CBE 40445

8/21/20

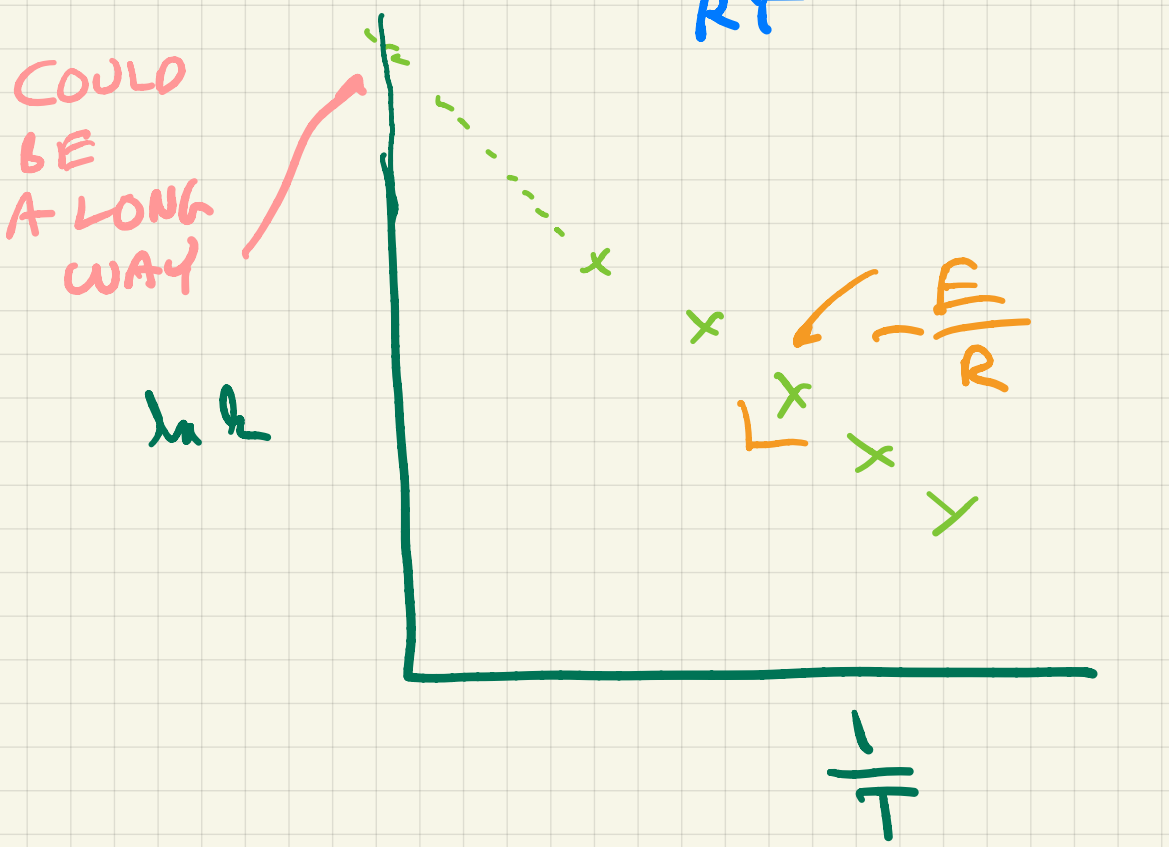
- DATA ANALYSIS
  - NOISY DATA
- 'FUNDAMENTAL' ASPECTS OF CHEMICAL KINETICS
  - TRANSITION STATE THEORY
- CHAPT - 3
  - CHEMICAL REACTORS

