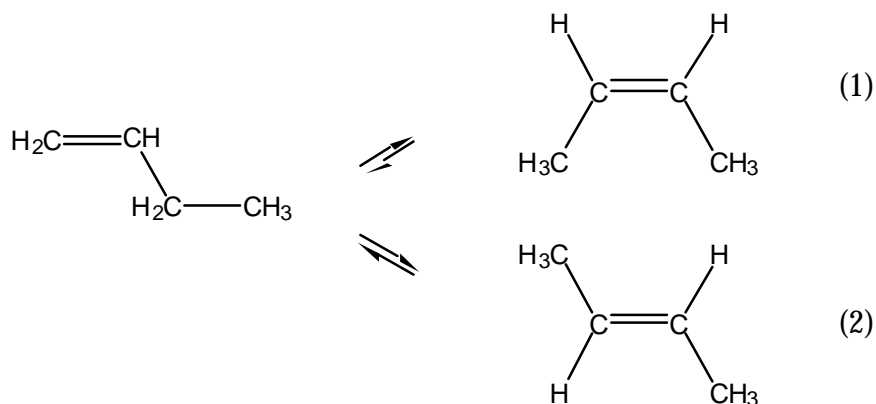## CATALYTIC ISOMERIZATION OF BUTENE

Introduction

The purpose of this experiment is to give you some experience in studying a solid-catalyzed gas reaction in a flow reactor. The reaction is the isomerization of the olefin 1-butene to a mixture of cis- and trans-2-butenes:

Freshly dried, activated alumina is used as the catalyst. The over-all isomerization of 1-butene can be treated as a reversible first-order reaction, although the reaction scheme is actually rather complicated, including the mutual isomerization of cis- and trans-2-butene. The equilibrium constants for reactions (1) and (2), as well as the *equilibrium* ratio of trans- to cis-2-butene, are shown in Table 1 for a number of temperatures.

Table 1

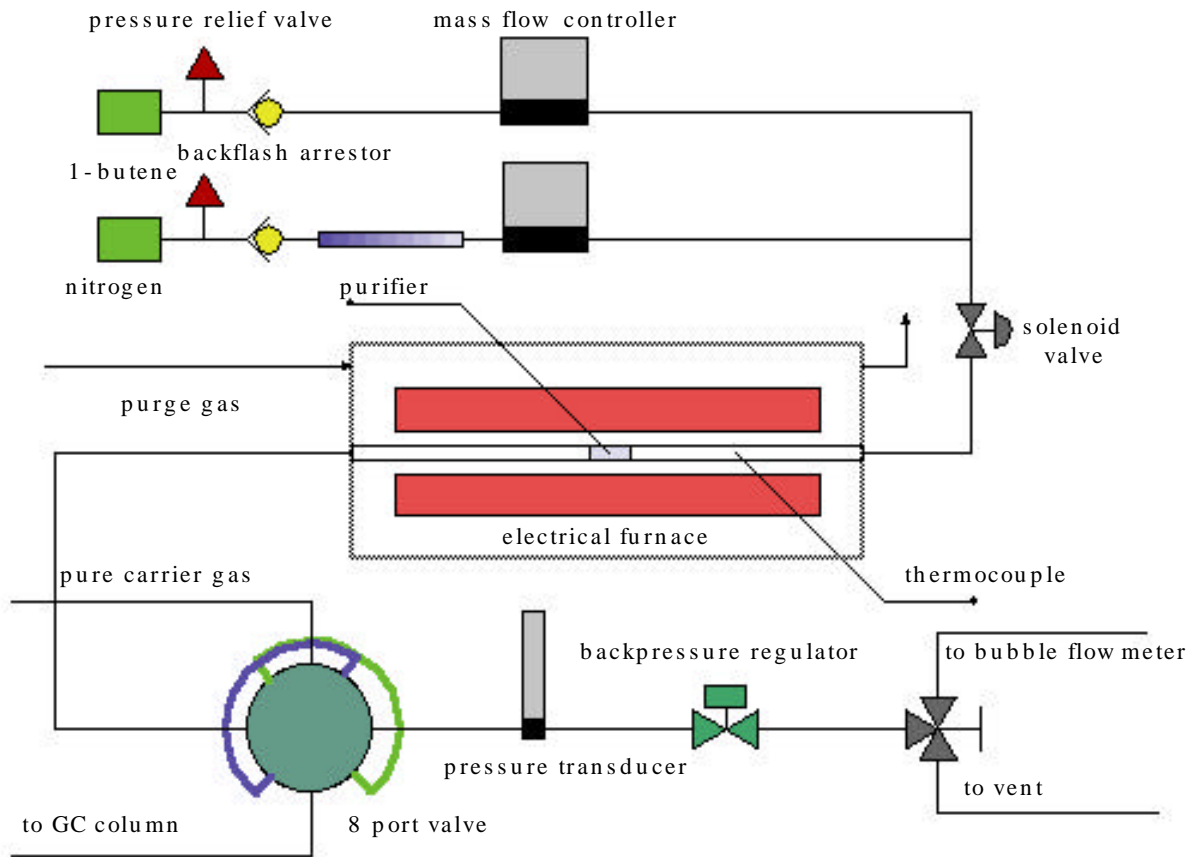| T(K)	K_{eq} Reaction (1)	Reaction (2)	$(trans/cis)_{eq}$
300	9.03	32.9	3.62
400	4.34	10.6	2.44
500	2.70	5.31	1.97
600	1.90	3.32	1.75

