(*) Q+A WED @ 7-8 Keyes 105

TEST @ 5-7, THURS.

2.25.19

RXN Mechanism

Frequency Factor (accounts for collision frequency + geometry)

$k = Ae^{-Ea/RT}$ $\quad f = e^{-Ea/RT}$

- f = fraction of molecules with enough energy to react.
- f increases exponentially w T (as does k)

rearranging → $\ln(k) = \ln(A) - \frac{Ea}{RT}$

$\ln(k) = \ln(A) - \frac{Ea}{R}\left(\frac{1}{T}\right)$

$y = b + mx$

@ T_2 to k@ T_1:

$\ln(K_1) = \ln A - \frac{Ea}{R}\left(\frac{1}{T_1}\right)$

$\ln(K_2) = \ln A - Ea/R\left(\frac{1}{T_2}\right)$

$\ln\left(\frac{K_1}{K_2}\right) = \frac{Ea}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

Ex) First order RXN has a $k = 2.75 \cdot 10^{-2}\ s^{-1}$ @ 20°C. (+273)
What is value of k @ 60°C (+273) if $Ea = 75.5$ kJ/mol?

$\ln\left(\frac{K_1}{K_2}\right) = \frac{Ea}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

$\ln\left(\frac{(2.75 \cdot 10^{-2})}{k_2}\right) = \frac{(75.5)(10^3)}{8.314}\left(\frac{1}{333} - \frac{1}{293}\right)$

$\ln\left(\frac{2.75 \cdot 10^{-2}}{k_2}\right) = -3.72$

to get rid of ln, raise both sides to e.

$\frac{2.75 \cdot 10^{-2}}{k_2} = e^{-3.72}$

$\frac{2.75 \cdot 10^{-2}}{k_2} = 0.0242$

$1.14\ s^{-1} = k_2$

Elementary RXN

Overall RXN: $NO_2 + CO \rightarrow NO + CO_2$

Rate = $k[NO_2]^2$

Elementary RXN - actual physical encounter between individual Molecules.

$A + B \rightarrow$ products

Represents Actual collision.

Rate = $k[A][B]$ • you can write rate law based on elementary RXN.

unimolecular: $A \rightarrow B$ ∴ Rate = $k[A]$

bimolecular: $A + A \rightarrow C + D$ ∴ Rate = $k[A]^2$

termolecular: $A + B + C \rightarrow$ products ∴ Rate = $k[A][B][C]$

(*) The Molecularity of an elementary RXN tells how many molecules are involved in that step of the Mechanism.

A 2 step Mechanism:

$NO_2 + CO \rightarrow NO + CO_2$

Step 1: $NO_2 + NO_2 \rightarrow NO + NO_3$

Step 2: $NO_3 + CO \rightarrow NO_2 + CO_2$

$NO_2 + CO \rightarrow NO + CO_2$

Intermediate bc it is produced and then used in second step.

(*) Mechanism - A set of steps that describe how the RXN occurs on a molecular level - makeup the overall RXN.

>> What Limits the Rate? <<

- The overall RXN cannot occur faster than the slowest RXN in mechanism = Rate determining step.

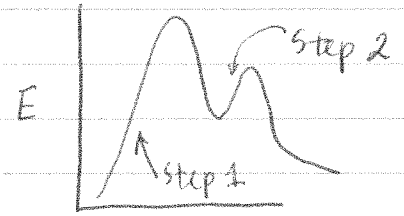
K_1: $NO_2 + NO_2 \rightarrow NO + NO_3$ ← slow

K_2: $NO_3 + CO \rightarrow NO_2 + CO_2$ ← fast

$NO_2 + CO \rightarrow NO + CO_2$

Rate = Rate of RDS

$= k_1[NO_2]^2$



>> Deducing Mechanisms <<

$H_2 + 2ICl \rightarrow I_2 + 2HCl$

$Rate = k[H_2][ICl]$

What is the Mechanism?

Step 1: $H_2 + ICl \rightarrow HCl + HI$ ← slow — HI: intermediate

Step 2: $HI + ICl \rightarrow HCl + I_2$

$H_2 + 2ICl \rightarrow I_2 + 2HCl$

Ex 2) $2NO + Br_2 \rightleftharpoons 2NOBr$

$NO + Br_2 \rightleftharpoons NOBr_2$

slow → $NOBr_2 + NO \rightarrow 2NOBr$

Rate determined here!

rate $= k[NO]^2[Br_2]$

(*) suggests that first step is not the slowest bc rate law is not simple!