ChE 344
Reaction Engineering and Design

Lecture 4: Tuesday, Jan 18, 2022

Stoichiometry tables, $C_A = f(X)$

Reading for today's Lecture: Chapter 4.1, 4.2

Reading for Lecture 5: Chapter 4.3

Lecture 4: Stoichiometry and relation of concentration to conversion
Related Text: Chapter 4.1-4.2

Variables

For a reaction with A as the limiting reactant:

$$aA + bB \longrightarrow cC + dD$$

$$\frac{a}{a}A + \frac{b}{a}B \longrightarrow \frac{c}{a}C + \frac{d}{a}D$$

$$\delta = \frac{\text{change in number of moles with reaction}}{\text{moles A reacted}} = \frac{c + d - b - a}{a}$$

$$y_{A0} \equiv \frac{P_{A0}}{P_0} = \frac{N_{A0}}{N_{T0}} = \frac{F_{A0}}{F_{T0}}$$

$$\varepsilon = y_{A0}\delta$$

$$\theta_j = \frac{\text{initial/inlet number of moles "j"}}{\text{initial/inlet number of moles "A"}} = \frac{N_{j0}}{N_{A0}} = \frac{F_{j0}}{F_{A0}} = \frac{C_{j0}}{C_{A0}} = \frac{y_{j0}}{y_{A0}}$$

Stoichiometry Tables (for A as limiting reactant)

Batch

Species	Symbol	Initial	Change	Remaining
Reactant A	A	N_{A0}	$-N_{A0}X$	$N_A = N_{A0}(1-X)$
Reactant B	B	$N_{A0}\Theta_B$	$-b/a\ N_{A0}X$	$N_B = N_{A0}(\Theta_B - b/a\ X)$
Product C	C	$N_{A0}\Theta_C$	$+c/a\ N_{A0}X$	$N_C = N_{A0}(\Theta_C + c/a\ X)$
Product D	D	$N_{A0}\Theta_D$	$+d/a\ N_{A0}X$	$N_D = N_{A0}(\Theta_D + d/a\ X)$
Inert	I	$N_{A0}\Theta_I$		$N_{A0}\Theta_I$
Total		N_{T0}		$N_T = N_{T0}(1+\varepsilon X)$

Flow

Species	Symbol	Inlet	Change	Outlet
Reactant A	A	F_{A0}	$-F_{A0}X$	$F_A = F_{A0}(1-X)$
Reactant B	B	$F_{A0}\Theta_B$	$-b/a\ F_{A0}X$	$F_B = F_{A0}(\Theta_B - b/a\ X)$
Product C	C	$F_{A0}\Theta_C$	$+c/a\ F_{A0}X$	$F_C = F_{A0}(\Theta_C + c/a\ X)$
Product D	D	$F_{A0}\Theta_D$	$+d/a\ F_{A0}X$	$F_D = F_{A0}(\Theta_D + d/a\ X)$
Inert	I	$F_{A0}\Theta_I$		$F_{A0}\Theta_I$
Total		F_{T0}		$F_T = F_{T0}(1+\varepsilon X)$

For gas-phase, volume can change. No change in volume for liquid!

$$V = V_0\frac{N_T}{N_{T0}}\frac{T}{T_0}\frac{P_0}{P};\ v = v_0\frac{F_T}{F_{T0}}\frac{T}{T_0}\frac{P_0}{P};\ C_A = C_{A0}\frac{(1-X)}{1+\varepsilon X}\frac{T_0}{T}\frac{P}{P_0};\ C_j = C_{A0}\frac{(\theta_j - \frac{\nu_j}{\nu_A}X)}{1+\varepsilon X}\frac{T_0}{T}\frac{P}{P_0}$$

In the final equation, for C_j, remember if we write the reaction in terms of limiting reactant A, $\nu_A = -1$.

Last time, rate laws.

Power law

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

α is reaction order in A

β is reaction order in B

Gives units for *k* → 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) as written

Non-elementary reactions

Where rate law is different than from stoichiometry.

For non-elementary reactions, can have negative orders.

