ChE 4190 | **EXAM 1** | **July 6, 1998**

Open Books and Notes

I. 60 pts.

Simultaneous reactions of hydrogenation and isomerization take place in a certain organic synthesis. The normal isomer (N) isomerizes to the iso isomer (I) while N is also hydrogenated to $N\text{-}H_2$ by hydrogen supplier $S\text{-}H_2$. This can be written short hand:

$$N + S\text{-}H_2 \xrightarrow{k_1} N\text{-}H_2 + S \qquad r_1 = k_1 C_N C_{S\text{-}H2}$$

$$N \xrightarrow{k_2} I \qquad r_2 = k_2 C_N$$

For this particular case, we know that $C_{N,O} = 1.8$ moles/lt, $C_{S\text{-}H2,O} = 2.0$ moles/lt, $k_1 = 2.5$ lt/mole-min and $k_2 = 0.6\ \text{min}^{-1}$.

It is already known that we need to make 1.0 moles/lt of $N\text{-}H_2$ (the hydrogenation product).

a) 40 pts.

Compute the concentration of I that would be formed when $C_{N\text{-}H2} = 1.0$ moles/lt.

b) 20 pts.

Set up a single integral which contains only time and one concentration (i.e., eliminate all concentrations except one) to solve for the time required for $C_{N\text{-}H2}$ to reach 1.0 moles/lt also starting with $C_{N,O} = 1.8$ moles/lt and $C_{S\text{-}H2,O} = 2.0$ moles/lt. (You do not need to solve the integral).

II. 40 pts.

The overall reaction for the thermal decomposition of acetaldehyde is:

$$CH_3\,CHO \longrightarrow CO + CH_4$$

Given the mechanism:

Initiation: $CH_3\,CHO \xrightarrow{k_1} CH_3\bullet + CHO\bullet$

Propogation $CH_3\bullet + CH_3CHO \xrightarrow{k_2} CH_3CO\bullet + CH_4$

$CH_3CO\bullet \xrightarrow{k_3} CH_3\bullet + CO$

Termination: $2CH_3\bullet \xrightarrow{k_4} C_2H_6$

$2CHO\bullet \xrightarrow{k_5} CHOOCH$

What order do you expect to observe in CH_3CHO?

Solution :

I. a) $r_1 = k_1 C_N C_{S-H2}$

$r_2 = k_2 C_N$

$$-\frac{dC_N}{dt} = k_1 C_N C_{S-H2} + k_2 C_N$$

$$-\frac{dC_{S-H2}}{dt} = k_1 C_N C_{S-H2}$$

$$\frac{dC_N}{dC_{S-H2}} = 1 + k_2/k_1 \frac{1}{C_{S-H2}}$$

$$\int_{1.8}^{C_N} dC_N = \int_{2.0}^{C_{S-H2}} \left(1 + \frac{k_2}{k_1 C_{S-H2}}\right) dC_{S-H2}$$

$$C_N - 1.8 = C_{S-H2} - 2.0 + (k_2/k_1) \ln\left(\frac{C_{S-H2}}{2.0}\right)$$

when one mole of $N-H_2$ is formed, 1 mole of C_{S-H2} has reacted, so $C_{S-H2} = 1.0$

③

$$C_N - 1.8 = 1.0 - 2.0 + \frac{0.6\ \text{min}^{-1}}{2.5\ \text{lt/mole-min}} \ln\left(\frac{1.0}{2.0}\right)$$

$$C_N = 1.8 - 1.0 + 0.24 \ln(1/2) = 0.6336$$

$$C_I = \underbrace{1.8 - 0.6336}_{\text{total } C_N \text{ reacted}} - \underbrace{1.0}_{C_N \text{ reacted to form N-H2}}$$

$$\boxed{C_I = 0.1664}$$

b) $$-\frac{dC_N}{dt} = k_1 C_N C_{S\text{-}H_2} + k_2 C_N$$

If we could eliminate $C_{S\text{-}H_2}$ using $C_{S\text{-}H_2} = f(C_N)$, we could solve this integral for time. However, we know $C_N = f(C_{S\text{-}H_2})$ rather than the other way around, so it is easier to solve for the time required to react one mole of S-H2 which is the same as the time required to form 1 mole of N-H2

$$-\frac{dC_{S-H2}}{dt} = k_1 C_N C_{S-H2}$$

$$-\frac{dC_{S-H2}}{dt} = k_1\left[\left(C_{S-H2} - 0.2\right) + \frac{k_2}{k_1}\ln\left(\frac{C_{S-H2}}{2}\right)\right] C_{S-H2}$$

$$\boxed{\int_{2.0}^{1.0} \frac{dC_{S-H2}}{\left[\left(C_{S-H2} - 0.2\right) + \frac{k_2}{k_1}\ln\left(\frac{C_{S-H2}}{2}\right)\right] C_{S-H2}} = -k_1 \int_0^t dt}$$

II. for chain rxn, rate is equal to the rate of the propogation step:

$$-\frac{d[CH_3CHO]}{dt} = k_2[CH_3\cdot][CH_3CHO] + k_3[CH_3CHO]$$

Need to eliminate $[CH_3\cdot]$

Use S.S. approximation.

