D. Arrhenius Equation

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

- complex!

R = constant = .00831

A = constant unique to each reaction

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

Math: ln both sides

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

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 (½ or $1/10^{th}$ or 10 times faster...)

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

$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C$ fast, but reversible

$C + D \xrightarrow{k_2} E + F$ slow

$A + B + D \longrightarrow E + F$ $\quad r = k[A][B][C]$

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.

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

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

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

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 $\boxed{r = k'[A][B][D]}$