ChE 344
Reaction Engineering and Design

Lecture 3: Thursday, Jan 13, 2022

Rate Laws

Reading for today's Lecture: Chapter 3

Reading for Lecture 4: Chapter 4.1, 4.2

Lecture 3: Introduction to Rate Laws
Related Text: Chapter 3

Space time: $\frac{V}{v_0} = \tau$; Space velocity $= \frac{1}{\tau}$

Reaction orders (overall reaction order determines units of rate constant)

$$-r_A = kC_A^{\alpha}C_B^{\beta}; n = \alpha + \beta$$

Elementary Rate Laws

Powers in the rate law agree with magnitude of stoichiometric coefficient of the reaction as written.

$$aA + bB \rightarrow C; \frac{-r_A}{a} = kC_A^{a}C_B^{b}$$

Relative rates (true even if the reaction is not elementary)

$$aA + bB \rightarrow cC + dD$$

$$\frac{r_j}{v_j} = r; r = \frac{r_A}{-a} = \frac{r_B}{-b} = \frac{r_C}{c} = \frac{r_D}{d}$$

v_j is the stoichiometric coefficient of species j. It is positive if j is a product, and negative if j is a reactant. For example, if the reaction is elementary 'as written' above:

$$r = \frac{-r_A}{a} = \frac{-r_B}{b} = \frac{r_C}{c} = \frac{r_D}{d} = kC_A^{a}C_B^{b}$$

Temperature dependence of rate constant (Arrhenius equation)

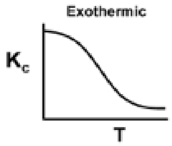
$$k(T) = A\exp\left(-\frac{E_a}{RT}\right) \quad \text{or} \quad k(T) = k(T_1)\exp\left(\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right)$$

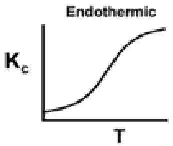
Arrhenius plot: $\ln(k) = \ln(A) - \frac{E_a}{R}\frac{1}{T}$

Temperature dependence of concentration equilibrium constant

$$K_C(T) = K_C(T_1)\exp\left[-\frac{\Delta H_{rxn}}{R}\left(\frac{1}{T} - \frac{1}{T_1}\right)\right]$$

Equilibrium constant can tell you whether a reaction is irreversible (→) or reversible (⇄).





Where do rate laws come from? (not covered in Lecture 3)

Collision theory: Frequency of collisions qualitatively gives you the frequency factor/pre-exponential factor for Arrhenius equation, and the concentration dependence (reaction orders).

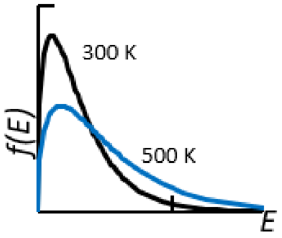
Maxwell-Boltzmann distribution gives you the probability of a collision having a certain energy.

$$f(E,T)dE = \frac{2\pi}{(\pi RT)^{3/2}}\exp\left[\frac{-E}{RT}\right]E^{1/2}dE$$

The integral of the probability gives you the fraction of collisions with energy above some threshold energy (E_a).

$$F(E > E_a, T) = \int_{E_a}^{\infty} f(E,T)dE = \frac{2}{\sqrt{\pi}}2\left(\frac{E_a}{RT}\right)^{1/2}\exp\left[\frac{-E_a}{RT}\right]$$

The $\exp\left[\frac{-E_a}{RT}\right]$ is where the exponential portion in the Arrhenius equation comes from! At higher temperatures, a higher fraction of molecular collisions have higher kinetic energies.



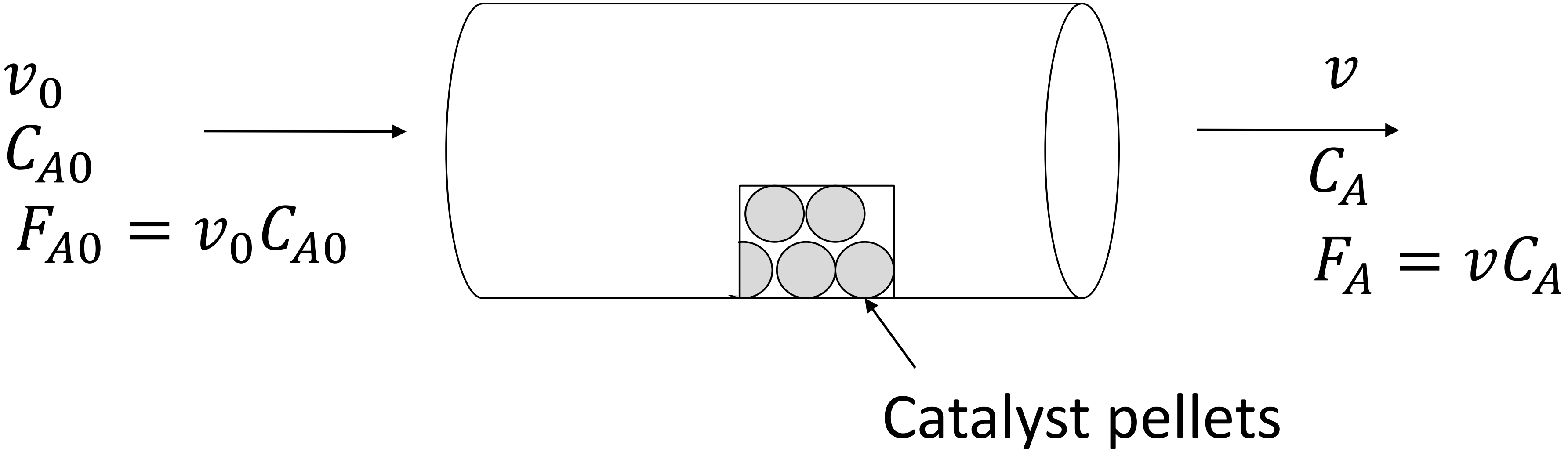
From Lecture 2: Design equation for a PBR using conversion.

How large does my PBR need to be to reach 80% conversion?

