

CATALYTIC HYDROLYSIS OF ETHYL ACETATE

A. SAFETY

SAFETY IS OF OVERRIDING IMPORTANCE. IT IS IMPERATIVE THAT YOU:

1. Wear eye protection at all times.
2. Wear jeans or slacks, a long sleeved shirt, and sturdy shoes that give good traction on possibly wet floors.
3. Guard against electrical hazards by making sure that all equipment is grounded using three-wire plugs and other means.
4. Handle with great care any solvents or other potentially volatile, flammable, toxic, or otherwise dangerous chemicals. Note that ethyl acetate is volatile and flammable. Obtain and read the MSDS (Material Safety Data Sheet) for ethyl acetate. The TA will prepare the roughly 4% aqueous ethyl acetate feed solution, using distilled water.
5. Guard against falls, burns, cuts, and other physical hazards. Use heavy gloves to open or close hot steam or condensate valves.
6. THINK FIRST OF SAFETY IN ANY ACTION YOU TAKE. If not certain, ask the TA or faculty member before you act.

B. OVERVIEW

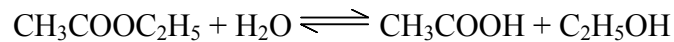
This experiment involves the hydrolysis of a 4% solution of ethyl acetate, with an ion exchange resin acting as a catalyst. The feed solution is heated by hot water in a stainless steel heat exchanger and then passes through a jacketed bed of catalyst beads. When a steady state has been reached the acetic acid in the reactor effluent is titrated (to a phenolphthalein end point) with NaOH to determine the conversion. Runs made at several different feed rates and temperatures allow the activation energy of the reaction to be determined, and the possibility of diffusion control to be examined.

The apparatus includes a temperature indicator/controller that can be used to control the power to the water heater. The controlled temperature is that of the water leaving the water heater, or that of the reactor effluent. Thus the apparatus can be used to study the transient behavior of a feedback control system as a function of the PID controller parameters, and also as a function of the variable delay corresponding to the choice of controlled variable and reactor feed rate. However the long time constants associated with cooling the hot water make control experiments less than ideal.

C. INTRODUCTION

The purpose of this experiment is to investigate the kinetics of the acid-catalyzed hydrolysis of ethyl acetate, using an anion ion-exchange resin as the catalyst. The temperature and flow rate dependence of the calculated reaction rate constant, and then the activation energy of the reaction, will be determined. The possible existence of transport effects will be examined.

The reaction to be studied is the liquid-phase hydrolysis of ethyl acetate (EtAc) to ethanol (EtOH) and acetic acid (HAc):



The catalyst is Rohm and Haas Amberlyst 15 ion exchange resin in the acid form. (The resin is supplied in the acid form, and can be restored to acid form by contact with strong acid, e.g. 1 N HCl or H₂SO₄, if needed.) The material used in this experiment is 20-50 mesh, 840 to 297 micrometer diameter, say 0.05 cm as an average. Presenting the catalyst in resin form, as essentially an insoluble acid, eliminates the need for subsequent neutralization or removal from the hydrolysate that would be required if a soluble acid were used, but requires that the ester be transported to, and the alcohol and acid be transported from, a phase boundary (the surface of the ion exchange resin). Thus it is possible that the rate at which the process proceeds will be limited by transport, reaction rate, or a combination of both.

By appropriate variation of flow rates, concentrations, and temperature you are expected to quantify the factors affecting the reaction rate. Under the conditions of the experiment, the reaction may be treated as first-order with respect to the ethyl acetate and as essentially irreversible (see below).

It is important to understand that the resin in this experiment functions as a true catalyst, no consumption of acid or net exchange of ions taking place. Thus, this fixed-bed reactor operation can operate at a steady-state, and the "breakthrough curve" behavior characteristic of an ion exchange separation process is not encountered.

D. THEORY

Let the reaction be



with A = ethyl acetate (EtAc), B = acetic acid (HAc), D = ethanol (EtOH). Let C be the EtAc concentration, let V be the running volume (we neglect volume occupied by the catalyst in defining the volume) of a plug flow reactor of total volume V_F, and let Q be the volumetric flow rate. Assuming first-order reaction, the steady state reactor equation is

$$\begin{aligned} & dC/dV = -(1/Q)kC, C(0) = C_0 \\ \text{for} & \\ & 0 \leq V \leq V_F \end{aligned}$$

and with k the reaction rate constant, assumed to be a function of temperature T (Kelvin) only.

This linear equation is easily integrated to give

$$C(V_F) = C_0 \exp(-kV_F/Q)$$

where V_F is the total volume of the reactor. From the stoichiometry we have

$$C_F = C(V_F) = C_0 - C_B$$

where C_B is the effluent concentration of acetic acid (gmol/cm^3), determined by titration. The feed concentration C_0 is found from the fact that the feed is made up by diluting 400 cm^3 of EtAc (MW = 88.11) to 10 L with distilled water. The density of EtAc is $0.895 \text{ gm}/\text{cm}^3$ at 25 C. The feed solution is thus 0.406 M.

From the integrated equation we have

$$kV_F/Q = \ln(C_0/C_F)$$

or

$$k = (Q/V_F)\ln(C_0/C_F)$$

If k follows an Arrhenius dependence on absolute temperature T (K), namely

$$k(T) = b_1 \exp[(-E/R)((1/T) - (1/298.16))]]$$

where E is the activation energy, R is the gas constant, and b_1 is a parameter equal to the rate constant at 25 C, then a plot of $\ln(k)$ vs. $1/T$ will be a straight line with slope $-E/R$. Note that, if Q is held constant while T is varied, a plot of $\ln(k)$ vs. $1/T$ will also have slope $-E/R$.

