CBE 40445

8/17/20

- QUICK REVIEW OF REACTION MECHANISMS AND REACTION KINETICS RULES
- 1ST, 2ND AND MORE COMPLEX REACTION KINETICS

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

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

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

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

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

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

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

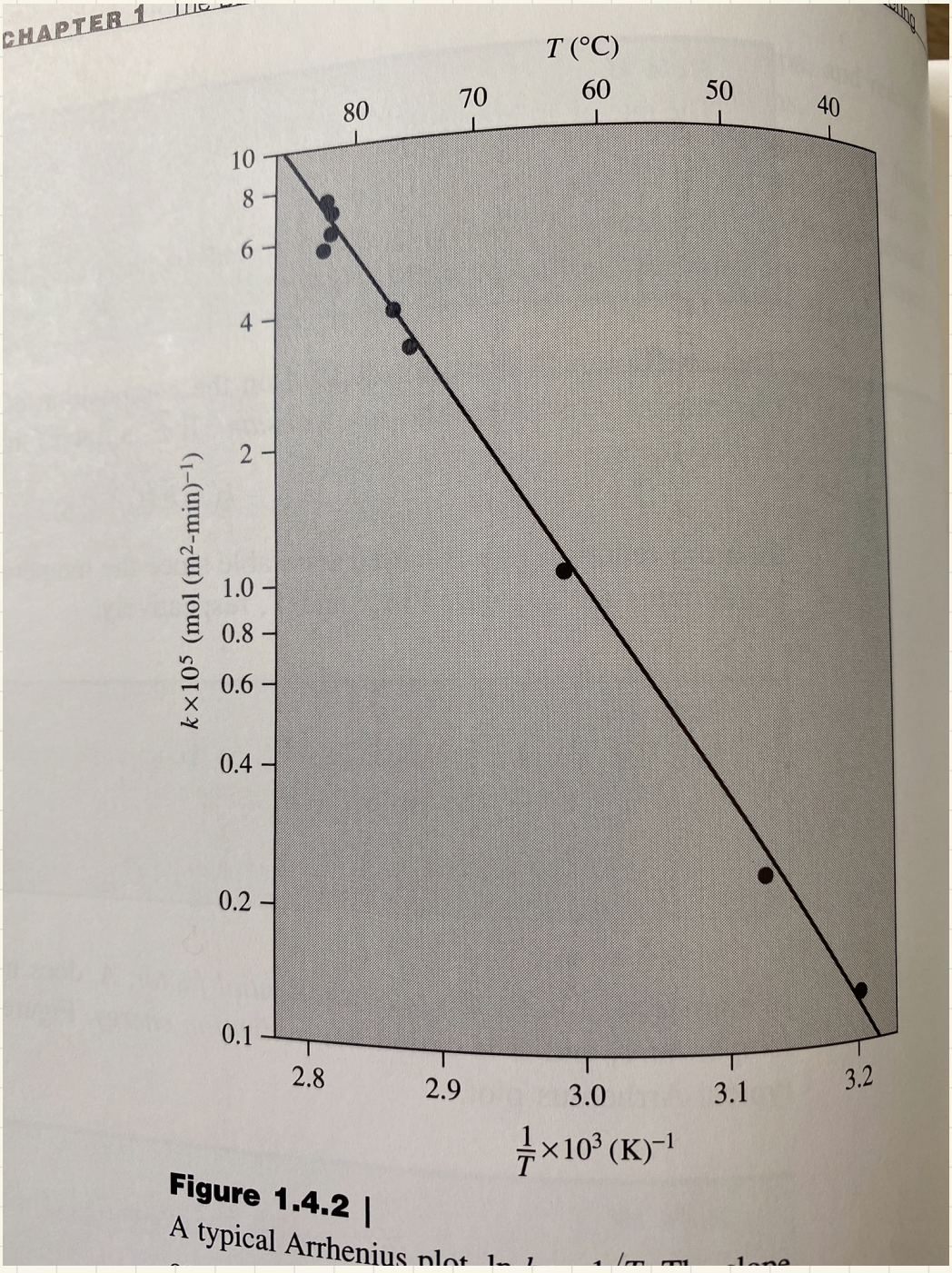


Figure 1.4.2 |
A typical Arrhenius plot. $\ln k$ vs. $1/T$. The slope

- $F(c_i) = \prod_i c_i^{d_i}$ ← 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'

CHEMICAL KINETICS

CONCEPTUAL IDEA:

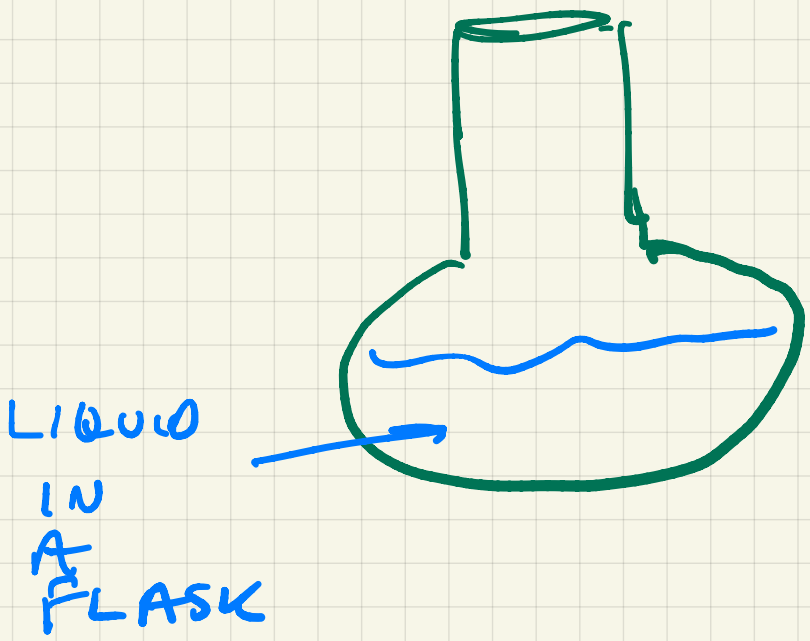
QUANITFY RATE OF SPECIFIED CHEMICAL REACTIONS..

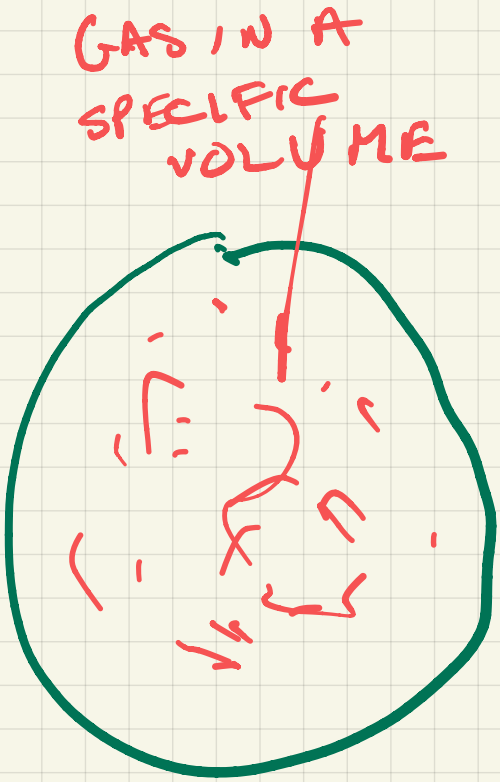
$$A \rightarrow \text{PRODUCTS}$$

$$A + B \rightarrow M$$

$$A + B \xrightarrow{CAT} M$$

ADDRESS A SPECIFIC CASE





START WITH MASS BALANCE:

$$A \rightarrow M$$

MOLES OF A IN REACTOR

$$\frac{d(C_A V)}{dt} = \wedge$$

RATE AT WHICH A IS CONSUMED BY REACTION

$$\frac{d(C_A V)}{dt} = -k C_A V$$

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

$-k C_A$: RATE OF A REACTION / VOLUME

V : VOLUME

FOR THIS CASE, WE WON'T ADD ANYTHING SO V=CONST

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

COULD ALSO WRITE

$$r = \frac{1}{V_i V} \frac{dm_i}{dt} = -\frac{1}{V} \frac{dm_A}{dt} = k C_A$$

AND SINCE $f_A = 1 - \frac{C_A}{C_{A0}}$

$$C_A = C_{A0}(1 - f_A)$$

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

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

START WITH MASS . . .

