Chemical Reaction Engineering I

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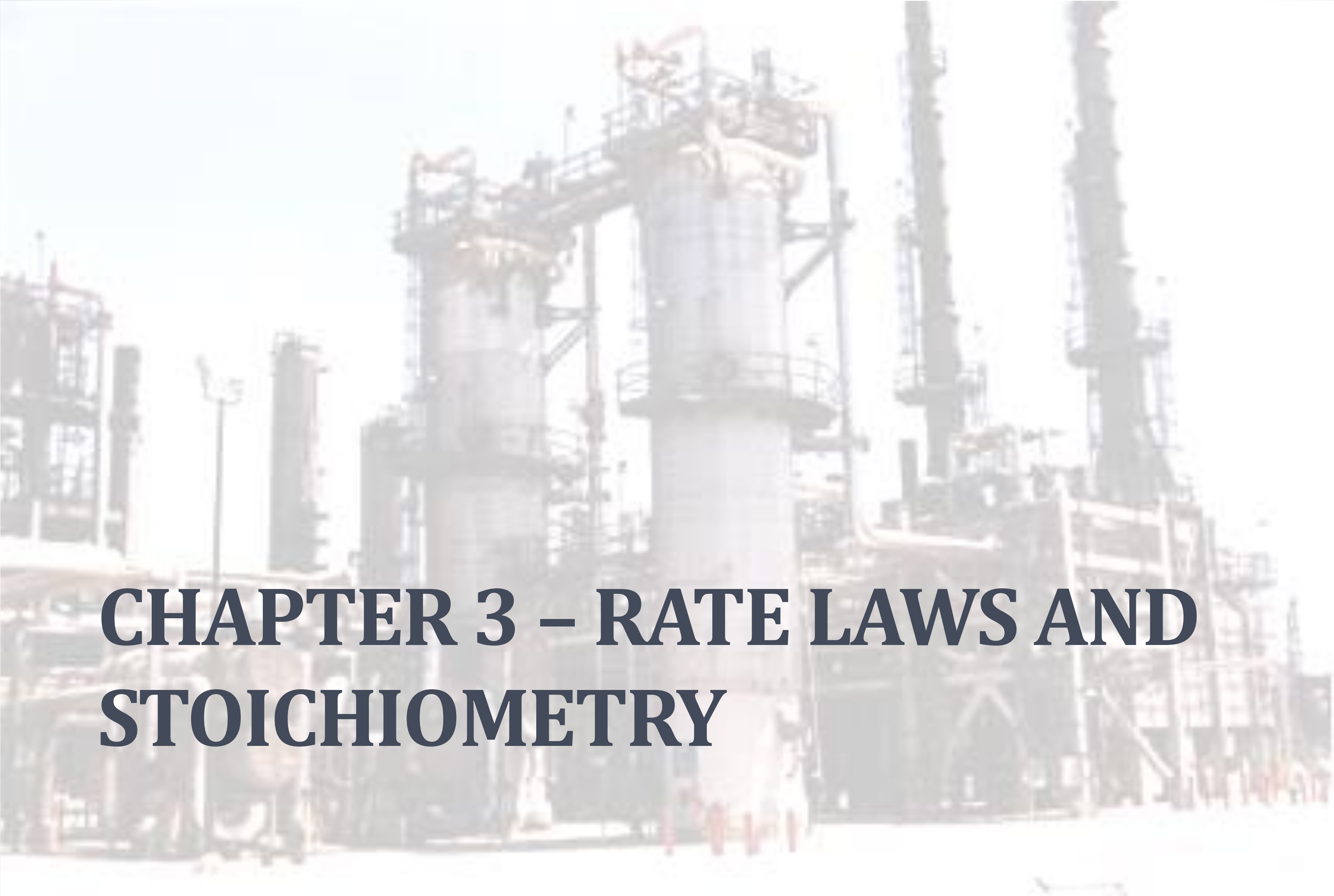


CHAPTER 3 – RATE LAWS AND STOICHIOMETRY

Success is measured not so much by the position one has reached in life, as by the obstacles one has overcome while trying to succeed.

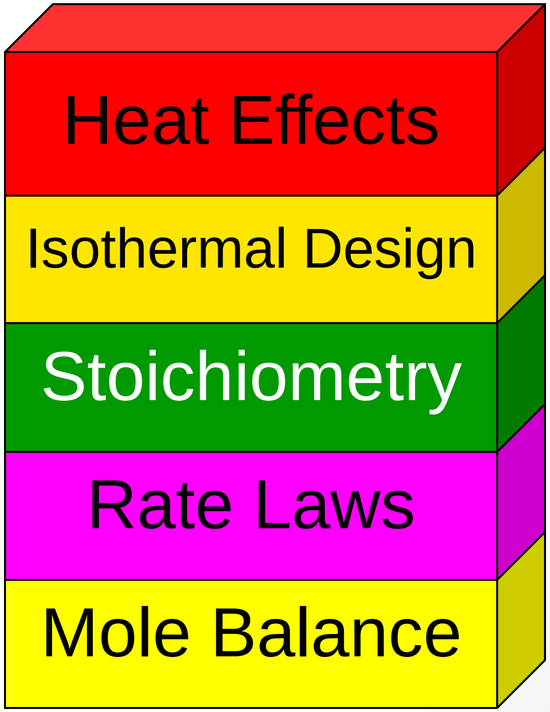
Booker T. Washington

Learning Outcomes

- After completing chapter 3, you will be able to
  - write the relationship between the relative rates of reaction.
  - write a rate law and define reaction order and activation energy.
  - set up a stoichiometric table for both batch and flow systems and express concentration as a function of conversion.
  - write $-r_A$ solely as a function of conversion, for both liquid-phase and gas-phase reacting systems, given the rate law and then entering concentration.
  - calculate the equilibrium conversion for both gas and liquid phase reactions.

CRE Algorithm

- Building Block 1 - **Mole Balances**
  - Size CSTRs and PFRs given $-r_A = f(X)$
  - Conversion for Reactors in Series
- Building Block 2 - **Rate Laws**
  - Reaction Orders
  - Arrhenius Equation
  - Activation Energy
  - Effect of Temperature



Heat Effects

Isothermal Design

Stoichiometry

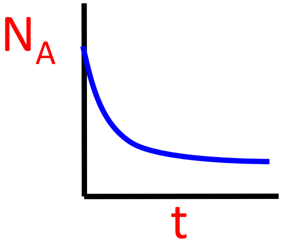
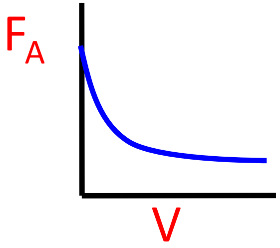
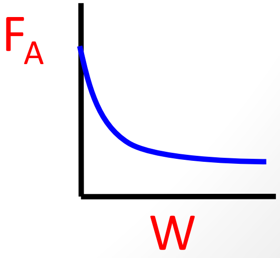
Rate Laws

Mole Balance

Review Chapter 1

Reactor Mole Balances Summary

The GMBE applied to the four major reactor types
(and the general reaction A→B)

Reactor	Differential	Algebraic	Integral	
Batch	$\frac{dN_A}{dt} = r_A V$		$t = \int_{N_{A0}}^{N_A} \frac{dN_A}{r_A V}$	
CSTR		$V = \frac{F_{A0} - F_A}{-r_A}$		
PFR	$\frac{dF_A}{dV} = r_A$		$V = \int_{F_{A0}}^{F_A} \frac{dF_A}{dr_A}$	
PBR	$\frac{dF_A}{dW} = r'_A$		$W = \int_{F_{A0}}^{F_A} \frac{dF_A}{r'_A}$	

Definition of Conversion

- Consider the generic reaction:

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

- Choose **limiting reactant A as basis** of calculation:

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

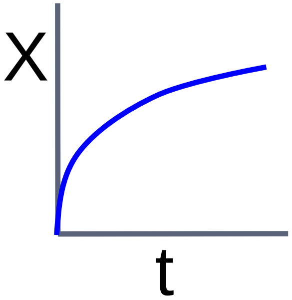
- Define **conversion**, X_A: the number of moles of A that have reacted per mole of A fed to the system

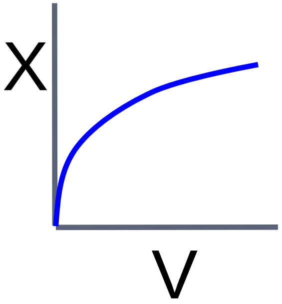
$$\boldsymbol{X_A = \frac{moles\ A\ reacted}{moles\ A\ fed}}$$

