Chem Lecture 04/03/14

Thinking like a chemist about Kinetics IV

Rxn coordinate

Quiz

① $A + B \rightarrow C$ (fast)

$C + B \rightarrow F$ (fast)

$F \rightarrow G$ (slow)

overall rxn? rate expressions

Answer: rate = $k[A][B]^2$

overal rxn ↓

$A + 2B \rightarrow G$

rate = $k[F]$

$[F] = k_2[B][C]$

$[C] = k_3[A][B]$

$[F] = k_2[B][A][B]$

$[F] = k[A][B]^2$

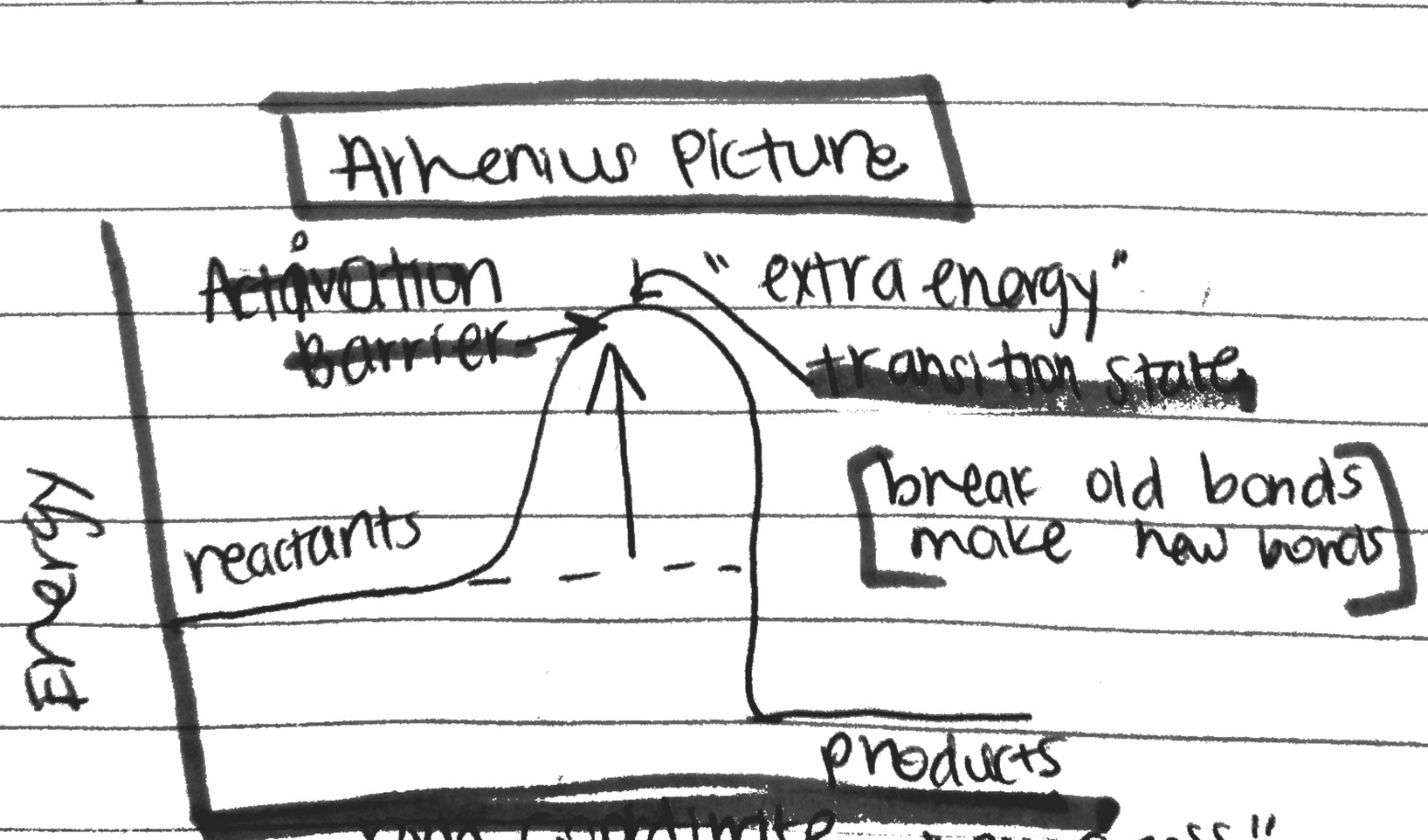
$rate = k[A][B]^2$

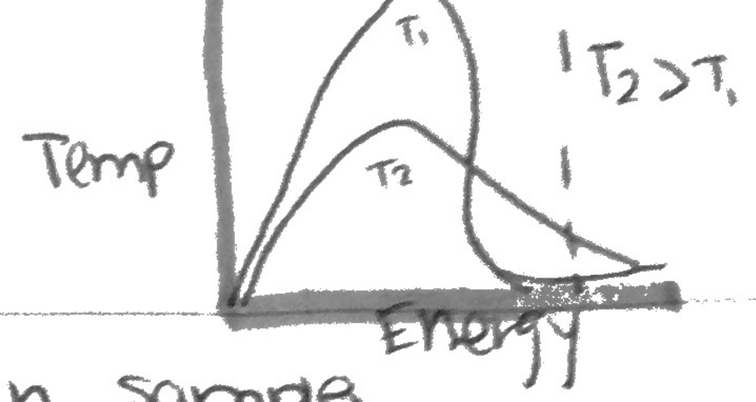
Factors that affect speed of rxn

- ~~Concentration~~ / Amount ("more stuff ⇒ faster) More collisio
  - Medium (compounds in contact) "collisions
  - Catalysts
  - Temp → rxns are faster @ ↑ temp "faster"

fine powder or hunk of rock?

Arhenius Picture





② Given Temp the molecule in sample
Ⓑ have distribution of energies

Arrhenius law

- rate constant (k) a function of temp.

pre exponential factor

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

fraction of molecules

* ↑ temp, the more molecule have enough energy to cross over barrier

Ⓐ rate @ infinite temp.
(not all interactions between molecules w/ sufficient energy will lead to products)