The present experiment is open-ended, in the sense that a "cook-book" procedure cannot be given that will guarantee a particular quantitative result. One important reason for this is that

the reaction rate (or rate constant) under given conditions depends on the particular alumina used as catalyst and on its detailed thermal treatment prior to your testing. However, it is known that the reaction can proceed with essentially no deactivation during continuous operation for a period of hours. The isomerization is also a convenient model reaction because the heat of reaction is very small (1-2 kcal/mole), and, with proper reactor and furnace design, it is not difficult to operate isothermally.

Apparatus and Procedure

The equipment is shown schematically below. Pure 1-butene is allowed to flow from a compressed gas cylinder through a mass flow controller and then into a reactor (1/4" S.S.) containing the catalyst, activated alumina. The reactor is surrounded by a tube furnace with temperature controller. The reactor effluent, containing the various butene isomers, is injected by an eight port sampling valve into the gas chromatograph column for quantitative analysis. Although the butenes are not particularly toxic, their odor is disagreeable, so the effluent is finally led outdoors (preferably after passage through an activated charcoal trap). The pressure in the reactor is adjustable using a backpressure regulator and transduced to the control computer via a pressure transducer. In case of emergency shutdown, a solenoid valve can be actuated to cut off any influent. The volumetric flow rate can also be measured using a bubble flow meter in case that some uncalibrated gas is used in this system.There is also a nitrogen gas inlet line reserved in the system for in situ catalyst preparation and possible multiple reactant reactions.

pressure relief valve   mass flow controller

backflash arrestor

1-butene

nitrogen   purifier

solenoid
valve

purge gas

electrical furnace

pure carrier gas   thermocouple

backpressure regulator   to bubble flow meter

pressure transducer

to GC column   8 port valve

to vent

The frame of the reactor rack is built with Unistrut® bars. Three layers are made so there is enough space to hold all the hardware. The furnace is on the top layer; the eight port sampling valve and the gas chromatography are on the middle layer; all the electrical supporting parts are on the bottom layer.
[picture 1]

The electrical furnace has its own temperature controller. By replacing the temperature sensor of the furnace with the thermocouple whose tip goes into the catalyst, we are able to get the temperature inside the catalyst to be the exact set temperature. The same signal from the thermocouple is also transmitted to the computer so the temperature can also be shown on the computer screen. A second thermocouple is put before the catalyst bed and the temperature is readable from the control computer.