Same as PFR, just swap catalyst weight (W) for reactor volume and r_A' for r_A

$$\boxed{-r_A' = F_{A0}\frac{dX}{dW}}$$

$$\boxed{W_{PBR} = F_{A0}\int_0^X \frac{dX}{-r_A'}}$$

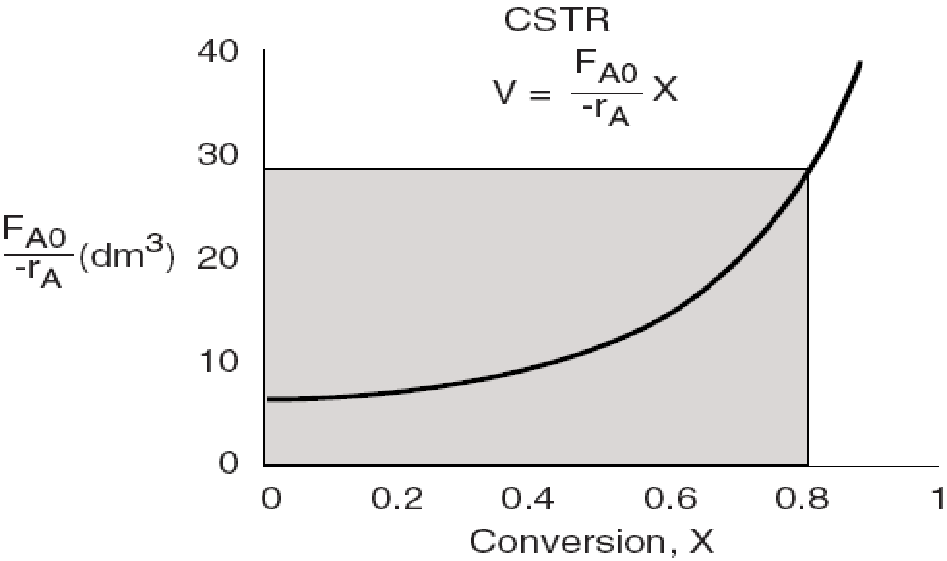


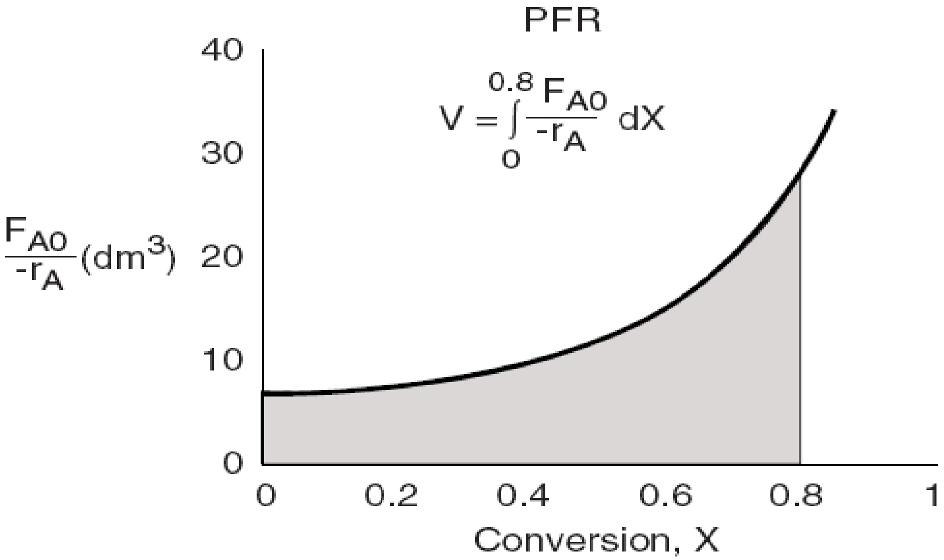
Last time: Generalized Mole Balance Equation in Conversion

$X \equiv$ moles A reacted / moles A fed

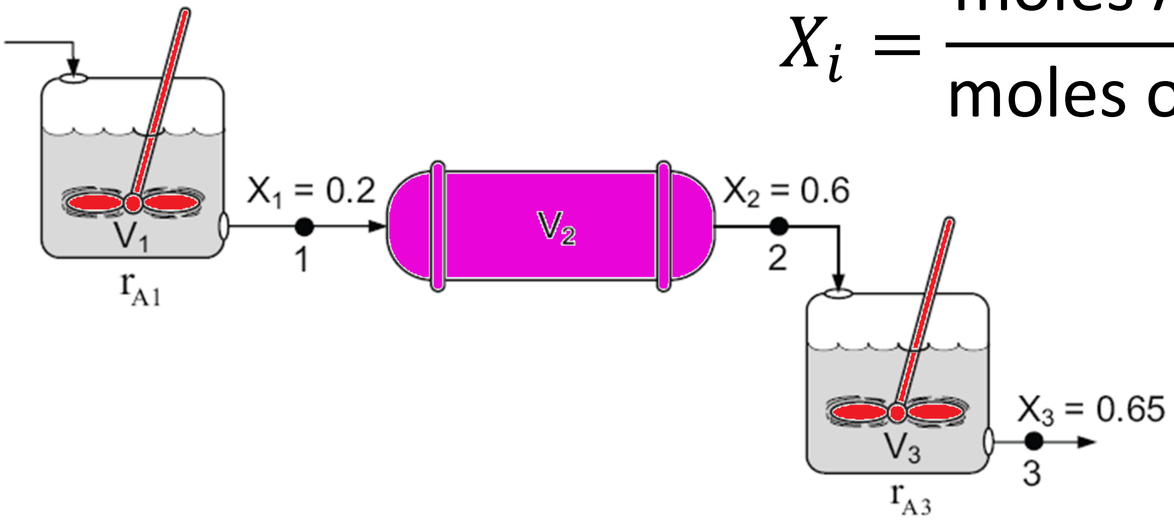
Reactor	Differential	Algebraic	Integral
Batch	$N_{A0}\frac{dX}{dt} = -r_A V$		$t = N_{A0}\int_0^X \frac{dX}{-r_A V}$
CSTR		$V_{CSTR} = \frac{F_{A0}X}{-r_A}$	
PFR	$F_{A0}\frac{dX}{dV} = -r_A$		$V_{PFR} = F_{A0}\int_0^X \frac{dX}{-r_A}$
PBR	$-r'_A = F_{A0}\frac{dX}{dW}$		$W_{PBR} = F_{A0}\int_0^X \frac{dX}{-r'_A}$

