ChE 321 **Washington State University**
Kinetics and Reactor Design **Department of Chemical Engineering**
Spring, 2001 **Richard L. Zollars**

You will have one hour (60 minutes) to complete this exam which consists of three (3) problems. You may use any books, notes, etc. that you have brought with you. Remember that the majority of the points on any problem will be given for clearly demonstrating that you know how to solve the problem. Thus, it is not necessary to complete all of the math necessary to reach a final numerical answer to receive most of the points for any problem. Make sure that you have completed each problem to the point where only calculations remain before taking the time to finish the calculations on any problem. Each problem statement may also contain information that is not necessary for the solution of the problem.

1) (45 pts)

The chemicals A and B can undergo two reactions in the liquid phase as shown below

$$A + B \xrightarrow{k_1} D$$

$$A + B \xrightarrow{k_2} U$$

where D is a desirable product and U is an undesirable product. The reaction rate expressions for these two reactions are:

$$rate_D = k_1 [A][B]$$

$$rate_U = k_2 [A]^2 [B]$$

A liquid stream containing both A and B enters a CSTR at a flow rate of 5 liter/min. The concentration of A in the inlet stream is 2 mole/liter and the concentration of B is 1 mole/liter. The inlet stream enters the reactor at a temperature of 20EC (293 K). The reactor operates at a temperature of 100EC (373 K). Use the data below

Kinetic Data:

$k_1 = 9.68\text{x}10^5$ exp(-6000/T) liter/mole-min for T in K

k_1(373 K) = 0.1 liter/mole-min

$k_2 = 1.33\text{x}10^5$ exp(-5000/T) liter^2/mole^2-min for T in K

k_2 (373 K) = 0.2 liter^2/mole^2-min

Thermodynamic Data:

C_{pA} = 40 cal/mole-EC

C_{pB} = 50 cal/mole-EC

C_{pD} = 90 cal/mole-EC

C_{pU} = 90 cal/mole-EC

)H_{r1} = -15,000 cal/mole (does not change with temperature)

)H_{r2} = -12,000 cal/mole (does not change with temperature)

Reactor Data:

UA = 120 cal/~~liter-~~min-EC

T_{hx} = 20EC

to answer the following:

a) What is the concentration of A and B inside the reactor? What is the volume of the reactor?

b) What is the instantaneous selectivity in the reactor? What is the overall selectivity in the reactor?

c) What modifications to the reactor and/or operating conditions would you recommend to increase the overall selectivity for these reactions?

SOLUTION

a) Let’s first write the material balances for A and B and the energy balance. For a CSTR these are:

$$
\begin{aligned}
0 &= F_{A_{in}} - F_{A_{out}} - k_1 C_A C_B V - k_2 C_A^2 C_B V \\
0 &= F_{B_{in}} - F_{B_{out}} - k_1 C_A C_B V - k_2 C_A^2 C_B V \\
UA(T_{hx} - T) &= \Delta H_{r_1} (k_1 C_A C_B V) + \Delta H_{r_2} \left(k_2 C_A^2 C_B V\right) + \int_{T_{in}}^{T_{out}} \left(F_{A_{in}} C_{p_A} + F_{B_{in}} C_{p_B}\right) dT
\end{aligned}
$$

Since $F_i = v_o C_i$ we know that F_{Ain} = 5 liter/min*2 mole/liter = 10 mole/min and F_{Bin} = 5 mole/min*1 mole/liter = 5 mole/min. Substituting the other known values into these equations gives

$$
\begin{aligned}
&0 = 10 - 5C_A - 0.1C_A C_B V - 0.2 C_A^2 C_B V \\
&0 = 5 - 5C_B - 0.1C_A C_B V - 0.2 C_A^2 C_B V \\
&120(20 - 100) = -15000(0.1C_A C_B V) - 12000\left(0.2 C_A^2 C_B V\right) + \int_{20}^{100} (10(40) + 5(50))\, dT
\end{aligned}
$$

This looks like we have to solve three equations in three unknonwns (C_A, C_B, and V). If you subtract the material balance for B from the material balance for A you get

$$0 = 10 - 5C_A - (5 - 5C_B)$$

or

$$C_B = C_A - 1$$

Using this in the material balance for A and the energy balance and simplifying gives

$$
\begin{aligned}
&0 = 10 - 5C_A - 0.1C_A (C_A - 1)V - 0.2C_A^2 (C_A - 1)V \\
&120(20 - 100) = -1500\left(C_A (C_A - 1)V \right) - 2400\left(C_A^2 (C_A - 1)V \right) + 650 * (100 - 20))
\end{aligned}
$$