Discuss with your neighbors:

For A → B, in a flow reactor, for a given conversion, under which conditions is $V_{CSTR} < V_{PFR}$?

$$V_{PFR} = \int_0^X \frac{-F_{A0}}{r_A} dX$$

$$V_{CSTR} = \frac{F_{A0} X}{-r_A}$$

A) Zero order in A $\quad r_A = -k$

B) First order in A $\quad r_A = -kC_A$

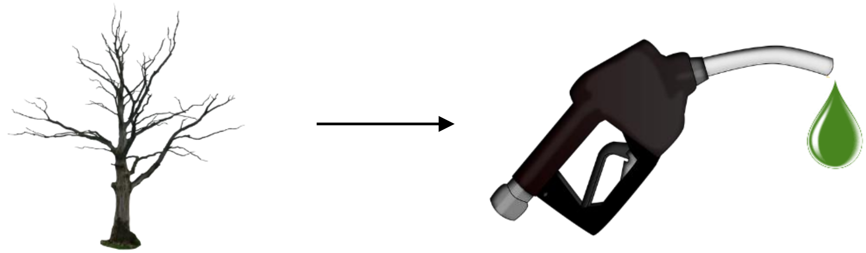
C) Order = -1 in A $\quad r_A = -kC_A{}^{-1}$

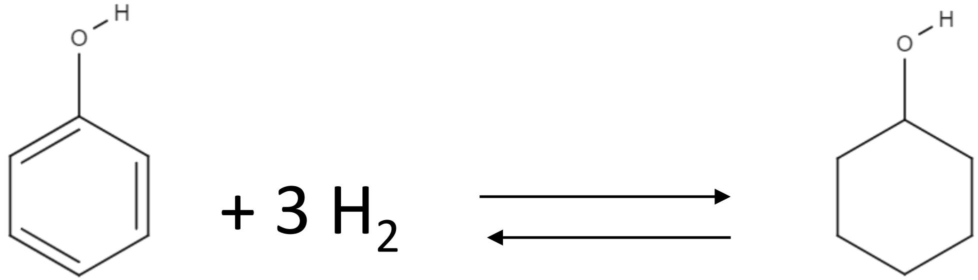
D) Second order in A $\quad r_A = -kC_A{}^2$

Another way to think about this, as soon as A enters the CSTR its concentration decreases to that of outlet. This is good (faster reaction) only if the order in A is negative!

Question: When is K_C "large enough"?

Example: Hydrogenation of model compounds of lignin.

Waste Biomass  Renewable Fuel



$A \quad + 3B$ ~~$\rightleftarrows$~~ $\rightarrow \quad C$

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

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

K_C >2000 at room temperature, I could not detect the reverse reaction, or any reactants at equilibrium (X ≈ 1 at equilib.).

However, at ~300 °C, K_C is only ~0.03! Exothermic

Temperature considerations: Conc. equilib. constant

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

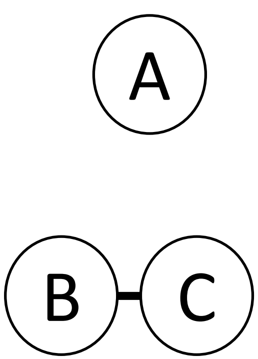
Temperature dependence for rate constant (Arrhenius eqn.)

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

Where does this T dep. of k come from?

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

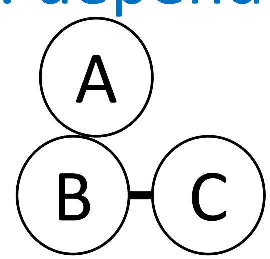
<u>Reactants</u>



<u>Collision</u>

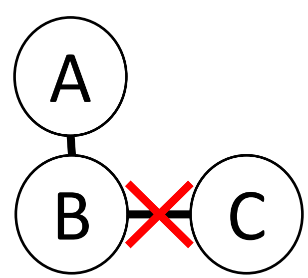
Freq. factor (A)

