Tubular Reactor

Instruction Manual

CET-MKII

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Disclaimer

Should you have any queries or comments, please contact the Armfield Customer Support helpdesk (Monday to Thursday: 0830 – 1730 and Friday: 0830 - 1300 UK time). Contact details are as follows:

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(0) 1425 478781 (calls charged at local rate)	+44 (0) 1425 478781 (international rates apply)
Email: support@armfield.co.uk	
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Use with CEX Service Unit

This instruction manual describes the use of the CET-MKII Tubular Reactor in conjunction with the CEXC Computer Controlled Service Unit.

An alternative instruction manual is available from Armfield that describes the use of the CET-MKII in conjunction with the CEX Service Unit. Please contact Armfield if a copy of this instruction manual is required. Contact details are included later in this document.

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.

Tubular reactors are often used when continuous operation is required but without back-mixing of products and reactants.

The Armfield CET MkII Tubular Reactor is specially designed to allow detailed study of this important process. It is one of five reactor types which are interchangeable on the Reactor Service Unit (CEXC), the others being CEM MkII - Continuous Stirred Tank Reactor, CEB MkIII – Transparent batch 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. This means that the inaccurate and inconvenient process of titration, which was formally used to monitor the reaction progress, is no longer necessary.

CEXC fitted with CET MkII tubular reactor

Equipment Diagrams

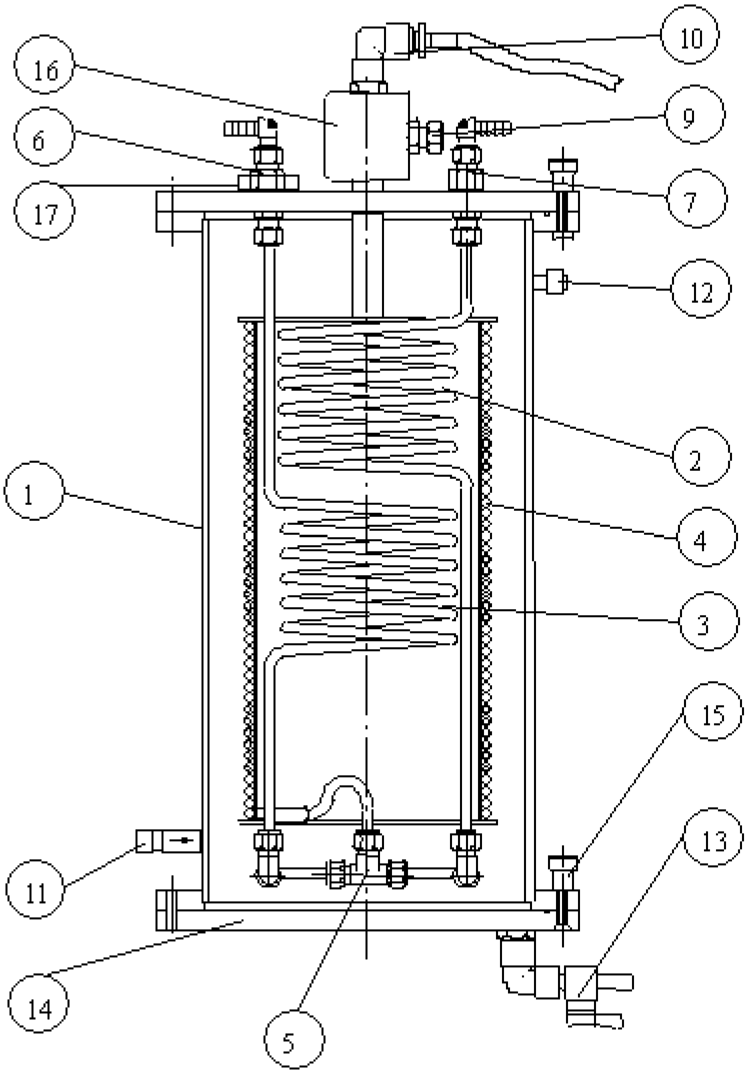


Figure 1: Front View of CET-MKII Tubular Reactor

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 **CET-MKII Tubular 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

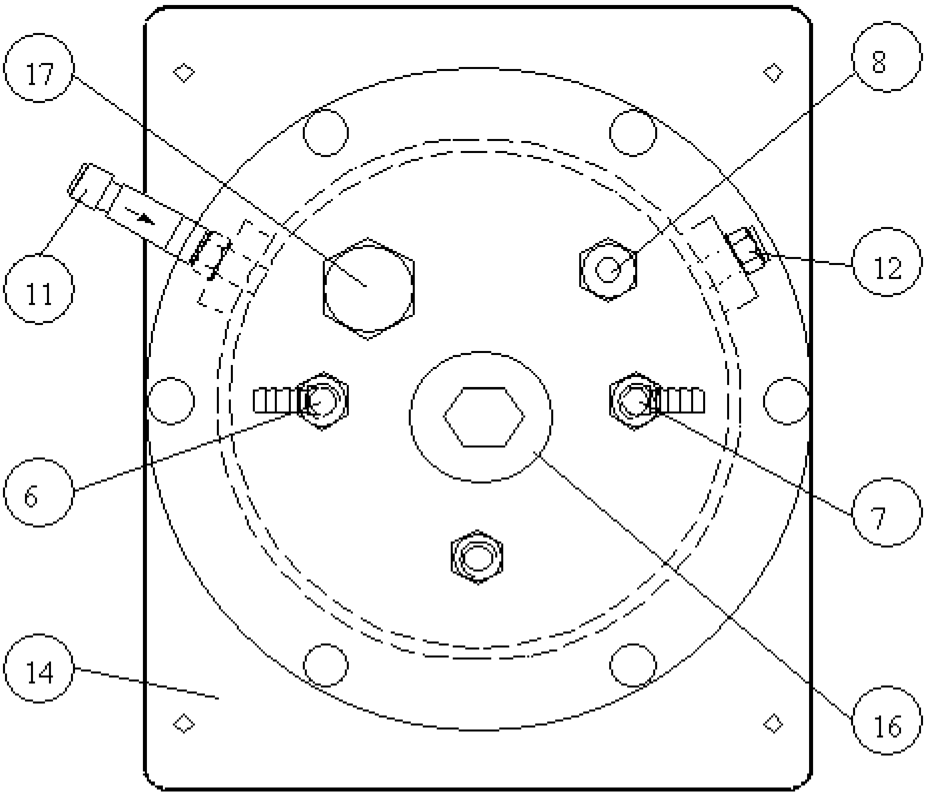
Where necessary, refer to the drawings in the Equipment Diagrams section.