E. APPARATUS (see the schematic diagram below)

Tubular Reactor

The reactor consists of a 3.8 cm ID, 53 cm long borosilicate tube surrounded by a water jacket. The catalyst section is supported by a 60 mesh stainless steel screen in a Teflon ring at each end. The catalyst is packed to a depth of about 36 cm. The entrance and exit sections of the reactor are packed with glass beads to reduce dead volume and flow maldistribution. Flow through the jacket and the reactor is upward, in order to remove any air or vapor bubbles. A 1/16" stainless jacketed copper-constantan thermocouple is located in the reactor effluent stream, and is connected to an Omega CNI16 temperature indicator/controller.

Feed

The feed is supplied to the reactor from a 20 L tank by a magnetic-drive centrifugal pump. The feed consists of a mixture of absolute ethyl acetate in distilled water (0.406 M), 400 ml of EtAc diluted to 10 L. (EtAc MW = 88.11, density = 0.895 gm/ml)

Temperature Control

To obtain isothermal operation of the reactor at any desired temperature, the feed is preheated in a small stainless steel ITT heat exchanger (1 ft² area) and the reactor is jacketed. A magnetic-drive centrifugal pump circulates hot water from a 10 L electrically heated (1500 W) vessel through the heat exchanger and the jacket in parallel. The input to the active controller is a 1/16 inch stainless steel jacketed copper-constantan thermocouple mounted in the effluent line of the heater. When the controller parameters have been properly tuned (typically PB1 = 2 to 10 C, RES = 3000 sec, RATE = 0 sec), the controller will hold the reactor effluent temperature within 0.2 C of the set point. (The heater contains a thermal switch that limits the temperature to about 65 C. Thus the controller set point should be limited to about 62.5 C. If the thermal switch is activated, it may take an hour or more to reset, due to slow cooling of the insulated water tank.)

Reactor Feed Rate

A rotameter (nominal calibration: 150 mm location of the stainless steel ball is 133 ml/min) is used to monitor the feed flow rate. Either the rotameter may be calibrated initially, or the flow rate for each run can be measured by collecting a known volume (typically 100 ml) for a measured time, in which case the rotameter is used only to monitor constancy of flow during the run. Note that the rotameter floats tend to oscillate quite strongly, for unknown reasons, and thus accurate flow rate measurements are best obtained by collecting and timing a fixed volume of reactor effluent. The needle valve downstream of the reactor should be used to set the flow rate. This location maintains maximum pressure on the reactor, and reduces the possibility that ethyl acetate will vaporize at the higher temperatures.

Sample Analysis

Equipment for titrating the product stream samples includes a 50 ml burette, phenolphthalein indicator, and 1 N NaOH titrating solution (40 g NaOH/L). Typically a 100 ml sample is collected in an Erlenmeyer flask, a few drops of phenolphthalein dissolved in ethanol are added, and the sample is titrated to a phenolphthalein end point (very sharp) using 1.0 N NaOH.

F. PROCEDURE

Make runs at several, typically three, flow rates at roughly 30 C, then increase the reactor temperature to about 40 C and again make three runs, and then repeat at about 50 C. For each flow rate, allow 300 to 500 ml of liquid to pass through the reactor and then titrate a sample of product. Continue to titrate samples until the concentration of acetic acid is essentially constant. Note that at the highest temperature some of the EtAc may vaporize in the heat exchanger or catalyst bed. Look for and record the presence of bubbles in the bed.

Use for each temperature three flow rates, roughly 25, 50, and 100 ml/min. Thus 9 runs in total are required. (Since the water heater cools very slowly, the low temperature runs should be made first.)

G. DATA ANALYSIS

The first goal of the data analysis is to calculate the reaction rate constant k for each run. For runs at the same temperature, k will be plotted as a function of flow rate Q . Then, for runs at the same flow rate Q , a plot of $\ln(k)$ vs. $1/T$ will be examined and the activation energy will be determined from the

slope of the plot, if the data lie close to a straight line.

If the activation energy is independent of flow rate, the implication is that the reaction is not diffusion controlled. If, however, the activation energy is lower at low flow rates, the implication is that the reaction is diffusion controlled.

We may also plot k vs. Q at constant T . If k does not depend on Q the reaction is not diffusion controlled. If k increases with Q we have evidence for diffusion control.

We now want to see if the reaction rate is controlled by diffusion through the fluid film at the particle interface. By diffusion control we mean that a 1% reduction in the fluid film transfer coefficient will lead to a 1% increase in the observed reaction rate. Note that, at steady state, the rate of transport across the film is equal to the rate of reaction in the particle, so that it is incorrect to say that the reaction is faster than the transport rate when the reaction is diffusion controlled. We will calculate the concentration gradient needed to transfer EtAc at the observed reaction rate across the fluid film, and compare this to the maximum concentration gradient available, namely the average of the inlet and outlet concentrations of EtAc. If the required gradient is relatively small, then the fluid film resistance is not controlling.

Finally, if the reaction is fully diffusion-controlled, the EtAc concentration in the catalyst pores is essentially zero, and the reaction rate constant k will be equal to the overall mass transfer coefficient per unit volume $k_f a_p$. As shown below, $k_f a_p$ can be calculated from the modified Wilke-Hougen correlation (1).