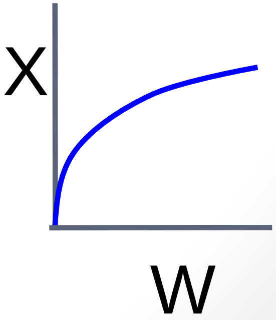
Review Chapter ٢

Reactor Mole Balances Summary in terms of conversion, X

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

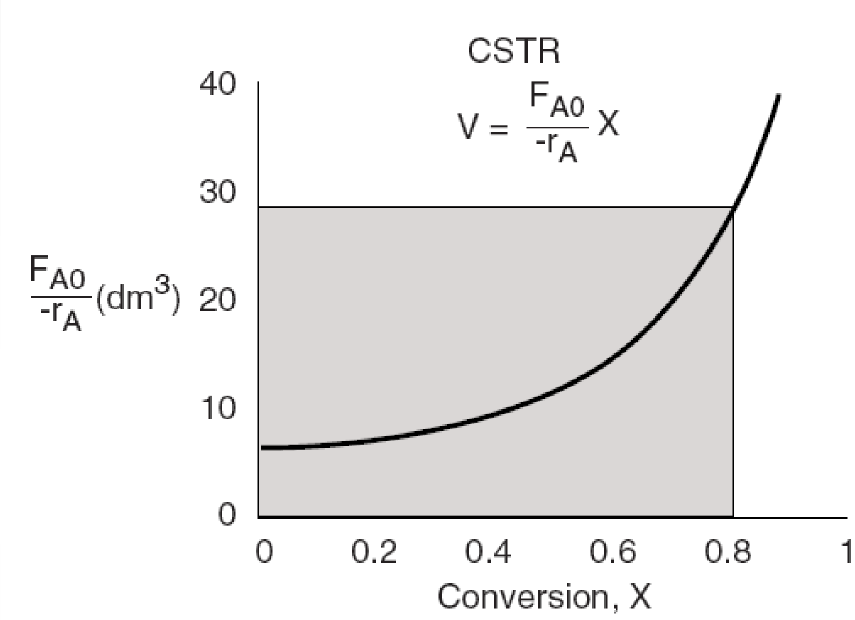


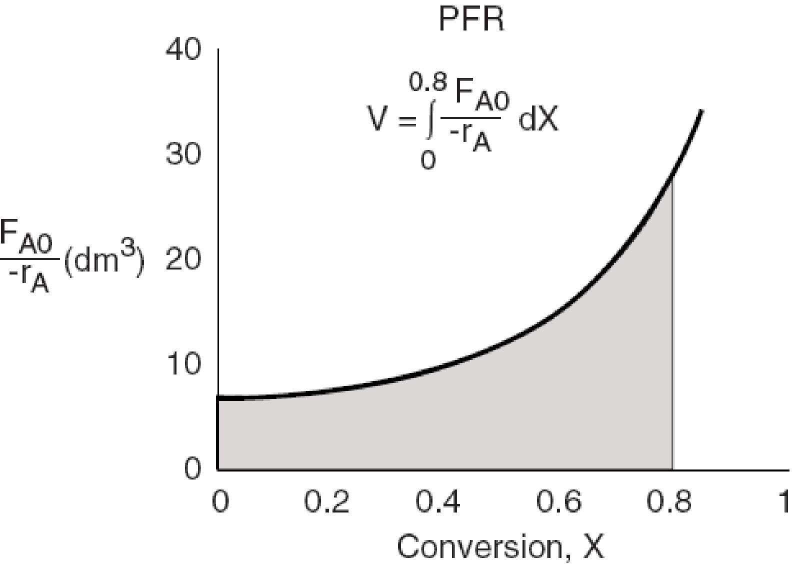




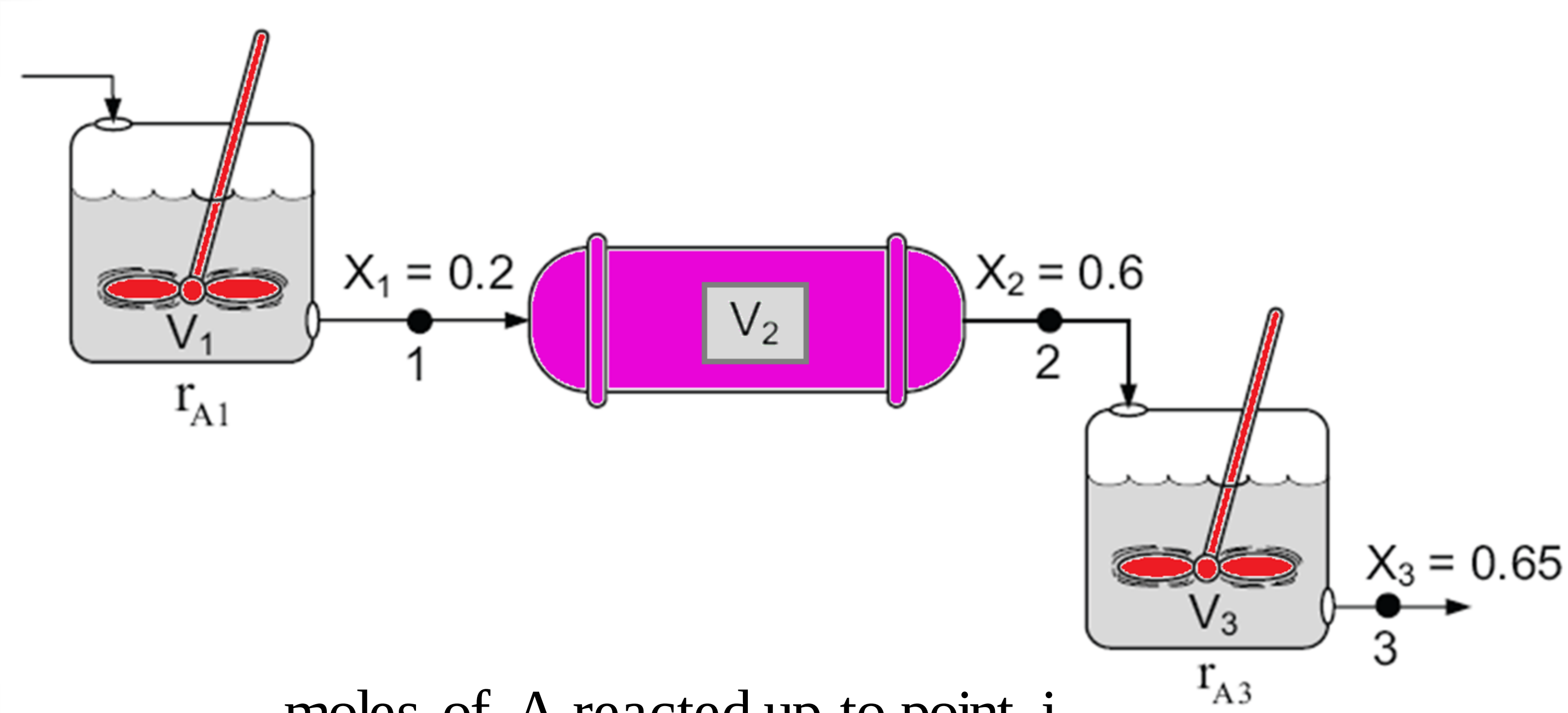
Review Chapter ٢

Levenspiel Plots





Reactors in Series

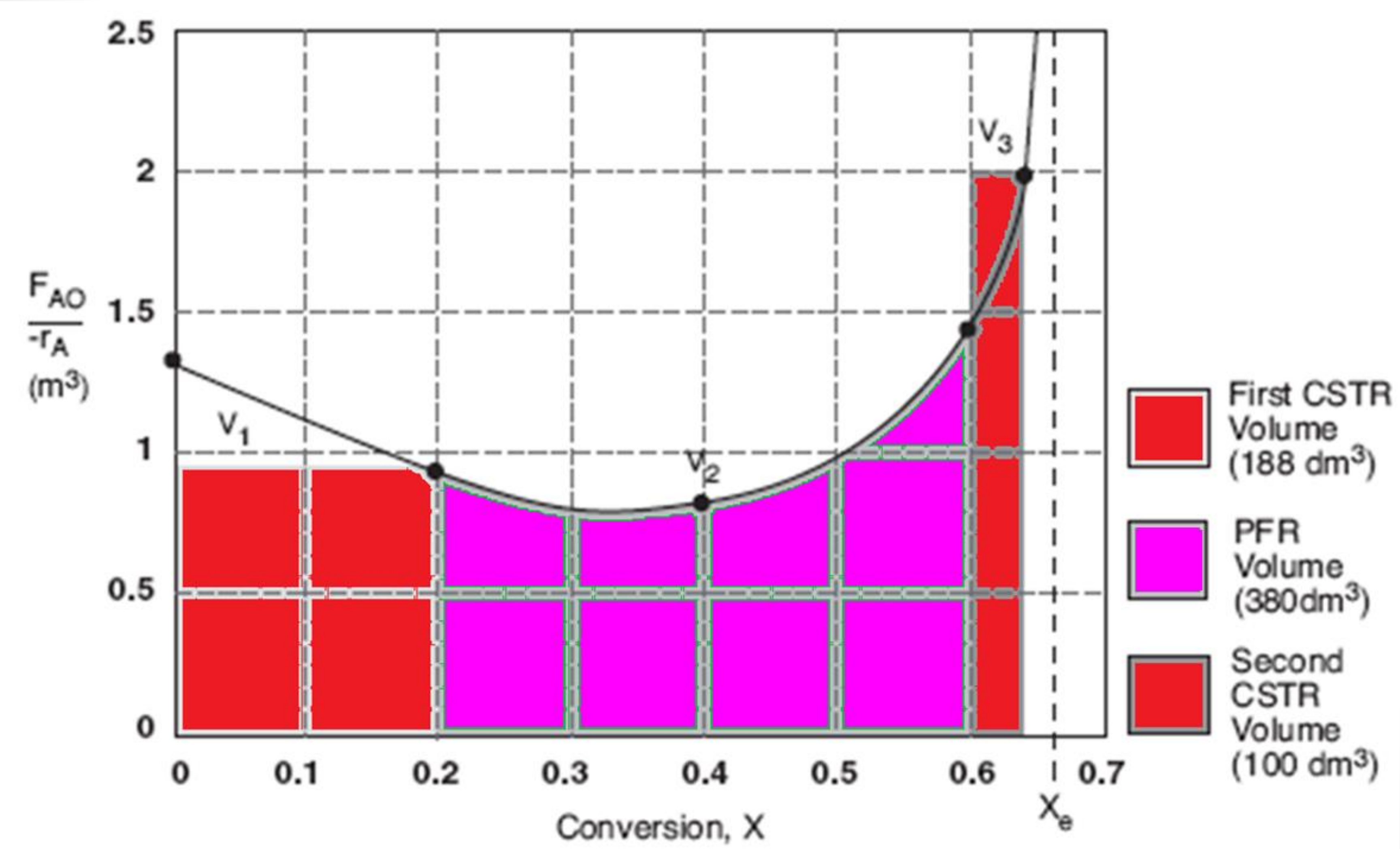


$$X_i = \frac{\text{moles of A reacted up to point } i}{\text{moles of A fed to first reactor}}$$

Only valid if there are no side streams

Review Chapter ٢

Reactors in Series



Space Time, τ

- **Space time τ** is the time necessary to process one reactor volume of fluid at entrance conditions.

$$\tau = \frac{V}{\upsilon_0}$$

Space Velocity

- $SV \equiv \frac{v_0}{V}$ $SV = \frac{1}{\tau}$
- **liquid-hourly space velocity, LHSV** $LHSV = \frac{v_{0|liquid}}{V}$
- **gas-hourly space velocity, GHSV**

$$GHSV = \frac{v_{0|STP}}{V}$$

Expressing other Components Conversion in Terms of X_A

$$A + \frac{b}{a}B \longrightarrow \frac{c}{a}C + \frac{d}{a}D \qquad X_A \equiv \frac{\text{moles A reacted}}{\text{moles A fed}}$$

BATCH SYSTEM:

Longer reactant is in reactor, more reactant is converted to product (until reactant is consumed or the reaction reaches equilibrium)

∴ Conversion (X_j) is a function of time (t) in the batch reactor

$$N_A = N_{A0} - [N_{A0}][X_A]$$

Moles A in reactor at time t = Moles A fed - Moles A consumed

$$\rightarrow N_A = N_{A0}(1 - X_A)$$

reactant

product

$$N_B = N_{B0} - \frac{b}{a}(N_{A0}X_A) \qquad N_C = N_{C0} + \frac{c}{a}(N_{A0}X_A)$$

$$N_D = N_{D0} + \frac{d}{a}(N_{A0}X_A) \qquad N_I = N_{I0} \quad (\text{inert component})$$

Types of Reactions

- **Homogeneous reaction =** involves only one phase.
- **Heterogeneous reaction =** involves more than one phase, and the reaction usually occurs at the interface between the phases.
- **An irreversible reaction** = proceeds in only one direction and continues in that direction **until** the reactants are exhausted.
- **A reversible reaction =** can proceed in either direction, depending on the concentrations of reactants and products relative to the corresponding equilibrium concentrations.