Overview

The reactor vessel (1) is set on a baseplate (14) which is designed to be located on the four studs of the CEXC service unit and then secured by thumbnuts (15). The positioning of the reactor on the service unit is illustrated. The reactor is positioned on the service unit with the non-return valve sited on the left and towards the rear.

The tubular reactor in which the chemical reaction takes place is a flexible coil (4) wound around an acrylic former. Total volume of the reactor coil is 0.466 L.

In order to maintain a constant temperature throughout the reactor coil, the coil bundle is submerged in circulating water which is automatically maintained at a pre-selected temperature by the PID temperature controller which is incorporated in the Armfield Software. The actual temperature of the circulating water and therefore the reactants is relayed to the controller by a k-thermocouple (T1) which is held in gland (8) in the lid. Water enters from the circulator at the non-return valve (11) - this prevents water draining back through the vessel of the circulator when the pump is stopped. Water leaves the reactor at overflow (12) and returns to the circulator.



A filling plug (17) is provided on the top of the reactor vessel to allow the vessel to be filled with clean water. This plug (with sealing washer) must be fitted when the hot water circulator on the CEXC service unit is in operation. Otherwise air will enter pushing down the water level of the reactor and over filling the HWC vessel.

Sockets at the rear of the service unit are provided to connect the conductivity probe and temperature sensors to the instrumentation.

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

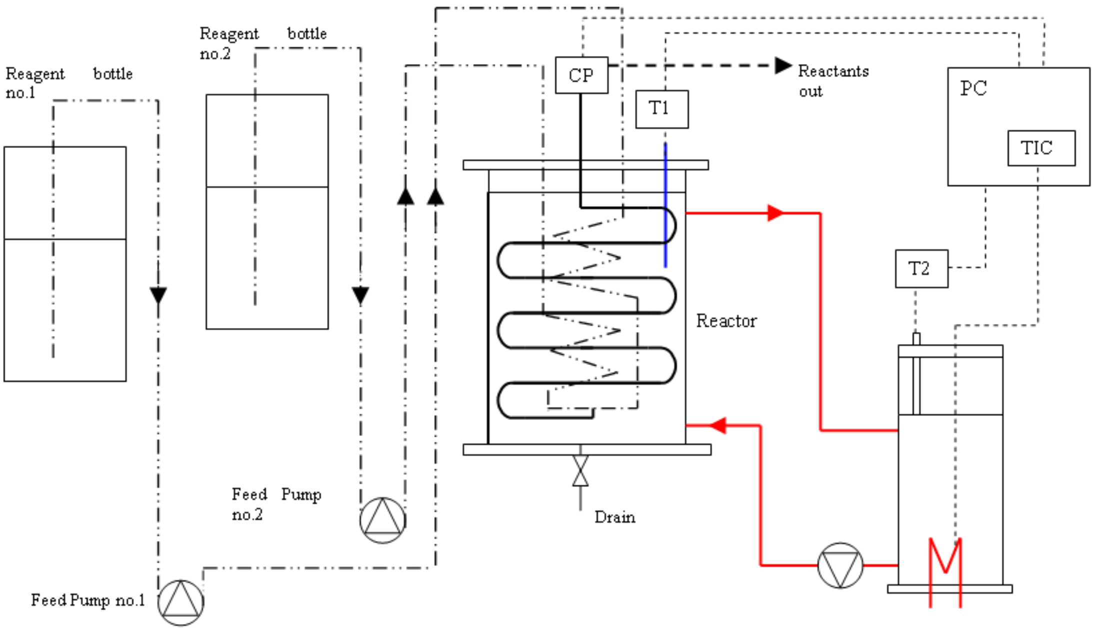
Both temperature values and conductivity values are data logged using a PC in conjunction with the Armfield software interface.

When not in use, the reactor can be drained using the valve (13) in the base.

Flow of materials

Reactants are pumped from the two feed bottles supplied by the peristaltic pumps and enter the reactor through connectors (6) and (7) in the lid of the vessel. Each reactant is pre-heated by heat transfer coils (2) and (3) before being blended together in "T" fitting (5).

The reactants pass up through the reactor coil and leave the reactor vessel through the conductivity probe housing (16). This housing allows the conductivity probe (CP) to be held in the stream of reactants emerging from the reactor. Flexible tubing from the hose nozzle (10) is used to guide the reactants to drain.



CET- MKII Tubular 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.

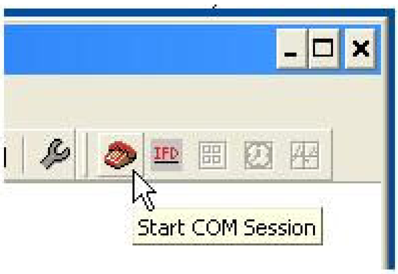
Installing the PC Software

Before operating CET-MKII 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 CET-MKII onto the CEXC

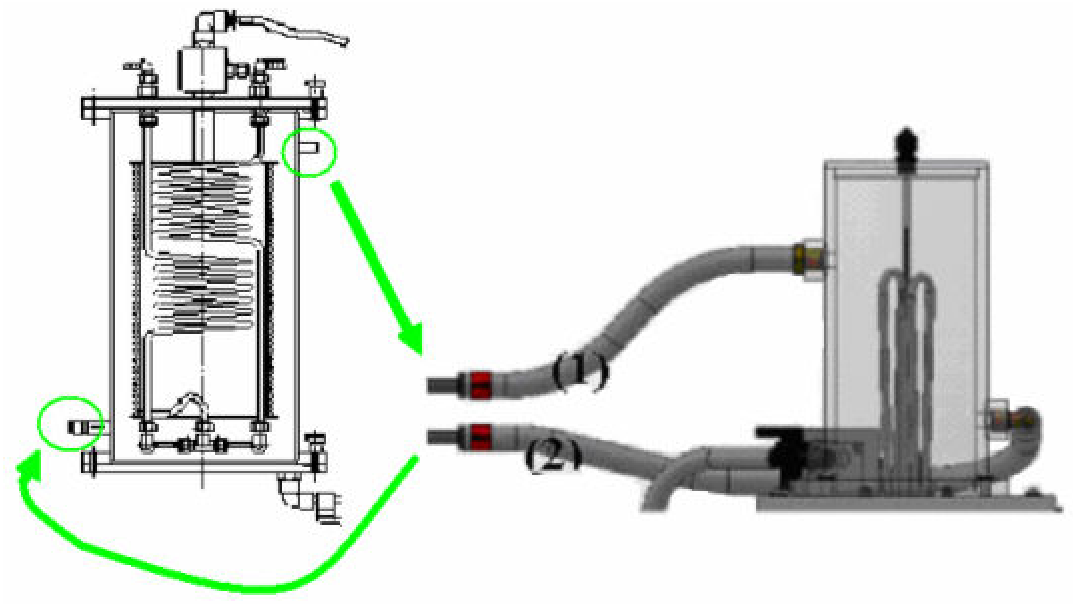
- The reactor vessel is set on a baseplate which is itself located on four studs on the service unit and secured by thumbnuts. Fit the CET-MkII assembly to the CEXC using the 4 locating studs and black thumbnuts. Position the reactor is on the left hand side of the reactor towards the rear.

