Chemical Engineering Laboratory Manual

v 0.08, last updated March 17, 2006

This document is a collection of manuals of Chemical Engineering-related experiments that have been offered at various times in the past few years. The Undergraduate Laboratory course structure has been modified, and as a result, students will now perform 40 experiments over 4 semesters. In the interim period before the new course structure is ratified, these experiments will run under the existing course/credit structure. Several new experiments are due to be phased in, to better integrate concepts from different courses. In addition to descriptions of the various experiments, this manual contains (i) discussion of relevant aspects of Safety that students are expected to observe during their experimentation, and (ii) basic principles of data analysis that are expected to be followed in presenting their results.

Course-specific details (including the evaluation procedure followed and the rotation schedule) may be obtained on the UG lab webpage http://www.che.iitb.ac.in/courses/uglab/uglabs.html

UG Lab Coordinators
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1 Determination of Apparent Porosity

The Evacuation Method

General: The evacuation method of the determination of apparent porosity is applicable to all types of refractories.

Evacuating Apparatus: An apparatus capable of reducing the pressure to a value not greater than 25 mm of mercury, shall be used.

Immersion Liquid: Water may be used, unless the test material is unstable in contact with it. Liquid paraffin may be used with all types of refractory material but it shall be fractionated before use and the fraction boiling below 200°C shall be rejected.

Test specimen - Test specimen measuring 65 x 65 x 40 mm shall be cut from the brick or shape as to remove the original surface of the refractory under test. For this purpose a cut-off grinding wheel is recommended. Any loosely adhering grog or dust shall be removed from the test piece before use.

Procedure

- Dry the test specimen at 110°C and weigh after cooling to room temperature in a desiccator. This weighing and all subsequent weighings shall be made to an accuracy of 0.1 g.

- Place the test specimen after weighing in an empty vacuum desiccator. Reduce the pressure in the desiccator to a value not greater than 25 mm of mercury. Admit the immersion liquid slowly till the specimen is covered. Allow the specimen to stand under reduced pressure for at least 5 to 6 hours. Air shall then be allowed to enter the vessel and the test specimen held in a sling of fine thread, shall be weighed (S) while suspended in the immersion liquid of the same density as that in the desiccator.

- Lift the test piece slowly from the immersion liquid by means of a sling. The sides of a test piece will drain during this operation and the globules of liquid that form on the under-sided and between the sling and the top surface shall be removed by brief contact with the edge of a piece of filter paper. Care should be taken that the filter paper does not come into contact with the surface of the test piece since the removal of too much liquid will lead to large errors than the removal of insufficient liquid. Then weigh the soaked test piece suspended in air (W).

- Obtain the exterior volume (V) in cubic centimeters of the test specimen by subtracting the suspended weight (S) from the saturated weight (W) and the actual volume of open pores (V1) in cubic centimeters by subtracting the dry weight (D) from the saturated weight (W).

Calculation

Obtain the apparent porosity (P) in percent from either of the following formulae

\[
P = \frac{V_1}{V} \times 100 \quad P = \frac{W - D}{W - S} \times 100
\]

The Boiling Water Method

General - The boiling water method of the determination of apparent porosity is applicable to burnt bricks only.

Test Specimen - Test specimen as given under 9.1.4 shall be used.
Procedure

1. Dry the test specimen at 110°C and weigh after cooling to room temperature in a desiccator. This weighing and all subsequent weighings shall be made to an accuracy of 0.1 g.

2. Place the test specimen in distilled water and boil for two hours, and then allow to cool to room temperature while still immersed in water. During boiling, ensure that the test specimen is not in contact with the heated bottom of the container.

3. Heat the specimen in a container which does not give off scale. After boiling and cooling, weigh the test specimen (S) while suspended in water.

4. Immediately after obtaining the suspended weight remove the test specimen from water, blot lightly with a moistened towel and weigh in air (W).

5. The exterior volume of the test specimen (V) and true volume of open pores (V1) as in 9.1.5.4 and calculate the apparent porosity as given in 9.1.6.

Determination of true specific gravity and true density

Objective

This test determines the true specific gravity and true density of refractory materials under prescribed conditions. It is not applicable to materials attacked by water.

Apparatus

Analytical Balance and Weights
50-ml Pycnometer Bottle with Capillary Tube Stopper
Thermometer
Drying Oven
Weighing Bottle
Desicator
A suitable apparatus to produce a vacuum of 12 to 25 mm mercury pressure.

Preparation of Sample

1. Take two pieces of the size of a walnut from different positions of a solid specimen in such a way as to exclude any part of the original exterior surface (skin).

2. Crush the pieces between hardened steel surfaces to a maximum particle size of 3 mm thoroughly mix the crushed material and reduce by quartering to a test sample of 50 g.

3. If the material submitted for testing is already crushed or ground thoroughly mix a representative portion of at least 500 g and reduce by quartering to a test sample of 50 g.

4. Grind the entire 50-g sample in an agate mortar to such a fineness that it will pass through IS Sieve 15. Do the grinding either by hand or by mechanical sample grinder so constructed as to prevent the introduction of any impurity.

5. Remove by a magnet any magnetic material introduced in crushing or grinding.
6. Take care in all stages of preparation of the test sample not to exclude any portions that are difficult to grind, and avoid any selective sampling.

Procedure

1. Dry the 50 g sample to constant weight at 105°C to 110°C and place in a glass stoppered weighing bottle. Make duplicate tests on material from the 50-g sample. Record all weights to the nearest 0.001 g.

2. Dry the pycnometer and stopper at 105°C, cool in a desiccator, weigh (p) on an analytical balance. Then fill the pycnometer with distilled water at room temperature (t°C), and again weigh (W1) with the stopper in place. Then empty the pycnometer and again dry.

3. Place approximately 8 to 12 g of the sample in the dry pycnometer; weigh the pycnometer, stopper and sample (W). Fill the pycnometer to one-fourth to one half of its capacity with distilled water, and boil the water (See Note 1) at atmospheric or under reduced pressure for approximately 10 to 15 minutes. After boiling, fill the pycnometer with distilled water (See Note 2), cool to room temperature (t°C) in a water-bath, insert the stopper, wipe off excess water from the stopper and the pycnometer thoroughly with a lintless towel. Then weigh the pycnometer and contents (W2).

Note 1: Exercise caution during boiling so that it is not sufficiently vigorous to cause loss of the sample due to popping. If the boiling is done at atmospheric pressure, it is advisable to insert with the stopper a thin strip of paper before the boiling operation.

Note 2: Fill the pycnometer so that there is an overflow of water through the capillary tube when the stopper is inserted. When wiping the excess water from the tip of the stopper, do it in such a way as not to withdraw any water from the capillary tube. Any variation in room temperature (t) when obtaining weights (W1) and (W2) will introduce an appreciable error. Therefore, obtain them at the same temperature within the limits of 0.3°C. Use a constant temperature bath controlled to 0.1°C.

Calculations

Calculate the true specific gravity in accordance with the following formula:

\[
\text{Specific gravity} = \frac{W - P}{(W - P) - (W_1 - W_2)} \tag{1.2}
\]

where \( t \) = temperature of the material and the water in °C, \( W \) = weight in g of the stoppered pycnometer and sample, \( P \) = weight in g of the stoppered pycnometer, \( W_2 \) = weight in g of the stoppered pycnometer, sample, and water, and \( W_1 \) = weight in g of the stoppered pycnometer filled with water.

The true density of the sample may be determined without additional measurement in accordance with the following formula:

\[
\text{True Density} = \text{Specific gravity} \times (d_w - d_a) \tag{1.3}
\]
where $d_w = \text{density of water at the temperature at which the test was carried out}$, and $d_a = \text{density of air at the temperature at which the test was made}$.

Report the determinations to the nearest 0.001. Calculate also the following from the obtained results.

Note: These are however, not included in the said I.S.Specification

i) Bulk density  
ii) Water absorption

**Porosity**

**Porosity Effects:**
- Density (Bulk),
- Thermal Conductivity
- Thermal resistance of the body
- Strength at room temperature as well as at high temperature
- Permeability
- Corrosion or Chemical attack
- Surface properties (smoothness etc.),
- Absorption

**TYPES OF PORES**
- Open or apparent,
- Closed or sealed
- Continuous or isolated
- Size of pore: big, medium, small
- Distribution: Well distributed or appearing as defects such as holes, cracks, etc.

Porosity is always expressed in percentage.

- Apparent porosity (Open) %: $(\text{Open pore volume/Bulk volume}) \times 100$
- Sealed porosity %: $100 \times (\text{Sealed pore volume/B Volume})$
- True porosity %: $100 \times (\text{Total pore volume/B Volume})$

**Open Porosity**

Open porosity is found out from:
- Wt. of the body in air: W
- Wt. of the body in water: D
- Saturated wt. of the body with water: S

Sealed porosity is known by finding out the density of the body (True density).

$$\text{Total Bulk volume} = \text{Open pore volume} + \text{closed pore volume} + \text{Volume of the material}$$

If water affects the material than other liquid is to be used, and then the density of the liquid has to be taken into account.

**Porosity is affected by**

- The nature of the material. Certain materials have micro porosity and cannot be easily reduced. Hence porosity of the body prepared from the material is higher, e.g. DIATOMACEOUS EARTH.
• Particle size, shape, arrangement of the particles from which the body is prepared.

• Method of preparation, Hand Moulding, machine or hydraulic moulding, slip-casting, extrusion and fusion etc.

• Amount of water used during fabrication

• Physical and chemical reactions that occur when materials is fired in the furnace to get the final shape such as phase change accompanied by expansion and contraction, bloating, moulding, frothing, decomposition of carbonates, sulphated etc., burning of carbon and organic materials, loss of water of crystallization etc.

• Temperature of firing and time. At higher temperatures the body reduces its porosity due to one or more of the following reasons:
  - Melt formation
  - Crystallisation or recrystallisation
  - Diffusion : Solid-solid, solid-liquid

• Fusion and cast or well sintered refractories may have very low porosities, even less than 1 per cent.

• Normal refractories which have been fired in the furnace to get the final shape have 10 to 30 per cent porosity

• Insulating refractories porosity may vary between 50 and 80 per cent.
2 Residence Time Distribution

Objective

To determine the residence time distribution in the given configuration for pulse and step inputs.

Concept

The main objective of this experiment is to introduce the concept and measurement of residence time distribution and to emphasize its use in the reactor design. The three basic reactor models viz., batch, back mix (CSTR) and PFR are based on ideal concepts. We often apply these models to determine the conversion and other parameters. However, owing to non-ideality prevalent in the ‘real’ systems, the conversion obtained may not be the true conversion. How do we account for this non-ideality? The residence time distribution (RTD) or more precisely the E(t) function may be looked upon as a correction factor to account for the non-ideality. The causes of non-ideality could be channeling and back mixing in the case of a PFR and dead zones and non-uniform mixing in the case of a CSTR.

Theory

Imagine that 10 atoms are injected in a PFR in a short time. Since, there is no axial mixing in the PFR, ideally all these atoms should come out of the reactor at the same time. However, this is not the case with the real system. Different atoms take different time to come out of the reactor. The time the atoms have spent in the reactor is called the residence time and the distribution of the various atoms coming out the reactor with respect to time is called the residence time distribution. RTD can be determined experimentally by injecting an inert chemical, molecule, or atom, called tracer, into the reactor at some time t=0 and then measuring the tracer concentration ‘C’ in the exit stream as a function of time. Pulse and step inputs are the two commonly used methods of injection.

Pulse Input

In a pulse input, an amount of tracer No is suddenly injected in one shot into the feed stream entering the reactor in as short time as possible. The outlet concentration is then measured as a function of time. The effluent concentration-time curve is referred to as the C curve in the RTD analysis. If we select an increment of time Δt sufficiently small that the concentration of tracer, C(t), exiting between time t and t + Δt is essentially constant, then the amount of tracer material, ΔN, leaving the reactor between time t and t + Δt is

\[ \Delta N = C(t)v\Delta t \]  \hspace{1cm} (2.1)

where, v is the effluent volumetric flow rate. In other words, ΔN is the amount of material that has spent an amount of time between t and t + Δt in the reactor. If we now divide by the total amount of material that was injected into the reactor, N0, we obtain

\[ \frac{\Delta N}{N_0} = \frac{vC(t)}{N_0}\Delta t \]  \hspace{1cm} (2.2)

which, represents the fraction of the material that has a residence time in the reactor between time t and t + Δt.
For a pulse injection we define
\[ E(t) = \frac{vC(t)}{N_0} \] (2.3)
so that
\[ \frac{\Delta N}{N_0} = E(t)\Delta T \] (2.4)
This quantity \( E(t) \) is called the residence time distribution function. It describes in a quantitative manner how much time different fluid elements have spent in the reactor.
Re-writing the above equations in the differential form,
\[ dN = vC(t)dt \] (2.5)
and integrating, we obtain
\[ N_0 = \int_0^\infty vC(t)dt \] (2.6)
The volumetric flow rate \( v \) is constant, and so we can define \( E(t) \) as:
\[ E(t) = \frac{C(t)}{\int_0^\infty C(t)dt} \] (2.7)
The integral in the denominator is the area under the \( C \) curve.

**Step Input**
Consider a constant rate of tracer addition to a feed that is initiated at time \( t = 0 \). Before this time no tracer was added to the feed. Thus, we have
\[ C_0(t) = \begin{cases} 0 & t < 0 \\ C_0 & t \geq 0 \end{cases} \] (2.8)
The concentration of the tracer in the feed to the reactor is kept at this level until the concentration in the effluent is indistinguishable from that in the feed; the test may then be discontinued.
The output concentration from a vessel is related to the input concentration by the convolution integral:
\[ C_{out}(t) = \int_0^t C_{in}(t - t')E(t')dt' \] (2.9)
Because the inlet concentration is a constant with time, \( C_0 \), we can take it outside the integral sign. Thus,
\[ C_{out}(t) = C_0 \int_0^t E(t')dt' \] (2.10)
Dividing by \( C_0 \) yields
\[ \left[ \frac{C_{out}}{C_0} \right]_{\text{step}} = \int_0^t E(t')dt' = F(t) \] (2.11)
Thus, the normalized concentration vs. time profile gives the \( F \) curve. The relation between \( E(t) \) and \( F(t) \) is:
\[ \frac{dF(t)}{dt} = E(t) \] (2.12)
For a laminar flow reactor, the velocity profile is parabolic with the fluid in the center of the tube spending the shortest time. By using a similar analysis as shown above, we obtain the complete RTD function for a laminar flow reactor as:

\[
E(t) = \begin{cases} 
0 & t < \tau/2 \\
\tau^2/2t^3 & t \geq \tau/2 
\end{cases}
\]

(2.13)

We can also determine the dispersion number in the following manner:

\[
T_m = \frac{\int_{0}^{\infty} t C dt}{\int_{0}^{\infty} C dt} = \frac{\sum t_i C_i \Delta t_i}{\sum C_i \Delta t_i}
\]

(2.14)

The variance is defined as:

\[
\sigma^2 = \frac{\sum t_i^2 C_i \Delta t_i}{\sum C_i \Delta t_i} - t_m^2
\]

(2.15)

\[
\sigma^2_\theta = \frac{\sigma^2}{t_m^2}
\]

(2.16)

The Dispersion number is defined as \(D/uL\) and is given by:

\[
\sigma^2_\theta = \frac{\sigma^2}{t^2} = \frac{2}{uL} - 2 \left( \frac{D}{uL} \right)^2 \left( 1 - \exp^{n/L/D} \right)
\]

(2.17)

**Apparatus**

**OUTLINE OF THE SET-UP**

The set-up consists of three CSTRs and 2 PFRs (LFRs) which can be connected in series or parallel. Two reservoirs are provided for the continuous phase (water) and tracer (dilute NaOH solution) respectively. Peristaltic pumps are used to pump the water and tracer to the reactor/s. The dispensing mode available with the pumps can be used to give a pulse input. The concentrations at the exit of the reactor/s is/are monitored by conductivity probes.

Figure 2.1: Experimental setup
Procedure

1. Check whether both the reservoirs (water and tracer) are full.
2. Measure the volume of the reactors in the given configuration.
3. Adjust the flowrates of both the fluids so that they are in the given range of residence time.
4. Start the flow of water through the reactors and allow the system to attain steady state (w.r.t. flowrate).
5. Prepare about 100 ml of 5 M NaOH solution for pulse input study.
6. Purge the pump tubing (to be used for dispensing) with the prepared solution.
7. Activate the dispensing mode on the pump and set the quantity to dispensed. Set the flow at the maximum value so that the set quantity will be dispensed at the maximum flowrate, thus, acting as a pulse input.
8. At a particular time instant press the ‘start’ button on the pump and simultaneously start the ‘stop watch’. Prior to dispensing, ensure that the valve on the feed line is open.
9. Note down the conductivity w.r.t. time at every half residence time intervals. Initially (till two residence times) note down the values at every 10 sec time interval. The time span can be eventually increased when the change in conductivity is not rapid.
10. Continue till the conductivity values attain or approach the initial values.
11. For step input study, start the flow of water through the reactors and allow steady state to be attained.
12. Purge the tracer pump tubing with the solution from the reservoir. Ensure that the flowrate is the same as that adjusted at the start.
13. At a particular time instant, stop the flow of water and simultaneously start the flow of tracer.
14. Note down the conductivity values w.r.t. time at every 10 sec time interval initially followed by 30 sec later when the change in the conductivity values is not rapid.
15. Continue till the conductivity values become steady.

Calculations

Pulse Input

1. Plot concentration (conductivity) $C$ vs. $t$
2. Calculate $E(t)$ using equation 2.7
3. Calculate $E_{theo}(t)$

$$E_{theo}(t) = \frac{\tau^2}{24\beta}$$  \hspace{1cm} (PFR)

$$E_{theo}(t) = \frac{1}{\tau} \exp^{-t/\tau}$$  \hspace{1cm} (CSTR)
4. Plot $E_{\text{exp}}(t)$ and $E_{\text{theo}}(t)$ vs. $t$.

5. Calculate the mean residence time ($t_m$).

6. Calculate variance ($\sigma^2$), $\sigma_\theta^2$ and $D/uL$ using equations $2.15-2.17$ [only in the case of LFR].

7. Calculate and plot $E_{\text{exp}}(t)$ and $E_{\text{theo}}(t)$ for given configuration.

**Step Input**

1. Plot concentration (conductivity) vs. $t$.

2. Evaluate $F_{\text{theo}}(t)$ using equation $2.12$.

3. Plot $F_{\text{exp}}(t)$ i.e. $C/C_0$ and $F_{\text{theo}}(t)$ vs. $t$.

4. Obtain the equation for the F-plot by curve fitting.

5. Differentiate this with respect to $t$ to obtain $E_{\text{exp}}(t)$.

6. Plot $E_{\text{exp}}(t)$ vs. $t$.

7. Evaluate $F_{\text{theo}}(t)$ for given configuration and plot $F_{\text{theo}}(t)$ and $F_{\text{exp}}(t)$ vs. $t$.

**Results**

<table>
<thead>
<tr>
<th></th>
<th>Single reactor</th>
<th>Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$t_m$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$D/uL$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Comments**
3 Continuous Reactive Distillation

Reactive Distillation

Reactive Distillation (RD) is a combination of reaction and distillation in a single vessel owing to which it enjoys a number of specific advantages over conventional sequential approach of reaction followed by distillation or other separation techniques. Improved selectivity, increased conversion, better heat control, effective utilization of reaction heat, scope for difficult separations and the avoidance of azeotropes are a few of the advantages that are offered by RD. The introduction of an in situ separation process in the reaction zone or vice versa leads to complex interactions between vapor-liquid equilibrium, mass transfer rates, diffusion and chemical kinetics, which poses a great challenge for design and synthesis of these systems. RD being a relatively new field, research on various aspects such as modeling and simulation, process synthesis, column hardware design, non-linear dynamics and control is in progress. The suitability of RD for a particular reaction depends on various factors such as volatilities of reactants and products along with the feasible reaction and distillation temperature. Hence, the use of RD for every reaction may not be feasible. Exploring the candidate reactions for RD, itself is an area that needs considerable attention to expand the domain of RD processes. Although invented in 1921, the industrial application of reactive distillation did not take place before the 1980’s.

The esterification of acetic acid with alcohols like n-butanol, ethanol, isobutyl alcohol and amyl alcohol fall in a typical class of reacting systems. Butyl acetate is an industrially important chemical with wide applications as a versatile solvent. n-Butyl acetate is manufactured by the esterification of acetic acid with n-butanol in the presence of suitable acid catalyst. The alcohol is sparingly soluble in water and the ester is almost insoluble. Another interesting feature of this system is that it is associated with the formation a minimum boiling ternary azeotrope of ester, alcohol and water, which is heterogeneous in nature. Hence, in a typical reactive distillation column that consists of both reactive and non-reactive zones, the heterogeneous azeotrope or a composition close to the azeotrope can be obtained as the distillate product. Moreover, the aqueous phase that forms after the condensation of the vapor is almost pure water. Depending on the requirement either of the phases can be withdrawn as a product and the other phase can be recycled back as reflux. The pure ester i.e. butyl acetate is the least volatile component in the system is realized as a bottom product.

In reactive distillation scheme, the option of using a conventional reactor for partial reaction followed by a reactive distillation column has been reported to have offered better economics. The simulation studies on the butyl acetate synthesis have also indicated that this option can be better than conducting the entire reaction in a reactive distillation column. The present work is aimed at performing a detailed experimental investigation on a reactive distillation column operated in such a mode.

Experimental

Material and Catalysts

The packing used in the reactive distillation column were KATAPAK-S embedded with Amberlyst-15 catalyst and non-catalytic HYFLUX high efficiency low pressure drop wire mesh distillation packing.
KATAPAK-S: KATAPAK-S (S implies Sandwich) is a structured catalyst support for use in gas-liquid reaction systems such as trickle bed reactors, bubble columns or reactive distillation processes, in which catalyst granules can be embedded (Fig. 3.1). It is suitable for many catalytic applications, such as esterifications, etherification, and hydrogenations reaction. KATAPAK-S is immobilized between two sheets of metal wire gauze, forming "sandwiches". Each of these sheets is corrugated, resulting in a structure with flow channels of a defined angle and hydraulic diameter. The sandwiches are assembled with the flow channels in opposed orientation, so that the resulting unit is characterized by an open cross-flow structure pattern. The sandwich exists of 16 triangular channels, with a total of 32 cross-overs. A single triangular channel has a base of 36 mm, and a height of 18 mm. There is a 2 mm gap between the bases of adjoining triangular channels (Fig. 3.2). Inside such a sandwich, catalyst particles are present; the liquid flows inside these packed channels. When taking two of these sandwiches and placing them together, the space in between the two sandwiches is geometrically nearly equal to the inside of a packed channel. The channels that will be formed by this space are referred to as the open channels; no catalyst particles are present in the open channels. The gas flows through these open channels.

HYFLUX: HYFLUX is structured tower packings made of stainless steel 304 and 316, are particularly useful when a moderate to large number of theoretical stages have to be accommodated in a limited height of the tower. HYFLUX is manufactured from a multitude of fine metallic wires which are knitted into a tube which is flattened, crimped, plied and custom formed to meet exacting specifications Fig. 3.3.

The open structure formed due to the proprietary lay of the filaments, the unique stitches employed and the special crimping and plying form tortuous channels for liquids which can continuously combine, divide and recombine for optimum mixing and contact with vapour. This results in

![Figure 3.1: KATAPAK-S Structure](image-url)
Figure 3.2: Reconstruction of KATAPAK-S, a set of intersecting triangular tubes

Figure 3.3: HYFLUX noncatalytic Packing
intimate mixing between vapour passing upward through the controlled interconnecting passageways and the thin film of liquid flowing down the capillary wire network of the packing. The unique interaction results in high mass transfer rates (maximum separation efficiency) while maintaining low resistance to flow (low AP / theoretical stage).

Specifications

<table>
<thead>
<tr>
<th>Specification</th>
<th>Requirement</th>
</tr>
</thead>
<tbody>
<tr>
<td>HETP</td>
<td>[ \geq 100 \text{ to } 200 \text{ mm in production columns} ]</td>
</tr>
<tr>
<td></td>
<td>[ \geq 75 \text{ mm in pilot/laboratory stills} ]</td>
</tr>
<tr>
<td>NTU/metre</td>
<td>[ \leq 10 \text{ in production columns} ]</td>
</tr>
<tr>
<td></td>
<td>[ \leq 13 \text{ in pilot/laboratory stills} ]</td>
</tr>
<tr>
<td>( \Delta P / \text{theoretical plate} )</td>
<td>[ 0.05 - 0.75 \text{ mm Hg} ]</td>
</tr>
<tr>
<td>Vapour load</td>
<td>[ 0.2 - 2.75 \text{ F factor (m/s} \sqrt{kg/M^3}) ]</td>
</tr>
<tr>
<td>Liquid load</td>
<td>[&lt;0.7 \text{ m}^3/\text{m}^2 \text{ h} ]</td>
</tr>
<tr>
<td>Liquid holdup</td>
<td>[3 \text{ to } 8 \text{ (w/w)} ]</td>
</tr>
</tbody>
</table>

Apparatus and Procedure

The experimental setup of a laboratory scale reactive distillation plant is as shown in Figure 3.4. A 3m tall distillation column of inside diameter 54 mm that operates at atmospheric pressure was used. The reboiler (3 lit) was externally heated with the help of a heating mantle. The non-reactive rectifying and stripping sections were packed with Evergreen HYFLUX packing made out of fine metallic wires. The middle reactive zone was packed with Sulzer KATAKAK-S packing embedded with ion exchange resins Amberlyst-15 as a catalyst. All the sections are 1m tall in height. A proper insulation with external wall heating arrangement was provided to minimize the heat losses to the surrounding. The reaction mixture consisting of acetic acid, butanol, butyl acetate and water or an equilibrium mixture from the batch reactor is fed continuously to the column through a rotameter. An electronically driven metering pump is used to transfer the liquid from the feed tank to the column. In the condenser, two immiscible phases are formed, an aqueous phase i.e. almost pure water and an organic phase containing water, butanol and butyl acetate. The feed is preheated before introducing it to the column. Phase separator with the condenser is used to provide reflux to the column and to continuously withdraw water formed during the reaction. Temperature sensors Pt 100 are provided at different locations in the column to measure these temperatures (Position 1- Position 8).

Analysis

The samples were analyzed using Gas Chromatograph (GC, C-911, Mak Analytica India Ltd.) equipped with thermal conductivity detector (TCD). The column used for the analysis was porapack-Q with hydrogen as carrier gas at the flow rate of 20 ml/min. Injector and detector
Figure 3.4: Experimental setup
were maintained at 220°C and 150°C respectively. The oven temperature was maintained isothermally at 240°C to get best resolution in less time. The results obtained by GC were confirmed by independent titrations using standard sodium hydroxide solution. The samples were also analyzed by titrating them against NaOH using phenolphthalein as indicator.

Observations

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<th>Values</th>
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Steady State Column Profile

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4 Verification of Debye-Huckel Theory

Aim
To determine experimentally the activity coefficient of cupric ions in aqueous solutions and compare them with those estimated using Debye Huckel theory.

Apparatus
Ion meter provided with cupric electrode, automatic temperature compensator, copper sulphate (CuSO$_4$.5H$_2$O), other copper salts, pipette, volumetric flask, beakers.

Theory
Thermodynamic state of the solution can be characterized by the chemical potential, $\mu_i$ of the constituent species. The gradient of the chemical potential provides the driving force for the diffusion of the species. For the equilibrium of the phases in contact, the chemical potential of each of the species should be equal in all phases. It is therefore necessary to measure and predict the chemical potential of species in the solutions.

It is convenient to express chemical potential $\mu_i$ in terms of its activity $a_i$ defined as

$$\mu_i = \mu_i^0 + RT \ln a_i$$  \hspace{1cm} (4.1)

where $\mu_i^0$ is the chemical potential of species $i$ in the standard state (arbitrarily chosen), $R$ is the Universal gas constant and $T$ is the temperature.

For an electrolyte species $a_i$ can be expressed in terms of the molality of the ion:

$$a_i = \frac{\gamma_i m_i}{m_i^0}$$  \hspace{1cm} (4.2)

where $m_i$ is the molality of $i$, mol/kg of solvent; $m_i^0$ is the molality in the solution at standard state, and $\gamma_i$ is the activity coefficient of $i$.

The activity coefficient is the measure of the interaction of species $i$ with the other species in the solution. The standard state is chosen as a fictitious state where $\gamma_i = 1$ (corresponding to the ideal solution where all the interactions are extinguished). $m_i^0$ is (but not always) actually chosen as 1 molal.

In the solution, an electrolyte dissociate into cations and anions

$$M_pX_q \rightarrow pM^{Z_+}+qX^{Z_-}$$

$$pZ_+ + qZ_-=0$$  \hspace{1cm} (4.3)

Due to electrostatic interactions, cations are surrounded by anions and vice versa, it is not possible to determine chemical potential of the individual ions. We can determine the chemical potential of the salt as

$$\mu = p\mu_+ + q\mu_-$$

$$= p\mu_+^0 + q\mu_-^0 + pRT \ln a_+ + qRT \ln a_-$$

$$= p\mu_+^0 + q\mu_-^0 + pRT \ln \left(\frac{m_+}{m_+^0}\right) + qRT \ln \left(\frac{m_-}{m_-^0}\right) + pRT \ln \gamma_+ + qRT \ln \gamma_-$$  \hspace{1cm} (4.4)
We define
\[ \gamma_{\pm} = \left( \gamma^p_{\pm} \gamma^q_{\pm} \right)^{1/2} \] (4.5)
as the mean activity coefficient. Thus
\[ \mu = p\mu^0_+ + q\mu^0_- + pRT \ln \left( \frac{m_+}{m^0_+} \right) + qRT \ln \left( \frac{m_-}{m^0_-} \right) + (p + q)RT \ln \gamma_{\pm} \]
\[ = p\mu_+ + q\mu_- \] (4.6)

where
\[ \mu_+ = \mu^0_+ + RT \ln \left( \frac{m_+}{m^0_+} \right) \]
\[ \mu_- = \mu^0_- + RT \ln \left( \frac{m_-}{m^0_-} \right) \] (4.7)

The above equation allows us to express the chemical potential of individual ions in terms of the mean activity coefficient. However, it is to be understood that does not correspond to the individual ion but to the pair of ions (cation and anion)

**Debye-Huckel Law**

Debye-Huckel theory has been developed for very dilute ionic solution in which electrostatic interactions dominate. The theory neglects all other interactions. The following equation has been derived based on the mean field and point charge assumptions
\[
\log \gamma_{\pm} = -|z_+ z_-| A \left( \frac{I}{m^0} \right)^{1/2}
\] (4.8)

Where \( I \) represents the ionic strength of the solution and is given by
\[ I = \frac{1}{2} \left( m_+ z^2_+ + m_- z^2_- \right) \] (4.9)

It is generally agreed to use \( m^0 = 1 \), and
\[ A = \frac{0.509}{(T/298)^{3/2}} \] (4.10)

At 25°C, the value of \( A \) is 0.509.

The test of the theory is to plot \( \log \gamma_{\pm} \) versus \( \sqrt{I/m^0} \). The plot should be the straight line. This is indeed true up to \( m/m^0 = 0.04 \). Beyond this point the following equation holds,
\[
\log \gamma_{\pm} = \frac{|z_+ z_-| A \left( \frac{I}{m^0} \right)^{1/2}}{1 + B \left( \frac{I}{m^0} \right)^{1/2}}
\] (4.11)

However, \( B \) is not a universal constant but depends on the nature of the cations and anions. Hence \( B \) needs to be regressed from the experiments.
Measurement of Activity and Mean Activity Coefficient

One of the techniques for the measurement of the activity coefficient is to use a specific ion electrode. This electrode adsorbs specific ion. As a result of this adsorption, the potential of the electrode changes in proportion to the chemical potential of the ion in the solution. The Nernst equation governs the electrode potential.

\[ E = E_0 + \frac{2.303 \times 10^3 RT}{z_i F} \log(a_i) \]  

(4.12)

Where \( z_i \) is the valency of the ion and \( F \) = Faraday constant. \( E \) is the potential of the electrode (mV) and \( E_0 \) is the reference potential. Writing

\[ a_i = \frac{\gamma \pm m_i}{m_i^0} \]  

(4.13)

we get

\[ E = E_0 + \frac{2.303 \times 10^3 RT}{z_i F} \log \left[ \frac{m_i}{m_i^0} \right] \]  

(4.14)

At very low concentrations,

\[ E = E_0 + \frac{2.303 \times 10^3 RT}{z_i F} \log \left[ \frac{m_i}{m_i^0} \right] + \frac{2.303 \times 10^3 RT}{z_i F} \left| z_+ z_- \right| A \left( \frac{I}{m^0} \right)^{1/2} \]  

(4.15)

At very low concentration the activity coefficient term can be neglected. In this case the plot of \( E \) versus \( \log m_i/m_i^0 \) is the straight line with slope

\[ S = \frac{2.303 \times 10^3 RT}{z_i F} \]  

(4.16)

and the intercept is \( E_0 \).