Last time, Levenspiel plots





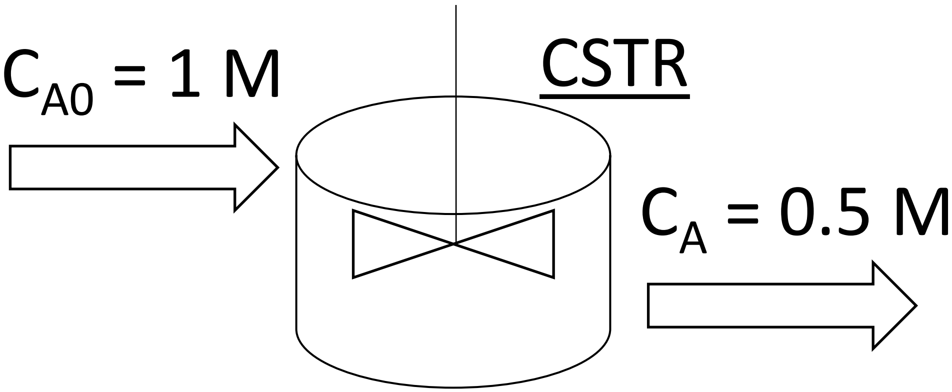
Levenspiel plots can also be used for reactors in series



$$X_i = \frac{\text{moles A reacted up to point i}}{\text{moles of A fed to first reactor}}$$

Only valid if there are no side streams

Conceptually: Why different volumes for the same X in a CSTR vs. PFR? Let's look at the reactor concentration for a simple reaction where we want to X = 0.5: $A \rightarrow B$

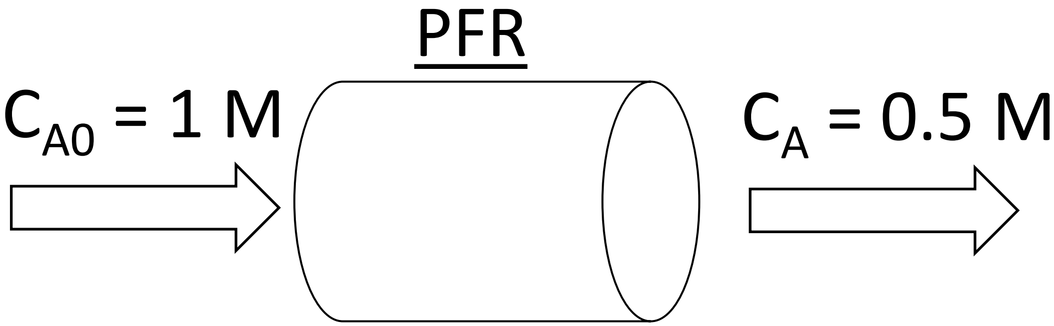


C_{A0} = 1 M

CSTR

C_A = 0.5 M

Rate in **all** of the reactor calculated at C_A = 0.5 M



PFR

C_{A0} = 1 M

C_A = 0.5 M

Rate in the reactor calculated at $C_A > 0.5$ M (depending where you are in reactor)

If higher C_A increases the rate of reaction (positive order) the rate will be overall higher in a PFR! Less volume needed

Sometimes rather than volume we will use “space time” in flow reactors: Time to process one reactor volume of fluid

For liquid phase:

A → B

Say CSTR:

$$V_{CSTR} = \frac{F_{j0} - F_j}{-r_j}$$

In liquid phase there is no expansion due to change in number of moles so v=v_0.

$$\frac{F_{A0}X}{kC_{A0}(1-X)} = \frac{Xv_0}{k(1-X)}$$

Can get (for liquid phase CSTR):

$$\overbrace{\left(\frac{V_{CSTR}}{v_0}\right)}^{\tau \equiv space\ time} = \frac{X}{k(1-X)}$$

Here spacetime is how long to replace one volume of CSTR.

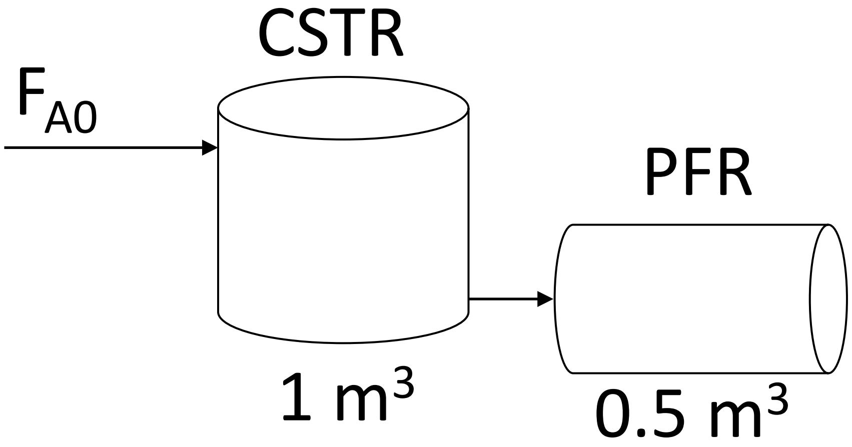
For a PFR it is how long a ‘plug’ takes to go through a PFR

(defined same way $\frac{V_{PFR}}{v_0}$).

$$\frac{1}{\tau} = space\ velocity$$

Sometimes called LHSV, liquid hourly space velocity, while GHSV is the gas hourly space velocity.

Example problem: CSTR and PFR in series (order matters!)



$F_{A0} = 1$ mol/min

$v_0 = 1\ m^3$/min

$$C_{A0}v_0 = F_{A0}$$

A → B, 1st order in A

$k = 1\ min^{-1}$

$$V_{CSTR} = \frac{F_{A0}(X_{out} - X_{in})}{-r_A} = \frac{F_{A0}(X_{out} - X_{in})}{kC_{A0}(1 - X_{out})} = \frac{v_0(X_{out} - X_{in})}{k\ (1 - X_{out})}$$

$$kV_{CSTR} = v_0(X_{out} - X_{in}) + kX_{out}V_{CSTR}$$

$$kV_{CSTR} + v_0X_{in} = (v_0 + kV_{CSTR})X_{out}$$

$$\frac{kV_{CSTR} + v_0 X_{in}}{v_0 + kV_{CSTR}} = X_{out}$$

$$\frac{1(1) + 1(0)}{1 + 1(1)} = 0.5 = X_{out}$$

Could solve second reactor as a fresh reactor (new F_{A0}, F_{B0}, reset X to 0, then solve), or could continue (but don't mix and match!)