Molecularity of Reaction

- The ***molecularity*** of a reaction is the number of **atoms,** ions, or molecule **involved** (colliding) in a reaction **step.**
- The terms ***unimolecular, bimolecular*** and ***termolecular*** refer to reactions involving, respectively, one, two, or three atoms (or molecules) interacting **or** colliding in **any** one reaction step.
- Most common ***unimolecular*** reaction example:

$$ {}_{92}U^{238} \rightarrow {}_{90}Th^{234} + {}_{2}He^{4} \qquad -r_U = kC_U $$

Molecularity of Reaction

- The **true** ***bimolecular*** reactions that exist are reactions involving free radical, such as

$$\mathrm{Br}\bullet + \mathrm{C_2H_6} \rightarrow \mathrm{HBr} + \mathrm{C_2H_5}\bullet$$

$$-r_{\mathrm{Br}\bullet} = kC_{\mathrm{Br}\bullet}C_{\mathrm{C_2H_6}}$$

- Probability of a ***termolecular*** reaction occurring is almost nonexistent, and in most instances the reaction pathway follows a series **of *bimolecular*** reactions as in the case of the reaction

$$2\mathrm{NO} + \mathrm{O_2} \rightarrow 2\mathrm{NO_2}$$

Building Block 2

Rate Laws

- **Rate law** (kinetic expression):
  - the algebraic **equation** that relates $-\boldsymbol{r_A}$ to the species concentrations is

- **Power Law Model:**

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

α order in A

β order in B

Overall Rection Order :

$$\mathrm{n} = \alpha + \beta$$

Building Block 2

Rate Laws

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

- A reaction follows an **elementary rate law** if the reaction orders just happens to agree with the stoichiometric coefficients for the reaction as written.
- e.g. If the above reaction follows an **elementary rate law**

$$-r_A = k_A C_A^2 C_B$$

  - 2nd order in A, 1st order in B, overall 3rd order

- Rate Laws are **determined by experimental observation**

Building Block 2

Rate Laws

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

- Rate Laws could be non-elementary.
- For example, reaction could be:
  - Second Order in A $\quad -r_A = k_A C_A^2$
  - Zero Order in B $\quad -r_B = k_B C_A^2$
  - Overall Second Order $\quad r_C = k_C C_A^2$