The slope of the plot deviates somewhat from the above equation. One reason is the dynamics of the electrode. It takes a long time for the electrode to reach equilibrium. The other reason is the error due to the omission of the correction. To correct for the second contribution we plot

\[ E^* = E_i - \frac{2.303 \times 10^3 RT}{z_i F} \left| z_+ z_- \right| A \left( \frac{I}{m^0} \right)^{1/2} \]  

(4.17)

We obtain the slope and the intercept of the modified plot

\[ E^* = E_0 + S \log \left( \frac{m_i}{m_i^0} \right) \]  

(4.18)

At higher concentrations

\[ \frac{E - E^*}{S} = \log \gamma \]  

(4.19)

where \( E^* \) is the value extrapolated from the above equation. This allows us to compute \( \log \gamma \).

Verification of Debye-Hückel Theory

1. Plot \( \log \gamma \) versus \( \sqrt{I} \) for the entire range of the concentration.
2. Find the region where it is a straight line.
3. Find the slope and check whether it matches with the theory.
4. At high concentration find \( B \) so that the modified D-H theory yields the best fit to the experimental data.
Procedure

1. Preparation the solution of 10000 ppm (0.16M) Cu+++ from CuSO$_4$.5 H$_2$O. From that solution prepare the solution of 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 100, 1000, 3000, 5000, 6000, 7000, 8000, 9000, 10000 by serial dilution.

2. Plug the Cupric electrode (filled with filling solution) to the ion meter.

3. Rinse the electrode with distilled water and wipe with a tissue paper.

4. Immerse the electrode in 1 ppm solution. One should wait for at least 3 minutes or till the meter shows ready whichever is longer. Then note down the potential reading as shown in the meter.

5. Then take out the electrode, rinse it with distilled water, blot dry with tissue paper and immerse in the next solution (2ppm), note down the reading shown by the meter.

6. Follow the same procedure as above and measure the potential of all solutions. It is advisable to start with the solution of lower concentration and move onto the higher concentrations in the ascending order.

7. Plot the potential at lower concentration (1- 10 ppm) on a $E$ versus log $C$. This results in an approximate straight line given by the Nernst equation

$$ E = E_0 + 2.303 \frac{RT}{zF} \log C $$

The intercept of the line with the Y axis gives $E_0$. At higher concentrations, the potential is given by

$$ E = E_0 + 2.303 \frac{RT}{zF} \log a $$

In this equation $a$ is the only unknown and can be calculated. The activity coefficient is then calculated

$$ \gamma = \frac{a}{C} $$

(4.20)

Compare the experimental value of activity coefficient with those calculated using Debye Hückel theory.
# Data Sheet for D-H Theory

Observation Table for experimental method

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<th>log C</th>
<th>$E$ (mV)</th>
<th>log a</th>
<th>a</th>
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Observations:

1. Value of $E_0 =$
2. Value of slope =$
Observation Table for theoretical method

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<th>$\log \gamma$</th>
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Observation:

1. $B =$
## Results

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5 Ion Exchange Columns

Aim

To plot the breakthrough curve of strong acid cation exchange Amberlyst resins, and determine their capacity by batch and continuous flow processes.

Theory

Ion Exchangers

Of all different natural and synthetic products which show ion exchange properties, the most important are ion-exchange resins, ion-exchange coals, mineral ion exchangers, and synthetic inorganic exchangers. Ion exchangers owe their characteristic properties to a peculiar feature of their structure. They consist of a framework held together by chemical bonds or lattice energy which carries a positive or negative surplus charge. Counter ions of opposite charge move throughout the framework and can be replaced by other ions of same sign. For example, the framework of a cation exchanger can be regarded as a macromolecular or crystalline polyanion, while the framework of an anion exchanger can be regarded as a polycation.

Ion Exchange Resins

These constitute the most important class of ion exchangers. Their framework called the matrix, consists of an irregular, macromolecular, 3-D network of hydrocarbon chains. The matrix carries ionic groups such as SO$_3^-$, COO$^-$ in cation exchangers and NH$_3^+$, NH$_2^+$ in anion exchangers. Ion exchange resins are thus cross linked polyelectrolytes. The matrix of the resins is hydrophobic. However, hydrophilic components are introduced by the incorporation of ionic groups such as SO$_3$H. Linear hydrocarbon macromolecules with such molecules are soluble in water. So ion exchange resins are made insoluble by introduction of cross-links which Interconnect the various hydrocarbon chains. An ion-exchange resin is practically one single macromolecule. Its dissolution would require rupture of C-C bonds. Thus resins are insoluble in all solvents by which they are not destroyed. The matrix is elastic and can swell by taking up solvent, a fact referred to as "heteroporosity" or "heterodictality".

The chemical, physical, and mechanical stability and the ion-exchange behavior of the resins depend primarily on the structure and the degree of cross-linking of the matrix and on the nature and number of fixed ionic groups. The degree of cross-linking determines the mesh width of the matrix and thus the swelling ability of the resin and the mobility of the counter ions in the resin, which in turn determine the rates of ion-exchange in the resin. Highly cross linked resins are harder and more resistant to mechanical breakdown.

Amberlyst-15 with sulphonic acid functionality is our resin of interest. It is a highly porous, macroreticular ion-exchanger prepared by a variation of the conventional pearl-polymerization technique. In pearl polymerization, monomers are mixed, and a polymerization catalyst such as benzoyl peroxide is added. The mixture is then added to an agitated aqueous solution kept at the temperature required for polymerization.

The mixture forms small droplets, which remain suspended. A suspension stabilizer is added to prevent agglomeration of droplets. In the case of Amberlyst, an organic solvent which is a good solvent for the monomer, but a poor solvent for the polymer is added to the polymerization mixture.
As polymerization progresses, the solvent molecules are squeezed out by the growing copolymer regions. In this way, spherical beads with wide pores are obtained.

**Selectivity**

Ion exchangers prefer one species over another due to several causes:

1. The electrostatic interaction between the charged framework and the counter ions depend on the size and valence of the counter ion.
2. In addition to electrostatic forces, other interactions between ions and their environment are effective.
3. Large counter ions may be sterically excluded from the narrow pores of the ion exchanger.

All these effects depend on the nature of the counter ion and thus may lead to preferential uptake of a species by the ion exchanger. The ability of the ion-exchanger to distinguish between the various counter ion species is called selectivity.

**Separation Factor**

The preference of the ion exchanger for one of the two counter ions is often expressed by the separation factor, defined by

\[ \alpha = \frac{m'_a m_b}{m_a m'_b} = \frac{C'_a C_b}{C_a C'_b} = \frac{x'_a x_b}{x_a x'_b} \]  

(5.1)

The molal selectivity coefficient, which is used for theoretical studies, is defined as

\[ K_A^B = \frac{M^{|Z_B|} A |Z_A|}{M^{|Z_A|} B |Z_B|} \]  

(5.2)

The selectivity of the ion exchange process depends on the properties of the ion exchanger used and the composition of the aqueous phase. In the case of two ions having the same charge and very similar radii, the selectivity due to the properties of the ion exchanger (such as acidity, basicity, and the degree of cross linking) is not sufficient for ensuring effective separation. In such a case, an appropriate complexing agent has to be added to the aqueous phase: the selectivity attained is then either due to the difference in the stability constants or to the different charges or structures of the complexes formed. Increased selectivity can be brought about in many ways. For eg., one can exploit the preference of an exchanger for highly charged ions in dilute solutions, or one can choose a chelating resin.

**Capacity**

Capacity is defined as the number of counter-ion equivalents in a specified amount of material. Capacity and related data are primarily used for two reasons: for characterizing ion-exchange materials, and for use in the numerical calculation of ion-exchange operations. Capacity can be defined in numerous ways:

1. **Capacity (Maximum capacity, ion-exchange capacity)** Definition: Number of inorganic groups per specified amount of ion-exchanger
2. **Scientific Weight Capacity**
   Units: meq/g dry H⁺ or Cl⁻ form

3. **Technical Volume Capacity**
   Units: eq/liter packed bed in H⁺ or Cl⁻ form and fully water-swollen

4. **Apparent Capacity (Effective Capacity)**
   Definition: Number of exchangeable counter ions per specified amount of ion exchanger.
   Units: meq/g dry H⁺ or Cl⁻ form (apparent weight capacity). Apparent capacity is lower than maximum capacity when inorganic groups are incompletely ionized; depends on experimental conditions (pH, conc., etc.)

5. **Sorption Capacity**
   Definition: Amount of solute, taken up by sorption rather than by exchange, per specified amount of ion exchanger

6. **Useful Capacity**
   Definition: Capacity utilized when equilibrium is not attained. Used at low ion-exchange rates. Depends on experimental conditions (ion-exchange rate, etc.)

7. **Breakthrough Capacity (Dynamic Capacity)**
   Definition: Capacity utilized in column operation. Depends on operating conditions

8. **Concentration of fixed ionic groups**
   Definition: Number of fixed ionic groups in meq/cm³ swollen resin (molarity) or per gram solvent in resin (molality). Depends on experimental conditions (swelling, etc.). Used in theoretical treatment of ion-exchange phenomena

A

\[ Q_v = \frac{(1 - b) \times d \times (100 - W)}{100 \times Q_w} \]

- \( Q_v \): volume capacity in equivalents per liter packed bed.
- \( Q_w \): Scientific weight capacity in milliequivalents per gram.
- \( b \): fractional void volume of packing
- \( W \): water content of the resin in weight percent
- \( d \): density of the swollen resin in grams per ml

B

The molality of fixed groups in meq/g is

\[ m = \frac{(100 - W) \times Q_w}{W \times (1 + \sum Q_i \times MQ_w \times 10^{-3})} \]

The molarity of fixed groups in meq/ml is

\[ X = \frac{d \times (100 - W) \times Q_w}{100 \times (1 + \sum Q_i \times MQ_w \times 10^{-3})} \]

**Batch Process**

**Apparatus**

Stirred tank reactor with stirrer, belt, stand, pipette, resins, copper sulphate solution, test tubes (15), ion meter, cupric electrode, Ionic Strength Adjustor (ISA), volumetric flasks
Procedure

1. Calibrate the ion meter using cupric nitrate standards of concentrations 0.6355 ppm, 6.355 ppm, 63.55 ppm, and 127.1 ppm.

2. Take known weight of resins in the stirred tank reactor. Fit the reactor on the stand and attach the belt to the stirrer which is adjusted on the pulleys. Switch on the stirrer.

3. Pour quickly calculated volume of 800 ppm cupric sulphate solution into the tank and start the timer.

4. Withdraw 1 ml samples from the tank using a pipette at every 40 seconds for about 10 minutes.

5. Dilute the samples to 50 ml in volumetric flasks and measure their concentrations using ion meter.

6. Plot a graph of concentration vs. time.

7. The amount of cupric ions consumed is calculated from the initial and final concentrations.

Calculations

Initial concentration - \( C_0 \) ppm

Final concentration - \( C_f \) ppm

Qty. of cupric ions used

\[
Q = \frac{(C_f - C_0) \times 250}{1000000}
\]

Capacity of resins = \( \frac{Q}{63.55} \) eq/g of resin

Observation Table

<table>
<thead>
<tr>
<th>S.N.</th>
<th>Time (min)</th>
<th>Cu ion concentration (ppm)</th>
</tr>
</thead>
</table>

Graph

Plot a graph of concentration versus time.

Continuous Process

Procedure

1. Take 10 g resins and prepare a slurry with distilled water. Charge the column with the slurry such that there are no air bubbles trapped.

2. Keep adding cupric sulphate solution to the resin, and let it flow out at approximately 1 ml/min.
3. After every 20 ml, measure out 1 ml of effluent, dilute it to 50 ml in the volumetric flask and measure its concentration in the ion meter.

4. A graph of concentration versus volume is plotted.

Observation Table

<table>
<thead>
<tr>
<th>S.N.</th>
<th>Time (min)</th>
<th>Cu ion concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
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</tbody>
</table>

Graph

Plot a graph of concentration versus time.

Results and Comments
6 Gas-Liquid and Liquid-Liquid Reaction

Aim

- To synthesize styrene chlorohydrin from styrene, water and chlorine,
- To study chlorination in bubble column and stirred contactor, and
- To study heterogeneous reaction between styrene and hypochlorous acid in stirred contactor and stirred disc contactor.

Reactions

\[
\begin{align*}
H_2O + Cl_2 & \rightarrow HOCl + HCl \quad \text{(gas-liquid reaction)} \\
C_8H_8 + HOCl & \rightarrow C_8H_9ClO \quad \text{(liquid-liquid reaction)}
\end{align*}
\]

Application

This is a typical traditional process of converting olefin to its epoxide (or oxide) (Figure 6.1). Most of the Propylene/Ethylene oxide in earlier days was being produced by this process. The chlorohydrin produced in this process is further hydrolysed by sodium/calcium hydroxide to the oxide. Styrene oxide, which is fine chemical, may also be manufactured by this route. It is used to synthesize phenyl ethyl alcohol by hydrogenation process. Phenyl ethyl alcohol is used as an ingredient in perfumes, deodorants etc.

There are two steps in the process of synthesis of styrene chlorohydrin. In the first step chlorination of water takes place and hypochlorous acid forms whereas in second step heterogeneous reaction between styrene and hypochlorous acid takes place to form styrene chlorohydrin. The alternate way to produce hypochlorous acid is through reaction between hydrogen peroxide and hydrochloric acid. But in this reaction chances of unreacted HCl remaining are more and that will affect second step. So the chlorination of water in controlled conditions favors the reaction to form hypochlorous acid. One must note the limitation of this process that large amount wastes such as sodium/calcium chloride is generated; chlorine is a loss as it does not appear in the final product. Hence, in spite of being a popular route in old days, people are shifting towards more environmentally friendly catalytic oxidations with either oxygen or hydrogen peroxide. However, fine chemical industry still prefers this route for olefin oxides like styrene oxide.

Apparatus

The laboratory experimental set-up for synthesis of styrene chlorohydrin consists of following reactors:

1. Bubble column and Mechanically agitated reactor with chlorine gas supply
2. Stirred contactor and Stirred disc contactor.
Figure 6.1: The flow sheet for production of olefin oxide. The process within double dotted line is to be studied in laboratory.
Procedure

Gas-Liquid reaction: Formation of HOCl

1. Prepare 2.5 wt% NaOH solution (about 10 L).
2. Start both the cryostats for chilling system (set temperature at -1°C).
3. In the first step of the process, pass chlorine gas through the sparger at the bottom of column (measure flow rate).
4. Measure pH and analyze for HOCl concentration at various time intervals till HOCl concentration reaches 30 g/L.

Liquid-Liquid reaction: Chlorohydrination

1. Make an emulsion of styrene (50 mL) and water (500 mL) using high speed agitator in mechanically agitated reactor and lower down the temperature to 1°C by passing chilled water through jacket .
2. Add HOCl solution in such a way that the temperature remains 1-4°C till completion of reaction. The reaction is instantaneous and exothermic. Keep the record of HOCl added.
3. There will be two distinct phases (lower organic and upper aqueous one). Separate the aqueous and organic phases. Analyze aqueous phase for unreacted HOCl by titration method and organic phase for products by using gas chromatography (GC) with FID detector.

Analysis

Analysis of HOCl (Titration Method)

- Chemicals:
  - Potassium iodide (KI crystals), Sodium thiosulphate (Na₂S₂O₃.5H₂O), Starch, Acetic acid
- Reagents:
  1. Sodium thiosulphate titrant: Make 0.5 N sodium thiosulphate solution by adding 125 gm of Na₂S₂O₃.5H₂O in 1 L of distilled water.
  2. Starch: Boil 2 gm of starch in 100 mL of distilled water.

Procedure

1. Make 10 mL of HOCl sample and measure pH (make sure it is above 4).
2. Make 25 mL of HOCl sample in conical flask with ice chips to maintain low temperature. Add acetic acid if pH is higher than 5 in such way that pH drops in the range of 3.5 to 5.
3. Add 1 gm of KI crystals and 1 mL of starch indicator and brown colour appears.
4. Titrate it with sodium thiosulphate solution till the brown colour disappears. This is end point of titration. Note down the burette reading.
5. Calculate the conc. of HOCl (g/L) = 1.05 × B.R. (mL)
Analysis of organic phase for styrene chlorohydrine

Gas Chromatography

Theory and background  Gas chromatography is the technique of analysis of the components in liquid or gaseous mixture. The method exploits the difference in the affinity toward a given solid (usually an adsorbent) of the various components present in the mixture. Based on this difference the components are separated and analyzed with the help of various detectors, such as flame ionized detector, thermal conductivity detector, atomic absorption detector, since the analysis is based on gas-liquid interactions it works only for the components, that are either are in gaseous phase or that can be converted in the gaseous state (or vapor state) under the given conditions.

The instrument  The schematic diagram of the GC instrument is shown in Figure 6.2. The sample to be analyzed is injected in the injector port of the column through which a carrier inert gas flows at the desired flow rate. The injection volume is decided based on whether it is gas or liquid sample and on the sensitivity of the detector. The column contains a stationary phase; the injector temperature is maintained in such a way that the sample, if in a liquid form is vaporized at the injector port. The vaporized sample flows through the column over the stationary phase when the sample comes in contact of the stationary phase some components which have stronger affinity lag behind while some with less affinity flow with the carrier. Hence at the detector port the component appears at different time interval. These times correspond to residence times of the respective components. Apart from the nature from a stationary phase, temperature of the column and carrier flow rate also strongly influence the separation (or resolution) of the component. Hence one has to choose the right combination of these parameters while separating a given sample mixture. At the detector, component is detected and a voltage signal is generated that is proportional to the amount of component present in the sample.

Flame ionization detector (FID)  The component is burnt and the voltage signal is proportional to the concentration of ion generated. The continuous air (or oxygen) and hydrogen supply to this detector is essential for flame generation. This detector can only detect the component that burn (e.g. hydrocarbon). Hence non-burnable components such as water can not be analyzed using FID.

Figure 6.2: Schematic diagram of a Gas Chromatograph
Analysis of Samples

1. Take 2 mL of organic phase and filter it through a bed of sodium sulphate to remove the water from organic phase.
2. Inject (0.05 mL) sample of filtered organic phase
3. Prepare the calibration chart using authentic sample of styrene chlorohydrin.

Observations

Table 1: The variation of HOCl concentration with time

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Temp (°C)</th>
<th>pH</th>
<th>Burette reading (ml)</th>
<th>HOCl conc. (g/L)</th>
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<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Temperature (°C)</th>
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<td>Start</td>
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<tr>
<td>End</td>
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<thead>
<tr>
<th>Styrene: HOCl (vol)</th>
<th>Rxn time (min)</th>
<th>Param. studied</th>
<th>Area % (from GC analysis)</th>
<th>RPM</th>
<th>Remarks</th>
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Results

Yield of Styrene chlorohydrin is

\[
\text{Yield} = \left( \frac{\text{area of SCH in chromatogram}}{\text{total area in chromatogram} - \text{area of SCH in chromatogram}} \right) \times 100\%
\]

Questions

1. Calculate the chlorine and NaOH requirements in the process?
2. What is the necessity of NaOH in the chlorine absorber?
3. List different parameters involved in the process that you would like to investigate to possibly obtain the better performance?
4. Can you think of any other gas - liquid or liquid - liquid contactor that can be used for the reactions involved? Give the relative merits and demerits?
7 High Performance Thin Layer Chromatography

Aim

The objective of this experiment is to train you with the HPTLC instrument and measurement of concentrations of the components in the liquid mixtures.

Apparatus

Sample bottles, TLC plate, syringe, HPTLC applicator and scanner, etc.

Chemicals

Benzophenone, Benzhydrol, methanol, toluene, hexane, etc.

Theory

High performance thin layer chromatography (HPTLC) is an important technique for identification and separation of mixtures of organic compounds. It is used for following different situations:

1. Identification of components of a mixture (using appropriate standards)
2. Following the course of a reaction,
3. Analyzing fractions collected during purification,
4. Analyzing the purity of a compound.

In TLC, components of the mixture are partitioned between an adsorbent (the stationary phase, usually silica gel) and a solvent (the mobile phase) which flows through the adsorbent.

In TLC, a plastic, glass or aluminum sheet is coated with a thin layer of silica gel. A very small amount of a solution of the substance to be analyzed is applied in a small spot with a capillary tube, 1cm from the bottom of the TLC plate as shown in Figure 7.1-A.

The TLC is developed in a chamber, which contains the developing solvent (the mobile phase). A truncated filter paper placed in the chamber serves to saturate the chamber with mobile phase. As the mobile phase rises up the TLC plate by capillary action, the components dissolve in the solvent and move up the TLC plate. Individual components move up at different rates, depending on intermolecular forces between the component and the silica gel stationary phase and the component and the mobile phase as shown in Figure 7.1-B.

The stationary phase is hydrated SiO$_2$ and is very "polar". It is capable of strong dipole-dipole and H-bond donating and accepting interactions with the "analytes" (the components being analyzed). More polar analytes interact more strongly with the stationary phase in move very slowly up the TLC plate. By comparison, the mobile phase is relatively nonpolar and is capable of interacting with analytes by stronger London forces, as well as by dipole-dipole and H-bonding. More nonpolar analytes interact less strongly with the polar silica gel and more strongly with the less polar mobile phase and move higher up the TLC plate.

Once the solvent is within 1-2 cm of the top of the TLC sheet, the TLC is removed from the developing chamber and the farthest extent of the solvent (the solvent front) is marked with a pencil.
The solvent is allowed to evaporate from the TLC sheet in the hood. The spots are visualized using a UV lamp. (The TLC plates we will use contain a fluorescent indicator, which "glows" green under 254 nm UV light. If a compound on the TLC absorbs that light, it will appear as a dark spot). These spots are shown in Figure 3. The center of the spots are located and marked with a pencil and the distances between the origin and the center of the spots are measured.

The \( R_f \) is defined as the distance the center of the spot moved divided by the distance the solvent front moved (both measured from the origin). \( R_f \) values can be used to aid in the identification of a substance by comparison to standards. The \( R_f \) value is not a physical constant, and comparison should be made only between spots on the same sheet, run at the same time. Two substances that have the same \( R_f \) value may be identical; those with different \( R_f \) values are not identical.

Figure 7.1: Schematic diagram of HPTLC

**Procedure**

1. Prepare the five different concentrations of the benzophenone and benzhydrol in 2 mL of methanol or acetone.
2. Prepare the four different mixtures of both components (unknown compositions) in 2 mL methanol or acetone.

3. Prepare a TLC developing Chamber. Place a truncated filter paper in the jar so that when solvent is added the solvent will wick up the filter paper and saturate the chamber with solvent.

4. Add solvent to the jar to a depth of 1/2 cm.

5. Apply the spots of prepared solutions on the TLC plate (1 cm from the bottom of the plate) by using applicator.

6. In the first five lanes, spot pure benzophenone solution, middle five lanes, spot your pure benzhydrol solution, and last four lanes, spot your unknown concentrations of liquid mixtures. (You may want to visualize your spots using the UV lamp to make sure you can see the spots before developing the TLC).

7. Develop your TLC in toluene and hexane (50:50) solvent system. When the solvent has migrated within 1-2 cm from the top of the plate, remove the TLC. Allow the solvent to evaporate from the TLC in the hood.

8. When your TLC is complete, empty the developing solvent into the waste jar in the hood. Remove the filter paper from the jar and place the open jar and the filter paper in your hood and allow the solvent to evaporate. DO NOT wash the jars with water or acetone. Simply allow the solvent to evaporate completely before reusing the jar for the next analysis.

9. Visualize your TLC under a UV lamp.

10. Analyze the TLC plate by using the scanner.

Exercise

1. Present calibration curves of two components and concentrations of the two components in the given liquid mixtures.

2. What are the different chromatography methods? Explain each method in briefly.

3. What are the advantages of the HPTLC method?

4. What are the different manual errors encounters in the analysis using the HPTLC method?
8 Metal Recovery from a Dilute Solution by an Electrochemical Method

Aims

Toxic heavy metal ions in wastewater can be reduced by electro deposition of metals at a cathode (Graphite)

1. Evaluate the current and energy consumption of the process.
2. Determine the reaction rate constant of the electro deposition reaction, its activation energy, and the effect of mass transfer on the rate constant.

Perform the electrolysis experiment to reduce toxic metal ions (Cu\(^{++}\)) from an initial concentration of 500-1000 ppm to a low level acceptable for discharge as required by Pollution Control Board regulations. By measuring the concentration changes of the metal ion at various controlled anode-to-cathode cell voltages, and water circulation rates, determine the reaction rate constant, its activation energy, and the effect of mass transport of metal ions on rate of electrodeposition reaction. By measuring the amount of metal recovered and the total electric charges used in the electrolysis, also calculate the current efficiency (\(\eta\)) and energy requirement of the process.

Electrolytic System and Data Analysis

In this experiment, a flow-through electrochemical cell is operated in a recirculation mode.

Composition of Electrolyte

Copper sulphate (CuSO\(_4\)-5H\(_2\)O) - Cu\(^{++}\) = 500-1000 ppm
Sodium sulphate (Na\(_2\)SO\(_4\)) = 0.05M

The cathodic and anodic reactions in the cells are

\[
Cu^{++} + 2e^- \rightarrow Cu \quad (\text{cathode})
\]

\[
H_2O \rightarrow (1/2)O_2 + 2H^+ + 2e^- \quad (\text{anode})
\]

The copper electro deposition is a first-order reaction with respect to cupric ion concentration in the waste water. By assuming a uniform concentration throughout the solution tank and electrolytic cell, the concentration change of cupric ion at a given set of controlled anode-to-cathode cell voltage, wastewater circulation rate can be described by

\[
\frac{C}{C_0} = \exp(-kat) \quad (8.1)
\]

where \(C\) = concentration of cupric ion in waste water at time \(t\), \(C_0\) = initial concentration of cupric ion, \(k\) = First order reaction rate constant for deposition of Cu\(^{2+}\) at cathode. \(a = A/V_{sol}\), where \(A\) = total area of cathode (2 dm\(^2\)), \(V_{sol}\) = volume of wastewater in the solution tank.

According to equation [8.1], a plot of \(\ln C\) vs \(t\) yields a straight line, and the value of \(ka\) can be evaluated from the slope. The values of \(ka\) depend on flow rate of electrolyte, temperature and cathode potential. The cathode potential can be changed by varying the cell voltage.
The instantaneous current efficiency ($\eta_i$) of copper deposition reaction at a given electrolysis time can be evaluated by calculating the rate of change of cupric ion concentration, $dC/dt$, from experimental curve $C$ vs $t$ (sec) curve and by comparing the value to the current ($I$), at the same electrolysis time, according to Faraday’s law.

$$\text{Current efficiency}(\eta_i)\% = \frac{V_{\text{sol}}(dC/dt)}{I/nF} \times 100 \quad (8.2)$$

Where $F = 96500\text{C/equiv}$, and $n =$ number of electrons (2 equiv/mol). The average current efficiency is obtained by comparing the mass of Cu recovered at the end of the experiment,

$$\text{Average Current efficiency}(\eta_{av})\% = \frac{W}{(M/nF)\int_0^\theta I \, dt} \times 100 \quad (8.3)$$

Where $\theta =$ Total electrolysis time in seconds and $W =$ mass of copper deposited at the cathode.

$$W = V_{\text{sol}}(C_0 - C_{\text{final}})$$

$M =$ Atomic weight of copper (63.5g/mol).

The energy consumption per kg of copper recovered is calculated by integrating the current $I$ and voltage curve with respect to the time according to,

$$\text{Energy (kWh/kg-metal)} = \frac{\int_0^\theta I E_{\text{cell}} \, dt}{3600 \times 1000W} \quad (8.4)$$

Where $E_{\text{cell}} =$ cell voltage and $W =$ weight of copper deposited (kg).

**Experimental Method**

The experimental setup is shown in Figure [8.1]. Electrolyte containing 500-1000 ppm Cu$^{2+}$ and 0.05M Na$_2$SO$_4$ prepared in tap water is circulated through electrolytic cell at various flow rates. Electrolysis started by applying a constant anode-to-cathode cell voltage (2-6V) from DC power supply. Measure (1) cell current ($I$) in amperes,(2) Cell voltage (Volts), (3) cupric ion concentration either by spectrophotometer or simple titration with EDTA, and (4) solution pH by pH meter, at specific time intervals.

**Results and Calculations**

**Experiment 1**

Plot semi log plot of cupric ion concentration versus electrolysis time (sec) for controlled cell voltage and flow rate of electrolyte. Show that the concentration of cupric ion decreases logarithmically with the time as in equation [8.1]. Calculate the effective volumetric reaction rate constant $k_a$ (sec$^{-1}$) from slope of the graph.
Cell voltage = (V), Flow rate = 1/sec

<table>
<thead>
<tr>
<th>Cupric ion conc. (ppm)</th>
<th>Time (sec)</th>
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<tbody>
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</table>

**Experiment 2**

**Reaction rate constant** \((ka)\): Plot \(ka\) versus cell voltage for series of runs at fixed flow rate of electrolyte. Show that value of \(ka\) varied linearly with cell voltage as described by Ohm’s law. This indicates ohmic resistance of the electrolyte played an important role in the copper deposition reaction. Change the cell voltage after 1800 sec intervals and measure \(ka\).

<table>
<thead>
<tr>
<th>Flow rate = 1/sec</th>
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</thead>
<tbody>
<tr>
<td>Cell voltage (V)</td>
</tr>
<tr>
<td>(ka) (sec(^{-1}))</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>3.5</td>
</tr>
<tr>
<td>4</td>
</tr>
<tr>
<td>4.5</td>
</tr>
</tbody>
</table>

**Experiment 3**

**Current efficiency and Energy requirement:** The main side reaction at the cathode is reduction of \(H_2O\) molecules to \(H_2\) gas and \(OH^-\) ions.

\[
2H_2O + 2e^- = H_2 + 2OH^-
\]  

(8.5)

The \(OH^-\) ions generated from the above reaction neutralizes the \(H\) ions and thus pH changes with time.

Find instantaneous cathode current efficiency \((\eta_i)\) and at end experiment find the average current efficiency \((\eta_{av})\) by using equations 8.2 & 8.3 respectively. Also calculate the energy requirement by using formula 8.4.

<table>
<thead>
<tr>
<th>Flow rate = 1/sec, Controlled cell voltage = V, Average Current = Amp, Average current efficiency ((\eta_a)) =</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (sec)</td>
</tr>
<tr>
<td>1800</td>
</tr>
<tr>
<td>3600</td>
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<tr>
<td>5400</td>
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<tr>
<td>7200</td>
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</tbody>
</table>
Plot instantaneous cathode current efficiency ($\eta_i \%$) versus time, for a controlled cell voltage. The average current efficiency ($\eta_{av}$) can be calculated by integrating the $\eta_i$ with respect to time and dividing the result with the total electrolysis time of an experimental run.

**Experiment 4**

**Mass Transfer Aspects of Electrodeposition Reaction:** For electrodeposition of metal from a dilute solution, the rate-controlling step is generally the transport of metal ions from the bulk solution to the cathode surface. Increasing the solution velocity near cathode enhances the mass transfer rate.

Log-log plot of the effective volumetric reaction rate $ka$ (sec$^{-1}$) versus flow rate of electrolyte should give a straight line. This linear relationship shows a strong mass transfer influence on the rate of the copper deposition in the present system.

But if the copper deposition reaction is controlled by mass transfer, the reaction rate constant would be expected to be independent of the cell voltage. The fact that $ka$ increases with increase in both cell voltage and flow rate, this suggests that the copper deposition from dilute solution is under a mixed control of mass transfer and ohmic resistance of the electrolyte.

<table>
<thead>
<tr>
<th>Cell voltage = Volts, Average Current (I) = Amps</th>
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<table>
<thead>
<tr>
<th>log $ka$ (sec$^{-1}$)</th>
<th>log flow rate</th>
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**Estimation of Cu**

**By Spectrophotometer**

2. Enter the program no. 984, Press "Enter" key.
3. Adjust the wavelength as displayed (810nm) by rotating the knob on right hand side of instrument.
4. Place Zero or Blank sample vial in cell compartment put the vial cover.
5. Press "Zero" key.
6. Now replace the blank solution vial with the vial containing unknown Cu$^{2+}$ solution,
7. Place the vial cover, and press "Read" key.
8. Spectrophotometer will display the concentration of Cu$^{2+}$ in ppm.
By EDTA titration method

1. Pipette out 20 ml of electrolyte from cell outlet in 250ml conical flask.
2. Add few drops of ammonia (1 - 1.5 ml) till solution turns deep blue.
3. Add 20 ml of distilled water.
4. Add 4-5 drops of aqueous solution of Fast Sulphon Black-F indicator.
5. Titrate against 0.01M/0.05M EDTA solution.
6. End point of titration is when colour changes from blue to green.
7. 1ml of 0.01mol EDTA = 0.6354mg of Cu.
8. If EDTA is 0.05M, then 1 ml of 0.05M EDTA = 3.177mg of Cu

Reference: Chemical Engineering Education, 2002, Page 144-155

Figure 8.1: Electrolytic Cell for Copper Recovery from a Dilute Solution
Electrosynthesis of Manganese (III) Acetate in a Packed Bed Reactor

Introduction

The use of metal ion catalysts for oxidation of aromatic hydrocarbons is well established. Manganese (III) ion, which is one of the metal ion catalysts, has a special significance because of its use as oxidizing agent for the synthesis of organic compounds. The manganese (III) ion is generally used in the form of acetate.

