Transparent Batch Reactor

Instruction Manual

CEB-MKIII

ISSUE 3

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General Overview

THIS INSTRUCTION MANUAL SHOULD BE USED IN CONJUNCTION WITH THE MANUAL SUPPLIED WITH THE CEXC COMPUTER CONTROLLED CHEMICAL REACTOR SERVICE UNIT.

This Manual provides the necessary information for operating the equipment in conjunction with the CEXC Computer Controlled Chemical Reactor Service Unit, and for performing a range of Teaching Exercises designed to demonstrate the basic principles of Chemical Reactors theory and use.

Batch reactors are used widely in industry at all scales. Batch reactors are tanks, commonly provided with agitation and a method of heat transfer (usually by coils or external jacket). This type of reactor is primarily employed for relatively slow reactions of several hours duration, since the downtime for filling and emptying large equipment can be significant. Agitation is used to maintain homogeneity and to improve heat transfer.

The Armfield CEB MkIII Transparent Batch Reactor is specially designed to allow detailed study of this important process. It is one of five reactors types which are interchangeable on the Computer Controlled Reactor Service Unit (CEXC), the others being CEM MkII - Continuous Stirred Tank Reactor, CET MkII - Tubular Reactor, CEY Plug Flow Reactor and CEZ Laminar Flow Reactor.

Reactions are monitored by conductivity probe as the conductivity of the solution changes with conversion of the reactants to product and visually due to the use of indicators.

CEXC fitted with CEB MkIII Transparent batch reactor

Note: If CEB-MKIII is to be used with a CEX rather than CEXC, then optional temperature sensor STS4 will be required if it is required to measure reactor temperature (the temperature sensor supplied with CEX is used to control the hot water temperature in isothermal operation).

Equipment Diagrams

Figure 1: CEB MkIII Transparent Batch Reactor

Important Safety Information

Introduction

All practical work areas and laboratories should be covered by local safety regulations **which must be followed at all times**.

It is the responsibility of the owner to ensure that all users are made aware of relevant local regulations, and that the apparatus is operated in accordance with those regulations. If requested then Armfield can supply a typical set of standard laboratory safety rules, but these are guidelines only and should be modified as required. Supervision of users should be provided whenever appropriate.

Your **CEB MkIII Transparent Batch Reactor** has been designed to be safe in use when installed, operated and maintained in accordance with the instructions in this manual. As with any piece of sophisticated equipment, dangers exist if the equipment is misused, mishandled or badly maintained.

Water Borne Hazards

The equipment described in this instruction manual involves the use of water, which under certain conditions can create a health hazard due to infection by harmful micro-organisms.

For example, the microscopic bacterium called Legionella pneumophila will feed on any scale, rust, algae or sludge in water and will breed rapidly if the temperature of water is between 20 and 45°C. Any water containing this bacterium which is sprayed or splashed creating air-borne droplets can produce a form of pneumonia called Legionnaires Disease which is potentially fatal.

Legionella is not the only harmful micro-organism which can infect water, but it serves as a useful example of the need for cleanliness.

Under the COSHH regulations, the following precautions must be observed:

- Any water contained within the product must not be allowed to stagnate, ie. the water must be changed regularly.

- Any rust, sludge, scale or algae on which micro-organisms can feed must be removed regularly, i.e. the equipment must be cleaned regularly.

- Where practicable the water should be maintained at a temperature below 20°C. If this is not practicable then the water should be disinfected if it is safe and appropriate to do so. Note that other hazards may exist in the handling of biocides used to disinfect the water.

- A scheme should be prepared for preventing or controlling the risk incorporating all of the actions listed above.

Further details on preventing infection are contained in the publication "The Control of Legionellosis including Legionnaires Disease" - Health and Safety Series booklet HS (G) 70.

Electrical Safety

The equipment described in this Instruction Manual operates from a mains voltage electrical supply. It must be connected to a supply of the same frequency and voltage

as marked on the equipment or the mains lead. If in doubt, consult a qualified electrician or contact Armfield.

The equipment must not be operated with any of the panels removed.

To give increased operator protection, the unit incorporates a Residual Current Device (RCD), alternatively called an Earth Leakage Circuit Breaker, as an integral part of this equipment. If through misuse or accident the equipment becomes electrically dangerous, the RCD will switch off the electrical supply and reduce the severity of any electric shock received by an operator to a level which, under normal circumstances, will not cause injury to that person.

At least once each month, check that the RCD is operating correctly by pressing the TEST button. The circuit breaker **MUST** trip when the button is pressed. Failure to trip means that the operator is not protected and the equipment must be checked and repaired by a competent electrician before it is used.

Hot Surfaces and Liquids

The unit incorporates a pumped electric water heater, and is capable of producing temperatures that could cause skin burns.

Before disconnecting any of the pipes or tubing:

- Stop all the pumps.

- Leave time for the water to cool

- Check that the temperature is at a safe level

Do not touch any surfaces close to 'Hot Surfaces' warning labels, or any of the interconnecting tubing, whilst the equipment is in use.

Chemical Safety

Details of the chemicals intended for use with this equipment are given in the Operational Procedures section. Chemicals purchased by the user are normally supplied with a COSHH data sheet which provides information on safe handling, health and safety and other issues. It is important that these guidelines are adhered to.

- It is the user's responsibility to handle chemicals safely.

- Prepare chemicals and operate the equipment in well ventilated areas.

- Only use chemicals specified in the equipment manuals and in the concentrations recommended.

- Follow local regulations regarding chemical storage and disposal.

Description

Where necessary, refer to the drawings in the <u>Equipment Diagrams</u> section.

The Reactor Vessel

The reactor vessel is a double skinned glass vessel with one litre and a half of internal working volume. It is set on a baseplate which is designed to be located on the four studs of the CEXC service unit and then secured by thumbnuts. The reactor is supported by three pillars; position the reactor on the CEXC service unit such that a single pillar is to the front.
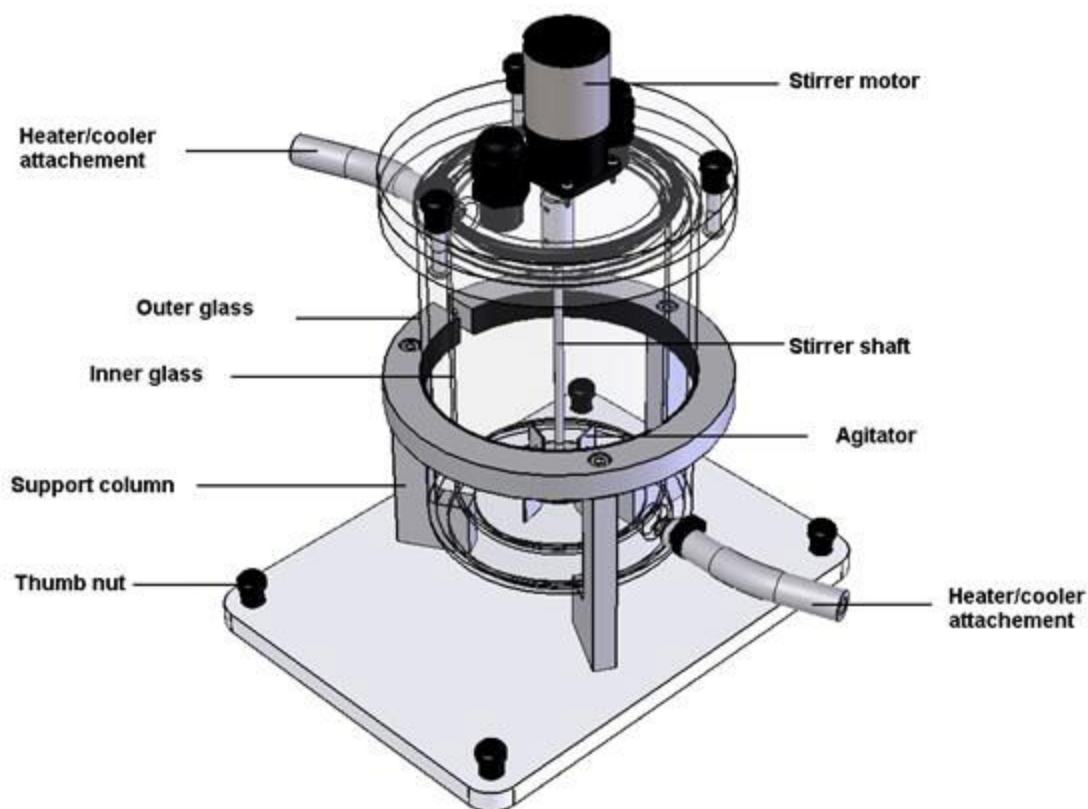
CEB MKII Transparent Batch Reactor

Hot water from the CEXC or cold water from CW17 can be recirculated to the jacket for temperature control purposes. Either the hot water circulator or the CW-17 chiller is connected to the 'Heater/Cooler attachments'. **Note:** the water inlet is at the bottom of the reactor jacket and the water outlet is at the top of the reactor jacket.

