CBE 40445

8/14/20

REVIEW: "EQUILIBRIUM"

PHASE EQ. $f_i^{I} = f_i^{II}$

FROM $\Delta G = 0$

CHEMICAL EQ

$$K_a = \exp\left(-\frac{\Delta G_{RXN}^{\circ}}{RT}\right)$$

$$K_a = \left(\frac{a_M^m \, a_N^n}{a_A^a \, a_B^b}\right)$$

$$a = \frac{\bar{f}_i}{\bar{f}_i^{\,0}}$$

STANDARD STATE

$$\frac{\partial \ln K_a}{\partial T} = \frac{\Delta H^{\circ}}{RT^2}$$

$$K_a = \left[\frac{X_M^m \, X_N^n}{X_A^a \, X_B^b}\right]\left[\frac{\phi_M^m \, \phi_N^n}{\phi_A^a \, \phi_B^b}\right]\left(\frac{P}{P^\circ}\right)^{m+n-a-b}$$

NOW CONSIDER FRAMEWORK HOW TO DESCRIBE RATE OF REACTIONS

BOOK KEEPING . . .

EXTENT OF REACTION:

$$\phi(t) = \frac{n_i(t) - n_i^0}{\nu_i}$$

$n_i(t)$: MOLES RIGHT NOW

n_i^0: INITIAL MOLES

ν_i: STOICHIOMETRIC COEFFICIENT

FRACTIONAL CONVERSION

$$f(t) \equiv \frac{\phi(t)}{\phi_{max}} \qquad 0 \le f(t) \le 1$$

$$f_l = -\nu_l \frac{\Phi}{n_l^0} = 1 - \frac{n_l}{n_l^0}$$

FRACTION OF REACTANTS THAT HAVE BEEN "USED UP"

USUALLY CONSIDER THE "LIMITING" REACTANT. (THE ONE THAT WOULD RUN OUT FIRST)

$$\frac{\phi(t)}{\phi_{max}}$$

$$\frac{n_i(t) - n_i^0}{V_i}$$

$$\frac{\dfrac{n_i(t) - n_i^0}{V_i}}{\dfrac{n_i^0}{V_i}}$$

$$\frac{n_i(t)}{n_i} - 1$$

RATE OF REACTION

$$\frac{d\phi}{dt} \quad \left(\frac{\text{MOLES}}{\text{TIME}}\right)$$

WE USUALLY NORMALIZE THIS TO VOLUME OF DEVICE

$$r = \frac{1}{V}\frac{d\phi}{dt}$$

$$dn_i = \nu_i \, d\phi \qquad \left(n_i = n_i^0 + \nu_i \phi(t)\right)$$

$$r = \frac{1}{\nu_i V}\frac{dn_i}{dt}$$

USEFUL !! VARIABLES

$$r = \frac{1}{\nu_i V}\frac{d(C_i V)}{dt}$$

BUT FOR A HOMOGENEOUS SYSTEM ...

FOR CASES WITH A HETEROGENEOUS CATALYST...

RATE / MASS

$$r = \pm \frac{1}{g_m} \frac{d\phi}{dt} \quad \left(\frac{\text{MOLE}}{\text{MASS TIME}}\right)$$

RATE / AREA

$$r = \pm \frac{1}{SA} \frac{d\phi}{dt} \quad \left(\frac{\text{MOLE}}{\text{AREA TIME}}\right)$$

IT IS INTERESTING TO READ THE AUTHOR'S EXPOSITION ABOUT

REACTION INTERMEDIATES

SURFACE COMPOSITION

MECHANISMS...

- EVEN APPARENTLY SIMPLE REACTIONS COULD HAVE MULTISTEP PROCESSES

CONSIDER AN APPARENTLY SIMPLE REACTION (GAS PHASE)

$$C_2H_4 + H_2 \rightarrow C_2H_6$$

WOULD YOU EVER DO THIS FOR $?

BUT ACTUALLY!