$$k = Ae^{-Ea/RT} \rightarrow \ln k = \ln A - Ea/RT$$

$$\ln k = \ln A + \left(\frac{Ea}{R}\right)\left(\frac{1}{T}\right)$$
$$y = b + m\,x$$

③ Activation Energy for rxn?

$$\text{slope} = -\frac{Ea}{R} = -1.2 \times 10^4$$

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

Ⓑ $1 \times 10^5 \frac{J}{mol}$

$$(-)\frac{+Ea}{8.314\frac{J}{kmol}} = -1.2 \times 10^4 \left(-\frac{}{kmol}\right)J$$

★ more molecules have "sufficient" energy to get over barrier = BIG effect

Transition State Theory

- only there for an extremely short time (higher barrier → slow)

$(CH_3)_3CCl + OH^- \longrightarrow (CH_3)_3C^+ + OH^- + Cl^-$ (1st step)

$Cl^- + OH^- + (CH_3)_3C^+ \longrightarrow (CH_3)_3COH + Cl^-$ (2nd step)

overall rxn: $(CH_3)_3CCl + OH^- \longrightarrow (CH_3)_3COH + Cl^-$

slowest step → highest barrier

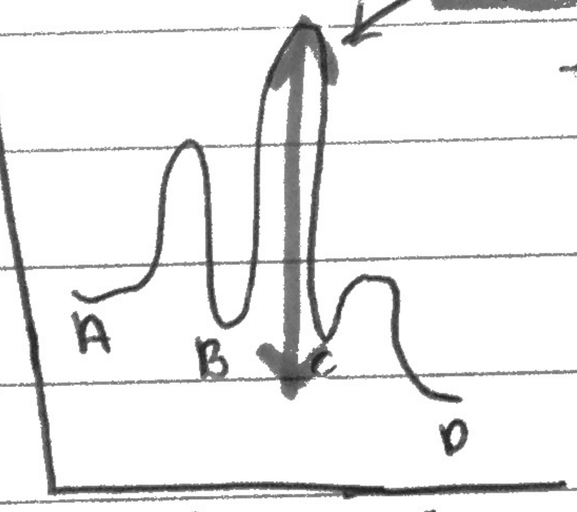
- 3 barriers (steps)
- 2 intermediates

Clickers

A → B

B → C

C → D



Overall rxn: A → D

★ Adding catalyst to rxn mixture changes activation energy

- catalyst: lowers the activation energy, not part of overall rxn
  - (ex) enzyme, speeds rxn process, not all used up (consumed)
  - changes the mechanism