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

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

$$r_0 = k\,(3.77\times10^{-2})^3 = 110\,(3.77\times10^{-2})^3$$

$$r_0 = 5.89\times10^{-3} \text{ moles/lt-min}$$

points

$$r_A = \nu_A r = (-1)(5.89\times10^{-3}) = -5.89\times10^{-3} \frac{\text{moles}}{\text{lt-min}}$$

$$r_B = +\nu_B r = -1.18\times10^{-3}$$

$$r_c = \nu_c r = +5.89\times10^{-3}$$

b) Must use f_B since B is limiting

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

$$\therefore\ f_B = 0.5$$

$$r = k C_A C_B^2$$

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

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

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

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	1/2
B	1	0
C	0	1/2
	2	1

$$\delta_B = \frac{1-2}{2} = -1/2$$

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

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

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

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

$$k_{60} = 280$$

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

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

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

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

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

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

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

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

sep. variables

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

Integral Tables:

$$-\frac{1}{(-1)(1-f_B)}\Bigg|_0^{1/2} - 1/2 \left[\frac{1}{(-1)^2} \ln(1-f_B) + \frac{1}{1-f_B}\right]_0^{1/2}$$

$$= 2k C_{A0}^2 t$$

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

$$1 - 1/2 [\ln(1/2) + 1] = 2k C_{A0}^2 t$$

$$1/2 + \ln 2 = 2(280)(3.66 \times 10^{-2})^2 t$$

pts

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

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

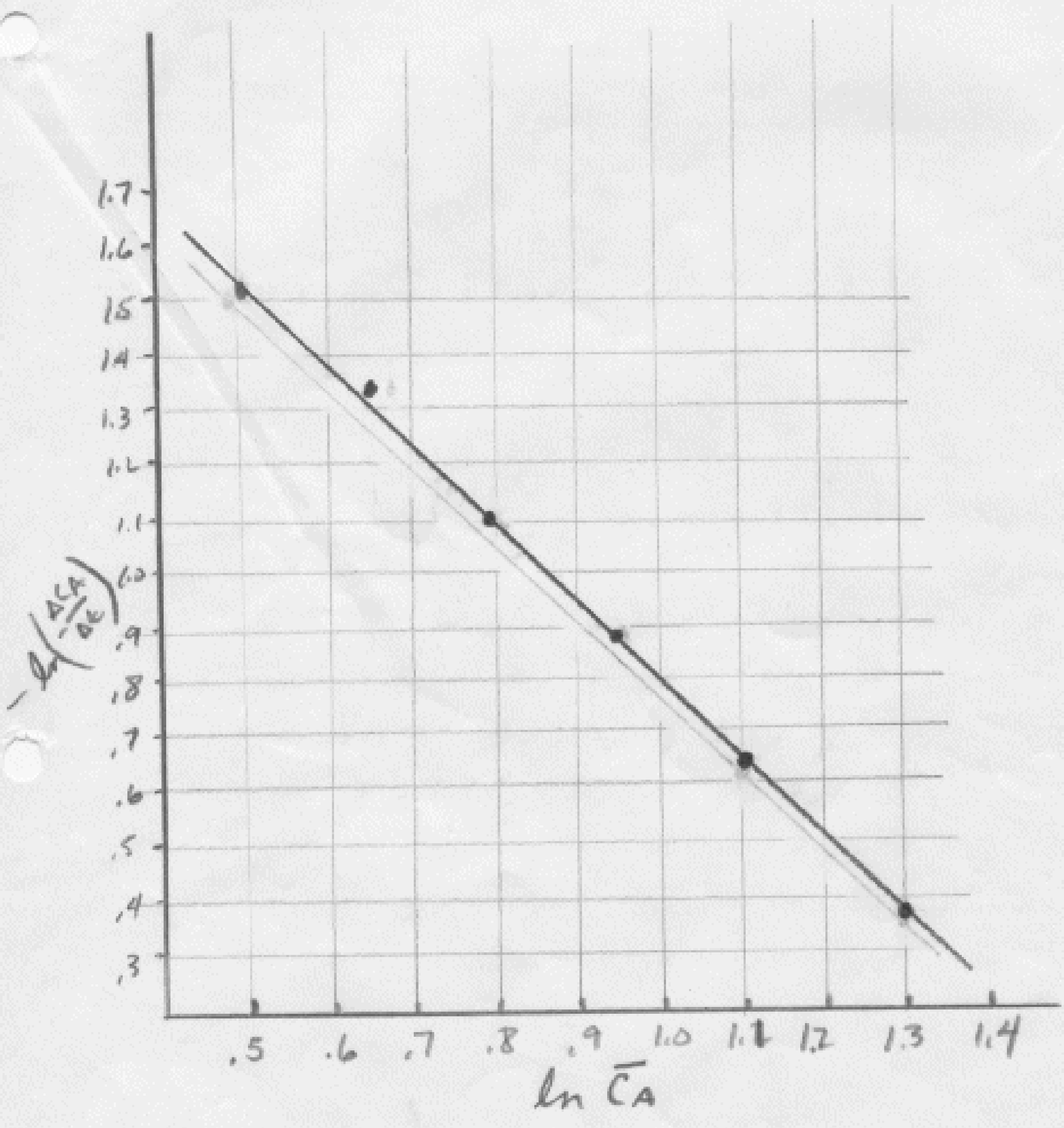
$$\text{slope} = n = \frac{1.514 - .317}{1.30 - .51} = 1.45$$

$$-.635 = \ln k + 1.45(1.11)$$ (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
$\ln \bar{C}_A$