The catalyst to be used is an ASTM reference material, N10131 alumina (Al_2O_3). 0.1985 gram is loaded in the reactor tube and two small pieces of glass wool keep the catalyst in place. A reactor temperature of ca. 400°C should be sufficient to obtain reasonable conversions (30-50%) of 1-butene at a volumetric flow rate (measured at room temperature) of ca. 30 ml/min.

Instead of manual injections, an electric actuator driven eight port sampling valve is used in the new design to achieve remote operation. This sampling valve has two sample loops

installed. In position A, loop 1 is loaded while the mobile phase flows through loop 2 and into the packing column. In position B, loop 2 is loaded while the mobile phase flows through loop 1 and into the packing column. The rotating shaft is driven by an electric actuator, which is powered by 110 VAC and remotely controlled by TTL level logic signals.
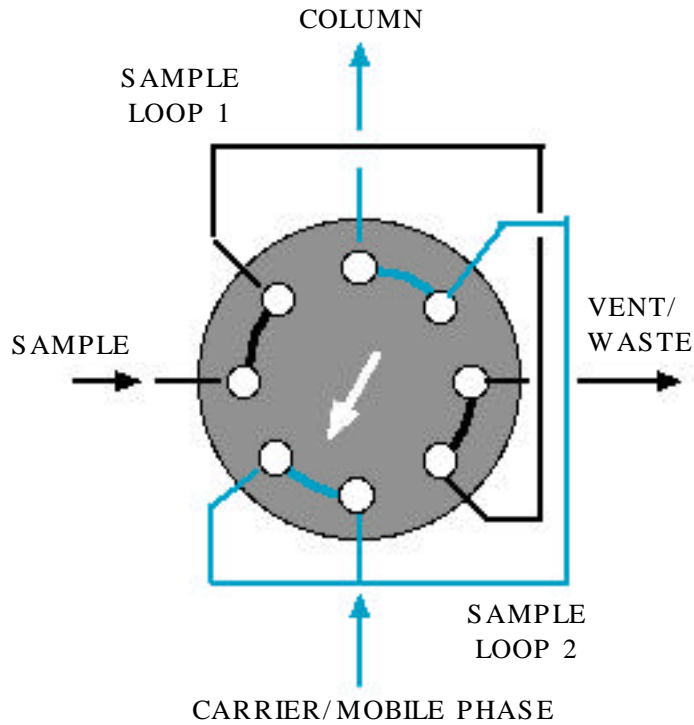
Position A of the eight port valve

COLUMN

SAMPLE
LOOP 1

SAMPLE

VENT/
WASTE

SAMPLE
LOOP 2

CARRIER/ MOBILE PHASE
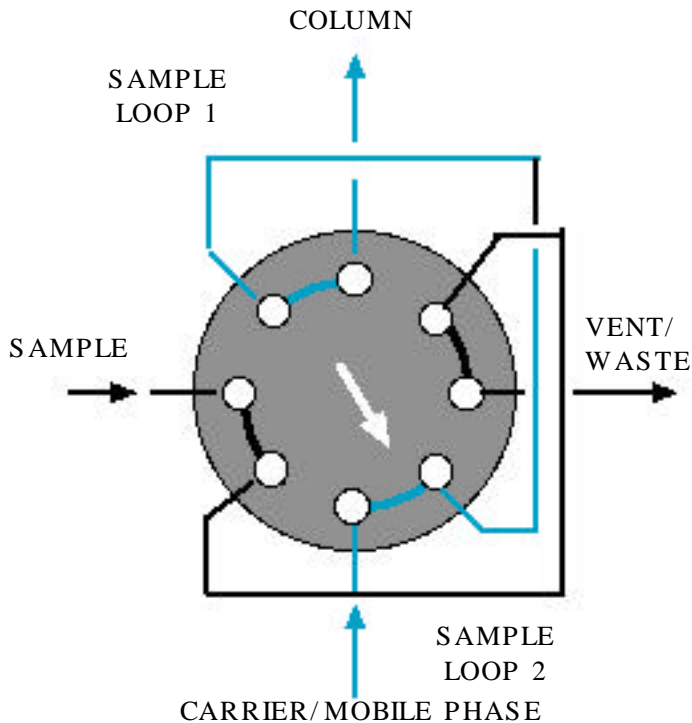
Position B of the eight port valve