- Fit the reagent bottles into the molded channel on the CEXC. Fit tubing on the left hand side of each of the two feed pumps into the bottles through the hole in the lid.

- Connect the remaining two pipes from the feed pumps to the connectors on lid of the reactor as shown.

- 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.

Connecting the HWC to CET-MKII



- Connect suction pipe of the HWC (1) to overflow pipe mounted high on the side of the reactor.
- Connect the supply pipe of the HWC (2) to the non return valve mounted low down on the left rear side of the reactor.
- Fill the reactor with water (preferably deionised) using the fill plug on the top plate of the reactor up to overflow height to prevent water from filling HWC vessel.
- Refit the plug.

Connection to the 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.

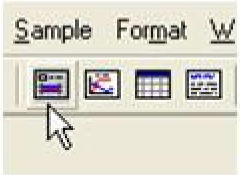
Connection to a PC for Control and Data Logging

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

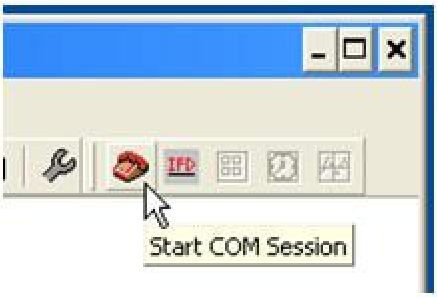
Switch on the PC and connect the USB lead from the CEXC to the PC.

Load the CET 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 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.

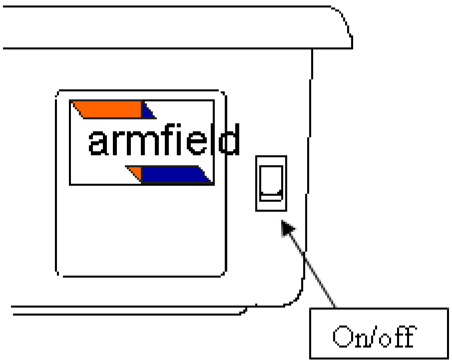
Operating the PC Software

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.



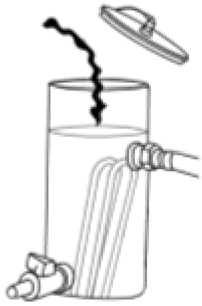
Filling the feed bottles

Unscrew the feed bottle caps and pour solutions in using a suitable funnel if necessary.

Operating the 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 30mm from the top.

Top up the level of this vessel as necessary to maintain the level above the tip of the level electrode (typically 30mm from the top of the vessel).



Heater is controlled from a PC via the CET-MKII 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.

See PID Settings for Experiment with Heater.

Operating the Data Logger and Software

The Tubular Reactor is controlled using the CET-MKII software supplied, which allows real-time monitoring and data logging of all sensor outputs and control of the heater unit and pumps. 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 > CET).

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 controlled from the Mimic Diagram screen in the software. This shows all the sensor outputs, and includes controls for the pumps and the Hot water Circulator. There is an extra temperature ‘T3’ and ‘Low conductivity’ plug with outputs on the software for extra connections made by the user.

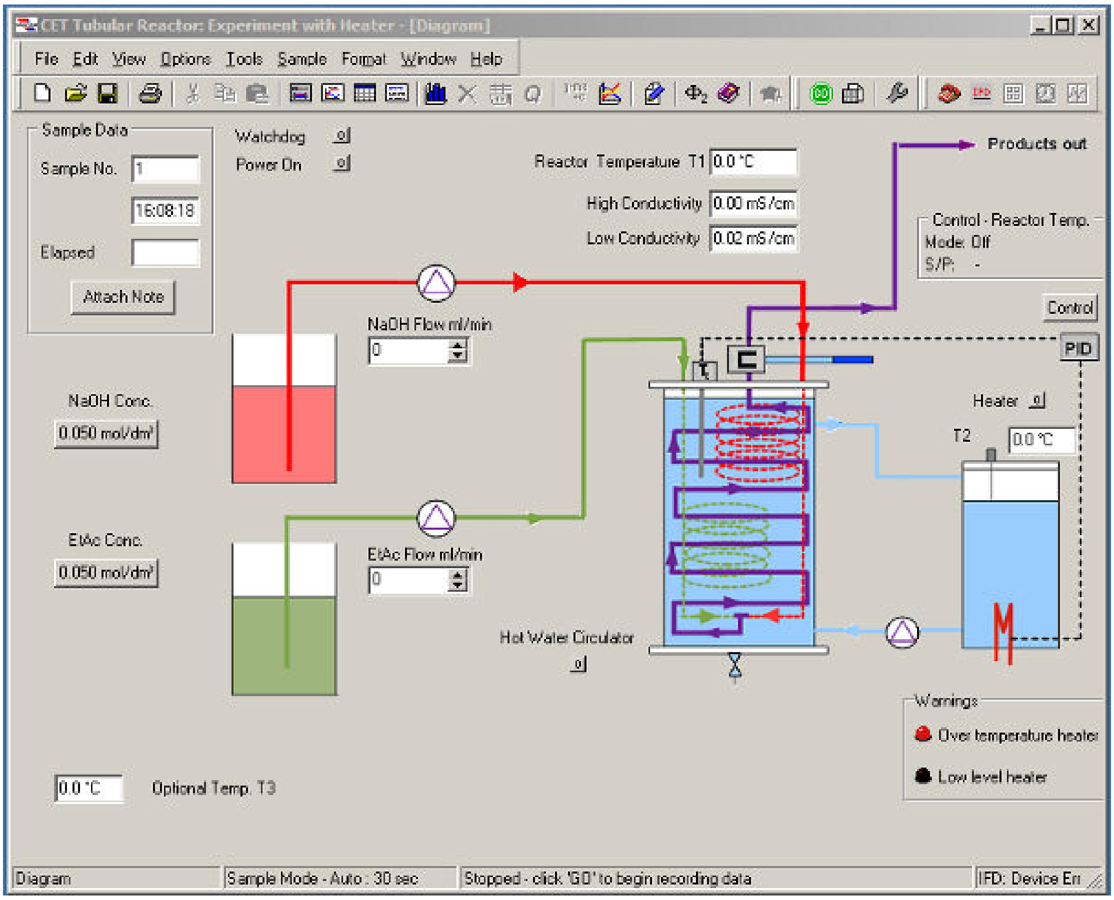
Feed pump speeds are controlled using up/down arrows or typing the flow rate in a value between 0 and the maximum of 150ml/min. Click on the appropriate POWER ON symbol to start up the pumps.