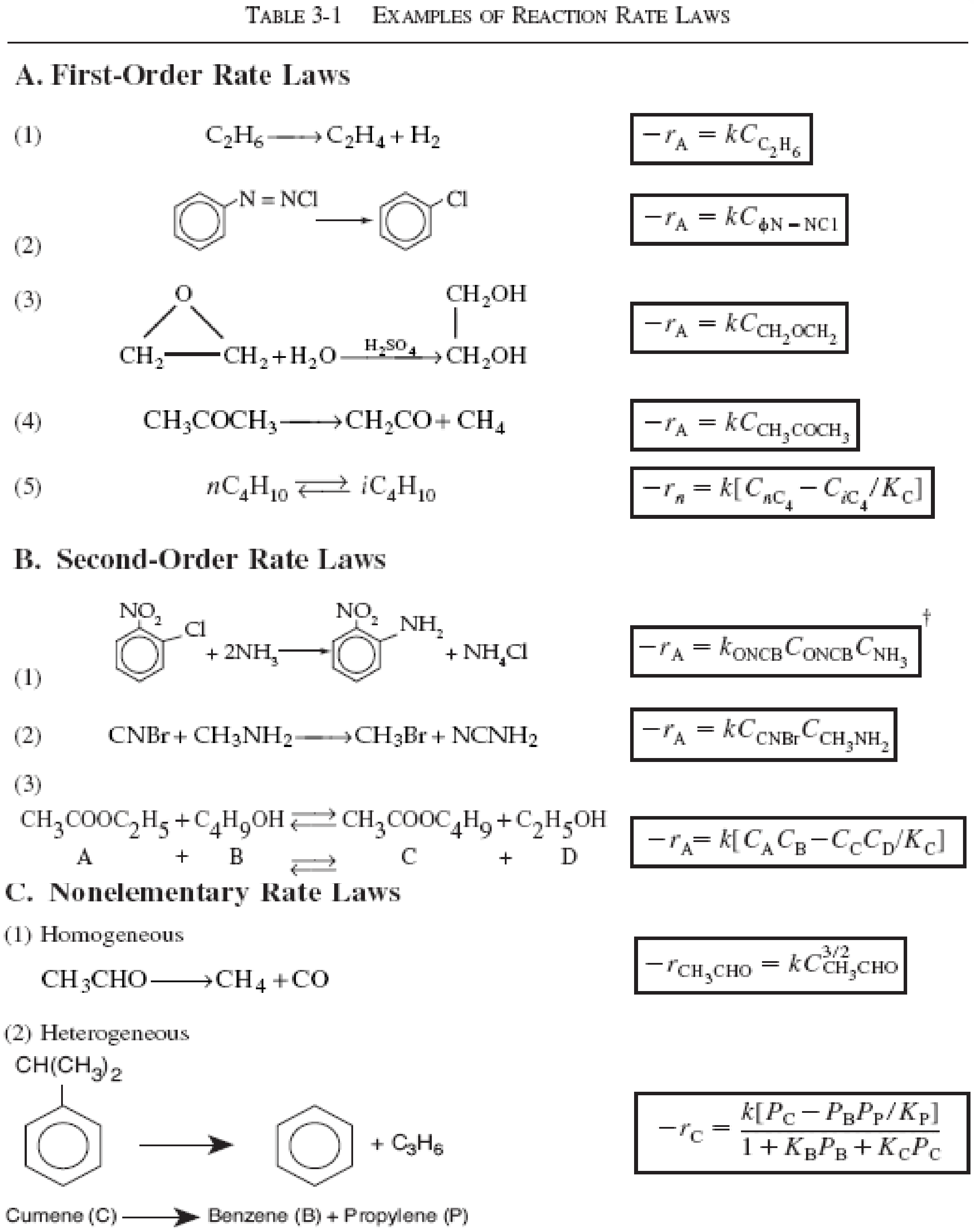


TABLE 3-1 EXAMPLES OF REACTION RATE LAWS

A. First-Order Rate Laws

	Reaction	Rate law
(1)	$C_2H_6 \longrightarrow C_2H_4 + H_2$	$-r_A = kC_{C_2H_6}$
(2)	N = NCl ⟶ Cl	$-r_A = kC_{\phi N-NCl}$
(3)	O CH_2—$CH_2 + H_2O \xrightarrow{H_2SO_4}$ CH_2OH—CH_2OH	$-r_A = kC_{CH_2OCH_2}$
(4)	$CH_3COCH_3 \longrightarrow CH_2CO + CH_4$	$-r_A = kC_{CH_3COCH_3}$
(5)	$nC_4H_{10} \rightleftarrows iC_4H_{10}$	$-r_n = k[C_{nC_4} - C_{iC_4}/K_C]$

B. Second-Order Rate Laws

	Reaction	Rate law
(1)	NO_2 Cl + $2NH_3$ ⟶ NO_2 NH_2 + NH_4Cl	$-r_A = k_{ONCB}C_{ONCB}C_{NH_3}$ †
(2)	$CNBr + CH_3NH_2 \longrightarrow CH_3Br + NCNH_2$	$-r_A = kC_{CNBr}C_{CH_3NH_2}$
(3)	$CH_3COOC_2H_5 + C_4H_9OH \rightleftarrows CH_3COOC_4H_9 + C_2H_5OH$ $A + B \rightleftarrows C + D$	$-r_A = k[C_AC_B - C_CC_D/K_C]$

C. Nonelementary Rate Laws

	Reaction	Rate law
(1) Homogeneous	$CH_3CHO \longrightarrow CH_4 + CO$	$-r_{CH_3CHO} = kC^{3/2}_{CH_3CHO}$
(2) Heterogeneous	$CH(CH_3)_2$ ⟶ $+ C_3H_6$ Cumene (C) ⟶ Benzene (B) + Propylene (P)	$-r_C = \dfrac{k[P_C - P_BP_P/K_P]}{1 + K_BP_B + K_CP_C}$

Relative Rates of Reaction

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

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

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

Relative Rates of Reaction

$$2\mathrm{A} + \mathrm{B} \rightarrow 3\mathrm{C}$$

Given $$-r_A = 10\ \frac{mol}{dm^3 \cdot s}$$

Then $$\frac{r_A}{-2} = \frac{r_B}{-1} = \frac{r_C}{3}$$

$$-r_{\mathbf{B}} = \frac{-r_A}{2} = 5\ \frac{mol}{dm^3 \cdot s}$$

$$r_C = \frac{-3}{2} r_A = 15\ \frac{mol}{dm^3 \cdot s}$$

Reversible Elementary Reaction

$$2A+B \underset{k_{-A}}{\overset{k_A}{\rightleftarrows}} 3C$$

$$-r_A = k_A C_A^2 C_B - k_{-A} C_C^3 = k_A \left[C_A^2\, C_B - \frac{C_C^3}{k_A / k_{-A}} \right]$$

$$-r_A = k_A \left[C_A{}^2 C_B - \frac{C_C^3}{K_e} \right]$$

Reversible Elementary Reaction

$$2A+B \underset{k_{-A}}{\overset{k_A}{\rightleftarrows}} 3C$$

Reaction is: First Order in A
Second Order in B
Overall third Order

$$[-r_A] = \frac{moles}{dm^3 s} \qquad C_A = \frac{moles}{dm^3}$$

$$[k] = \left[\frac{-r_A}{C_A C_B^2}\right] = \frac{mole/dm^3/s}{\left(mole/dm^3\right)\left(mole/dm^3\right)^2} = \frac{dm^6}{mole^2 s}$$

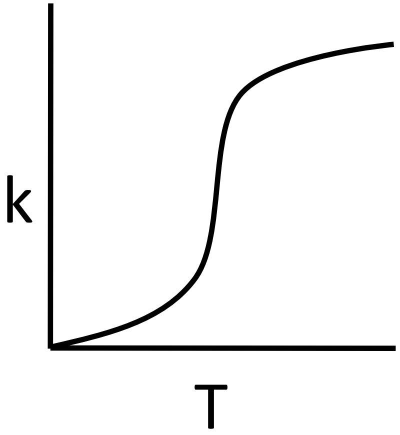
The Reaction Rate Constant

- The quantity k is referred to as either the **specific reaction rate or the reaction rate constant**.
- The **rate constant** k is not truly a constant; it is merely independent of the concentrations of the species involved in the reaction.
- It is almost always strongly **dependent on temperature**.
- It depends on whether or not a **catalyst** is present, and in gas-phase reactions, it may be a function of **total pressure**.
- In liquid systems it can also be a function of other parameters, such as **ionic strength** and **choice of solvent**.
  - These other variables normally exhibit much less effect on the specific reaction rate than temperature does **with the exception of supercritical solvents**, such as super critical water.

Arrhenius Equation

k is the specific reaction rate (constant) and is given by the Arrhenius Equation, where:

$$\boxed{k = Ae^{-E/RT}}$$



$$T \rightarrow \infty \quad k \rightarrow A$$

$$T \rightarrow 0 \quad k \rightarrow 0$$

$$A \approx 10^{13}$$

Arrhenius Equation

where:

E = Activation energy (cal/mol)

R = Gas constant (cal/mol*K)

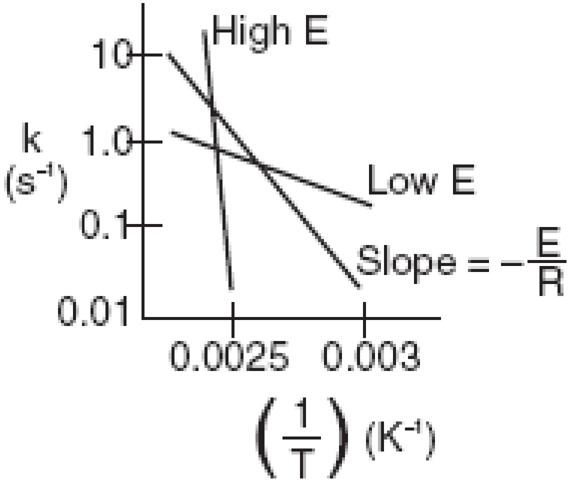
T = Temperature (K)

A = Frequency factor (same units as rate constant k)

(units of A, and k, depend on overall reaction order)

$$\ln k_A = \ln A - \frac{E}{R}\left(\frac{1}{T}\right)$$

Semilog Plot



Reaction Coordinates

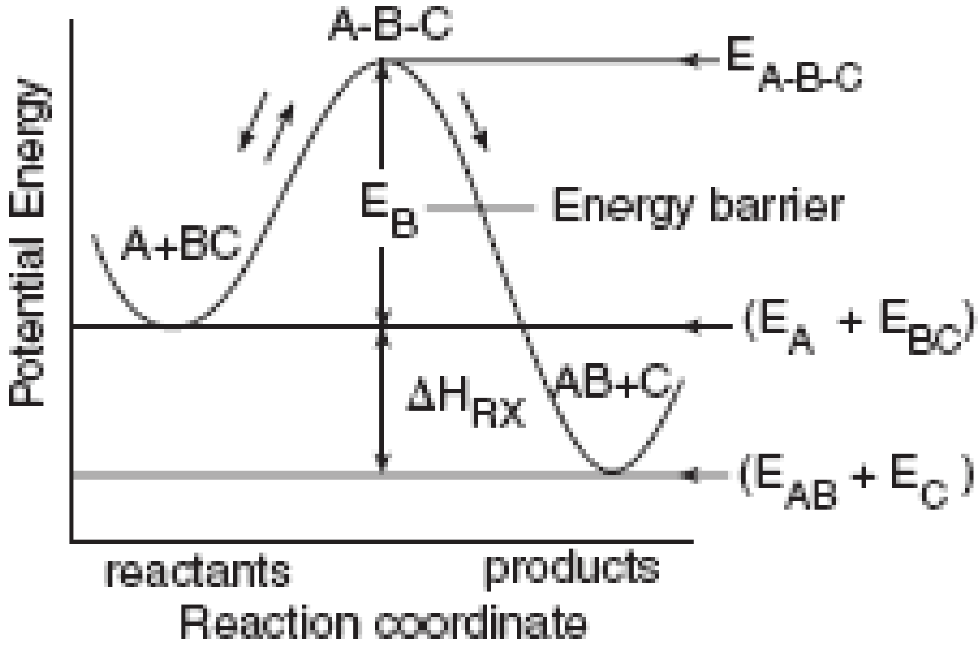
- The activation energy can be thought of as a barrier to energy transfer (from the kinetic energy to the potential energy) between reacting molecules that must be overcome.
- One way to view the barrier to a reaction is through the **reaction coordinates**.
- These coordinates denote the energy of the system as a function of progress along the reaction path as we go from reactants to an intermediate to products.