The manganic acetate \([\text{(CH}_3\text{CO}_2\text{)}_3\text{Mn.2H}_2\text{O}]\) can be regenerated from, manganous acetate \([\text{(CH}_3\text{CO}_2\text{)}_2\text{Mn.4H}_2\text{O}]\) by common oxidizing agents such as, Potassium permanganate, peracid, and lead (IV) oxide. More attractively, however, it can be generated electrolytically, there by, obviating the use of additional chemicals.

Aim

To study Effect of, 1) flow rate of electrolyte, 2) Current density, and 3) bath composition in electrolytic preparation of Mn(III) acetate in laboratory.

Approach

The packed-bed reactor as shown in Figure 9.1 is for electro-synthesis of Mn (III) acetate. A known composition of electrolyte is introduced into the reactor from the bottom, by peristaltic pump. When required flow rate adjusted and current is supplied to the cell.

Figure 9.1: 1) Electrolytic cell, 2 & 3) Inlet & Outlet for electrolyte 4) Perforated Graphite anode, 5) Carbon Particulates, 6) Perforated Ti, cathode, 7) DC Source

At a particular intervals the out is collected and Mn (III) is routinely determined either by UV spectrophotometry at 456nm, a wave length where only Mn(III) is absorbed, or by treating with measured excess of ferrous ammonium sulphate solution and back titration with standard potassium dichromate solution.
Electrolytic Reaction

The regenerative oxidation occurs at the anode according to the reaction:

\[ Mn(II) \rightarrow Mn(III) + e^- \]  \hspace{1cm} (9.1)

As a competing reaction oxygen is evolved,

\[ 2OH^- \rightarrow (1/2)O_2 + H_2O + 2e^- \]  \hspace{1cm} (9.2)

The reaction occurring at the cathode is,

\[ H^+ + e^- \rightarrow (1/2)H_2 \]  \hspace{1cm} (9.3)

Experimental Procedure

Prepare the following solution of known composition, about 100-200ml

1. Mn(II) acetate.4H2O 80-100mM
2. Sodium Acetate 400-470mM
3. Acetic acid (Conc.) 90-95%
4. Water 10-5%

1. Take 15-20 carbon particulates. Find the surface area of about 5-6 particulates. Find average area. \((\pi dl + 2\pi r^2)\)

2. Introduce carbon particles in electrolytic reactor. These particles will rest on perforated graphite anode. Introduce perforated Titanium Cathode from the top of reactor, so that it should not touch carbon particles.

3. Start the peristaltic pump. Allow to flow the solution. (usually flow rate is 1 ml/min to 5 ml/min)

4. Pass the current. Collect the outlet solution; find the concentration of Mn (III) acetate either by titration method or by spectrophotometer.

Observations and Calculations

Experiment 1: Effect of current density on current efficiency

<table>
<thead>
<tr>
<th>Time (sec)</th>
<th>Current density (mA cm(^{-2}))</th>
<th>Current efficiency (\eta)%</th>
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Given: 1) Bath Composition: 2) Flow rate =
Experiment 2: Effect of flow rate on current efficiency

Given: 1) Bath Composition: 2) Current density (mA/cm$^2$) =

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<tr>
<th>Time (sec)</th>
<th>Flow rate (ml/min)</th>
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Calculation of current efficiency

Current efficiency $C_e(\eta) = 100\Delta cF/I_t t$, where $\Delta c$ is the amount of Mn (III) acetate (mol), $I_t$ is the total current in ampere, $F$ is Faraday constant (Amp./mol/e), $E$ is applied voltage, $M$ is Molar mass of Mn (III) acetate (kg/mol), $t$ is the electrolysis period in seconds, $n$ is the number of electrons involved in electrode reaction.

The Energy consumption $E_c$ can be calculated as

$$E_c = nFE/MC_e$$

Estimation of Mn(III) by back titration

1. Pipette out known volume of electrolyte.
2. Add known volume of (in excess) 0.1N Ferrous Ammonium Sulphate.
3. Add 1-2 ml of conc. sulphric acid & 1-5 drops of N-phenyl anthranalic acid as indicator.
4. Titrate against 0.1N Potassium dichromate.
5. Colour change is from green to violet red.

UV Spectrophotometric method

At wavelength 456 nm only Mn (III) absorbs. Prepare a calibration chart for various known concentrations of Mn (III) solution. Find the unknown Concentration.
10 Hydrodynamics of packed columns

Aim
To study the pressure drop and flooding characteristics in a packed column.

Theory
Chemical engineering operations commonly involve the use of packed and fluidized beds. These are devices in which a large surface area for contact between a liquid and a gas (absorption, distillation) or a solid and a gas or liquid (adsorption, catalysis) is obtained for achieving rapid mass and heat transfer, and particularly in the case of fluidized beds, catalytic chemical reactions. You will find a good deal of information about flow through packed and fluidized beds in the book by McCabe and Smith and Perry’s Handbook (1997). Here, we can discuss the experimental analysis to find out pressure drop and flooding characteristics in a packed column.

A typical packed bed is a cylindrical column that is filled with a suitable packing material. The liquid is distributed as uniformly as possible at the top of the column and flows downward, wetting the packing material. A gas is admitted at the bottom, and flows upward, contacting the liquid in a countercurrent fashion. An example of a packed bed is an absorber. Here, the gas contains some carrier species that is insoluble in the liquid (such as air) and a soluble species such as carbon dioxide or ammonia. The soluble species is absorbed in the liquid, and the lean gas leaves the column at the top. The liquid rich in the soluble species is taken out at the bottom.

From a fluid mechanical perspective, the most important issue is that of the pressure drop required for the liquid or the gas to flow through the column at a specified flow rate. To calculate this quantity we rely on a friction factor correlation attributed to Ergun. Other fluid mechanical issues involve the proper distribution of the liquid across the cross-section, and developing models of the velocity profile in the liquid film around a piece of packing material so that heat/mass transfer calculations can be made. Design of packing materials to achieve uniform distribution of the fluid across the cross-section throughout the column is an important subject as well. Here, we only focus on the pressure drop issue. Pressure drop for the dry packing is calculated by

\[
\Delta P \frac{g_c \epsilon^3 d_p \rho_g}{Z(1 - \epsilon) G'^2} = \frac{A(1 - \epsilon)}{Re} + B
\]

where \(\Delta P\) = pressure drop, lb./in.\(^2\), or psi; \(Z\) = depth of the packed bed, ft.; \(G' = \rho V\) = gas velocity, lb./hr.-ft.\(^2\); \(\rho_g\) = fluid density, lb./ft.\(^3\); \(\mu\) = fluid viscosity, lb./hr.-ft. (centipoise \(\times 2.42 = \) lb./hr.-ft.) (centistokes \(\times 0.3876 \times\) density, lb./ft.\(^3\) = lb./hr.-ft.). \(d_p\) = effective particle diameter, ft. \(\epsilon\) = interparticle void fraction, dimensionless \(g_c\) = acceleration of gravity (32.2 ft./s\(^2\)).

Pressure drops are correlated in terms of \((\Delta P/L)\), the pressure drop per unit length of packing. The term, \((\Delta P/L)\), is usually expressed as "psi per foot of packing".

Pressure drop in the irrigated packing as continuous range:

\[
\frac{\Delta P}{Z} = m \times 10^{-8} 10^{(nL'/\rho_l)} \frac{G'^2}{\rho_g}
\]

\[
d_p = \frac{6(1 - \epsilon)}{a_p}
\]

where packing surface \(a_p\) is in (m\(^2\)/m\(^3\)).
Experimental procedure

1. Check that the liquid in all the manometers is at the equal levels.

2. Dry Packing Pressure Drop:
   (a) Introduce the air into the column at a low flow rate without the liquid flow. Allow the gas to run for 5 to 10 minutes till the liquid columns in the manometers are stabilized. Record the pressure drop across the packing $\Delta P$ in the manometer C and air flow rate in the manometer A.
   (b) Increase the air flow rate and again record $\Delta P$ vs. gas flow rate. Take minimum six reading by increasing the gas flow rate, covering the whole range in the manometer C.

3. Pressure Drop in the Irrigated Packing:
   (a) Stop the gas flow and fill the water in the column to be completely submerged and wet the packing. Allow the air bubbles to escape. When the packing is completely wet drain off the water.
   (b) Adjust a small water flow rate and allow it to run for a few minutes. Introduce the air at a small flow rate. Allow the system to come to steady state and take the readings, in the manometer.
   (c) Increase the gas rate while keeping the liquid rate same and record the manometer readings. A minimum six gas rates covering the whole gas flow range have to be taken for each liquid rate.
   (d) Cut off the air flow and again repeat the procedure 3a, 3b and 3c for an increased liquid rate. This procedure has to be repeated for at least five liquid flow rates covering the whole range of the manometer.

4. Measurement of the packing properties:
   (a) Measure the height of the packing ($Z$) by a scale.
   (b) Column diameter: Fill the water in the column and rain a measured empty height in a measuring cylinder. The column in diameter $D$ can be calculated.
   (c) Void fraction: Fill the column with the water so as to completely submerge the packing. Drain the water and collect the water volume drained as the water level falls from the top to bottom of the packing. Calculate the void fraction ($\epsilon$) from this.
   (d) Measure the geometrical dimensions of the packing and calculate $a_p$ and other important packing properties.

5. Observation and data presentation:
   (a) Data from the literature: (For the packing:)
      
      \begin{align*}
      (1) \quad & \epsilon = \\
      (2) \quad & a_p/\epsilon \text{ (wet packed)} =
      \end{align*}
   
   (b) Calibration data of flow rate vs. $\Delta P$ to be provided.
   (c) $\Delta P/Z$ vs. $G$, with $L'$ parameter.
<table>
<thead>
<tr>
<th>Liquid flow (kg/hr.m²)</th>
<th>Gas flow (kg/hr.m²)</th>
<th>$\Delta P/Z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L_0$</td>
<td>min gas rate</td>
<td>kg/cm²/m</td>
</tr>
<tr>
<td>L1 (min 5 flow rates)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

6. Calculate and report the following:

- Height of the packing $Z$ (m):
- Calculate column diameter $D$ (cm):
- Void fraction $\epsilon$:
- Types of the packing:
- Nominal packing diameter
- Height of other geometrical dimensions:
- Packing surface = $a_p$:
- Packing factor (from literature and calculated):

**Conclusions and Comments**

1. Plot $(\Delta P/Z)$ vs. $G'$ on a log-log plot with $L'$ including $L' = 0$ as parameter. Report the slope of $(\Delta P/Z)$ vs. $G'$ and compare with that in equations 10.1 and 10.2.

2. From $(\Delta P/Z)$ vs. $G'$ plots identify and report
   - (a) The flooding and loading points
   - (b) Critical liquid flow rate.

3. With the $L'$ and $G'$ values at the flooding point found in 10.2 with the help of generalized correlation:

   \[
   \log \left( \frac{L'}{G'} \right)^{1/2} \left( \frac{\rho_g}{\rho_l} \right) = \log \left( \frac{G'^2 a_p}{\epsilon^2 \mu_l^{0.2}} \right) g_c \rho_g \rho_l
   \]

   Here $L'$ is the liquid mass flux (lbm/ft² s) based on the area of the empty column, $G'$ is the gas mass flux (lbm/ft² s), $\rho_g$ is the gas density (lbm/ft³), $\rho_l$ is the liquid mass density (lbm/ft³), $\mu_l$ is the liquid viscosity (centipoises), and $g_c$ is the acceleration of gravity (32.2 ft/s²). Note that $Y$ is not dimensionless $a_p$ is a packing surface factor found in Perry Table 18-5 (ft⁻¹),

   Calculate the dynamic $(a_p/\epsilon^3)$, and compare with the values calculated and reported in the literature.

4. Give your comments on the results and possible sources of errors and precautions.

**Sample calculation of Pressure drop**

We have a plot in which the abscissa X is $X = (L'/G')(\rho_g/\rho_l)^{0.5}$ and the ordinate Y is $Y = [G'^2(a_p/\epsilon^3)\mu_l^{0.2}]/(\rho_g\rho_l g_c)$ (see Perry’s Handbook (Fifth Edition, Figure 18-39)). As an example, consider an air flow rate of 6.0 ft³/min at STP, a water flow rate of 1200 g/s, and a column ID of 4 inches (corresponding to a column area of 0.0872 ft²),

\[
G = (6 \times 29)/(359 \times 60)(1/0.0872) = 0.0926 \text{lbm/ft}^2\text{s}
\]
\[
L = \frac{1200}{(453.6 \times 60 \times 0.0872)} = 0.506 \text{lbm/ft}^2\text{s}
\]
\[
\mu = 1.0 \text{ centipoise}, \ F_p = 1000 \ (1/\text{ft}), \ \phi = 1, \ \rho_l = 62.3 \ \text{lbm/ft}^3, \ \rho_g = \frac{29}{359}(273.2/298.2) = 0.0740 \ \text{lbm/ft}^3 \text{ and}
\]
\[
X = \frac{(0.506/0.0926)(0.0740/62.3)0.5}{0.188,}
\]
\[
Y = \frac{(0.09262 \times 1000 \times 10.2)/(0.074 \times 62.3 \times 32.2)}{0.0578}
\]
Based on Figure 18-39 in Perry, the gas phase pressure drop per foot of packing is about 1.40 inches of water. If the packing height is 30 inches the predicted pressure drop is 3.5 inches of water.

References


11 Differential Distillation

Aim
To verify the Rayleigh’s equation for a differential distillation in a binary system

Theory
In the case of a differential distillation, the vapour at any time is in equilibrium with the liquid from which it rises but changes continuously in the composition. Thus, the mathematical approach used must be differential. Assume that $L$ mol of liquid in the still of composition $x$ mol fraction $A$ and that an amount $dD$ mol of distillate is vaporized, of mol fraction $y^*$ in equilibrium with the liquid.

Material Balance
The rate of depletion of liquid is equal to the rate of distillate output. The instantaneous rate of depletion of a component in the liquid is therefore, In - out = accumulation

$$0 - dD = dL \quad (11.1)$$

Taking balance on more volatile component,

$$0 - y^*dD = d(Lx) \quad (11.2)$$

$$0 - y^*dD = xdL + Ldx \quad (11.3)$$

$$y^*dL = xdL + Ldx \quad (11.4)$$

Therefore rearrangement gives,

$$\int_F^W \frac{dL}{L} = \int_{x_w}^{x_F} \frac{dx}{y^* - x} \quad (11.5)$$

This equation can be integrated to get the following form which is called the Rayleigh’s Equation,

$$\ln \frac{F}{W} = \int_{x_w}^{x_F} \frac{dx}{y^* - x} \quad (11.6)$$

where, $F = \text{moles of feed of composition } x_F$, $W = \text{moles of residual liquid of composition } x_W$, $W$ and $x_w$ can be obtained by material balance,

$$F = D + W \quad (11.7)$$

$$F x_F = D x_D + W x_W \quad (11.8)$$

The integral in eqn. (11.5) can be solved analytically (provided the relationship between $y^*$ and $x$ is available) or graphically (calculating the area under the curve for the plot of $1/(y^* - x)$ vs $x$.)
Procedure

1. Prepare a calibration plot of mole fraction \((x)\) vs. refractive index \((n)\) of pure components \(A\) and \(B\).

2. Weigh 8 nos. of tagged stoppered conical flasks.

3. Start the flow of water through the condenser.

4. Fill 3/4th (approx. 300 ml) volume of the distillation flask with a mixture of \(A\) and \(B\) of known composition \((x_F)\). The mixture is weighed \((w)\) before charging in the distillation flask.

5. Start heating at a slow rate. When the mixture starts boiling, collect the distillate in a weighed 50 ml flask. After approximately 30 ml of the distillate has been collected, remove the flask and collect next 8 to 10 drops of the distillate in tagged test-tube and then put another flask for the collection of the distillate. This procedure should be repeated for collecting 8 distillate samples.

6. Measure the refractive indices (RI) of the samples collected in the test-tubes \((\eta_{1t}, \eta_{2t}, \ldots, \eta_{12t})\). Weigh the samples collected in the conical flasks \((w_1, w_2, \ldots, w_{12})\). Measure the RI of the bulk from each of the flasks \((\eta_{1b}, \eta_{2b}, \ldots, \eta_{12b})\).

Observations and Calculations

Data from the literature

1. Molecular weights of \(A\) and \(B\).

2. Refractive indices of \(A\) and \(B\).

3. Densities of \(A\) and \(B\).

4. Vapour liquid equilibrium data for \(A\) and \(B\) at atmospheric pressure.
Calibration data for mole fraction vs. RI

<table>
<thead>
<tr>
<th>S.N.</th>
<th>Mole fraction of A</th>
<th>RI</th>
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<tbody>
<tr>
<td>1</td>
<td>0</td>
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<td>2</td>
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<td>3</td>
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<td>10</td>
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<tr>
<td>11</td>
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</table>

Calculations

1. Calculate $D$ (amount of distillate) (from weighed 30 ml sample) and $x_D$ (distillate composition) (from refractive index of 30 ml sample) for each sample.

2. Calculate $W$ (amount of residue still left in the flask) and $x_W$ (composition of residue) using Eqn. 11.7 and 11.8 for each fraction.

3. Calculate $y^*$ (vapor phase composition) for each sample (from Refractive index of 8 drops collected.)

4. Calculate $x$ (liquid phase composition in equilibrium with $y^*$) using Raoult’s law.

5. Complete the following Table.

<table>
<thead>
<tr>
<th>S.N.</th>
<th>$F$</th>
<th>$x_F$</th>
<th>$D$</th>
<th>$x_D$</th>
<th>$W$</th>
<th>$x_W$</th>
<th>$y^*$</th>
<th>$x$</th>
<th>$\ln(F/W)_i$</th>
<th>$1/(y^*-x)$</th>
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<td>1</td>
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</table>

6. Calculate $\ln(F/W) = \ln(F/W)_1 + \ln(F/W)_2 + ... + \ln(F/W)_8$
7. Plot $1/(y^* - x)$ vs $x$ and measure the area under the curve.

8. Now verify Eqn. 11.6.

9. Calculate

$$\% \text{ Error} = \left| \frac{\ln(F/W) - \int_{x_0}^{x_F} dx/(y^* - x)}{\ln(F/W)} \right| \times 100$$
12 Distillation with Total Reflux

Aim

To determine the overall efficiency of the plate column, operating under total reflux for a binary system and number of transfer units for a packed column.

Theory

Overall efficiency = \frac{\text{Number of theoretical stages}}{\text{Number of actual stages}} \quad (12.1)

Fenske’s equation is

\[ N_M + 1 = \frac{\log \left( \frac{X_D - X_W}{1 - X_D} \right)}{\log \alpha_{av}} \quad (12.2) \]

\[ \alpha_{av} = \sqrt{\alpha_{top} \times \alpha_{bottom}} \quad (12.3) \]

\( N_M \) = number of theoretical stages at total reflux, and \( \alpha_{av} \) = average relative volatility.

Procedure

1. Prepare a calibration chart of refractive index (RI) vs. mole fractions of components \( A \) and \( B \).

2. Fill approximately 2/3rd volume of the distillation flask with a mixture of \( A \) and \( B \).

3. Start water circulation through the condenser.

4. Close the bottom sample "draw out" cock to prevent the overflow of liquid through the sample line during the experiment. Open the top sample "draw out" cock to allow the air to escape when the heating is started. Switch on the heating mantle and allow the flask temperature to rise.

5. When the vapours rise to the top of the column, close the top "draw out" cock and increase the heating rate if necessary. After about 30 min, note the top and the bottom temperatures. If some milky liquid appears near the top "draw out" or the sample line, drain it in a small conical flask and discard. This could be due to the formation of emulsion of the organic liquid with moisture.

6. When the top and the bottom temperatures become steady (based on two successive readings taken at 10 min time interval) it indicates that the system has attained steady state and the samples may be withdrawn.

7. 2 to 4 ml of top sample is collected in a test-tube after purging off some quantity. The test-tube should be immediately closed to avoid losses. Determine the RI of the sample.

8. Count the number of actual plates in the column.
Figure 12.1: Schematic of the setup

1. Condenser
2. Reboiler

Packed Column

Tray Tower
Apparatus

Observations

Data from the literature

1. Molecular weights of $A$ and $B$.
2. Refractive indices of $A$ and $B$ at ambient temperature.
3. Densities of $A$ and $B$ at ambient temperature.

Calibration data for mole fraction vs. RI

<table>
<thead>
<tr>
<th>S.N.</th>
<th>Mole fraction of $A$</th>
<th>RI</th>
</tr>
</thead>
</table>

Observations

1. Number of actual stages in the column.
2. Top temperature ($\degree$C)
3. Bottom temperature ($\degree$C)
4. RI of top and bottom samples
5. Mole fraction of top sample ($X_D$)
6. Mole fraction of residue ($X_B$)

Calculations

1. Calculate the number of stages (theoretical) by McCabe Thiele method and calculate the overall efficiency by equation $12.1$
2. Calculate the number of stages by Enthalpy-Composition method and calculate the efficiency by equation $12.1$
3. Calculate the number of stages by Fenske’s equation (equations $12.2$ and $12.3$ and calculate the efficiency by equation $12.1$
4. Calculate number of transfer units (NTU) for a packed column.

$$NTU = \int_{y_B}^{y_D} \frac{dy}{y^n - y}$$

5. Comment on the precaution and the sources of error.
13 Gas-Liquid Absorption

Objectives

1. Study hydrodynamic characteristics of packed columns.
2. Determine flooding characteristics of columns with three different packing.
3. Estimate mass transfer coefficient for absorption of ammonia into water.

Theory

Packed columns are used in chemical industry to absorb a gas from a mixture of gases or strip a volatile substance from a liquid. The columns are, usually, countercurrent gas-liquid contactors in which gas flows upward and liquid downward. To provide large interfacial area for mass transfer between gas and liquid, the columns are filled with packing.

Design of the column involves estimation of diameter of the column and height of the packing required for specified separation. The diameter is determined from flooding characteristics of the column and, the height is found from mass transfer characteristics of the packing and the gas-liquid system.

Flooding depends on pressure drop across the column, it being higher at the bottom and lower at the top to allow the gas to flow upward. The gas flow is usually turbulent and in a dry column, the pressure drop rises with gas flow with an exponent of 1.8 to 2.0 - a typical feature of turbulent flow. The pressure drop rises with an increasing flow of liquid because liquid fills up the column and the space for gas flow is reduced. Up to the loading point, the pressure drop follows the same relation as in dry run. Beyond the loading point, the pressure drop rises rapidly with gas flow and the liquid hold up in the column also rises. Eventually, at the flooding point, the pressure drop rises drastically and the liquid may splash back from the column. The gas velocity corresponding to the flooding point is called flooding velocity and the column is operated at some fraction of this velocity, say 60%.

Tower height is determined by packing characteristics, namely, interfacial area, mass transfer coefficient of the gas-liquid system and extent of separation. Refer to Cussler (1984) for derivation of governing equation for tower height.

Experimental Set-up

Figure 13.1 shows the experimental apparatus. It consists of three glass columns, each of 5 cm internal diameter and one meter packed height. Each column is packed with a different packing (Raschig Rings, Pall rings and Intalox saddles). Examine the gas and liquid connections made to the columns. Gas and liquid should flow through only one column at a time. The pressure drop across the column is recorded with a differential pressure transmitter, which is connected to the computer (note that there is no read out for the transmitter). Air and ammonia flows are adjusted with rotameters; the two streams are mixed to produce a mixture of specified concentration (work with dilute concentrations, less than 5% ammonia). Liquid flow is manipulated with a peristaltic pump, which can be controlled by a computer. The temperature of the column is obtained with an RTD connected to the computer. The dissolved ammonia gas concentration is measured by Ion Selective Electrode instrument for ammonia.
Figure 13.1: Experimental Apparatus for studying hydrodynamics of a packed column and ammonia absorption
Procedure

Flooding

First, study dry-run pressure drop by flowing only air through one of the columns. Set air flow at 10 LPM and work your way up by raising it in increments of 10 LPM. Record the pressure drop for all air flows. Then, allow liquid to flow into the column and measure the pressure drop for increasing flow rates of gas. Use five different liquid flows starting from about 1.5-5 LPM. For each liquid flow, raise the gas flow slowly in increments of 10 LPM and record pressure drops. Repeat the above procedure for the other two packings.

Mass transfer

The packed height of the columns is one meter. From the equation given below, find HTU and then mass transfer coefficient for air/ammonia mixture and water system. Use mass balance to estimate gas phase concentration of ammonia in the outlet.

Report

It should include objectives, description of experimental apparatus, raw data and analysis of flooding and mass transfer.
14 Thermal Conductivity of Insulating Powder

Introduction

Thermal conductivity is one of the important properties of the materials and its knowledge is required for analyzing heat conduction problems. Physical meaning of the thermal conductivity is how quickly heat passes through a given material. Thus the determination of this property is of considerable engineering importance. There are various methods of determination of thermal conductivity suitable for different materials. The present apparatus is suitable for finding out thermal conductivity of materials in the powdered form.

Theory

Consider the transfer of heat by conduction through the wall of a hollow sphere formed by insulating powdered layer packed between two thin copper spheres. Let \( r_i \) = radius of inner sphere in meters, \( r_o \) = radius of outer sphere in meters. \( T_i \) = surface temperature of the inner sphere, °C \( T_o \) = surface temperature of the outer sphere, °C

Being a thin surface and copper, which is highly conductive, the thermal resistance of both the surfaces is neglected. Applying Fourier Law of heat conduction for thin spherical layer of radius \( r \) and thickness \( dr \) with temperature difference \( dT \), the heat transfer rate,

\[
Q = -K \frac{4\pi r^2}{dr} dT
\]

where \( K \) = thermal conductivity (W/m°C), and \( Q \) = heat transfer rate (W). Separating variables,

\[
\frac{q}{4\pi K} \frac{dr}{r^2} = -dT
\]

Integrating from \( r_i \) to \( r_o \) and \( T_i \) and \( T_o \)

\[
q = \frac{4\pi k r_i r_o (T_i - T_o)}{r_i - r_o}
\]

From the experimental values of \( q, T_i \) and \( T_o \) the unknown thermal conductivity \( K \), can be determined as,

\[
K = \frac{q(r_o - r_i)}{4\pi r_i r_o (T_i - T_o)}
\]

Apparatus and Specifications

The apparatus consists of two thin walled concentric copper spheres. The inner surface houses the heating coil. The insulating powder is packed between the two shells. The power supply to heating coil is adjusted by using a dimmerstat and is measured by voltmeter and ammeter. Thermocouples are used to measure the temperatures \( T_i \) and \( T_o \).

Under steady state conditions the temperatures are noted and also the Voltmeter, Ammeter readings are recorded. These reading in turn enable to find out the thermal conductivity of the insulating powder packed between two shells. We assume the insulating powder as an isotropic material and the value of the thermal conductivity to be constant. One dimensional heat conduction in the radial is assumed across the powder layer and thermal conductivity can be determined as above under steady state conditions.
Specifications

Radius of the inner copper sphere, $r_i = 50$ mm  
Radius of the outer copper sphere, $r_o = 100$ mm  
Voltmeter - 0 to 200 volts  
Ammeter - 0 to 2 Amps.  
Temperature Indicator - 0 to 300 °C  
Dimmerstat 0 to 2 A, 0 to 230 V  
Heater Coil- strip heating element Sandwiched between mica sheets.

Experimental Procedure

1. Make the necessary electrical connections and give AC input to supply mains.
2. Keep the heat input constant throughout the experiment at various values by adjusting the dimmerstat, from 20 to 200 volts.
3. Wait till a satisfactory steady state condition is reached.
4. Note down the readings in the observation table as given below.
   (a) Voltmeter reading ($V$) = Volts  
   (b) Ammeter reading ($I$) = Amps.  
   (c) Heater Input ($VI$) = Watts  
   (d) Temperature of Inner sphere $T_i$ = °C  
   (e) Temperature of outer sphere $T_o$ = °C  
5. Heat transfer rate, $q = VI$ Watts

The observations and results are tabulated and repeated for different wattages.
15 Heat Transfer by Combined Natural Convection and Radiation

Theory

In many engineering problems a surface loses or receives thermal energy simultaneously by convection and radiation. For example, when a hot body is exposed to its surroundings at a lower temperature, it loses heat both by convection and radiation and the two mechanisms of heat transfer act in parallel. The total rate of heat transfer is the same of the heat transfer rates by convection and radiation as given by

\[ q = q_c + q_r = h_c A(T_s - T_a) + A\sigma(T_s^4 - T_a^4) \]  \hspace{1cm} (15.1)

where

- \( q_c, q_r \) = heat transfer rates by convection and radiation
- \( A \) = heat transfer area of the body.
- \( h_c \) = average convection heat transfer coefficient either natural convection or forced convection or both depending on the prevailing conditions
- \( T_s \) = Surface temperature of the body
- \( T_a \) = Ambient temperature
- \( \epsilon_s \) = emissivity of the surface
- \( \sigma \) = Stefan-Boltzman constant of radiation

Equation 15.1 can also be written as

\[ \frac{q}{A} = (h_c + h_r)(T_s - T_a) \]  \hspace{1cm} (15.2)

where \( h_r \) = radiation heat transfer coefficient

\[ h_r = \frac{q_r}{A(T_s - T_a)} = \frac{\epsilon_s\sigma(T_s^4 - T_a^4)}{T_s - T_a} \]  \hspace{1cm} (15.3)

Heat Transfer COefficient for Natural Convection

The heat transfer coefficient for natural convection on vertical planes and cylinders is given by

\[ Nu = \frac{h_c L}{K} = c(Gr Pr)^n = C(Ra)^n \]  \hspace{1cm} (15.4)

where \( Nu = h_c L/K \) = Nusselt number, \( Gr = (L^3 \rho^2 g \beta \delta T)/\mu^2 \) = Grashof number, \( Pr = C_p \mu/L \) = Prandtl number, \( Ra = Gr Pr \) = Raleigh number.

Notation: \( L = \) length, \( \rho = \) density, \( \mu = \) viscosity, \( \alpha = \) coefficient of thermal expansion, \( \beta = 1/T \) for gases (\( T \) is in K), \( c_p = \) specific heat, \( K = \) conductivity.

For Rayleigh Number between \( 10^4 \) and \( 10^9 \), equation 15.4 is given by

\[ Nu = \frac{h_c L}{K} = 0.59(Gr Pr)^{0.25} \]  \hspace{1cm} (15.5)
The physical properties of the fluid to be used in eq. (15.5) should be evaluated at the film temperature. The film temperature is defined as

\[ T_f = \frac{T_s + T_a}{2} \]  

(15.6)

where \( T_s \) = Surface temperature, \( T_a \) = Free stream temperature (i.e. the temperature outside the boundary layer), Ambient Temperature.

**Total Heat Transfer**

When a body is heated to a certain temperature and allowed to cool, then the rate of heat transfer (or loss) to the surroundings at any time can be written as

\[ q = m c_p \frac{dT}{dt} \]  

(15.7)

where \( m \) = mass of the body in kg, \( c_p \) = specific heat of the body, \( T \) = temperature in K, \( t \) = time in s.

Under the condition of Natural Convection and radiation, the total rate of heat loss as given by eq. (15.7) is equal to eqs. (15.1) & (15.2).

**Experimental Procedure**

Determine the mass of the cylinder and its surface area for heat transfer. Heat the metallic cylinder to about 350°C. Support the heated cylinder on a wooden stand with the help of three glass rods. As soon as the temperature falls to 300°C, start recording the temperature at intervals of 5 minutes till the surface temperature reaches about 100°C.

**Calculations**

Plot temperature versus time graph, find out the slope at the required temperature, and calculate total heat loss from equation (15.7). Knowing natural convective heat transfer coefficient from Eq. (15.5) the rate of heat transfer due to radiation and radiation heat transfer coefficient \( h_r \) can be calculated from Eq. (15.2). From knowledge of \( h_r \), the emissivity of the surface \( \epsilon_s \) can be calculated from eq. (15.3). Perform the calculation as a function of temperature between 100 to 300°C.