We now have two equations in two unknowns that must be solved simltaneously. Doing this gives C_A = 1.05 mole/liter (so $C_B = C_A - 1$ = 0.05 mole/liter) and V = 292.2 liter.

b) In a CSTR the instatntaneous and overall selectivities are the same. Since we have both CA and CB lets do the selectivity as the ratio of the reaction rates. Thus

$$S = s = \frac{rate_D}{rate_U} = \frac{k_1 C_A C_B}{k_2 C_A^2 C_B} = \frac{A_1}{A_2} \exp\left(-(E_1 - E_2)/T\right) \frac{1}{C_A} = \frac{9.68 \times 10^5}{1.33 \times 10^5} \exp(-1000/373) \frac{1}{1.05}$$

$$S = s = 0.475$$

c) The selectivity expression above shows that the concentration of B does not affect selectivity. This leaves only C_A and T as parameters affecting the selectivity.   To increase the selectivity we want C_A low and T high. In terms of C, operating in a single CSTR is the best. We might try diluting the inlet stream to lower the concentration of A. Elevating the reactor temperature would also increase the selectivity.

2) (30 pts)

Chemical A decomposes to form B and C according to the stoichiometric relation

$$A \rightarrow B + C$$

This reaction occurs when A is exposed to light, but only when some other species is present. The mechanism for this reaction is thought to occur via the following steps:

1) Light energy is absorbed by some species (call it D) converting it to an active species (call the active species D*).
2) D* may give up this absorbed energy as heat and return to the neutral species, D.
3) D* may interact with A, transferring the energy from D* to A, giving an activated A (call it A*) and neutral D.
4) The activated A species (A*) then decomposes to give B and C.

Show that this mechanism is consistent with the observed stoichiometry. Derive a rate expression for the disappearance of A that is consistent with this mechanism. Remember that the rate expression must not contain concentrations of any intermediate species. In this case, however, the light intensity (call it I_{light}) and the concentration of the neutral transfer species ([D]) may appear in the rate expression since neither of these are reaction intermediates.

SOLUTION

The mechanism can be expressed as the following steps:

$$D + light \underset{k_{-1}}{\overset{k}{\leftrightarrow}} D*$$

$$D* + A \xrightarrow{k_2} D + A*$$

$$A* \xrightarrow{k_3} B + \quad C$$

Adding all of theses steps together gives

$$A + light \rightarrow B + C$$

Since light is not a chemical compound it would not show up in the stoichiometry so the mechanistic steps do give rise to the observed stoichiometry.

Species A disappears in the middle reaction. Thus the rate of disappearance of A is given by

$$r_A = -k_2 [A][D^*]$$

Since D* is an intermediate we need to find a way to express [D*] in terms of species that are not intermediates. Writing the expression for the rate of reaction of D* gives

$$r_{D^*} = k_1 [D] I_{light} - k_{-1} [D^*] - k_2 [A][D^*]$$

Using the pseudo-steady state approximation this rate should be zero. Solving for [D*] gives

$$[D^*] = \frac{k_1 [D] I_{light}}{k_{-1} + k_2 [A]}$$

Now substitute this into the expression for the reaction rate of A to get

$$r_A = k_2 [A] \frac{k_1 [D] I_{light}}{k_{-1} + k_2 [A]} = \frac{k_1 k_2 [A][D] I_{light}}{k_{-1} + k_2 [A]}$$

3) (25 pts)

The concentration of species A, which is the reactant in a chemical reaction, varies with time as shown in the table below.

Time (min)	C_A (mole/liter)
2	1.85
4	1.37
6	1.02
8	0.75
10	0.56

The reaction is thought to be second order with respect to the concentration of A. If the reaction is second order, what is the rate constant? Is the reaction second order with respect to A? In answering this latter question it is not sufficient to only answer yes or no – you must give some argument supporting your answer.