A turbine agitator works to provide efficient mixing and heat transfer. The agitator is driven by an electric motor mounted on the lid of the reactor. The speed of the motor can be controlled by using Amrfield software interface. The socket for the electrical motor plug is sited at the rear of the service unit.
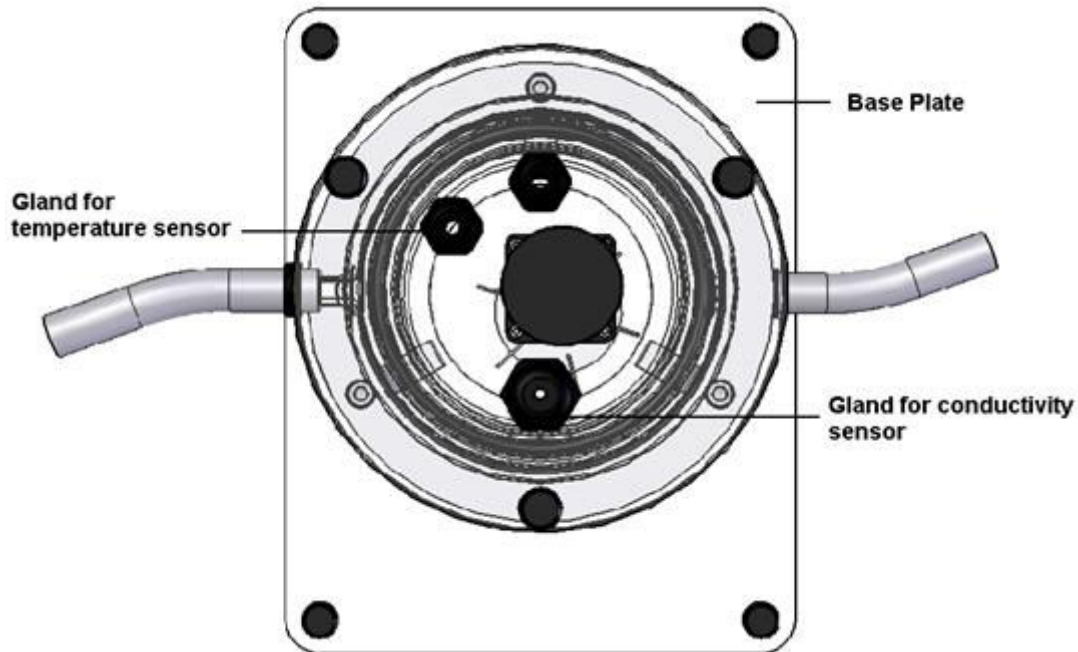
Reactor Lid

Glands in the reactor lid house the conductivity and temperature sensor provided with the CEXC service unit. The larger of the two glands is for the conductivity probe. The glands are unscrewed by hand, the sensors inserted completely into the reactor until they rest a few cm from the bottom and then the glands re-tightened by hand. Sockets at the rear of the service unit are provided to connect each sensor. The conductivity probe is connected to the 3 pin socket marked 'HIGH COND'. The temperature sensor is connected to the k-thermocouple socket marked 'T1'. Both temperature values and conductivity values are data logged using a PC in conjunction with the Armfield software interface.

An additional temperature sensor 'T2' is supplied with CEXC that allows the Hot Water Circulator temperature to be also monitored. Therefore T2 temperature sensor must be immersed in the Hot Water Circulator vessel through the hole in the lid.

There is an extra temperature 'T3' and 'Low conductivity' plug at the rear of the service unit with outputs on the software for extra connections made by the user. If solutions with low conductance are used, connect the conductivity probe to the socket marked as 'LOW COND' and conductivity values will be data logging more accurately in a low range.
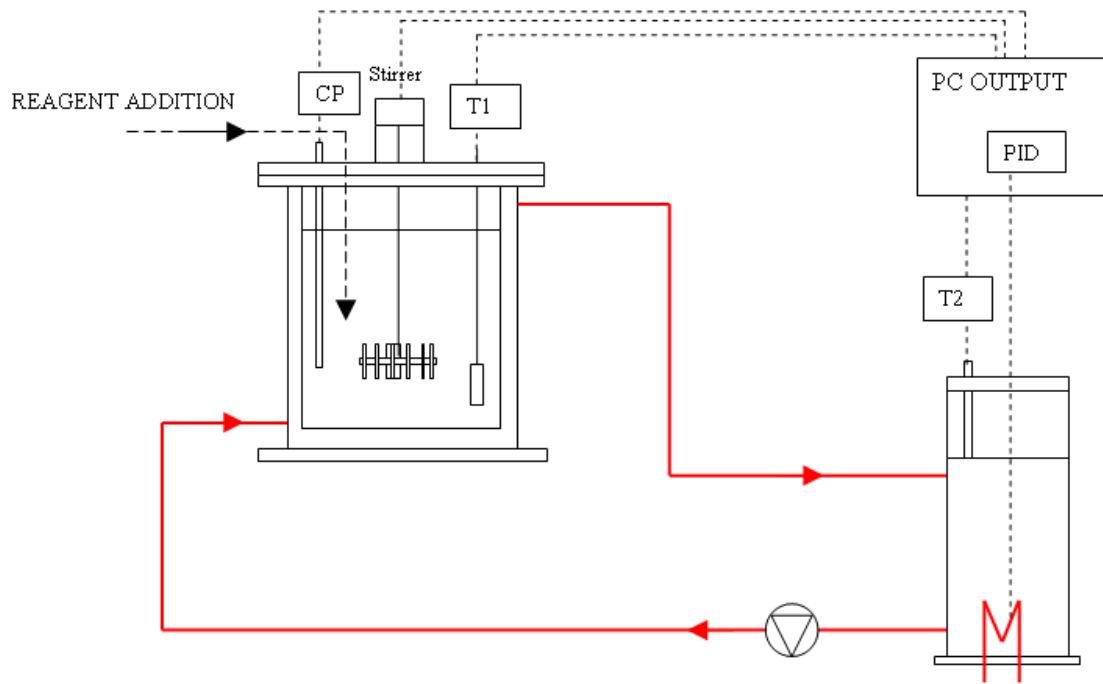
CEB MkIII Transparent Batch Reactor

Installation

Advisory

Before operating the equipment, it must be unpacked, assembled and installed as described in the steps that follow. Safe use of the equipment depends on following the correct installation procedure.

Installing the PC Software

Before operating CEB-MKIII it will be necessary to install the software from the CD-ROM supplied with CEXC onto an appropriate PC (PC not supplied).

For instructions on how to install and run the software insert the CD-ROM into the optical drive on the PC (PC not supplied) then choose 'Help' from the menu.

After installing and running the software on the PC, instructions on how to operate the software can be obtained by choosing the 'Help' tab in the top right hand corner of the screen as shown below:

Note that when operating the software for the first time it will be necessary to enable the USB virtual COM port by choosing the Red telephone icon (Start COM session).

Full instructions about enabling the port are included in the Help menus.

Installing the Equipment

Mounting the CEB MKIII onto the CEXC

- The reactor vessel is set on a baseplate which is itself located on four studs on the service unit and secured by thumbnuts. The feed bottles provided with CEXC are not required with the batch reactor configuration.

- Plug the temperature sensor and conductivity sensor supplied with CEXC into the appropriate sockets at the rear of the service unit then insert the sensors through the appropriate glands in the lid of the reactor. Check that the sensors are fully immersed then tighten the glands.

- Connect the stirrer plug to the socket located on the rear of the CEXC.

Connecting the HWC to CEB MKIII
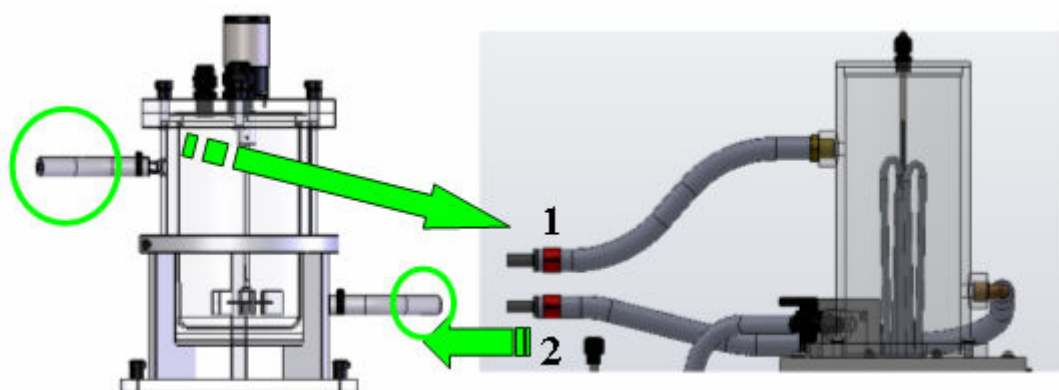
- Connect return pipe of the HWC (1) to the connection at the top of the reactor vessel.

