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KINETICS & REACTOR DESIGN

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What next???

If the going is real easy, beware, you may be headed down hill and don't know it.

Source: Unknown

When the going gets tough, the tough get going

After this chapter you will be able to write the rate of reaction as a function of conversion for both gas phase and liquid phase contacting systems

Rationale for moving ahead

Earlier we saw that if we had $-r_A$ as a function of X , $[-r_A = f(X)]$ we could size many reactors and reactor sequences and systems.

How do we obtain $-r_A = f(X)$?

We do this in two steps

1. Rate Law – Find the rate as a function of concentration,

$$-r_A = k \text{ fn } (C_A, C_B \dots)$$

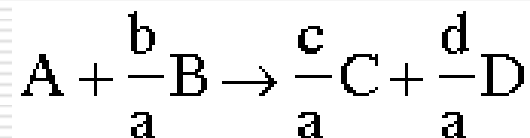
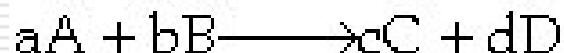
2. Stoichiometry – Find the concentration as a function of conversion

$$C_A = g(X)$$

Basic definitions

- Homogeneous reaction: One phase
 - Heterogeneous reaction: 2 phase, interface
 - Irreversible reaction
 - Reversible reaction
-
- Molecularity: Number of atoms, molecules or ions involved in a reaction step
-
- Unimolecular
 - Bimolecular
 - Tetramolecular

Relative rates of reactions



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

The Reaction:



is carried out in a reactor. If at a particular point, the rate of disappearance of A is 10 mol/dm³/s, what are the rates of B and C?

Reaction Order and Rate Laws

Consider the general equation $aA + bB \longrightarrow cC + dD$

We will choose A as our basis of calculation $A + \frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D$

The basis of calculation is most always the limiting reactant.

$$-r_A = k_A (T) \text{ fn } (C_A, C_B \dots) \quad \leftarrow \text{ **RATE LAW** }$$

k is the specific rate of reaction or rate constant

Power law models

$$-r_A = k_A (T) \text{ fn } (C_A, C_B \dots)$$

Experiments

Theory

Order of a reaction

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

α order in A

β order in B

Overall Reaction Order = $\alpha + \beta$

The order of a reaction refers to the powers to which the concentrations are raised in the kinetic rate law.

The unit of $-r_A$ is always in terms of concentration per unit time while the units of rate constant will vary with the order of the reaction. For $A \rightarrow \text{Products}$ with reaction order n ,

$$k = (\text{Concentration})^{1-n} / \text{time}$$

Order of a reaction

Strictly speaking the reaction rate is in terms of the activities,

$$a_i = \gamma_i C_i$$

For many reacting systems the activity co-efficient does not change appreciably during the course of the reaction and they are absorbed into the specific reaction rate

DIY

- 1. What are zero, first, second and third order reaction?**
- 2. What are the units of k for the above?**

Elementary reactions

A reaction follows an elementary rate law if and only if the stoichiometric coefficients are the same as the individual reaction order of each species. For the reaction in the previous example $A + B \rightarrow C + D$ the rate law would be: $-r_A = k C_A C_B$

If $2NO + O_2 \rightarrow 2NO_2$, then $-r_{NO} = k_{NO} (C_{NO})^2 C_{O_2}$,

Is this reaction elementary!



Non-elementary reactions

If the rate law for the non-elementary reaction

is found to be $-r_A = kC_A^2 C_B$ $A + B \rightarrow C + D$

then the reaction is said to be 2nd order in A, 1st order in B, and 3rd order overall.

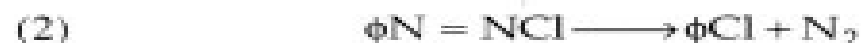
The overall order of the reaction does not have to be an integer nor does the order have to be an integer with respect to any individual component. For e.g. $\text{CO} + \text{Cl}_2 \rightarrow \text{COCl}_2$ (phosgene synthesis)