In the present experiment you will use a SRI model 8610 with a FID detector. A 1/8"OD, 6' long chromatogrphy column packed with 0.19% picric acid Gaphpc-GC at column temperature of 35°C has given good resolution of the butene isomers. The retention times for the three compounds are respectively 2.0 minutes for 1 butene, 2.8 minutes for trans-2-butene and 3.6 minutes for cis-2-butene. Although you might not expect to obtain exactly the same residence times in your experiments, their relative order of appearance from the column should be the same with respect to one another. The sensitivity of the detector is almost the same for the different butene isomers [Why?] and in this experiment it will be assumed to be the same. Determination of the absolute concentrations of the individual isomers would require construction of a calibration curve, with the use of gas samples of different, but known, sizes. This isomerization reaction can be followed, however, without the need to construct the calibration curve [Why?]

Note: You should read the handout on the operation of a gas chromatograph, posted separately.

The gas chromatography data are collected by a 286 IBMPC which is devoted on running peaksimpleII. We did not use the controller computer to gather gas chromatography data because we already own a GC data acquisition system based on MSDOS.

A low end pentium desktop PC purchased from Gateway2000 is used as controller computer. The interface between the desktop PC and all the electronic parts on the reactor rack is implemented by an AD/DA board and a multiplexer. The AD/DA board, Model 203 from Lawson Labs, is a high-resolution device for translating voltages into digital form. The board

communicates with a host computer over a RS-232 serial link. It has a single 20-bit differential analog input channel, two 14-bit analog outputs, a digital input, and 8 digital outputs. The model 17B multiplexer that is also obtained from Lawson Labs expands the single analog input to sixteen. Of the eight digital outputs, four are used as address lines for 17B; one for furnace on/off; one for solenoid valve on/off; two for eight port valve. The two analog outputs are used as voltage setpoints for the two mass flow controllers. On the 17B multiplexer, 5 channels are used. Two channels are for mass flow controllers; two channels are for temperature transmitters; one is for the pressure transducer.