- Connect the supply pipe of the HWC (2) to the connection at the bottom of the reactor vessel.

Connection to electricity supply
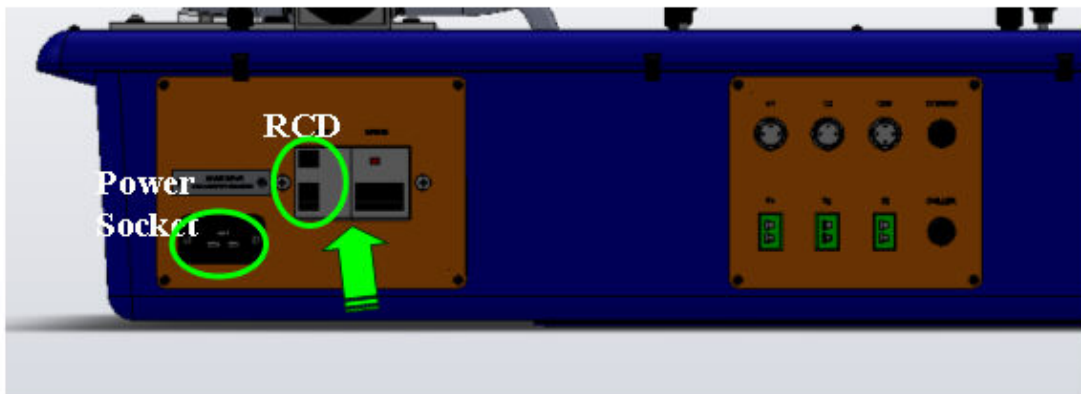
- Check that the voltage specified on the equipment matches the supply voltage.

  NOTE: this unit **must** be earthed.

- Connect the power socket at the rear of the plinth to a suitable mains electricity supply.

- Ensure that circuit breakers and RCD are ON (up).

- The on/off switch for the apparatus is located on the orange panel on the front of the plinth. Switch on the apparatus.

Connection to a PC for Control and Data Logging

Ensure that the software has been installed as described in the section 'Installing the PC software'.

Switch on the PC and connect the USB lead from the CEXC to the PC.

Load the CEM software then choose the appropriate experiment from the menu. For detailed information about operating the software refer to the section Operating the PC Software.

Display the mimic diagram by choosing View then Diagram or via the mimic diagram icon from the top toolbar:
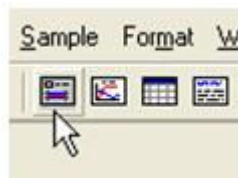
If operating the software for the first time enable the virtual COM port using the red telephone icon in the top toolbar:

Refer to the section Operating the PC Software if necessary.

Connect the mains supply to the CEXC then switch on the CEXC. Click the 'Power On' button on the mimic diagram:

Confirm that the appropriate measured variables are displayed on the mimic diagram.

The software is ready for use.

Priming the hot water circulator (HWC)

- Fill HWC vessel with water up to the low level tip (30cm from top).

- Switch on the Hot Water Circulator. Level of water in the vessel will decrease as reactor jacket is filled. Keep filling the HWC vessel until the level in the vessel is stable and over the Low level tip.
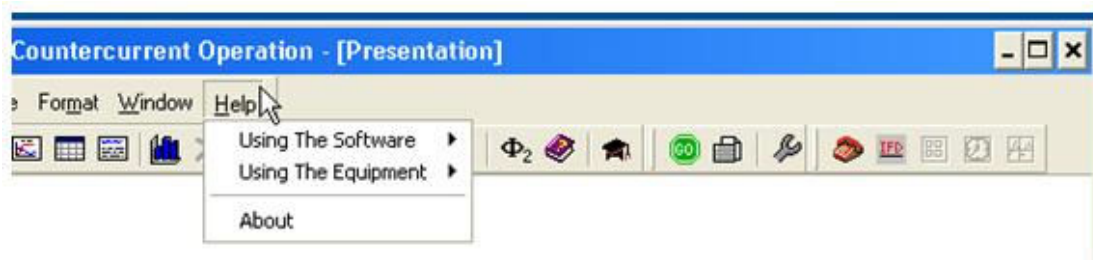
Operation

Where necessary, refer to the drawings in the Equipment Diagrams section.

The apparatus must be set up in accordance with the Installation section. Additionally, ensure that you have read the Important Safety Information at the beginning of this manual.

Operating the PC Software

Details about operating the software can be obtained by choosing the 'Help' tab in the top right hand corner of the screen as shown below:

Operating the Equipment

Switching on the unit

The unit is switched on using the switch on the front of the unit. The circuit breakers and RCD device located at the rear of the unit should be turned on beforehand.
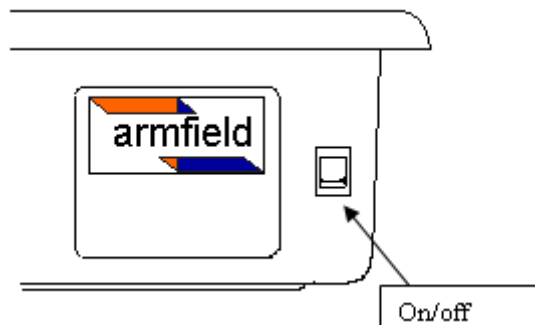
Operation Hot Water Circulator

The hot water circulator vessel should be filled with water before use, and drained after use if the equipment is not going to be used for some time. When use fill the vessel by pouring clean (preferably demineralised) water until the level is approximately 20 mm from the top.

Top up the level of this vessel as necessary to maintain the level above the tip of the level electrode (typically 20 mm from the top of the vessel).
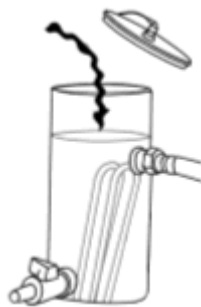
Heater is controlled from a PC via the CEB software. A PID controller within the software maintains the heater setting based on the temperature measured by the chosen temperature sensor. The Set Point temperature, proportional Band and the Integral and Derivative times may be adjusted by the user. Alternatively the heater power setting may be entered manually as a percentage value, using the same controller window as for the PID settings.

Operation of Data Logger and Software

The Armfield CEB MkIII reactor is controlled using the CEB software supplied with the CEXC, which allows real-time monitoring and data logging of all sensor outputs and control of the heater unit. Recorded results can be displayed in tabular and graph format. The software runs on a Windows™ PC which connects to the CEXC using a USB interface.

Installation of the software is described in the Installation Guide, and the software must be installed before connecting the PC to the CEXC. The software may then be run from the Start menu (Start > Programs > Armfield Chemical Reactor Software > CEB). Operation of the software is described in a walkthrough presentation within the software, and also in the online Help Text accessible via the software Help menu. Operation and setting of specific controls is also provided within the experiments described in this manual.

Mimic Diagram and software

The equipment is usually controlled from the Mimic Diagram screen in the software. This shows all the sensor outputs, and includes controls for the stirrer and the Hot water Circulator. The stirrer is controlled from the software using the up/down buttons or typing in directly a value between 0 and 100%.

Concentration and volume values must be filled in the boxes on each experiment so that software will carry out the convenient calculations.