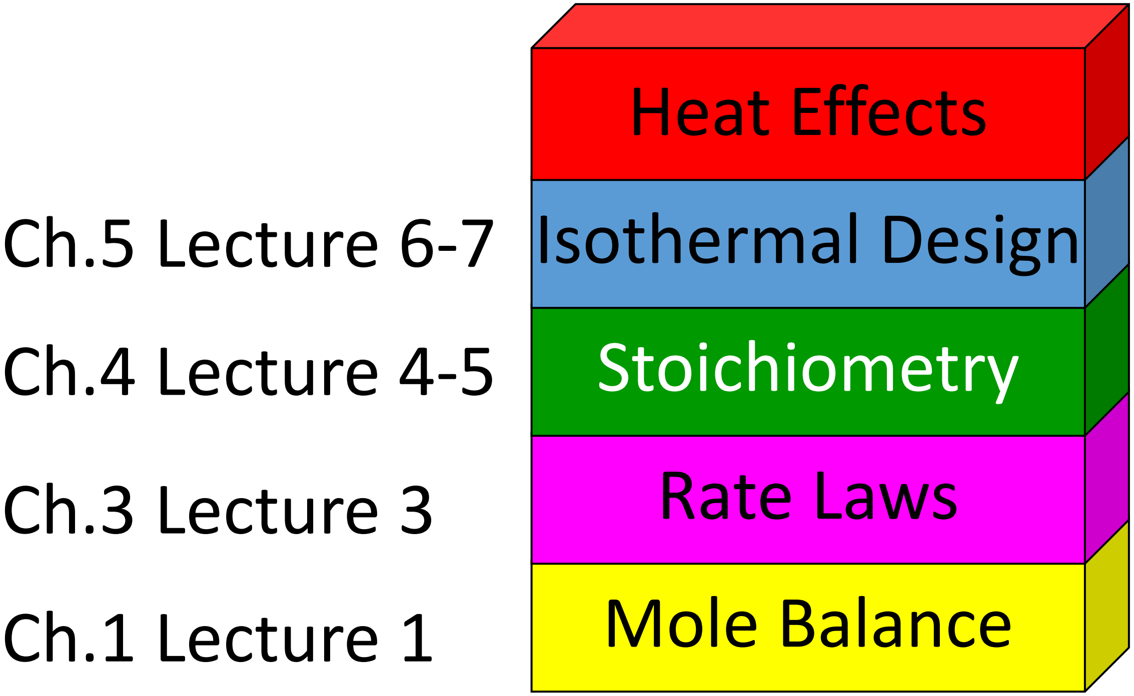
$$V_{PFR} = \int_{X_{in}}^{X_{out}} \frac{-F_{A0}}{r_A} dX = \int_{\underset{\nwarrow 0.5}{X_{in}}}^{X_{out}} \frac{v_0}{k\,(1 - X)} dX$$

$$= \int_{X_{in}}^{X_{out}} \frac{1}{(1 - X)} dX = -\ln(1 - X_{out}) + \ln(1 - X_{in})$$

$$X_{out} = 1 - \exp\left[\ln(1 - X_{in}) - k\frac{V_{PFR}}{v_0}\right]$$

Today: Continuing in our Chemical Reacting Engineering algorithm with Rate Laws

Remember they show us the shape of Levenspiel plots!



Heat Effects

Ch.5 Lecture 6-7 Isothermal Design

Ch.4 Lecture 4-5 Stoichiometry

Ch.3 Lecture 3 Rate Laws

Ch.1 Lecture 1 Mole Balance

Why are rate laws important?

We need $r_A = f(X)$ to be able to determine reactor sizes needed to reach a certain conversion.

$$-r_A = [k(\mathrm{T})][\mathrm{f}(C_A, C_B\ldots)]$$

Recall that k is our rate ‘constant’ (but actually a function of temperature as we will learn today)

$C_i = f(X)$

As your reaction proceeds (conversion increases), naturally the concentrations will change! A rate law allows you to understand how this change influences your rate

For a generic reaction

aA + bB ⇄ cC + dD

Power law

$$-\frac{r_A}{a} = kC_A^{\alpha}C_B^{\beta}$$

α is reaction order in A

β is reaction order in B

Overall order is $n = \alpha + \beta$

Elementary rate law

The powers in the rate law agree with the magnitude of the stoichiometric coefficient (i.e., α = a, β = b)

Example: 1A + 2B → C

$$-r_A = kC_A^1C_B^2 = kC_AC_B^2$$

We would say A is first order and B is second order

C is zero order

Many reactions are non-elementary and may have complex relations with concentrations

(Just a simplified example, we won’t derive until we discuss catalysis later in the course)

$$-r_A = k\frac{C_A C_B}{(1 + C_A + C_B)^2}$$

If $C_A \gg C_B + 1$

$$-r_A \approx k\frac{C_A C_B}{(C_A)^2}$$

$$-r_A \approx k(C_A)^{-1}C_B$$

Negative one order in A when C_A is high!

If $C_A \ll C_B + 1$

$$-r_A \approx k\frac{C_A C_B}{(1 + C_B)^2}$$

$$-r_A \approx kC_A\frac{C_B}{(1 + C_B)^2}$$

Positive one order in A when C_A is low!

Units of rate constant *k* are determined by order of reaction!

Recall: reaction rate has units mol/(volume*time)

Concentration has units of mol/volume

Zero order overall

$-r_A = k$

k has units of mol/(volume*time)

First order overall

$-r_A = kC_A^1$

k has units of (time^{-1})

Second order overall

$-r_A = kC_A^1 C_B^1$

k has units of volume/(mol*time)

$-r_A = kC_A^2$

Discuss with your neighbors:

You are running the following reaction in a flow reactor, and when you decrease C_A (without changing anything else), your amount of B produced per hour goes down. Which of the following *cannot* be the rate law?

$$A \rightarrow B$$

A) $r_A = -kC_A$ ← Elementary

[✓ B) $r_A = -k$]

Positive non-zero order only

C) $r_A = -k(C_A)^{3/2}$

D) $r_A = -k(C_A)^{1/2}$

Recall relative rates $r_j = \nu_j r$ where r is the rate of reaction

aA + bB ⇄ cC + dD

Stoichiometric coefficient of j

$$\frac{-r_A}{a} = \frac{-r_B}{b} = \frac{r_C}{c} = \frac{r_D}{d}$$

Example: Elementary rate law $A + 2B \rightarrow 4C$

$$\frac{-r_A}{1} = \frac{-r_B}{2} = \frac{r_C}{4}$$

In the book, Prof Fogler uses rate constants with a subscript

$$-r_A = k_A C_A C_B^2;\ -r_B = k_B C_A C_B^2;\ r_C = k_C C_A C_B^2 = 4k_A C_A C_B^2$$

In lecture slides I will use a single rate constant relative to the written reaction.

$$r_A = \nu_A k C_A C_B^2 = -k C_A C_B^2$$
$$r_B = \nu_B k C_A C_B^2 = -2k C_A C_B^2$$
$$r_C = \nu_C k C_A C_B^2 = 4k C_A C_B^2$$

How about moving from irreversible to reversible reactions?