5

$$\frac{d[CH_3\cdot]}{dt} = 0 = k_1[CH_3CHO] - k_2[CH_3\cdot][CH_3CHO] + k_3[CH_3CO\cdot] - 2k_4[CH_3\cdot]^2$$

need $[CH_3CO\cdot]$

$$\frac{d[CH_3CO\cdot]}{dt} = 0 = k_2[CH_3\cdot][CH_3CHO] - k_3[CH_3CO\cdot]$$

$$[CH_3CO\cdot] = \frac{k_2[CH_3\cdot][CH_3CHO]}{k_3}$$

$$0 = k_1[CH_3CHO] - k_2[CH_3\cdot][CH_3CHO] + k_2[CH_3\cdot][CH_3CHO] - 2k_4[CH_3\cdot]^2$$

$$[CH_3\cdot] = \sqrt{\frac{k_1}{2k_4}}[CH_3CHO]^{1/2}$$

initiation

$$r = -\frac{d[CH_3CHO]}{dt} = k_2\sqrt{\frac{k_1}{2k_4}}[CH_3CHO]^{1/2}[CH_3CHO] + k_1[CH_3CHO]$$

$$r = k_{OBS}[CH_3CHO]^{3/2}$$

$$\boxed{N_{OBS} = 3/2}$$

This exam comes from 1981 back when I used to give hard exams. It represents more difficult work than I would normally expect on your first exam. However, it does require students to perform many rudimentary calculations such as the concentration of ideal gases, and the fundamental definition of fractional conversion, and as such, should be workable by an average student.

Please try to work the exam before looking at the solution.

I. 70 points

The gas phase, irreversible, <u>elementary</u> reaction:

$$A + 2B \rightarrow C$$

takes place at 2 atmospheres constant pressure. At 50°C, the rate constant (expressed in units containing g-moles, liters, and minutes) is 110. Initially, an equimolar mixture of A & B with no C or inerts is present. Assume ideal gases. The activation energy is 20 Kcal/mole.

a) Calculate r, r_A, r_B, and r_C initially.

b) Calculate r when one fourth of the A is reacted.

c) Calculate r initially if the temperature is changed to 60°C.

d) How long will it take to react one fourth the A at 60°C?

II. 30 points

The liquid phase, constant density, irreversible reaction:

$$A \rightarrow B$$

has been studied in a batch reactor at constant temperature. The following data has been reported:

t(min)	C_A(moles/lt)
0.00	4.00
1.00	3.31
2.00	2.78
3.00	2.37
4.00	2.04
5.00	1.78
6.00	1.56

Use the differential approach to calculate the reaction order and the rate constant. What are the units of the rate constant?

CHE 4190

EXAM I, Feb 12, 1981 Solution

I)

a) start w/ calc. C_A & C_B

$$P_i V = n_i RT$$

$$\frac{P_i}{RT} = C_i$$

$$P_{A0} = P_{B0} = 1 \text{ atm}$$

$$\frac{1 \text{ atm}}{(.08205)(50+273)} = C_{A0} = C_{B0} = 3.77 \times 10^{-2} \text{ moles/lt}$$

calc. r

$$r = k C_A C_B^2 \quad \text{(elementary, irreversible)}$$

$$r_0 = k(3.77 \times 10^{-2})^3 = 110(3.77 \times 10^{-2})^3$$

$$r_0 = 5.89 \times 10^{-3} \text{ moles/lt-min}$$

$$r_A = -\nu_A r = (-1)(5.89 \times 10^{-3}) = -5.89 \times 10^{-3} \ \frac{\text{moles}}{\text{lt-min}}$$