ELEMENTARY REACTIONS

$$C_2H_4 + H_2 \xrightarrow{k_1} C_2H_5^{\cdot} + H^{\cdot}$$

$$H^{\cdot} + C_2H_4 \xrightarrow{k_2} C_2H_5^{\cdot}$$

$$C_2H_5^{\cdot} + H_2 \rightarrow C_2H_6 + H^{\cdot}$$

$$C_2H_5^{\cdot} + H^{\cdot} \rightarrow C_2H_6$$

CONSIDER OZONE DECOMPOSITON

$$2O_3 \longrightarrow 3O_2$$

$$O_3 \xrightarrow{k_1} O_2 + O^{\cdot}$$

$$O_2 + O^{\cdot} \xrightarrow{k_2} O_3$$

$$O^{\cdot} + O_3 \longrightarrow 2O_2$$

OR

$$H_2 + Br_2 \longrightarrow 2HBr$$

INITIATION $\quad Br_2 + \text{"LIGHT"} \longrightarrow 2Br^{\cdot}$

PROPAGATION $\quad Br^{\cdot} + H_2 \longrightarrow HBr + H^{\cdot}$

PROPAGATION $\quad H^{\cdot} + Br_2 \longrightarrow HBr + Br^{\cdot}$

TERMINATION $\quad 2Br^{\cdot} \longrightarrow Br_2$

IF YOU KNOW ELEMENTARY STEPS OR INTERMEDIATES, THIS COULD ENLIGHTEN KINETICS.

(MOST?)

IN MANY CASES, YOU WON'T KNOW MUCH ABOUT THIS AND JUST WILL USE THE DATA YOU HAVE.

IN SOME EXTREME SENSE...

TRACKING DOWN INTERMEDIATES OR SURFACE SPECIES BECOMES: ZOOLOGY ...

BASIC "RULES" OF RATES OF SINGLE REACTIONS

- REACTION RATE DECREASES AS REACTANTS ARE USED UP (AT CONST T.)