- From the sample volume (typically 20 ml), and the volume and normality of the NaOH (typically 1 or 0.1 N) used in the HAc titration, calculate the effluent EtAc concentration C_F . The feed concentration C_0 is found from the fact that the feed is made up by diluting 400 cm³ of EtAc (MW = 88.11) to 10 L with distilled water. The density of EtAc is 0.895 gm/cm³ at 25 C. The feed is thus 0.406 M.
- From the volumetric flow rate Q (ml/s), based on the timed collection of 50 to 100 cm³ of effluent, and the feed and effluent EtAc concentrations C_0 and C_F , calculate the overall reaction rate N (gmol EtAc/s).
- From the modified Wilke-Hougen correlation (1)

$$k_f a_p = 2.62(D_f Q/A)^{0.5} d_p^{-1.5}$$

- Calculate the overall mass transfer coefficient per unit volume $k_f a_p$ (1/s). Here D_f is the diffusion coefficient of EtAc, which may be assumed as 0.2×10^{-4} cm²/s, Q is the volumetric flow rate (cm³/s), A is the cross-sectional area of the bed (cm²), and d_p is the particle diameter, which is 0.5 mm for the Rohm and Haas Amberlyst 15 resin. The bed diameter is 3.8 cm, and the bed length is measurable. From these calculate the bed area A and volume V_F .
- Calculate the concentration difference ΔC needed to transfer the reacting EtAc through the fluid film from

$$\Delta C = N/k_f a_p V_F$$

and then calculate the concentration ratio

$$r = \Delta C / [(C_0 + C_F)/2]$$

If r is large, the fluid film resistance is controlling. Conversely, if r is small, the concentration gradient across the film is small and the reaction is controlled by the kinetics of diffusion and reaction in the catalyst pores.

As an alternate and perhaps better procedure, compare the calculated reaction rate constant k with the overall mass transfer coefficient $k_f a_p$ from the Wilke-Hougen correlation. If they are roughly equal, we have evidence for diffusion control. If k is less than $k_f a_p$, we have evidence for reaction control.

H. Sample Calculation

Typical data:

Sample Volume = 100 ml = 0.1 L

Collection time = 2.0 min = 120 s

1.0 N NaOH volume = 20 ml = 0.020 L

Reactor temperature = 55 C

Q = flow rate = 100/120 = 0.833 cm³/s

The concentration of acetic acid in the effluent sample is

$$(20/1000)L \cdot 1.0 \text{ (gmol/L)} / 0.1 \text{ L} = 0.200 \text{ gmol/L}$$

Since the feed contains 0.406 gmol/L EtAc, the conversion is 0.200/0.406 = 49.3%.

Considering the rate constant k (1/s), we have

$$k = (Q/V_f) \ln(C_f/C)$$

where Q = volumetric feed rate (cm³/s), V_f = reactor volume (cm³), C_f = feed concentration (gmol/L), and C = effluent concentration (gmol/L). With $Q = 0.833$, $V_f = 200$, $C_f = 0.406$, and $C = 0.200$, we have

$$k = 0.00283 \text{ s}^{-1}$$

Evaluating, with area $A = 10 \text{ cm}^2$ and $D = 0.2 \cdot 10^{-4} \text{ cm}^2/\text{s}$ and $d_p = 0.05 \text{ cm}$,

$$k_f a_p = 2.62(D_f Q/A)^{0.5} d_p^{-1.5} =$$

$$2.62 (0.2 \cdot 10^{-4} \cdot 0.833/10)^{(1/2)} \cdot 0.05^{(-1.5)} = 0.3025 \text{ s}^{-1}$$

Since the rate constant the associated with fluid film mass transfer is much larger than the rate constant associated with reaction, we conclude that the overall rate is controlled by the catalytic reaction.

I. REPORT

From the feed and effluent concentrations for each run, determine the apparent rate constant k for each flow-temperature combination. For a fixed temperature, plot the rate constant as a function of volumetric flow rate Q (cm^3/s). If k does not depend on Q , you have strong evidence that the process is not diffusion controlled. If k increases with Q , the converse is true. For a fixed flow, plot $\ln(k)$ as a function of $(1/T)$. The slope of the line (if the line is straight) is $-E/R$, where E is the activation energy. (In general the activation energy for a chemical reaction is greater than E for a diffusion-controlled process.) Calculate the apparent activation energy.

Discuss how calculated quantities (from both experiment and theory) may be uncertain because of uncertainties in the quantities from which they were calculated. (For example, are departures from linearity in the $\ln(k)$ vs. $(1/T)$ plot significant, and how reproducible are the effluent concentration values?)

Discuss the control factors of the reaction: Is it mass transfer rate controlled or surface reaction rate controlled? Is there a transition from one to the other? How would you control the system to enhance the reaction rate depending on the rate-controlled step?

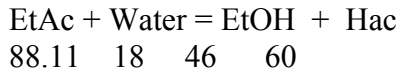
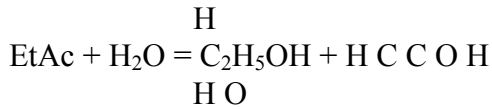
(Optional) For the control system part of the experiment, report the nature of the response (e.g. large or small amplitude oscillations, oscillatory or exponential approach to a steady state, large or small offset at the steady state) as a function of water flow rate, SP1, PB1, and RES. Recommend best controller parameter values.

J. REFERENCES

1. Perry, R.H. and C.H. Chilton, "Chemical Engineers' Handbook, 5th Ed." McGraw-Hill, New York (1973), Section 16-20.
2. Anon., Dowex: "Ion Exchange," Dow Chemical Co., Midland, Mich. (1958) esp. sec. 3, pp. 12-18, and p. 69.
3. Kunin, R. "Ion Exchange Resins 2nd ed." Wiley, New York, (1958) esp. Ch. 12, Catalysis with Ion Exchange Resins.
4. "Encyclopedia of Polymer Technology," Ion Exchange Polymers.

K. NOTES

o Stoichiometry



o Feed concentration based on 400 ml EtAc in 10 L of solution:

$$[(400 \text{ ml}) (0.985 \text{ g/ml}) (1 \text{ gmol}/88.11 \text{ g})]/10 \text{ L} = 0.406 \text{ M}$$

o The ID of the glass reactor is 37 mm. The length of the catalyst bed can easily be measured, and thus the bed volume can be determined. The liquid contained in the reactor is, roughly, 100 ml.

o The feed should be made up using distilled water to avoid cations like calcium which bind to the ion exchange resin.

o The temperature, as indicated on the temperature indicator/controller, is accurate to within a few degrees. But the controller instruction book shows how a correction can be added so that the reading is exactly correct at a given temperature. This requires that the thermocouple be immersed in a stirred Dewar filled with hot water at, say, 50 C, as measured by an accurate mercury-in-glass thermometer.

o Use the valve at the reactor outlet to control the flow rate. This keeps maximum pressure on the fluid in the reactor, and minimizes vaporization of the ethyl acetate.

o The power cord is provided with GFCI ground fault protection unit. If a short develops, this unit will trip and cut off power to the experiment. Before resetting the unit the cause of the short should be corrected. Note that the power cord must be plugged into a three-wire grounded outlet. It is recommended that the GFCI unit be tested before the power strip is turned on.