$$k = A \exp\left(\frac{-E}{RT}\right)$$

$$\frac{k}{A} = \exp\left(\frac{-E}{RT}\right)$$

$$\ln\left(\frac{k}{A}\right) = -\frac{E}{RT}$$

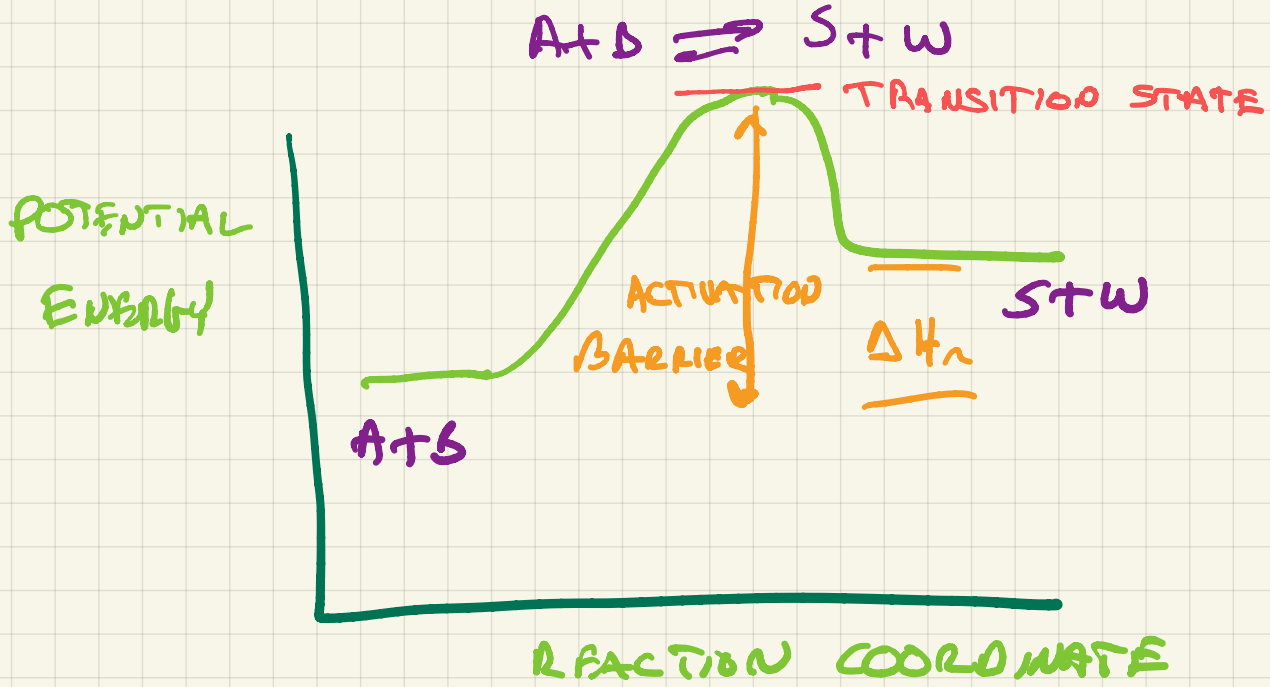
$$\ln k = -\frac{E}{RT} + \ln A$$



JUST GET A FROM E + k

PRESUMABLY THESE ARE BASED ON A NUMBER POINTS

"TRANSITION STATE THEORY"



$$A + B \rightleftharpoons S + W$$

SO WE EXPECT THAT

AT EQUILIBRIUM

$$k_1 C_A C_B = k_2 C_S C_W$$

$$K_C = \frac{k_1}{k_2} = \frac{C_S C_W}{C_A C_B}$$

NOW INCLUDING A TRANSITION STATE: $k_1 C_A C_B = k_2 C_S C_W = \lambda C_{TS}$

IF WE CONSIDER REACTANTS GOING TO TRANSITION STATE:

RATE OF FORWARD REACTION → $k_1 C_A C_B = \lambda C_{TS}$

$(A + B \rightleftharpoons TS)$

WHICH GIVES...

$$k^{\ddagger} = \frac{C_{TS}}{C_A C_B}$$

(IF YOU BELIEVE THIS..)

THEN SOME THERMO:

ALL FOR $A+B \rightleftharpoons TS$

$$RT \ln K^{\ddagger} = -\Delta G_0^{\ddagger} = -\Delta H_0^{\ddagger} + T\Delta S_0^{\ddagger}$$

THUS

$$C_{TS} = \exp\left[\frac{\Delta S_0^{\ddagger}}{R_c}\right] \exp\left[\frac{-\Delta H_0^{\ddagger}}{RT}\right] C_A C_B$$

($K^{\ddagger}$)

AGAIN THERMO!