The electrical connection diagram is shown below:
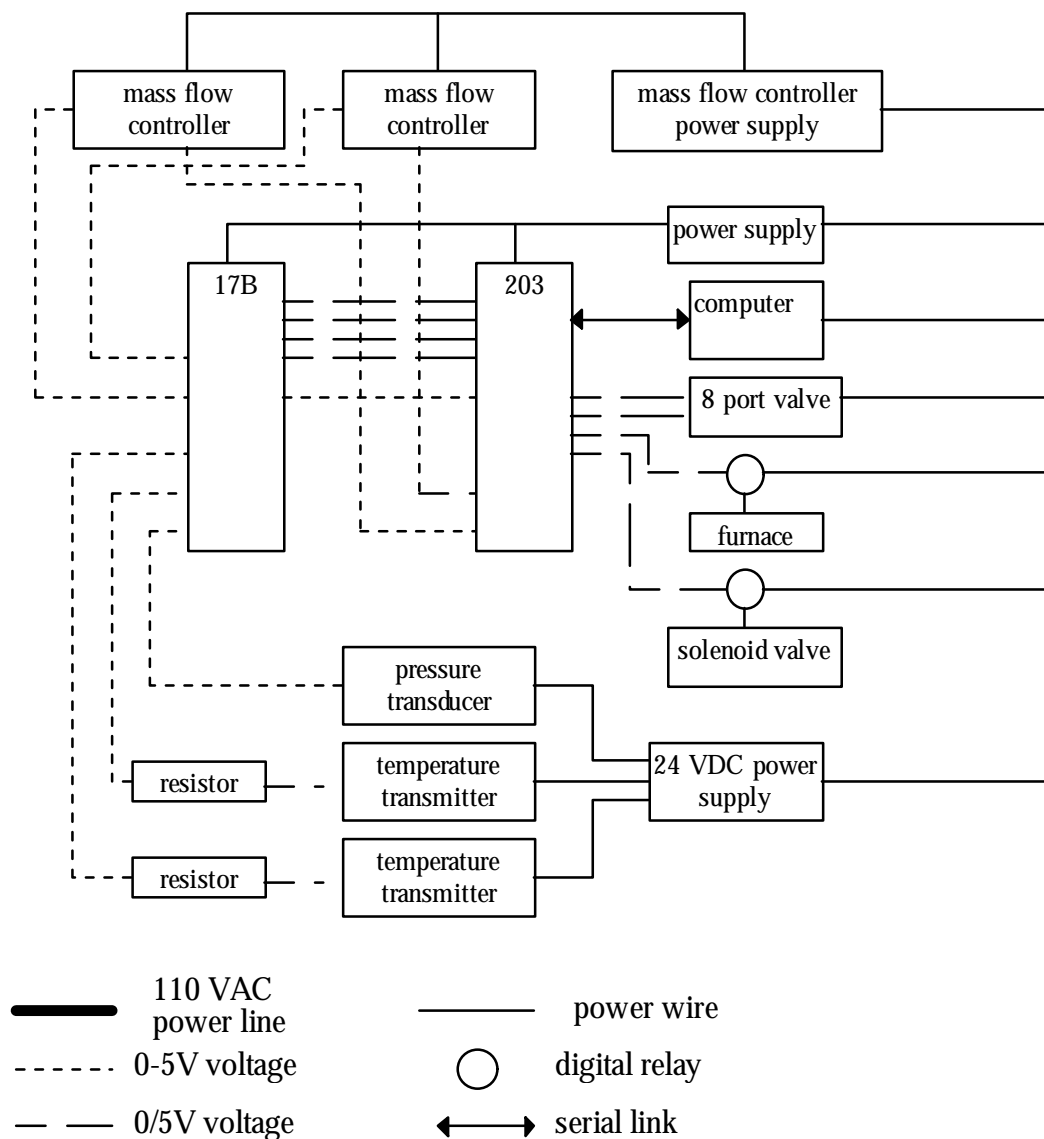
A Windows95 program is developed to build a bridge between the AD/DA board and the operator. After double clicking the icon for the program, PFR_controller, the connection between the desktop PC and M203 is built up and two windows pop out. One is simulation of a real time