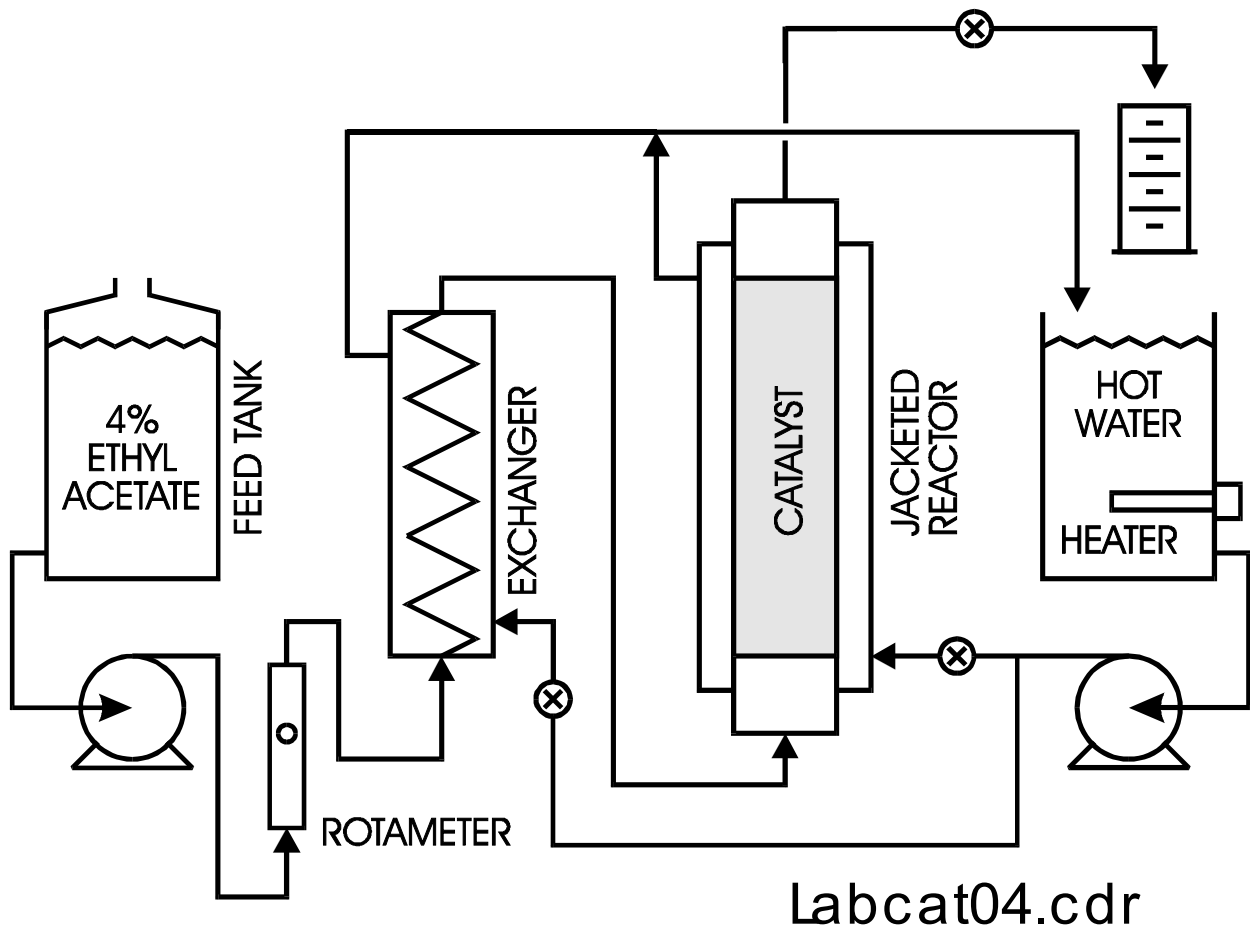
o The jacketed glass reactor vessel is supported in a frame consisting of four 1/2" aluminum rods connected to 1/2" aluminum end plates. Three 10-32 machine screws in each end plate exert pressure on stainless reactor heads which contact the reactor via 1/8" (#226) Teflon O-rings. It is most important that these screws be tightened sequentially, evenly (so the heads are not cocked), and with minimal force (not much more than finger tight), force sufficient only to prevent leaks. Use an Allen wrench to adjust these screws.

o If the reactor has to be removed, it is recommended that the two 1/4" - 20 bolts that hold the frame to the back board be removed, and the reactor in its frame then be moved horizontally away from the

jacket water line connections. Do not exert strong side forces on the glass jacket connectors.

o The rotameter flow rate is 133 ml water/min when the stainless float is at 150 mm.