- IRREVERSIBLE REACTION RATE EXPRESSION

$$r = k(T)\,\bar{F}(C_i, T)$$

- EXPECT "ARRHENIUS" BEHAVIOR

$$k = \bar{A} \exp\left[-\frac{E_A}{RT}\right]$$

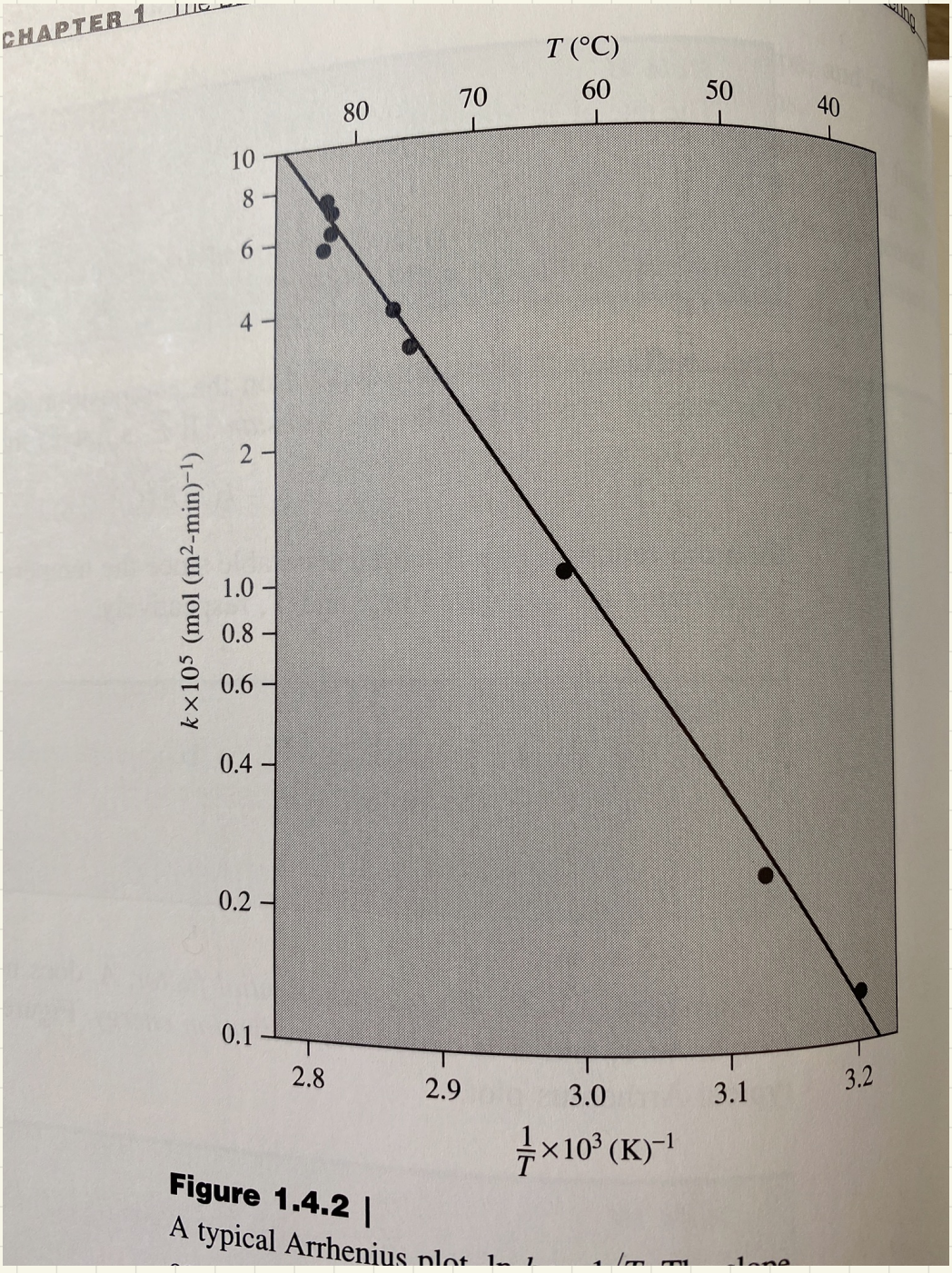


Figure 1.4.2 |
A typical Arrhenius plot. $\ln k$ vs. $1/T$. The slope

- $F(c_i) = \prod_i c_i^{d_i}$ ← OR MORE COMPLEX FUNCTION...

$$r = k c_A^{\bar{a}} c_B^{\bar{b}}$$

CONSIDER $H_2 + Br_2 \rightarrow 2HBr$

WOULD WE EXPECT:

$$r = k c_{H_2} c_{Br_2} \quad ?$$

NO!! YOU HAVE SEEN SEQUENCE OF ELEMENTARY STEPS...

$$H_2 + Br_2 \longrightarrow 2HBr$$

$$Br_2 + \text{"LIGHT"} \longrightarrow 2Br^{\cdot}$$

$$Br^{\cdot} + H_2 \longrightarrow HBr + H^{\cdot}$$

$$H^{\cdot} + Br_2 \longrightarrow HBr + Br^{\cdot}$$

$$2Br^{\cdot} \longrightarrow Br_2$$

$$\lambda = \frac{k_1 C_{H_2} C_{Br_2}^{1/2}}{k_2 + \frac{C_{HBr}}{C_{Br_2}}}$$

- REVERSIBLE REACTIONS CAN BE WRITTEN AS A FORWARD AND A REVERSE RATE

$$r = r_+ - r_-$$

$$r_+ = k_+ \bar{F}_+(c_i)$$

$$r_- = k_- \bar{F}_-(c_i)$$

IF THE FORWARD & REVERSE RATES ARE EQUAL, THEN THE REACTION IS IN EQUILIBRIUM

IN AN IDEALIZED CASE:

$$K_c = \frac{k_+}{k_-}$$

'EQUILIBRIUM' CONSTANT

BUT ONLY IF THE "RATE" EXPRESSIONS ARE 'SYMMETRIC'

EXAMPLE RATES

$$A \longrightarrow \text{PRODUCTS}$$

WOULD EXPECT

$$r = k C_A \quad \left(\frac{\text{MOLES}}{\text{VOLUME}}\right)$$

$$\left(\frac{1}{\text{TIME}}\right)$$

$$r = \frac{1}{V_i V}\frac{dn_i}{dt} = -\frac{1}{V}\frac{dn_A}{dt} = k C_A$$

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

WHICH I LIKE ALOT BETTER THAN!

$$\frac{df_A}{dt} = k(1 - f_A)$$

WE WILL USE BOTH ....