**Data**

Physical properties of Air at 1 atm pressure

<table>
<thead>
<tr>
<th>T (K)</th>
<th>( \rho ) (kg/m³)</th>
<th>( c_p ) (kJ/kg°C)</th>
<th>( 10^5 ) (kg/m s)</th>
<th>K</th>
<th>Pr</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>1.1774</td>
<td>1.0057</td>
<td>1.8462</td>
<td>0.02624</td>
<td>0.708</td>
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<tr>
<td>350</td>
<td>0.9980</td>
<td>1.0090</td>
<td>2.075</td>
<td>0.03003</td>
<td>0.697</td>
</tr>
<tr>
<td>400</td>
<td>0.8826</td>
<td>1.0140</td>
<td>2.286</td>
<td>0.03365</td>
<td>0.689</td>
</tr>
<tr>
<td>450</td>
<td>0.7833</td>
<td>1.0207</td>
<td>2.484</td>
<td>0.03787</td>
<td>0.683</td>
</tr>
</tbody>
</table>

Metal brass cylinder, \( D = 5.1 \) cm, \( H=7.65 \) cm, \( W = 1.28 \) kg
Specific Heat (Brass) 0.091 kcal /kg °C
Ambient Air temperature \( T_a = \) Room Temperature
16 Boiling and Condensation Studies

INTRODUCTION

Boiling and condensation are vital links in the transfer of heat from hot to cold regions in countless applications, e.g. thermal and nuclear power generation in steam plants, refrigeration, refining, heat transmission, etc.

THEORY

1. BOILING: When a liquid at saturation temperature is in contact with the surface of a solid (usually metal) at a higher temperature, heat is transferred to the liquid and a phase change (evaporation) of some of the liquid occurs. The nature and the rate of this heat transfer changes considerably as the temperature difference between the metal surface and the liquid is increased.

Although "boiling" is a common process, the production of vapor bubbles is a very interesting and complex process. Due to surface tension, the vapor inside a bubble must be at a higher pressure than the surrounding liquid. The pressure difference increases as the diameter of the bubble decreases, and is insignificant when the bubble is large. However, when the bubble is minute, an appreciable pressure difference exists. The pressure inside the bubble is the vapor pressure corresponding with the saturation temperature. Thus when no bubbles exist (or are very small) it is possible for the liquid temperature in the region of the heat transfer surface to be well above the temperature of the bulk of the liquid. (This will be close to the saturation temperature corresponding with the pressure at the free liquid vapor interface). The formation of bubbles normally associated with boiling is influenced by the foregoing.

2. CONVECTIVE BOILING: When the heating surface temperature is slightly hotter than the saturation temperature of the liquid, the excess vapor pressure is unlikely to produce bubbles. The locally warmed liquid expands and convection currents carry it to the liquid vapor interface where evaporation takes place, and thermal equilibrium is restored. Thus in this mode, evaporation takes place at small temperature differences and with no bubble formation.

3. NUCLEATE BOILING: As the surface becomes hotter, the excess of vapor pressure over local liquid pressure increases and eventually bubbles are formed. These occur at nucleating points or cavities in the surface, which form the nucleus for the formation of a bubble. As soon as a bubble is formed, it expands rapidly as the warmed liquid evaporates into it. The buoyancy detaches the bubble from the surface and another starts to form.

Nucleate boiling is characterized by vigorous bubble formation and turbulence. Exceptionally high heat transfer rates and heat transfer coefficients with moderate temperature differences occur in nucleate boiling, and in practical applications the boiling is nearly always in this mode.

4. FILM BOILING: Above the critical surface -liquid temperature difference it is found that the heating surface becomes "Vapor locked" and the liquid is unable to wet the surface. When this happens there is considerable reduction in heat transfer rate and if the heat input to the metal is not immediately reduced to match the lower ability of the surface to transfer heat, the metal temperature will rise until radiation from the surface plus the limited film boiling heat transfer, is equal to energy input.
If the energy input is in the form of work (including electrical energy) there is no limit to the temperature which can rise until a failure or a "burnt out" occurs. If the source is radiant energy from, for example, a combustion process, a similar failure can occur, and many tube failures in the radiant action of advanced boilers are attributed to this cause. Immersion heaters must obviously design with sufficient area so that the heat flux never exceeds the critical value. The consequence of a "burn out" in a nuclear power plant will be readily appreciated.

5. **CONDENSING HEAT TRANSFER:** Condensing of a vapor onto a cold surface may be "filmwise" or "dropwise". When filmwise condensation occurs, the surface is completely wetted by the condensate and condensation is onto the outer layer of the liquid film the heat passing through the film and into the surface largely by conduction.

By treating a surface with a suitable compound, it may be possible to promote "dropwise" condensation. When this occurs the surface is not wetted by the liquid and the surface becomes covered with the beads of liquid which coalesce to form drops which then fall away leaving the surface bare for a repetition of the action. Heat transfer coefficients with dropwise condensation are higher than with filmwise owing to the absence of the liquid film.

**SPECIFICATIONS AND EXPERIMENTAL SETUP**

**Dimensions of the heating surface**
- Effective length = 29.5 mm
- Diameter = 12.7 mm
- Surface area = 0.0013 m² (including area of end)
- Condenser surface area = 0.032 m²
- Maximum permitted surface Temperature = 220°C
- Heater Cut-out Temperature = 170°C
- Fluid: R11 Trichloro-fluoromethane CCl₃F (NO OTHER FLUID SHOULD BE USED)
- Quantity of fluid: (Liquid level to be not less than 50 mm above heating element) Approximately 0.55 L
- Heat Transfer to surroundings from the chamber = 0.8 WK⁻¹

**Dimensions of glass chamber:**
- Nominal diameter = 80 mm
- Length = 300 mm
- Volume = 0.0015 m³
- Specific Heat capacity of water = 4.18 KJ kg⁻¹ K⁻¹
- 1 bar = 105 Nm⁻² = 100 KNm⁻²

The panel consists the chamber with thick walled glass cylinder (80 mm bore × 300 mm long), with nickel plated brass end plates. The chamber houses the heating element and the condenser. The heating element with 300 Watt "High watt density cartridge heater swaged into a thick walled copper sleeve to give a uniform surface temperature. Effective heating surface area is approximately 13 cm². The condenser with 9 coils nickel plated copper tube if mean surface area approximately 0.032 m².

Besides the chamber, Voltmeter and Ammeter to measure electrical input to the heating element, ranges 0 to 250 volts and 0 to 3 A respectively and Variable Transformer to give infinitely variable heat input to the heating element. Charging and Drain valve fitted to lower end plate-to charge or discharge R11. Single Point Digital temperature indicator with 10°C resolution indicates the
temperature of the surface of the heating element. There is a long glass thermometer (0 to 50°C and 150 mm) to measure (i) Water inlet and outlet temperatures (ii) R11 liquid temperature and (iii) R11 vapor temperature. On the left corner of the panel, pressure Gauge ranging from -100 to +250 KN m$^{-2}$ gauge to indicate pressure in chamber. On the right side of the panel, Water flow meter, tapered glass tube with stainless steel float and control valves, range 0 to 50.

DESCRIPTION OF EXPERIMENTAL SETUP

A high "Watt density" electric heating element in a copper sleeve submerged in R11 liquid is mounted horizontally in a vertical glass cylinder. The temperature of the copper sleeve is measured by a thermocouple and digital indicator. The electric input to the heater may be varied from 0 to approximately 300 watts by a variable transformer, the actual heat transfer rate being obtained from the product of the Voltmeter and Ammeter readings. A controller incorporated in the temperature indicator switches off electric input if the temperature of the heating surface exceeds a pre-set value. At the upper end of the cylinder is nickel plated coil of a copper tube through which cooling water flows. This coil condenses the R11 vapor produced by the heat input and the liquid formed returns to the bottom of the cylinder for re-evaporation. A cooling water flow meter used in conjunction with glass thermometers measuring the cooling water temperature, enables the rate of heat transfer at the condenser to be measured. Glass thermometers are also mounted inside the glass cylinder to indicate the temperature of R11 liquid and vapor.

OBSERVATIONS AND RESULTS

Visual Demonstration of Convective, Nucleate and Film Boiling (Three Modes of Boiling) Turn on the electrical and water supplies and adjust both to low settings. Allow the digital thermometer to stabilize. Observe this and the liquid temperature at frequent intervals.

Carefully watch the liquid surroundings the heater. Convection currents will be observed, and at the same time liquid will be seen to collect and drip on the condenser coils, indicating that evaporation is proceeding although at a low rate. Increase the wattage in increments, keeping the vapor pressure at any desired constant value by adjusting the cooling water flow rate. Nucleate Boiling will soon start and will increase until vigorous boiling is seen, the temperature differences between the liquid and the metal being still quite moderate (200K). Increase the power input and at about 200 and 300 watts the nature of the boiling will be seen to change dramatically and at the same time the metal and liquid temperature difference rise quickly. The rate of evaporation falls to a low level and the water flow rate must be reduced to maintain a steady pressure. The electrical input should be now reduced to about 60 watts. Careful examination of the heater surface will show that it is now enveloped in an almost unbroken film of vapor and this is the cause of the reduced heat transfer rate.

The electrical power input should be now reduced to zero. It will be found that as the metal-liquid temperature difference falls to about 40 K the boiling suddenly becomes vigorous as film boiling reverts to nucleate boiling.

DEMONSTRATION OF FILMWISE CONDENSATION AND MEASUREMENT OF OVERALL HEAT TRANSFER COEFFICIENT

The filmwise condensation which occurs with R11 can be clearly seen, and the resistance offered by the liquid is readily appreciated. The overall heat transfer coefficient between the condensing vapor
and water may be found as follows: Adjust the voltage and the water flow rate until the desired pressure and condensing rate is established. When conditions are stable, note the water flow rate \(m_w\), water inlet and outlet temperatures \(T_i, T_o\) and the saturation temperature of R11 \(T_s\), Voltage \(E\) and Current \(I\).

**CALCULATIONS**

Heat transfer rate of cooling coil,

\[
Q_w = M_w C_p (T_i - T_o) \tag{16.1}
\]

Heat transfer rate from heater

\[
Q_e = E \times I \tag{16.2}
\]

Heat transfer to surroundings (by difference) = \(Q_e - Q_w\)

Log mean temperature difference,

\[
\phi_m = \frac{\phi_1 - \phi_2}{\ln \frac{\phi_1}{\phi_2}} \tag{16.3}
\]

\[
\phi_1 = T_s - T_i \tag{16.4}
\]

\[
\phi_2 = T_s - T_o \tag{16.5}
\]

Overall heat transfer coefficient

\[
U = \frac{Q_w}{A \phi_m} \tag{16.6}
\]

Where \(A\) = surface area of the condenser.

**ESTIMATION OF CONDENSATION COEFFICIENTS**

For the horizontal tube, condensation coefficients is given by

\[
C_o = h \left( \frac{k^2}{k^3 \rho^2 g} \right)^{1/3} = 1.51 Re^{-1/3} \tag{16.7}
\]

\(C_o\) = Condensation number

\(Re\) = Film Reynolds number

\(k\) = Condensate loading per unit length of tube, m/L

\(m\) = total condensate flow rate, Kg/s

\(L\) = length of the tube, m

The physical properties should be evaluated at film temperature, \(T_f = (T_s + T_w)/2\)

Where \(T_s\) = Saturation temperature, \(T_w\) = wall temperature

The condensation coefficient for a horizontal tube can also be estimated by,

\[
h = 0.725 \left( \frac{k^3 \rho^2 g \lambda}{\Delta D_o \mu} \right)^{1/4} \tag{16.8}
\]

\(D_o\) = tube diameter, m

\(\lambda\) = latent heat of condensation, J/Kg

\(\Delta t = T_s - T_w\)

The condenser coil may be approximated as a stack of horizontal tubes, and the length of tube in
each horizontal row may be estimated as $D_e$, where $D_e = \text{Coil diameter}$. There are, say, $n$ turns, i.e., $n$, rows of tubes, then,

$$\Gamma = \frac{m}{n \pi D_e} \quad (16.9)$$

$$m = \frac{Q_w}{\lambda} \quad (16.10)$$

$\lambda = \text{latent heat of condensation}$.

Average condensation coefficient for a stack of tubes is shown as

$$h_w = h_1^{-1/4} \quad (16.11)$$

$h_1 = \text{condensate coefficient for the top tube in stack}; \; N = \text{No. of tubes in a stack}$.

For a coil, the inside film coefficient can be obtained as

$$h_{i:e} = (1 + 3.5 \frac{d_{ie}}{D_e})h_i \quad (16.12)$$

$h_i = \text{film coefficient for a straight pipe}$

$d_{ie} = \text{tube diameter}$

$D_e = \text{Coil diameter}$

Overall coefficient for a coil can be estimated from eq. (9) and (10) and taking into account the thermal resistance of the tube. The estimated and the experimental coefficients can be compared. This may be repeated at other water flowrates, other saturation temperatures and other condensation heat fluxes. The observations and results can be tabulated.
17 Heat Transfer Through a Submerged Helical Coil in an Agitated Vessel (Under Unsteady-State Conditions)

Aim

To evaluate overall and individual film heat transfer coefficients for cooling hot liquids in a stirred vessel, by means of cooling water, flowing through the helical coil submerged in the vessel.

Equipment

An insulated cylindrical vessel, helical coil, propeller type impeller, driven by fractional horse power motor, immersion heater, a variac to control the speed of the motor, thermometers, stop watch, bucket and a balance.

Procedure

1. Clean the tank and the copper helical coil with fine emery paper and place the helical coil inside the tank on a wooden support.

2. Charge the tank with appropriate amount of given liquid so as to make the depth of the liquid equal to the diameter of the vessel.

3. Fix up the shaft of the propeller to the shaft of the fractional horse power motor and adjust the depth of the impeller from the bottom of the tank, such that the depth is equal to 1/3rd of the tank diameter.

4. Start the agitator and set its speed to a fairly high value, say 1000 r.p.m., So as to give complete mixing and hence uniform temperature inside the tank.

5. Heat the vessel liquid by means of an immersion heater to about 800°C and then keep the heater on, admit cold water through the helical coil and adjust its flow rate to a desired value such that the Reynolds number is greater than 104 (say 5Kg per minute).

6. Stop heating the liquid and let the temperature of the hot vessel liquid fall gradually. As the temperature of the tank liquid reaches to 700°C, start recording the temperature of the tank liquid and outgoing liquid as a function of time. Continue recording till the temperature difference between the vessel liquid and the outgoing coil liquid drops down to 450°C.

7. Follow the same procedure for at least three more different flow rates of the coil liquid in turbulent flow (say 7Kg/min, 10Kg/min)
Observations

<table>
<thead>
<tr>
<th>Time (θ min)</th>
<th>T_h °C</th>
<th>T_c °C</th>
<th>T_ca °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>70</td>
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</tr>
</tbody>
</table>

T_h = temperature of vessel liquid at any time, θ
T_c = temperature of outgoing coil liquid at any time, θ
T_ca = temperature of incoming coil liquid at zero time.
N = speed of the agitation, rph.
M_h = mass of hot liquid in the vessel, Kg.
W = flow rate of cold water in the coil, Kg/hr.

Theory

Heat lost by the vessel liquid during small interval of time dθ, due to temperature drop dT_h is given by \(-M_h C_{p,h} dT_h\), Kcal. Heat carried away by the coil liquid during the small interval, dθ is equal to \((W c dq)C_{p,c}(T_c-T_ca)\) Kcal. Heat transfer through the wall of the helical coil during the interval dθ = \(U_0A_0\Delta T_{lm}.dθ\). Heat lost from the vessel liquid to the surrounding during the interval dθ is dq_s.

Accumulation of heat inside the coil during the interval (dθ) = \(M_C C_{p,c}dt_c/2\), where \(M_C\) is the mass of the liquid inside the coil. Therefore,

\[-M_h C_{p,h} dT_h = U_0A_0\Delta T_{lm}.dθ + dq_s\] (17.1)

and

\[U_0A_0\Delta T_{lm}.dθ = W_C C_{pc}(T_c-T_ca)dθ + M_C C_{pc} dT_c/2\] (17.2)

If the vessel is properly insulated, the heat loss to the surroundings is negligible and consequently equation (17.1) reduces to

\[-M_h C_{p,h} dT_h = U_0A_0\Delta T_{lm}.dθ\] (17.3)

Since during the small interval, the accumulation or depletion of heat inside the coil is inappreciable compared to the amount of the heat carried away by the coil liquid, the term \(M_C C_{pc}dt_c/2\) can be dropped from the equation (17.2). The equation (17.2) becomes

\[U_0A_0\Delta T_{lm}.dθ = W_C C_{pc}(T_c-T_ca)dθ\] (17.4)

From the equation (17.4)

\[U_0A_0\frac{T_c - T_{ca}}{\ln(T_h - T_{ca})/(T_h - T_c)} = W_C C_{pc}(T_c-T_ca)dθ\]
or

$$\ln \left( \frac{T_h - T_{ca}}{T_h - T_c} \right) = \frac{U_0 A_0}{W_c C_{pc}} \tag{17.5}$$

or

$$\frac{(T_h - T_{ca})}{(T_h - T_c)} = e^{\frac{U_0 A_0}{W_c C_{pc}}} = K \text{(say)} \tag{17.6}$$

or \((T_h - T_{ca})/K = T_h - T_c\).

$$T_c = T_h - \frac{T_h}{K} + \frac{T_{ca}}{K} = T_h \left( 1 - \frac{1}{K} \right) + \frac{T_{ca}}{K} \tag{17.7}$$

**Method of Calculation**

**Method 1**

Make a plot of \(T_c\) against \(T_h\) and calculate the slope of the graph by the method of least squares. From the calculated slope, find out the value of \(K\). Knowing the value of \(K\), calculate \(U_0\) from equation \([17.6]\). This method of calculating \(U_0\) is valid only when \(T_{ca}\) (incoming coil liquid temperature at zero time) is constant.

**Method 2**

When \(T_{ca}\) is also a variable, find the average value of \(K\) for all readings by using equation \([17.6]\) and then calculate \(U_0\) from the same equation using the average value of \(K\).

**Method 3**

From equation \([17.3]\) and \([17.4]\)

$$- M_h C_{ph} dt_h = W_C C_{pc}(T_c - T_{ca}) d\theta$$

$$- M_h C_{ph} dt_h = W_C C_{pc} \left[ T_h \left( 1 - \frac{1}{K} \right) + \frac{T_{ca}}{K} - T_{ca} \right] d\theta = W_C C_{pc} \left( 1 - \frac{1}{K} \right) (T_h - T_{ca}) d\theta$$

or

$$- \int_{T_{hi}}^{T_h} \frac{dt_h}{T_h - T_{ca}} = \frac{W_C C_{pc}}{M_h C_{ph}} \left( 1 - \frac{1}{K} \right) \int_0^\theta d\theta$$

Assuming \(T_{ca}\) to be constant,

$$\ln \left( \frac{T_{hi} - T_{ca}}{T_h - T_{ca}} \right) = \frac{W_C C_{pc}}{M_h C_{ph}} \left( 1 - \frac{1}{K} \right) \theta \tag{17.9}$$

where \(T_{hi}\) = temperature of vessel liquid at \(\theta = 0\). If we plot \(\ln(T_{hi} - T_{ca})/(T_h - T_{ca})\) against \(\theta\), we will get a straight line passing through the origin. Calculate the slope by the method of least squares and from the slope find out the value of \(K\). Use this value of \(K\) to evaluate \(U_0\) from equation \([17.6]\).
Method 4

From equation [17.3]

\[
\int_{T_{hi}}^{T_h} = \frac{U_0 A_0}{M_h C_{ph}} \int_{0}^{\theta} = \frac{U_0 A_0 \theta}{M_h C_{ph}}
\] (17.10)

Plot \(1/T_{lm}\) against \(T_h\) and evaluate the area under the curve for different values of \(\theta\) (or \(T_h\)). From the area calculate \(U_0\) by equation [17.10] for different values of \(\theta\). Calculate the mean value of \(U_0\) for the duration of run.

Calculation of \(H_{IC}\)

Inside film heat transfer coefficient \(h_i\), for turbulent flow inside straight circular tube is given by the Sieder and Tate equation:

\[
\text{Straight tube } h_i = 0.023 \frac{K}{d_i} Re^{0.8} Pr_b^{1/3} \left( \frac{\mu_b}{\mu_w} \right)^{0.14}
\] (17.11)

Inside coil film heat transfer coefficient \(h_{ic}\), for turbulent flow inside the helical coil is given by the following equation:

\[
\text{Straight tube: } h_{ic} = \left( 1 + 3.5 \frac{d_i}{D_c} \right) h_i
\] (17.12)

Where, \(d_i = \) inside tube diameter, \(D_c = \) Helix diameter

Calculation of \(H_{oc}\)

Coil outside film heat transfer coefficient, \(h_{oc}\), can be calculated by subtracting metal wall resistance as well as inside coil film resistance from the overall resistance, neglecting the dirt film resistance.

\[
\frac{1}{U_0 A_0} = \frac{1}{h_{oc} A_0} + \frac{1}{h_{ic} A_i} + \frac{X}{K_m A_m}
\] (17.13)

\[
\frac{1}{U_0} = \frac{1}{h_{oc}} + \frac{d_0}{d_i} \frac{1}{h_{ic}} + \frac{d_0}{d_m} \frac{X}{K_m}
\] (17.14)

\[
\frac{1}{h_{oc}} = \frac{1}{U_0} - \frac{d_0}{d_i} \frac{1}{h_{ic}} - \frac{d_0}{d_m} \frac{X}{K_m}
\] (17.15)

\[
h_{oc} = \frac{1}{U_0} - \frac{d_0}{d_i} \frac{1}{h_{ic}} - \frac{d_0}{d_m} \frac{X}{K_m}
\] (17.16)

where \(K_m = \) thermal conductivity of the tube wall, \(d_m = \) mean diameter of the coil tube.

Observations and Specifications

Data:-
\(n = 11\),
\(d_0 = 1.27 \times 10^{-2} \text{ m}\);
\(D_c = 24 \text{ cm}\);
\(H = D_t = 30 \times 10^{-2} \text{ m}\);
\(C_{pc} = 0.998 \text{ Kcal/(kg}^\circ\text{C)}\)
$C_{ph} = 0.466 \text{ Kcal/(kg} \cdot ^\circ \text{C)}$

$A_0 = \pi d_0 \times \pi D_c \times n = \pi \times 1.27 \times 10^{-2} \times \pi 30 \times 10^{-2} \times 11 = 0.3480 \text{ m}^2$.

mass of oil = $M_h = \pi D^2/4 \times H \times \rho_{oil} = = \pi(30)^2/4 \times 30 \times 0.86 = 18.25 \text{ Kg}$.

Oil Used: - SERVOTHERM medium oil (Essotherm 500 or hytherm 500 oil)

Flow rate of water = 4.0 Kg/min = 240 Kg/hr

$T_h =$ temperature of oil in vessel in $^\circ \text{C}$

$T_{ca} =$ inlet temperature of cold water in $^\circ \text{C}$

$T_c =$ outlet temperature of cold water in $^\circ \text{C}$

**Specimen Calculations**

**Method I**

\[ T_c = T_h(1 - \frac{1}{K}) + \frac{T_{ca}}{K} \{\text{from } y = mx + c\} \] 

(17.17)

$T_h =$ temperature of vessel liquid at any time, $T_c =$ temperature of outgoing cooling fluid, $T_{ca} =$ temperature of incoming cooling fluid. $K$ is determined as follows: Calculate slope using least square method. If $T_c$ is plotted against $T_h$ then

\[ \text{Slope } m = \frac{\sum XY}{S_i^2} \]

Now, $S_i^2 = \frac{1}{n-1}[\sum^n_i X_i^2 - \frac{1}{n}(\sum^1_i X_i)^2]S_X Y = \frac{1}{n-1}[\sum^n_i X_i Y_i - \frac{1}{n}(\sum^1_i X_i)(\sum^n_i Y_i)]$ where $n$ is number of readings

Calculation for flow rate of 4.0 kg/min i.e. 240 kg/hr $\sum T_{h2} = \sum X_i = 1054$; $\sum T_c = \sum Y_i = 684$; $\sum X(i)^2 = 54510$

Therefore $S = \frac{1}{20}[54510 - \frac{1}{20}(1054)^2] = 80.46 \sum X_i Y_i = 34599.75$; therefore $S_X Y = \frac{1}{20}[34599.75 - \frac{1}{20}(1054)(684)] = 13.47$

Slope $m = \frac{\sum XY}{S_i^2} = \frac{13.47}{80.46} = 0.167 = (1 - \frac{1}{K})$ therefore $K = 1.2$

$U_0 = \frac{W_c C_{pe} d \ln K}{A_0} = 3.388 \frac{kcal}{\text{min.m}^2 \cdot ^\circ \text{C}} = 203 \frac{kcal}{\text{hr.m}^2 \cdot ^\circ \text{C}}$

**Method II**

Not applicable, because $T_{ca}$ is not a variable in our experiment.

**Method III**

\[ \ln \frac{T_{hi} - T_{ca}}{T_h - T_{ca}} = \frac{W_c C_{pe}}{M_h C_{ph}} (1 - \frac{1}{K}) \int_0^\theta d\theta \]

(17.18)
$T_{ca} = \text{constant} = 28.5^\circ C$

The graph of $\ln \left( \frac{T_h - T_{ca}}{T_i - T_{ca}} \right) V \theta$, is a straight line passing through origin. Slope is calculated by the method of least squares.

$$Slope = \frac{W_c C_{pc}}{M_h C_{ph}} (1 - \frac{1}{K}) \quad (17.19)$$

Therefore $K = \frac{1}{1 - \frac{\text{slope} \cdot M_h C_{ph}}{W_c C_{pc}}} \therefore$ therefore let $X = ln \left( \frac{t_h - t_{ca}}{t_i - t_{ca}} \right)$

slope for flow rate = 4 kg/min = 240 kg/hr $\sum \theta = \sum X_i = 210 \sum X_i^2 = 2870$

$$S_i^2 = \frac{1}{19} [2870 - \frac{(210)^2}{20}] = 32 \quad (17.20)$$

$$\sum Y_i = \sum ln \left( \frac{t_h - t_{ca}}{t_i - t_{ca}} \right) = 15.25 \sum X_i Y_i = 201.86 \quad (17.21)$$

$$S_{XY} = \frac{1}{19} [201.86 - \frac{1}{20} \cdot (210)^2 (15.25)] = 2.197 \quad Slope = \frac{S_{XY}}{S_i^2} = \frac{2.197}{35} = 0.06728 \quad (17.22)$$

$$K = \frac{1}{1 - \frac{\text{slope} \cdot M_h C_{ph}}{W_c C_{pc}}} = \frac{1}{1 - \frac{0.06728 \cdot 18.25 \cdot 0.446}{43.998}} = 1.083 \quad (17.23)$$

$$U_0 = \frac{W_c C_{pc}}{A_0} = 88.65 \frac{kcal}{hr.m^2.\circ C} \quad (17.24)$$

Method IV

$$\Delta T_{lm} = \frac{T_c - T_{ca}}{\ln \frac{T_h - T_{ca}}{T_i - T_{ca}}} \quad (17.25)$$

$$\int_{T_{hi}}^{T_h} dT_h \Delta T_{lm} = \frac{U_0 A_0}{M_h C_{ph}} \int_0^\theta d\theta = \frac{U_0 A_0 \theta}{M_h C_{ph}} \quad (17.26)$$

A graph of $1/\Delta T_{lm}$ vs $T_h$ is plotted and area under the curve is determined for different intervals of $T_h$, then $U_0$ is calculated.

Flow rate 4 kg/min (240 kg/hr). It may be noted that $A_{th} = \text{indicated area under the curve from } T_{hi} \text{ to } T_h$. $M_h = 18.25 \text{ kg}; C_{ph} = 0.47 \text{ kcal/ (kg } \circ C); A_0 = 0.3480 \text{ m}^2$
Calculation of Heat Transfer Coefficient

For turbulent flow in a straight tube
The following equation was given by Sieder & Tate;

\[
h_{i \text{ straight tube}} = 0.023 \left( \frac{K_i}{d_i} \right) Re_b^{0.8} Pr_b^{1/3} \left( \frac{\mu_b}{\mu_w} \right)^{0.14}
\]  
(17.27)

where \( K_i \) = conductivity of the fluid.

For Helical Coil

\[
h_{ic} = \left( 1 + 3.5 \frac{d_i}{D_c} \right) h_{i \text{ straight tube}}
\]  
(17.28)

\[
K_i = 0.527 \text{ kcal hr.m}^{-2}\text{C}
\]  
(17.29)

\[
Re = \frac{d_i v \rho}{\mu} = \frac{4W_c}{\pi d_i \mu_b} > 10^4 \text{ (Turbulent flow)}
\]  
(17.30)

\[
v = \frac{W}{A \rho Pr^{1/3}} = \left( \frac{C_p \mu}{K} \right)^{1/3} = 1.796
\]  
(17.31)

To Calculate \( h_{OC} \)

\[
\frac{1}{h_{OC}} = \frac{1}{U_0} - \left( \frac{d_0}{d_i} \right) \frac{1}{h_{ic}} - \frac{d_0}{d_m} K_m; d_m = \frac{d_o - d_i}{\ln \frac{d_o}{d_i}}
\]  
(17.32)

\( K_m \) = mean thermal conductivity of the coil material (copper) = 333.72 \text{ kcal hr.m}^{-2}\text{C}

\( x \) = thickness of the tube = \( \frac{d_o - d_i}{2} \) = 1.27 - 0.95

Tabulate the calculated results and comment about the results.
18 Heat Transfer Through Coiled Tubes in an Agitated Vessel (Under Steady-State Conditions)

Aim

Determination of coil side heat transfer coefficient while transferring heat from an agitated liquid in a vessel to cold water flowing through the coil, submerged in the vessel under steady state conditions.

Introduction

Studies on heat transfer in stirred vessels, equipped with a helical coil, are helpful in the design of units like isothermal batch or continuous flow stirred tank reactors. A stirred vessel with a helical coil can also be used a heat exchanger for heating or cooling of process liquors.

The outside coil film heat transfer coefficient, $h_{oc}$, is in general, a function of the physical properties of the vessel liquid, the design, dimensions, speed and location of the stirrer, the geometry of the coil ($d_i$ and $D_c$) and details of construction (flat bottom, hemispherical bottom etc.) , size and condition (baffled or un baffled) of vessel. $h_{oc}$ is correlated in terms of dimensionless groups, incorporating all the variables under consideration.

For dimensionally similar systems,

$$
\frac{h_{oc} D_t}{K} = C \left( \frac{D_a^2 N \rho}{\mu} \right)^d \left( \frac{C_p \mu}{K} \right)^e \left( \frac{\mu}{\rho_w} \right)^f
$$

where $D_t$ = vessel diameter, $D_a$ = agitator diameter, $N$ = agitator speed r.p.h.

The inside coil film heat transfer coefficient, $h_{ic}$, is a function of the physical properties of the coil liquid, its flow rate and the curvature ration ($d_i/D_c$).

Apparatus

The apparatus consists of

1. A lagged, flat bottom cylindrical vessel with a helical coil,

2. A turbine type agitator, connected to a fractional horse power motor, and auto transformer to control the speed of agitator,

3. Precision thermometer to measure the temperature of hot vessel liquid ($T_h$), coil liquid ($T_{c1}$, $T_{c2}$) and jacket side hot water ($T_{j1}$, $T_{j2}$),

4. Stop watch, tachometer etc.

Procedure

1. Clean the copper helical coil with fine emery paper.

2. Change the measured quantity of the, given liquid into the vessel so as to make the depth of the liquid equal to the diameter of the vessel.

3. Fix the stirrer in the vessel in such a way that the depth of the agitator measured from the bottom of the tank is equal to 1/3rd the tank diameter.
4. Keep the stirrer speed at 600 r.p.m. by measuring it with the tachometer.

5. Admit the hot water into the jacket side and constant flow rate (6 to 7 kg/min) and temperature of 600°C.

6. When vessel liquid is heated up to about 400°C admit the cold water through coil at the rate which will give \( Re = 10^4 \) (5Kg/min, 10Kg/min).

7. At the steady state, note down, inlet and outlet temperatures of coil liquid, temperature of vessel liquid, flow rate of cold liquid and speed of agitator.

8. Repeat the above procedure by changing the cold water flow rate for the range of \( 10^4 < Re < 10^5 \).

**Calculations**

1. Heat gained by coil liquid, \( q_c = W_c C_p,c(T_{c2} - T_{c1}) = U_o A_o \Delta T_{lm} \) Kcal/hr, where

   \[
   A_o = (\pi d_o)(\pi d_c n) \text{ m}^2,
   \]

   \( d_o \) = outer diameter of the coil tube

   \( d_c \) = mean helix diameter

   \( n \) = number of turns of the coil

   \[
   \Delta T_{lm} = \frac{(T_h - T_{c1}) - (T_h - T_{c2})}{\ln \frac{T_h - T_{c1}}{T_h - T_{c2}}}
   \]

   Calculate \( U_o \).