CATALYTIC HYDROLYSIS OF ETHYL ACETATE



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'--tolact01.bas acetate parameter estimation    4-7-01
COMMON SHARED n, abt, avctr, nxp, npara, ldb1
DIM SHARED ystr(301), y(301), bb(301, 3), r(301), btb(3, 3), btr(3)
DIM SHARED a(30, 30), anv(30, 30), B(30), x(30), asav(30, 30), bsav(30)
DIM SHARED d(30, 30), lr(30), lc(30), sc(30), tst(30, 30)
DIM SHARED bp(3), bpzr(3), bpu(3), xx(30), ybase(301)
'-----for odes
'--jsrk arguments:neq,nstep,delt,yrk(),yy(),gg(),ak1(),ak2(),ak3()
DIM SHARED cc(1, 501, 3), dd(50, 10), plott(50, 3)
COMMON SHARED bb1, bb2, bb3, neq, nstep, delt, tt, trk, nrk, beta
'-----
DECLARE SUB gjlsc ()
SCREEN 12
WINDOW (-50, -.2)-(550, 1.8)
OPEN "runs.inn" FOR INPUT AS #1
OPEN "runs.out" FOR OUTPUT AS #2
'#####
COLOR 14
PRINT "ANALYSIS OF CATALYTIC ACETATE HYDROLYSIS KINETIC DATA"
PRINT ""
COLOR 10
PRINT "This program (tolact01.bas) analyzes, and carries out "
PRINT "a non-linear regression parameter estimation using, data"
PRINT "from the Catalytic Hydrolysis of Ethyl Acetate experiment. "; ""
PRINT "Input data are contained in file runs.inn. Each line "
PRINT "of the file contains the data for a run, as follows: "
PRINT "temperature (C), sample volume (ml), volume of 1.0 N NaOH, "
PRINT "EtAc feed concentration (gmol/L), sample collection time "
PRINT "(min), assigned run identifier "
PRINT ""
COLOR 9
INPUT "Enter to continue."; dd
COLOR 10
PRINT "When the program executes you will supply the number of"
PRINT "runs to be analyzed, which may be less than the number "
PRINT "of runs contained in file runs.inn. This allows less"
PRINT "reliable runs, located at the end of the file, to be included"
PRINT "in, or excluded from, from the analysis."
PRINT ""
PRINT "Assuming isothermal plug flow operation and first-order"
PRINT "kinetics, the rate constant k for a run is given by "
PRINT ""
PRINT "      k = (Q/Vf) ln(C0/Cf)  "
PRINT ""
PRINT "where Q is the volumetric flow rate (L/min), Vf is the "
PRINT "reactor volume (assumed = 0.2 L), C0 is the feed "
PRINT "concentration (gmol EtAc/L), Cf is the effluent EtAc"
PRINT "concentration as determined by titration of the sample "
PRINT "and k is the rate constant (min^-1)."
PRINT ""
PRINT "The program proceeds by reading and printing the input "
PRINT "data. Then for each run the program calculates and prints"
PRINT "the run identifier (run number), temperature, Cf, percent"
PRINT "conversion of EtAc, and the rate constant. "
PRINT ""
COLOR 9
INPUT "Enter to continue."; dd
COLOR 10
PRINT "Next an Arrhenius plot ln(rate constant) vs. T (K)^-1 is "

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PRINT "generated, with the expectation that a straight line with "
PRINT "negative slope =  $-E_{act}/R$  will be obtained. "
PRINT " "
PRINT "We now assume that the rate constant is given by"
PRINT " "
PRINT "     $k = b_1 \exp((-b_2/R)(1/T) - (1/298.16))$  "
PRINT " "
PRINT "where the parameter  $b_1$  is the rate constant at 25 C and "
PRINT "parameter  $b_2$  is the activation energy (cal), and R is"
PRINT "the gas constant. "
PRINT ""
PRINT "The program proceeds to estimate values for  $b_1$  and  $b_2$ "
PRINT "by using a standard Gauss-Newton iterative algorithm"
PRINT "that minimizes the sum of the squared residuals "
PRINT ""
PRINT "     $r_j = k_j^* - k_j$ "
PRINT ""
PRINT "where  $k_j^*$  is the experimental rate constant for the  $j$ th"
PRINT "run and  $k_j$  is the calculated value based on the equation"
PRINT "above. "
PRINT ""
PRINT "When the iterative process has converged, the least-squares "; ""
PRINT "values of  $b_1$  and  $b_2$  are printed out."
PRINT ""
COLOR 9
INPUT "Enter to continue."; dd
COLOR 10
'-----
abt = .0001
avctr = .0001
'--
npara = 2 '--number of parameters determined
CLS
COLOR 11
PRINT "Input from file runs.inn, output to file runs.out."
INPUT "Enter number of runs, typically 17 or 20. "; nrun
CLS
nxp = nrun '--number of runs = exptl points
n = npara '--matrix order for Gauss-Jordan reduction solution of normal eqns
bpzr(1) = 2 '-- $k(298.16)*100$ 
bpzr(2) = 50 '-- $(E_{act}/100)/R_g$ 
deltb1 = .1 '--increment to  $b_1$ 
deltb2 = 1 '--increment to  $b_2$ 
'-----use load ystr
'--load data from file runs.inn
PRINT "run identifier, temperature, sample volume, NaOH, feed conc., sample time"
'--
FOR krun = 1 TO nrun
INPUT #1, dd(krun, 1), dd(krun, 2), dd(krun, 3), dd(krun, 4), dd(krun, 5),
dd(krun, 6)
PRINT USING "####.###"; dd(krun, 6); dd(krun, 1); dd(krun, 2); dd(krun, 3);
dd(krun, 4); dd(krun, 5)
NEXT krun
'--
COLOR 9
INPUT "Enter to continue."; dd
COLOR 10
'--columns = temp, volume, naoh, cfeed, time, nrun

