ChE 344
Reaction Engineering and Design

Lecture 5: Thursday, Jan 20, 2022

Stoichiometry: Reversible reactions

Reading for today's Lecture: Chapter 4.2, 4.3

Reading for Lecture 6: Chapter 5.1-5.4

Homework 1 due tomorrow 11:59pm

Lecture 5: Stoichiometry and equilibrium conversion for reversible reactions
Related Text: Chapter 4.3

Reminder: Reversible reactions

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

Two rate constants, k_f (forward rate constant) and k_r (reverse rate constant). For elementary reaction:

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

Please note that when we say it is elementary, that is referring to how the reaction is originally written ($2A + B \rightleftarrows 3C$), including the stoichiometric coefficients as written. If you rewrite the reaction to be in terms of a limiting reactant, that would not change the rate law. For example, if we were to take the elementary reaction above and rewrite it as ($A + \frac{1}{2}B \rightleftarrows \frac{3}{2}C$), the rate law is **still**:

$$-\frac{r_A}{2} = -r_B = \frac{r_C}{3} = k_f C_A^2 C_B - k_r C_C^3$$

because it was elementary for the originally written reaction.

Concentration equilibrium constant:

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

Equilibrium conversion

For irreversible reactions, conversion will go to 1, but for reversible reactions it goes to X_{eq}. We can determine this conversion if we know the concentration equilibrium constant. From last lecture for a gas-phase reaction where volume changes:

$$C_j(X) = C_{A0}\frac{\left(\theta_j - \frac{\nu_j}{\nu_A}X\right)}{1 + \varepsilon X}\frac{T_0}{T}\frac{P}{P_0}$$

This is a more general form of what we wrote in class, when we used terms like (-b/a) in the numerator instead of $-\frac{\nu_j}{\nu_A}$. Remember ν_j is the stoichiometric coefficient of species j. The symbol here is a "nu". I don't use it in class unless necessary because it looks very similar in writing to a v (which we use for volumetric flow rate). They are two different things! An example of the concentration of B for $A \rightleftarrows B$:

$$C_B(X) = C_{A0}\frac{\left(\theta_B - \frac{\nu_B}{\nu_A}X\right)}{1 + \varepsilon X}\frac{T_0}{T}\frac{P}{P_0} = C_{A0}\frac{\left(\theta_B - \frac{+1}{-1}X\right)}{1 + \varepsilon X}\frac{T_0}{T}\frac{P}{P_0} = C_{A0}\frac{(\theta_B + X)}{1 + \varepsilon X}\frac{T_0}{T}\frac{P}{P_0}$$

Equilibrium is where the net rate of reaction is zero. We can use that along with the concentrations as a function of conversion to solve for X_{eq}. For instance:

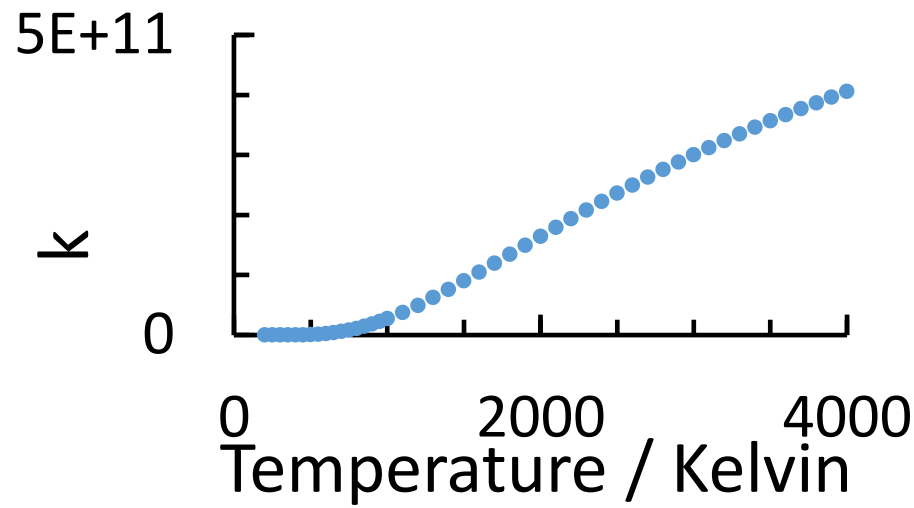
$$K_C = \frac{\left(C_C(X_{eq})\right)^3}{\left(C_A(X_{eq})\right)^2 C_B(X_{eq})}$$

Equilibrium conversion (for the same K_C) can change if volume varies (gas-phase), so long as there is a change in stoichiometry of the reaction (i.e., $\delta \neq 0$).