Reaction Coordinates

For the reaction:

$$A + BC \Leftrightarrow A ::: B ::: C \rightarrow AB + C$$

The reaction coordinate is:



Why is there an Activation Energy?

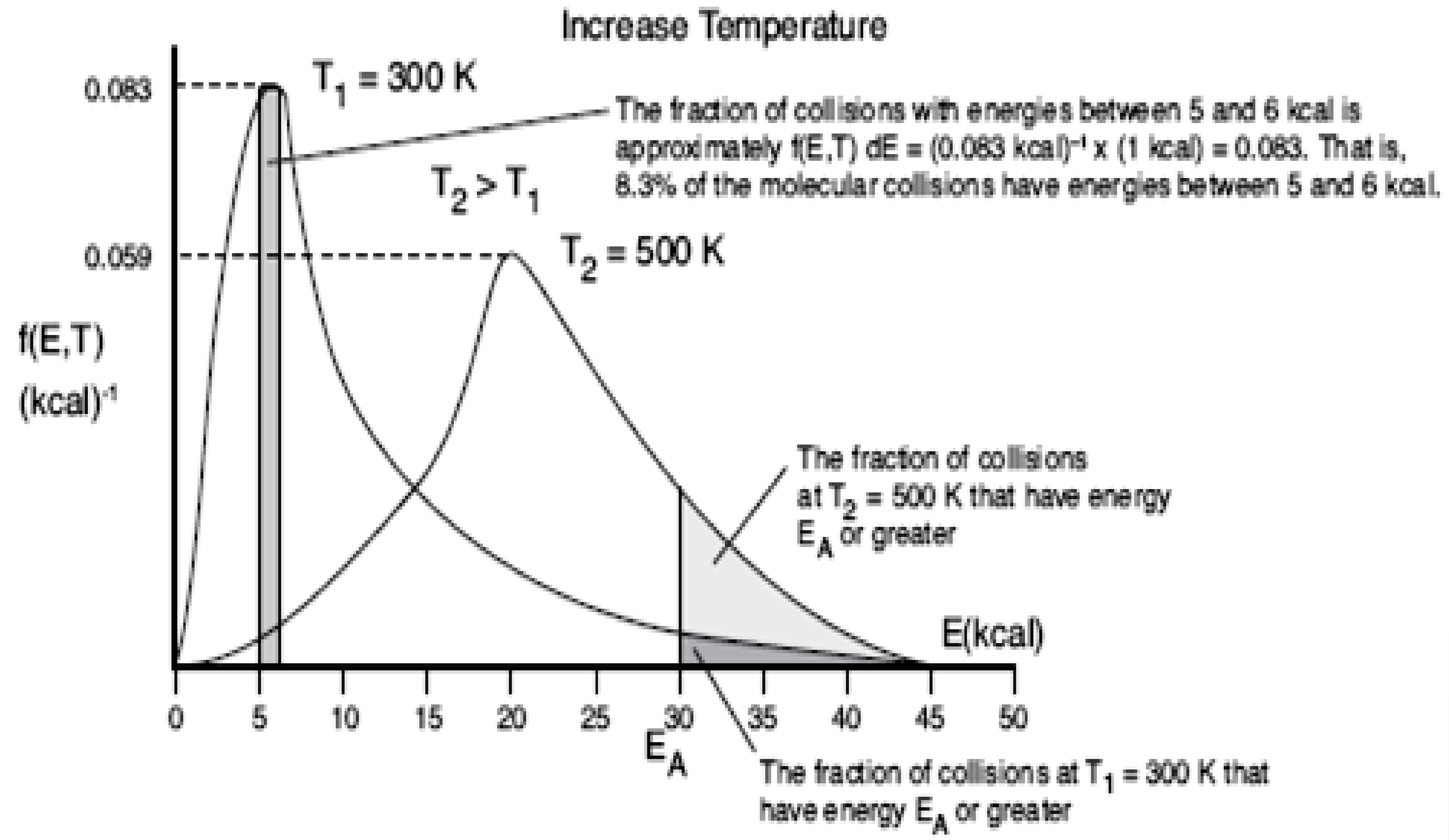
- For the reaction to occur, the reactants must overcome an energy barrier (**activation energy, $\mathbf{E_A}$**). In order to react,
  1. The molecules need energy to disort or stretch their bonds in order to break them and thus form new bonds
  2. As the reacting molecules come close together, they must overcome both stearic and electron repulsion forces.

Why is there an Activation Energy?

- One can also view the activation energy in terms of **collision theory**.
- By increasing the temperature, we increase the kinetic energy of the reactant molecules.
- This kinetic energy can in turn be transferred through molecular collisions to internal energy to increase the stretching and bending of the bonds, causing them to reach an activated state, vulnerable to bond breaking and reaction.

Why is there an Activation Energy?

- The energy of the individual molecules falls within a



The fraction of collisions with energies between 5 and 6 kcal is approximately f(E,T) dE = (0.083 kcal)$^{-1}$ x (1 kcal) = 0.083. That is, 8.3% of the molecular collisions have energies between 5 and 6 kcal.

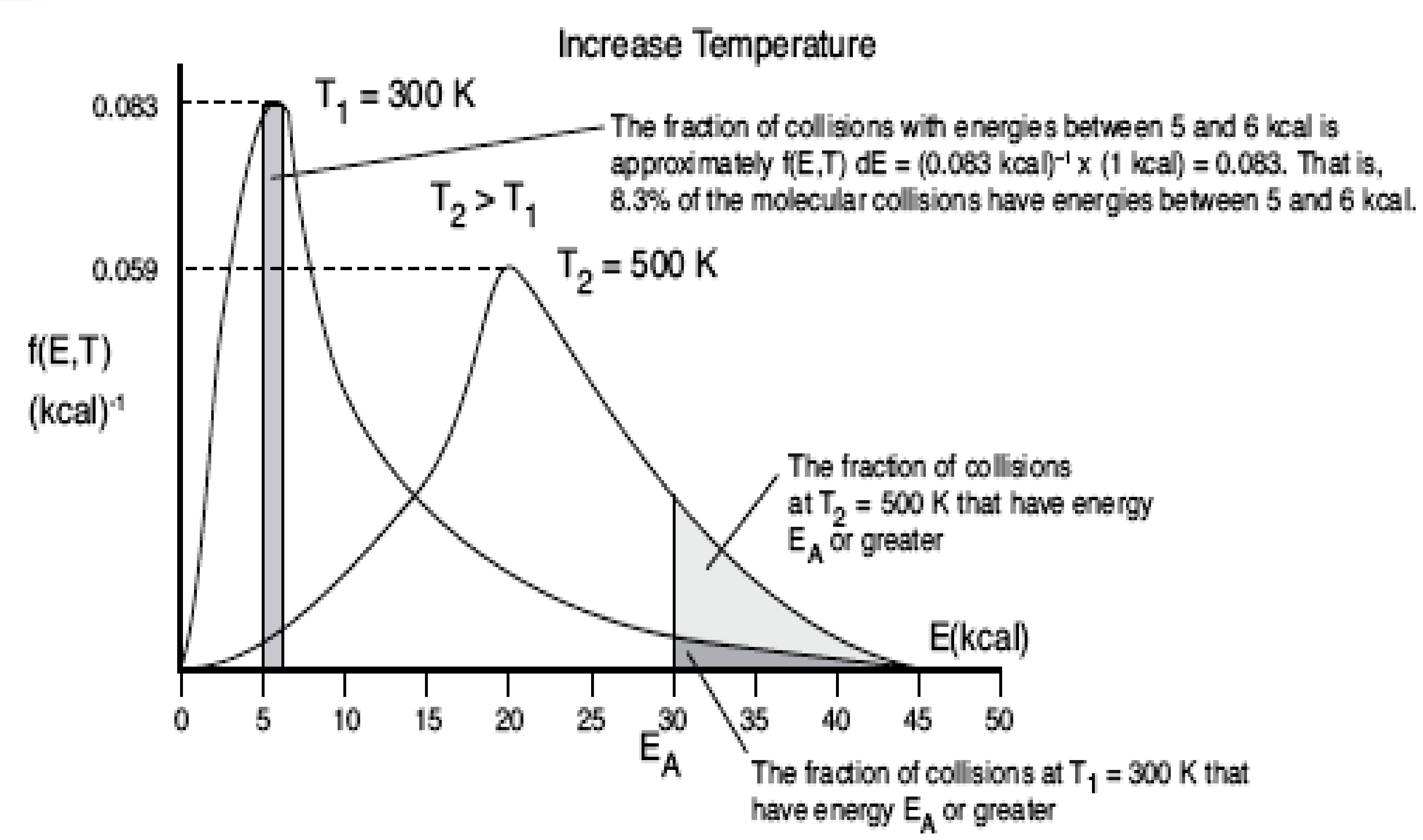
The fraction of collisions at T_2 = 500 K that have energy E_A or greater

The fraction of collisions at T_1 = 300 K that have energy E_A or greater

Why is there an Activation Energy?