Concentration values must be typed in on each experiment so that software will carry out the subsequent calculations.

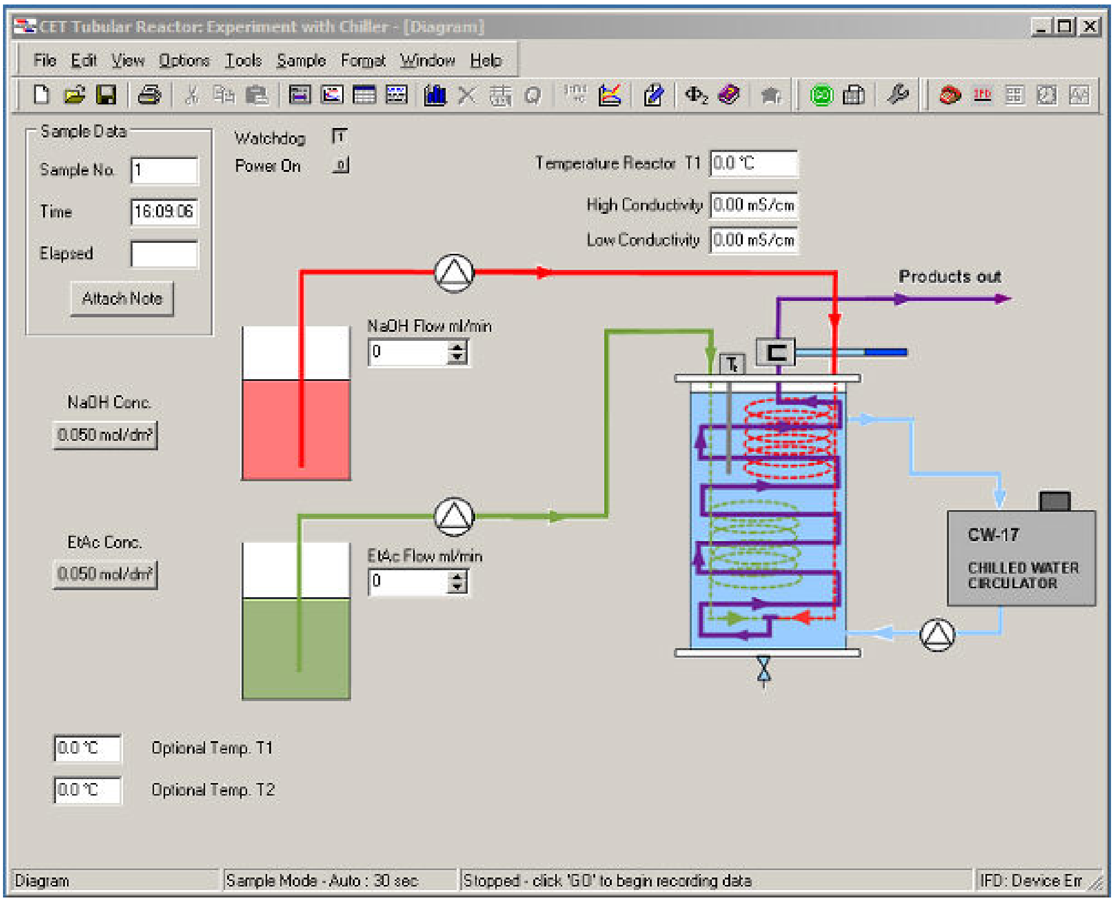
Conductivity and temperature values will be monitored on the screen and data logged when ‘GO’ is clicked.

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

CET-MKII Tubular reactor can be used with heater or with Chiller. When the Heater is used settings on the software are required. When using the Chiller CW-17 PID settings are not required. See the installation guide for appropriate controller settings when using the CW-17.



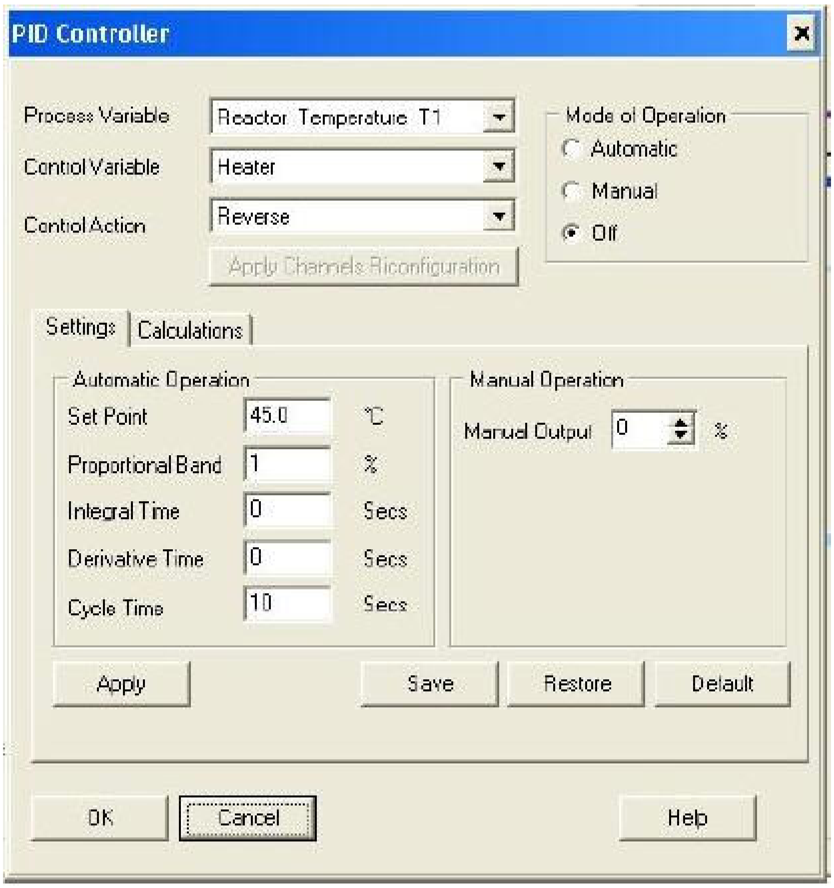
CET-MKII Tubular Reactor with Heater



CET-MKII Tubular Reactor with Chiller

Controlling the Hot Water Circulator (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.

