to the desired value, e.g. 5 liters/min.
6. The stirrer is run at the lowest speed at which the contents of the vessel are adequately stirred. (It is important to ensure that the diffuser and oxygen electrode are so located that air bubbles are not carried into contact with the electrode. This would lead to false oxygen readings.)
7. Once the air flow has been established at the required steady rate, oxygen reading data are taken at intervals of 2 minutes, until the oxygen level is approaching saturation.
8. Temperature of the water is also recorded at each reading of oxygen concentration in the course of the experiment. The average temperature should be used in subsequent calculations.
9. The experiment is repeated at different stirrer speeds.

#### Safety Issues:

In this experiment sodium sulphite and cobaltous chloride solutions are used in the aeration process. They are both hazardous in case of ingestion and inhalation. Cobaltous chloride is also hazardous in case of skin contact and eye contact, while sodium sulphite is slightly hazardous. Therefore, at all times wear lab coats, eyewear and gloves. In case of skin or eye contact flush contacted areas with plenty of water. Remove contaminated clothing or contact lenses. In case of ingestion do not induce vomiting unless directed to do so by medical personnel. Never give anything by mouth to an unconscious person. Loosen tight clothing such as collar, tie or waistband. In case of inhalation immediately get a breath of fresh air.

### 7.8.5. Report Objectives

1. Calculate the value of  $D_t$  for each reading.
2. Plot these  $D_t$  values on a logarithmic scale against  $t$  (arithmetic scale).
3. Calculate  $K_s$  from the graph.
4. Calculate the oxygenation capacity  $R_{(10)}$
5. Comment on the effects of the rate of mixing on values of  $R_{(10)}$  and  $K_s$ .
6. Plot oxygenation capacity against variable stirrer speeds and derive a mathematical relationship if possible.