- The activation energy has been equated with a minimum energy that must be possessed by reacting molecules before the reaction will occur.
- The fraction of the reacting molecules that have an energy E_A or greater is shown by the shaded areas.
  - The molecules in the shaded area have sufficient kinetic energy to cause the bond to break and reaction to occur.

Why is there an Activation Energy?



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Algorithm

How to find $-r_A = f(X)$

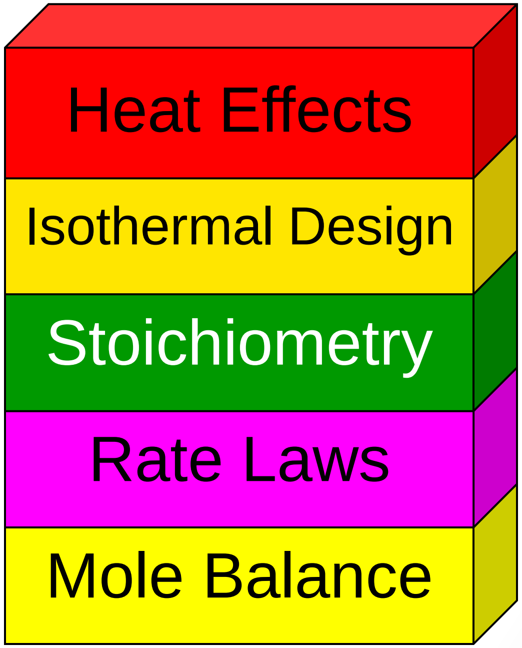
Step 1: Rate Law $-r_A = g(C_i)$

Step 2: Stoichiometry $(C_i) = h(X)$

Step 3: Combine to get $-r_A = f(X)$

CRE Algorithm

- Building Block 1 - **Mole Balances**
  - Size CSTRs and PFRs given $-r_A = f(X)$
- Building Block 2 - **Rate Laws**
  - Reaction Orders
  - Arrhenius Equation
- Building Block 3 - **Stoichiometry**
  - Stoichiometric Table
  - Definitions of Concentration
  - Calculate the Equilibrium Conversion



Heat Effects

Isothermal Design

Stoichiometry

Rate Laws

Mole Balance

Algorithm

How to find $-r_A = f(X)$

Step 1: Rate Law $-r_A = g(C_i)$

Step 2: Stoichiometry $(C_i) = h(X)$

Step 3: Combine to get $-r_A = f(X)$

Building Block 3:

Stoichiometry

- We shall set up **Stoichiometry Tables** using species A as our basis of calculation in the following reaction.
- We will use the stoichiometric tables to express the concentration as a function of conversion.
- We will combine $C_i = f(X)$ with the appropriate rate law to obtain $-r_A = f(X)$.

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

A is the limiting reactant.

Stoichiometry

$$N_A = N_{A0} - N_{A0}X$$

For every mole of A that reacts, ***b/a*** moles of B react. Therefore moles of B remaining:

$$N_B = N_{B0} - \frac{b}{a}N_{A0} = N_{A0}\left(\frac{N_{B0}}{N_{A0}} - \frac{b}{a}X\right)$$

Let $\Theta_B = \frac{N_{B0}}{N_{A0}}$

Then:

$$N_B = N_{A0}\left(\Theta_B - \frac{b}{a}X\right)$$

$$N_C = N_{C0} + \frac{c}{a}N_{A0}X = N_{A0}\left(\Theta_C + \frac{c}{a}X\right)$$

Batch System

Stoichiometry Table

Species	Symbol	Initial	Change	Remaining
A	A	N_{A0}	$-N_{A0}X$	$N_A=N_{A0}(1-X)$
B	B	$N_{B0}=N_{A0}\Theta_B$	$-\frac{b}{a}N_{A0}X$	$N_B = N_{A0}\left(\Theta_B - \frac{b}{a}X\right)$
C	C	$N_{C0}=N_{A0}\Theta_C$	$+\frac{c}{a}N_{A0}X$	$N_C = N_{A0}\left(\Theta_C + \frac{c}{a}X\right)$
D	D	$N_{D0}=N_{A0}\Theta_D$	$+\frac{d}{a}N_{A0}X$	$N_D = N_{A0}(\Theta_D + \frac{d}{a}X)$
Inert	I	$N_{I0}=N_{A0}\Theta_I$	----------	$N_I=N_{A0}\Theta_I$
		N_{T0}		$N_T=N_{T0}+\delta N_{A0}X$

where: $\Theta_i = \frac{N_{i0}}{N_{A0}} = \frac{C_{i0}\upsilon_0}{C_{A0}\upsilon_0} = \frac{C_{i0}}{C_{A0}} = \frac{y_{i0}}{y_{A0}}$ and $\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1$

δ = change in total number of mol per mol A reacted

Stoichiometry Constant Volume Batch System

Note: **If** the reaction occurs in the liquid phase

or

if a gas phase reaction occurs in a rigid (e.g. steel) batch reactor

Then $V = V_0$

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

$$C_B = \frac{N_B}{V} = \frac{N_{A0}}{V_0}\left(\Theta_B - \frac{b}{a}X\right) = C_{A0}\left(\Theta_B - \frac{b}{a}X\right)$$

Stoichiometry Constant Volume Batch System

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

Suppose $-r_A = k_A C_A^2 C_B$

Batch: $V = V_0$

$$-r_A = k_A C_{A0}{}^3 (1 - X)^2 \left(\Theta_B - \frac{b}{a} X \right)$$

Equimolar feed: $\Theta_B = 1$

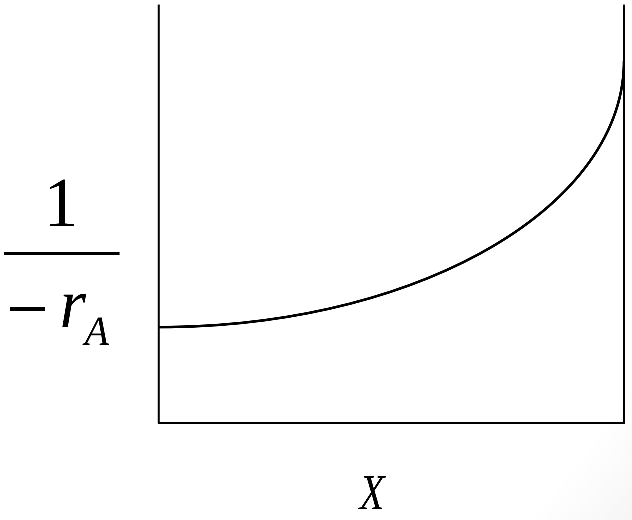
Stoichiometric feed: $\Theta_B = \frac{b}{a}$

Stoichiometry Constant Volume Batch System

If $-r_A = k_A C_A^2 C_B$, then

$$-r_A = C_{A0}{}^3 (1-X)^2 \left(\Theta_B - \frac{b}{a} X \right)$$ Constant Volume Batch

and we have $-r_A = f(X)$



Batch Reactor - Equilibrium Conversion - Example

Calculate the equilibrium conversion for gas phase reaction, X_e.