Choose Reactor Temperature as PROCESS VARIABLE to control, set the PID loop as convenient and click 'Hot Water Circulator' symbol. Then click 'Power on' and water will start to recirculate.

PID Settings for Experiment with Heater

Process variable = Reactor Temperature (T1)

Control Variable = Heater

Control Action = Reverse

SP = Chosen by the user   IT = 0   Cycle time = 10

PB = 1   DT = 0

Operating the CET-MkII

There are two modes of operation with the CET Tubular Reactor: Experiment with HEATER and with CHILLER.

When using the Chiller CW-17 PID settings are not required. See the installation guide for appropriate controller settings when using the CW-17.

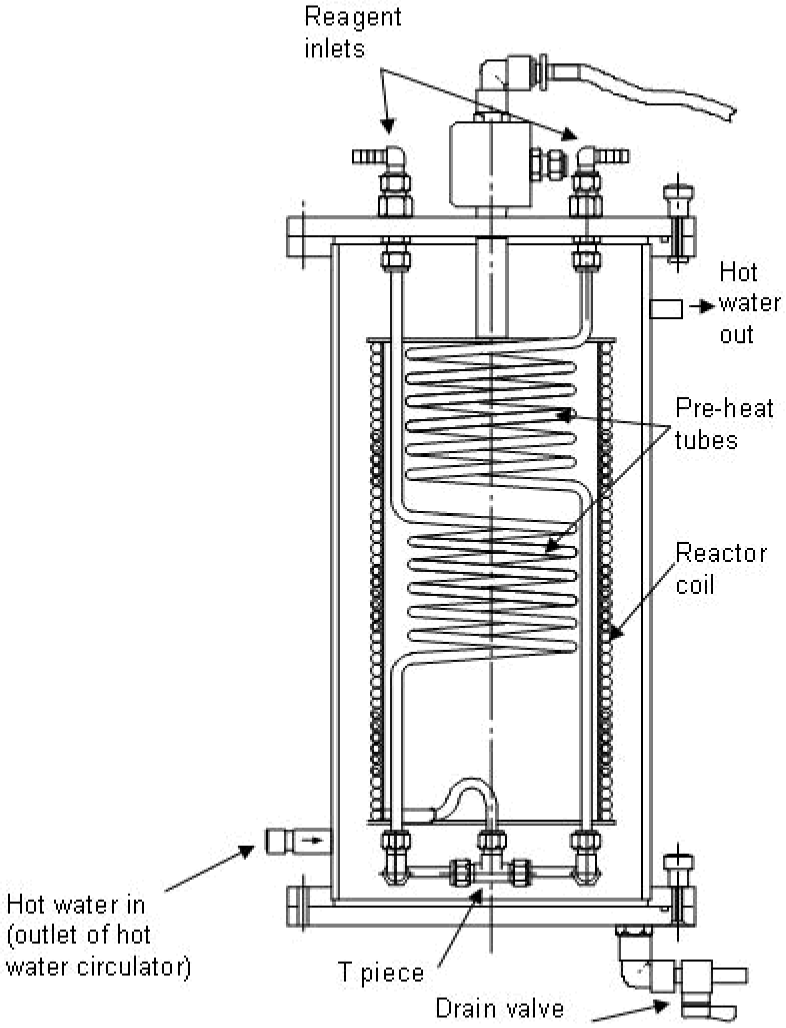
When using the Heater the temperature sensor T1 supplied with CEXC, which is Reactor Temperature on the software, should be set as the Process Variable to be controlled in the PID loop. This sensor must be immersed in the reactor vessel and will be data logged.

The temperature and conductivity sensors must be situated well below the liquid surface inside the reactor.

The volumetric ratio in which the reactants are mixed is defined by the relative flow rates of the two pumps. If the pumps are operated at the same flow rate then the reactants are mixed in equal volumes.

The residence time in the reactor is defined by the total flow rates of the two feed pumps. The total volume of the reactor coil is approximately 466 mL. Dividing this volume by the combined flow rates of the feed pumps in mL/s will yield the residence time in seconds.

The extent of conversion of the reactants is determined from the conductivity, which is measured by the conductivity probe fitted in the housing where the liquid stream exits the reactor. It is important that the probe is inserted into the housing with the electrode access holes in the glass surround in line with the flow.



Equipment Specifications

Dimensions

Pre-heat coils (each)

Total length: 1.2m

Internal diam: 4.9mm

Total vol of coil: 0.02L

Reactor coil

Total length: 20.9m

Internal diam: 5.0mm

Total vol of coil: 0.466L

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.

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.

The temperature conditioning circuit (which provides the reading from the thermocouples supplied with the CEXC service unit) is located on a printed circuit board inside the plinth on the right-hand side. 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.

If a thermocouple calibrator is available:

Connect Thermocouple calibrator simulator to T1 input socket, located at the rear of the plinth. 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 an extra thermocouple is used).

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.

When the conditioning circuit has been re-calibrated, replace the front panel of the electrical console and re-install the sensors in the appropriate place on the CEXC service unit.

Conductivity probe calibration

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 in the Routine Maintenance section.

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

Laboratory Teaching Exercises

Index to Exercises

Exercise A - To determine the rate constant using a tubular reactor

Exercise B - To determine the kinetic constant of a reaction using an indicator for visually monitoring

Exercise C - To investigate the effect of throughput on conversion

Exercise D - To demonstrate the temperature dependence of the reaction and the rate constant

Nomenclature

Symbol	Name	Unit
A	cross sectional area of tubular reactor	(cm^2)
a_μ	sodium hydroxide conc. in feed vessel	(mol/dm^3)
a_0	sodium hydroxide conc. in mixed feed	(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. (same subscripts as above for a)	(mol/dm^3)
c	sodium acetate conc. (same subscripts as above for a)	(mol/dm^3)
F	total volume feed rate	(dm^3/s)
F_a	volumetric feed rate of sodium hydroxide	(dm^3/s)
F_b	volumetric feed rate of ethyl acetate	(dm^3/s)
k	specific rate constant	
L	overall length of tubular reactor	(cm)
r	reaction rate	
t_R	residence time	(s)
t	elapsed time	(s)
T	reactor temperature	(K)

V	volume of reactor	(dm^3)
X_a	conversion of sodium hydroxide $= \frac{a_0 - a_1}{a_0}$	
X_c	conversion to sodium acetate $= \frac{c_1 - c_0}{c_\infty}$	
Λ	conductivity	(Siemens/cm)
Λ_0	initial conductivity	
Λ_1	conductivity at time t	
Λ_∞	conductivity after ∞ time	
Λ_a	sodium hydroxide conductivity	
Λ_c	sodium acetate conductivity	
Ă	Arrhenius frequency factor	
E	activation energy	(J/mol)
R	gas constant	(J/mol K)

Common Theory

The Armfield Continuous Tubular Flow Reactor is designed to demonstrate the mechanism of a chemical reaction in such a reactor as well as the effects of varying the process conditions such as reaction temperature, reactant concentration, feed rate etc.