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'--First we calc k* = kstr for each run from the exptl data.  Then we
'  calc k from the params b1 and b2 and T.  Then we want k and
'  k* to agree, in a least-squares sense.
vf = .2 '--reactor volume - L
b1 = 10
b2 = 20
'-----calcs for each run
'PRINT "nrun,naoh,volume,deltc,cfeed,cfinal,conver,kstr"
PRINT "nrun, temp, cfinal, conver, kstr"
'--
FOR jj = 1 TO nrun
temp = dd(jj, 1)          '-- deg C
cfeed = .406              '--gmol/L
naoh = dd(jj, 3) / 1000   '--L
volume = dd(jj, 2) / 1000 '--L
time = dd(jj, 5)         '--min
runn = dd(jj, 6)         '--run identifier
deltc = naoh * 1 / volume '--gmol/L
cfinal = cfeed - deltc   '--effluent EtAc concentration
IF cfinal <= 0 THEN PRINT "cfinal error"; cfinal; runn
IF cfinal <= 0 THEN INPUT "enter"; dd
flow = volume / time    '--L/min
vf = .2 '--L
kstr = 100 * (flow / vf) * LOG(cfeed / cfinal)
conver = 100 * naoh / (.406 * volume)
PRINT USING "####.###"; runn; naoh * 1000; volume * 1000; deltc; cfeed; cfinal;
conver; kstr
PRINT #2, USING "####.###"; runn; temp; cfinal; conver; kstr
PRINT USING "####.###"; runn; temp; cfinal; conver; kstr
'--
'INPUT "enter to continue"; dd
ystr(jj) = kstr
plott(jj, 1) = 1 / (temp + 273.16)
plott(jj, 2) = LOG(kstr)
plott(jj, 3) = runn
NEXT jj
'-----
INPUT "End ystr - hit enter for Arrhenius plot."; dd
'-----ARRHENIUS PLOT
CLS
'WINDOW (.003, -.7)-(.0033, 4.5)
WINDOW (.00295, -.7)-(.00335, 4.5)
LOCATE 5: PRINT "          ln(rate constant)"
LOCATE 28: PRINT "          1/T(K)"
COLOR 13
LINE (.003, 0)-(.0033, 3.6), , B
COLOR 11
x = 0
y = 0
'--
FOR jj = 1 TO nrun
FOR ii = 1 TO 200000: NEXT ii
xbk = x
ybk = y
x = plott(jj, 1)
y = plott(jj, 2)
runn = plott(jj, 3)
LOCATE 1, 1: PRINT "Run identifier, 1/T, ln(k)"; : PRINT USING "####.#####";
runn; x; y

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COLOR 11
CIRCLE (x, y), .000003
NEXT jj
'-----
820
INPUT "Enter 1 to continue with parameter estimation."; dd
IF dd <> 1 THEN GOTO 820
niter = 100
'--
FOR j = 1 TO npara
bp(j) = bpzr(j) '--load initial guesses into bp
NEXT j
'--
'=====MAIN LOOP KKK
FOR kkk = 1 TO niter
CLS
'--
FOR j = 1 TO npara
PRINT "j,bp"; : PRINT USING "#####.###"; j; bp(j)
NEXT j
'--
IF ldb1 > 0 THEN INPUT "enter kkk loop"; dd
'--call integ to find ybase
bpu(1) = bp(1)
bpu(2) = bp(2)
trk = 0
'--
FOR k = 1 TO nxp
ybase(k) = bpu(1) * EXP((-bpu(2) / 1.987) * 100 * ((1 / (dd(k, 1) + 273.16)) - (1 / 298.16)))
'PRINT "dd(k,1),ybase(k)"; : PRINT USING "#####.#####"; dd(k, 1); ybase(k)
'INPUT "enter"; dd
NEXT k
'--calc r
FOR k = 1 TO nxp
r(k) = ystr(k) - ybase(k)
NEXT k
'--
FOR k = 1 TO nxp
PRINT "k,ystr,ybase,r"; : PRINT USING "#####.###"; k; ystr(k); ybase(k); r(k)
NEXT k
'--
'INPUT "pause 2"; dd
'--
'PRINT "r"
'FOR ii = 1 TO 50000: NEXT ii
'--
ssb3 = ssb2
ssb2 = ssb1
ssb1 = ss
ss = 0
'--
FOR k = 1 TO nxp
ss = ss + r(k) ^ 2
NEXT k
'--
stdvn = SQR(ss / nxp)
'-----check convergence after 10 iterations
IF kkk > 10 THEN dd1 = ABS((ssb3 - ss) / (ss + .5))

```

```

IF kkk <= 10 GOTO 120
IF dd1 < .01 GOTO 7000 '--check convergence
120
'--
'CLS
PRINT "bp(1),bp(2)"; : PRINT USING "#####.###"; bp(1); bp(2)
PRINT "kkk,stdvn,ssb3,ssb2,ssb1,SS"; : PRINT USING "#####.##"; kkk; stdvn; ssb3;
ssb2; ssb1; ss

'INPUT "pause"; dd
'--
FOR ii = 1 TO 20000: NEXT ii
'--
FOR k = 1 TO nxp
'IF ldb1 > 0 THEN PRINT "k,ybase,r"; : PRINT USING "#####.###"; ybase(k); r(k)
NEXT k
'--vary b1
bpu(1) = bp(1) + deltb1
bpu(2) = bp(2)
trk = 0
'--
FOR jj = 1 TO nxp
y(jj) = bpu(1) * EXP((-bpu(2) / 1.987) * 100 * ((1 / (dd(jj, 1) + 273.16)) - (1 /
298.16)))
NEXT jj
'--
FOR k = 1 TO nxp
'PRINT "k,y"; : PRINT USING "#####.###"; k; y(k)
NEXT k
'--calc column 1 of bb
FOR k = 1 TO nxp
bb(k, 1) = (y(k) - ybase(k)) / deltb1
NEXT k
'--vary b2
bpu(1) = bp(1)
bpu(2) = bp(2) + deltb2
trk = 0
'--
FOR jj = 1 TO nxp
y(jj) = bpu(1) * EXP((-bpu(2) / 1.987) * 100 * ((1 / (dd(jj, 1) + 273.16)) - (1 /
298.16)))
NEXT jj
'--
FOR k = 1 TO nxp
'PRINT "k,y"; : PRINT USING "#####.###"; k; y(k)
NEXT k
'--
'--calc column 2 of bb
FOR k = 1 TO nxp
bb(k, 2) = (y(k) - ybase(k)) / deltb2
NEXT k
'--
FOR k = 1 TO nxp
'PRINT "k,bb"; : PRINT USING "#####.###"; k; bb(k, 1); bb(k, 2)
NEXT k
'--
'INPUT "end print B"; dd
'CLS
'--calc BTB

```