Consider the following **elementary** reaction with K_C=20 dm^3/mol and C_{A0} = 0.2 mol/dm^3.
Find X_e for a **constant volume batch reactor.**

$$2A \Leftrightarrow B$$

$$-r_A = k_A\left[C_A{}^2 - \frac{C_B}{K_C}\right]$$

Batch Reactor - Example

Calculate X_e

$$C_{A0} = 0.2\, mol/dm^3$$

$$K_C = 20\, dm^3/mol$$

Step 1: $\dfrac{dX}{dt} = \dfrac{-r_A V}{N_{A0}}$

$$2A \Leftrightarrow B$$

Step 2: rate law: $-\mathrm{r_A} = \mathrm{k_A C_A^2 - k_B C_B}$

$$-r_A = k_A\left[C_A{}^2 - \frac{C_B}{K_C}\right]$$

$$\mathrm{K_C} = \frac{\mathrm{k_A}}{\mathrm{k_B}}$$

Batch Reactor - Example

Symbol	Initial	Change	Remaining
A	N_{A0}	$-N_{A0}X$	$N_{A0}(1-X)$
B	0	$\frac{1}{2} N_{A0}X$	$N_{A0} X/2$

Totals: $N_{T0}=N_{A0}$ $N_T=N_{A0} - N_{A0} X/2$

@ equilibrium: $-rA = 0$ $0 = C_{Ae}^2 - \dfrac{C_{Be}}{K_C}$

Stoichiometry: $A \rightarrow B/2$

Constant Volume: $V = V_0$

$$C_{Ae} = \frac{N_{Ae}}{V} = C_{A0}\left(1 - X_e\right) \qquad C_{Be} = C_{A0}\frac{X_e}{2}$$

Batch Reactor - Example

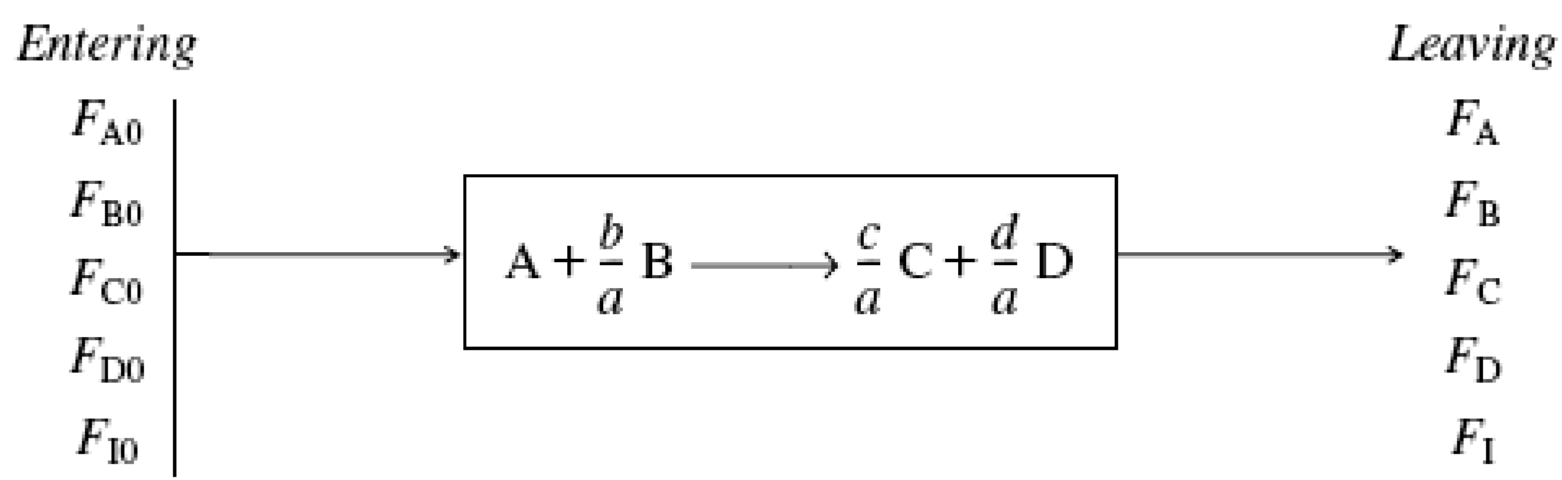
$$K_e = \frac{C_{Be}}{C_{Ae}^2}$$

$$K_e = \frac{C_{A0}\frac{X_e}{2}}{\left[C_{A0}(1-X_e)\right]^2} = \frac{X_e}{2C_{A0}(1-X_e)^2}$$

$$2K_eC_{A0} = \frac{X_e}{(1-X_e)^2} = 2(20)(0.2) = 8$$

$$\boxed{X_{eb} = 0.703}$$

Flow System –
Stoichiometry Table



Species	Symbol	Reactor Feed	Change	Reactor Effluent
A	A	F_{A0}	$-F_{A0}X$	$F_A=F_{A0}(1-X)$
B	B	$F_{B0}=F_{A0}\Theta_B$	$-\frac{b}{a}F_{A0}X$	$F_B = F_{A0}\left(\Theta_B - \frac{b}{a}X\right)$

Where: $\Theta_i = \frac{F_{i0}}{F_{A0}} = \frac{C_{i0}\upsilon_0}{C_{A0}\upsilon_0} = \frac{C_{i0}}{C_{A0}} = \frac{y_{i0}}{y_{A0}}$

Flow System – Stoichiometry Table

Species	Symbol	Reactor Feed	Change	Reactor Effluent
C	C	$F_{C0}=F_{A0}\Theta_C$	$+\frac{c}{a}F_{A0}X$	$F_C=F_{A0}\left(\Theta_C+\frac{c}{a}X\right)$
D	D	$F_{D0}=F_{A0}\Theta_D$	$+\frac{d}{a}F_{A0}X$	$F_D=F_{A0}\left(\Theta_D+\frac{d}{a}X\right)$
Inert	I	$F_{I0}={}_{A0}\Theta_I$	----------	$F_I=F_{A0}\Theta_I$
		F_{T0}		$F_T=F_{T0}+\delta F_{A0}X$

Where: $\Theta_i=\frac{F_{i0}}{F_{A0}}=\frac{C_{i0}\upsilon_0}{C_{A0}\upsilon_0}=\frac{C_{i0}}{C_{A0}}=\frac{y_{i0}}{y_{A0}}$ and $\delta=\frac{d}{a}+\frac{c}{a}-\frac{b}{a}-1$

Concentration – Flow System $C_A=\frac{F_A}{\upsilon}$

Stoichiometry

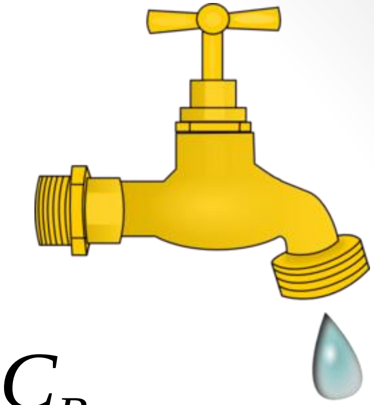
Concentration Flow System: $C_A = \frac{F_A}{\upsilon}$

Liquid Phase Flow System: $\upsilon = \upsilon_0$

$$C_A = \frac{F_A}{\upsilon} = \frac{F_{A0}(1-X)}{\upsilon_0} = C_{A0}(1-X)$$

$$C_B = \frac{N_B}{\upsilon} = \frac{N_{A0}}{\upsilon_0}\left(\Theta_B - \frac{b}{a}X\right) = C_{A0}\left(\Theta_B - \frac{b}{a}X\right)$$

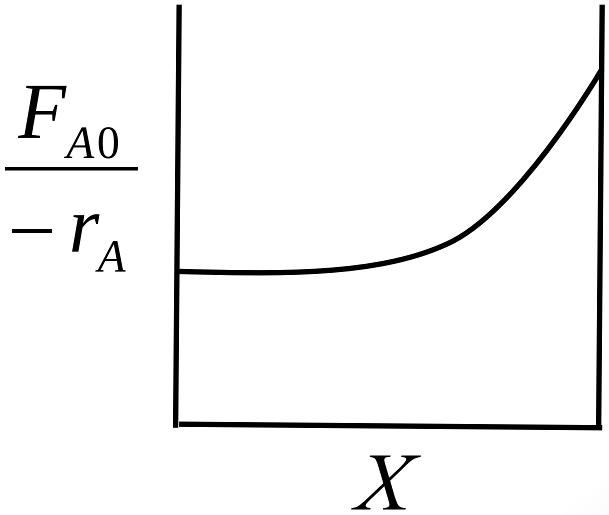
Liquid Systems



If the rate of reaction were $-r_A = kC_AC_B$

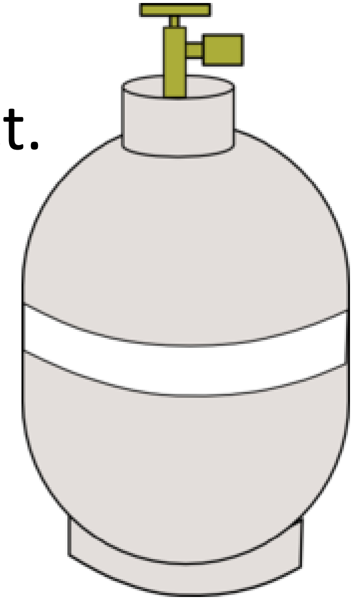
then we would have $-r_A = C_{A0}{}^2(1-X)\left(\Theta_B - \frac{b}{a}X\right)$

This gives us $-r_A = f(X)$



Stoichiometry for Gas Phase Flow Systems

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$



4 mol of reactants gives 2 mol of product.