The software also automatically generates a series of 'Watchdog' pulses, required by the plc, ensuring that the hardware shuts down safely in case of a software or communications failure.
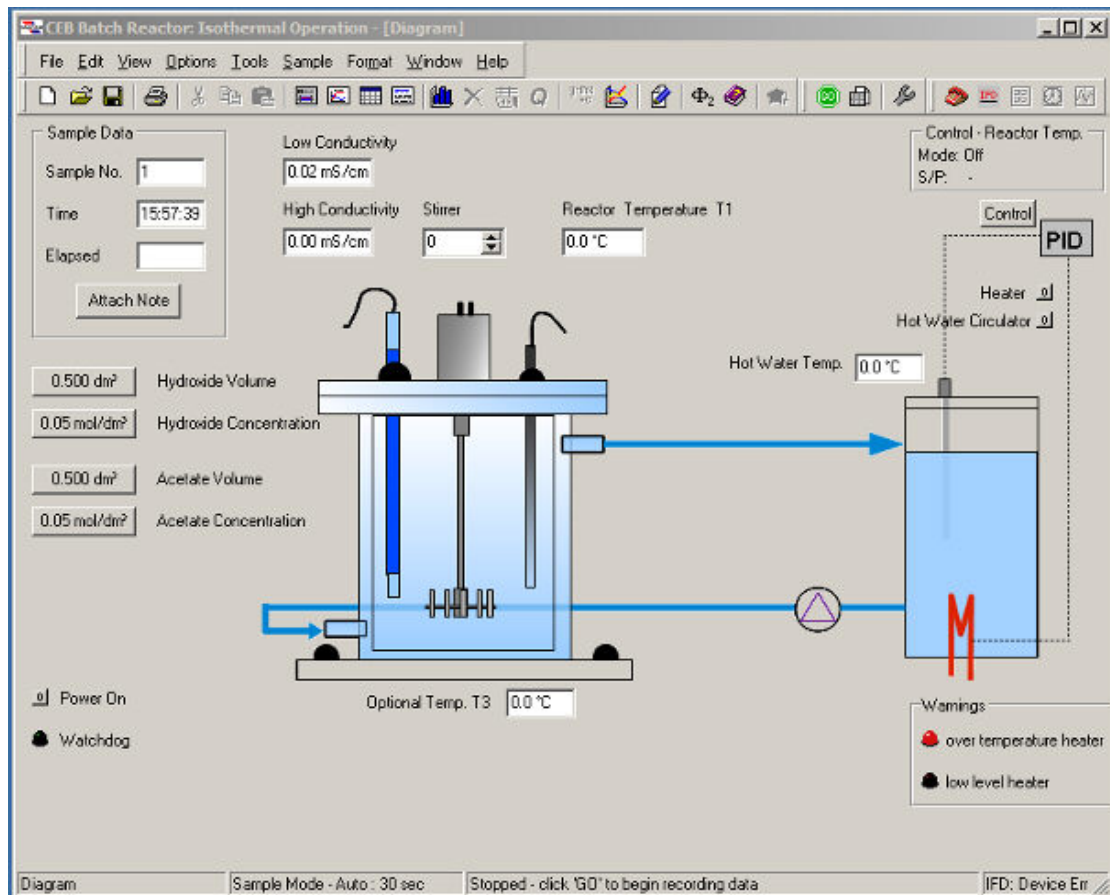
Controlling the HWC

The heater is controlled by a controller in the software. Click on the appropriate CONTROL symbol to open the controller window.
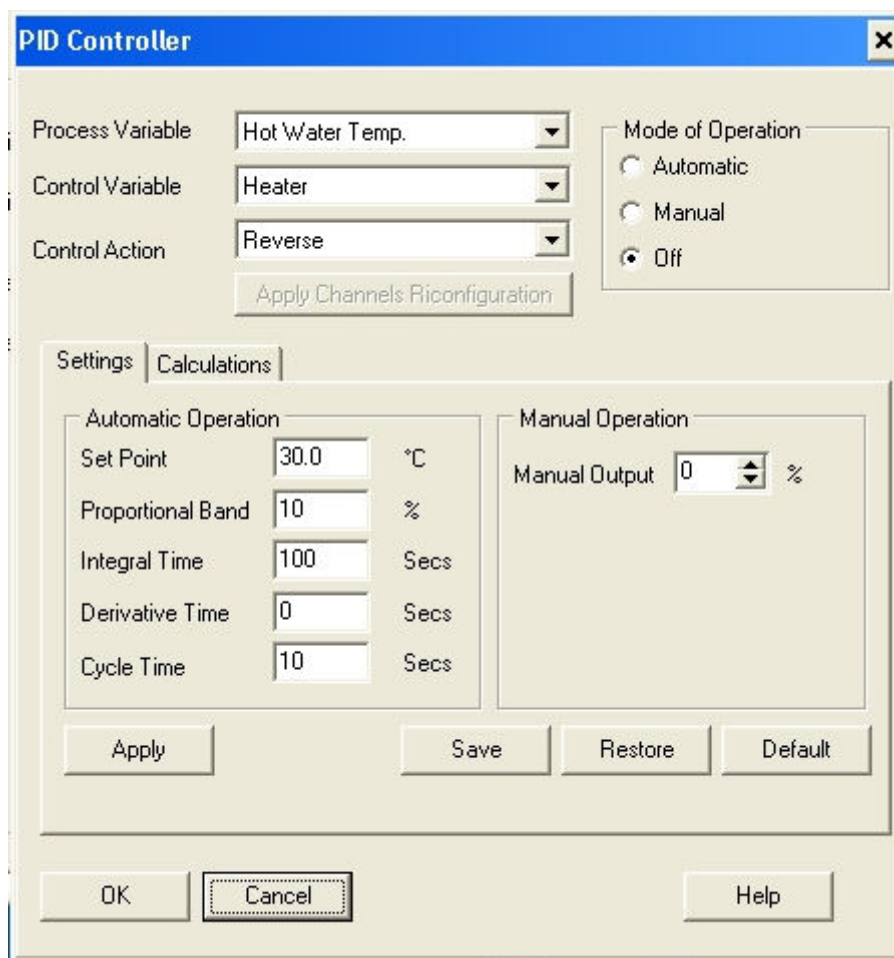
Control can be either closed loop (Automatic) which uses the temperature sensor immediately following the heater as the process variable in a PID loop, or open loop (Manual) where the user defines the percentage time the heaters are 'ON' for, and hence the output power.

When performing a reaction it is best to use Automatic control as this produces stable temperatures most rapidly, and maintains these conditions by varying the heater power.

Operating the CEB MkIII

There are two modes of operation with the CEB batch reactor: **Isothermal** and **Adiabatic** operation. The temperature and conductivity sensors must be situated well below the liquid surface inside the reactor.

Isothermal Operation

When operating isothermally the temperature sensor T2 supplied with CEXC should be set as the temperature sensor to be controlled in the PID loop box on the software. This sensor must be immersed in the vessel of the Hot Water Circulator. On the other hand the other temperature sensor T1 is used to monitor the reaction temperature during the experiments.

PID settings need to be adjusted to suit the experiment conditions. When using the Chiller CW-17 PID settings are not required. See the installation guide for appropriate controller settings when using the CW-17.

In the case of Isothermal Operation the PID settings recommended are:

Note these values are suitable when the controlling sensor is T2 which is fitted in the HWC vessel.

The setpoint can be varied as required to suit the experiment.

Adiabatic Operation

When operating the batch reactor adiabatically, temperature control is not required so either Chiller or HWC are not required.

The contents of the reactor are stirred by an agitator which is driven by an electrical motor/gearbox combination mounted on the lid. The motor is connected to the electrical supply by a jack plug which is plugged into a socket at the rear of the CEXC service unit. The agitator speed is adjusted using the Armfield software interface supplied with the reactor. See mimic Adiabatic Operation Diagram below.
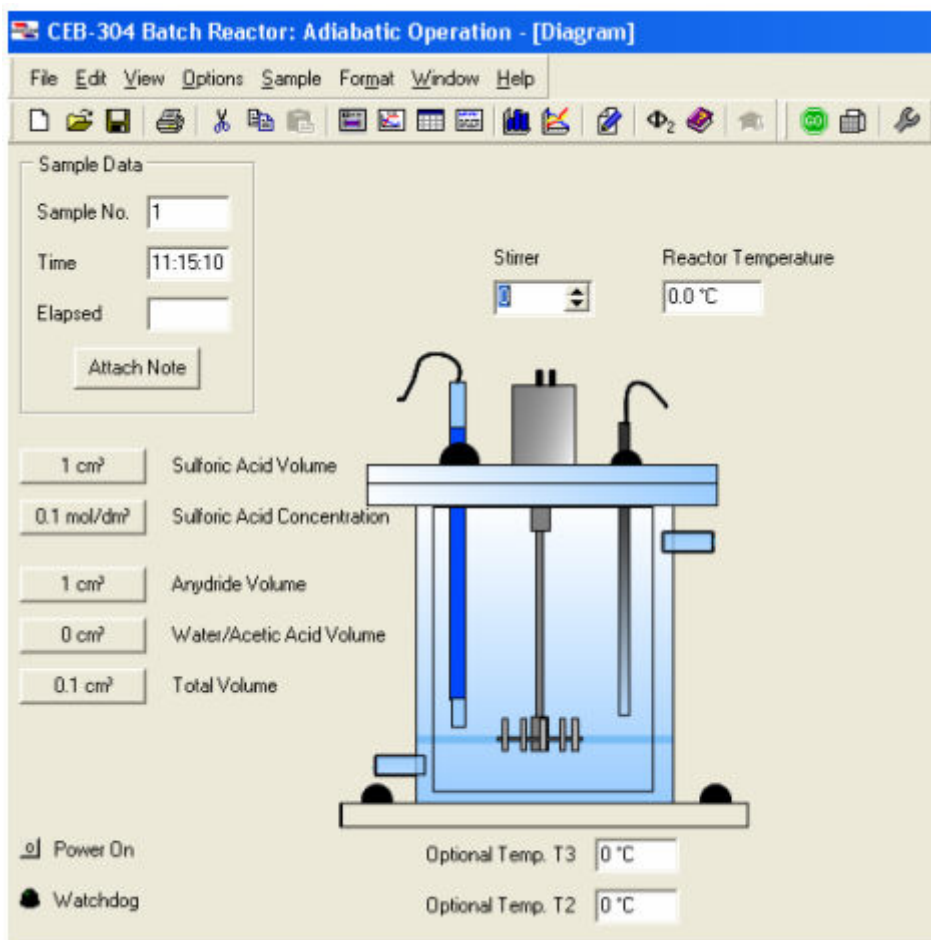
Ensure that protective gloves are worn when handling any of the substances used in the reactor. Once the experiment is finished wash the reactor with distilled water.