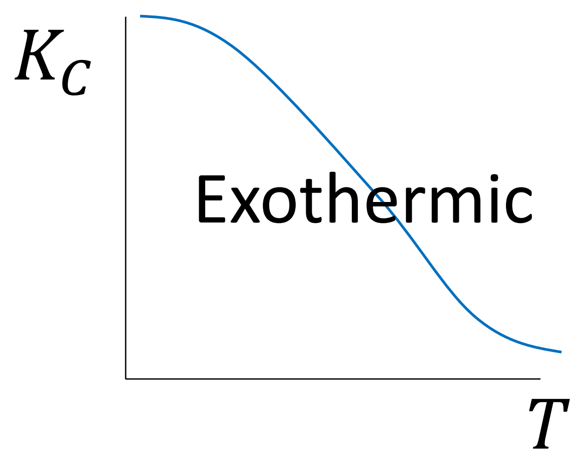
Differences between k (rate constant) and K_C (conc. equilibrium constant):

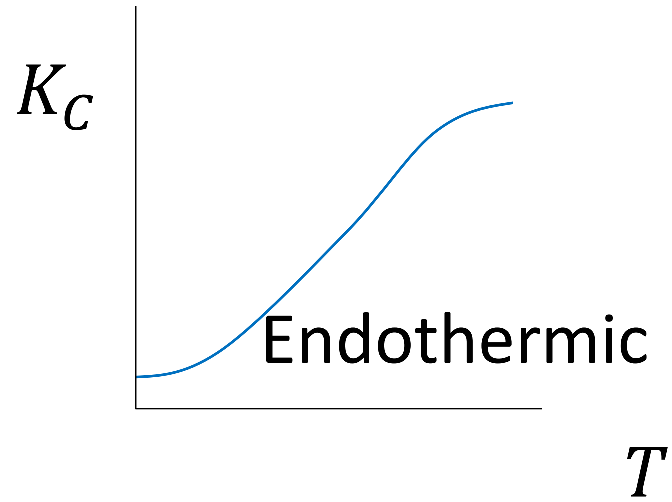
E_a is always positive, so k will always increase with T.

For reversible reactions, BOTH k_f and k_r increase with T. But their ratio will change depending on if it is an exo- or endothermic reaction



ΔH_{rxn} can be positive OR negative, so K_C can increase OR decrease with T





Review of some terms from last few lectures

V = physical volume of reactor (of gas or of liquid)

v = total volumetric flow rate

If A is your limiting reactant we have the following definitions:

$\theta_j \equiv N_{j0} / N_{A0}$ or F_{j0}/F_{A0}

$X \equiv$ moles A reacted / moles A fed $= \frac{F_{A0} - F_A}{F_{A0}}$

$y_{A0} = \frac{N_{A0}}{N_{T0}} = \frac{F_{A0}}{F_{T0}}$ = Amount of A relative to total (inlet/initially)

$$\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1$$ = Change in number of moles / Moles A reacted

$$\varepsilon = y_{A0}\delta$$ = Change in # moles for complete conversion / Total moles fed

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

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

From volume changing

Discuss with your neighbors

For the following reaction, what is the elementary rate law for $-r_A$, and what are δ, and ε?

$$A + 2B \rightarrow C$$

F_{A0} = 1 mol min^{-1}

F_{B0} = 1 mol min^{-1}

F_{C0} = 0 mol min^{-1}

F_{I0} = 1 mol min^{-1}

F_{T0} = 3 mol min^{-1}

B is limiting reactant!

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

A) $-r_A = kC_AC_B^2$; δ= -1 ; ε = -1/3

B) $-r_A = kC_AC_C$; δ= -2 ; ε = -2

C) $-r_A = kC_BC_C$; δ= -1 ; ε = -1

D) $-r_A = kC_AC_B^2$; δ = +2 ; ε = -2/3

δ=1/2- 1/2 -1 = **-1**

y_{B0} = 1 /(1+1+1) = 1/3

ε=-1 * 1/3 = **-1/3**

B is limiting reactant in this problem

Why is it important to write in terms of the limiting reactant?

Let's say instead we (incorrectly) used A as our limiting reactant (i.e., we define conversion wrt A).

$-r_A = kC_AC_B^2$; $\delta = -2$; $\varepsilon = -2/3$

This doesn't look so bad… but what if we think about our flow rates?

$$F_A = F_{A0}(1 - X)$$

$$F_B = F_{A0}(\theta_B - 2X)$$

Looks ok so far, but what would F_B out of the reactor be for 75% conversion (X = 0.75)?