points

$$r_B = +\nu_B r = -1.18 \times 10^{-3}$$

$$r_C = \nu_C r = +5.89 \times 10^{-3}$$

b) Must use f_B since B is limiting

When 1/4 the A is used up, 1/2 the B is used up

$$\therefore f_B = 0.5$$

$$r = k C_A C_B^2$$

$$C_A = \frac{C_{A0} - \frac{1}{2} C_{B0} f_B}{1 + \delta_B f_B}$$

$$C_B = \frac{C_{B0}\ (1 - f_B)}{1 + \delta_B f_B}$$

$$r = \frac{110\ (C_{A0} - ½ C_{B0} f_B)(C_{B0})^2 (1-f_B)^2}{(1 - ½ f_B)^3}$$

w/ $f_B = .5$, $C_{A0} = C_{B0} = 3.77 \times 10^{-2}$

$$\boxed{r = 2.62 \times 10^{-3}}$$

$$\delta_B = \frac{V|_{f_B=0} - V|_{f_B=1}}{V|_{f_B=0}}$$

	Start	Finish
A	1	½
B	1	0
C	0	½
	2	1

$$\delta_B = \frac{1-2}{2} = -½$$

c) Need to calc k_{60}, Find A

$$110 = A \exp(-20000/1.987\ (273+50))$$

$$A = 3.70 \times 10^{15}\ lt^2/mole^2 \cdot min$$

$$k_{60} = 3.70 \times 10^{15} \exp(-20000/1.987\ (273+60))$$

$$k_{60} = 280$$

$$C_{A0} = C_{B0} = \frac{1}{(.08205)(273+60)} = 3.66 \times 10^{-2}$$

$$\boxed{r = 280\ (3.66 \times 10^{-2})^3 = 1.37 \times 10^{-2}}\ \frac{moles}{lt \cdot min}$$

d) $r = k\, C_A\, C_B^2$

$$\frac{C_{B0}}{(1 + \delta_B f_B)} \frac{df_B}{dt} = 2k \left(\frac{C_{A0} - ½ C_{B0} f_B}{1 + \delta_B f_B}\right)\left(\frac{C_{B0}(1 - f_B)}{1 + \delta_B f_B}\right)^2$$

since $C_{A0} = C_{B0}$ & $\delta_B = -1/2$

$$\cancel{\frac{C_{A0}}{1-\frac{1}{2}f_B}}\ \frac{df_B}{dt} = 2k\left(\cancel{\frac{C_{A0}-\frac{1}{2}C_{A0}f_B}{1-\frac{1}{2}f_B}}\right)\left(\frac{C_{A0}(1-f_B)}{1-\frac{1}{2}f_B}\right)^2$$

$$\frac{df_B}{dt} = 2k\,C_{A0}^2\ \frac{\cancel{(1-\frac{1}{2}f_B)}(1-f_B)^2}{(1-\frac{1}{2}f_B)^{\cancel{2}}}$$

$$\frac{df_B}{dt} = 2k\,C_{A0}^2\ \frac{(1-f_B)^2}{(1-\frac{1}{2}f_B)}$$

sep. variables

$$\int_0^{1/2}\frac{1}{(1-f_B)^2}\,df_B - \frac{1}{2}\int_0^{1/2}\frac{f_B}{(1-f_B)^2}\,df_B = 2k\,C_{A0}^2\int_0^t dt$$

Integral Tables:

$$-\frac{1}{(-1)(1-f_B)}\Bigg|_0^{1/2} - \frac{1}{2}\left[\frac{1}{(-1)^2}\ln(1-f_B) + \frac{1}{1-f_B}\right]_0^{1/2} = 2k\,C_{A0}^2\,t$$

$$\left[\left(\frac{1}{.5}\right)-1\right] - \frac{1}{2}\left[\ln(\tfrac{1}{2}) - \cancelto{0}{\ln(1)} + \frac{1}{.5} - 1\right] = 2k\,C_{A0}\,t$$

$$1 - \frac{1}{2}\left[\ln(\tfrac{1}{2}) + 1\right] = 2k\,C_{A0}^2\,t$$

$$\frac{1}{2} + \ln 2 = 2(280)(3.66\times10^{-2})^2\,t$$

$$\boxed{t = 1.59 \text{ min}}$$

pts

II) $A \rightarrow B$

$$-\frac{dC_A}{dt} = kC_A^n$$

approximate w/ diff. approach

$$-\frac{\Delta C_A}{\Delta t} = kC_A^n$$

$$\ln\left(-\frac{\Delta C_A}{\Delta t}\right) = \ln k + n \ln C_A$$

C_A	t	$-\Delta C_A$	$\ln\left(-\frac{\Delta C_A}{\Delta t}\right)$	$\ln(C_A)_{AVG}$
4	0	.69	-.371	1.30
3.31	1	.53	-.635	1.11
2.78	2	.41	-.892	0.95
2.37	3	.33	-1.109	0.79
2.04	4	.26	-1.347	0.65
1.78	5	.22	-1.514	0.51
1.56	6			