The reaction chosen 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.

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 CET-MKII Reactor

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

$$\text{Volume of concentrate} = \frac{\text{Mol Wt}}{10} \times \frac{1}{\text{Density}} = \frac{88.11}{10 \times 0.90} = 9.79 \text{ ml per litre of solution}$$

Therefore add 9.79ml of concentrated Ethyl Acetate to 900 ml 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 1000 ml.

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.

Dilution of Sodium Hydroxide for use with CET-MKII Reactor

Armfield recommends the use of a 0.1M solution of Sodium Hydroxide in the CET MkII reactor. This may be made by adding 4.0g of NaOH to 960ml of deionised water then making up the solution to 1000ml.

Exercise A - To determine the rate constant using a tubular reactor

Theory

The rate expression can be shown to be $r = k.a.b$

where if a_μ is equal to b_μ this simplifies to $r = k.a^2$

In the general case the order of reaction n is not known and is shown by $r = k.a^n$

The rate constant can be determined using the CET-MkII Tubular Reactor.

We can show that $kta_\mu = \frac{X_a}{1 - X_a}$ (for a second order reaction)

From this equation it can be seen that a plot of $\frac{X_a}{1 - X_a}$ against time t will give a straight line of slope ka_μ.

If the inlet concentration a_μ is known, k can be determined.

The reaction:

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

Sodium Hydroxide + Ethyl Acetate → Sodium Acetate + Ethyl Alcohol

can be considered equi-molar and first order with respect to both sodium hydroxide and ethyl acetate i.e. second order overall, within the limits of concentration (0 - 0.1M) and temperature (20 - 40°C) studied.

The reaction carried out in a Tubular Reactor eventually reaches steady state when a certain amount of conversion of the starting reagents has taken place.

The steady state conditions will vary depending on concentration of reagents, flowrate, volume of reactor and temperature of reaction.

Method

Make up 2.5 litre batches of 0.1M sodium hydroxide and 2.5 L of 0.1M ethyl acetate.

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

Remove the lids of the feed bottles and carefully fill with the reagents. Refit the lids and fit the silicone pipe from the pumps.

The experiments involve the collection and storage of conductivity data. The USB port located at the front of the Service Unit must be connected to the computer. This will enable data logging of the conductivity, flow rates and temperature sensors at selected time intervals over a selected period of time.

Ensure the conductivity probe and temperature sensor has been installed in accordance with the Installation section.

Start the software using the option of the experiment with heater.

It has been determined that the degree of conversion of the reagents affects the conductivity of the reactor contents so that recording the conductivity with respect to time using the Armfield data logger can be used to calculate the amount of conversion.

Prior to priming the hot water circulating system, fill the reactor with water. Fill the vessel to a level above the overflow (return to the circulator), just below the reactor lid, using a suitable hose from a domestic supply through the temperature sensor gland (8) in the lid. A non-return valve (11) prevents water flowing out of the reactor via the inlet. Ensure the thermocouple is re-fitted and the gland tightened securely by hand before releasing the outlet tubing.

Set PID controller loop according to the settings for an Experiment with Heater described in operation section.

Adjust the set point of the PID to 30°C.

Change PID ‘mode of operation’ to ‘Automatic’.

Switch on the Hot Water Circulator by clicking ‘Hot Water Circulator’ and then ‘Power On’. The temperature of the water in the reactor vessel will begin to rise and within 10-15 min will be automatically maintained at the desired set-point (30°C in this instance).

When temperature reactor is steady type in the value of the concentration of both solutions on the software.

Switch on the pumps by typing the flow rate in the software and instigate the data logger program (or begin taking readings if no computer is being used).

Reactants will flow from both feed bottles and enter the reactor through the connections in the lid. Each reactant passes through pre-heat coils submerged in the water in which they are individually brought up to the reaction temperature. At the base of the tubular reactor coil, the reactants are mixed together in a "T" connection and begin to pass through the coil. The reacting solution will emerge from the coil through connector (16) in the lid where a probe senses continuously the conductivity which is related to degree of conversion. For an accurate conductivity reading, no bubbles are allowed in the reactant pipe.

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

Interpretation of Results

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 EXCEL so that the results can be displayed in tabular and graphical form.

On conclusion of the experiment using the Armfield data logger, a set of readings of conductivity with time will be stored in the computer.

At this point, this data can be transferred onto the spreadsheet.

Start the spreadsheet program.

Note that Armfield software performs all the calculations during experiment. However, it is recommended to go through all the procedure and calculations for better understanding.

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

F_a =

F_b =

a_μ =

b_μ =

c_μ =

T =

V =

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

$$a_0 = \frac{F_a}{F_a + F_b} \cdot a_\mu$$

$$b_0 = \frac{F_b}{F_a + F_b} \cdot b_\mu$$

c_∞	=	b_o	for $b_o < a_o$
c_∞	=	a_o	for $b_o \geq a_o$
$\Lambda_{c\infty}$	=	$0.070[1+ 0.0284(T-294)]\ c_\infty$	for $T \geq 294$
Λ_{ao}	=	$0.195[1+ 0.0184(T-294)]\ a_o$	for $T \geq 294$
Λ_o	=	Λ_{ao}	assumes $c_o = 0$
a_∞	=	0	for $a_o < b_o$

$a_\infty = (a_o - b_o)$ for $a_o \geq b_o$

$\Lambda_{a\infty} = 0.195[1 + 0.0184(T-294)]\, a_\infty$ if $a_\infty \neq 0$

$\Lambda_\infty = \Lambda_{c\infty} + \Lambda_{a\infty}$

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:

$$a_1 = (a_\infty - a_0)\left[\frac{\Lambda_0 - \Lambda_1}{\Lambda_0 - \Lambda_\infty}\right] + a_0$$

$$c_1 = c_\infty\left[\frac{\Lambda_0 - \Lambda_1}{\Lambda_0 - \Lambda_\infty}\right]$$ for $c_0 = 0$

$$X_a = \frac{a_0 - a_1}{a_0}$$

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

To calculate the specific rate constant, k:

The overall mass balance at steady-state condition may be written as:

Input – Output ± Reaction = 0

i.e. for a reactant a in a reactor of volume V

$$\frac{d(Va_1)}{dt} = F \cdot a_0 - F \cdot a_1 - V \cdot k \cdot a_1^2$$

For the continuous reactor operating at steady state the volume may be assumed constant and

$$k = \frac{F}{V} \cdot \frac{a_0 - a_1}{a_1^2} = \frac{(F_a + F_b)}{V} \cdot \frac{(a_0 - a_1)}{a_1^2}$$ $mol/dm^3\ sec$

The steady state concentration of NaOH in the reactor a_1 may be used to calculate the specific rate constant k.