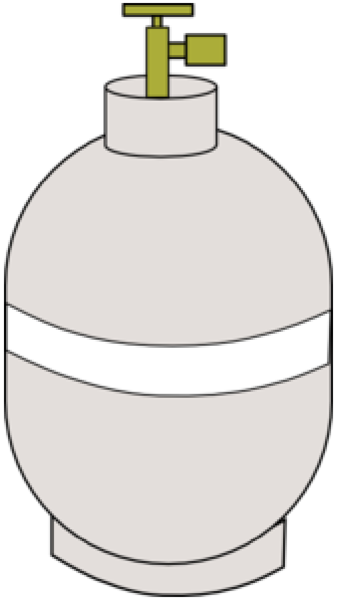
→ the molar flow rate will be changing as the reaction progresses.

Because equal **numbers of moles** occupy equal **volumes** in the gas phase at the same temperature and pressure.

→ the volumetric flow rate will also **change.**

Stoichiometry for Gas Phase Flow Systems

Combining the compressibility factor equation of state with $Z = Z_0$



Stoichiometry:

$$C_T = \frac{P}{ZRT}$$

$$C_{T0} = \frac{P_0}{Z_0 R_0 T_0}$$

$$F_T = C_T \upsilon$$

$$F_{T0} = C_{T0} \upsilon_0$$

We obtain:

$$\boxed{\upsilon = \upsilon_0 \frac{F_T}{F_{T0}} \frac{P_0}{P} \frac{T}{T_0}}$$

Stoichiometry for Gas Phase Flow Systems

$$C_A = F_A/\upsilon = \frac{F_A}{\upsilon_0\left(\frac{F_T}{F_0}\right)}\left(\frac{P}{P_0}\right)\left(\frac{T_0}{T}\right) = \frac{F_{T0}}{\upsilon_0}\frac{F_A}{F_T}\left(\frac{P}{P_0}\right)\left(\frac{T_0}{T}\right)$$

Since $C_{T0} = F_{T0}/\upsilon_0$,

$$C_A = F_A/\upsilon = C_{T0}\frac{F_A}{F_T}\left(\frac{P}{P_0}\right)\left(\frac{T_0}{T}\right)$$

Using the same method,

$$C_B = C_{T0}\left(\frac{F_B}{F_T}\right)\left(\frac{P}{P_0}\right)\left(\frac{T_0}{T}\right)$$

Stoichiometry for Gas Phase Flow Systems

The total molar flow rate is: $\mathrm{F_T = F_{T0} + F_{A0}\delta X}$

Substituting F_T gives: $\upsilon = \upsilon_0 \dfrac{F_T}{F_{T0}} \dfrac{P_0}{P} \dfrac{T}{T_0}$

$$\upsilon = \upsilon_0 \left(\frac{F_{T0} + F_{A0}\delta X}{F_{T0}} \right) \frac{T}{T_0} \frac{P_0}{P} = \upsilon_0 \left(1 + \frac{F_{A0}}{F_{T0}} \delta X \right) \frac{T}{T_0} \frac{P_0}{P}$$

$$\upsilon = \upsilon_0 \left(\frac{F_{T0} + F_{A0}\delta X}{F_{T0}} \right) \frac{T}{T_0} \frac{P_0}{P} = \upsilon_0 \left(1 + \frac{F_{A0}}{F_{T0}} \delta X \right) \frac{T}{T_0} \frac{P_0}{P}$$

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

For Gas Phase Flow Systems

Concentration Flow System: $C_A = \dfrac{F_A}{\upsilon}$

Gas Phase Flow System: $\upsilon = \upsilon_0 (1 + \varepsilon X) \dfrac{T}{T_0} \dfrac{P_0}{P}$

$$C_A = \frac{F_A}{\upsilon} = \frac{F_{A0}(1 - X)}{\upsilon_0 (1 + \varepsilon X) \frac{T}{T_0} \frac{P_0}{P}} = C_{A0} \frac{(1 - X)}{(1 + \varepsilon X)} \frac{T_0}{T} \frac{P}{P_0}$$

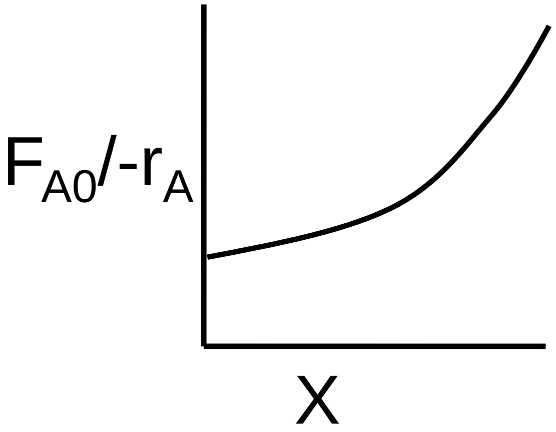
$$C_B = \frac{F_B}{\upsilon} = \frac{F_{A0}\left(\Theta_B - \frac{b}{a} X\right)}{\upsilon_0 (1 + \varepsilon X) \frac{T}{T_0} \frac{P_0}{P}} = C_{A0} \frac{\left(\Theta_B - \frac{b}{a} X\right)}{(1 + \varepsilon X)} \frac{T_0}{T} \frac{P}{P_0}$$

For Gas Phase Flow Systems

If $-r_A = kC_AC_B$

$$-r_A = k_A C_{A0}^2 \left[\frac{(1-X)}{(1+\varepsilon X)} \frac{\left(\Theta_B - \frac{b}{a}X\right)}{(1+\varepsilon X)} \left(\frac{P}{P_0}\frac{T_0}{T}\right)^2 \right]$$

This gives us



For Gas Phase Flow Systems

where

$$\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1$$

$$\delta = \frac{\text{change in total number of moles}}{\text{mole of A reacted}}$$

$$\varepsilon = \left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1 \right) \frac{F_{A0}}{F_{T0}} = y_{A0}\delta$$

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

$$\varepsilon = \frac{\text{change in total number of moles for complete conversion}}{\text{total number of moles fed to the reactor}}$$

Equilibrium Conversion (X_{ef}) for Gas Phase Flow Reaction System

Example:

- Consider the following elementary reaction where

$$2\mathrm{A} \Leftrightarrow \mathrm{B} \qquad -r_A = k_A\left[C_A{}^2 - \frac{C_B}{K_C}\right]$$

K_C = 20 dm³/mol and C_{A0} = 0.2 mol/dm³.

- Calculate Equilibrium Conversion for an isothermal isobaric **flow reactor (X_{ef})**.

Gas Flow Example (X_{ef})

$$2A \Leftrightarrow B$$

$$X_{ef} = ?$$

Solution:

Rate Law:

$$-r_A = k_A \left[C_A^2 - \frac{C_B}{K_C} \right]$$

Stoichiometry

$$\mathrm{A} \rightarrow \frac{1}{2}\mathrm{B}$$

Gas Flow Example (X_{ef})

Species	Feed	Change	Effluent
A	F_{A0}	$-F_{A0}X$	$F_A = F_{A0}(1-X)$
B	0	$+F_{A0}X/2$	$F_B = F_{A0}X/2$
Total	$F_{T0}=F_{A0}$		$F_T = F_{A0} - F_{A0}X/2$

Stoichiometry: Gas isothermal $T = T_0$

Gas isobaric $P = P_0$

$$\upsilon = \upsilon_0 (1+\varepsilon X)$$

$$C_A = \frac{F_{A0}(1-X)}{\upsilon_0(1+\varepsilon X)} = \frac{C_{A0}(1-X)}{(1+\varepsilon X)}$$

$$C_B = \frac{F_B}{\upsilon} = \frac{F_{A0}X/2}{\upsilon_0(1+\varepsilon X)} = \frac{C_{A0}X}{2(1+\varepsilon X)}$$

Gas Flow Example (X_{ef})

$$-r_A = k_A\left[\left(\frac{C_{A0}(1-X)}{(1+\varepsilon X)}\right)^2 - \frac{C_{A0}X}{2(1+\varepsilon X)K_C}\right]$$

Pure A → $y_{A0} = 1$

$C_{A0} = yA_0 P_0/RT_0, CA_0 = P_0/RT_0$

$$\varepsilon = y_{A0}\delta = (1)\left(\frac{1}{2}-1\right) = -\frac{1}{2}$$

At equilibrium: $-rA = 0$

$$2K_C C_{A0} = \frac{X_e(1+\varepsilon X_e)}{(1-X_e)^2}$$

Gas Flow Example (X_{ef})

$$2K_C C_{A0} = \frac{X_e(1+\varepsilon X_e)}{(1-X_e)^2}$$

$$\varepsilon = -\frac{1}{2}$$

$$2K_C C_{A0} = 2\left(20\frac{dm^3}{mol}\right)\left(0.2\frac{mol}{dm^3}\right) = 8$$

$$8 = \frac{X_e - 0.5X_e^{\ 2}}{\left(1-2X_e + X_e^{\ 2}\right)}$$

$$8.5X_e^{\ 2} - 17X_e + 8 = 0$$

$$\boxed{X_{ef} = 0.757}$$

For Batch System:

$$X_{eb} = 0.703$$