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

NOW FRACTIONAL CONVERSION

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

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

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

$$\frac{df}{(1-f)} = k\,dt$$

$$-\int_{f=0}^{f} \frac{-df}{(1-f)} = \int_0^t k\,dt$$

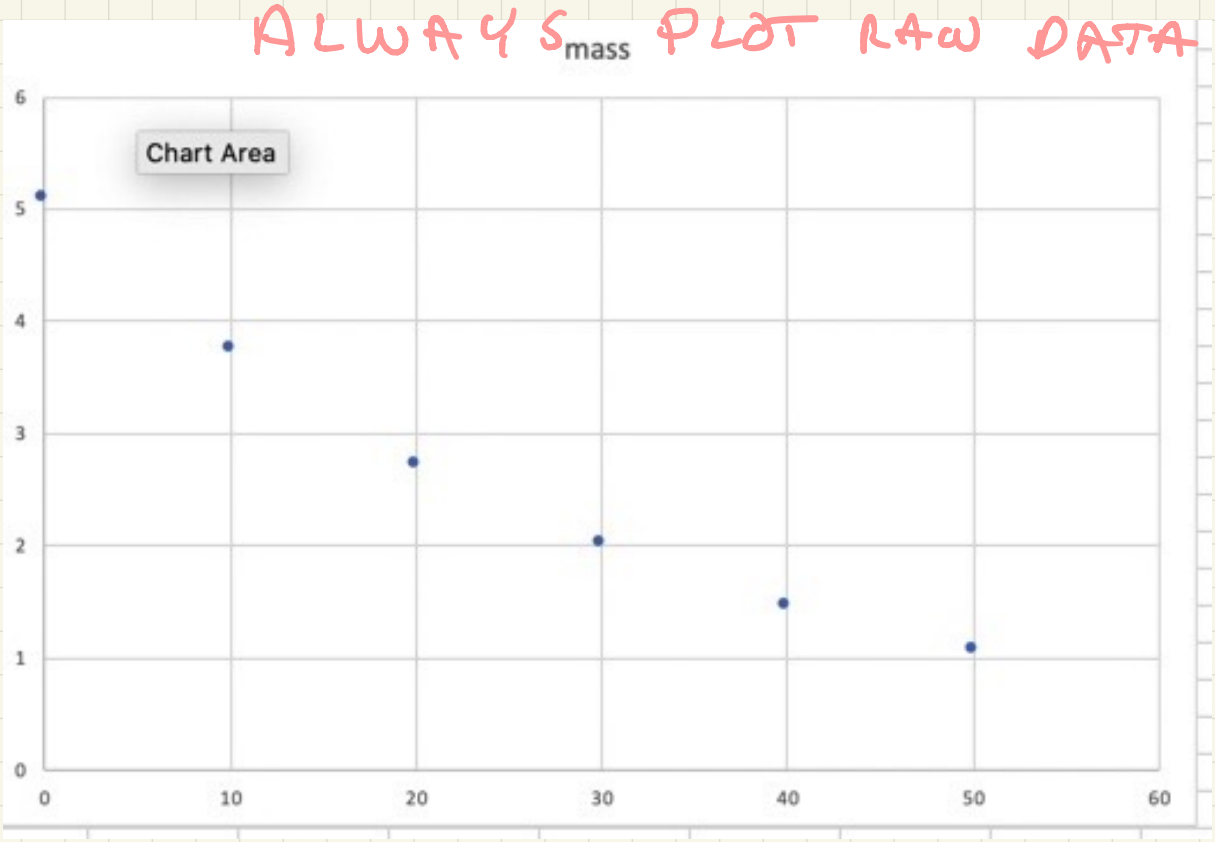
COLLECTED!