SOME OBSCURE DATA

DECOMPOSITION OF DIBROMOSUCCINIC ACID

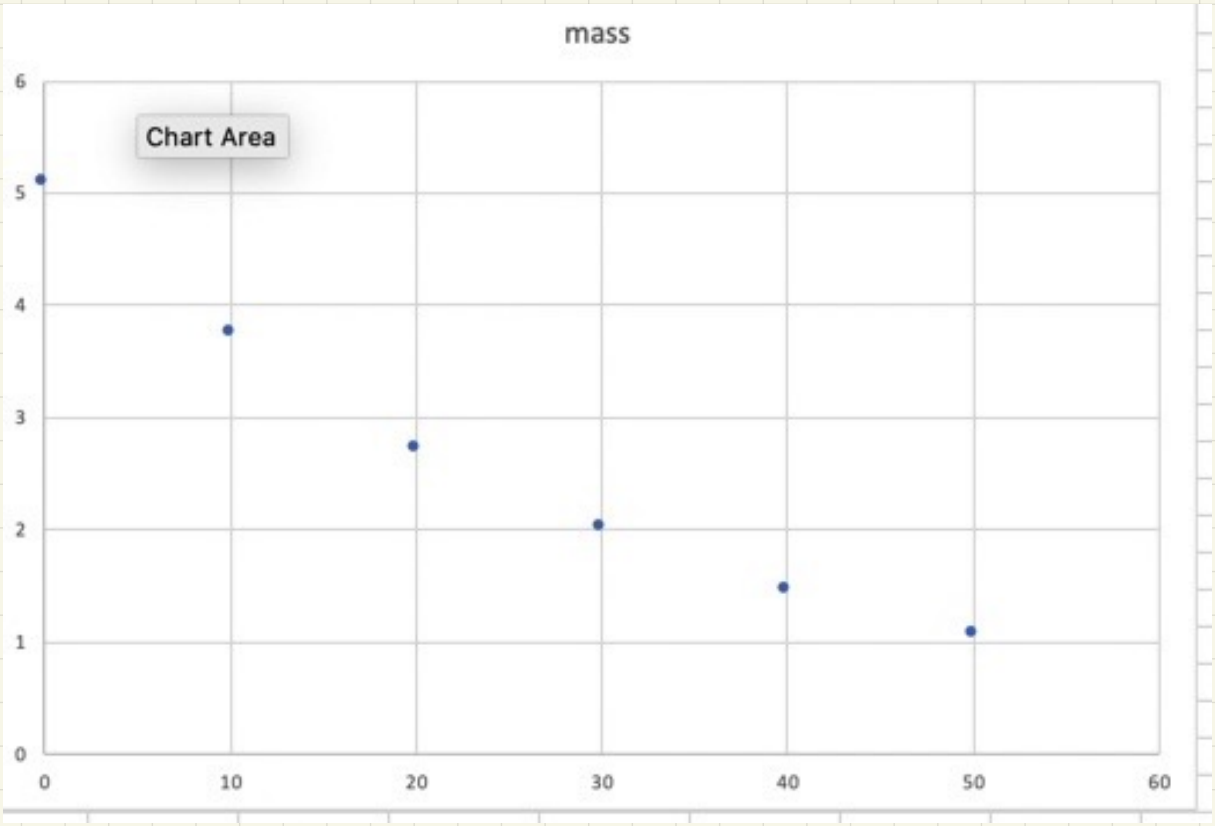
$C_2H_2Br_2(COOH)_2$

T (MIN)	MASS ACID (g)	f
0	5.11	0
10	3.77	.26
20	2.74	.46
30	2.02	.60
40	1.48	.71
50	1.08	.79

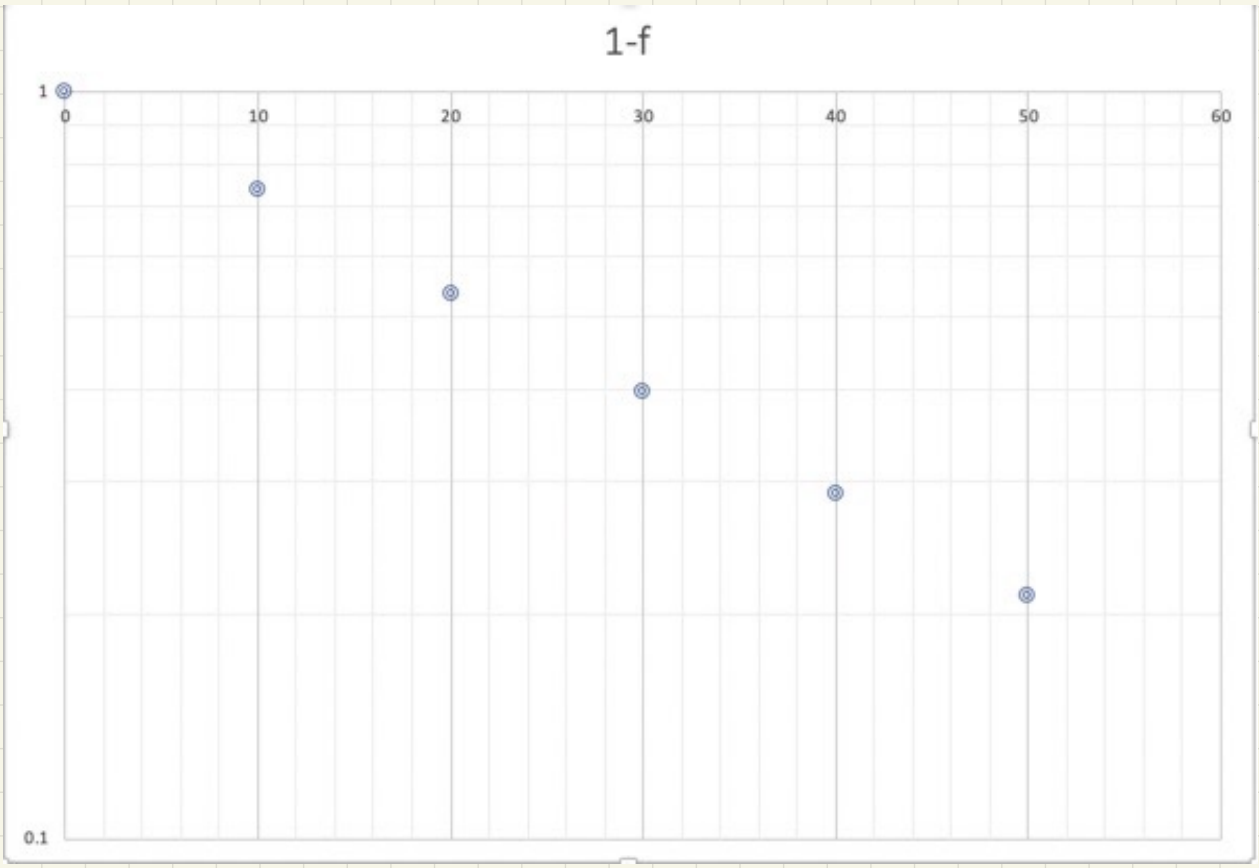
$$\frac{dm}{dt} = -km \qquad m = m^\circ(1-f)$$