plotter. It displays the two temperatures, two mass flow rates and the pressure. both left and right axis ranges can be adjusted by activating appropriate dialogs from the menu bar. The time axis range is default set at 60 seconds and is also changeable by activating a dialog window at runtime. Another window is a real time monitor. The schematic drawing of the reaction system is shown in this window. All the data that are received by the AD/DA board, including the on/off status of the electrical furnace and solenoid valve, are shown at proper places and refreshed every second. The sample injection can be remotely done by simply clicking on a menu item. The operator is also able to shut down the electrical furnace or the solenoid valve in the same manner.
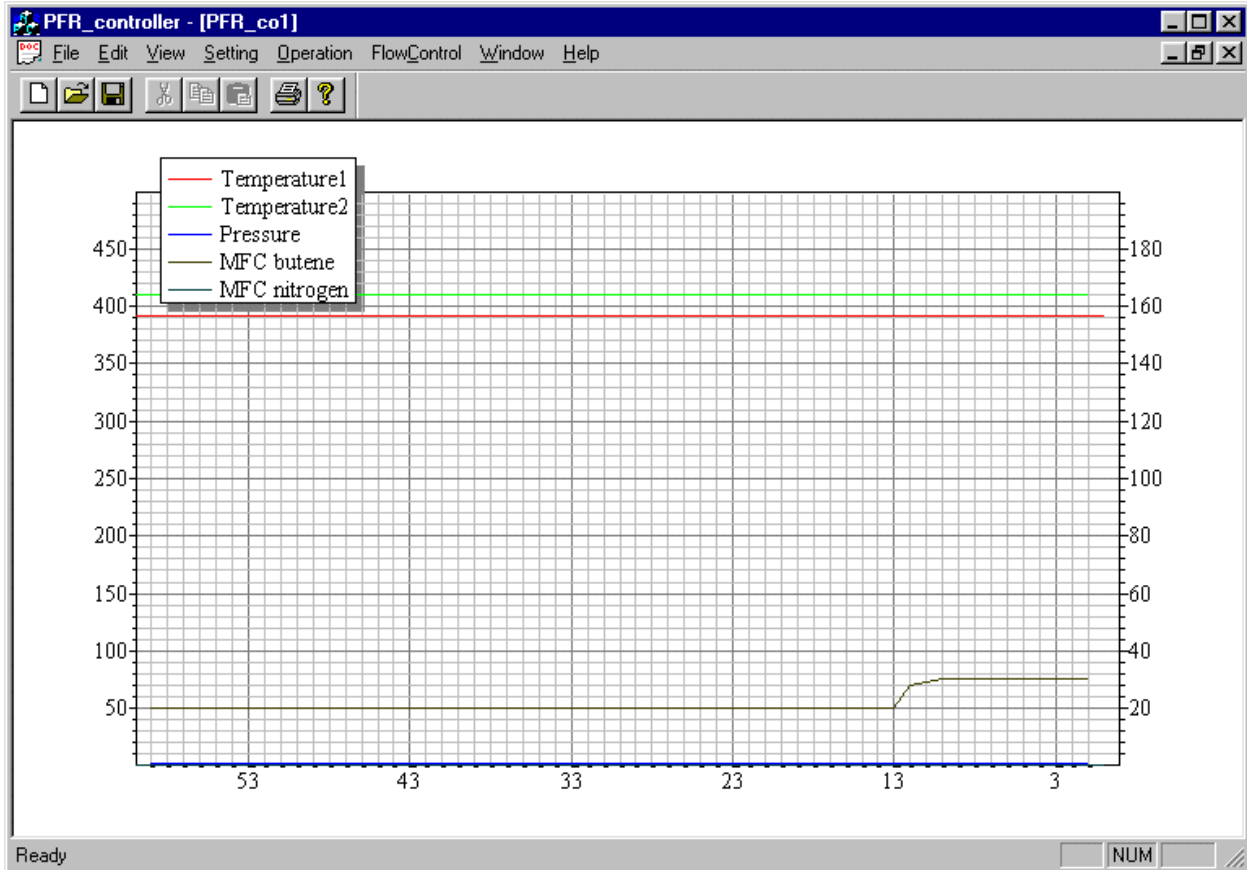
PFR_controller window

