Example Problems

1) A common rule of thumb is that the rate of a reaction doubles for every 10°C rise in temperature. What activation energy does this suggest at a temperature of 25°C?

Solution:

$$k_1 = A e^{-E/RT_1}$$

$$k_2 = 2k_1 = A e^{-E/RT_2}$$

$$\ln k_1 = \ln A - E/RT_1$$

$$\ln 2k_1 = \ln A - E/RT_2$$

subtract

$$\ln \frac{k_1}{2k_1} = E/R \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \tfrac{1}{2} = E/1.987 \left(\frac{1}{273+35} - \frac{1}{273+25} \right)$$

$$\ln \tfrac{1}{2} = E \left(-5.483 \times 10^{-4} \right)$$

$$\boxed{E = 12641 \text{ cal/mole}}$$

2) The reaction:

$$SO_2Cl_2 \rightarrow SO_2 + Cl_2 \quad \text{(irreversible)}$$

or $A \rightarrow B + C$

was studied in a constant volume batch reactor at 279.2°C. The following data was obtained:

t(min)	0	3.4	15.7	28.1	41.1	54.5	68.3	82.4	96.3
P_T (mmHg)	322.5	325	335	345	355	365	375	385	395

Initially, only SO_2Cl_2 was charged into the reactor. P_T is the total pressure in the reactor. Assume ideal gasses for all calculations.

a) Assume an n^{th} order reaction in A (SO_2Cl_2) and derive an expression for dP_T/dt as a function of P_T

b) determine n

c) what is the value of k?

Solution:

a) Write the total pressure as a function of C_A.

$$N_T = N_A + N_B + N_C$$

$$N_T = N_A + (N_{A0} - N_A) + (N_{A0} - N_A)$$

$$N_T = 2N_{A0} - N_A$$

$$P_T = \frac{N_T RT}{V} = \frac{2N_{A0} - N_A}{V} RT$$

$$P_{A0} = \frac{N_{A0} RT}{V}$$

$$P_T = 2P_{A0} - \frac{N_A}{V} RT$$

$$P_T = 2P_{A0} - C_A RT \qquad 1)$$

for a const. vol. n^{th} order rxn

$$-\frac{dC_A}{dt} = k_1 C_A^n \qquad 2)$$

differentiate eqn 1)

$$\frac{dP_T}{dt} = -\frac{dC_A}{dt} RT$$

sub into 2)