$\rightarrow$ $\rightleftarrows$

$$\mathrm{k}_{\mathrm{forward}} = k_f$$

$$2A + B \rightleftarrows 3C$$

$$\mathrm{k}_{\mathrm{reverse}} = k_r$$

If elementary rate law:

$$\frac{r_A}{-2} = \frac{r_B}{-1} = \frac{r_C}{3} = k_f C_A^2 C_B - k_r C_C^3 = k_f \left[C_A^2 C_B - \frac{C_C^3}{k_f / k_r} \right]$$

$$= k_f \left[C_A^2 C_B - \frac{C_C^3}{K_C} \right]$$

$$K_C = k_f / k_r$$

Conc. equilibrium constant

If elementary!

If K_C is very large, $k_f \gg k_r$, and the reaction can be assumed to be irreversible!

From thermodynamics:

Equilib. concentrations

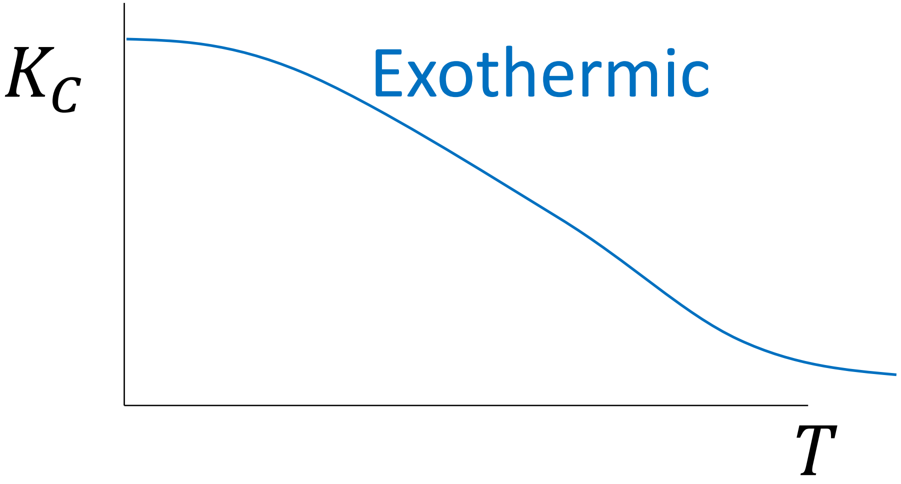
$$K_C = \prod_i C_{i,eq}^{\nu_i} = \frac{C_{C,eq}^3}{C_{A,eq}^2 C_{B,eq}}$$

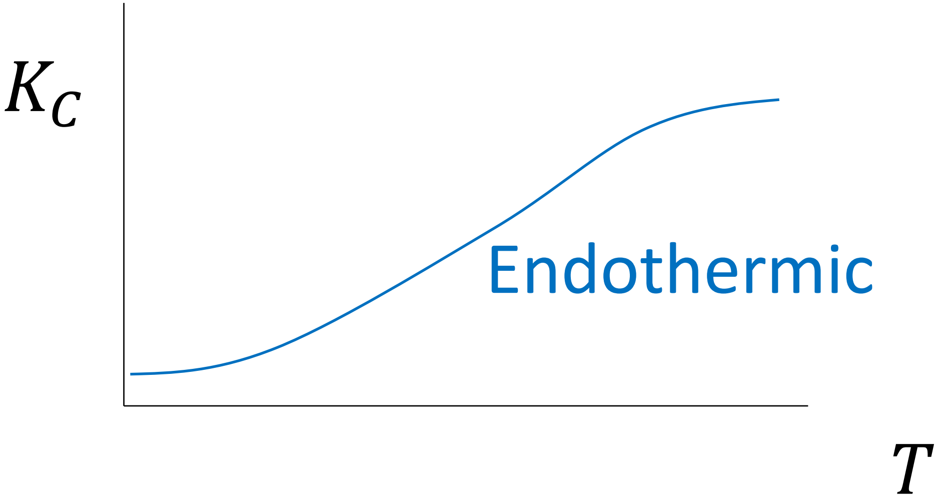
If K_C is very large, $C_{B,eq}$ and $C_{A,eq}$ approach zero (X → 1)

$$K_C(T) = K_C(T_1)\exp\left[-\frac{\Delta H_{rxn}}{R}\left(\frac{1}{T} - \frac{1}{T_1}\right)\right]$$

An exothermic reaction has a ΔH_{rxn} that is negative.

An endothermic reaction has a ΔH_{rxn} that is positive.





$$K_C = \frac{C_{C,eq}^3}{C_{A,eq}^2 C_{B,eq}}$$

$$-\frac{r_A}{2} = k_f \left[C_A^2 C_B - \frac{C_C^3}{K_C} \right] = k_f C_A^2 C_B - k_r C_C^3$$

At equilibrium, no reaction: $r_A = 0$

$$C_{A,eq}^2 C_{B,eq} = \frac{C_{C,eq}^3}{K_C}$$

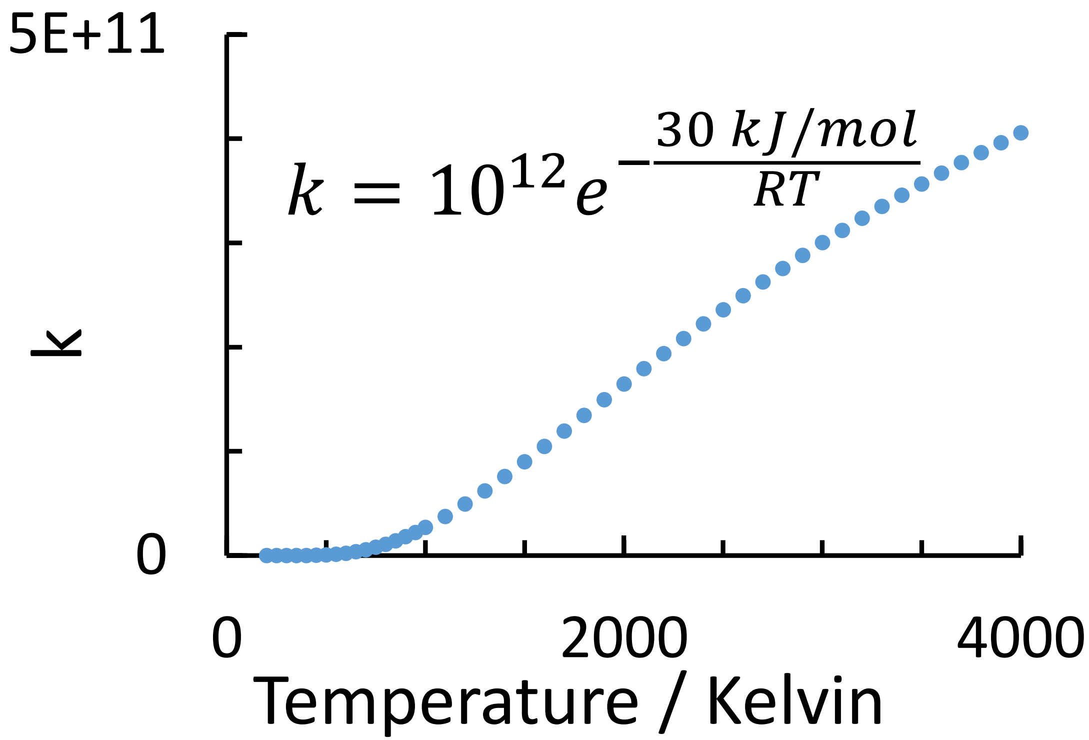
$$K_C = \frac{C_{C,eq}^3}{C_{A,eq}^2 C_{B,eq}}$$