Equipment Specifications

Environmental Conditions

This equipment has been designed for operation in the following environmental conditions. Operation outside of these conditions may result reduced performance, damage to the equipment or hazard to the operator.

a. Indoor use;

b. Altitude up to 2000m;

c. Temperature 5°C to 40°C;

d. Maximum relative humidity 80% for temperatures up to 31°C, decreasing linearly to 50% relative humidity at 40°C;

e. Mains supply voltage fluctuations up to ±10% of the nominal voltage;

f. Transient over-voltages typically present on the MAINS supply;

   Note: The normal level of transient over-voltages is impulse withstand (over-voltage) category II of IEC 60364-4-443;

g. Pollution degree 2.

   Normally only nonconductive pollution occurs.

   Temporary conductivity caused by condensation is to be expected.

   Typical of an office or laboratory environment

Routine Maintenance

Responsibility

To preserve the life and efficient operation of the equipment it is important that the equipment is properly maintained. Regular maintenance of the equipment is the responsibility of the end user and must be performed by qualified personnel who understand the operation of the equipment.

General

The equipment should be disconnected from the electrical supply when not in use. After use the feed bottles, reactor vessel, sump tray and pipework should be washed through with water to remove chemical residues and then drained.

RCD Test

Test the RCD by pressing the TEST button at least once a month. If the RCD button does not trip when the Test button is pressed then the equipment must not be used and should be checked by a competent electrician.

Temperature sensors calibration

The temperature sensors are calibrated before delivery and should not require re-calibration. However should calibration become necessary follow the below procedure. This should only be done once the unit has fully warmed up.

The temperature conditioning circuit (which provides the reading from the conductivity probe supplied with the CEXC service unit) is located on a printed circuit board inside the plinth on the right-hand side. This circuit is calibrated before despatch and should not require re-calibration. However, should re-calibration become necessary the appropriate calibration potentiometers can be located using the diagram given in the CEXC manual (Routine Maintenance).

Connect CEXC service unit to a PC and start up the Armfield software. Open mimic diagram screen where T1, T2 and T3 windows are displayed.

If a thermocouple calibrator is available:

Connect Thermocouple calibrator simulator to T1 input socket. Set to 25ºC and adjust VR1 (T1 ZERO) and VR2 (T1 SPAN) on the PCB to give 25ºC displayed on PC. Check accuracy at 15º and 40ºC.

Repeat the same procedure for T2 by adjusting VR3 (T2 ZERO) and VR4 (T2 SPAN) on the PCB to give 25ºC displayed on PC, and VR5 (T3 ZERO) and VR6 (T3 SPAN) for T3.

If a thermocouple calibrator is not available:

Temperature sensor T1, T2 and T3 should be dipped into crushed ice, and then adjust the ZEROS to give 0ºC, then sensors should be dipped into boiling water and then adjust the SPANS to 100ºC.

Calibration of the conductivity sensor

The conductivity conditioning circuit (which provides the reading from the conductivity probe supplied with the CEXC service unit) is located on a printed circuit board inside the plinth on the right-hand side. This circuit is calibrated before despatch and should

not require re-calibration. However, should re-calibration become necessary the appropriate calibration potentiometers can be located using the diagram given in the CEXC manual (Routine Maintenance).

Ensure the equipment has been connected to the electrical supply and switched on for at least 20 minutes. Start up the Armfield software for the specific reactor. To access the PCB remove the panel on the right hand side of the plinth by removing the four fixing screws.

Disconnect the conductivity probe from the socket at the back of the plinth. Connect an AC Voltmeter (Range AC mV) to pins 1 and 2 of the vacant socket and adjust potentiometer VR10 on the PCB to give a reading of 50 mV (RMS) on the Voltmeter (probe excitation voltage).

Disconnect the Voltmeter then reconnect the probe to the socket having removed the probe from the appropriate reactor fitted to the CEXC.

High conductivity Calibration

Fill a small beaker with a Conductivity standard solution (e.g. 0.1M KCl giving a conductivity of 12.88 mS at 25°C) and measure the temperature of the standard solution using a suitable thermometer. From the table supplied determine the actual conductivity of the solution at the measured temperature.

Immerse the probe into the Conductivity standard solution in the beaker then adjust potentiometer VR7 to give a reading of the standard solution in the 'High conductivity' box on the software to match the conductivity.

Low conductivity Calibration

Fill a small beaker with a Conductivity standard solution (e.g. 0.01M KCl giving a conductivity of 1.41mS at 25°C) and measure the temperature of the standard solution using a suitable thermometer. From the table supplied determine the actual conductivity of the solution at the measured temperature.

Immerse the probe into the Conductivity standard solution in the beaker then adjust potentiometer VR8 to give a reading of the Standard solution in the 'Low conductivity' box on the software.

When the conditioning circuit has been re-calibrated replace the panel and re-install the probe in the appropriate reactor on the CEXC service unit.

12.88 mS/cm at 25ºC 0.1 M KCl

ºC	mS/cm	ºC	mS/cm
5	8.22	20	11.67
10	9.33	21	11.91
15	10.48	22	12.15
16	10.72	23	12.39
17	10.95	24	12.64
18	11.19	25	12.88
19	11.43	26	13.13

1.413 mS/cm at 25ºC 0.01 M KCl

ºC	mS/cm	ºC	mS/cm
5	0.896	20	1.278
10	1.02	21	1.305
15	1.147	22	1.332
16	1.173	23	1.359
17	1.199	24	1.386
18	1.225	25	1.413
19	1.251	26	1.441

1.413 mS/cm at 25ºC 0.01 M KCl

Laboratory Teaching Exercises

Index to Exercises

Nomenclature

Symbol	Name	Unit
a_0	initial sodium hydroxide conc.	(mol/dm^3)
a_1	sodium hydroxide conc. in reactor at time t	(mol/dm^3)
a_∞	sodium hydroxide conc. in reactor after ∞ time	(mol/dm^3)
b	ethyl acetate conc.	(mol/dm^3)
	(same subscripts as above for a)	
c	sodium acetate conc.	(mol/dm^3)
	(same subscripts as above for a)	
C	acetic anhydrite conc. at time t	(mol/dm^3)
C_0	acetic anhydrite conc. at t = 0	
k	specific rate constant	
r	reaction rate	(s)
t_r	reaction time	(s)
t	elapsed time	(s)
T	reactor temperature	(K)
V	volume of reactor	(dm^3)
X_a	conversion of sodium hydroxide $= \dfrac{a_0 - a_1}{a_0}$	
X_c	conversion to sodium acetate $= \dfrac{c_1 - c_0}{c_\infty}$	
Λ	conductivity	(Siemens/cm)

Λ_o	initial conductivity	
Λ_1	conductivity at time t	
Λ_∞	conductivity after ∞ time	
Λ_a	sodium hydroxide conductivity	
Λ_c	sodium acetate conductivity	
k_0	Arrhenius frequency factor	
E	Activation energy (J/mol)	
R	gas constant	(J/mol K)
ρ	density	(kg/dm³)
H	molar enthalpy	(J/mol)
$\overline{C_p}$	mean heat capacity	(J/kg K)

Common Theory

The Armfield batch reactor is designed to demonstrate the mechanism of a chemical reaction in a reactor, as well as the effects of varying process conditions such as reaction temperature, reagent concentrations etc.

The reaction chosen for the isothermal demonstration is the saponification of ethyl acetate by sodium hydroxide, as it can be carried out under safe conditions of temperature and pressure and is well documented. The use of indicators allows to follow the reaction by changing the colour as the reaction takes place.