Conc. dependence

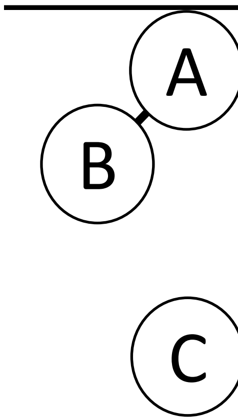


<u>Bonds break/make</u>

Activation energy (E_a)



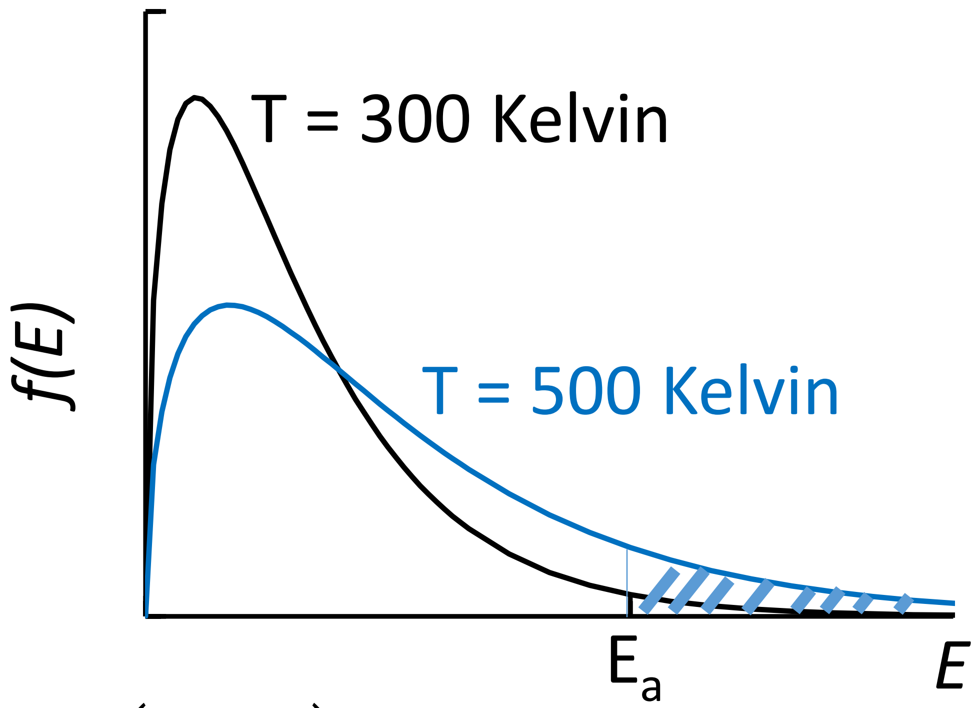
<u>Products</u>



Maxwell Boltzmann energy distribution (temp. dependent)

Fraction of molecules with energy $E > E_a$

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



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

Collisions, or opportunities to react per time (A)