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

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

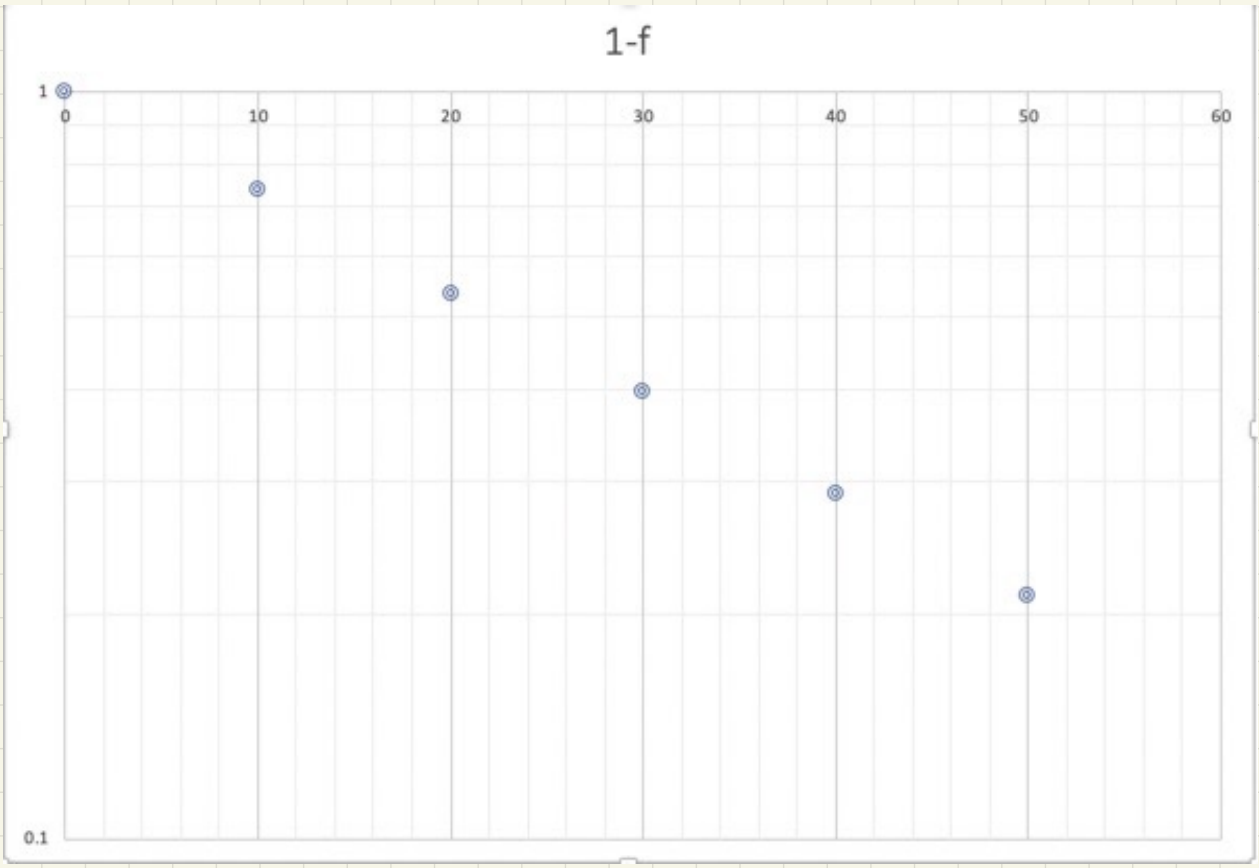
WE EXPECT DATA TO FOLLOW THIS ↑

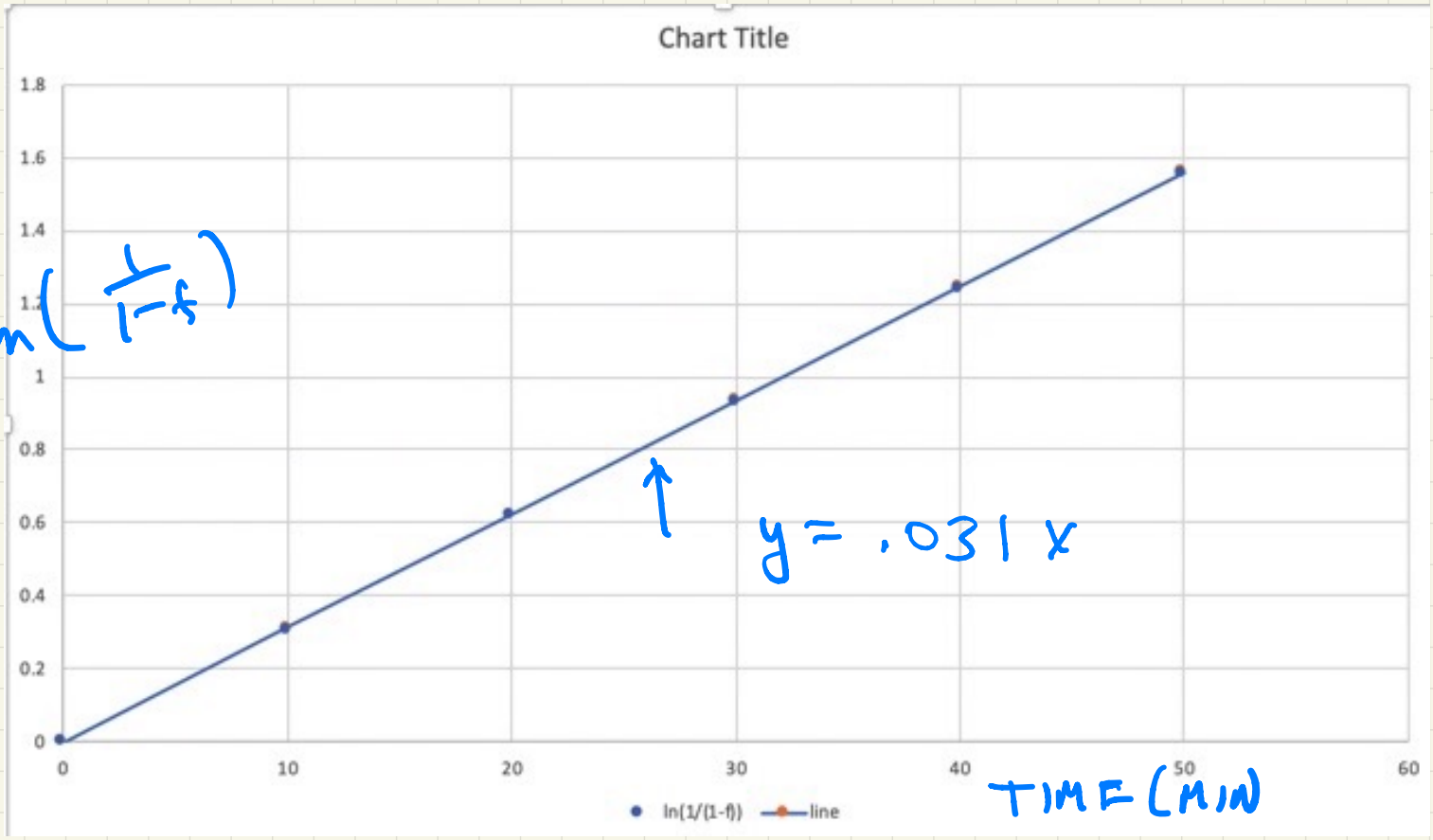
ALWAYS PLOT RAW DATA



PLOT 1-f ON LOG SCALE:

(LOOK'S GOOD WE EXPECT 1S ORDER MODEL TO WORK)





THIS ONE WAS EASY!!