```

FOR j1 = 1 TO npara
FOR j2 = 1 TO npara
btb(j1, j2) = 0
'--
FOR k = 1 TO nxp
btb(j1, j2) = btb(j1, j2) + bb(k, j1) * bb(k, j2)
NEXT k
'--
NEXT j2
NEXT j1
'--
FOR j = 1 TO npara
FOR k = 1 TO npara
PRINT USING "#####.###"; btb(j, k);
NEXT k
PRINT ""
NEXT j
'--
det = btb(1, 1) * btb(2, 2) - btb(1, 2) * btb(2, 1)
PRINT "det"; : PRINT USING "#####.###"; det
'--calc BTr
FOR j = 1 TO npara
btr(j) = 0
FOR k = 1 TO nxp
btr(j) = btr(j) + bb(k, j) * r(k)
NEXT k
NEXT j
'--
'--
FOR j = 1 TO npara
B(j) = btr(j)      '--b is input given vector to GJR
NEXT j
'--
FOR j = 1 TO npara
FOR k = 1 TO npara
a(j, k) = btb(j, k)
NEXT k
NEXT j
'--use gjlsc to find xx = b increment
CALL gjlsc
'--
FOR j = 1 TO n
PRINT "b,db from gjlsc,btr"; : PRINT USING "#####.###"; bp(j); x(j); btr(j)
NEXT j
'--
'FOR ii = 1 TO 1000000: NEXT ii
FOR ii = 1 TO 100000: NEXT ii
'INPUT "pause"; dd
'--plot ybase and ystr
CLS
LOCATE 1, 1
'--
FOR j = 1 TO nxp
FOR ii = 1 TO 500: NEXT ii
'PRINT "j,ystr,ybase"; : PRINT USING "#####.###"; j; ystr(j); ybase(j)
NEXT j
'--
'INPUT "pause 3"; dd
'FOR ii = 1 TO 500000: NEXT ii

```

```

'--update params
beta = .2
beta = .5
'--
FOR j = 1 TO npara
bp(j) = bp(j) + beta * x(j)
NEXT j
'--
NEXT kkk
'=====END KKK LOOP
INPUT "Enter to continue."; dd
CLS
7000 '--converged
PRINT "converged, kkk"; : PRINT USING "####"; kkk
PRINT "BTB"; : PRINT USING "#####.###"; btb(1, 1); btb(1, 2); btb(2, 1); btb(2,
2)
PRINT "BTB-1"; : PRINT USING "####.#####"; anv(1, 1); anv(1, 2); anv(2, 1);
anv(2, 2)
'--
COLOR 10
PRINT ""
PRINT "Best Parameters"
PRINT "Best b1 = rate const (1/min) at 25 C = "; : PRINT USING "####.###"; bp(1)
/ 100
PRINT "Best b2 = activation energy (cal) = "; : PRINT USING "#####.#"; bp(2) *
100
'--
PRINT #2, "Best Parameters"
PRINT #2, "Best b1 = rate const (1/min) at 25 C = "; : PRINT #2, USING
"####.###"; bp(1) / 100
PRINT #2, "Best b2 = activation energy (cal) = "; : PRINT #2, USING "#####.#";
bp(2) * 100
800
INPUT "Enter 1 to stop."; dd
IF dd <> 1 GOTO 800
'--
STOP
END

SUB gjlsc STATIC
'-- subroutine GJLSC4(ndim, n, a, b, abt, avctr, anv, x, det)
'----gauss jordan linear equation solution and matrix inversion
'   ndim=array dimension, n=matrix order, a=nxn matrix,
'   b=given vector, avctr=abt=parameter(typically 1.0e-06),
'   anv=inverse of a, x=solution vector,
'   abs(det)=abs(determinant of scaled a), -1<=det=>1
'--save a in asav
FOR j = 1 TO n
  bsav(j) = B(j)
  FOR k = 1 TO n
    asav(j, k) = a(j, k)
  NEXT k
NEXT j
'--
FOR l = 1 TO n
  lr(l) = 0
  lc(l) = 0
  x(l) = 0
NEXT l

```

```

'--
det = 1
'--
FOR kc = 1 TO n
  s = 0
  FOR kr = 1 TO n
    s = s + a(kr, kc) ^ 2
  NEXT kr
sc(kc) = SQR(s)
'----remove scaling
IF SQR(s) < abt THEN PRINT USING "#####.##"; kc; sc(kc)
'--
'  FOR kr = 1 TO n
'    a(kr, kc) = a(kr, kc) / sc(kc)
'  NEXT kr
'--
NEXT kc
'-----
FOR j = 1 TO n
'--
  FOR k = 1 TO n
    anv(j, k) = 0
    d(j, k) = 0
  NEXT k
'--
  d(j, j) = 1
NEXT j
'--choose a row, if row has a pivot go to next row,
'  if row has no pivot choose a column, if
'  column has a pivot go to next column, if
'  column has no pivot see if pivot is more than max,
'  if more than max update max and pivot row and column
'=====MAIN kk LOOP processes a and b and d
FOR kk = 1 TO n
amx = 0
jpv = 0 '--pivot row
kpv = 0 '--pivot column
'--
  FOR jrow = 1 TO n '-----pick a row
'--scan list of rows
    FOR l = 1 TO n '--scan list of rows
      IF jrow = lr(l) THEN GOTO 20 '-- go to 20 if row has a pivot
    NEXT l
'--row is ok, now scan down column
FOR jcol = 1 TO n '-----pick a column
'--
  FOR l = 1 TO n '--scan list of columns
    IF jcol = lc(l) THEN GOTO 22
  NEXT l
'--a(jrow,jcol) is a possible pivot
  IF ABS(a(jrow, jcol)) < amx THEN GOTO 22
'-----jr,jc is the best pivot so far
jpv = jrow
kpv = jcol
amx = ABS(a(jpv, kpv))
22
NEXT jcol
'-----end jcol loop
20

```