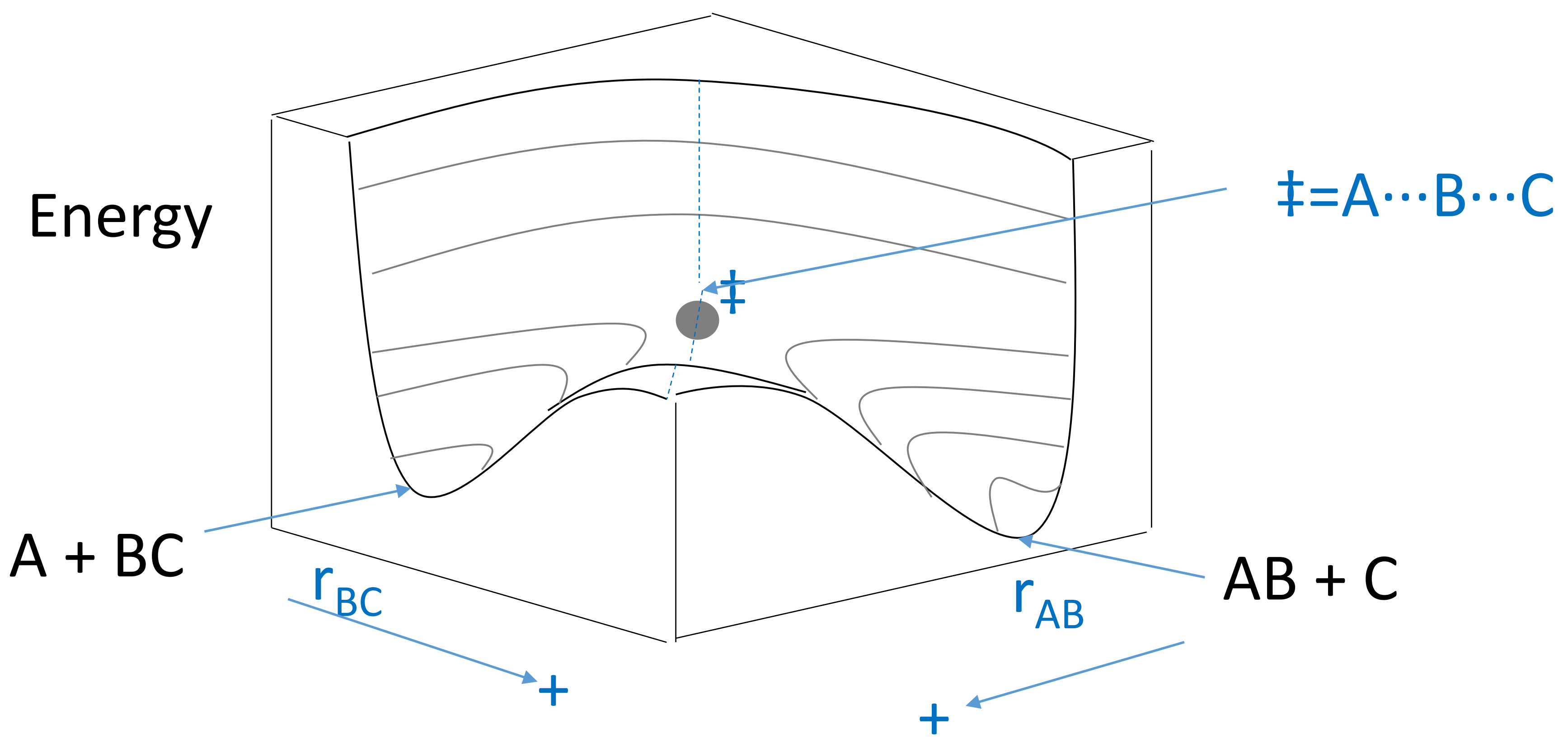
Fraction of opportunities that result in a reaction ($\exp\left(-\frac{E_a}{RT}\right)$)

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:

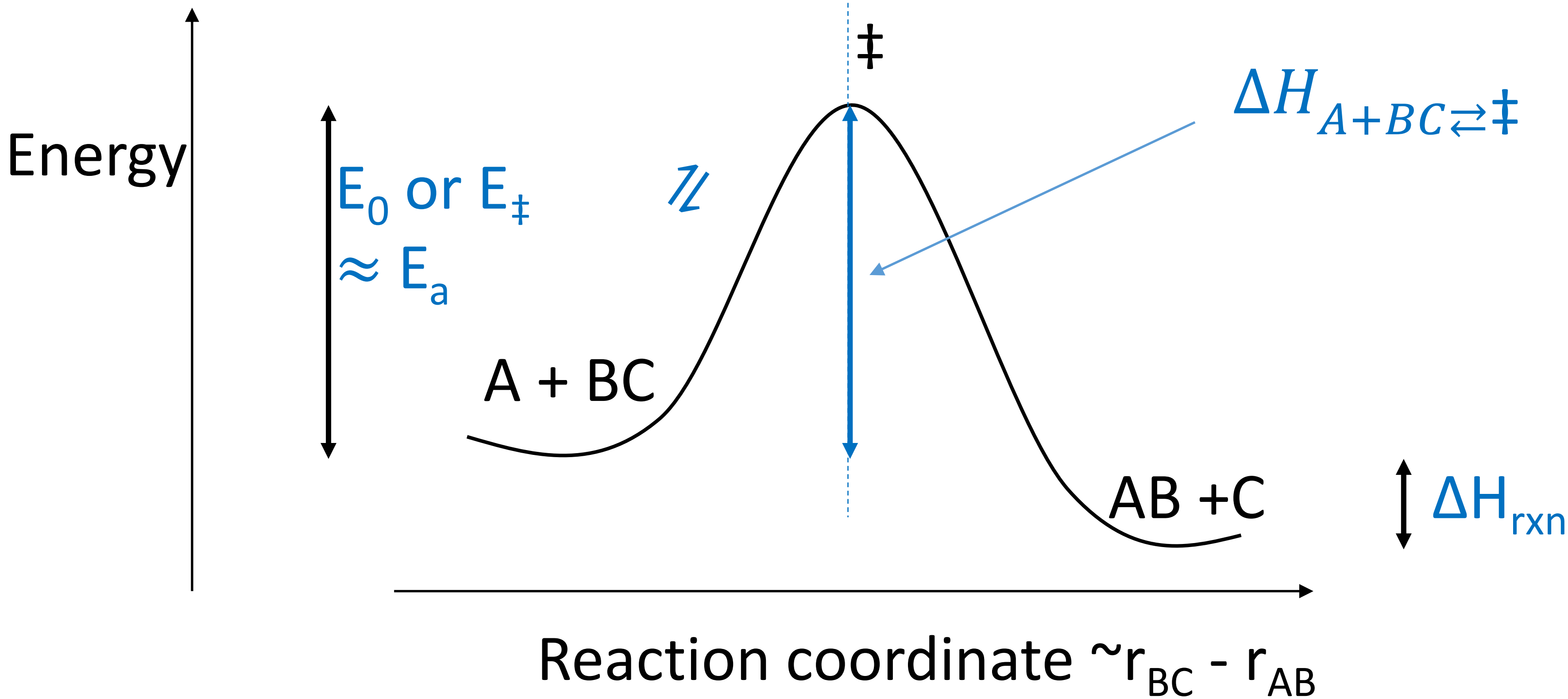
Every configuration has an associated energy.

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



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



Reaction coordinate: Way of saying how far along is an <u>individual</u> molecular reaction (different than conversion!)

- Here it might be is atom B closer to C (like the reactant) or closer to A (like the product)

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

$$A + BC \rightleftarrows \ddagger$$

$$\Delta H_{A+BC \rightleftarrows \ddagger} \approx E_a$$

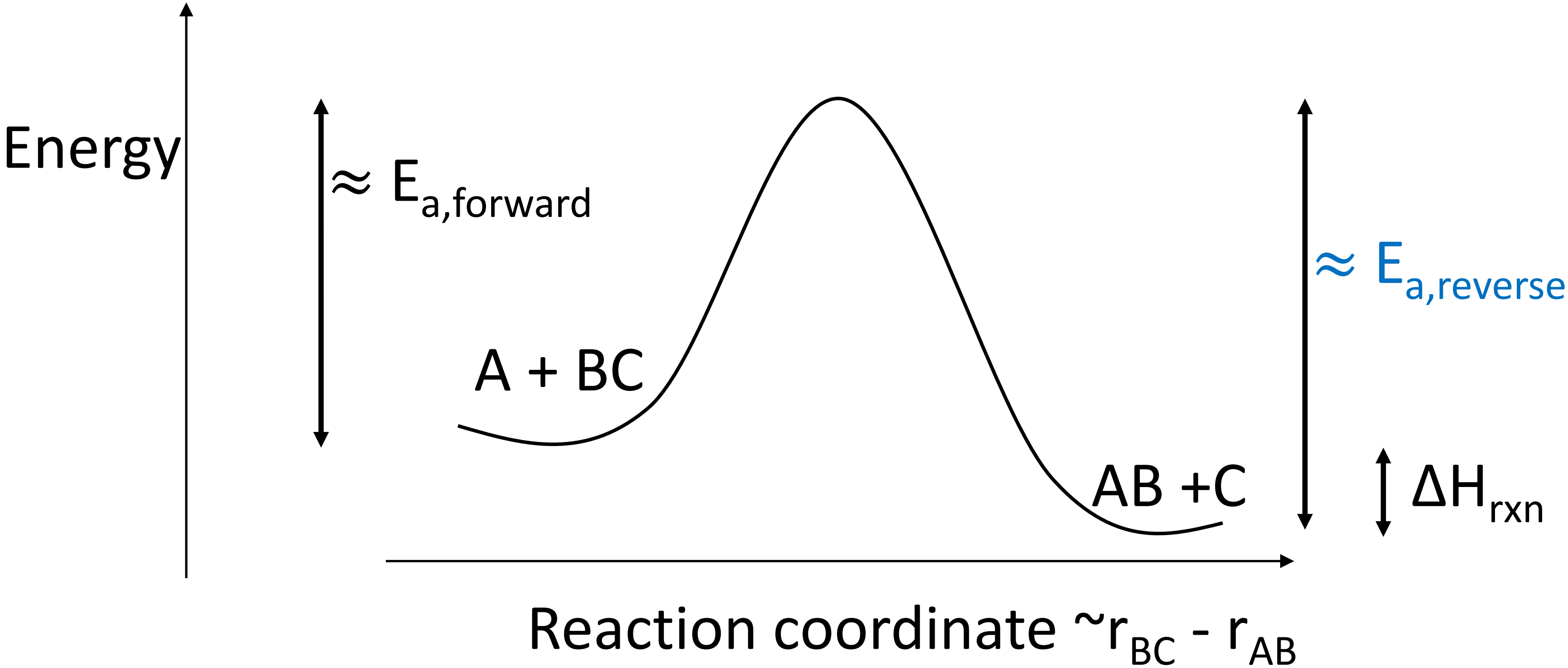
In this specific case with the transition state,