The reaction chosen for the adiabatic demonstration is the hydrolysis of acetic anhydride. This involves the use of glacial acetic acid and sulphuric acid as well as acetic anhydride.

Although it may be possible to carry out demonstrations using other chemicals, it is not advisable as the materials of construction of the reactor may not be compatible.

Before carrying out reactions involving any other reagents please refer to Armfield Ltd. for advice.

Dilution of Ethyl Acetate for use with CEB MKII Batch Reactor

Armfield recommends the use of a 0.1M solution of Ethyl Acetate in the CEB MkIII reactor. This should be made by diluting concentrated Ethyl Acetate as follows:

$$Volume\ of\ concentrate = M\left(\frac{mol}{litre}\right) \times \frac{1}{Density} = 0.1 \times \frac{88.11}{0.90} = 9.79\ ml\ per\ litre\ of\ solution$$

Therefore add 4.895ml of concentrated Ethyl Acetate to 400ml of deionised or distilled water.

Shake the mixture vigorously until the two liquids have mixed. Add further water to make up the final volume to 500ml.

Note: The practice of making a strong solution (e.g. 1M) then further diluting this to the required concentration (e.g. 0.1M) cannot be applied when using Ethyl Acetate. The required dilution should be made directly as stated above.

To get the colourful solution add 0.00394 gr of Crystal Violet to the 500ml of Ethyl Acetate to make up a final solution of $1 \cdot 10^{-5}$ Mol/l of CV when both reagents are mixed.

Dilution of Sodium Hydroxide for use with CEB MKII Batch Reactor

Armfield recommends the use of a 0.1M solution of Sodium Hydroxide in the CEB MkIII reactor. This may be made by adding 50ml of NaOH 1M to 450ml of distilled water then making up the solution to 500ml.
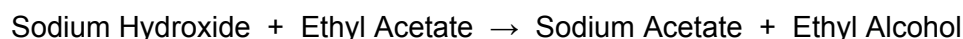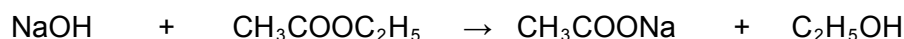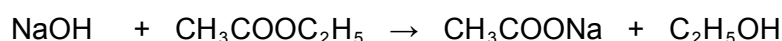
Exercise A - Isothermal Operation

Objective

To find the reaction rate constant in a stirred batch reactor.

Theory

The reaction:

$$NaOH \quad + \quad CH_3COOC_2H_5 \quad \rightarrow \quad CH_3COONa \quad + \quad C_2H_5OH$$

Sodium Hydroxide + Ethyl Acetate $\rightarrow$ Sodium Acetate + Ethyl Alcohol

Assuming that the initial concentrations are equal and that the amount of reagent used up after time t is X then the concentrations at time t are:

$$NaOH \quad + \quad CH_3COOC_2H_5 \quad \rightarrow \quad CH_3COONa \quad + \quad C_2H_5OH$$

$$a\text{-}X \quad + \quad a\text{-}X \quad \rightarrow \quad X \quad + \quad X$$

From the kinetic analysis of a general second order reaction it can be shown that:

$$k \cdot t = -\frac{X}{a(a-X)} \tag{1}$$

where k is the reaction rate constant and t is the time of reaction. Using notation from the nomenclature:

$$X = a_0 - a_1$$

substituting for X in equation (1) above gives:

$$k \cdot t = -\frac{a_0 - a_1}{a_0 \cdot a_1}$$

Hence a plot of $\dfrac{a_0 - a_1}{a_0 \cdot a_1}$ against t gives a straight line of gradient k.

Method

Make up 0.5 litre batches of 0.1M sodium hydroxide and 0.5 of 0.1M ethyl acetate (containing $1 \cdot 10^{-5}$ Mol/l Crystal Violet)

IMPORTANT: It is essential when handling these chemicals to wear protective clothing, gloves and safety spectacles.

Open Armfield Software and choose 'Isothermal operation'

Set up the Hot Water Circulator as detailed in the Operation section.

Adjust settings on the PID loop as detailed in Operation procedure for Isothermal Operation and set point to 25°C.

Charge the batch reactor with 0.5 litres of the sodium hydroxide solution. Set the reactor agitator to '50%' and press 'Power on' to start the agitation. Then press 'Hot Water Circulator' and water will start to recirculate through jacket reactor and vessel.

As the experiment involves the collection and storage of conductivity data, the data output port in the plinth must be connected to the computer with Armfield Interface data logger. This will enable data logging of the conductivity, temperatures and stirrer speed values at selected time intervals over a selected period.

Ensure the conductivity and temperature sensors have both been installed in accordance with the Installation section.

Collection of data will be until a stable condition is reached in the reactor and this takes approximately 30 minutes. It is advisable to set the data collection period to, say, 45 minutes.

Switch on the Hot Water Circulator. The temperature of the sodium hydroxide in the reactor vessel will begin to rise and will be automatically maintained at the desired set-point (25°C in this instance) by the action of the HWC in the jacket.

Carefully add to the reactor 0.5 litres of the ethyl acetate solution and instigate the data logger program (or begin taking readings if no computer is being used).

It has been determined that the degree of conversion of the reagents affects the conductivity of the reactor contents. By recording the conductivity with respect to time, either manually or using the Armfield Data Logger, the amount of conversion can be calculated.

If time permits the experiment should be repeated as above but with the temperature controller set to 35°C, or at other temperatures below room temperature like 15ºC. It is also recommended to repeat the experiment at another stirrer speed to study the effect of the mixing on conversion.

When temperature is below room temperature, the use of a Chiller is required. Connect the Chiller system as detailed in the OPERATIONAL PROCEDURES section of the CEXC manual.

It is recommended to fit the CEXC temperature probe T2 into the HWC vessel hole for better PID control, as described in Isothermal operation section, and the use of the T1 temperature sensor also supplied to follow the temperature in the reactor.

Interpretation of results

Armfield Interface data logger performs all the calculations while the experiment takes place. However if better understanding of the experiment is needed, follow below procedure to calculate the specific rate constant and effect of the temperature on the specific rate constant.

Having recorded the conductivity of the contents of the reactor over the period of the reaction, the conductivity measurements must now be translated into degree of conversion of the constituents.

Both sodium hydroxide and sodium acetate contribute conductance to the reaction solution whilst ethyl acetate and ethyl alcohol do not. The conductivity of a sodium hydroxide solution at a given concentration and temperature however, is not the same as that of a sodium acetate solution at the same molarity and temperature and

a relationship has been established allowing conversion to be inferred from conductivity:

The calculations are best carried out using a spreadsheet such as Microsoft™ Excel so that the results can be displayed in tabular and graphical form.

On conclusion of the experiment, the set of readings of conductivity with time will need to be transferred to the computer as two columns of data.

Now enter the following known constants from the experiment using the Nomenclature. Ensure use of correct units.

a_μ = (Sodium Hydroxide conc. in feed bottle)

a_0 = (Sodium Hydroxide conc. in mixed feed) $= \dfrac{a_\mu \cdot V_a}{V_a + V_b}$

b_μ = (Ethyl acetate conc. in feed bottle)

b_0 = (Ethyl acetate conc. in mixed feed) $= \dfrac{b_\mu \cdot V_b}{V_a + V_b}$

c_μ =

T   = (Reactor temperature, T1)

V   = (Total volume in the reactor vessel)

Using the spreadsheet, calculate the values of c_∞, a_∞, $\Lambda_{c\infty}$, Λ_{a0}, Λ_o, $\Lambda_{a\infty}$ and Λ_∞ from the following formulae:

c_∞	=	b_0	for $b_0 < a_0$
c_∞	=	a_0	for $b_0 \geq a_0$
$\Lambda_{c\infty}$	=	$0.070[1+ 0.0284(T-294)]\, c_\infty$	for $T \geq 294$
Λ_{a0}	=	$0.195[1+ 0.0184(T-294)]\, a_0$	for $T \geq 294$
Λ_o	=	Λ_{a0}	assumes $c_0 = 0$
a_∞	=	0	for $a_0 < b_0$
a_∞	=	$(a_0 - b_0)$	for $a_0 \geq b_0$
$\Lambda_{a\infty}$	=	$0.195[1+ 0.0184(T-294)]\, a_\infty$	if $a_\infty \neq 0$
Λ_∞	=	$\Lambda_{c\infty} + \Lambda_{a\infty}$	

For the values of each of the above, the spreadsheet can be used to calculate values of sodium hydroxide concentration (a_1) and sodium acetate concentration (c_1) and the degree of conversion (X_a) and (X_c) for each of the samples of conductivity taken over the period of the experiment.