System Layout
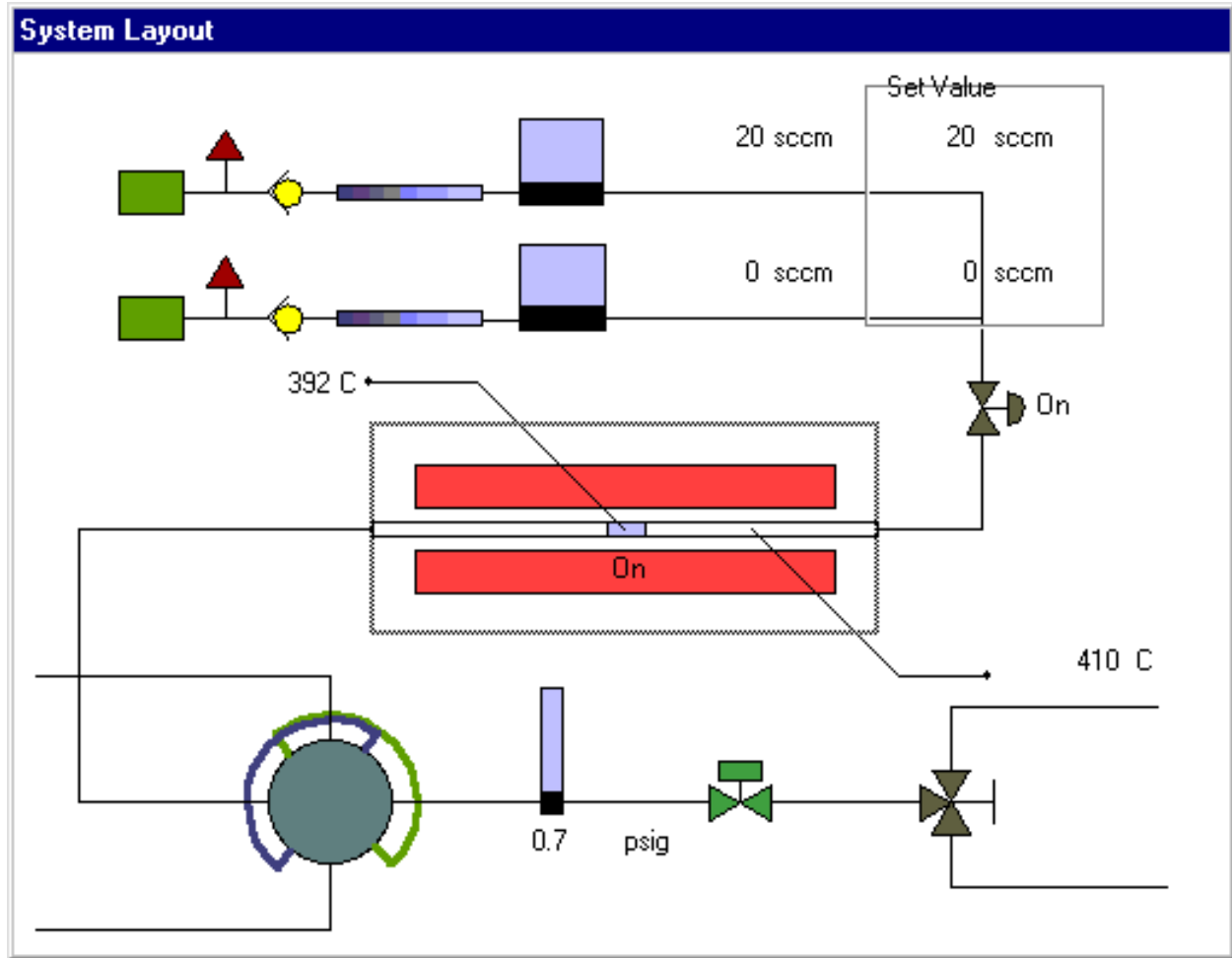
real time monitor window

The computer program, PFR_controller, is developed using Visual C++ 5.0 and runs on Windows95 platform. Parts of the codes come from adaptation of works done by Samuel R. Blackburn, Jörg König and Jan Vidar Burger. A serial communication layer, a M203 driver and an operator interface layer constitute the whole structure of the program.

To run this experiment, both gas chromatography and reaction system should be set up properly.

Brief procedure descriptions are suggested below. It is not very necessary to follow every step exactly if you know what you are doing.