SO THAT: $k C_A C_B = \lambda C_{TS}$

NOW A RATE

$$\Lambda = k_1 C_A C_B = \lambda \exp\left[\frac{\Delta S_0^{\ddagger}}{R}\right] \exp\left[\frac{-\Delta H_0^{\ddagger}}{RT}\right] C_A C_B$$

CONTINUING WITH SOME ASSUMPTIONS OF T. S.

UNIVERSAL FLEQUENCY

$$\lambda = \frac{k_B T}{h}$$

k_B ← BOLTZMAN CONSTANT

h ← PLANK CONSTANT

WHICH GIVES:

GENERAL RELATION!

$$k = \left(\frac{k_B T}{h}\right) \exp\left[\frac{\Delta S_0^{\neq}}{R}\right] \exp\left[\frac{-\Delta H_0^{\neq}}{RT}\right] C_A C_B$$

SO BACK TO ARRHENIUS...

$$\bar{A} = \left(\frac{k_B T}{h}\right) \exp\left[\frac{\Delta S_0^{\neq}}{R}\right]$$

$$E = \Delta H_0^{\neq}$$

WE SEE LINEAR DEPENDENCE ON T, BUT USUALLY THIS IS SMALL COMPARED TO EXPONENTIAL

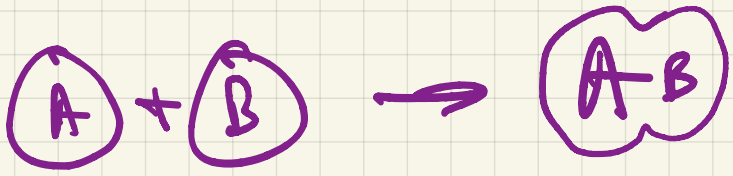

S = k log W
LVDWIG
BOLTZMANN
1844 – 1906
Dr PHIL PAULA
BOLTZMANN
GEB. CHIARI
ARTHUR
BOLTZMANN

$$\bar{A} = \left(\frac{kT}{h}\right) \exp\left[\frac{\Delta S_j^{\ddagger}}{R}\right]$$

SO $\Delta S_j^{\ddagger}$ $A + B \rightarrow TS$

EXPECT MOLECULAR CONFIGUATION TO BE IMPORTANT

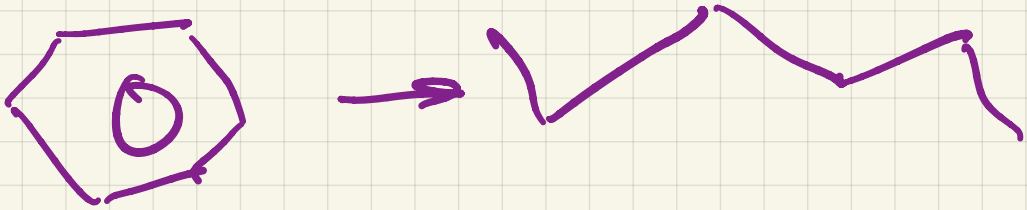
AS ΔS_0 ↑ A ↑



$\Delta S < 0$

$\Delta S \sim \left(\frac{10\ J}{MOLE\ K}\right)$

$R = 8.314 \frac{J}{MOLE}$



$\Delta S > 0$

$\exp\left[\frac{\Delta S_j^{\ddagger}}{R}\right]$ COULD BE $O(1)$

OR MAYBE

$.1 \leq \exp\left[\frac{\Delta S_j^{\ddagger}}{R}\right] \leq 10$

THUS AS A BASELINE!

$$\overline{A} \hat{=} \frac{\overline{kT}}{h} \tilde{=} 10^{13}/s$$

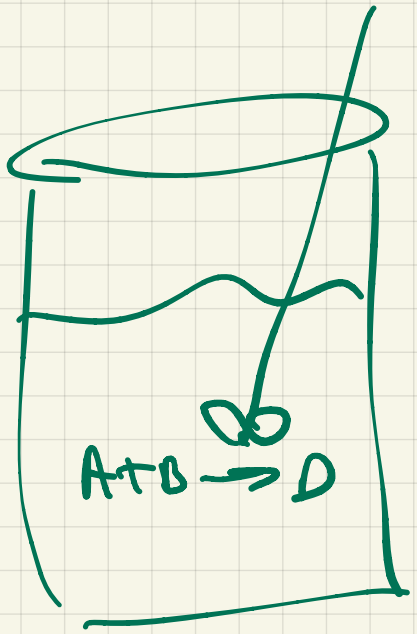
D & D NOTE THAT MOST OF THE TIME $\Delta H_j^{\ddagger}$, $\Delta S_j^{\ddagger}$ ARE NOT REALLY KNOWN..