$$K_{C,A+BC \rightleftarrows \ddagger}(T) = K_{C,A+BC \rightleftarrows \ddagger}(T_1) \exp\left[-\frac{\Delta E_a}{R}\left(\frac{1}{T} - \frac{1}{T_1}\right)\right]$$

The larger E_a is, the smaller $K_{C,A+BC \rightleftarrows \ddagger}$ will be. Temperature dependence is same as Arrhenius!

The smaller K_C is, the lower the concentration of transition states (‡). This means fewer species to react to the products, so the reaction rate is lower!

$$K_C = \prod_i C_{i,eq}^{\nu_i} = \frac{C_{\ddagger,eq}}{C_{A,eq} C_{BC,eq}}$$



From this, we can see that:

$$k_f = A_f e^{-\frac{E_{a,f}}{RT}} \qquad k_r = A_r e^{-\frac{E_{a,r}}{RT}} \qquad \frac{k_f}{k_r} = \frac{A_f}{A_r} e^{-\frac{E_{a,f}-E_{a,r}}{RT}}$$

and $E_{a,f} - E_{a,r} = \Delta H_{rxn}$

If ΔH_{rxn} is very negative (exothermic), $E_{a,f} << E_{a,r}$. A larger barrier leads to $k_f >> k_r$, or an irreversible reaction

Problem solving strategy

- Generalized mole balance equation (aka reactor design eqn.)
- Design equations in terms of conversion of limiting reactant
- Rate laws in terms of concentrations

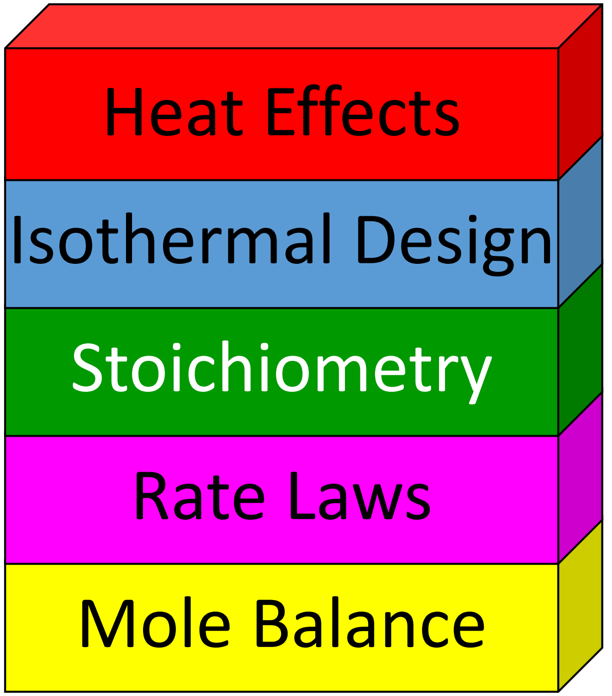
Today: Concentrations in terms of conversion, where we need to consider stoichiometry