Comment upon the results obtained.

Note: It is recommended that this experiment should be repeated at various other concentrations to investigate the relationship between the specific rate constant (*k*) and the temperature of reaction.

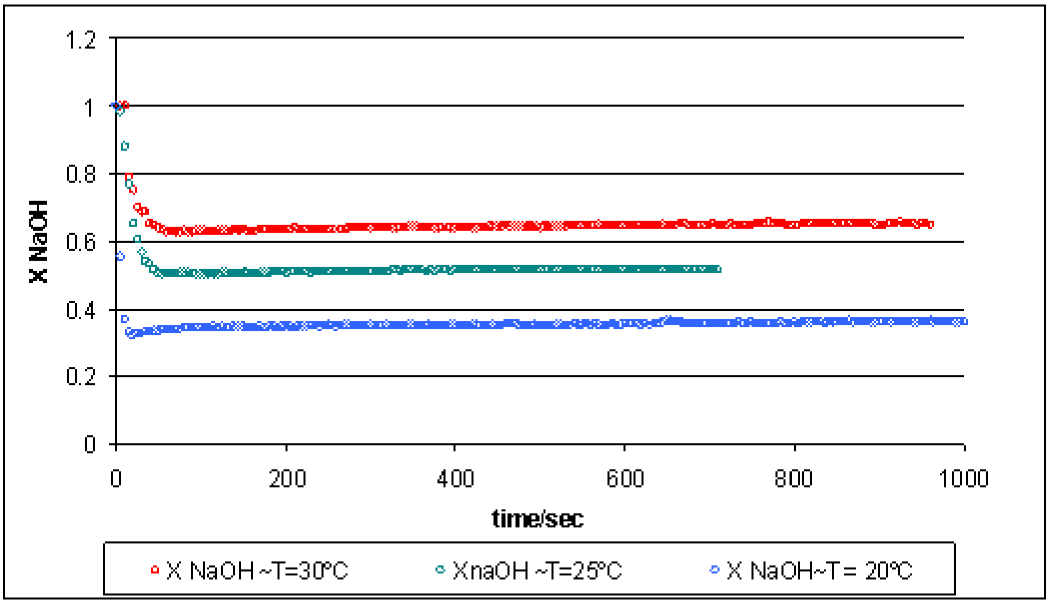


Figure A1: Conversions of NaOH at different temperatures

Rinse the feed bottles with demineralised water and pump the water through the reactor to rinse out the chemicals. The reactor can be left with water in the coil ready for the next experiment.

When removing the CET-MkII reactor from the service unit always drain using the drain valve under the baseplate first.

Exercise B - To determine the kinetic constant of a reaction using an indicator for visually monitoring

The experimental procedure is identical to that of Exercise A with the exception that Ethyl acetate solution will contain 0.01% w/w of Indigo carmine to monitor the change in colour while the reaction takes place.

Method

The ethyl acetate solution has to content Indigo Carmine at 0.01% p/p. This indicator is an acid base non toxic indicator with a change range between 11.5 and 13 of pH going through dark blue to greenish yellow.

Exercise C - To investigate the effect of throughput on conversion

Theory

For a tubular reactor, the mass balance for a reactant is represented by:

$$\int_{a_1}^{a_0} \frac{da}{r_a} = \frac{AL}{F}$$

For the reaction between ethyl acetate and sodium hydroxide, it is equi-molar and is second order in nature, thus

r = k.a.b

where k is the kinetic rate constant.

Arranging for initial concentrations of a and b to be equal $r = k.a^2$

$$\int_{a_1}^{a_0} \frac{da}{ka^2} = \frac{AL}{F}$$

$$\frac{AL}{F} = t_R$$ the residence time

Integrating,

$$\frac{1}{a_0} - \frac{1}{a_1} = k \cdot t_R$$

Fractional conversion,

$$X_a = \frac{a_0 - a_1}{a_0}$$

Therefore,

$$k \cdot t_R \cdot a_0 = \frac{X_a}{1 - X_a}$$

Thus the conversion factor $\frac{X_a}{1-X_a}$ is directly proportional to t_R the residence time for constant reaction temperatures (T).

Method

The experimental procedure is identical to that of Exercise A with the exception that flow rates of reactants can be varied to change the residence time of the reactants in the reactor.

Calculate the degree of conversion of the reactants at steady state using conductivity readings (from data logger and spreadsheet as described in Exercise A) for different values of F_a and F_b. Exercise A used flows of 80ml/min so it is suggested that flows of 40ml/min and 60ml/min are used for this experiment. Plot t_R against $\frac{X_a}{1-X_a}$.

Comment on the graph obtained.

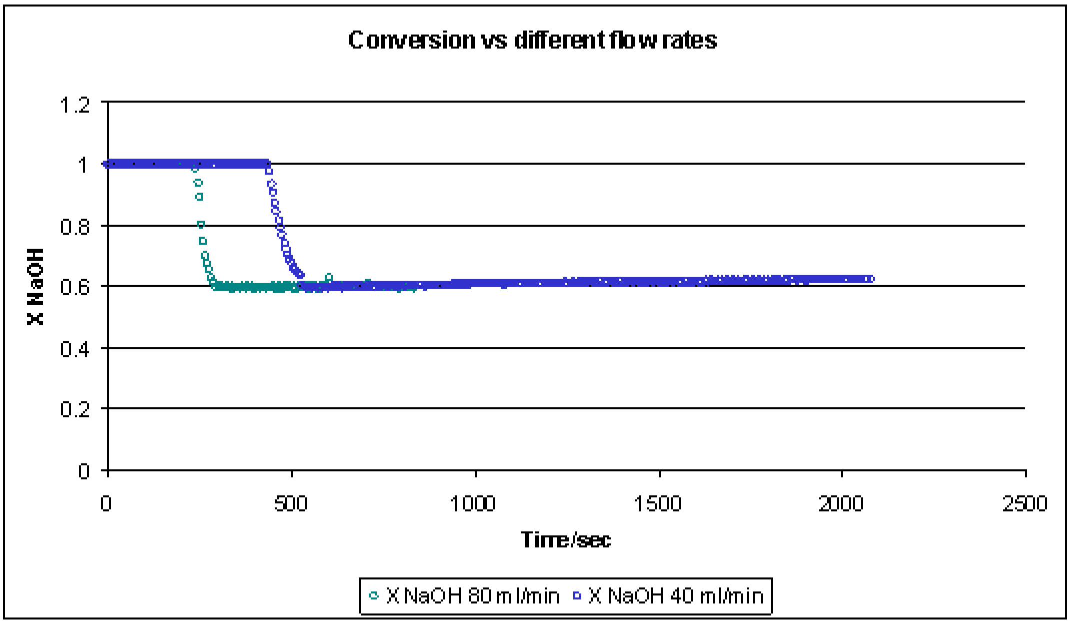


Figure 2: Conversions of NaOH at different flow rates

Exercise D - Demonstrate the temperature dependence of the reaction and the rate constant