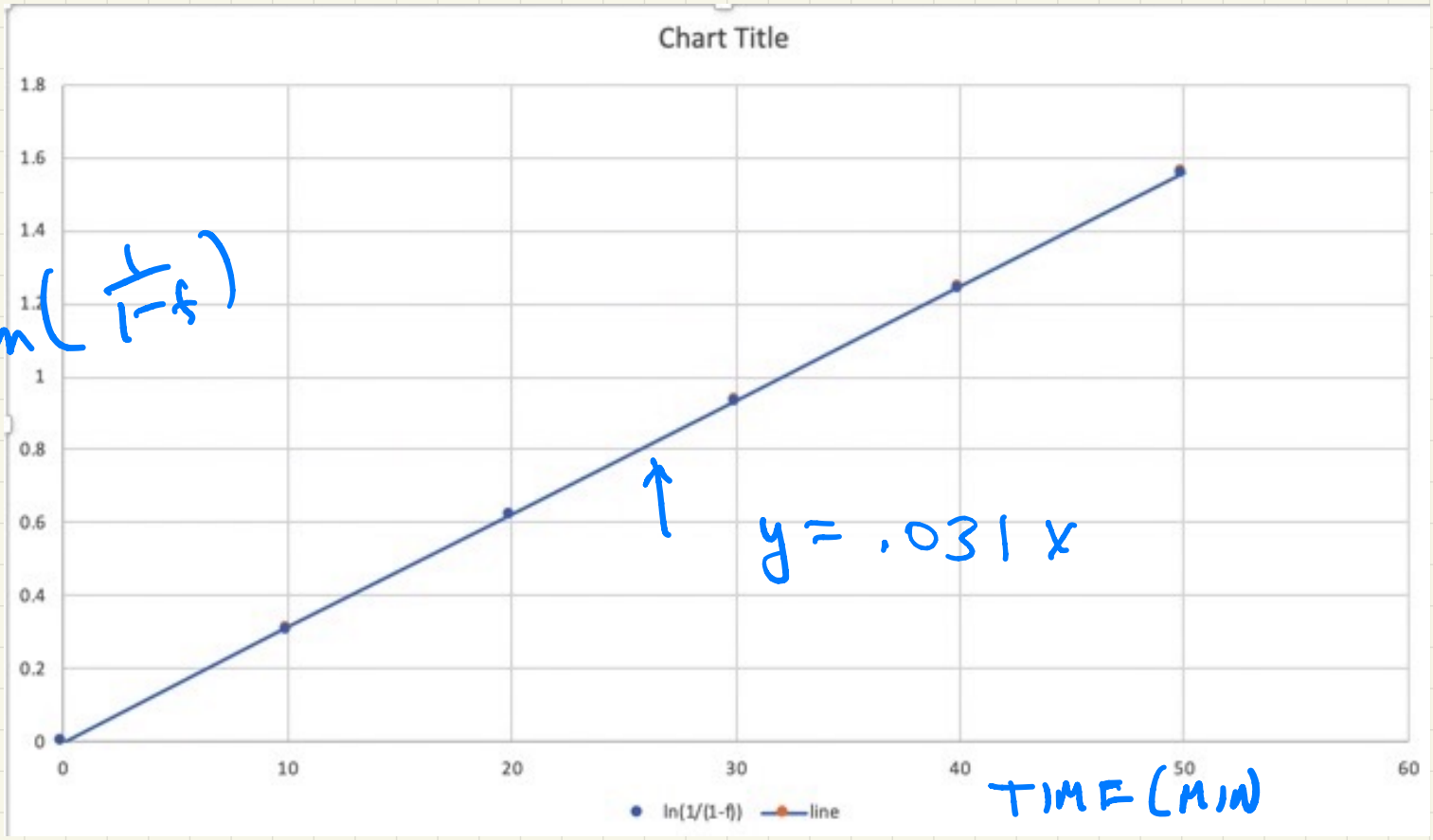
$$\frac{df}{dt} = k(1-f) \qquad f = 0 \text{ @ } t = 0$$

$$\ln\left(\frac{1}{1-f}\right) = kt$$



PLOT 1-f ON LOG SCALE:





THIS ONE WAS EASY!!