see graph

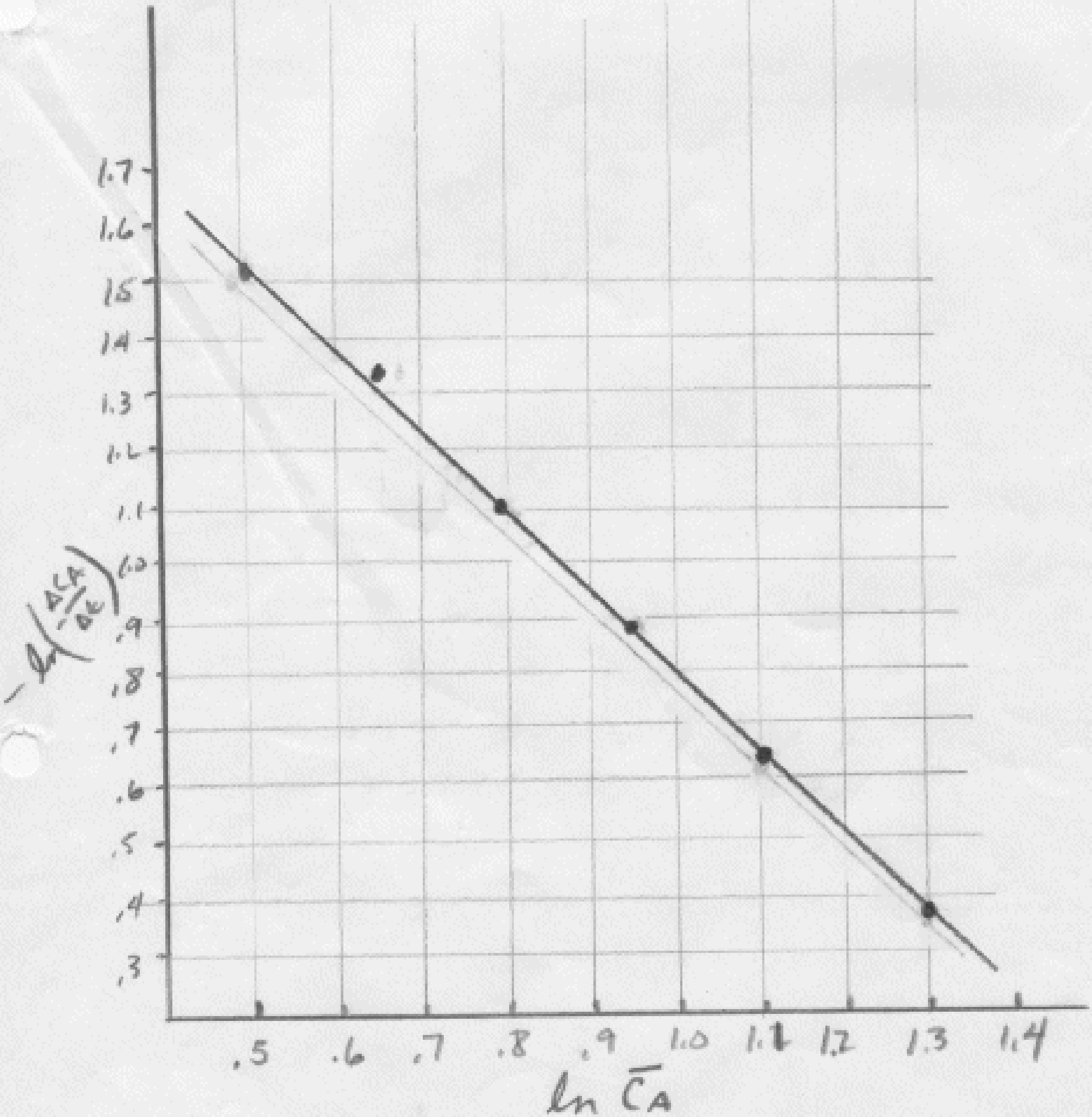
$$\text{slope} = n = \frac{1.514 - .317}{1.30 - .51} = 1.45$$

$$-.635 = \ln k + 1.45(1.11)$$ (Pick point

$$\ln k = -2.24$$

$$k = 0.106 \ \frac{lt^{.45}}{mole^{.45}\ min}$$

10 pts



1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
.9
.8
.7
.6
.5
.4
.3
$-\ln\left(\frac{\Delta C_A}{\Delta t}\right)$
.5
.6
.7
.8
.9
1.0
1.1
1.2
1.3
1.4
$\ln \bar{C}_A$