SO MOST OF THE TIME WE USE ARRHENIUS..

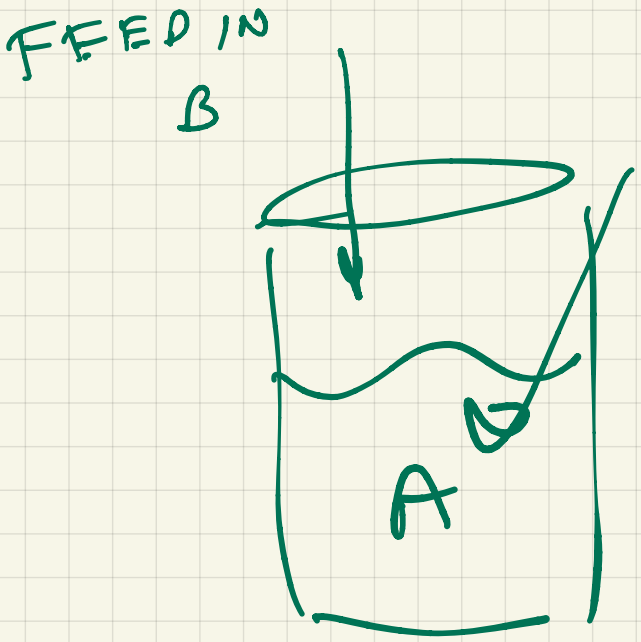
CHAPTER 3

HOW DO WE GET KINETIC DATA?

IN A LAB, YOU USUALLY USE A BATCH OR SEMI BATCH REACTOR



BATCH



SEMI BATCH

(MOLES)

MASS BALANCE

SPECIES i

RATE OF CHANGE OF MOLES OF i IN REACTOR = FLOW RATE OF i INTO REACTOR − FLOW RATE OF i OUT OF REACTOR

+ RATE AT WHICH i IS PRODUCED/CONSUMED BY REACTION

THUS INTERMS OF MOLES...

$$\frac{dN_i}{dt} = 0 - 0 + \nu_i \cdot r \cdot V$$

r: REACTION RATE / VOLUME

V: VOLUME

ν_i: STOICHIOMETRIC COEFFICIENT

GENERALLY AN INITIAL VALUE PROBLEM

COULD ALSO WRITE

$$\frac{d}{dt}VC_i = \nu_i \cdot r \cdot V$$

IF $r = kC_A$ $\quad A \rightarrow S$

$$\frac{dVC_A}{dt} = -kC_A V$$

IF V = CONST

$$V\frac{dC_A}{dt} = -kC_A V$$

COULD ALSO WRITE:

$$M_i^0 \frac{df_i}{dt} = -\nu_i \mathcal{N} V \qquad f_i(t=0) = 0$$

SUPPOSE $A + B \longrightarrow S$

$$\mathcal{N} = k C_A C_B$$

$$C_{A0} \neq C_{B0}$$

$$dC_A = dC_B$$

$V = \text{CONST}$

$$C_{A0} - C_A = C_{B0} - C_B$$

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

$$\frac{dC_A}{dt} = -k C_A (C_{B0} - C_{A0} + C_A)$$

$$\frac{dC_A}{C_A (C_A - (C_{A0} - C_B))} = k\,dt$$

$$\frac{dC_A}{C_A\left(C_A - (C_{A0} - C_{B0})\right)} = k\,dt$$

$$\ln\left(\frac{C_{A0}\left(C_A(t) - (C_{A0} - C_{B0})\right)}{C_{A0} - C_{B0}}\right) = kt$$