PFR operation procedure:

WARNING: UNPLUG THE POWER LINE FOR THE EIGHT PORT VALVE BEFORE YOU RUN THE PFR_CONTROLLER. PLUG IT IN AFTER YOU START UP THE PFR_CONTROLLER.

1. Plug in the main power cable to the wall electrical outlet.
2. Connect the serial port with the M203 board serial cable. Have the computer, titanic, power on.
3. Have the exhaust pipe hooked in the vent.
4. Follow the procedure to set up GC.
5. Follow the procedure to run peaksimple.
6. Open the 1-butene valve. (DO NOT play with regulator!)
7. Run PFR_Controller by double clicking it.
8. Plug in the 8-port valve power line.
9. Setup ther flow rate: select FLOWCONTROL/SETUP FLOW RATE and set up the butene flow rate you want; leave nitrogen flow rate at zero.
10. Setup the temperature mannually, which means that you set it on the furnace panel.
11. After the furnace temperature stabilizes, select OPERATION/INJECTION in the menu of PFR_controller and press the space bar of the PACKARD BELL(NOT the pentium machine, but the old 286! I suppose PeaksimpleII is running on that machine at this time and is at standby mode. If not, read peaksimpleII part).
12. Follow the procedure of peaksimpleII to collect data.

FID ignition:

        To make the GC run, the first thing is to set up the necessary gas flows for the GC. In this particular application, hydrogen is used as carrier gas and FID uses hydrogen and air. Hydrogen is supplied by a gas tank. Air is supplied through wall faucet.
1. First, hydrogen gas tank valve and another needle valve after the regulator should be opened counterclockwise. (You should not adjust anything ON the PRESSURE REGULATOR)
2. Air faucet should be opened in the same manner.
3. Open two valves on either side of a hydrogen purifier at the right side of the rack.
4. Set the head pressures of the GC as follows:
5. Head pressure of hydrogen: 12 psi
6. Head pressure of air: 14 psi
7. Head pressure of carrier gas: 16 psi
8. Turn on the power of the GC. (The switch is on the left side of the GC)
9. Open the red cover of the GC, push forward the ignition switch (NOT the KNOB), hold it for 1 second until you hear the 'pop' noise. To verify if the flame is on, a glossy metal suface may be used to cover the FID gas exit hole (don't block it) for a few seconds. After remove the metal piece, you should be able to tell a thin layer of water on the metal surface if the FID is ignited.

Running peaksimp II:

        The program is under the directory: c:\peaksimp. (If the computer is unbootable, go into CMOS setup, set up the hard disk as type number 3). Type in peak2 to run the program after the power of GC is turned on. Select CONTROL/LOAD in the menu to activate a dialog window. Choose Butene.con and click ok. Select Control/channels in the menu. In the dialog activated

choose 'compon' button in the second line. Choose load to activate another window and then
choose butene.cpt. Click ok several times to return to the main window. To start an analysis
cycle, hit space bar. The analysis will end automatically in 5 minutes, or it can be stopped
manually by hitting 'end' button. Once an analysis cycle ends, choose analysis/results to see a
table of species, retention time and peak area. At the left side of the main window, there are some
useful buttons. They are 'zero', 'zoom out' and 'zoom in'. Try to click them and find out how
they work.

Shutdown procedure:

Pretty much the reverse. Figure it out yourself.

Variables to be Studied (as many as possible)

1.   Once the reactor temperature is stable, does the extent of isomerization of 1-butene
        remain constant with time, at fixed flow rate?

2.   How does the extent of isomerization vary with flow rate, at constant temperature?

3.   What are the observed ratios of the trans-2-butene to cis-2-butene peak areas? Are the
        ratios consistent with the equilibrium value at your operating temperature? If not, why
        not?

4.   Calculate rate constants for these reactions assuming first order mechanisms. (You will
        have to explain the procedure for doing this during the oral before the experiment!)

5.   Determine the effect of a 30°C temperature change on the apparent first-order rate
        constant? What is the apparent activation energy?