Same for an elementary reaction!

Reaction rates depend on temperature through rate constant

Arrhenius equation

$$k = Ae^{-\frac{E_a}{RT}}$$



A = Preexponential factor/frequency factor (same units as k)

R = ideal gas constant, 8.314 J mol^{-1} K^{-1}

E_a = activation energy, units J mol^{-1} (or kJ/mol)

T in Kelvin (important it is in absolute temp!)

Often, you will have information about k at a given temperature, but need to know it at a different temperature.

For *k* that is known at a given temperature T_1

$$k(T_1) = A\exp\left(-\frac{E_a}{RT_1}\right)$$

You can solve for *k* at a temperature T

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

$$\frac{k(T)}{k(T_1)} = \frac{A}{A}\frac{\exp\left(-\frac{E_a}{RT}\right)}{\exp\left(-\frac{E_a}{RT_1}\right)} = \exp\left(\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right)$$

$$k(T) = k(T_1)\exp\left(\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right)$$

E_a is essentially always positive. With this in mind…

Discuss with your neighbors:

The rate constant, *k*, at 300 Kelvin is 1 s^{-1}. The activation energy, E_a, is 99.6 kJ/mol. What is k at 350 Kelvin? Hint: You should not need a calculator (but feel free to if you want).

$$k(T) = k(T_1)\exp\left(\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right)$$

[✓ A) 300 s^{-1}]

