

D. Arrhenius Equation

$$k = Ae^{-E_a/RT}$$

$R = \text{constant} = .00831$

$A = \text{constant unique to each reaction}$

- complex!

- Qual: ① larger $E_a \Rightarrow$ smaller k
 ② higher temp $\Rightarrow$ larger k

Math: $\ln$ both sides

graphical solution a) $\ln k = \frac{-E_a}{.00831} \left(\frac{1}{T} \right) + \ln A$

$y = mx + b$
 Graph k vs. $1/T$,
 $\Rightarrow$ solve for E_a and A

b) 2-Point Solution

$$\ln \left(\frac{k_2}{k_1} \right) = \frac{E_a}{.00831} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

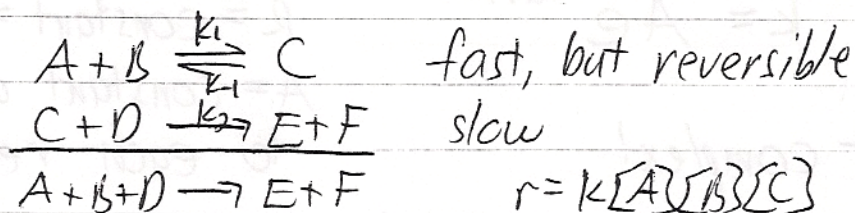
E_a in kJ/mol
 T in Kelvin

Applications

- ① Given k 's at 2 temps, can find E_a
- ② Given E_a and the k at one temp, can find the k at any other
- ③ Given E_a and the k_1 at one temp, then can find whatever temp is needed to produce a desired k_2 ($1/2$ or $1/10^{th}$ or 10 times faster...)

Derivation of Rate Law When 1st Step
Isn't Slow

13-22



- ① Intermediates (C) don't build up. They reach a steady state, (usually very low concentration) in which formation = destruction

rate formation = rate destruction

$$k_1[A][B] = k_{-1}[C] + k_2[C][D]$$

since step 2 is slow, it probably makes a small contribution to the rate of destruction and can be dropped.

$$\text{Thus } k_1[A][B] = k_{-1}[C]$$

$$\text{Rearranged: } [C] = \frac{k_1[A][B]}{k_{-1}}$$

$$\text{② Overall rate given by slow step: } r = k_2[C][D]$$

$$\text{Substituting for } [C] \quad r = \frac{k_2 k_1}{k_{-1}} [A][B][D]$$

since $\frac{k_2 k_1}{k_{-1}}$ is itself constant, overall

$$r = k' [A][B][D]$$