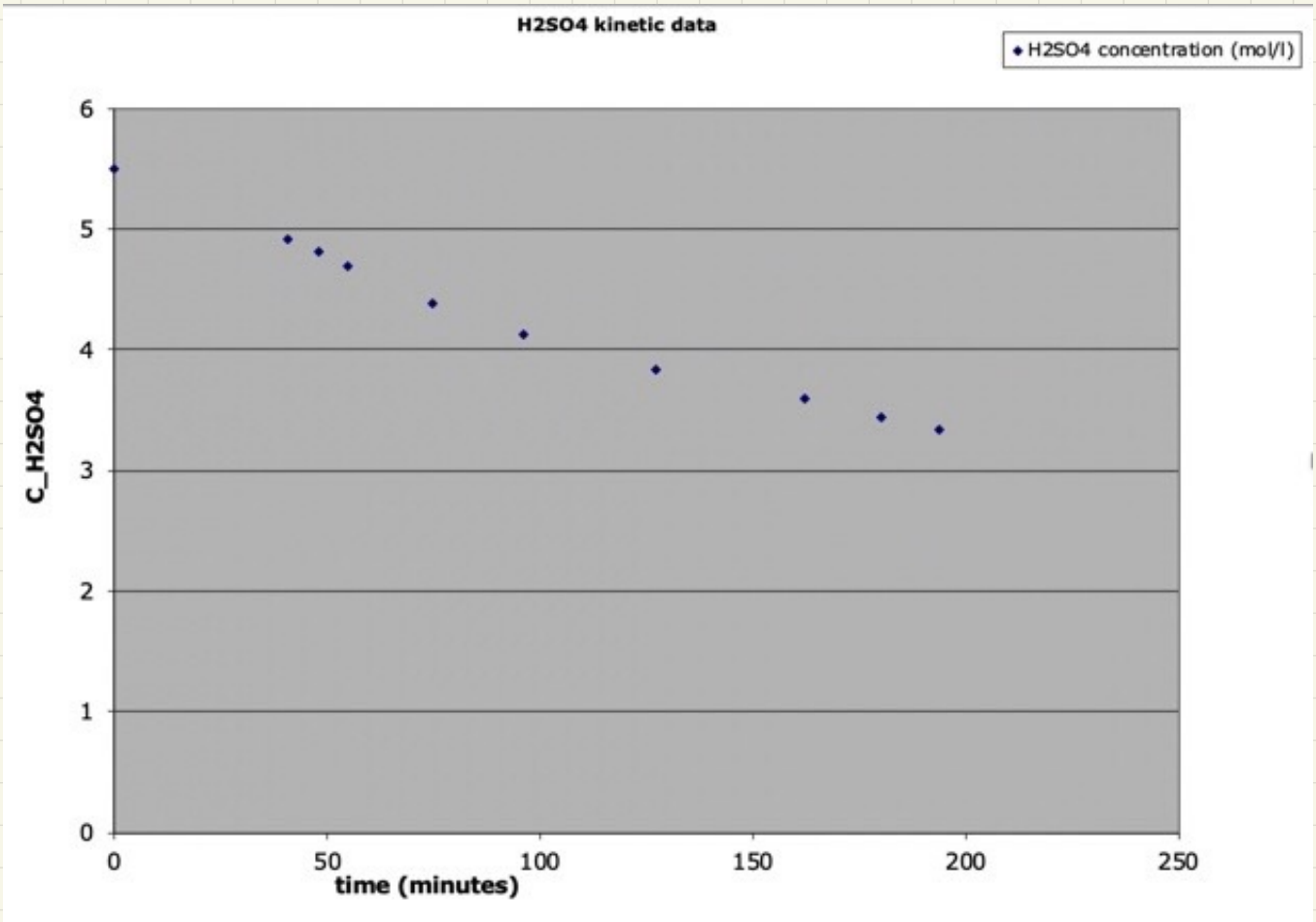
SOME MORE DATA

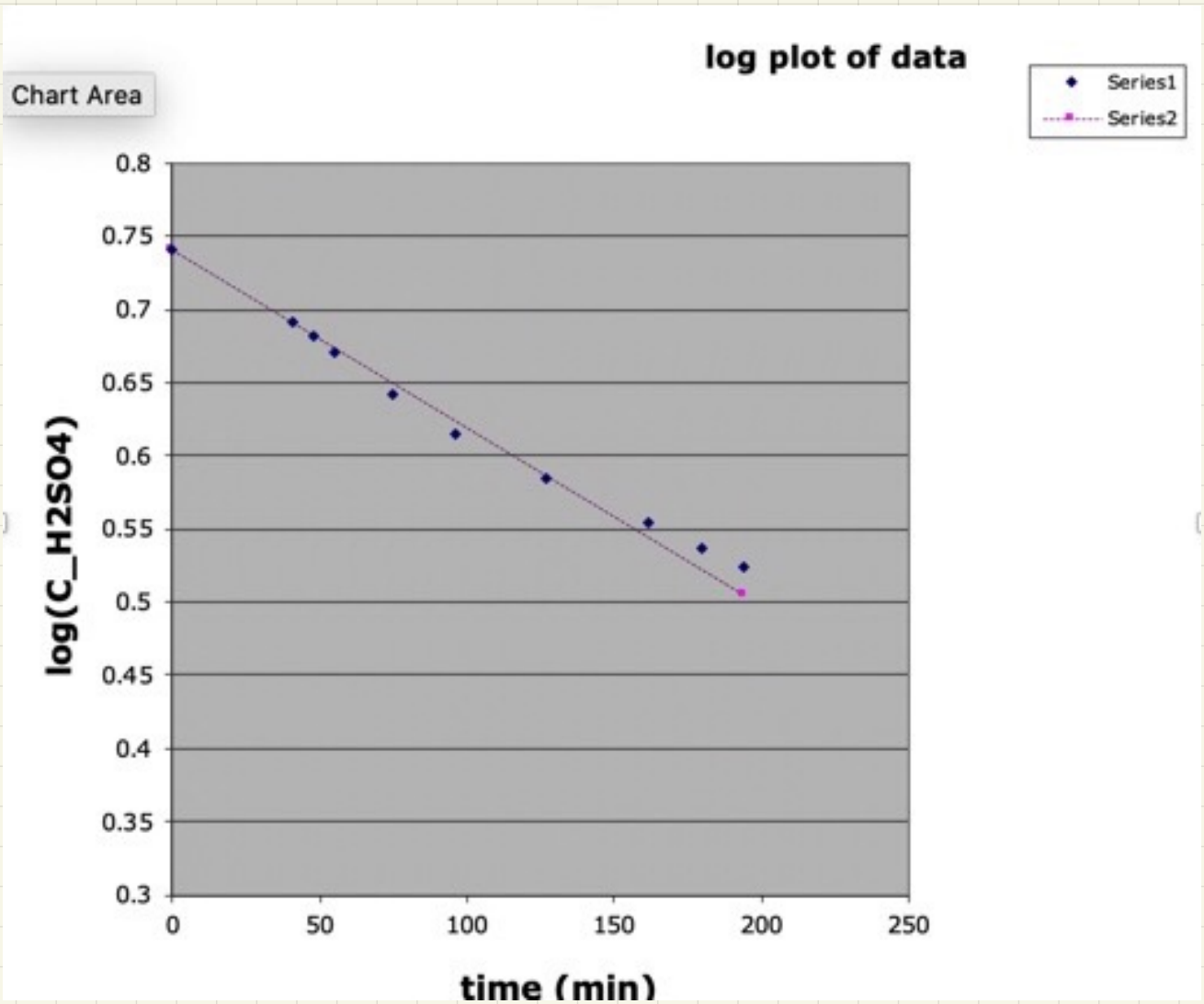
H_2SO_4 + DIETHYLSULFATE

$(C_2H_5)_2SO_4$

$\longrightarrow 2\,C_2H_5SO_4H$

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...