B) 300 $\text{M}^{-1}\ \text{s}^{-1}$

C) 0.1 s^{-1}

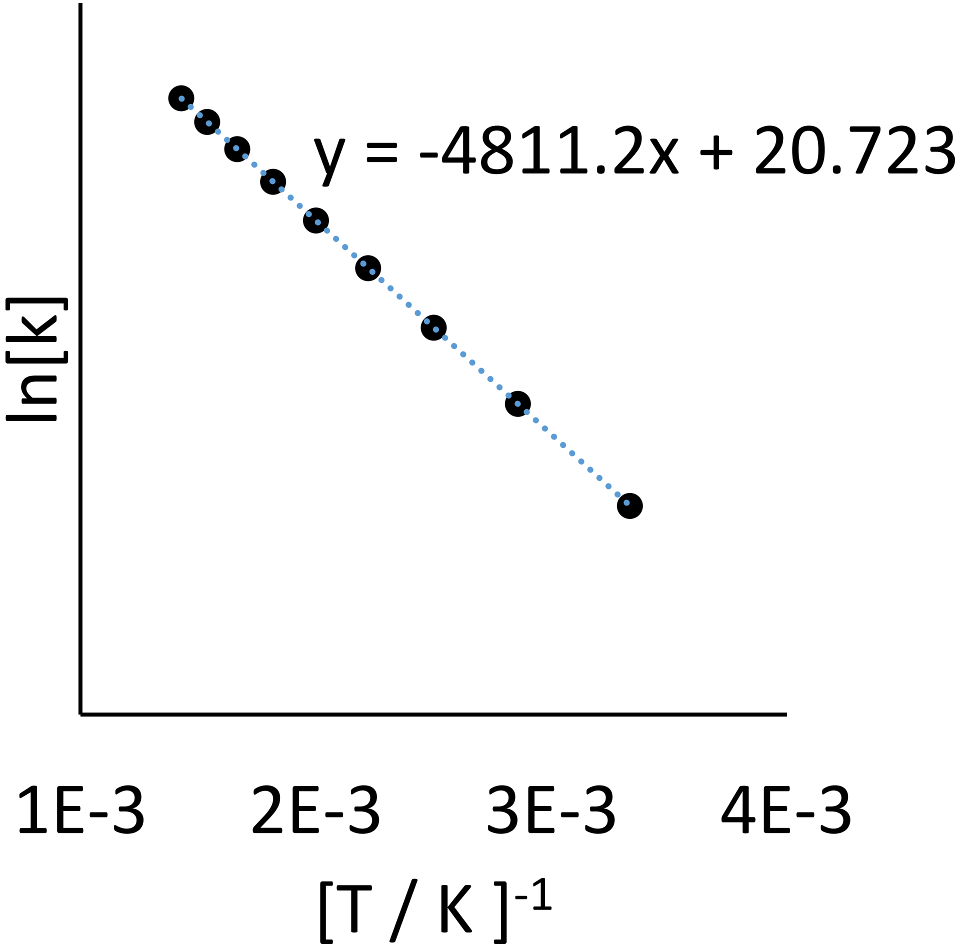
D) 0.0033 s^{-1}

Won’t change units, positive E_a means rate constant goes up with temperature

$$= 1s^{-1}\exp\left(\frac{99.6\ kJmol^{-1}}{8.314\ J\ mol^{-1}K^{-1}}\right.$$

$$\left. * \left(\frac{1}{300\ K} - \frac{1}{350\ K}\right)\right)$$

The effective activation barrier can be extracted using an Arrhenius plot



$$k = Ae^{-\frac{E_a}{RT}}$$

$$\ln[k] = \ln\left[Ae^{-\frac{E_a}{RT}}\right]$$

$$\ln[k] = \ln[A] - \frac{E_a}{RT}$$

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

$-E_a/R = -4811.2$

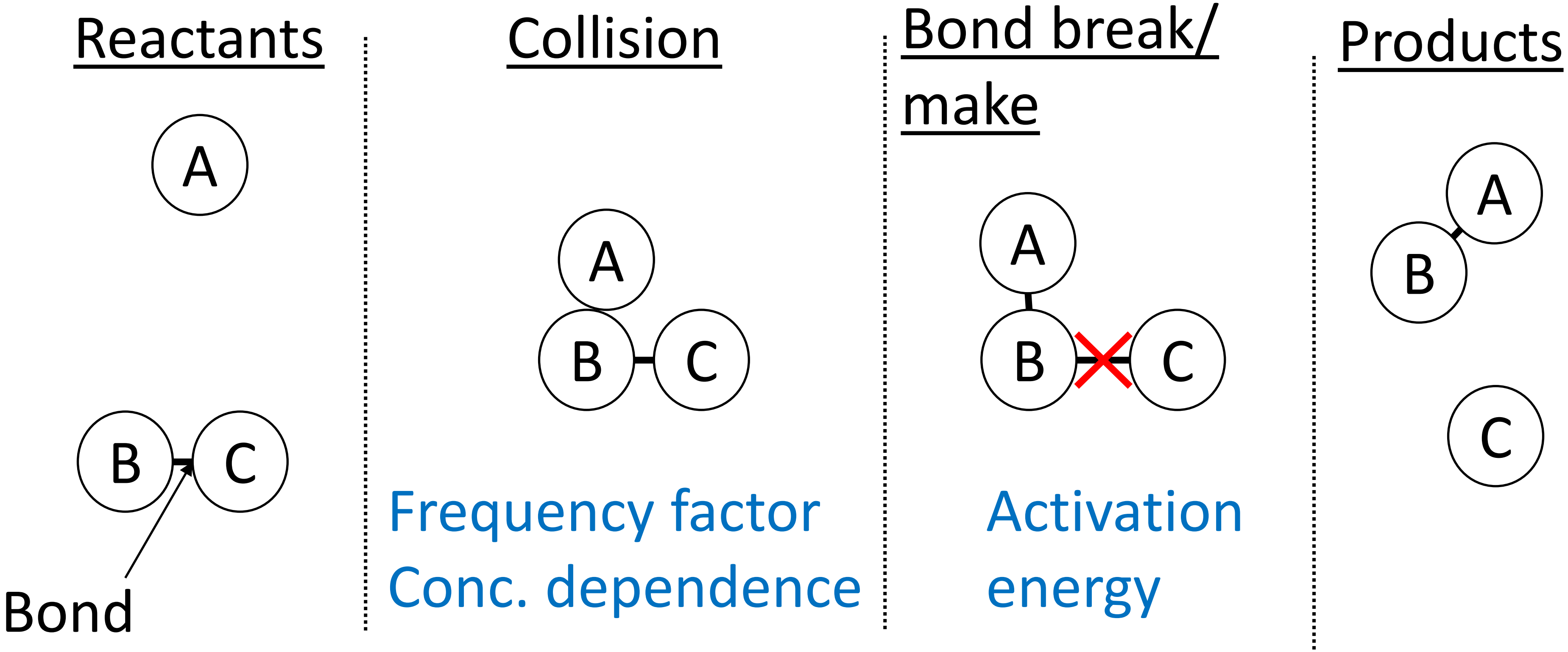
$E_a = 40\ \mathrm{kJ\ mol^{-1}}$

Why do rate laws have the form we see and why is there an activation energy? One way to think about it.

Qualitatively it is because the reactants must:

1. collide (higher concentration = more chance for collisions)
2. break/make new bonds which takes energy (E_a)!

$$A + BC \longrightarrow AB + C$$



Reactants

Bond

Collision

Frequency factor
Conc. dependence

Bond break/make

Activation energy

Products

The energy to make/break bonds comes from the kinetic energy of the molecules when they collide.
The distribution of velocities of the reacting molecules relative to one another is given by the Boltzmann distribution.

$$f(U,T) = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left[\frac{-mU^2}{2k_B T}\right] U^2$$

k_B = Boltzmann's constant = 1.38 x 10^{-23} J/molecule/K
m = Reduced mass, *g*
U = Relative velocity, *m/s*
T = Absolute Temperature, K
$f(U,T)$ = distribution of relative velocities
$f(U,T)\mathrm{d}U$ = fraction of relative velocities from U to $U+\mathrm{d}U$

$$f(U,T) = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left[\frac{-mU^2}{2k_B T}\right] U^2$$

e = Kinetic energy per molecule (not mole)

e = ½ *mU*^{2}

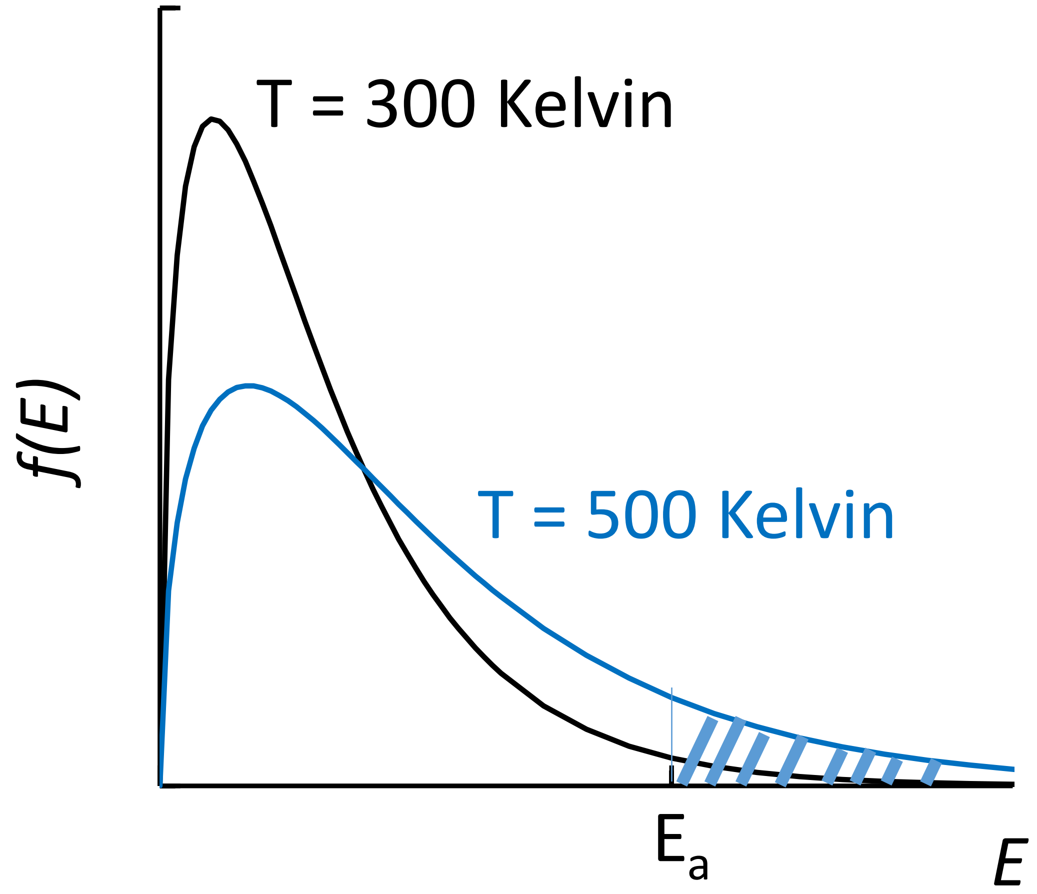
$$f(e,T) = \frac{2\pi}{(\pi k_B T)^{3/2}} \exp\left[\frac{-e}{k_B T}\right] e^{1/2}$$