θ_B=1, F_B= 1 mol min^{-1} (1- 1.5) = -0.5 mol min^{-1}

Uh oh! This is why it is very important to start off by identifying your limiting reactant, and we want to define our conversion based off of that species!

Last time, stoichiometry tables for limiting reactant 'A'

Batch stoichiometric table

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

Includes inert

No inert

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

$N_T = N_{T0} + N_{A0} * \delta * X$ $\quad$ $C_j = N_j/V$

$N_T = N_{T0}(1 + \varepsilon X)$ $\quad$ j is some species, T is Total

Flow stoichiometric table (replace N with F)

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}		$F_I = F_{I0}$

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

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

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

$C_j = F_j/v$

v is volumetric flow rate, V is volume of reacting species

For liquid-phase reaction

$v = v_0$

$$C_A = \frac{F_A}{v} = \frac{F_A}{v_0} = \frac{F_{A0}(1-X)}{v_0} = C_{A0}(1-X)$$

$V = V_0$

$$C_A = \frac{N_A}{V_0} = \frac{N_{A0}(1-X)}{V_0} = C_{A0}(1-X)$$

For a reaction that is first order in A and B: And stoich same

$$-r_A = kC_A C_B = kC_{A0}^2 (1-X)(\theta_B - X)$$

Now we have $-r_A(X)$. We could couple this with a design equation (e.g., batch reactor design equation)

$$\frac{dX}{dt} = -r_A \frac{V}{N_{A0}} = -r_A \frac{1}{C_{A0}} = kC_{A0}^1 (1-X)(\theta_B - X)$$

This design equation can then be solved analytically or numerically to get (for batch reactor) conversion vs. time

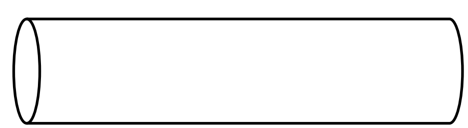
$$\frac{dX}{dt} = kC_{A0}^{\mathbf{1}}\,(1 - X)(\theta_B - X)$$

$$\int \frac{1}{(1 - X)(\theta_B - X)} dX = \int kC_{A0}^{\mathbf{1}}\ dt$$

Recall: If A is your reactant, for an irreversible rxn in batch reactor with no V change, C_A will go down with time, while X will go up.

For <u>gas-phase</u> reaction (where gas volume can change)

$$C_A = \frac{F_A}{v} = \frac{F_A}{v_0 \frac{F_T}{F_{T0}} \frac{T}{T_0} \frac{P_0}{P}} = \frac{F_{A0}(1 - X)}{v_0} \frac{1}{1 + \varepsilon X} \frac{T_0}{T} \frac{P}{P_0}$$



Discuss with your neighbors

A liquid stream containing 1 mol/dm^3 of A, 2 mol/dm^3 of B, and 0.5 mol/dm^3 of C enters a reactor. The irreversible reaction $A + B \rightarrow C$ proceeds to a conversion of A of 75% (X = 0.75). What is the outlet concentration of C?

A) 0.75 mol/dm^3

B) 1.25 mol/dm^3

C) 2 mol/dm^3

D) 2.5 mol/dm^3

Limiting reactant = A

Liquid, so constant volume: $v = v_0$

$C_{C0} = 0.5$ M, $C_{A0} = 1$ M

$\Theta_C = 0.5 \text{ M} / 1 \text{ M} = 0.5$

$F_C = F_{A0} (\Theta_C + c/a\ X)$

$F_C/v_0 = F_{A0}/v_0(\Theta_C + c/a\ X)$

$X = 0.75$

$C_C = C_{A0} (0.5 + X) = 1 \text{ M} \times (1.25)$

Recall reversible vs. irreversible reactions

$\rightleftarrows$ $\rightarrow$

$$2A + B \underset{k_{reverse}}{\overset{k_{forward}}{\rightleftarrows}} 3C$$

If elementary:

$$-\frac{r_A}{2} = -r_B = \frac{r_C}{3} = k_f C_A^2 C_B - k_r C_C^3$$

At some point, when there is enough of species C present:

$$k_f C_A^2 C_B = k_r C_C^3$$

At this point, when the rate of forward and reverse reaction are equal, we say we are at equilibrium. The corresponding conversion is what we call our equilibrium conversion (X_{eq}). For reversible reactions, X_{eq} < 1.