2. Calculation of \( h_i \) and \( h_o \) by Wilson’s plot: plot the graph of \( 1/U_o \) vs \( 1/V_i^{0.8} \) and find out the intercept and slope of this graph.
19 Heat Transfer in a Packed Bed

Aim

To determine the wall heat transfer coefficients in a packed bed and establish the relationship between Nusselt number and Reynolds number, further to compare the packed bed heat transfer coefficients, \( h_{ip} \), to those obtained by empty tube for the same flow rates.

Theory

The presence of solid packing increase the wall heat transfer coefficients in a packed bed several times over that in an empty tube at the same fluid flow rate. It is found that the ratio of the coefficients in the packed bed to that in the empty pipe varies in the ratio of diameter of the packing to that of the tube. An enhancement in the wall heat transfer coefficient in a packed bed is due to the turbulence caused by higher local fluid velocity inside the voids of the solid packing. This turbulence tends to prevent the build up of a slow moving layer of fluid next to the wall and also increases the radial heat transfer within the fluid to the tube. Leva has correlated fixed bed heat transfer coefficients over a wide range of variables. Leva’s correlation is given as follows,

\[
\frac{h_{ip}D_I}{k} = 0.813 \left( \frac{D_pG}{\mu} \right)^{0.9} \exp \left( -\frac{6d_p}{D_I} \right) \quad \text{For } dp/dt < 0.35 \quad (19.1)
\]

\[
\frac{h_{ip}D_I}{k} = 0.125 \left( \frac{D_pG}{\mu} \right)^{0.75} \quad \text{For } 0.35 < dp/dt < 0.60 \quad (19.2)
\]

Apparatus

Hot water with constant inlet temperature as heating medium, Platform scale balance, Stop watch, Weighing container and, Auxiliary piping and pumping equipment, Experimental setup as specified.

Experimental Setup

A 5.0 cm i.d. copper tube is fitted with an external jacket. The packing is 3/8" \( \times \) 3/8" raschig rings, filled inside the tube up to 45.7 cm length and rest on a perforated plate, (with 3 mm holes) having 45% hole area. The packed bed exchanger is equipped with thermometers to measure the inlet and outlet temperatures of cold water and hot water flowing respectively on the tube side and jacket side.

Data

Inner diameter of packed tube \( (D_I) = 50 \) mm.
Outer diameter of packed tube \( (D_o) = 60.6 \) mm.
Inner diameter of jacket \( (D_I) \) jacket = 86 mm.
Length of packed test section = 457.2mm.
Raschig Ring Dimensions: Length = 13.6 mm, Inner diameter = 7.6 mm, Outer diameter = 13.6 mm.
Procedure

1. Admit the cold water through the packed tube and set its flow rate to the desired value as indicated by the calibrated Rota meter.

2. Admit hot water through the jacket at 60°C and at constant flow rate of about 10 kg/min.

3. When the steady state is reached, record the inlet and outlet temperatures of cold water and hot water.

4. Determine the exact flow rates of cold water and hot fluid by weighing the liquids collected in a known interval of time (the weight of the liquid collected in a container or bucket should be above 5 kg.

5. Repeat the above procedure for several flow rates. Flow rate of cold water in the packed bed should be in the range of 2 to 7 kg/min for constant operating conditions of heating medium.

Observations

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Flow Rate of cold Water $W_c$, kg/hr</th>
<th>Inlet Temp of cold water $t_{c1}$, °C</th>
<th>Outlet temp of cold Water $t_{c2}$, °C</th>
<th>Flow Rate of hot water $W_h$, kg/hr</th>
<th>Inlet temp of hot water $t_{h1}$, °C</th>
<th>Outlet temp of hot water $t_{h2}$, °C</th>
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</table>

If Steam is used as Heating Medium: Steam Pressure; Steam Temperature $t_s$°C; Steam Condensate Rate, $W_s$ kg/hr.

Method of Calculation

Heat gained by cold water, $q_c = w_c c_p c (T_{c2} - T_{c1})$ kcal/hr
Heat lost by hot water, $q_h = w_h c_p h (T_{h2} - T_{h1})$ kcal/hr.

$q_h = q_c$ (within 5 % error); $q_{avg} = U_i A_i \Delta T_{lm}$ where

$$\Delta T_{lm} = \frac{(T_{h2} - T_{c1}) - (T_{h1} - T_{c2})}{\ln \frac{T_{h2} - T_{c1}}{T_{h1} - T_{c2}}}$$ (19.3)

$A_i =$ inside heat transfer area = $\pi d_i L$ m²,
$d_i =$ inner diameter of the tube, m
$L =$ length of test section, m

Calculate values of $U_i$ for the several runs taken.
Method - I

Calculation of $h_0$:
For laminar flow

$$\frac{h_0 D_e}{k} = 1.86Re^{1/3}Pr^{1/3} \left( \frac{D}{L} \right)^{1/3} \left[ \frac{\mu}{\mu_w} \right]^{0.14}$$

When hot water is used as heating medium in the concentric annulus, $h_0$ can be estimated from the following equations:
For laminar flow:

$$\frac{h_0 D_e}{k} = 1.75 \left[ \frac{WC_p}{K_L} \right]^{1/3} \left( \frac{\mu}{\mu_w} \right)^{0.14}$$  \hspace{1cm} (19.4)

Or, for turbulent flow

$$\frac{h_0 D_e}{k} = 0.023 \left( \frac{D_p \rho}{\mu} \right)^{0.8} \left( \frac{C_p \mu_t}{k} \right)^{0.14} \hspace{1cm} (19.5)

D_e = \text{equivalent diameter} = \frac{D_1 - D_2}{2}

h_0 \text{ and } D_e \text{ are obtained by Wilson's plot, viz, } \frac{1}{U_0 V_0} \text{ vs } \frac{1}{U_i V_i^{0.8}}$$

The hydraulic radius = $4 \times$ cross sectional area/wetted perimeter = $(D_1^2 - D_2^2)/(D_1 + D_2) = D_1 - D_2$

Where $D_1 =$ inner diameter of inner packed tube, $D_2 =$ outer diameter of inner packed tube, and if the flow is intermediate between laminar and turbulent flow regions, use Colburn’s $J_h$ factor charts.

Calculation of $h_i$

1. For clean surfaces

$$\frac{1}{U_i A_i} = \frac{1}{h_0 A_O} + \frac{X}{K_m A_m} + \frac{1}{h_i A_i}$$

Knowing $h_0$, $U_i$ and metal wall resistance, we can calculate $h_i$ from the above equation.

2. Calculate $h_i$ in a packed bed by Leva’s correlations given in equations (1) and (2) and compare them with the experimental value obtained above by equation (8)

Film Coefficients for an Empty Tube

If water flow inside the tube is fully developed turbulent flow, then using Wilson’s plot, viz, $1/U_0$ vs $1/V_i^{0.8}$ to obtain $h_0$ and $h_i$. $V_i =$ superficial fluid velocity inside the packed bed, (m/hr).

Estimation of $h_i$ for an Empty Tube

Calculate the inside film heat transfer coefficient for the empty tube for each of the mass flow rates used. Here $A_i = \pi d_i^2/4$ where $d_i =$ inside diameter of the tube.

Calculate $N_{Re} = \frac{D_i \rho}{\mu}$ and use the appropriate equation to calculate the inside film heat transfer coefficients in circular tubes, from equation given below, depending upon the type of flow. Use Colburn’s $J_h$ factor for the intermediate flow regimes, viz, $2100 < N_{Re} < 10^4$. Compute the ratio of $h_{ip}/h_i$ i.e. wall film heat transfer coefficient of a packed bed relative to that of an empty tube. Tabulate the values of this ratio and plot them against $N_{Re}h_{ip}/h_i$ vs $d_p e/u$

Useful data $C_{pc} = 0.9986\text{ kcal/kg}^\circ\text{C}$, $C_{pb} = 0.9978\text{ kcal/kg}^\circ\text{C}$, $K_{water} = 0.539\text{ kcal/hr.m.}^\circ\text{C}$, $\mu|_{35^\circ\text{C}} = 7.49 \times 10^{-4}\text{ kg/m.s}$
Results

Conclusions
20  Finned Tube Heat Exchanger

Objective

To determine the efficiency of given longitudinal/pin fin and compare it with the theoretical value for the given fin.

Apparatus

1. Longitudinal fin heat exchanger.
2. Pin fin heat exchanger.
3. Bare pipe without fins.
4. Steam generator to generate steam at constant pressure. The steam generator is also provided with temperature indicator and a dead weight safety valve.

Procedure

1. IMPORTANT INSTRUCTIONS: Follow instructions 1 and 2 without fail, otherwise electrical heater will burn out.
2. Open the drain valve provided at the bottom of steam generator and drain out the water from steam generator completely.
3. Close the drain valve and charge 4 lit. of water through charging valve provided at the top of the steam generator and close it. Ensure that the dead weight safety valve is free.
4. Start the electrical heater of steam generator. Initially supply full voltage to the electrical heater. Steam will start forming within about 15-20 min. of switching on the heater. During this period, keep open the valve to one of the test sections (either longitudinal fin heat exchanger or pin fin heat exchanger). Also keep the needle valve at the end of test section open. Once the steam generation starts, the finned tube heat exchanger will start getting heated up and condensate will start coming out of the needle valve provided at the bottom of condensate collector. When the test section (finned tube heat exchanger) is fully heated up, steam will start coming out of the needle valve. Now regulate the needle valve in such a way that only condensate comes out of it. At this point of time also regulate the voltage supplied to the electrical heater so as to keep the pressure in the steam generator constant. The pressure can be regulated between 0-1 atm. gauge as per the requirement.
5. Once the test section (finned tube heat exchanger along with bare pipe without fins) is fully heated, drain out completely the condensate it any. Close the needle valve on condensate drain line simultaneously starting the stop-watch. Collect the condensate accumulated at an interval of 15 min. for finned tube heat exchanger and 30 min. for bare pipe. If the quantity of condensate collected is same for 2 to 3 consecutive readings (within experimental accuracy), note down the volume of condensate collected and time interval.
6. Repeat the procedure given in 4 for pin fin heat exchanger as well as bare pipe.
Theory

In a heat exchanger, the two fluids namely; hot and cold, are separated by a metal wall. Under this condition the rate of heat transfer will depend on the overall resistance to heat transfer given by the equation:

\[
\frac{1}{U_i A_i} = \frac{1}{h_i A_i} + \frac{x}{K A_{lm}} + \frac{1}{h_o A_o}
\]  

(20.1)

where,

- \(U_i\) = Overall heat transfer coefficient based on inner area [Kcal/hr m² °C]
- \(U_o\) = Overall heat transfer coefficient based on outer area [Kcal/hr m² °C]
- \(h_i, h_o\) = Inside and outside film heat transfer coefficients [Kcal/hr m² °C]
- \(A_i, A_o\) = Inside and outside surface area [m²]

When viscous liquids are heated in a double pipe heat exchanger or any standard tubular heat exchanger by condensing steam or hot fluid of low viscosity, the film heat transfer coefficient of the viscous liquid will be much smaller than that on the hot fluid side and will therefore, become controlling resistance for heat transfer. This condition is also present in case of air or gas heaters where the gas side film heat transfer coefficient will be very low (typically of the order of 0.01 to 0.005 times) compared to that for the liquid or condensing vapour on the other side. Since, the heat transfer coefficient of viscous fluid or gas cannot be improved much, the only alternative is to increase the area available for heat transfer on that side so that its resistance to heat transfer can be reduced. To conserve space and to reduce the cost of equipment in these cases, certain type of heat exchange surfaces, called extended surfaces, have been developed in which outside area of tube is increased many fold by fins and other appendages.

Two types of fins, are in common use viz; longitudinal fins and transverse fins. Longitudinal fins are used when the direction of flow of the fluid is parallel to the axis of tube and transverse fins are used when the direction of the flow of the fluid is across the tube. Spikes, pins, studs or spines are also used for either direction of flow.

The outside area of a finned tube consists of two parts: the area of fins and the area of bare tube not covered by the bases of fins. A unit area of fin surface is not as efficient as a unit area of bare tube surface because of the added resistance to the heat flow by conduction through the fin at its base. The expression for fin efficiencies can be derived by solving the general differential equation of heat conduction with suitable boundary conditions. Generally three boundary conditions are used:

1. Fin of infinite length so that there is no heat dissipation from its tip, or in other words temperature at the tip of fin is same as that of the surrounding fluid.

2. Insulated tip. This condition even though cannot be realized in practice, but considering that the tip area is negligible as compared to the total fin area, heat dissipated from tip can be neglected and hence, \(dt/dx\) is assumed to be zero at the tip.

3. Finite heat dissipation from the tip. Even though the assumption of insulated tip is invalid, most of the fins are treated under this category, and longitudinal fin efficiency for this case is given by the expression:

\[
\eta_{fin} = \frac{\tanh(mL)}{mL}
\]  

(20.2)
where
\[ m = \sqrt{\frac{hC}{KA}} \]

- \( m \) = film heat transfer coefficient from the fin surface [Kcal/hr m\(^2\)\(^\circ\)C]\n- \( h \) = circumference of the fin [m]\n- \( C \) = thermal conductivity of fin material [Kcal/hr m\(^\circ\)C]\n- \( A \) = cross-sectional area of fin [m\(^2\)]

From the above equation, it can be seen that the fin efficiency is a function of \( mL \), and as the value of \( mL \) increases, the fin efficiency decreases. A reasonable value of fin efficiency will be around 50 to 75% for which \( mL \) should have a value between 1 and 2. If the fin height \( L \) should be sufficient (of the order of 5 to 8 cm), then it can be seen that the value of \( h \) should be around 10 to 20 which can be given by air in natural convection. The value of film heat transfer coefficient for any other liquid in natural convection, or any gas in forced convection will be much higher than 20. Thus, the given set-up is used for heat transfer to air in natural convection region.

**Observations**

1. Finned Tube:
   1. Height of fin (L) : cm.
   2. Width of fin (W) : cm.
   3. Thickness of fin (b) : cm.
   4. Number of fins (N) : 4
   5. O.D. of fin tube : cm.
   6. Thermal conductivity of fin material (K) : Kcal/hr m\(^\circ\)C

2. Bare Tube:
   1. Length of tube (l) : cm.
   2. O.D. of tube : cm.
   3. \( T_{\text{ambient}} \) : \(^\circ\)C

**Calculations**

1. Circumference of fin (C):
   \[ C = 2(w + b) = m. \] (20.3)

2. Cross-sectional area of fin (A):
   \[ A = wxb = m^2 \] (20.4)

3. Fin area available for heat transfer:
   \[ A_F = CxLxN = m^2 \] (20.5)

4. Tube area available for heat transfer in finned tube heat exchanger:
   \[ A_B = (\Pi D - Nb)xw = m^2 \] (20.6)
5. Total area of finned tube heat exchanger:

\[
A_t = A_F + A_B = m^2
\]  
(20.7)

6. Heat given out by steam through finned tube heat exchanger (\(Q_1\)):

\[
Q_1 = (m_1x)x\lambda = Kcal/hr
\]  
(20.8)

7. Heat given out by steam through bare tube (\(Q_2\)):

\[
Q_2 = (m_2x)x\lambda = Kcal/hr
\]  
(20.9)

where \(\lambda\) = latent heat of vaporization of water at steam pressure (Kcal/Kg)

8. Film heat transfer coefficient from bare tube (\(h\)):

\[
h = \frac{Q_2}{(Ax\Delta T)} = Kcal/hrm^2°C;
\]

\[
A = \Pi DL = m^2;
\]

\[
\Delta T = (T_{steam} - T_{ambient}) = °C
\]

9. \(m = \sqrt{(hC/KA)} =
\]

10. \(mL =
\]

11. \(\eta_{fin} (Theoretical) = \tanh mL/mL
\]

12. Amount of heat actually dissipated by fin:

\[
Q_{fin} = Q_1 - (A_B \times h \times \Delta T) = Kcal/hr
\]  
(20.10)

13. Amount of heat that can be dissipated by ideal fin:

\[
Q_{ideal} = A_F \times h \times \Delta T = Kcal/hr
\]  
(20.11)

14. Observed value of fin efficiency:

\[
\eta(\text{Observed}) = \frac{Q_{fin}}{Q_{ideal}} =
\]  
(20.12)

Conclusion
21 Heat Transfer in Laminar Flow

Objective

To determine the overall heat transfer coefficient making use of logarithmic mean temperature difference. From overall heat transfer coefficient, determine the individual film heat transfer coefficient and verify the Seider-Tate equation for laminar flow heat transfer.

Apparatus

1. Stainless steel double pipe heat exchanger with facility to measure inlet and outlet temperature of hot fluid with accuracy of 0.1°C. The inlet and outlet temperatures of cold fluid is measured with liquid in glass thermometer of 1°C accuracy.


3. Hot fluid circulation pump with speed variation mechanism. Bare pipe without fins.

4. Cold fluid circulation pump with speed variation mechanism. Steam generator to generate steam at constant pressure. The steam generator is also provided with temperature indicator and a dead weight safety valve.

5. An insulated stainless steel tank with bottom discharge to measure the flow rate of hot fluid.

Procedure

1. Connect 15 amp. and 5 amp. plug pins to stable 230 V A.C. electric supply. Care should be taken to connect these two pins in different phases of the power supply.

2. Switch on the dual temperature indicator cum controller. Check the set point of the controller. The set point should be set around 65 to 70°C.

3. Ensure that the valve at the bottom of measuring tank is open. Open the valve on the outlet line of the hot fluid tank. Switch on the power supply to hot fluid circulation pump and slowly increase the speed of the pump by regulating the voltage supplied to it by adjusting the regulator knob. Initially run the pump at slow speed. Check the inlet and outlet temperatures of the fluid indicated by digital thermometer. Note down the temperature difference between inlet and outlet temperatures, which gives zero error. (Digital thermometers can give errors upto 1°C which is generally very difficult to bring down). After noting down the zero error in the digital thermometers, switch on the heater of the hot fluid tank by switching on the D.P. switch (main switches).

4. Connect the suction line of cold fluid circulation pump to cold water supply line. (It is preferable to have 15 - 30 lit. capacity container with bottom outlet connected to pump suction line and cold water supply falling freely in the container to keep water level in it at a constant height. This will ensure constant flow rate of cooling water through the heat exchanger). Adjust the cooling water flow rate through the heat exchanger such that its temperature rise is restricted to about 2 - 3°C. Keep this flow rate constant throughout the experiment.
5. Adjust the flow rate of hot fluid through the heat exchanger by adjusting the speed of hot fluid circulation pump. Measure the flow rate of hot fluid by closing the valve at the bottom of measuring tank and noting down the time required for liquid level to rise between two marks. (The minimum flow rate of hot fluid should at least be 70 c.c./sec. in order to have laminar flow through the heat exchanger). As soon as the liquid level in measuring tank reaches the top mark, open the ball valve at the bottom of the measuring tank in order to avoid the overflow of fluid from the tank.

6. Note down the inlet and outlet temperatures indicated by digital thermometer on the control panel after steady state is reached. Also note down the inlet and outlet temperatures of cooling water.

7. Repeat step 5 & 6 for at least 6 different flow rates of hot fluid.

**Theory**

In a heat exchanger, heat is transferred from hot fluid to cold fluid through metal wall, which generally separates these two fluids. Heat transfer through metal wall is always by conduction while on both sides of metal wall it is generally by convection. Generally resistance offered to heat transfer by the metal wall is negligible as compared to resistance offered by convection. The wall temperature is always between local temperatures of the two fluids. The actual value depends upon individual film heat transfer coefficient on either sides.

At low Reynold’s number \((Re < 2100)\), the flow pattern is laminar and the fluid flows in an ordered manner along generally parallel "Filament like" streams which do not mix. It follows that in this type of flow, that the heat transferred to and through the fluid is essentially by conduction.

When heat is transferred through resistances in series, the total resistance to heat transfer is the sum of individual resistances in series. Thus, for heat exchanger, one can write,

\[
\frac{1}{U_i A_i} = \frac{1}{h_i A_i} + \frac{x}{K A_{lm}} + \frac{1}{h_o A_o}
\]

OR

\[
\frac{1}{U_i} = \frac{1}{h_i} + \frac{\Delta T A_i}{K A_{lm}} + \frac{A_i}{h_o A_o}
\]

Once the heat exchanger material and its geometry is fixed, then the metal wall resistance \(x/K A_{lm}\) becomes constant. Similarly, if the flow rate of cold fluid is fixed and its mean temperature does not differ much for different flow rates of hot fluid, then the resistance by the outside film will remain almost constant. Thus, the overall heat transfer coefficient will depend upon the value of inside film heat transfer coefficient alone. If flow through inner tube is in the turbulent flow regime, then Sieder-Tate equation can be used to predict the inside film heat transfer coefficient.

\[
Nu = 1.86(Re)^{1/3}(Pr)^{1/3}
\]

If the bulk mean temperature does not differ much for different flow rates, then all the physical properties will remain nearly the same and equation (3) can be re-written as:

\[
Nu = \text{constant} \times \text{(velocity)}^{1/3}
\]
Substituting equation (4) in equation (2), one can write it as:

\[
\frac{1}{U_i} = \text{constant}_1 \frac{1}{u^{1/3}} + \text{constant}_2
\]

Thus, the graph of \(1/U_i \) vs \(1/u^{1/3} \) (which is known as Wilson plot) should be a straight line with a slope equal to \(\text{constant}_1 \) and intercept equal to \(\text{constant}_2 \). From this graph, inside film heat transfer coefficient can be calculated which can be used to verify Sieder-Tate equation.

**Observations**

1. Inside diameter of inner tube \((d_1)\) = 1.0 cm.
2. Outside diameter of inner tube \((d_2)\) = 1.27 cm.
3. Inside diameter of outer tube \((D_1)\) = 2.20 cm.
4. Length of heat exchanger \((L)\) = 85 cm.
5. Inner heat transfer area of heat exchanger \((A)\) = m\(^2\)
6. Zero error of hot fluid digital thermometers = °C
7. Volume of measuring tank between bottom and middle mark \((V_1)\) = c.c.
8. Volume of measuring tank between bottom and upper mark \((V_2)\) = c.c.

**Observation Table**

<table>
<thead>
<tr>
<th>Obs.No.</th>
<th>Hot fluid temp. °C</th>
<th>Cold fluid temp. °C</th>
<th>Time reqd for hot fluid level to rise between two marks (t) sec.</th>
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<tbody>
<tr>
<td></td>
<td>inlet ((T_1))</td>
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</table>
### A: Table of Calculated Results

<table>
<thead>
<tr>
<th>Obs. No.</th>
<th>Volumetric flow rate of hot fluid (c.c./sec)</th>
<th>Amount of heat transferred</th>
<th>Velocity of hot fluid</th>
<th>LMTD ( \Delta T_{lm} ) °C</th>
<th>Overall heat transfer coefficient ( U ) (Kcal/hr m²°C)</th>
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<tbody>
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</table>

### B: Table of Calculated Results

<table>
<thead>
<tr>
<th>Obs. No.</th>
<th>( 1/(V^{1/3}) )</th>
<th>( 1/U )</th>
<th>Inside film heat transfer coefficient ( h_i ) (Kcal/hr m²°C)</th>
<th>Nusselt No. ( Nu )</th>
<th>Reynold’s No. ( Re )</th>
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### Calculations

1. Cross-sectional area of inner tube:

\[
S = \frac{\pi}{4}d_1^2 = \text{cm}^2
\]

2. Inside heat transfer area of heat exchanger:

\[
A = \pi d_1 L = \text{cm}^2
\]

3. Prandtl number of hot fluid at mean temperature:

\[
Pr = \frac{C_p \mu}{K} =
\]
Sample Calculation for Reading No. :

1. Volumetric flow rate of hot fluid:

\[ V = \frac{V_1 \text{ (or } V_2)}{t} = \text{ c.c./sec.} \]

2. Velocity of hot fluid through heat exchanger:

\[ u = \frac{V}{\rho} = \text{ cm/sec.} \]

3. Amount of heat transferred:

\[ Q = \left( \frac{V \times \rho \times 3600}{1000} \right) \times C_p \times (T_1 - T_2) = \text{ Kcal/hr} \]

4. Logarithmic mean temperature difference (LMTD):

\[ LMTD = \frac{(T_1 - t_1) - (T_2 - t_2)}{\ln \left( \frac{T_1 - t_1}{T_2 - t_2} \right)} = \circ C \]

5. Overall heat transfer coefficient:

\[ U = \frac{Q}{A \Delta T_{lm}} = \text{ Kcal/hr m}^2 \circ C \]

6. Value of intercept or graph of \( f \) vs \( \left[ 1/(u^{1/3}) \right] \) or \( h_o = 1/\text{Intercept = Kcal/hr m}^2 \circ C \)

7. Inside film heat transfer coefficient:

\[ h_i = \frac{1}{\left( \frac{T_i}{T_f} \right) - \left( \frac{T_i}{T_o} \right)} = \text{ Kcal/hr m}^2 \circ C \]

8. Nusselt’s number:

\[ Nu = \frac{h_i d_i}{K} = \]

9. Reynold’s number:

\[ Re = \frac{d_1 u \rho}{\mu} = \]

Plots

1. Plot the graph of \( 1/U \) vs \( 1/(u^{1/3}) \) on linear scale. (This should be a straight line)

2. Plot the graph of Nusselt number vs Graetz number on log - log scale. Pass a straight line through this and find its slope.

Results

Conclusions
22 Heat Transfer in Turbulent Flow

Aim

To determine the overall heat transfer coefficient making use of logarithmic mean temperature difference. From overall heat transfer coefficient, determine the individual film heat transfer coefficients and verify the Dittus-Boelter equation for turbulent flow heat transfer.

Apparatus

1. Stainless steel double pipe heat exchanger with facility to measure inlet and outlet temperature of hot fluid with accuracy of 0.1°C. The inlet and outlet temperatures of cold fluid is measured with liquid in glass thermometer of 1°C accuracy.
2. A stainless steel insulated tank with a heater.
3. Hot fluid circulation pump with speed variation mechanism.
4. Cold fluid circulation pump with speed variation mechanism.
5. An insulated stainless steel tank with bottom discharge to measure the flow rate of hot fluid.

Theory

In a heat exchanger, heat is transferred from hot fluid to cold fluid through metal wall which generally separates these two fluids. Heat transfer through metal wall is always by conduction while on both sides of metal wall it is generally by convection. Generally resistance offered to heat transfer by the metal wall is negligible as compared to resistance offered by convection. The wall temperature is always between local temperatures of the two fluids. The actual value depends upon individual film heat transfer coefficient on either sides. At higher Reynolds's number ($Re > 10,000$), the ordered flow pattern of laminar flow regime is replaced by randomly moving eddies thoroughly mixing the fluid and greatly assisting heat transfer. However, this enhancement of film heat transfer coefficient is accompanied by much higher pressure drop which demands higher pumping power. Thus, although desirable, turbulent flow is usually restricted to fluids of low viscosity. When heat is transferred through resistances in series, the total resistance to heat transfer is the sum of individual resistances in series. Thus, for heat exchanger, one can write,

$$\frac{1}{U_i A_i} = \frac{1}{h_i A_i} + \frac{\Delta x}{K A_{lm}} + \frac{1}{h_0 A_0}$$

(22.1)

Or

$$\frac{1}{U_i} = \frac{1}{h_i} + \frac{\Delta x A_i}{K A_{lm}} + \frac{A_i}{h_0 A_0}$$

(22.2)

Once the heat exchanger material and its geometry is fixed, then the metal wall resistance ($\Delta x/K A_{lm}$) becomes constant. Similarly, if the flow rate of cold fluid is fixed and its mean temperature does not differ much for different flow rates of hot fluid, then the resistance by the outside film will remain almost constant. Thus, the overall heat transfer coefficient will depend upon the value of inside film heat transfer coefficient alone. If flow through inner tube is in the turbulent flow regime, then Dittus-Boelter equation can be used to find out inside film heat transfer coefficient.

$$Nu = 0.023(Re)^{0.8}(Pr)^n$$

(22.3)
If the bulk mean temperature does not differ much for different flow rates, then all the physical properties will remain nearly the same and equation (3) can be re-written as:

\[ Nu = \text{constant} \times (\text{velocity})^{0.8} \]  \hspace{1cm} (22.4)

Substituting the above equation in equation (2), we get:

\[ \frac{1}{U_i} = \text{constant}_1 \frac{1}{u^{0.8}} + \text{constant}_2 \]  \hspace{1cm} (22.5)

Thus, the graph of \(1/U_i\) vs \(1/u^{0.8}\) (which is known as Wilson plot) should be a straight line with a slope equal to \(\text{constant}_1\) and intercept equal to \(\text{constant}_2\). From this graph, inside film heat transfer coefficient can be calculated which can be used to verify Dittus-Boelter equation.

**Procedure**

1. Connect 15 amp and 5 amp plug pins to a stable 230 V A.C. electric supply. Care should be taken to connect these two pins in different phases of the power supply.

2. Switch on the dual temperature indicator - controller. Check the set point of the controller. The set point should be set around 65 to 70°C.

3. Ensure that the valve at the bottom of measuring tank is open. Open the valve on the outlet line of the hot fluid tank. Switch on the power supply to hot fluid circulation pump and slowly increase the speed of the pump by regulating the voltage supplied to it. Initially run the pump at slow speed. Check the inlet and outlet temperatures of the fluid indicated by digital thermometer. Note down the temperature difference between inlet and outlet temperatures, which gives zero error (Digital thermometers can give errors upto 1°C which is generally very difficult to bring down). After noting down the zero error in the digital thermometer, switch on all the (three) heaters of the hot fluid tank by switching on their respective main switches.

4. Connect the suction line of cold fluid circulation pump to cold water supply line. (It is preferable to have 15 - 30 lit. capacity container with bottom outlet connected to pump suction line and cold water supply falling freely in the container to keep water level in it at a constant height. This will ensure constant flow rate of cooling water through the heat exchanger). Adjust the cooling water flow rate through the heat exchanger such that its temperature rise is restricted to about 3-4°C. Keep this flow rate constant throughout the experiment.

5. Adjust the flow rate of hot fluid through the heat exchanger by adjusting the speed of hot fluid circulation pump. Measure the flow rate of hot fluid by closing the valve at the bottom of measuring tank and noting down the time required for liquid level to rise between two marks. (The minimum flow rate of hot fluid should at least be 40 cc/s. to maintain Reynold’s number above 10,000 in the heat exchanger). As soon as the liquid level in measuring tank reaches the top mark, open the ball valve at the bottom of the measuring tank in order to avoid the overflow of fluid from the tank.

6. Note down the inlet and outlet temperatures indicated by digital thermometer on the control panel after steady state is reached. Also note down the inlet and outlet temperatures of cooling water.

7. Repeat step 5 & 6 for at least 6 different flow rates of hot fluid.
Observations

1. Inside diameter of inner tube \((d_1) = \) cm.
2. Outside diameter of inner tube \((d_2) = \) cm.
3. Inside diameter of outer tube \((D_1) = \) cm.
4. Length of heat exchanger \((L) = \) cm.
5. Inner heat transfer area of heat exchanger \((A) = \) m².
6. Zero error of hot fluid digital thermometers = °C
7. Volume of measuring tank between bottom and middle mark \((V_1) = \) cm³.
8. Volume of measuring tank between bottom and upper mark \((V_2) = \) cm³.

Observation Table

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Calculations

1. Cross-sectional area of inner tube:
   \[ S = \frac{\pi}{4} d_1^2 = \text{cm}^2 \]
2. Inside heat transfer area of heat exchanger:
   \[ A = \pi d_1 L = \text{cm}^2 \]
3. Prandtl number of hot fluid at mean temperature:
   \[ Pr = \frac{C_p \mu}{K} = \]
4. Volumetric flow rate of hot fluid:
   \[ V = \frac{V_1 \text{ (or } V_2)}{t} = \text{c.c./sec.} \]
2. Velocity of hot fluid through heat exchanger:

\[ u = \frac{V}{\rho} \text{ cm/sec.} \]

3. Amount of heat transferred:

\[ Q = \left( \frac{V \times \rho \times 3600}{1000} \right) \times C_p \times (T_1 - T_2) = \text{Kcal/hr} \]

4. Logarithmic mean temperature difference (LMTD):

\[ LMTD = \frac{(T_1 - t_2) - (T_2 - t_1)}{\ln \left( \frac{T_1 - t_2}{T_2 - t_1} \right)} = ^\circ C \]

5. Overall heat transfer coefficient:

\[ U = \frac{Q}{A\Delta T_{lm}} = \text{Kcal/hr m}^2\text{C} \]

6. Value of intercept or graph of f vs \([1/(u^{1/3})](1/h_o)\) = or \(h_o = 1/\text{Intercept} = \text{Kcal/hr m}^2\text{C} \)

7. Inside film heat transfer coefficient:

\[ h_i = \frac{1}{[(\frac{1}{T_i}) - (\frac{1}{h_o})]} = \text{Kcal/hr m}^2\text{C} \]

8. Nusselt’s number:

\[ Nu = \frac{h_i d_i}{K} = \]

9. Reynold’s number:

\[ Re = \frac{d_1 u p}{\mu} = \]

**Plots**

Plot the graph of \(1/U_i\) vs \(1/u^{0.8}\) on linear scale. (This should be a straight line).