Switch *e* (kJ/molecule) to *E* (kJ/mol), and k_B to *R*

$$f(E,T) = \frac{2\pi}{(\pi RT)^{3/2}} \exp\left[\frac{-E}{RT}\right] E^{1/2}$$

$$f(E,T)dE = \frac{2\pi}{(\pi RT)^{3/2}} \exp\left[\frac{-E}{RT}\right] E^{1/2} dE$$

Fraction of collisions with energy E and E + dE



Fraction of molecules with energy E > E_a

$$F(E > E_a, T) = \int_{E_a}^{\infty} f(E,T)dE$$

Fraction of collisions with energy greater than E_a

$$F(E > E_a, T) = \frac{2}{\sqrt{\pi}} 2 \left(\frac{E_a}{RT}\right)^{1/2} \boxed{\exp\left[\frac{-E_a}{RT}\right]}$$

Back to Arrhenius equation:

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

Collisions, or opportunities to react per time

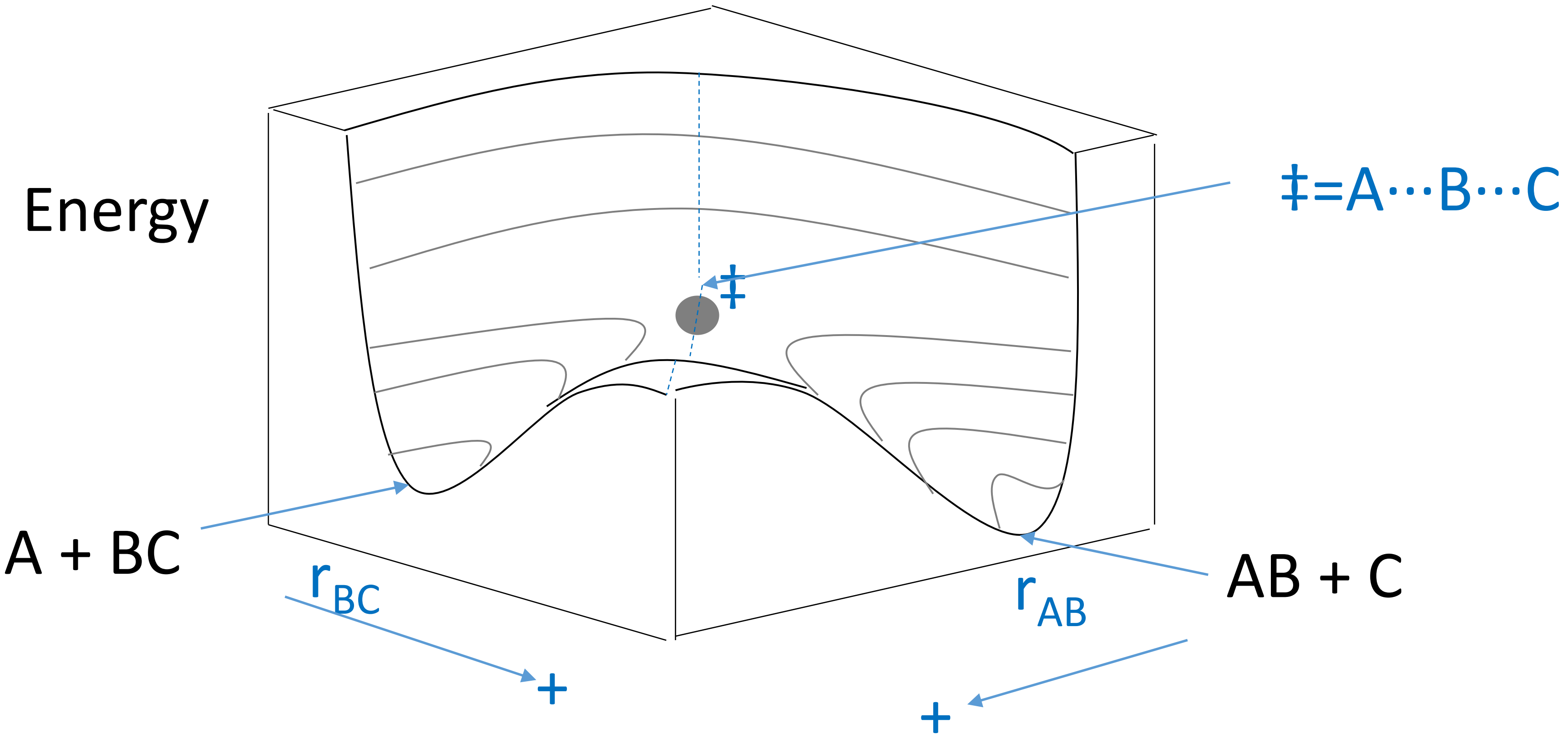
Fraction of opportunities that result in a reaction

Rate constant will never exceed *A*, because as $T \to \infty$, $\exp\left(-\frac{E_a}{RT}\right) \to 1$

Another way to explain Arrhenius- Potential Energy Surface:

Every configuration has an associated energy.

$$A + BC \rightarrow \ddagger \rightarrow AB + C$$



r_{BC} is the distance between B and C

The transition state (‡) is the highest energy position along the lowest energy pathway from reactant to product