Sample problem:
Decomposition of dinitrogen tetroxide

$$N_2O_4 \underset{k_r}{\overset{k_f}{\rightleftarrows}} 2NO_2 \qquad\qquad A \underset{k_r}{\overset{k_f}{\rightleftarrows}} 2B$$

Pure N_2O_4 at 340 K at 2 atm, F_{A0} = 3 moles min^{-1}.

K_C = 0.1 mol/L, k_f = 0.5 min^{-1}. Assume elementary reactions.

<u>Solve X_{eq} for constant volume batch reactor</u>

$$r_A = -k_f C_A + k_r {C_B}^2 = -k_f\left(C_A - \frac{k_r}{k_f}{C_B}^2\right)$$

$$r_A = -k_f\left(C_A - \frac{{C_B}^2}{K_C}\right)$$

$$C_A = \frac{N_A}{V} = \frac{N_{A0}(1-X)}{V} = C_{A0}(1-X)$$

Convert N_{A0}/V to C_{A0} because we are told to assume constant volume here, so $V = V_0$ (even though it is gas-phase).

$$C_B = C_{A0}\left(\theta_B + \frac{b}{a}X\right) = C_{A0}(0+2X) = 2C_{A0}X$$

$$K_C = \frac{C_{B,eq}{}^2}{C_{A,eq}} = \frac{\left(2C_{A0}X_{eq}\right)^2}{C_{A0}(1-X_{eq})} = \frac{4C_{A0}\left(X_{eq}\right)^2}{(1-X_{eq})}$$

$C_{A0} = y_{A0} * P_0/RT$, can convert from pressure to 0.072 mol/L

$y_{A0} = 1$; $P_0 = 2$ atm; $R = 0.082\ M^{-1}$ atm K^{-1}; $T = 340$ K

$$4(0.072\ \mathrm{M})\left(X_{eq}\right)^2 + 0.1\ \mathrm{M}\ X_{eq} - 0.1\ \mathrm{M} = 0$$

$$X_{eq,batch} = 0.441$$

Quad. formula

Discuss with your neighbors

For our decomposition of dinitrogen tetroxide reaction in a constant volume batch reactor:

$$N_2O_4 \underset{k_r}{\overset{k_f}{\rightleftarrows}} 2NO_2 \qquad\qquad A \underset{k_r}{\overset{k_f}{\rightleftarrows}} 2B$$

What if now K_C = 1 mol/L instead of K_C = 0.1 mol/L. What would be the new X_{eq}?

$$X_{eq,batch}(K_C = 0.1\ M) = 0.441$$

$$X_{eq,batch}(K_C = 1\ M) =???$$

A) $X_{eq,batch} = 0.811$

B) $X_{eq,batch} = 0.441$

C) $X_{eq,batch} = 0.221$

D) $X_{eq,batch} = 1.000$

$$\overset{k_f}{\underset{k_r}{A \rightleftarrows 2B}}$$

Pure N_2O_4 at 340 K at 2 atm, F_{A0} = 3 moles min^{-1}. K_C = 0.1 mol/L, k_f = 0.5 min^{-1}. Assume elementary reactions. No pressure drop, isothermal.

Solve X_{eq} for plug flow reactor: No longer constant volume!

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

$$\varepsilon = \delta y_{A0} = 1 * 1$$

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

$$C_B = \frac{F_B}{v} = \frac{C_{A0}2X}{1 + X}$$

$$K_C = 0.1\frac{mol}{L} = \frac{{C_{B,eq}}^2}{C_{A,eq}} = \frac{\left(\frac{C_{A0}2X_{eq}}{1+X_{eq}}\right)^2}{\frac{C_{A0}(1-X_{eq})}{1+X_{eq}}}$$

$$= \frac{4C_{A0}{X_{eq}}^2}{(1+X_{eq})(1-X_{eq})}$$

$$X_{eq,PFR} = 0.508$$

Note, for both of these mathematically you will get two solutions, one that is positive and one that is negative. The conversion must be positive in this case for mass to be conserved.

For our reaction:

$$A \underset{k_r}{\overset{k_f}{\rightleftarrows}} 2B$$

We get:

$$X_{eq,batch} = 0.441$$

$$X_{eq,PFR} = 0.508$$

The equilibrium conversion is higher in the flow system than in the batch (constant volume) system.

Thinking about Le Chatelier's principle, does this make sense?

Which system would have a higher pressure?

<u>Next Tuesday</u>:

More practice with isothermal reactor design!