**Conclusions**
23 Flow Through Piping Networks

Objectives

1. To identify the different types of pipes, fittings, valves and pumps
2. To visualize the flow through valves and pumps and make sketches of the same
3. To build a network using some of the above components
4. To measure the water flow rate through various sections of the piping network

Theory

The distribution of flow rates of a fluid in piping network is related to the resistance offered by different segments of the network.

Procedure

1. Observe the display of pipes, fittings, valves and pumps in the laboratory. For example note if the threads are on the outside/inside, clockwise/anti-clockwise; how the flanged ends are fitted together (do you need a gasket? why?), the fluid path through the different valves (how are globe and gate valves different? What are they used for? etc.)

2. Observe the partially open centrifugal pump. For example what are the types of impellers used? How are the open type and closed type impellers different? Where are the different impellers used and why? Which is the suction line and which is the discharge line? Is there a need to prime the pump? why?
3. Observe the partially open reciprocating pump and try to answer some of the questions above for this pump.

4. Build a piping network shown in the diagram using some of the available parts.

5. Find the flow rate through a water tap using a large measuring cylinder and a stop watch (what is the error involved in measuring flow rate?)

6. Connect the piping network to the tap and measure the flow rate at A, B and C of the piping network. However make sure that the flow rate out of the source tap is the same as in the earlier step (How would you do that?)

7. Relate the flow rates A, B and C of the piping network to the total inlet flow rate

8. In the hostel/home try to predict the flow rate distribution through the network and see whether your experimental results match your predictions.
24 Nature of Flow

Objectives

- To visually observe laminar and turbulent flow patterns.
- To determine the critical Reynolds number for transition from laminar to turbulent flow.
- To determine the friction-factor and to verify the relationship between $f$ and $N_{Re}$.

Theory

When a fluid flows in a pipe, tube or other conduit, the flow may be laminar or turbulent depending upon the conditions of flow. At low fluid velocities, the fluid moves without lateral mixing, as though a series of concentric conduits are sliding over one another. In such a flow, the streamlines remain distinct from one another over the entire length. This type of flow is called laminar flow. At high fluid velocities, eddies form in the fluids under motion causing lateral mixing and superimposition of turbulence on the primary motion of translation, thus disrupting the entire flow pattern. This type of flow is called turbulent flow.

The type of flow and the magnitude of turbulence is given by Reynolds number which is a dimensionless parameter given by $N_{Re} = \frac{\rho V D}{\mu}$. When the velocity of a fluid flowing in a conduit is gradually increased, the Reynolds number increases and at a particular value of $N_{Re}$, the flow changes from laminar to turbulent; this value of $N_{Re}$ is called upper critical Reynolds number.

Similarly, when the velocity of a fluid flowing at a high velocity in a conduit is gradually decreased, $N_{Re}$ decreases and at a particular value of $N_{Re}$, the flow changes from turbulent to laminar; this value of $N_{Re}$ is called the lower critical Reynolds number.

For a pipe flow, $N_{Re} = \frac{\rho V D}{\mu}$ where $\rho$ is the fluid density, $V$ is the linear velocity, $D$ is the inner diameter of the pipe, and $\mu$ is the fluid viscosity. This may be rewritten as $N_{Re} = \frac{\rho Q D}{A \mu} = \frac{m D}{A \mu}$ where $Q$ is the volumetric flow rate, $m$ is the mass flow rate, and $A$ is the cross-sectional area.

Another significant factor which is useful in the study of flow is the friction factor ($f$) defined as the ratio of wall shear stress to the product of the density and velocity head.

$$f = \frac{\Delta P g_c D}{2 L \rho V^2}$$

where $\Delta P$ is the pressure drop and $L$ is the length of the pipe. For laminar flow, $f = \frac{16}{N_{Re}}$. For turbulent flow,

$$f = 0.046 N_{Re}^{-0.2} \quad (50000 < N_{Re} < 10^6)$$
$$f = 0.0014 + (0.125 / N_{Re}^{0.32}) \quad (3000 < N_{Re} < 3 \times 10^6)$$

Procedure

1. Allow the water to fill the equipment and adjust the flow rate to the lowest possible value.

2. Adjust the flow rate of the dye solution so that its flow rate is the same as the velocity of water.
3. Note the two tank heights for every flow rate and observe the flow for different flow rates indicated by the dye solution.

4. Measure the volumetric flow rate using a measuring vessel and a stop watch.

5. Increase the flow rate of water in small increments and repeat the above steps.

6. From the highest flow rate decrease the flow rate in small decrements, and repeat the above steps.

Results

1. For each run comment on the observed characteristics of the dye flow.

2. Calculate the volumetric flow rate, linear velocity, friction factor and Reynolds number.

3. Determine the critical Reynolds number for the transition from laminar to turbulent flow, when the flow rate is increased in small steps. Is it the same for the transition of turbulent to laminar flow when flow is decreased in small steps?

4. Plot the graph of $f$ versus $N_{Re}$ and comment on the graph.

Frictional Losses in Pipe Fittings and Valves

Objectives

1. To determine the frictional losses across pipe fittings in a piping network
2. To determine the frictional losses across valves in a piping network

Theory

The resistance offered by a fitting is expressed as equivalent to the resistance offered by a length of a straight pipe of the same diameter as that of the fitting. This length is called the equivalent length of the fitting and length is expressed as the number of diameters of the pipe. Another method of expressing the resistance or frictional losses (FL) in fittings is by the number of velocity heads in a pipe of the same diameter

\[ FL_{fitting} = \frac{Kv^2}{2g} \]  

(25.1)

where \( K \) is the frictional loss constant, \( v \) the velocity and \( g \) the acceleration due to gravity. The pressure difference across fitting can be measured by a manometer or a pressure transducer

Procedure

1. Start the pump and wait until water flows in all sections of the piping network of interest in a steady state.
2. When steady is achieved measure the readings in the manometers across the fittings of interest.
3. Find flow rate of water. Find the frictional loss across each fittings and express the losses in terms of equivalent length and velocity heads.
26  Viscosity Measurement

Objectives

1. To measure the viscosity of a polymer solution using a Brookfield viscometer
2. To find the viscosity at various concentrations of the polymer

Theory

The resistance offered to flow is related to the viscosity of the liquid. A Brookfield viscometer uses this principle to determine the viscosity of a liquid.

Procedure

1. Familiarize yourself with the various adjustments on the Brookfield viscometer (rpm, spindle, start/stop etc?)
2. Prepare a solution of the given polymer in water
3. Determine the dial reading for that solution.
4. Convert the dial reading into viscosity using the monogram for the viscometer.
27 Agitation and Mixing

Objectives

1. To measure the power number for a agitated system
2. To relate the power number and Reynolds number in an agitated system

Theory

The Power number, $N_p$, is given as:

$$N_p = \frac{P}{\rho N^3 d^5}$$  \hspace{1cm} (27.1)

where $P$ is the power utilized for agitation, $\rho$, the fluid density, $N$, the impeller speed and $d$, the impeller diameter. The Reynolds number $N_{Re}$, for an agitated system is given by:

$$N_{Re} = \frac{\rho N d^2}{\mu}$$  \hspace{1cm} (27.2)

where $\mu$ is the fluid viscosity.

Procedure

1. Place the given viscous liquid in a mixer system and agitate it by setting the impeller speed to a particular value.
2. The torque developed can be measured by the dynamometer arrangement
3. Also, measure the impeller speed, impeller diameter and the temperature.
4. Vary the agitation speed using the variac.
5. Find the Power number and the Reynolds number for each run
6. Represent the relationship between Power number and Reynolds number, graphically.
Two Phase Flow in Vertical Tubes

Objectives

1. To visually observe the motion of a single slug and investigate experimentally the relation between the slug velocity and slug dimension.

2. To investigate experimentally the relation between gas flow rate and the gas volume fraction (void fraction) for the slug flow regime in two phase gas/liquid flow in a vertical tube.

Introduction

Two phase gas / liquid flow is important in a variety of chemical engineering applications such as the simultaneous transport of the gas and oil in horizontal pipelines or a vertical wells several flow regimes can occur, depending on many factors, including the orientation of the pipe the individual magnitudes of the liquid and gas flow rates and physical properties such as density, surface tension and viscosity.

For vertical pipes (the situation here), there are four principal flow regimes shown in Fig. 28.1 and which occur successively at ever increasing gas flow rates.

Figure 28.1: Two-phase flow regimes in a vertical tube: (a) bubble, (b) slug, (c) annular, and (d) mist flow. In each case, the gas is shown in white and the liquid is shaded or black.
1. Bubble flow in which the gas is dispersed as small bubbles throughout the liquid which is the continuous phase.

2. Slug flow in which the individual small bubbles have started to coalesce together in the form of slugs. The liquid phase is still continuous.

3. Annular flow in which the fast moving gas stream is now a continuous phase that encompasses central portion of the tube with the liquid forming a relatively thin film on the tube wall.

4. Mist flow in which the velocity of the continuous gas phase is so high that it reaches as far as the tube wall and entrains the liquid in the form of droplets.

In the experiment, you will be investigating the slug flow regime for the flow of air and water in the tube. In this regime, surface tension and viscosity are possibly relatively unimportant, especially in the tube of larger diameter: also, the liquid density plays only a small role in determining the shape of the slugs, but is important if pressure-drop calculations are needed.

**Principles and Theory**

The general situation is shown in the Fig. 28(a), in which the gas (air) and liquid (water) are traveling upwards together at individual volumetric flow rates $G$ and $L$ respectively, in a tube of internal diameter $D$. In general, there will be an upward liquid velocity $U_{Lm}$ across a plane A-A just ahead of gas slug. By applying continuity and considering the gas to be incompressible over short distances, the total upward volumetric flow rate of liquid across A-A must be the combined gas and liquid flow rates entering at the bottom, namely $G=L$. The mean liquid velocity at A-A is therefore $U_{Lm} = (G+L)/A$, where $A$ is the cross-sectional area of the tube.

Next, consider Fig. 28(b) which shows a slightly different situation: that of a single bubble, which is moving steadily upwards with a rise of velocity $U_b$ in an otherwise stagnant liquid. For liquid such as water and light oils that are not very viscous, the situation is one of the potential flow in the liquid. Under circumstances, Davies and Taylor[2] used on approximate analytical solution that gave

$$U_b = 0.35 \sqrt{gD} \quad (28.1)$$

in which $g$ is the gravitational acceleration. As part of this project, you will also be attempting to test equation 28.1 against both experiment and theory and possibly to determine a more appropriate value of the constant than 0.35

The situation of Fig. 28(a) is now shown enlarged in Fig. 28(c). The slug is no longer rising in a stagnant liquid as in Fig. 28(b) but in a liquid whose mean velocity just ahead of it is $U_{Lm}$. Further, near the "nose" O of the slug-at the center of the tube, where the velocity is the highest-the liquid velocity will be somewhat larger, namely about $1.2U_{Lm}$ as shown by Nickin, Wilkes, and Davidson[1] provided that the Reynolds number between slugs exceeds 8,000. Therefore, the actual rise velocity of the slug will be

$$U_s = 1.2 \frac{G+L}{L} + U_b = 1.2 \frac{G+L}{L} + 0.35 \sqrt{gD} \quad (28.2)$$

Now, by conservation of the gas we must have

$$G = U_s A\epsilon \quad (28.3)$$
Figure 28.2: Two-phase flow in a vertical tube: (a) gas and liquid ascending, (b) bubble rising in stagnant liquid, (c) bubble
in which \( \epsilon \) is the void fraction (the fraction of the total volume that is occupied by the gas). Hence, eliminating \( U_s \) between Equations 28.2 and 28.3 we obtain

\[
\frac{G}{\epsilon A} = 1.2 \frac{G + L}{A} + 0.35 \sqrt{gD}
\]

If \( G \) and \( L \) are known, Equation 28.4 gives the void fraction, which is very important in determining the pressure drop in a tube of height \( H \). Also note that the weight of the liquid, which occupies fraction \( (1 - \epsilon) \) of the total volume, is much greater than that of gas. Therefore, the Pressure drop is given to the first approximation by

\[
P_1 - P_2 = \rho L g H (1 - \epsilon)
\]

A secondary correction to Equation 28.5 would include the wall friction on the liquid "pistons" between successive gas slugs.

**Equipment**

A 12.5 mm diameter plastic tube of length 1.5 m is connected to air and water supply systems. Two flow meters for measuring flow rates of air and water (0-20 Ls\(^{-1}\) and 0-2 Ls\(^{-1}\)) are connected to respective supply line. A one HP motor pump is used in this experiment Values are for controlling the air and water supply.

**Procedure**

1. By turning the air flow on and of suddenly, form isolated single slugs. By measuring time taken to move up a known distance, determine the rise velocity. Use wide spectrum of slug lengths as possible and note down the slug length as accurately as you can in each case. Take plenty of measurements (at least 30).

2. Operate with a steady continuous stream of air so there is no net water flow rate: that is, with \( L = 0 \), Measure the volumetric flow rate of air \( G \), m\(^3\)s\(^{-1}\), the slug rise velocity, \( U_s \), ms\(^{-1}\), and (by quickly closing the valves in the tube) the void fraction, \( \epsilon \). Repeat for the variety of flow rates.

**Data Analysis**

1. For single slugs of air in stagnant water, Plot the rise velocity, \( U_b \) against the slug length to see if they are correlated. Compare with theory and discuss.

2. For steady slug flow, plot gas volume fraction with the gas flow rate. Compare with theory and discuss.
29 Determination of Partial Molar Enthalpies by Adiabatic Calorimetry

Objective

To determine the heat of mixing of binary system by adiabatic calorimetry and the partial molar enthalpies of two components.

Introduction

Calorimetry involves measurements of enthalpy changes in various processes like mixing, dilution, dissolution, crystallization, adsorption or in a chemical reaction. In addition, it is used for the determination of heat capacities. Calorimetry can be of two types: adiabatic or isothermal. In an adiabatic calorimeter no heat is exchanged with surroundings and hence temperature change is to be monitored during the process occurring in the calorimeter. In such a case the accuracy of measurement of any physical property using a calorimeter depends on the accuracy of temperature measurement and how good the adiabatic shield is.

A vacuum flask/Dewar flask is used as an adiabatic calorimeter. However, minute "heat leaks" are not uncommon. In order to reduce heat flow to or from the surroundings, the Dewar flask itself should be placed in a constant temperature container such as a large thermostat or insulated box whose temperature should be regulated as close to the contents of the Dewar flask as possible. Care should be taken so that "heat leak" does not occur through either the lid of the Dewar flask or openings in the lid. If the instrument is sensitive enough, stirring of the contents would also be controlled and its effect should be monitored in a blank experiment. Figure 29.1.

![Diagram of a Calorimeter](image.png)

Figure 29.1: A schematic diagram of a Calorimeter. D = Glass Dewar Flask of capacity 100 ml, S = Polypropylene Stopper, H = Resistance Heater, ST = Stirrer, T = Temperature Sensor
**Procedure**

**To find water-equivalent of calorimeter**

Since the various parts such as stirrer, heater, temperature sensor, stopper and walls of the flask absorb some heat it is necessary to know the calorimeter water-equivalent, $K$. For this purpose a known amount of heat, $Q$ (Joules) is supplied to the calorimeter containing (say) $m$ gm of water of heat capacity ($C_p$ (J/g K)). If $\Delta T$ is the observed temperature change, then:

$$Q = mC_p\Delta T + K\Delta T$$  \hspace{1cm} (29.1)

Hence $K$ can be calculated from Equation 29.1 the other quantities being known experimentally.

**To find heat capacity of a pure liquid or a solution**

As shown in Figure 29.1 the calorimeter is provided with a heating coil (in the form of a resistor). If a known current $I$ (amp) is passed for time $t$ (sec) through the heating coil. "Joule heating" will cause the temperature of the system to increase by (say) $\Delta T_h$ ($^\circ$C). The amount of energy supplied ($Q$) is

$$Q = IVt \text{ in Joules}$$  \hspace{1cm} (29.2)

where $V$ is the voltage drop across the heater resistance. Combining Equations 29.2 and 29.1

$$IVt = mC_p\Delta T + K\Delta T$$  \hspace{1cm} (29.3)

Using this equation, $C_p$ of a pure liquid of a solution may be determined (the other quantities being known experimentally).

**Experimental Measurements**

1. Find calorimeter constant $K$ by the procedure outlined above.


3. Add a certain volume of (but take weight) first liquid (1) to the calorimeter.

4. Allow thermal equilibrium to be attained and note the initial temperature $T_1$.

5. Add a known volume (take weight) of the second liquid (2). Stir and note the final and steady mixture temperature $T_2$. The resultant temperature change due to mixing is $\Delta T_m = (T_2 - T_1)$; this will be negative or positive depending on the sign of heat of mixing of the system. Note this $\Delta T_m$ against the mole fraction $x_1$ of liquid 1 in the final mixture. During this part of the experiment, the heating coil is kept "off". The total volume of the mixture should be about 85-90 ml.

6. Next the heating coil is switched on and the specific heat ($C_{pm}$) of the mixture is measured as outlined above in section "B". Again $\Delta T_h$ should be at least 3-4$^\circ$C.

Repeat the two previous steps (finding the heat capacity of a pure liquid, and generating experimental measurements) so that you obtained a range of $\Delta T_m$ and $C_{pm}$ corresponding to mole fraction $x_1$ ranging from 0 to 1.
Note that mixing occurs under non-isothermal conditions. It follows, therefore, if isothermal conditions of mixing were to be maintained, an amount of energy $Q_m$ would have to be added (or withdrawn), where

$$Q_m = (mC_{pm} + K)(-\Delta T_m) \quad (29.4)$$

where $m$ = total mass of the mixture.

**Calculations**

1. Estimate the quantity $Q_m$ for each composition of the mixture. Take at least 4-5 compositions,

2. Heat of mixing $\Delta h_m$ per mole solution, at mole fraction $x_1$ is given as $\Delta h_m = Q_m/(n_1 + n_2)$ Joules/mole, ($n_1$, $n_2$ = moles of components 1 and 2 in the mixture). Plot $\Delta h_m$ vs. $x_1$.

3. Calculate the partial molar enthalpies at the composition $x_1 = 0.5$ and $H_1^\infty$ & $H_2^\infty$.

4. Comment on the nature of the $\Delta h_m$ vs. $x_1$ curve with reference to the molecular properties of the components forming the mixture.
30 Ebulliometric Determination of Vapour Pressures

Objectives

1. To determine the vapour pressure at various temperatures for a pure substance and to calculate the correlation constants in the vapour pressure equation.

2. Estimation of the latent heat of vaporization for the substance from the vapour pressure data.

Introduction

When the vapor phase of a pure fluid is in equilibrium with its liquid phase, the equality of chemical potential, temperature, pressure in both phases leads to the Clausius-Clapeyron equation:

\[
\frac{d \ln P}{d(1/T)} = - \frac{\Delta H}{R \Delta Z_v} \tag{30.1}
\]

Most vapour pressure estimations and correlation equations stem from integration of Equation 30.1. When this is done, an assumption must be made regarding the dependence of the group \( \Delta H_v/\Delta Z_v \) on temperature. The simplest approach is to assume that the \( \Delta H_v/\Delta Z_v \) is constant and then Equation 30.1 on integration becomes (\( A \) being the integration constant):

\[
\ln P = A - \frac{B}{T} \tag{30.2}
\]

(\( T \) in K, and \( \Delta Z_v = Z_{vap} - Z_{liq} \), \( Z \) being the compressibility factor). The above equation is called Clausius-Clapeyron equation where, \( B \) is given as \( \Delta H_v/R\Delta Z_v \) (\( \Delta H_v \) = enthalpy of vaporization). A simple modification of the equation which has been widely used is known as Antoine equation:

\[
\ln P = A - \frac{B}{T + C} \tag{30.3}
\]

\( C = \) Constant, \( T = ^{\circ}C \). As an approximation at low pressures (< 1 atm), if \( \Delta Z_v \) is taken as 1.0, the latent heat of vaporization can be directly obtained from the slope of the plot of \( \ln P \) vs. \( 1/T \).

Experimental Procedure

1. Accurate data on equilibrium vapor pressures can be determined over a range 100 to 760 mm Hg using a specially designed glass ebulliometer connected to a manifold and pressure control system. The sample of the liquid, or solution whose vapour pressure is to be measured is, charged to fill the bulb of the ebulliometer. When the bulb is electrically heated, slugs of vapor bubbles with entrapped liquid rise in the tube (Cottrell Pump) to the flask chamber and are poured on the inner surface of the thermowell where vapour bubbles get disengaged from the liquid. The liquid stream along with the condensed vapor is recirculated till equilibrium is attained. The equilibrium state is indicated by the constancy of both the thermowell temperature and of the vapour condensation drop-rate through the drop-counter. The pressure of the ebulliometer is regulated via a stop-cock, the pressure being recorded by means of an absolute manometer. Electrical heating is regulated in order to minimize superheating and the ebulliometer is adequately insulated in order to minimize heat loss resulting in any subcooling of the liquid.
2. Once the pressure in the manifold is fixed at any value, the system will on its own adjust to the corresponding equilibrium temperature. Allow at least 20-25 minutes for this, but note the change of temperature with time (not needed to be reported in journal) so that you know when a steady temperature is reached.

3. Once temperature steadies, count the drop rate (per minute) of condensed vapour.

4. This drop rate is proportional to the steady state amount of the substance in the vapor phase (which is, of course, being condensed back into liquid). For vapour-liquid equilibrium the system $T$ remains constant as quality ($x$) going from 0 to 1. Experimentally low drop rate ($< 30$/min) correspond to low values of $x$, while very high drop rates ($> 110$/min) indicate high value of $x$. Experimentally both these extremes need to be avoided as these may make the system exist either in the supercooled or superheated region, which will yield an inaccurate equilibrium temperature measurement for a given pressure. At an intermediate drop rate the system is likely to be in the two-phase region with a medium quality. The temperature measured under such a condition will provide a relatively accurate equilibrium value of temperature.

5. Adjust the heat input to the ebulliometer bulb using the rheostat so that you obtain a drop rate in the intermediate range (40-90/min). The rheostat is very sensitive; no more than a change by a graduation is recommended at a time. After any such change, wait for system temperature to stabilize and then measure the drop rate.

6. Once you obtain a stable drop-rate in the intermediate range (and a corresponding temperature), change the rheostat reading by half a graduation (either increase or decrease as needed; note that increase in rheostat reading would increase heat input, and hence also the drop rate of condensed vapor), keeping the same pressure, and obtain another drop rate preferably within the same range, and note the stable temperature. Report the average of the two temperatures as the equilibrium temperature corresponding to the pressure of the manifold.

7. Obtain $P$ vs. $T$ data for at least 8 pressures in the range 100-760 mm Hg.

**Calculations**

1. Plot $\ln P$ vs. $1/T$.

2. Determine the correlation constants in the vapour pressure equation.

3. If the units of $P$ are changed from mm Hg to atm or Kg/cm$^2$, how does the behavior of the curve change?

4. Estimate latent heat of vaporization from the plot in (1).

5. How does the latent heat change with increasing temperature and pressure over a wide range? Under what condition is $\Delta H_v$ zero? Why?

6. The latent heat of vaporization is generally seen to be dependent on properties such as molecular weight and polarity. Explain why these properties are determinant to the enthalpy of vaporization.
31 Ebulliometric Determination of the ‘Infinite Dilution Activity Coefficient’ (IDAC)

Aim

1. To determine the value of the "Infinite Dilution Activity Coefficients" (IDAC) of a binary at 1 atm pressure using differential ebullometry and the limiting slope method.

2. To estimate the parameters in the activity coefficients correlations such as Van Laar/Wilson.

Theory

The greatest deviation from ideal solution behaviour occurs at infinite dilution. The infinite dilution activity coefficients are, therefore, appropriate indices to the degree of non-ideality of a solution. Further, the knowledge of infinite dilution activity coefficients allows phase equilibrium calculation to be performed as they may be used to determine the parameters of the activity coefficient model suitable for the binary mixture. Experimental determination of IDACs is based upon the following theoretical consideration. If the vapour phase is assumed to be ideal and the Poynting correction is negligible then the total system pressure at vapour-liquid equilibrium is given by:

\[ P = \gamma_1 P_1^0 x_1 + \gamma_2 P_2^0 x_2 \]  

(31.1)

\( P_i^0 \) = sat vapour pressure of the \( i^{th} \) species at the given temperature. This equation is differentiated at constant temperature to give:

\[ \frac{dP}{dx_1} = P_1^0 \left[ x_1 \frac{d\gamma_1}{dx_1} + \gamma_1 \right] + P_2^0 \left[ x_2 \frac{d\gamma_2}{dx_2} + \gamma_2 \right] \frac{dx_2}{dx_1} \]  

(31.2)

If we let \( x_1 \) approach zero and use the following relations:

\[ \frac{dx_2}{dx_1} = -1; \quad \frac{d\gamma_1}{dx_1} \text{ is finite at } x_1 = 0 \quad \gamma_2 \to 1 \quad x_2 \to 1 \quad \frac{d\gamma_2}{dx_2} \to 0 \quad P \to P_2^0 \]

Hence we get:

\[ \gamma_i^\infty = \frac{P_2^0 + (dP/dx_1)^\infty}{P_1^0} \]  

(31.3)

The following general relationship of the partial derivatives exists for the variables \( T \), \( P \) and \( x_1 \):

\[ \frac{\partial P}{\partial x_1} = - \left( \frac{\partial P}{\partial T} \right)_{x_1} \left( \frac{\partial T}{\partial x_1} \right)_P \]  

(31.4)

Evaluated at \( x_1 = 0 \), this becomes

\[ \left( \frac{\partial P}{\partial x_1} \right)^\infty_T = - \left( \frac{\partial P}{\partial T} \right) \left( \frac{\partial T}{\partial x_1} \right)^\infty_P \]  

(31.5)

Substituting (31.5) in (31.3) the value of \( \gamma_1^\infty \) can be obtained from isobaric data using the relation,

\[ \gamma_1^\infty = \frac{P_2^0 - (dP_2^0/dT)(dT/dx_1)^\infty}{P_1^0} \]  

(31.6)
If the Antoine’s equation for vapour pressures is used then,

\[
\frac{dP_0^2}{dT} = \frac{P_0^2 B}{(T + C)^2}
\]

(31.7)

where \( B \) and \( C \) are the Antoine constants for the component 2.

Further \( dT/dx_1|_P^\infty \) can be obtained from the limiting slope of the \( T \) vs \( x_1 \) curve as \( x_1 \to 0 \) by plotting the solution boiling temperature \( T \) versus mole fraction \( (x_1) \).

**Procedure**

Accurate data on infinite dilution activity coefficients can be obtained using ebulliometers. Three or four ebulliometers are connected to a manifold and a common pressure control system. The pure solvent \( (2) \) is charged to one of the ebulliometers and very dilute solutions of known concentrations of solute \( (1) \) (typically, in the range 0 – 5 mol percent) are charged to the remaining ebulliometers, each charge having a different concentration of the species (solute 1) present in dilute amounts. Since extremely small boiling temperature differences can be detected between that of the pure solvent and that of solutions, very dilute solutions may be used, thus increasing the accuracy of determination of the slope \( dT/dx_1|_P^\infty \).

1. Set the pressure of the entire manifold at the fixed value (typically it may be atmospheric) and switch on the heating supply to each ebulliometer. After the temperature has steadied for each ebulliometer, count the average drop rate of condensation of vapor per minute and record it against the temperature.

2. Alter the heat input to each ebulliometer by a very small amount (typically by about half a graduation on the rheostate controlling the heat input) and record any ensuing change of temperature. Ideally, the temperature should alter by a very small amount (if at all) and at its altered steady value measure the average drop rate as before.

3. For each ebulliometer obtain at least 3 – 4 sets of temperature and drop rate (which should not exceed 100/min) measurement.

**Calculations**

1. Plot temperature vs. Drop rate for each dilute solution separately. Extrapolate to zero drop rate to get the bubble point temperature of solution (why?)

2. Plot bubble point temperature vs. concentration (i.e. \( T \) vs. \( x_1 \)) to find the slope of the best straight line. Calculate \( \gamma_1^\infty \) using this slope and correlations developed in the preceding section.

3. Repeat the above for the other dilute and (with species 2 in dilute solution in species 1) to calculate \( \gamma_1^\infty \) (This data may be taken from the complementary experiment carried out by other groups).

4. At what temperature have \( \gamma_1^\infty \) and \( \gamma_2^\infty \) have been calculated? Does your system exhibit positive or negative deviation from Raoult’s law?

5. Determine the Van Laar or Wilson’s parameters and compare with literature data, if available.
Determination of the Dynamic Surface Tension of a surfactant by using Bubble Pressure Tensiometer

Aim
To determine the dynamic surface tension of a given surfactant solution using a maximum bubble pressure tensiometer.

Apparatus and Instruments
Volumetric flasks, conical flasks, beakers, pipette, bubble pressure tensiometer, etc.

Chemicals
Sodium dodecyl sulphate solution, acetone, distilled water.

Theory
1. Dynamic surface tension

With conventional surface tension measuring methods, such as the Wilhelmy plate method, the static surface tension is obtained, i.e. a statement is made about a completely formed surface which is in dynamic equilibrium. Surfactant solutions require a much longer time than water and other liquids to achieve this dynamic equilibrium. This is because of the molecular construction of the surfactants: they consist of a hydrophilic (water-attracting) "head" and a hydrophobic (water-repelling) "tail". As a result of this construction, the surfactant molecules accumulate at the surface; the "tail" projects from the surface and causes a reduction in the surface tension.

2. Dependency of the surface tension on the concentration

In addition to the chemical structure, the concentration also has a decisive influence on the surface tension. The equilibrium value of the surface tension decreases as the number of surfactant molecules
accumulating at the surface increases. It achieves its final value when the surface is completely occupied and offers no place for further molecules. If the concentration is further increased from this point then the surfactant molecules will accumulate within the solution and form aggregates, the so-called "micelles". The concentration at which this effect occurs is known as the "critical micelle formation concentration" (CMC). It is an important characteristic for surfactants. This means that methods for measuring the dynamic surface tensions should only be used above the CMC. In such a case the concentration only influences the chronological function of the surface tension and no longer has any influence on its static value. The following illustration shows the measuring ranges of static and dynamic methods (e.g. the bubble pressure method):

Figure 32.3: Schematic image of a micelle

Figure 32.4: Ranges of static and dynamic measuring methods

3. The bubble pressure method

An easy-to-use method for determining the dynamic surface tension is the method of measuring the maximum bubble pressure. In a bubble pressure tensiometer gas bubbles are produced in the sample liquid at an exactly defined bubble generation rate. The gas bubbles enter the liquid through a capillary whose radius is known. During this process the pressure passes through a maximum whose value is recorded by the instrument. The following illustration shows the pressure curve during bubble formation plotted as a function of time:

Figure 32.5: Bubble formation with time

1. The bubble is formed. Initially the pressure is below the maximum pressure; the radius of curvature of the air bubble is larger than the radius of the capillary.

2. The pressure curve passes through a maximum. At this point the air bubble radius is the same as that of the capillary; the air bubble forms an exact hemisphere. The following relationship exists between the maximum pressure \( \rho_{\text{max}} \), the hydro-static pressure in the capillary \( \rho_0 \), the inner radius \( r \) of the capillary and the surface tension:

\[
\sigma = \frac{(\rho_{\text{max}} - \rho_0)r}{2}
\]

3. After the maximum the "dead time" of the measurement starts. The pressure decreases again, the radius of the air bubble becomes larger.

4. The bubble finally escapes from the capillary and rises. The cycle begins again with the formation of the next bubble.
4. Variation of surface tension with the bubble frequency

For pure solvents the dynamic surface tension does not change with the bubble rate. In case of multi component solution, the surface tension increase with the increasing bubbling frequency. At higher frequency the surfactant molecule does not have adequate time to diffuse to and orient them at the gas/liquid interface. Hence the surface tension increases.