Ch.5 Lecture 6-7

C_i is a function of X!

r_A is a function of conc.

Mole balance, conversion



If we have a reaction of the form below in a batch reactor:

$$A + \frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D$$

What is the number of moles of A as a function of conversion?

Here A is our limiting reactant and conversion refers to conversion of A

Initially, there is N_{A0} moles of A. We define conversion with respect to A, so N_A at a given conversion is: $N_A = N_{A0}(1-X)$

Adding a few definitions to make things easier to write:

$$y_{A0} \equiv \frac{P_{\mathrm{A0}}}{P_0} = \frac{N_{\mathrm{A0}}}{N_{T0}} = \frac{F_{\mathrm{A0}}}{F_{T0}}$$

$$\Theta_j \equiv N_{j0} / N_{A0} = C_{j0} / C_{A0} = y_{j0} / y_{A0}$$

Can also have inerts (present, but not involved in rxn)

Batch stoichiometric table

$N_{j0} = N_{A0}\Theta_j$

Species	Symbol	Initial	Change	Remaining
Reactant A	A	N_{A0}	$-N_{A0}X$	$N_A = N_{A0}(1-X)$
Reactant B	B	N_{B0}	$-b/a\, N_{A0}X$	$N_B = N_{A0}(\Theta_B - b/a\, X)$
Product C	C	N_{C0}	$+c/a\, N_{A0}X$	$N_C = N_{A0}(\Theta_C + c/a\, X)$
Product D	D	N_{D0}	$+d/a\, N_{A0}X$	$N_D = N_{A0}(\Theta_D + d/a\, X)$
Inert	I	N_{I0}		$N_{I0} = N_{A0}\Theta_I$

$$N_T = \underbrace{N_{A0}(\Theta_D + \Theta_C + \Theta_B + 1 + \Theta_I)}_{N_{T0}} + \underbrace{\left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1\right)}_{\delta} N_{A0}X$$

$N_T = N_{T0} + N_{A0} * \delta * X$

$N_T = N_{T0} + N_{T0} * y_{A0} * \delta * X$

$$C_j = \frac{N_j}{V}$$

Total number of moles changes with reaction if δ is non-zero

Discuss with your neighbors:

For A + 2B + C + 4D → E, in a batch reactor:

C_{A0} = 0.1 M, C_{B0} = 0.2 M, C_{C0} = 0.6 M, C_{D0} = 0.2 M.

What is the limiting reactant?

A) A

B) B

C) C

D) D

D would be used up first, because it takes 4 moles of D for every one mole of A, or two moles of B. So D is the limiting reactant. The limiting reactant is not necessarily the molecule written first!

Continuing with problem above for practice:

Rewriting $A + 2B + C + 4D \rightarrow E$ in a form with D as limiting reactant/defining conversion:

$\frac{1}{4}A + \frac{1}{2}B + \frac{1}{4}C + D \rightarrow \frac{1}{4}E$

Now what would δ be?

$\delta = \frac{1}{4} - \frac{1}{4} - \frac{1}{2} - \frac{1}{4} - 1 = -1\frac{3}{4} = -1.75$

What this means is that for every one mole of D that is reacted, the total number of moles decreases by 1.75

This is not going to affect us so much for liquid-phase reactions, but remember from Lecture 2 that for **gas-phase** reactions the total number of moles is related to volume!