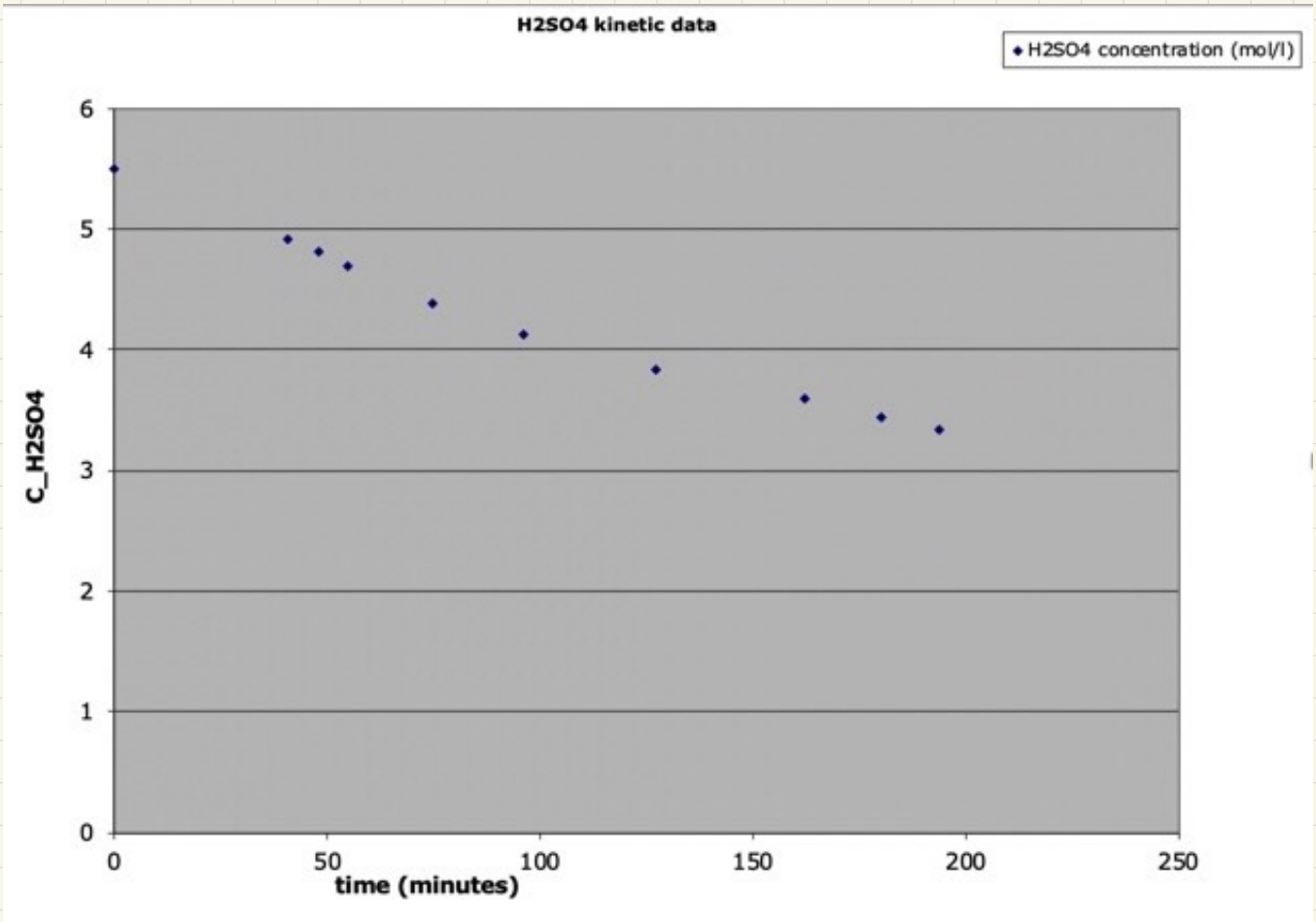
SOME MORE DATA

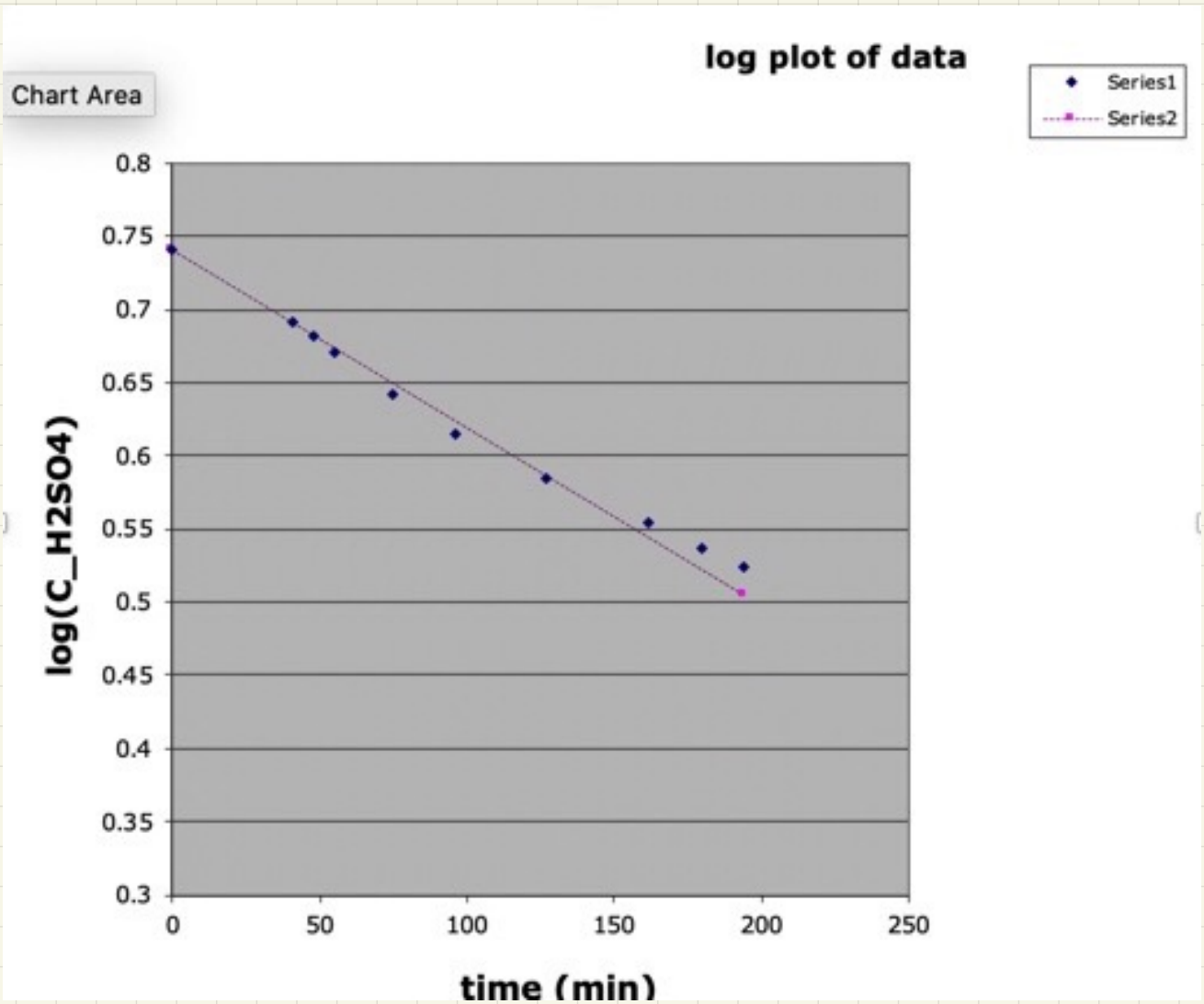
H_2SO_4 + DIETHYLSULFATE

$(C_2H_5)_2SO_4$

$\longrightarrow 2\,C_2H_5SO_4H$

time (min)	H2SO4 concentration (mol/l)
0	5.5
41	4.91
48	4.81
55	4.69
75	4.38
96	4.12
127	3.84
162	3.59
180	3.44
194	3.34





DOESN'T LOOK LIKE 1ST ORDER WILL WORK!!

HOW ABOUT 2ND ORDER

$$\frac{dC_{H_2SO_4}}{dt} = -k C_{H_2SO_4} C_{DiSO_4}$$

$$\frac{dC_{DiSO_4}}{dt} = -k C_{H_2SO_4} C_{DiSO_4}$$

CLEARLY:

$$dC_{H_2SO_4} = dC_{DiSO_4}$$

$$C_{H_2O_4}^{INITIAL} - C_{H_2SO_4} = C_{DISO_4}^{INITIAL} - C_{DiSO_4}$$

SO YOU CAN SUBSTITUTE FOR C_{DiSO_4} IF YOU NEED TO...