$$\frac{dP_T}{dt} = RT k_1 \left(\frac{2P_{A0} - P_0}{RT} \right)^n$$

$$\frac{dP_T}{dt} = \frac{k_1}{(RT)^{n-1}} \left(2P_{A0} - P_T \right)^n$$

b) assume 1^{st} order Rxn

$$\frac{dP_T}{dt} = k_1 (2P_{A0} - P_T)$$

$$-\int \frac{-dP_T}{(2P_{A0} - P_T)} = k_1 \int dt + C$$

$$-\ln (2P_{A0} - P_T) = k_1 t + C$$

@ $t = 0$, $P_T = P_{A0}$

$$-\ln P_{A0} = C$$

$$\ln \left(\frac{P_{A0}}{2P_0 - P_T} \right) = k_1 t$$

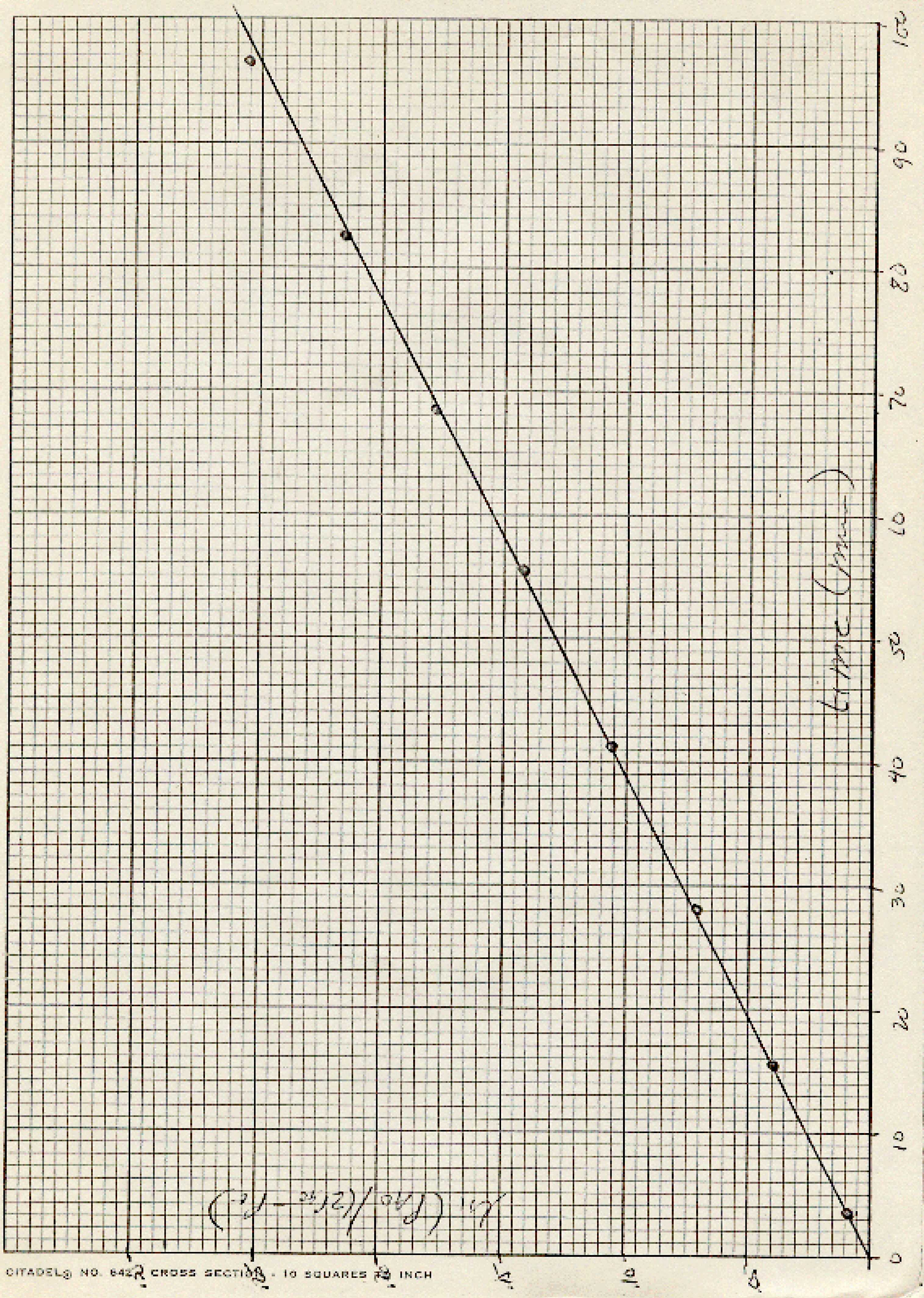
Plot $\ln\left(\frac{P_{A0}}{2P_{A0}-P_T}\right)$ vs t

$\ln\left(\frac{P_{A0}}{2P_{A0}-P_T}\right)$	t
0	0
0.008	3.4
0.040	15.7
0.072	28.1
0.106	41.1
0.141	54.5
0.178	68.3
0.215	82.4
0.255	96.3

Plot is straight (see next page)

$\therefore \quad n = 1$

c) slope $= k = \frac{0.26}{100} = 2.6 \times 10^{-3}\ \text{min}^{-1}$



CITADEL® NO. 642 CROSS SECTION - 10 SQUARES TO INCH

3) Liquid solutions of diazobenzene decompose irreversibly according to:

$$C_6H_5N_2Cl\,(\ell) \rightarrow C_6H_5Cl\,(\ell) + N_2(g)\uparrow$$

or $$A\,(\ell) \rightarrow B\,(\ell) + C\,(g)\uparrow$$

The kinetics are 1st order in A. In one experiment at 50°C, the initial concentration of $C_6H_5N_2Cl$ (A) was 10 gr/lt and the following amounts of N_2(g) were liberated:

time (min)	6	9	12	14	18	20	22	24	26	30
N_2 liberated cm^3 at 50°C 1 atm	19.3	26.0	32.6	36.0	41.3	43.3	45.0	46.5	48.4	50.3

Complete decomposition of A liberated 58.3 cm^3 of N_2. Calculate the rate constant.

Solution:

Since 1 mole of A produces 1 mole of C, we can calc. the frac. conv. of A as a function of time

$$f_A = \frac{V_{N_2}@\,any\,t}{V_{N_2}@\,t=\infty}$$

t	6	9	12	14	18	20	22	24	26	30
f_A	.331	.446	.559	.617	.708	.743	.772	.798	.830	.863

for a 1st order cnst. density rxn

$$-\frac{dC_A}{dt} = k_1 C_A$$

$$\cancel{C_{A0}} \frac{df_A}{dt} = k_1 \cancel{C_{A0}} (1 - f_A)$$

$$\int \frac{df_A}{1 - f_A} = k_1 \int dt \quad + C$$

$$\ln\left(\frac{1}{1 - f_A}\right) = k_1 t$$

$$k_1 = \frac{\ln\left(\frac{1}{1 - f_A}\right)}{t}$$

t	6	9	12	14	18	20	22	24	26	30
k_1 $\times 10^2$	6.70	6.56	6.82	6.86	6.74	6.79	6.72	6.66	6.82	6.63

$$k_{AVG} = 6.74 \times 10^{-2} \text{ min}^{-1}$$