Figure 32.6: Surface tension versus bubble frequency

Experimental Procedure

1. Measure the dynamic surface tension of pure acetone and pure water.

2. Make a 50 mM Sodium dodecyl sulphate (SDS) solution and measure its surface tension at a bubble frequency of 1 Hz.

3. Increase the bubble frequency to 2 Hz and note the surface tension.

4. Repeat the third step by increasing the bubble frequency by one unit, till the bubble frequency is 10 Hz.

5. Record the observations in a tabular form and plot a graph of dynamic surface tension of SDS solution v/s bubble frequency.

Questions

1. What are the different methods used for measurement of surface tension? Explain in brief.

2. What are the different types of surfactants? Explain each type with examples.
33 Vapour Liquid Equilibrium

Aim

To determine the vapour-liquid equilibrium data for the given binary system. (A = more volatile component. B = less volatile component).

1. To check the thermodynamic consistency of the data.

2. To present the thermodynamic characteristics and constants of Margules equation for the given system.

Theory

Vapour-liquid equilibrium data are the basic information of the system required for the design of equilibrium stages of a vapour-liquid separation equipment like distillation. Equilibrium data represent the composition of the mixture in the vapour phase \((Y)\) and that in the corresponding equilibrium liquid phase \((X)\) at equilibrium. The compositions are presented in mole fractions of the more volatile component \((A)\). Equilibrium compositions are functions of temperature and pressure. Therefore the data are reported under isothermal or isobaric conditions. However, isobaric data are required more often because industrial separations are carried out at constant pressure.

1. The vapour-liquid equilibrium data are presented as equilibrium compositions:

\[ Y_A = \frac{P_A}{\pi_A} \gamma_A X_A = K_A X_A \quad (33.1) \]

2. Relative Volatility:

\[ \alpha_{AB} = \frac{Y_A/(1 - Y_A)}{X_A/(1 - X_A)} \quad (33.2) \]

3. The Gibb’s-Duhem equation for the binary system for checking thermodynamic consistency of the data by the integral test:

\[ \int_0^1 \frac{\ln \gamma_1}{\gamma_2} dX_A = 0 \quad (33.3) \]

4. The Van Laar equations are

\[ \log \gamma_A = \frac{a}{1 + \frac{aX_A}{bX_B}} \]
\[ \log \gamma_B = \frac{b}{1 + \frac{bX_B}{aX_A}} \quad (33.4) \]

Many systems form an azeotrope where the equilibrium vapour and liquid compositions are the same i.e. \(Y_A = X_A\)

Experimental setup

The apparatus shown in Figure 33.1 is known as a vapour-liquid equilibrium still and has two essential parts: (1) Vaporizer, (2) Flash chamber or Equilibrium chamber. The binary liquid mixture is vapourized by an electrical heating coil in the vaporizer at a slow rate. The vapour from this rises to the equilibrium chamber. Vapour and liquid equilibrium at the temperature and pressure
Figure 33.1: Schematic diagram of VLE setup
of the chamber is established. The temperature or the chamber is recorded by the thermometer which extends well inside the equilibrium chamber. The pressure of the chamber may be regulated by connecting the vapour line to vacuum or pressure header. The vapour and liquid phases separate from each other in the flash chamber. The liquid flows down the liquid line through a water cooled joint to the feeder line, through which the mixture again goes back to the vaporizer. The still may be drained through the feeder line and may be charged through either the vapour or the liquid line.

**Procedure**

1. Prepare a calibration chart of composition vs. refractive index (R.I.) or density, for the two pure components A and B and their mixtures with $X_A$ varying from 0 to 1. Prepare the mixture of various compositions and determine the R.I. or density.

2. Prepare about 200 ml of mixture of A and B. The experiment should be started with the mixture richer in more volatile component (say 160 ml of A and 40 ml of B) so that in subsequent readings temperature increases. This mixture should be filled in the still through either of the limbs.

3. Check carefully that the electrical coil is completely submerged in the liquid (to avoid ignition) and the mixture is more than $2/3$rd level in the vaporizer. Switch on the power and slowly increase the power input in slow steps. Heating should be regulated so that there is no entrainment or foaming of the mixture from vaporizer to the flash chamber.

4. The circulation of the vapour and liquid will soon get established. Allow the system to approach equilibrium. This will be indicated by constant temperature of the thermometer at least for five minutes.

5. Take the liquid and vapour samples and determine the refractive index (or density). Also record the temperature and from R.I. (or density), determine $X_A$ and $Y_A$.

6. Drain out about 40 ml of mixture from the still and add about 40 ml of less volatile component. Repeat steps (1) to (5) and record the composition and temperature readings. Take at least six samples, covering whole range of compositions.

**Observations & Results**

1. More Volatile Component (A):

2. Less Volatile Component (B):

3. Properties of components (from literature/experimental)

<table>
<thead>
<tr>
<th>Component</th>
<th>Density at 30°C</th>
<th>Molecular Weight</th>
<th>Boiling Point</th>
<th>R.I at 30°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4. Report $X_A$ and $R.I$ for the whole range as follows:
5. Report $t - X - Y$ as follows:

<table>
<thead>
<tr>
<th>$X_A$</th>
<th>$R.I.$</th>
</tr>
</thead>
</table>

6. Calculate $K_A$, $\gamma_A$ and $\gamma_B$. Report in a data table the following: $t$, $X$, $Y$, $\gamma_A$, $\gamma_B$, $\ln(\gamma_A/\gamma_B)$, $K_A$.

<table>
<thead>
<tr>
<th>$t$, °C</th>
<th>$X_A$</th>
<th>$Y$</th>
</tr>
</thead>
</table>

7. Plot $\ln \gamma_A$, $\ln \gamma_B$ (on the same graph) and $\ln(\gamma_A/\gamma_B)$ vs $X_A$ (as another graph) and check for thermodynamic consistency. Find the difference in the positive and negative areas of $\ln(\gamma_A/\gamma_B)$ vs. $X_A$ (should be less than 20% due to experimental error).

8. Calculate the Van Laar constants $a$ and $b$ from

\[
    a = \log \gamma_A \left[ 1 + \frac{X_B \log \gamma_B}{X_A \log \gamma_A} \right]^2
\]

\[
    b = \log \gamma_B \left[ 1 + \frac{X_A \log \gamma_A}{X_B \log \gamma_B} \right]^2
\]

Comments
Total Protein Estimation by Lowry’s Method

Objective
To determine the concentration of proteins by Lowry’s method.

Reagents Required
1. BSA stock solution (1mg/ml),
2. Analytical reagents:
   (a) 50 ml of 2% sodium carbonate mixed with 50 ml of 0.1 N NaOH solution (0.4 gm in 100 ml distilled water.)
   (b) 10 ml of 1.56% copper sulphate solution mixed with 10 ml of 2.37% sodium potassium tartarate solution. Prepare analytical reagents by mixing 2 ml of (b) with 100 ml of (a)
3. Folin-Ciocalteau reagent solution (1N) Dilute commercial reagent (2N) with an equal volume of water on the day of use (2 ml of commercial reagent + 2 ml distilled water)

Principle
The phenolic group of tyrosine and tryptophan residues (amino acid) in a protein will produce a blue purple color complex, with maximum absorption in the region of 660 nm wavelength, with Folin-Ciocalteau reagent which consists of sodium tungstate molybdate and phosphate. Thus the intensity of color depends on the amount of these aromatic amino acids present and will thus vary for different proteins. Most proteins estimation techniques use Bovin Serum Albumin (BSA) universally as a standard protein, because of its low cost, high purity and ready availability. The method is sensitive down to about 10 µg/ml and is probably the most widely used protein assay despite its being only a relative method, subject to interference from Tris buffer, EDTA, nonionic and cationic detergents, carbohydrate, lipids and some salts. The incubation time is very critical for a reproducible assay. The reaction is also dependent on pH and a working range of pH 9 to 10.5 is essential.

Procedure
1. Different dilutions of BSA solutions are prepared by mixing stock BSA solution (1 mg/ml) and water in the test tube as given in the table. The final volume in each of the test tubes is 5 ml. The BSA range is 0.05 to 1 mg/ml.
2. From these different dilutions, pipette out 0.2 ml protein solution to different test tubes and add 2 ml of alkaline copper sulphate reagent (analytical reagent). Mix the solutions well.
3. This solution is incubated at room temperature for 10 mins.
4. Then add 0.2 ml of reagent Folin Ciocalteau solution (reagent solutions) to each tube and incubate for 30 min. Zero the colorimeter with blank and take the optical density (measure the absorbance) at 660 nm.
5. Plot the absorbance against protein concentration to get a standard calibration curve.
6. Check the absorbance of unknown sample and determine the concentration of the unknown sample using the standard curve plotted above.

<table>
<thead>
<tr>
<th>BSA (ml)</th>
<th>Water (ml)</th>
<th>Sample conc. (mg/ml)</th>
<th>Sample vol (ml)</th>
<th>Alk. CuSO₄ (ml)</th>
<th>Lowry reagent (ml)</th>
<th>O.D. 600 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>4.75</td>
<td>0.05</td>
<td>0.2</td>
<td>2</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>4.5</td>
<td>0.1</td>
<td>0.2</td>
<td>2</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>4</td>
<td>0.2</td>
<td>0.2</td>
<td>2</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>0.4</td>
<td>0.2</td>
<td>2</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>0.6</td>
<td>0.2</td>
<td>2</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>0.8</td>
<td>0.2</td>
<td>2</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>1.0</td>
<td>0.2</td>
<td>2</td>
<td>0.2</td>
<td></td>
</tr>
</tbody>
</table>

Write short notes on the following points in the report:

1. Beer-Lamberts law

References

2. Hartree E.E. (1972). Anal. Biochem. 48:422 (This modification makes the assay linear over a larger range than the original assay)
35 Determination of pK\textsubscript{a} by pH Titration Method

Objective

To determine the pK\textsubscript{a} values and buffering capacity of buffer solutions.

Requirements

Buffer stock solution (concentrated), pH meter, distilled water, wash bottle, volumetric flasks, measuring cylinders, beakers, and pipettes.

Glycine-NaOH buffer system:

1. 20 mM glycine
2. 200 mM NaOH

Glycine-HCl buffer system

1. 20 mM glycine
2. 200 mM HCl

Theory

The observation that partially neutralized solutions of weak acids or weak bases are resistant to pH changes on addition of small amounts of strong acid or strong base leads to the concept of "buffering". Buffers consist of an acid and its conjugate base, such as carbonate and bicarbonate, or acetate and acetic acid. The quality of a buffer is dependent on its buffering capacity (resistance to change in pH by addition of strong acid or base) and ability to maintain a stable pH upon dilution or addition of neutral salts. Because of the following equilibria, addition of small amounts of strong acid and strong base result in removal of only small amounts of the weakly acidic or basic species, therefore there is little change in the pH:

\[\text{HA (acid)} \leftrightarrow \text{H}^+ + \text{A}^- (\text{conjugate base})\]

\[\text{B (base)} + \text{H}^+ \leftrightarrow \text{BH}^+ (\text{conjugate acid})\]

The pH of a solution of a weak acid or base may be calculated from the Henderson-Hasselbalch equation:

\[\text{pH} = pK_a + \log \frac{[\text{basic species}]}{[\text{acidic species}]} \quad (35.1)\]

The pK\textsubscript{a} of a buffer is that pH where the concentrations of basic and acidic species are equal, and this basic form of equation is accurate between the pH ranges of 3 to 11. Below pH 3 and above pH 11 the concentration of the ionic species of water must be included in the equation. Since the pH range of interest to the biochemical engineer is 3 - 11 ranges, this can be ignored. From the Henderson-Hasselbalch equation an expression for buffer capacity (\(\beta = d[A^-]/d[pH]\)) may be deduced.
Procedure

1. pH Measurement: Mix all solutions thoroughly. The pH measurement may be made in original beakers. Do not change any control on the pH meter except as directed. With the meter on standby, rinse the electrode with deionized water, gently shake off the excess water, and immerse the electrode in the sample solution. Switch the meter to the pH mode, allow the reading to stabilize, and record the pH. Switch the meter back to the standby mode, rinse the electrode again, and leave the electrode immersed in deionized water. Repeat this procedure for all samples.

2. Glycine-NaOH buffer system: Prepare 50 ml 20 mM glycine solution and 100 ml of 200mM NaOH solution. Calibrate the pH meter with standard buffer solution at room temperature. Take 50 ml of glycine solution in a beaker and add 0.5 ml of NaOH solution and shake well to mix. Note the change in pH. Add subsequent quantities of NaOH with an increment of 0.5 ml each time and note observed pH at regular intervals. Take about 30-35 readings and generate the following observation table:

<table>
<thead>
<tr>
<th>Volume of NaOH added (ml)</th>
<th>Observed pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td></td>
</tr>
</tbody>
</table>

Results and Discussion

1. Plot the titration curve for the given buffer system.
2. Estimate the $pK_a$ for the different ionic species.
3. Derive Equation 35.1 Derive an equation for the buffering capacity in terms of $K_a$ and $[H^+]$.
4. When is $\beta$ maximum and what is its value at that condition?
5. List a few biological buffers and their range of operation. How do biological systems (cells, tissues etc.) maintain pH?

Further Reading

1. Read up the theory on buffering of blood.
2. How does the pH meter work?
36 Aseptic Culture Techniques

Objectives

To demonstrate the presence of microorganisms everywhere in the environment.

Introduction

In microbiological and biochemical engineering studies, one almost always deals with a pure culture or a mixture of known cultures, except perhaps in waste water treatment studies. Unless aseptic culture techniques are followed strictly, an originally pure culture will definitely become contaminated with other unwanted species. The use of a contaminated culture with unknown microorganisms will only lead to incredible results that are of little value. Thus, isolation and maintenance of a pure culture is of utmost importance in many microbiological studies. It is especially important to work with a well-characterized strain if the microorganism is used for a food preparation, as well as in antibiotic production where the product is to be taken internally.

The need for a clean working environment in biological engineering studies is a must and cleanliness is the prerequisite for any meaningful work. The environment we live in is full of microorganisms capable of surviving in any condition. This experiment is aimed at introducing you to the presence of microorganisms in the environment with the use of a simple microbiological technique.

Requirements

Nutrient agar plates, and incubator (at 37°C)

Procedure

Obtain the prepared petri dishes containing nutrient agar medium from the instructor and expose them to the following:

1. Exposure the plate to air for 30 minutes
2. Touch with unwashed fingers.
3. Touch with fingers washed with water and soap
4. Touch with fingers dipped in ethanol.
5. Kiss with moist lips
6. Press against the lab door knob.
7. Press against the bathroom doorknob.
8. Smear a little yogurt or milk.
10. Press against a tap handle.
11. Cough vigorously from 4-6 inches away.
12. The plates should be labeled appropriately and incubated upside down at 37°C.

13. Come back to the lab after 12 to 24 hours and note down what you find on the plates.

Observations

There are actually many more numbers and varieties of microorganisms in our immediate environment than those appearing on the incubated plates. Some of these will not grow in aerobic conditions or on glucose, but will flourish in different media. When working with microorganism, it is important that the working environment stays as clean as possible. For example, a minuscule puff of mold spores can drift in air for an extended period of time and contaminate many subsequent experiments. Some of the spores can withstand even the temperature existing inside an autoclave and emerge from the sterilization process in dormant but viable forms. In general, the chance of contamination is proportional to the number of microorganisms in the environment when the aseptic procedures are undertaken. It is important in a shared laboratory setting to practice good aseptic techniques and keep the working environment clean. Although microorganisms can’t be totally eliminated in our lab, their numbers can certainly be reduced drastically.

Questions

1. Describe the morphology of the colonies growing on the plates (color, texture, size, shape, elevation, number of colonies, etc.).

2. What is the role of agar in microbiological media?

3. Write a note on different types of microorganisms and their characteristics.

4. What are the methods available for the identification of microorganisms?

References


2. Collins, Microbiological methods - 5th Edn Butterworths, 1984
37 Kinetics of Alkaline Phosphatase

Objective
To study the kinetics of alkaline phosphatase.

Procedure

1. Sodium carbonate - sodium bicarbonate buffer: Dissolve 20 ml of 0.2 M solution of sodium carbonate (2.12 gm in 100 ml distilled water) and 230 ml of 0.2 M sodium bicarbonate (4.12 gm in 250 ml distilled water) to make up the volume 250 ml with pH 9 -9.2

2. 5 N sodium hydroxide solution (10 gm in 50 ml distilled water)

3. Substrate stock solution: Dissolve 0.1 gm of p-nitrophynyl phosphate in 25 ml of carbonate-bicarbonate buffer (prepared as above).

4. Enzyme solution: Dissolve 10 mg of alkaline phosphatase enzyme in 10 ml carbonate-bicarbonate buffer to get 1 mg/ml stock solution. Pipette out 0.1 ml of stock A and make-up the volume to 10 ml with buffer to obtain 0.01-mg/ml solution, which is used for further dilution.

Theory

Chemical reactions in biological systems occur in the presence of highly specific protein catalysts called enzymes. Enzymes catalyse the reaction rapidly under mild conditions in contrast to inorganic catalysts. The rate of enzyme-catalyzed reaction is influenced by different environmental conditions like concentration of substrate, pH, temperature. Presence of inhibitors and concentration of the enzyme itself. The rate of an enzyme-catalysed reaction can be measured by:

1. The disappearance of substrate, or

2. The appearance of the product.

In a typical experiment the enzyme and substrate are mixed and allowed to react for specific period of time; then amount of substrate disappeared or product formed is measured and this information will give the rate of activity of the enzyme per unit time.

To study an enzyme, an assay is necessary. The assay is a measurement of a chemical reaction, which might involve measuring the formation of the product. The enzymes phosphatases catalyse hydrolysis of phosphate esters to free inorganic phosphate in biological systems. There are two types of phosphatases depending on the pH environment in which they are active. We are going to study the alkaline phosphatase, which requires a pH of 9-9.2 for its activity. In order to measure the activity of enzyme the rate of formation of product can be followed. Here we make use of following reaction which results in the formation of yellow coloured product. p-nitrophenol the concentration of which can be measured using a simple colorimeter using appropriate filter (420 nm)

\[
p\text{-nitro phenyl phosphate} \rightarrow p\text{-nitro phenol} + \text{phosphate}
\]

Alkaline Phosphatase is an important enzyme in recycling phosphate within living cells. This enzyme catalyses the cleavage of phosphate group from a variety of compounds, including artificial
colourless substrate used in the present analysis p-nitro phenyl phosphate. One of the formed products p-nitro phenol, is yellow in basic solutions. The appearance and intensity of yellow colour in the reaction solution thus indicates the degree to which enzyme has acted upon substrate. Using the mathematical relationship between initial rate and substrate concentration (Michaelis-Mentin equation), reaction parameters like maximal reaction rate ($V_{\text{max}}$) and the Michaelis constant ($K_m$) can be determined from a hyperbolic graph. Linear graph methods like the Lineweaver-Burk plot can be used for easy determination of reaction parameters.

**Procedure**

1. Make the substrate dilutions as in the given table.
2. Prepare the 0.1 mg/ml enzyme solution (stock b) from the stock solution.
3. Mix substrate and enzyme solutions in given proportion and keep for 15 minutes.
4. Add 0.5 ml of 5N NaOH in each reaction solutions to stop the reaction.
5. Read the absorbance at 420 nm.
6. Prepare a serious of standard concentrations of p-nitro phenol in distilled water and measure the absorbance values at 420 nm against blank.
7. From the standard curve of p-nitro phenol, calculate the rate of the reaction and calculate amount of p-nitro phenol formed per second.
8. Plot reaction rate ($v$) against substrate concentration.
9. Data used for a Lineweaver-Burk double reciprocal plot to calculate kinetic parameters.

<table>
<thead>
<tr>
<th>Std (ml)</th>
<th>Buffer (ml)</th>
<th>Sub conc. (mg/ml)</th>
<th>Sub vol(ml)</th>
<th>Enz.vol(ml)</th>
<th>NaOH(ml)</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>4.5</td>
<td>0.4</td>
<td>1.9</td>
<td>0.1</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>4.0</td>
<td>0.8</td>
<td>1.9</td>
<td>0.1</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>3.0</td>
<td>1.6</td>
<td>1.9</td>
<td>0.1</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>2.5</td>
<td>2.0</td>
<td>1.9</td>
<td>0.1</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>2.0</td>
<td>2.4</td>
<td>1.9</td>
<td>0.1</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Stock</td>
<td>4.0</td>
<td>1.9</td>
<td>0.1</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Results**

1. Run a series of reactions with constant enzyme concentration at various substrate concentrations and measure the rate of reaction.
2. Plot graph of rate vs substrate concentration
3. Estimate $V_{\text{max}}$ from asymptote.
4. Estimate $K_m$ and $V_{\text{max}}$ using Lineweaver-Burk plot.
5. Describe the significance of parameters: Michaelis-Menten constant ($K_m$) and $V_{max}$.

6. Write brief notes on the effect of pH, temperature, enzyme concentration and presence of inhibitors on the activity of the enzymes.

7. Write about various types of enzyme inhibition.

References


48 Kinetics of a (Solid-Liquid) Esterification Reaction

Aim
To determine the reaction rate constants for the forward and backward reactions for esterification of acetic acid with butanol at different temperatures.

Reaction

\[ \text{CH}_3\text{COOH} + \text{C}_4\text{H}_9\text{OH} \rightleftharpoons \text{C}_4\text{H}_9\text{COOCH}_3 + \text{H}_2\text{O} \]

Acetic Acid + Butanol \rightleftharpoons Butyl Acetate + Water

Theory
The synthesis of butyl acetate is done through esterification of acetic acid with n-butanol. The ester has wide application as a versatile solvent in chemical industry. It is a reversible reaction that takes place in the presence of acid catalyst. The catalyst used in the present experiment is a solid heterogeneous catalyst. Hence, reaction takes place on the surface of the catalyst. If the reaction is performed in a batch reactor, the conversion will increase and the reaction rate will drop with respect to time. Eventually it will attain equilibrium.

Kinetic Model
Among all the models the simplest model is the pseudohomogeneous model given by the following rate equation:

\[ -\tau_{\text{CH}_3\text{COOH}} = k_1C_{\text{CH}_3\text{COOH}}C_{\text{C}_4\text{H}_9\text{OH}} - k_2C_{\text{C}_4\text{H}_9\text{COOCH}_3}C_{\text{H}_2\text{O}} \]  

(38.1)

where \( K \) is the reaction equilibrium constant (i.e. \( k_1/k_2 \)) that can be independently calculated using the following relation:

\[ \ln \frac{K}{K^0} = \frac{\Delta H_R^{0(l)}}{R} \left[ \frac{1}{T_0} - \frac{1}{T} \right] \]

(38.2)

where, \( K^0 = \exp\left[-\frac{\Delta G_R^{0(l)}}{R T_0}\right] \)

Data: \( \Delta H_R^{0(l)} = -3.887 \text{ kJ/mol} \), \( \Delta G_R^{0(l)} = -8.889 \text{ kJ/mol} \)

Apparatus
The set-up consists of five heating chambers whose temperature can be set independently thus, enabling conducting five runs at different temperatures simultaneously. The reaction is performed in a 300 ml glass reactors equipped with stirrer and condenser and placed in respective heating chambers for the attainment of the required temperature. The stirrer is driven by a motor with a control over the speed of agitation. The speed can be measured using a non-contact type tachometer. Digital temperature indicators are provided to measure the temperature of the reaction mixture in all the reactors.
Procedure

1. Set the temperatures of the heating chambers (at least four) at the desired levels and start heating.

2. Take measured quantities of acetic acid and n-butanol in the two reactors.

3. Place the reactors in the oil baths, start slow stirring and observe the reactor temperature.

4. Once the desired temperature of the reaction mixture is attained, add the measured quantity of cation exchange resin (Amberlyst-15) in the reactor. Consider this time as the zero reaction time. Increase the speed of agitation to 1200 rpm.

5. Remove samples from all the reactors. Keep removing the samples as per the time intervals indicated in the tables.

6. Titrate weighed quantity of the sample against 0.5 M NaOH. Record the titration readings and calculate conversions at every time interval.

Outline of the Process

Data

Mole ratio of reactants:
Amount of catalyst:
Figure 38.1: Schematic diagram of the Esterification setup
Observation and Results Table

<table>
<thead>
<tr>
<th>Chamber 1 Temperature = _____</th>
<th>Chamber 2 Temperature = _____</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (min)</td>
<td>Weight of sample (g)</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
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<tr>
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<td>20</td>
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<tr>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>45</td>
<td>45</td>
</tr>
<tr>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>$k_1$</td>
<td>$k_1$</td>
</tr>
<tr>
<td>$k_2$</td>
<td>$k_2$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chamber 3 Temperature = _____</th>
<th>Chamber 4 Temperature = _____</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (min)</td>
<td>Weight of sample (g)</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
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<td>45</td>
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<td>60</td>
<td>60</td>
</tr>
<tr>
<td>$k_1$</td>
<td>$k_1$</td>
</tr>
<tr>
<td>$k_2$</td>
<td>$k_2$</td>
</tr>
</tbody>
</table>

$k_0$ for forward reaction =
k_0$ for backward reaction =
$E$ for forward reaction =
$E$ for backward reaction =
Calculations

1. Calculate the conversion at all times for each temperature and plot the kinetic data \((X \text{ vs } t)\) for comparison, where \(X\) is conversion.

2. Calculate the reaction rate constant by Integration and Differential method

Integral Analysis

1. The rate equation can be integrated to give \(k_1t = f_1(X)\)
2. Find \(f_1(X)\)
3. Plot \(f_1 \text{ vs } t\) to get \(k_1\) and \(k_2\)

Differential Analysis

1. The rate equation can be written as \(dX/dt = k_1 \times f_2(X)\)
2. Find \(f_2(X)\)
3. Calculate \(dX/dt\) at each time interval for \(X \text{ vs } t\) plot.
4. Plot \(dX/dt \text{ vs } f_2(X)\).
5. Calculate \(k_1\) and \(k_2\) from the above plot.

Integral Analysis

1. Plot \(\ln k_1\) and \(\ln k_2\) vs \(1/T\).
2. Evaluate Arrhenius parameters \(k_0\) and \(E\) for both backward and forward reactions from the graph.

Conclusion and Comments

Questions

1. Suggest the algorithm to evaluate \(k_1\) by regression analysis.

2. If \(K\) is not known, how will you evaluate \(k_1\) and \(K\) from the kinetic data you have generated?
39 Batch Reactive Distillation

Aim
To examine the potential of batch reactive distillation in enhancing the reaction conversion.

Definition of Batch Reactive Distillation
Batch Reactive Distillation (BRD) is defined as a batch distillation system wherein reaction takes place in either reboiler or condenser or in the column or at more than one of these locations. It has a potential to lower the capital and energy cost of the process.

Theory
Consider the following reversible reaction.

\[ A + B \rightleftharpoons C + D \]  

(39.1)

The law of mass action for this reacting system is given by

\[ K = \frac{[C][D]}{[A][B]} \]  

(39.2)

If \( C \) is the desired product Le Chatelier’s principle says that if \( D \) can be removed simultaneously during the course of the reaction, the reaction can be shifted in the forward direction and conversion of \( C \) can be enhanced. Reactive distillation makes use of this concept and improves the yield of a reversible reaction.

Reaction of Interest
The reaction considered in the present experiment is esterification of acetic acid with butanol to give butyl acetate and water.

\[ CH_3COOH + C_4H_9OH \rightleftharpoons C4H9COOCH_3 + H_2O \]  

(39.3)

Butyl acetate is an industrially important chemical and finds application as a useful solvent in many processes.

The important limitation of reactive distillation is that the volatilities of the components involved should be favorable. For example, in the above system if one wants to remove \( D \), it should either have the highest volatility or it should form a minimum boiling azeotrope with one or more than one component in the system.

Table 1 gives the boiling points of the components involved in the reacting system.

<table>
<thead>
<tr>
<th>Components</th>
<th>Boiling Points °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic Acid</td>
<td>118</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>117.7</td>
</tr>
<tr>
<td>n-Butyl Acetate</td>
<td>126.3</td>
</tr>
<tr>
<td>Water</td>
<td>100</td>
</tr>
</tbody>
</table>
If we want to increase the conversion towards butyl acetate, we have to remove water efficiently during the course of reaction. The boiling points in the table may indicate that water and other components have close boiling points and the efficient removal of water may not be possible, as water will possibly carry other components along with it in the overhead product. However, in reality, it does not happen. Water forms ternary azeotrope with butanol and butyl acetate that boils at 87-90°C. Since this azeotrope has minimum boiling point, instead of pure water one gets distillate composition close to the ternary azeotrope (i.e. ternary mixture water, butanol and butyl acetate).

**Nature of Azeotrope**

The azeotrope can be either homogeneous or heterogeneous. If on condensation of vapour, the liquid form two phases, then the azeotrope is called as heterogeneous azeotrope. In the present case, the azeotrope is heterogeneous and form two phases. The aqueous phase is almost pure water and can be removed easily. Organic phase that consist of mainly butyl acetate and butanol can be recycled back to the column through reflux. Hence, ideally if one starts with stoichiometric mole ratio of butanol and acetic acid in the reactor, at end of the run, the system should contain only butyl acetate in the reactor if losses of butanol and other components with overhead aqueous phase are negligible. This conclusion is to be validated with the help of the present experiment.

**Apparatus**

The set up consists of two identical reactors ($R_1$ and $R_2$) of about 1 lit capacity. Both the reactors are externally heated with the help of a heating mantle. The reactors are also equipped with temperature sensors, turbine type impellers, baffles and drain valve for sample removal. The impellers are driven with the help of a common motor ($M$). The reactors are $R_1$ is connected to a distillation column ($D$) packed with ceramic raschig rings. The column is insulated using asbestos ropes. The overhead vapors are collected in the vertical condenser ($C_1$). A Dean Stark type arrangement has been used to provide reflux to the column. A cock is proved to withdraw the water formed in the reaction. The condenser ($C_2$) serves as a reflux condenser to reactor $R_2$.

**Procedure**

The two reactors namely $R_1$ and $R_2$ are each charged with 440 gms acetic acid and 550 gms of n-butanol and 100 gms of strong cation exchange (acidic) resin as catalyst.

1. Remove samples from reactors $R_1$ and $R_2$ and perform the titration analysis

2. Start the water supply to the condensers and switch on the power supply to heating mantles for both reactors $R_1$ and $R_2$ and Put the stirrer on and start slow stirring and wait for the reaction mixture to boil. Note down the temperatures.

3. Once the reaction mixture starts boiling, remove the sample (5 ml) from the bottom valves of both the reactors.

4. Increase the speed of agitation to the mark on the speed control device (it corresponds to 1000 rpm). The speed is such that the resin particles suspend well in the reaction mixture and the mass transfer resistance across the solid liquid interface becomes negligible. Remove the samples from both reactors.
5. From the reactor $R_1$, vapors move to the distillation column and eventually reach the condenser and get condensed. The condensate is collected in the Dean and Stark apparatus. You will observe that the condensate is a two phase mixture. Wait till the arm of this apparatus gets filled with liquid and the reflux begins.

6. Start removing water so as to maintain its level at the mark shown on the arm of the Dean and Stark apparatus.

7. Keep removing samples from the reactors $R_1$ and $R_2$ after every 10/15 mins from the respective bottom valves and note down various temperatures (top and bottom for reactor $R_1$ and only bottom for reactor $R_2$). Note the total amount of water removed (P). Make the correction for the hold up of water (5 ml) in Dean and Stark apparatus.

8. Collect samples of aqueous layer after every 10/15 min.

9. Remove samples of the organic layer after every 10/15 min.

10. Perform the analysis of all the samples by titration against standard NaOH. The analysis will give the indication of acid content in the mixture. When the acid content does not change with time, the saturation point is obtained. Stop the run at this stage. Put the stirrer and heating mantle off. Another indication for the saturation point is the constancy of reactor and top temperature with respect to time.

Procedure for Sample Removal

The sample from the reactor bottom may be collected by opening the drain valve. About 4-5 ml of the sample is collected in the sample bottle and the valve is closed. This liquid is disposed to the waste bottle and again a fresh sample is taken by following the above procedure. The initial quantity is rejected in order to purge the sampling line.

Outline of the Process

Analysis by Titration

1. Remove 2 ml sample in a conical flask by a pipette. The sample should be free from the resin particles.

2. Dilute the sample with water (about 25-30 ml).

3. Titrate with standard NaOH (0.1 N) solution and phenolphthalein as indicator.

Some important practical problems

During the experiment following things can go wrong. The students should take necessary action mentioned below or report to the instructor/demonstrator:

1. Because of the voltage fluctuations the speed of agitation may rise or fall suddenly. The regulator position may be adjusted accordingly in such case.

2. The drain valves may leak during the course of the run. The empty beaker (marked as "safety beaker") provided to you should be immediately placed below this valve and the instructor/demonstrator should be informed.
Figure 39.1: Schematic diagram of Batch Reactive Distillation
3. The stirrer of the reactor may stop suddenly. Inform the instructor/demonstrator immediately.