Recall volumes (Lecture 2) for gases
(remember liquids we assume no volume change)

Total volume

$$V = V_0 \frac{N_T}{N_{T0}} \frac{T}{T_0} \frac{P_0}{P}$$

Total volumetric flow rate

$$v = v_0 \frac{F_T}{F_{T0}} \frac{T}{T_0} \frac{P_0}{P}$$

$C_j = N_j/V$ or $C_j = F_j/v$

<u>Gases:</u>

$P_0V_0 = ZN_0RT_0$

$PV = ZNRT$

Z = compressibility factor,
Z = 1 for ideal gases

So for liquids, reaction affects concentrations by changing N_j.
But for gases, reaction can both change N_j **and** volume!

Flow stoichiometric table (replace N with F) (back to A as lim.)

Species	Symbol	Inlet	Change	Outlet
	A	F_{A0}	$-F_{A0}X$	$F_A = F_{A0}(1-X)$
	B	F_{B0}	$-b/a\, F_{A0}X$	$F_B = F_{A0}(\Theta_B - b/a\, X)$
	C	F_{C0}	$+ c/a\, F_{A0}X$	$F_C = F_{A0}(\Theta_C + c/a\, X)$
	D	F_{D0}	$+ d/a\, F_{A0}X$	$F_D = F_{A0}(\Theta_D + d/a\, X)$
	I	F_{I0}		$F_I = F_{I0}$

$$F_T = \underbrace{F_{A0}(\Theta_D + \Theta_C + \Theta_B + 1 + \Theta_I)}_{F_{T0}} + \underbrace{\left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1\right)}_{\delta} F_{A0}X$$

$$F_T = F_{T0} + F_{A0} * \delta * X$$

$$\varepsilon = y_{A0}\delta$$

$$F_T = F_{T0} + F_{T0} * y_{A0} * \delta * X = F_{T0}(1 + \varepsilon X)$$

Flow reactor concentrations for gas-phase (can also do the same thing with a batch reactor using $C_A = N_A / V$)

$$C_A = \frac{F_A}{v} = \frac{F_A}{v_0 \frac{F_T}{F_{T0}} \frac{T}{T_0} \frac{P_0}{P}}$$

We only do this part if the volume changes!

$$= \frac{F_{A0}(1-X)}{v_0} \frac{1}{1+\varepsilon X} \frac{T_0}{T} \frac{P}{P_0}$$

$$F_T = F_{T0}(1+\varepsilon X)$$

$$\varepsilon = y_{A0}\delta$$

$$C_A = C_{A0} \frac{(1-X)}{1+\varepsilon X} \frac{T_0}{T} \frac{P}{P_0}$$

For liquid or constant V it would just be: $C_A = C_{A0}(1-X)$

This does not mean total moles don't change in liquid, just that a change in total moles does not affect volume

Applying to all species, now we have the concentrations of all our reactants and products as a function of X.

Gas

$$C_B = \frac{C_{A0}(\theta_B - \frac{b}{a}X)}{1+\varepsilon X}\frac{T_0}{T}\frac{P}{P_0}$$

$$C_C = \frac{C_{A0}(\theta_C + \frac{c}{a}X)}{1+\varepsilon X}\frac{T_0}{T}\frac{P}{P_0}$$

$$C_D = \frac{C_{A0}(\theta_D + \frac{d}{a}X)}{1+\varepsilon X}\frac{T_0}{T}\frac{P}{P_0}$$

If we assume no pressure drop, and an isothermal reaction:

$$\frac{P}{P_0} = 1; \frac{T_0}{T} = 1$$

Why is this useful? Because now we can write our rate law as a function of conversion for gases, and use it to do reactor design! Remember our Levenspiel plots are using $F_{A0}/-r_A$ vs. X.

For example:

The elementary reaction,

$$A \rightarrow 2B$$

is running in an isothermal, gas-phase flow reactor with no pressure drop, with pure A as a feed. What's $-r_A(X)$?

Here, $\delta = 2/1 - 1 = +1$, $y_{A0} = 1$, $\varepsilon = +1$

$$-r_A = kC_A = kC_{A0}\frac{1-X}{1+X}$$

$$C_A = C_{A0}\frac{(1-X)}{1+\varepsilon X}\frac{T_0}{T}\frac{P}{P_0}$$