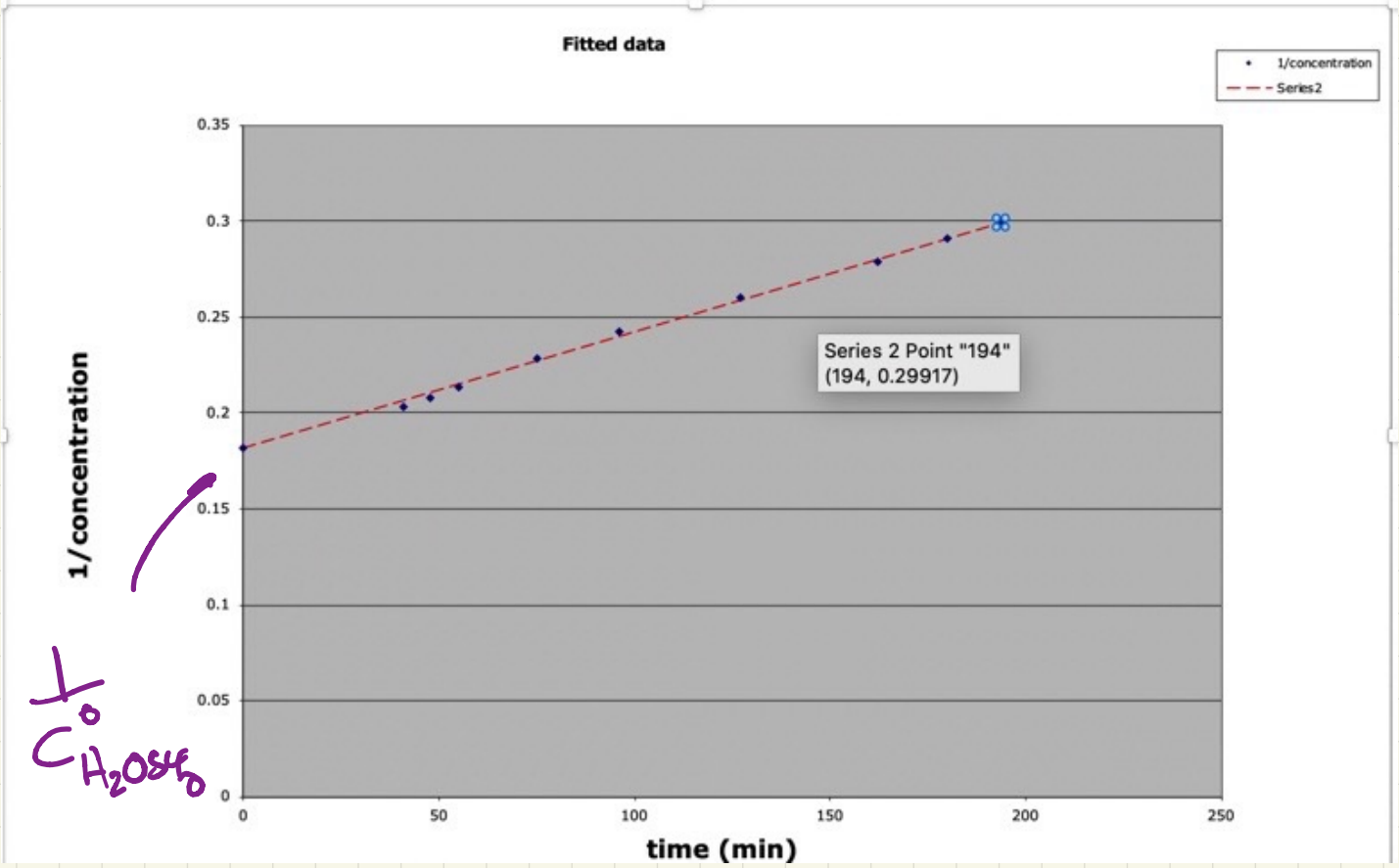
LETS CONSIDER

$$C^{0}_{H_2SO_4} = C^{0}_{DISO_4}$$

$$\frac{d C_{H_2SO_4}}{dt} = -k C^{2}_{H_2SO_4}$$

$$-\int_{C^{0}_{H_2SO_4}}^{C_{H_2SO_4}} \frac{d C_{H_2SO_4}}{C^{2}_{H_2SO_4}} = \int_{0}^{t} k \, dt$$

$$\left(\frac{1}{C_{H_2SO_4}} - \frac{1}{C^{0}_{H_2SO_4}} \right) = k t$$



k = SLOPE

$= 6.05 \times 10^{-4} \left(\frac{l}{\text{MOL-MIN}} \right)$