**OBSERVATIONS**

Titration reading of the reaction mixture: Readings when reaction mixtures from $R_1$ and $R_2$ start boiling:

**Observation Table**

**Reactor $R_1$ (batch reactive distillation)**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time (min)</th>
<th>Temperature</th>
<th>Titration Reading</th>
<th>Cumulative Amount of Water removed (P gms)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Top (Top)</td>
<td>Top (org)</td>
<td>Top (aq)</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>2</td>
<td>20</td>
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<tr>
<td>3</td>
<td>30</td>
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<tr>
<td>4</td>
<td>40</td>
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<tr>
<td>5</td>
<td>50</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Reactor $R_2$**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time (min)</th>
<th>Temperature</th>
<th>Titration Reading (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td></td>
<td></td>
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<tr>
<td>2</td>
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<td>4</td>
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<tr>
<td>5</td>
<td>50</td>
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</tr>
</tbody>
</table>

**Results**
Enhancement obtained in batch reactive distillation system =
\[
\frac{\text{Conversion in reactor } R_1 - \text{Conversion in reactor } R_2}{\text{Conversion in reactor } R_2}
\]

Conclusions and Comments

Questions

1. What is Le-Chatelier’s principle and how it is applied in the present experiment?
2. Why the reaction temperature changes with time?
3. What is azeotrope? Explain its relevance in the present experiment.
4. What if the azeotrope is not heterogeneous?
5. What is the effect of speed of agitation and particle size in this experiment?
6. Is batch reactive distillation an economically attractive option to the conventional approach (i.e. reaction followed by distillation)? Why?
7. Plot profiles of temperature, rate of water removal (only for \( R_1 \)) and conversion with respect to reaction time for both \( R_1 \) and \( R_2 \).
8. How much acetic acid is lost through distillate? Does that make a significant impact on the conversions calculated?
40 Micellar Catalysis

Aim
Study of instantaneous reaction by micellar catalysis.

Apparatus
Reaction kettle, stirrer with motor assembly, thistle funnel, pipette, syringe, standard flasks, etc.

Chemicals
Diethyl aniline (DEA), HCl, cetyl trimethyl ammonium bromide (CTAB)

Reaction

\[
\begin{array}{c}
\text{N(C}_2\text{H}_5)_2 \\
\text{[Ring]} \\
\text{N(C}_2\text{H}_5)_2\text{HCl}
\end{array}
+ \text{HCl} \rightarrow
\begin{array}{c}
\text{[Ring]} \\
\text{N(C}_2\text{H}_5)_2\text{HCl}
\end{array}
\]

Figure 40.1: Conversion of Diethyl Aniline to Diethylaniline hydrochloride

Theory
When the concentration of a surfactant in a solution exceeds certain limit known as critical micelle concentration (CC), surfactant molecules form micelles. Hydrophobic groups of surfactant molecules form the core of micelles while the hydrophilic head groups are located at the interface with water and the relatively small counter ions of the ionic micelle are located in steriod layer. Most of the counter ions are however located in the electrical double layer where they are completely dissociated to form charged aggregates and are able to exchange with ions in the bulk of the solution. Typically micelles have average radii of 12-30 Å. The size of the micelles is comparable to the molecular size. Due to this small size, micelles provide high interfacial area. Micelles can solubilize the sparingly soluble organic reactant. The counter ions located in the double layer can exchange ions with the bulk. However, due to small size, number density of micelles is quite high. All these properties make micelles to catalyze a reaction. The reaction can be studied using different surfactant; anionic as well as cationic and enhancement factor can be found. The above reaction is studied in presence of cationic surfactant certified (CTAB), cetyl trimethyl ammonium bromide at concentration above CC.
Rate Equation

\[ R = k_L [DEA^*](1 + q) \]  
(40.1)

Where, \( R \) = specific rate of extract of DEA into HCl, mol m\(^{-2}\) s\(^{-1}\), \( k_L \) = mass transfer coefficient, ms\(^{-1}\), [DEA\(^*\)] = solubility of DEA in aqueous phase, mol m\(^{-3}\).

\[ q = \frac{[HCl]}{[DEA^*]} \]  
(40.2)

Where, \( D_{DEA} \) and \( D_{HCl} \) are diffusivity of DEA and HCl respectively in the aqueous phase. If \( q \) is large, \( 1 + q \approx q \)

Hence, \( R = k_L [DEA^*]q \)

Therefore,

\[ R = k_L [HCl] \frac{D_{DEA}}{D_{HCl}}^{1/2} \]  
(40.3)

Material balance for HCl in the aqueous phase yields,

\[-V \frac{d[HCl]}{dt} = R \times A\]  
(40.4)

where, \( V \) is volume of aqueous phase. From the above equations

\[-V \frac{d[HCl]}{dt} = k_L [HCl] \frac{D_{DEA}}{D_{HCl}}^{1/2} A\]  
(40.5)

The initial condition is \( [HCl] = [HCl]_i \) at \( t = 0 \). The solution of the above equation is therefore,

\[ \ln \frac{[HCl]_i}{[HCl]} = k_L A \frac{D_{DEA}}{V \ D_{HCl}}^{1/2} \]  
(40.6)

Therefore, plot of \( \ln \frac{[HCl]_i}{[HCl]} \) vs \( t \) will give a straight line with Slope = \( (k_L A/V)(D_{DEA}/D_{HCl})^{1/2} \). The enhancement factor \( \phi \) is defined as:

\[ \phi = \frac{\text{slope in presence of surfactant}}{\text{slope in absence of surfactant}} \]

Procedure

1. In a model stirred cell reactor, add 250 ml of water.
2. Slowly add 85 ml of DEA by means of a funnel so that it spreads on the surface of water.
3. Position the impeller in the aqueous phase and set at a speed of 45-50 RPM so as to maintain a flat interface.
4. Add concentrated HCl through the thistle funnel into the aqueous phase to obtain a strength of 0.1 N. This is zero reaction time.
5. Aqueous phase sample (1 ml) is withdrawn by means of a syringe at a time interval of every 3 min. and diluted 300 times before analysis.
6. The reaction is monitored for 30 min.
7. The above procedure is repeated in presence of CTAB to observe the effect of micelles.
**Analysis**

The salt DEA-HCl formed in the aqueous phase shows an absorbance maxima at wavelength of 253 nm. All the aqueous phase samples are therefore analyzed on UV-VIS spectrophotometer at the wavelength of 253 nm.

**Calibration**

A standard plot is made of DEA-HCl of the following concentration:

1. $2 \times 10^{-3}$ M
2. $3 \times 10^{-3}$ M
3. $4 \times 10^{-3}$ M
4. $5 \times 10^{-3}$ M

**Observations**

$$\text{HCl} = \text{mol m}^{-3}$$

$$\text{DEA}^* = \text{mol m}^{-3}$$

**Observation Table I (without CTAB)**

<table>
<thead>
<tr>
<th>S.N.</th>
<th>Time (min)</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
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<tr>
<td>2</td>
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<tr>
<td>10</td>
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</tbody>
</table>

**Observation Table II (with CTAB)**

<table>
<thead>
<tr>
<th>S.N.</th>
<th>Time (min)</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
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<td>.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Results

1. Calculate $q$

$$q = \frac{[HCl]}{DEA^*} \left( \frac{D_{DEA}}{D_{HCl}} \right)^{\frac{1}{2}}$$

2. Slope in absence of CTAB =

3. Slope in presence of CTAB =

4. $k_L$ (without CTAB) = mol s$^{-1}$

5. $k_L$ (with CTAB) = mol s$^{-1}$

Result Table

<table>
<thead>
<tr>
<th>S.N</th>
<th>Time (min)</th>
<th>Concentration (without CTAB)</th>
<th>Concentration (with CTAB)</th>
<th>$\phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>2</td>
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<td>10</td>
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</tbody>
</table>

Conclusions and Comments
41 Homogeneous Reactions

Aim
To study kinetics of homogeneous reaction of quinoline (Q) with 1-bromobutane (BuBr).

Reaction

\[
\text{R}_3N + \text{R}'X \rightarrow \text{R}_3N^+ \text{R}'X^- \quad \text{(41.1)}
\]

These reactions are usually conducted by warming for a few hours, stoichiometric amounts of amine with the appropriate alkyl bromide/iodide.

A typical example of this, is alkylation of quinoline with 1-bromobutane. This reaction can be carried out at 80{\degree}C. Appreciable conversion can be obtained by mixing suitable amount of quinoline and 1-bromobutane in a reaction vessel and shaking for two hours.

Since quaternary salt is insoluble in the organic phase, it separates out from the reaction mixture. Formation of solid makes it difficult to accurately sample the reaction mass from analysis. This difficulty is solved by adding the second phase viz; water which extracts quaternary salt from the organic phase. Aqueous phase can be sampled for Br\(^{-}\) analysis. Reaction is first order with respect to quinoline and 1-bromobutane. The rate expression can therefore be written as:

\[
\frac{d}{dt}[\text{Br}^-] = k_2[n-\text{BuBr}][\text{C}_9\text{H}_7\text{N}] V_{\text{org}}
\]

Where, \([\text{Br}^-]\) is the concentration of bromide ions in the aqueous phase, mol m\(^{-3}\) s\(^{-1}\); \(V_{\text{aq}}\) is the volume of aqueous phase, cm\(^3\); \([n-\text{BuBr}]\) is the concentration of 1-bromobutane in organic phase, mol m\(^{-3}\); \([\text{C}_9\text{H}_7\text{N}]\) is concentration of quinoline in the organic phase, mol m\(^{-3}\); \(V_{\text{org}}\) is the volume of organic phase, cm\(^3\); \(k_2\) is the reaction rate constant, m\(^3\) mol\(^{-1}\) s\(^{-1}\).

Since conversion of n-BuBr during the experiment is small (< 10%), the concentration of both n-BuBr and quinoline can be assumed as constant. Therefore, a plot of \([\text{Br}^-]\) vs time is a straight line. The slope for this line is: \(S = k_2[n-\text{BuBr}]_i[C_9\text{H}_7\text{N}]_i(V_{\text{org}}/V_{\text{aq}})\) where \([n-\text{BuBr}]_i\) and \([C_9\text{H}_7\text{N}]_i\) represent the initial concentration of 1-bromobutane and quinoline respectively. The rate constant \(k_2\) can be estimated from the slope.
**Procedure**

1. Take 50 ml of Quinoline, 50 ml of 1-bromobutane and 100 ml of water in a reactor, set in water bath maintained at 80°C.

2. Withdraw sample from the aqueous phase. This corresponds to zero hour sample.

3. Stir the reaction mixture at 200-250 rpm so as to form a completely dispersed system.

4. Take samples from the aqueous phase at an interval of 20 min. after allowing the two phases to separate.

5. Continue the reaction for 2 hours.

6. The reaction is monitored, by analyzing for Br\(^{-}\) in the aqueous phase using a specific ion electrode meter.

**Analysis**

Selective ion electrode is provided along with the reference electrode and the Br\(^{-}\) electrode. The halide electrode consists of silver halide/silver sulfide membranes bonded into the tip of an epoxy electrode body. When the membrane is in contact with a halide solution, silver ions dissolve from the membrane surface and electrode develops a potential due to the silver ion concentration. This concentration is in turn, determined by the sample halide ion concentration. The meter is calibrated with standard bromide solution.

Aqueous phase sample (1 ml) which is withdrawn at every 20 min interval is quenched with a drop of concentrated HNO\(_3\) and then diluted to 100 ml in a standard volumetric flask. 50 ml of this is taken for analysis. Add 1 ml ionic adjuster (ISA) to this solution and read concentration in ppm on the meter.

**Observation Table**

<table>
<thead>
<tr>
<th>S.N.</th>
<th>Time (min)</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Calculations**

\[
k_2 = \frac{\text{slope} \times V_{aq}}{[n-\text{BuBr}]_i[C_9H_7N]_iV_{org}}
\]  

(41.3)

**Conclusions and Comments**
42 Interfacial (Liquid-Liquid) Nitration

Aim
To study the kinetics of nitration of nitrobenzene (NB) in a stirred cell reactor at a liquid-liquid interface.

Reaction

\[
\begin{align*}
\text{NO}_2^- + \text{HNO}_3 + \text{H}_2\text{SO}_4 &\rightleftharpoons \text{NO}_2(+) + \text{H}_3\text{O}^{}(+) + 2\text{H}_2\text{SO}_4^-
\end{align*}
\]

Figure 42.1: Nitrobenzene to Di-nitrobenzene

Reactants
1. Nitrobenzene (A.R.), \( \rho = 1.2 \text{ g/ml} \).
2. Nitrating mixture, \( \rho = 1.735 \text{ g/ml} \).

Equipment
Reaction Kettle, Impeller, Geared motor, Thistle funnel, Syringe, Standard flask, NaOH solution, Spectrophotometer.

Theory
The reaction involves electrophilic substitution of substrate i.e. nitrobenzene in presence of the nitrating mixture.

\[
\text{HNO}_3 + 2\text{H}_2\text{SO}_4 \rightleftharpoons \text{NO}_2(+) + \text{H}_3\text{O}^{}(+) + 2\text{H}_2\text{SO}_4^-
\]

i.e.

\[
\begin{align*}
\text{H}^- + \text{NO}_2^{} &\overset{\text{H}_2\text{SO}_4}{\rightleftharpoons} \text{HSO}_4^- + \text{H}_3\text{O}^{}(+) \\
\text{NO}_2^- &\overset{\text{H}_2\text{SO}_4}{\rightarrow} \text{H}_3\text{O}^{}(+) + \text{HSO}_4^-
\end{align*}
\]

The controlling step is the attack of \( \text{NO}_2^{(+)} \) on nitrobenzene.

\[
\text{Rate} = k'_2[R\text{NO}_2][\text{NO}_2]^+ = k_2[R\text{NO}_2][\text{HNO}_3]
\]

(42.1)

where \( k_2 = Kk'_2 \), and \( K \) is the extent of dissociation of HNO\(_3\) to yield \( \text{NO}_2^{(+)} \) ion. The reaction exhibits second order kinetics.
Industrial nitration involves two phase system; aqueous phase containing ions such as $\text{H}^+$, $\text{HSO}_4^-$, $\text{NO}_2^+$ and $\text{NO}_3^-$ and organic phase containing polar aromatic molecules. The charged species present in the bulk aqueous phase will tend to concentrate at the interface depending on the surface charge. Therefore, the reaction can occur in the interfacial mono-layer in addition to the reaction in the bulk. Thus, the overall rate of reaction may be written as:

$$R = R_i + R_b$$  \hspace{1cm} (42.2)

where $R$ = total rate of reaction, mol/h, and $R_i$ and $R_b$ = rate of reaction at interface and bulk respectively, mol/h. $R_i$ and $R_b$ can be expressed as:

$$R_i = k''_2[R\text{NO}_2]^*[\text{NO}_2]^*A \hspace{1cm} R_b = k_2[R\text{NO}_2][\text{HNO}_3]V$$  \hspace{1cm} (42.3)

where, $[\text{RNO}_2]^*$, $[\text{NO}_2]^*$ = concentration of nitrobenzene and nitronium ion per unit area of monolayer, mol/m$^2$, and $k''_2$ = interfacial reaction rate constant, m$^2$/mol h, and $A$ = interfacial area, m$^2$.

The rate of bulk reaction depends upon volume of the aqueous phase while it is independent of the interfacial area. Exactly opposite behaviour is exhibited by the interfacial reaction. The effect of the degree of agitation on the overall rate can therefore be studied in order to check whether one or the other mechanisms are dominant.

**Procedure**

1. Charge 100 ml of nitrating mixture to the Stirred Cell reactor.

2. Set the impeller at the interface.

3. With the help of thistle funnel, slowly add nitrobenzene (100 ml) so that it is evenly spread on the surface of the nitrating mixture.

4. Withdraw sample (1 ml) from the organic phase. This sample corresponds to zero reaction time.

5. Start the motor and set the impeller speed. The reaction is conducted at flat interface/dispersed system.

6. The reaction is monitored for the presence of m-dinitrobenzene (m-DNB) by withdrawing samples (0.5-1.0 ml) from the organic phase at an interval of every 15 min for 1.5 hrs. The sample is quenched with distilled water and the organic phase after separation is analyzed for m-DNB content by Janovsky test.
Analysis

The organic phase sample (0.1 g) is taken in a volumetric flask (25 ml) and diluted with acetone. 10 ml of this sample is taken in a beaker to which is added 0.6 ml of NaOH solution (0.25% by wt.). Violet colour starts developing. The sample is analyzed after 10 min on a UV-spectrometer. Note the absorbance at 573 nm wavelength ($\lambda$).

Calculations

Equation of the calibrating curve

$$y = 0.123x + 0.01719$$

where, $x =$ concentration of m-DNB in acetone (mg/l)

1. Concentration of m-DNB per weight of sample = 

$$\frac{x \times 10^{-6}}{\text{weight of sample per ml of acetone}}$$

2. % conversion based on HNO$_3$ taken

$$100 \times \frac{\text{moles of DNB formed}}{\text{wt. of sample}} \times \frac{\text{total weight of organic phase}}{\text{moles of HNO}_3 \text{ in nitrating mixture}}$$

Determine % conversion for each sample. Draw a graph of % conversion vs time. Slope obtained from the plot corresponds to the rate of reaction.

Observations and Results

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Wt. of sample taken for analysis</th>
<th>Absorbance</th>
<th>Concentration of DNB per weight of sample</th>
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Conclusions and Comments
A  Data Analysis

There are two common mistakes associated with most computations as observed in student reports: (1) lack of significance in computed answers, and (2) lack of understanding of the use of regression analysis. The lack of significance in most computations is the result of three causes: unnecessary use of all reported digits as displayed by calculators/computers, lack of knowledge of the least count associated with devices/measurements, and lack of understanding of how errors propagate during successive calculations. The main problem associated with regression analysis is the lack of thought which goes into verifying whether a linear model is appropriate. It is expected that you familiarize yourself with the discussion below, and analyze your data accordingly.

Number representation

Data may be represented by fixed-point or floating-point representations.

- **Fixed-point**: fixed number of decimal places: 1.000, 12.836, 36823.128
- **Floating point**: $0.1234 \times 10^5$ or $0.1234E05$, $-0.1386 \times 10^{-6}$ etc.

A significant aspect of data representation is the concept of significant digits. The numbers 1360, 1.360, 0.001360 all have 4 significant digits. It is important to appreciate that 1.360 is different from 1.36. In the context of measured values, this last digit of significance is a function of the least count of the measuring device.

Any number $a$ may be represented as $\pm m.10^e$ where $m$ is the mantissa ($0.1 \leq m < 1$) and $e$ is an integer. Usually $m$ is limited to 8 digits and hence $a$ is now stored as $\bar{a} = \pm \bar{m}.10^e$ where $\bar{m} = 0.d_1d_2...d_t$ and $d_1 > 0$, $t$ is usually 8 and $|e| < M$ ($M$ is the largest exponent that is allowed). For single precision calculations, $-38 < e < 38$ ($-125 < \exp_2 < 125$) where $\exp_2$ is the exponent in base 2 ($M=38$). Double precision uses $-308 < e < 308$ ($-1020 < \exp_2 < 1020$).

Numbers smaller than $10^{-38}$ would give underflow errors (which are handled by treating the value as 0) and values larger than $10^{38}$ cause overflow errors (problematic, because we cannot represent infinity on a computer).

Truncation and Round-off errors

Obviously, there could be loss of significance in the storage of numbers at lower precision. Decimal places are discarded by chopping them off (truncation) or by rounding them off. In both cases, there is a loss of significant digits. Rounding off involves discarding digits from $(k + 1)^{th}$ place onwards.

- If the number discarded is less than half the unit in the $k^{th}$ place, then the $k^{th}$ value is left unchanged (rounding down).
- If the number discarded is more than half the unit in the $k^{th}$ place, then add 1 to the $k^{th}$ value (rounding up).
- If the number discarded is half the unit in the $k^{th}$ place (i.e. = 5), round off to the nearest even decimal.
Therefore 3.45 and 3.55 when rounded off to one decimal place become 3.4 and 3.6. Rounding off 1.2535 to 3, 2 and 1 places gives 1.254, 1.25 and 1.3. Note that rounding off 1.25 to one place gives 1.2!

When $a = \pm m.10^e$ is approximated by $\tilde{a} = \pm \tilde{m}.10^e$, the relative rounding off error is (noting that $|m - \tilde{m}| \leq 10^{-t}/2$, and that $|m| \geq 0.1$)

$$\frac{|a - \tilde{a}|}{a} \sim \left|\frac{m - \tilde{m}}{m}\right| \leq \frac{10^{1-t}}{2}$$

Chopping off is obviously simpler, but errors would be larger. When $a = \pm m.10^e$ is approximated by $\tilde{a} = \pm \tilde{m}.10^e$, the relative truncation error is

$$\frac{|a - \tilde{a}|}{a} \sim \left|\frac{m - \tilde{m}}{m}\right| \leq 10^{1-t}$$

The absolute error when the true value $a$ is measured as $\tilde{a}$ is $\epsilon = a - \tilde{a}$. Example: $a = 10.2$ and $\tilde{a} = 10.5$ gives $\epsilon = -0.3$.

The relative error of $\tilde{a}$ is $\epsilon_\tilde{a} = (a - \tilde{a})/a = \epsilon/a$. But $a$ is usually unknown, and so this is approximated with $\epsilon_\tilde{a} = (a - \tilde{a})/\tilde{a} = \epsilon/\tilde{a}$. Usually $\epsilon$ is unknown, and so we use bounds such as $\beta$ where $|\epsilon| \leq \beta$ and $|\epsilon_\tilde{a}| \leq \beta_\tilde{a}$. While errors in the representation of individual numbers may look small, successive manipulation of such numbers would cause the total error to blow up.

**Error propagation**

Let $x = \tilde{x} + \epsilon_1$ and $y = \tilde{y} + \epsilon_2$ where $|\epsilon_1| \leq \beta_1$ and $|\epsilon_2| \leq \beta_2$

**Addition:**

$$|\epsilon| = |x + y - (\tilde{x} + \tilde{y})| = |(x - \tilde{x}) + (y - \tilde{y})| = |\epsilon_1 + \epsilon_2| \leq |\beta_1 + \beta_2|$$

**Subtraction:**

$$|\epsilon| = |x - y - (\tilde{x} - \tilde{y})| = |(x - \tilde{x}) - (y - \tilde{y})| = |\epsilon_1 - \epsilon_2| \leq |\beta_1 + \beta_2|$$

For both addition and subtraction, the error of the result is the sum of absolute errors.

**Multiplication:** The relative error $\epsilon_r$ of $\tilde{x}\tilde{y}$ is

$$|\epsilon_r| = \left|\frac{xy - \tilde{x}\tilde{y}}{xy}\right| = \left|x - \epsilon_1\right|\left|y - \epsilon_2\right| \approx \left|\frac{\epsilon_1 y + \epsilon_2 x - \epsilon_1 \epsilon_2}{xy}\right| \leq \frac{|\epsilon_1|}{|x|} + \frac{|\epsilon_2|}{|y|}$$

where we have assumed $|\epsilon_1\epsilon_2| \ll |\epsilon_1|$ and $|\epsilon_2|$.

**Division:** The real ratio may be written as

$$\frac{x}{y} = \frac{\tilde{x} + \epsilon_1}{\tilde{y} + \epsilon_2} = \frac{\tilde{x} + \epsilon_1}{\tilde{y}(1 + \epsilon_2/\tilde{y})} = \frac{\tilde{x} + \epsilon_1}{\tilde{y}} \left(1 - \frac{\epsilon_2}{\tilde{y}} + \frac{\epsilon_2^2}{\tilde{y}^2} - \ldots\right) \approx \frac{\tilde{x}}{\tilde{y}} + \frac{\epsilon_1}{\tilde{y}} - \frac{\epsilon_2}{\tilde{y}} \frac{\tilde{x}}{\tilde{y}}$$

where $\epsilon_1\epsilon_2$ and higher terms are neglected, and hence

$$\left|\frac{x/y - \tilde{x}/\tilde{y}}{x/y}\right| \approx \left|\frac{\epsilon_1}{x} \frac{\epsilon_2}{y}\right| \leq |\epsilon_r,1| + |\epsilon_r,2| \leq \beta_{r,1} + \beta_{r,2}$$

For both multiplication and division, the relative error of the result is the sum of relative errors.
Loss of accuracy

The causes of loss of accuracy usually are Floating point errors and Experimental errors.

Floating point errors

These are usually of 4 types:

1. Creeping roundoff/truncation: Using the definition of relative errors, \( x = \tilde{x}(1 + \epsilon_{r,1}) \) and \( y = \tilde{y}(1 + \epsilon_{r,2}) \) where \( \tilde{x} \) and \( \tilde{y} \) are the floating point representations of \( x \) and \( y \). Then the floating point representation of their sum would itself be stored as a floating point value \((\tilde{x} + \tilde{y})\). If the relative error in this representation itself is \( \epsilon_{r,3} \), then

\[
(\tilde{x} + \tilde{y}) = (\tilde{x} + \tilde{y})(1 + \epsilon_{r,3}) = (x(1 + \epsilon_{r,1}) + y(1 + \epsilon_{r,2}))(1 + \epsilon_{r,3})
\]

\[
= (x + y) + (x + y)\epsilon_{r,3} + (x\epsilon_{r,1} + y\epsilon_{r,2}) + (x\epsilon_{r,1} + y\epsilon_{r,2})\epsilon_{r,3}
\]

2. Negligible addition: adding a small number to a larger one with roundoff could result in the smaller number being drowned out. To 4 significant places (4S), \((0.0004 + 0.0004) + 1.000 = 1.001 \) but \((1.000 + 0.0004) + 0.0004 = 1.000\). Add the smallest numbers first, for better accuracy. This can be an issue for example, when computing the mean: for \( n \) values, the mean is computed by summing all the numbers using a loop, and then dividing by \( n \). It may be more reliable to sort the numbers and to then add them up.

3. Magnification: Errors get magnified usually on multiplication/division as explained before.

4. Loss of significant digits by subtraction cancellation

   Example: Subtraction cancellation of two numbers of ~same size: \( 0.1439 - 0.1426 = 0.0013 = 0.13 \times 10^{-2} \) with the loss of two significant digits.

   Example: Computing the ratio \( a/(b - c) \) can be problematic if \( b \) and \( c \) are of almost equal value.

<table>
<thead>
<tr>
<th>Calculation</th>
<th>signif. digits</th>
<th>( a/(b - c) )</th>
<th>( a(b + c)/(b^2 - c^2) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.81534/(35.724-35.596)=6.3698437...</td>
<td>5</td>
<td>6.3698</td>
<td>6.3698</td>
</tr>
<tr>
<td>0.8153/(35.72 - 35.60)</td>
<td>4</td>
<td>6.794</td>
<td>6.370</td>
</tr>
<tr>
<td>0.815/(35.7-35.6)</td>
<td>3</td>
<td>8.15</td>
<td>6.37</td>
</tr>
<tr>
<td>0.82/(36-36)</td>
<td>2</td>
<td>division by 0</td>
<td>6.4</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>-</td>
<td>6</td>
</tr>
</tbody>
</table>

Example: Quadratic roots: Find roots of \( x^2 - 40x + 2 = 0 \) to 4 significant digits.

- Method 1: For \( ax^2 + bx + c = 0 \),

\[
x_1 = \frac{-b + \sqrt{b^2 - 4ac}}{2a}, \quad x_2 = \frac{-b - \sqrt{b^2 - 4ac}}{2a}
\]

which gives \( x = 20.00 \pm \sqrt{398.0} = 20.00 \pm 19.95 \) which gives \( x_1 = 39.95 \) and \( x_2 = 0.05 \).
• Method 2:

\[ x_1 = -\frac{b + \sqrt{b^2 - 4ac}}{2a}, \quad x_2 = \frac{c}{ax_1} \]

using the observation that \( x_1 + x_2 = -\frac{b}{a} \) and \( x_1x_2 = \frac{c}{a} \). This gives \( x_1 = 39.95 \) and \( x_2 = 2.000/39.95 = 0.05006 \).

• Method 3: Use

\[ b_1 = -\frac{b}{2a}, \quad c_1 = \frac{c}{a}, \quad d = b_1^2 - c_1, \quad r_1 = \sqrt{d} \]

If \( b_1 < 0 \), use \( x_1 = -r_1 \) and if \( r_1 \neq 0 \), use \( x_2 = c_1/r_1 \). What roots does this method give?

Other tips

• Use fewer operations to reduce error: For example, use nested multiplication if possible. For \( y = a_0x^n + a_1x^{n-1} + \ldots + a_nx + a_{n+1} \), use a loop:

\[
y = 0; \quad \text{for } i=1 \text{ to } n+1, \quad y = y \times x + a_{i}; \quad \text{end}
\]

This results in \( 2n \) operations only, with one addition and one multiplication per iteration.

• Find alternate series forms. For example \( 1 + \cos(x) \) is difficult to measure at \( x \approx \pi \) since \( \cos(\pi) = -1 \) (subtractive cancellation). Instead use the identity \( 1 + \cos(x) = 2(\sin(x/2))^2 \).

• Store intermediate values in extended precision.

Regression analysis

Given a model where we believe that \( y = \alpha + \beta x \), we wish to estimate the ‘best-fit’ regression line \( y = a + bx \). First note that the values \( a \) and \( b \) represent the best possible estimates of \( \alpha \) and \( \beta \) given available experimental measurements \( (x_i, y_i) \). (\( \alpha \) and \( \beta \) are population parameters, and \( a \) and \( b \) represent sample estimates of those parameters).

We need a line such that \( (x_i, \hat{y}_i) = (x_i, a + bx_i) \). The deviations of the actual experimental points from the line are \( y_i - \hat{y}_i = d_i = y_i - a - bx_i \). The best fit line tries to minimize \( S = \text{sum of squared distances of points from the line} \) (hence called the method of least squares)

\[
S = \sum_{i=1}^{n} d_i^2 = \sum_{i=1}^{n} (y_i - a - bx_i)^2
\]

It can be shown that the best estimates of \( \beta \) and \( \alpha \) are

\[
b = \frac{L_{xy}}{L_{xx}}; \quad a = \bar{y} - b\bar{x}
\]

where

\[
\bar{x} = \frac{\sum_{i=1}^{n} x_i}{n}; \quad \bar{y} = \frac{\sum_{i=1}^{n} y_i}{n}
\]

\[
L_{xx} = \sum_{i=1}^{n} (x_i - \bar{x})^2 = \sum_{i=1}^{n} x_i^2 - n(\bar{x})^2; \quad L_{xy} = \sum_{i=1}^{n} (x_i - \bar{x})(y_i - \bar{y}) = \sum_{i=1}^{n} x_i y_i - n\bar{x}\bar{y}
\]
The sample correlation coefficient is a measure of association between the two continuous variables $x$ and $y$. $r = \frac{L_{xy}}{\sqrt{L_{xx}L_{yy}}}$ where $L_{yy}$ is $\sum_{i=1}^{n}(y_i - \bar{y})^2 = \sum_{i=1}^{n}y_i^2 - n(\bar{y})^2$. $r$ ranges from -1 to +1, and $r = 0$ indicates that $x$ and $y$ are not correlated. Clearly, $r$ is related to the slope of the best-fit line $b$. Note that $r$ is unchanged if the units of $x$ and $y$ are changed, or if the variables are themselves swapped ($x$ is called $y$ and vice-versa). $b$ however would be affected by swapping of variables or a change in units. $r$ indicates a linear relationship between the variables, whereas $b$ describes the precise linear relationship between them.

Notes

- The least-squares linear regression method assumes that the data fits a linear model. It is possible (and common) to get excellent regression values (close to 1), yet the data might instead be better described by a higher polynomial. Nonlinear regression approaches exist, but clearly even then, blind application of this statistical approach can be dangerous.

- A necessary aspect of accurate parameter estimation is identification of confidence intervals for the parameters involved. Belief in the estimates is increased on increasing the sample size (To increase your belief that a coin is fair, toss it more times). It is common to perform replicates to identify an average value. It is also important to compute from these replicates, the standard deviation associated with these measurements. These standard deviations are representations of the errors that we have already discussed. The propagation of errors reflects the situation that typically arises when the mean values of various variables are manipulated using various arithmetic operations, but propagation of standard deviations are ignored.

- A typical trick used in parameter evaluation of a nonlinear model is to first convert it to a linear form and then apply linear regression. For example, $y = \frac{ax}{b + x}$ may be inverted to yield the linear relationship $1/y = (1/a) + (b/a)(1/x)$. However while small values of $x$ (and therefore small errors in the measurement of $x$) may not significantly influence the shape of the hyperbolic curve (and estimation of parameters from that curve), they have a huge impact on the calculation of the slope and intercept of the inverted (linear) form.