These can be calculated and listed in columns (use spreadsheet COPY facility) alongside the readings of conductivity using the following equations:
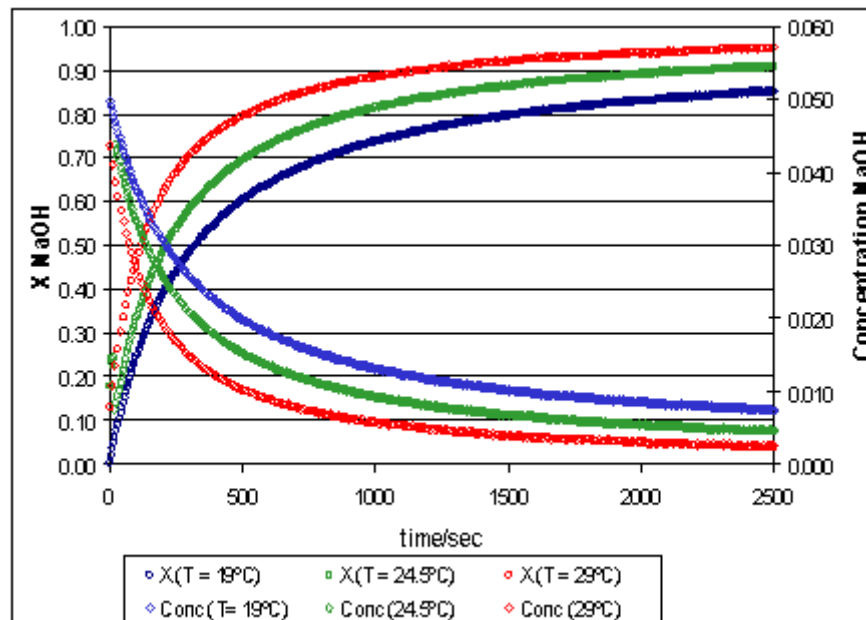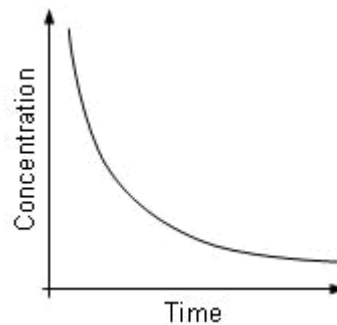
$$a_1 = (a_\infty - a_0)\left[\frac{\Lambda_0 - \Lambda_1}{\Lambda_0 - \Lambda_\infty}\right] + a_0$$

$$c_1 = c_\infty\left[\frac{\Lambda_0 - \Lambda_1}{\Lambda_0 - \Lambda_\infty}\right], \qquad \text{for } c_0 = 0$$
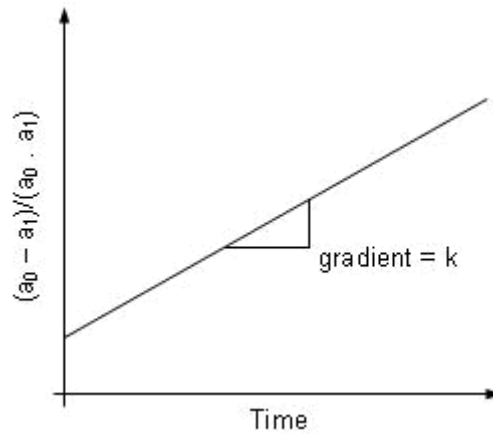
$$X_a = \frac{a_0 - a_1}{a_0}$$

$$X_c = \frac{c_1}{c_\infty}, \qquad \text{for } c_0 = 0$$

The concentration of NaOH can be plotted against time:

To calculate the specific rate constant, k:

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It is recommended that this experiment be repeated at various other reactor temperatures to investigate the relationship between the specific rate constant k and the temperature of reaction.

The effect of temperature on the reaction rate constant is determined by the activation energy of such a reaction, through the Arrhenius law:

$$k = k_0 \, e^{-E/RT}$$

where k_0 is the frequency factor, E is the activation energy, R is the ideal gases constant and T is the absolute temperature.
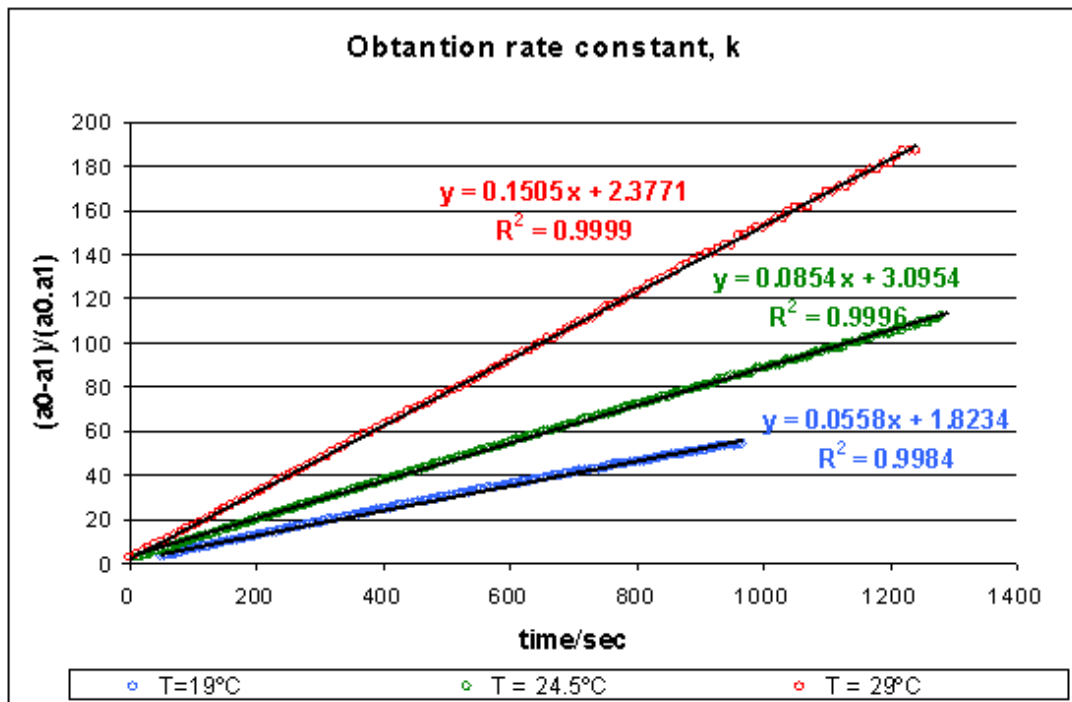
Once the kinetic constant at three different temperatures is known, for instance 15ºC, 20ºC and 25ºC, is straightforward to apply the Arrhenius law and calculate the frequency factor and the activation energy values for:

$$\ln k = \ln k_0 - \frac{E}{R}\frac{1}{T}$$

Rate constant vs temperature

$y = -7608.4x + 16.228$
$R^2 = 0.9995$
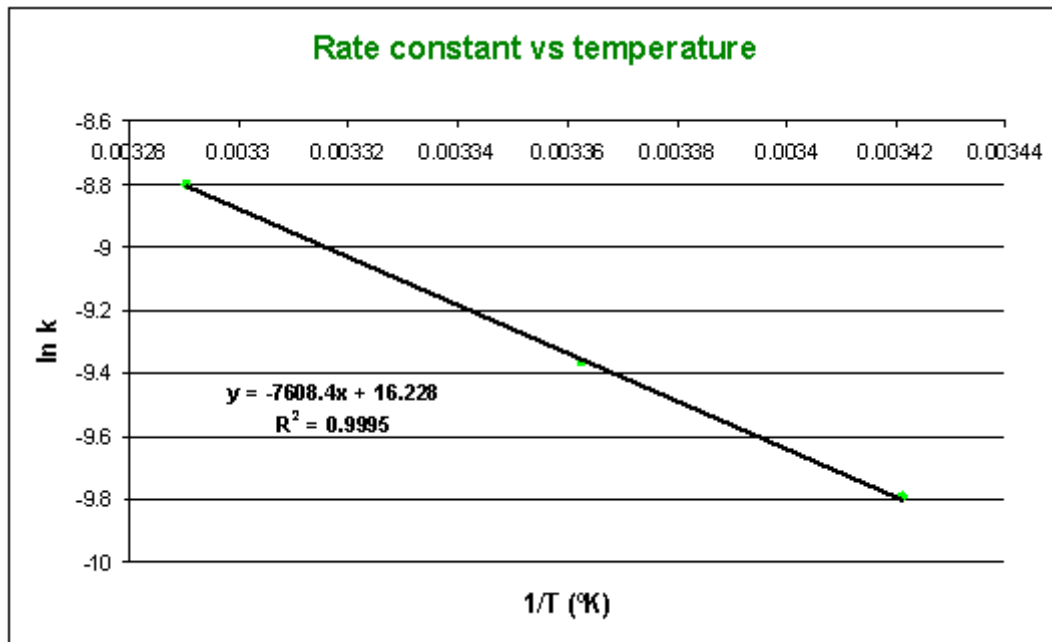
$\ln k_0 = 16.228 \qquad k_0 = 11.2 \cdot 10^{+6} \ m^3 / mol\,sec$

$\dfrac{E}{R} = 7608 \qquad E = 63.25 \ KJ / mol$

siendo R = 8.314 J K^{-1}mol^{-1}

Obtaining the reaction rate constant in function of the temperature:

$$\ln k(T) = 16.228 - 7608\,\frac{1}{T} \qquad T(^{\circ}K)$$

High activation energy implies a significant sensibility of the reaction kinetics to the temperature.