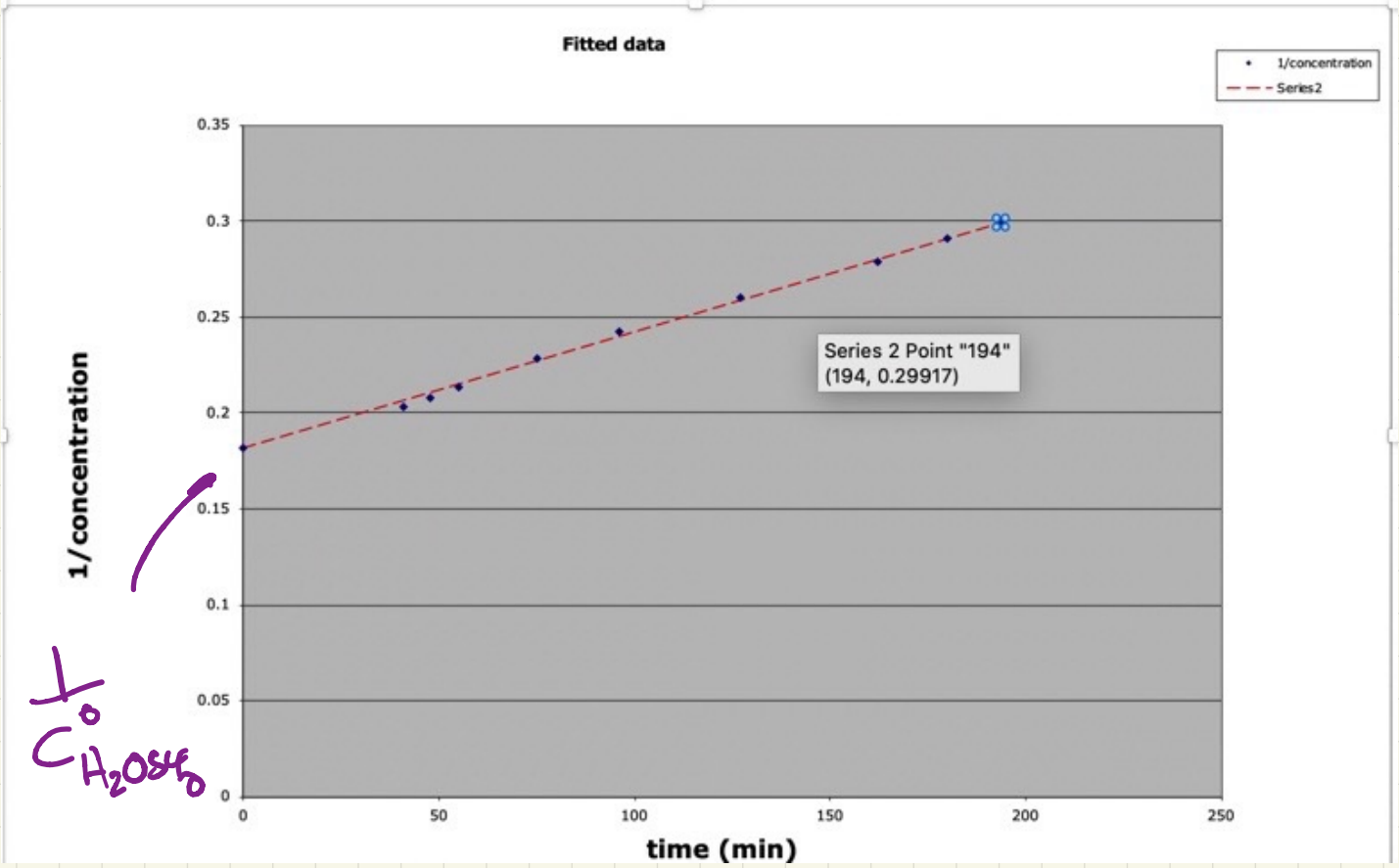
LETS CONSIDER

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

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

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

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



k = SLOPE

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

SUPPOSE A CATALYST, E IS USED

$$A \longrightarrow M$$

$$A + E \underset{k_n}{\overset{k_1}{\rightleftharpoons}} AE \xrightarrow{k_2} M + E$$

CORRECTIONS

$$\frac{dC_A}{dt} = -k_1 C_A C_E + k_n C_{AE}$$

$$\frac{dC_E}{dt} = -k C_A C_E + k_n C_{AE} + k_2 C_{AE}$$

JUST NEED 2 EQS

$$\frac{dC_{AE}}{dt} = k_1 C_A C_E - k_n C_{AE} - k_2 C_{AE}$$

$$\frac{dC_M}{dt} = k_2 C_{AE}$$

ASSUME $\frac{dC_{AE}}{dt} = 0$

AND $C_E^\circ = C_E + C_{AE}$

$$0 = \frac{dC_{AE}}{dt} = k_1 C_A C_E - k_{-1} C_{AE} - k_2 C_{AE}$$

SOLVE

$$C_{AE} = \frac{k_1 C_A C_E}{k_{-1} + k_2}$$

$$C_E^0 = C_E + C_{AE}$$

$$C_{AE} = \frac{k_1 C_A C_E^0}{k_1 C_A + k_2 + k_{-1}}$$

$$C_E = \frac{(k_2 + k_{-1}) C_E^0}{k_1 C_A + k_2 + k_{-1}}$$

THUS FOR $\frac{dC_A}{dt}$

$$\frac{dC_A}{dt} = -\frac{k_1 k_2 C_A C_E^0}{k_1 C_A + k_2 + k_{-1}}$$

$$\frac{dC_A}{dt} = - \frac{k_1 k_2 C_A C_E^0}{k_1 C_A + k_2 + k_n}$$

SOME LIMITS EXIST...