Theory

The rate of reaction as characterised by its rate constant *k* is strongly temperature dependent. This is generally expressed as the Arrhenius equation:

$$k = \breve{A} e^{-\frac{E}{RT}}$$

where E (activation energy [J/mol]) and R (gas constant [J/mol.K]) are constants, T [K] is the reaction temperature and Ă - frequency factor.

Therefore,

$$\ln k = \ln \breve{A} - \frac{E}{RT}$$

A logarithmic plot of k vs. 1/T will give a straight line.

Method

The procedure will be identical to that of Exercise A with the exception that the reaction will be carried out at different reactor temperatures.

Exercise A was carried out at 25°C. It is suggested that the reaction be carried out at a minimum of two further settings, say, 20°C and 30°C in order to plot the graph.

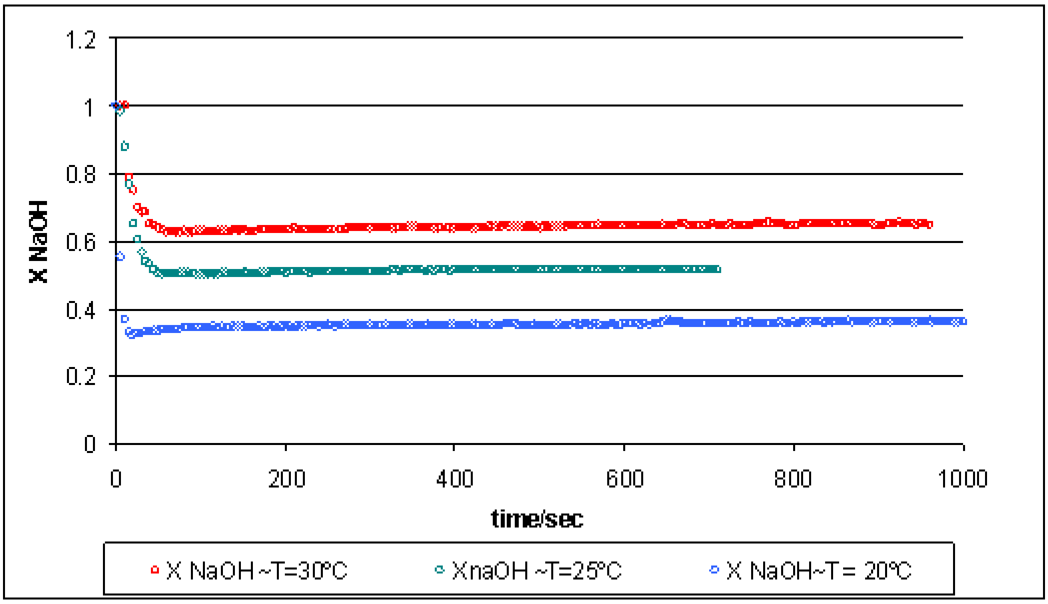


Figure D1: Conversions of NaOH at different temperatures

Plot 1/T vs. ln k and comment on the graph obtained.

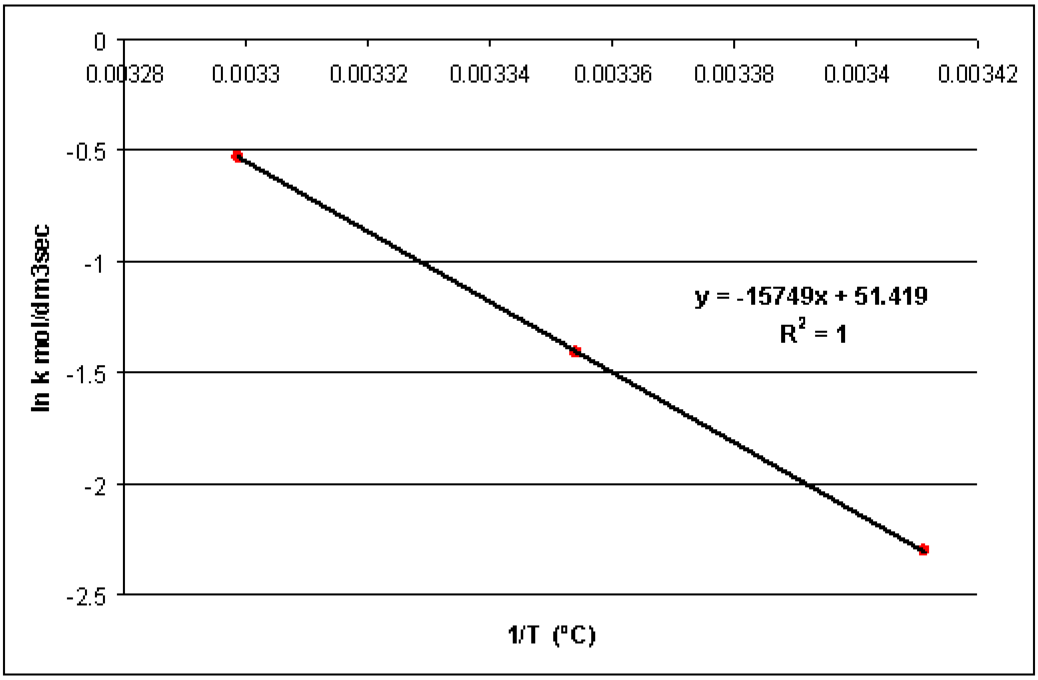


Figure D2: Variation of the Rate constant with Temperature

$$\ln \breve{A} = 51.419 \qquad \breve{A} = 2.142 \cdot 10^{+22}\ m^3/mol\,\text{sec}$$

$$\frac{E}{R} = 15749 \qquad E = 130.96\ KJ/mol$$

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

Obtaining the reaction rate constant in function of the temperature:

$$\ln k(T) = 51.42 - 15749\frac{1}{T} \qquad T(°K)$$

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

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