Exercise B - Reactant Concentration

Objective

To determine the effect of reactant concentration on the reaction rate.

Theory

In homogenous reaction systems, reaction rates depend on the concentration of the reactants. Collision theory indicates a rate increase if the concentration of one or both of the reactants is increased. However, the specific effect of concentration changes in a reaction system has to be determined by experimental methods. Increasing the concentration of substance A in reaction with substance B could increase the reaction rate, decrease it, or have no effect on it - depending on the particular reaction. It is important to recognise that the balanced equation for the net reaction does not indicate how the reaction rate is affected by a change in concentration of reactants.

The general form of the rate law is:

$$r = k[A]^n[B]^m$$

where:

r = reaction rate

k = rate constant

$[A]^n$, $[B]^m$ = molar concentrations of reactants

n, m = appropriate powers (based on experimental data)

Method

Use the same procedure as for Exercise A. Run the experiment using different initial concentrations of the reagents, for example, 0.1M, 0.08M and 0.02M. 0.5 litre of each solution will be required for each mixture tested.

Using the Armfield Data Logger in each experiment, graphs can be plotted relating reaction rate to concentration level for each of the reactants tested.

A logarithmic plot of reaction rate to concentration level will give a straight line of slope equal to the power of the relationship.

Hence the rate law for sodium hydroxide and ethyl acetate can be written in the form

$$r = k[a]^n[b]^m$$

Exercise C - Adiabatic Operation

WARNING: Extreme care should be taken whilst handling either acetic acid or acetic anhydride. Both chemicals are highly corrosive and care should be taken to avoid contact or inhalation of vapour.

DO NOT add acetic anhydride directly to sulphuric acid, as the reaction is violent and will cause the chemicals to be sprayed into the air.

The reaction described in this experiment should be carried out in a fume cupboard. On completion, the reaction products should be discarded according to local regulations (for example into a copious flow of cold water to a suitable drain), taking care to avoid inhalation of vapour.

Objective

To determine the rate equation for the hydrolysis of acetic anhydride to acetic acid in an adiabatic reactor.

Theory

The hydrolysis of acetic anhydride in water, in the presence of a catalyst of sulphuric acid is described by:

$$(CH_3CO)_2O + H_2O \rightarrow 2CH_3COOH$$
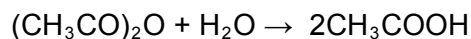
This reaction can be assumed to have simple power law kinetics of the form $r = -KC^n$, if the reaction is zero order in water. The concentration of the protonic acid remains constant for the duration of the run and thus k is a catalytic rate constant that includes this concentration, also in power law form. For any system of this particular type the instantaneous value of the acetic anhydride concentration can be eliminated between the material and thermal balance equations to give a linear equation (which can therefore be subjected to a statistical test). Use of this equation requires that values of the gradient of temperature with respect to time be found.

If the concentration of acetic anhydride at any time t is C, then the rate of the reaction is given by:

$$r = -\frac{dC}{dt} \tag{1}$$

with $C = C_0$ at t = 0. The heat generation rate is:

$$(-\Delta H) \cdot r = \rho \overline{C_p} \cdot \frac{dT}{dt} \tag{2}$$

with $T = T_0$ at t = 0. Substituting equation (1) in equation (2), integrating with respect to time and using the boundary conditions, we obtain:

$$(C_0 - C)(-\Delta H) = \rho \overline{C_p} \cdot (T - T_0) \tag{3}$$

For the n-th order case, the rate may be expressed in Arrhenius form:

$$r = kC^n = A \cdot e^{-E/RT} \cdot C^n \tag{4}$$

Using $\beta = \dfrac{\rho \overline{C_p}}{-\Delta H}$ and rearranging, equation (3) becomes:

$$C = C_0 - \beta(T - T_0)$$

Using equations (4) and (2), we obtain:

$$\beta \cdot \frac{dT}{dt} = A \cdot e^{(-E/RT)} \cdot \left[C_0 - \beta(T - T_0) \right]^n \tag{5}$$

Using $T = T_\infty$ when the reaction is complete gives:

$$(C_0 - 0) = \beta(T_\infty - T_0) \quad \text{and thus} \quad \beta = \frac{C_0}{(T_\infty - T_0)}$$

Substituting for β in equation (5) and rearranging, we have:

$$\frac{\dfrac{dT}{dt}}{\dfrac{T_\infty - T_0}{C_0} \cdot \left[C_0 - C_0 \cdot \dfrac{T - T_0}{T_\infty - T_0} \right]^n} = A \cdot e^{(-E/RT)}$$

Taking logarithms of both sides of this equation gives:

$$\ln|LHS| = \ln|A| - \left(\frac{E}{RT} \right) \tag{6}$$

and so a plot of ln(LHS) vs. 1/T should be linear with an intercept of ln(*A*) and a gradient of $-\dfrac{E}{R}$.

Method

Ensure the reactor has been set up with the special temperature sensor and computer interface for the adiabatic reaction as described in the Installation section.

If possible the reactants should be at approximately 30°C before mixing. If they are cooler than this, the reaction will take much longer to complete.

Charge the reactor with 100ml of acetic anhydride and 250ml of demineralised water.

Start the reactor agitator and adjust the variable speed drive to position '5.0'.

Add 150ml of glacial acetic acid (since the water and acetic anhydride are mutually insoluble, but are both soluble in acetic acid, this ensures that the reaction mixture is homogeneous - the acetic acid does not form part of the reaction).

Start the data logger program choosing 15 seconds as the interval between samples and 1500 seconds as the total running time of the experiment (a longer duration will

be required if the temperature of the reactants is less than 30°C). It is essential to log data until the temperature in the reactor begins to fall again.

Immediately add 25ml of 0.5M sulphuric acid as the catalyst. The reaction will commence.

Switch off the agitator.

When the reaction has completed, the temperature data can be viewed within the software, either in tabular or graphical format. The data should be saved as an excel file. It is then possible to carry out the second part of the analysis described above, by calculating the terms of equation (6), and plotting the graph.

In order to find dT/dt, it will be necessary to extract the linear region of data from a graph of temperature vs. time for the experiment. This will entail discarding the first few points, and also any points after the temperature reaches the peak value. See figure below

Several runs similar to that described above should be performed, using differing quantities of sulphuric acid catalyst (e.g. 15ml to 40ml in 5ml increments).
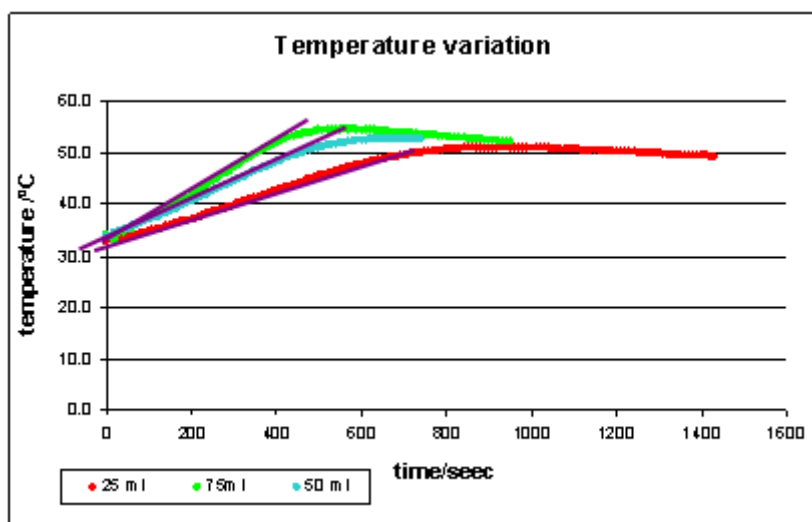
It will then be necessary to find the best value for n in equation (6) by trial and error, refining the value until the best straight line fit is obtained.

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