```

NEXT jrow
'-----end jrow loop
IF ABS(amx) < abt THEN PRINT "matrix singular"
IF ABS(amx) < abt THEN INPUT "singular - enter"; dd
IF ABS(amx) < abt THEN STOP
lr(kk) = jpv
lc(kk) = kpj
tmp = a(jpv, kpj) '--store pivot in tmp
'PRINT "found pivot kk, jpv, kpj"; : PRINT USING "####.##"; kk; jpv; kpj
'INPUT "enter to process matrix "; dd
'-----process a, d, and b
'--process pivot row
  FOR j = 1 TO n
    a(jpv, j) = a(jpv, j) / tmp
    d(jpv, j) = d(jpv, j) / tmp
  NEXT j
  B(jpv) = B(jpv) / tmp
'-----process all rows except one with pivot
FOR jr = 1 TO n '--choose a row to be processed
IF jr = jpv THEN GOTO 30
tmp2 = a(jr, kpj)
'--we place zeros above and below pivot at jpv and kpj
'--row = jr and column = jc
  B(jr) = B(jr) - a(jr, kpj) * B(kpj)
  FOR jc = 1 TO n '--scan cols of processed row
    IF jc <> kpj THEN a(jr, jc) = a(jr, jc) - a(jr, kpj) * a(jpv, jc)
    d(jr, jc) = d(jr, jc) - a(jr, kpj) * d(jpv, jc)
  NEXT jc
  a(jr, kpj) = 0
30
NEXT jr
'PRINT "picture of processed matrix a, kk"; kk
'--
FOR j = 1 TO n
FOR k = 1 TO n
IF ldb1 > 0 THEN PRINT USING "####.##"; a(j, k);
NEXT k
IF ldb1 > 0 THEN PRINT " "
NEXT j
'--
det = det * tmp '--update det
'--
NEXT kk
'=====end kk loop
'PRINT "fully processed matrix"
'--
'FOR j = 1 TO n
'FOR k = 1 TO n
'PRINT USING "####.##"; a(j, k);
'NEXT k
'PRINT ""
'NEXT j
'--
'PRINT "fully processed d = scrambled anv"
'--
FOR j = 1 TO n
FOR k = 1 TO n
'PRINT USING "####.##"; d(j, k);
NEXT k

```

```

'PRINT ""
NEXT j
'---
'PRINT ""
'PRINT "scrambled b"
'---
'FOR j = 1 TO n
'PRINT "j,b"; : PRINT USING "####.###"; b(j)
'NEXT j
'---
'INPUT "enter to unscramble"; dd
202
'-----unscramble b into x and d into anv
'PRINT "lr, lc"
'FOR j = 1 TO n
'PRINT USING "####.###"; lr(j); lc(j)
'NEXT j
'---
FOR j = 1 TO n
    l1 = lr(j)
    l2 = lc(j)
    x(l2) = B(l1)
'---
    FOR k = 1 TO n
        anv(l2, k) = d(l1, k)
    NEXT k
'---
NEXT j
'---
FOR j = 1 TO n
IF ldb1 > 0 THEN PRINT "gjlsc: lr,lc,b,x"; : PRINT USING "####.###"; lr(j);
lc(j); B(j); x(j)
NEXT j
'---
'PRINT "print anv"
'---
'FOR j = 1 TO n
'FOR k = 1 TO n
'PRINT USING "####.###"; anv(j, k);
'NEXT k
'PRINT ""
'NEXT j
'---
'PRINT ""
'--check A A-1
FOR j = 1 TO n
    FOR k = 1 TO n
        tst(j, k) = 0
        FOR l = 1 TO n
            tst(j, k) = tst(j, k) + asav(j, l) * anv(l, k)
        NEXT l
    NEXT k
NEXT j
'---
'--check unit matrix
FOR j = 1 TO n
FOR k = 1 TO n
IF j = k THEN tt = ABS(tst(j, k) - 1)
IF j <> k THEN tt = ABS(tst(j, k))

```

```

IF tt > .0001 THEN PRINT "unit matrix error, j,k,ujk"; j; k; tt
NEXT k
NEXT j
'INPUT "end test a a-1"; dd
'--
FOR j = 1 TO n
ax = 0
FOR k = 1 TO n
ax = ax + asav(j, k) * x(k)
NEXT k
IF ldb1 > 0 THEN PRINT "gjlsc: ax,b"; : PRINT USING "#####.###"; ax; bsav(j)
'IF ABS(ttt) > .0001 THEN PRINT "gjr a*x=b error"; j; ax; bsav(j)
'IF ABS(ttt) > .0001 THEN INPUT "error"; dd
NEXT j
'--
IF ldb1 > 0 THEN PRINT "A A-1"
FOR j = 1 TO n
FOR k = 1 TO n
IF ldb1 > 0 THEN PRINT USING "#####.###"; tst(j, k);
NEXT k
IF ldb1 > 0 THEN PRINT " "
NEXT j
'--
FOR j = 1 TO n
xx(j) = 0
FOR k = 1 TO n
xx(j) = xx(j) + anv(j, k) * bsav(k)
NEXT k
IF ldb1 > 0 THEN PRINT "j,xx"; : PRINT USING "#####.###"; j; xx(j)
NEXT j
'--check sum of pivot locations
lrs = 0
lcs = 0
'--
FOR l = 1 TO n
lrs = lrs + lr(l)
lcs = lcs + lc(l)
NEXT l
'--
ld = (n * (n + 1)) / 2
IF lrs <> ld THEN PRINT USING "#####.###"; lrs; ld
IF lcs <> ld THEN PRINT USING "#####.###"; lcs; ld
'--
END SUB

```