FOR C_A SUFFICIENTLY SMALL..

$$k_1 C_A << k_2 \text{ or } k_n$$

$$\frac{dC_A}{dt} \simeq - \frac{k_2 k_2 C_E^0}{(k_2 + k_2)} C_A$$

FIRST ORDER

$$= -K C_A$$

FOR C_A SUFFICIENTLY LARGE

$$k_1 C_A >> k_2 + k_n$$

ZERO ORDER

$$\frac{dC_A}{dt} : - k_2 C_{E_0} = -K$$

FIRST ORDER IN E^0

THIS FORM OF RATE EXPRESSION ARISES WHEN THERE IS AN INTERMEDIATE THAT COULD BE PRESENT IN LIMITED AMOUNTS (INDEPENDENT OF C_A)

k_2 DOESN'T CHANGE THE FORM

ARRHENIUS TEMPERATURE DEPENDENCE

ONE OF THE BASIC RULES OF KINETICS WAS TO EXPECT ARRHENIUS BEHAVIOR

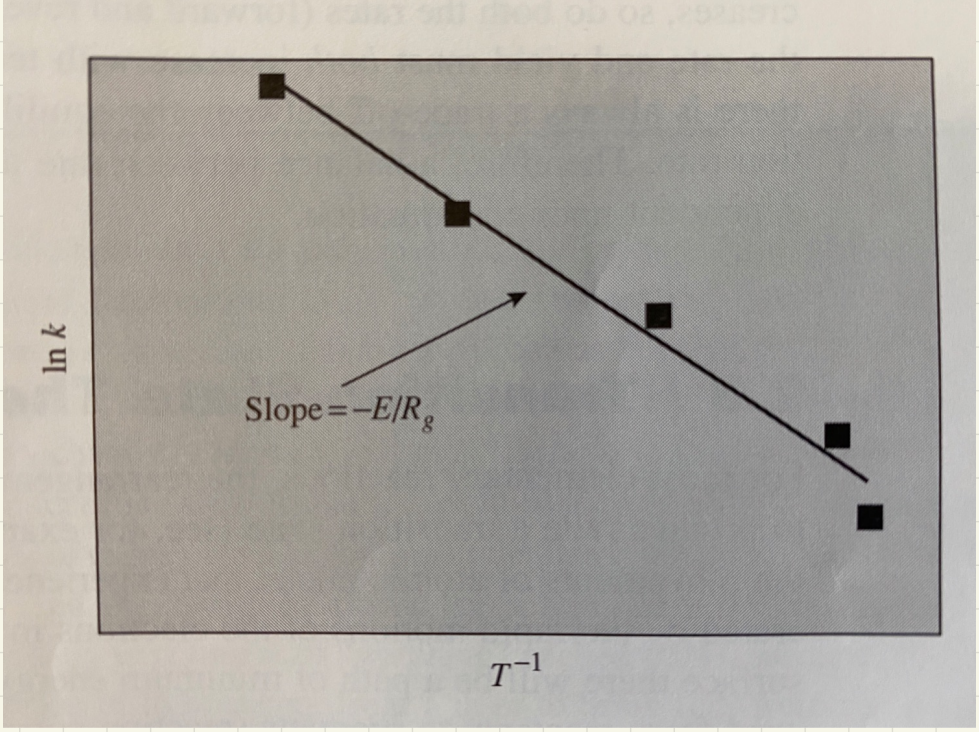
$$k = \overline{A} \exp\left[-\frac{E_A}{RT}\right]$$

IDEALLY NOT A FUNCTION OF T

OFTEN VERY SIGNIFICANT TEMP DEPENDENCE

$$2\,N_2O_5 \rightleftharpoons 2\,N_2O_4 + O_2$$

T (K)	k (s^{-1})
288	1.04×10^{-5}
298	3.38×10^{-5}
313	2.47×10^{-4}
323	7.59×10^{-4}
338	4.87×10^{-3}



AN OBVIOUS REASON FOR E TO VARY IS INTERNAL BONDING OF MOLECULE

WHILE A CAN ALSO CHANGE FOR DIFFERENT SYSTEMS,

A SUFFICIENT T IS NECESSARY TO MAKE REACTION OCCUR AT FINITE RATE.