SOLUTION

For a second order reaction the rate expression is given by

$$\frac{d\,C_A}{dt} = -k\,C_A^2$$

Rearranging this gives

$$\frac{d\,C_A}{C_A^2} = -k\,dt$$

Integrating both sides gives

$$\frac{1}{C_A} - \frac{1}{C_{A_o}} = kt$$

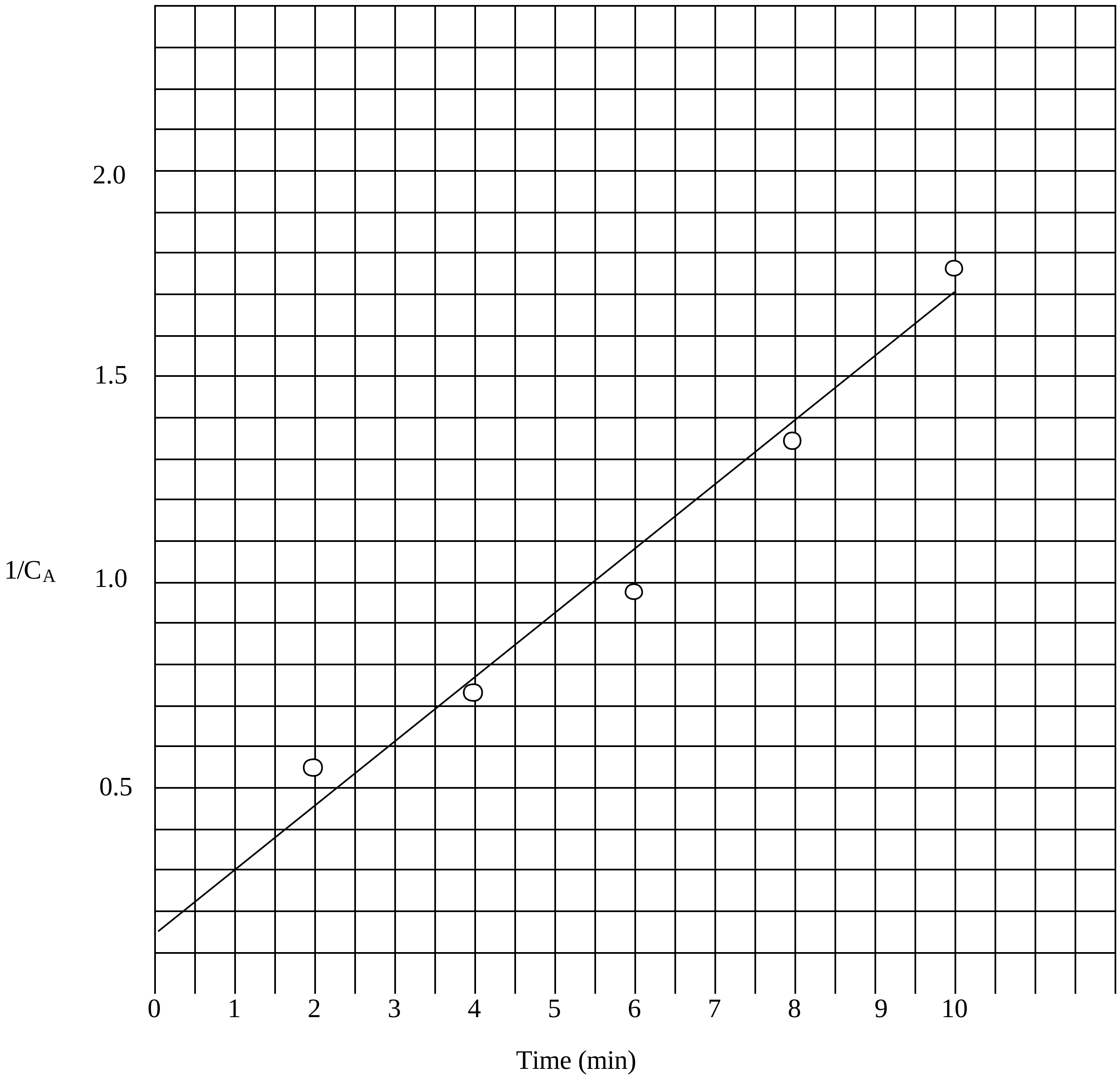
So a plot of $1/C_A$ should be a straight line with a slope = k. Take the original data and compute $1/C_A$.

Time (min)	C_A (mole/liter)	$1/C_A$ (liter/mole)
2	1.85	0.541
4	1.37	0.730
6	1.02	0.980
8	0.75	1.333
10	0.56	1.786

Plotting this on the axes provided gives the figure on the following page. A linear regression gives the results

Slope = 0.155 liter/mole-min
Intercept = 0.146 liter/mole
$r^2 = 0.985$

The straight line on the graph below represents the regression line. The slope should be the rate constant so for a second order reaction k = 0.155 liter/mole-min. The regression coefficient is large (0.98+) but looking at the data there is a definite bend upwards rather than random scatter about the regression line. Curvature indicates that this is not a second order reaction.


1/C_A
2.0
1.5
1.0
0.5
0
1
2
3
4
5
6
7
8
9
10
Time (min)