$$-r_{\text{CO}} = kC_{\text{CO}}C_{\text{Cl}_2}^{3/2}$$

TABLE 3-1. EXAMPLES OF REACTION RATE LAWS

A. First-Order Rate Laws

$$-r_A = kC_{C_2H_6}$$



$$-r_A = kC_{\phi N = NCl}$$



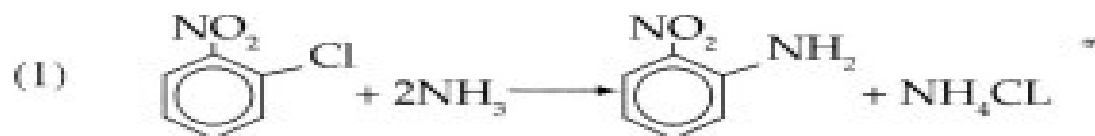
$$-r_A = kC_{CH_2OCH_2}$$



$$-r_A = kC_{CH_3COCH_3}$$



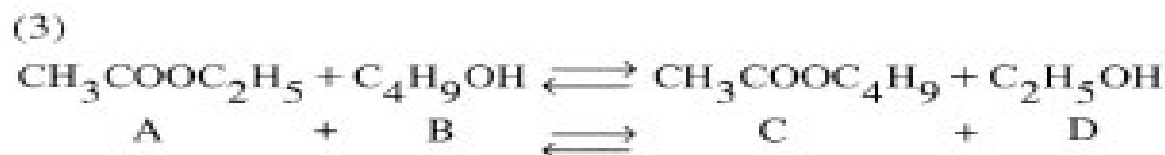
$$-r_n = k[C_{nC_4} - C_{iC_4}/K_C]$$

B. Second-Order Rate Laws

$$-r_A = k_{ONCB} C_{ONCB} C_{NH_3}^{\dagger}$$



$$-r_A = kC_{CNBr} C_{CH_3NH_2}$$

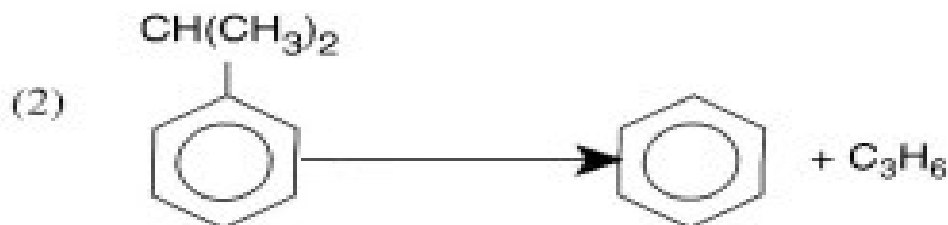


$$-r_A = k[C_A C_B - C_C C_D / K_C]$$

TABLE 3-1. EXAMPLES OF REACTION RATE LAWS (CONTINUED)

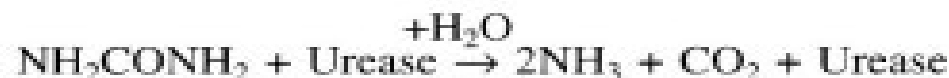
C. Nonelementary Rate Laws

$$-r_{\text{CH}_3\text{CHO}} = kC_{\text{CH}_3\text{CHO}}^{3/2}$$



Cumene (C) \longrightarrow Benzene (B) + Propylene (P)

$$-r_C = \frac{k[P_C - P_B P_P / K_P]}{1 + K_B P_B + K_C P_C}$$

D. Enzymatic Reactions (Urea (U) + Urease (E))

$$-r_U = \frac{kC_U}{K_M + C_U}$$

E. Biomass Reactions

$$-r_U = \frac{kC_S C_C}{K_S + C_S}$$

Note: The rate constant, k , and activation energies for a number of the reactions in these examples are given in the Data Base on the CD-ROM and Summary Notes.

Elementary reactions

Rate laws are determined experimentally. They are a function of the reaction chemistry and not on the type of reactor in which the reaction occurs.

CHECK LITERATURE BEFORE YOU RUN TO THE LAB

What is the reaction rate law for the reaction below if the reaction is elementary? What is r_B ? What is r_C ? Calculate the rates of A, B, and C in a CSTR where the concentrations are $C_A = 1.5 \text{ mol/dm}^3$, $C_B = 9 \text{ mol/dm}^3$ and $k_A = 2 \text{ (dm}^3/\text{mol)}^{(1/2)}(1/\text{s})$.

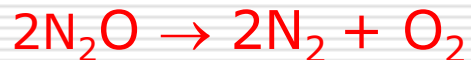


Non-elementary reactions

Sometimes reaction have complex rate expressions that cannot be separated into solely temperature dependent and concentration dependent portions

DECOMPOSITION OF NITROUS OXIDE

$$-r_A = \frac{k_A P_A P_B}{1 + K_A P_A}$$



**Rate
can be
in terms
of
partial
pressur
es**

$$-r_{\text{N}_2\text{O}} = k_{\text{N}_2\text{O}} C_{\text{N}_2\text{O}} / 1 + k' C_{\text{O}_2}$$

The concept of apparent reaction order

$$(1 \gg k' C_{\text{O}_2}) \text{ or } (1 \ll k' C_{\text{O}_2})$$

Things getting tougher by the day...



**For you and me
(making ppt's)**

When things go wrong, you'll find they usually go on getting worse for some time; but when things once start going right they often go on getting better and better.

But then, left to themselves, things always go from bad to worse

Be what nature intended you for, and you will succeed; be anything else and you will be ten thousand times worse than nothing

The reaction rate constant

- ❑ Not truly a constant
- ❑ Independent of the concentration of the species involved in the reaction
- ❑ Almost always strongly dependent on temperature
- ❑ Depends on whether a catalyst is present or not
- ❑ In gas-phase reactions, maybe a function of total pressure
- ❑ In liquid systems, it can be a function of other parameters such as ionic strength and choice of solvent
- ❑ Other parameters are less important and may assume importance for supercritical solvents

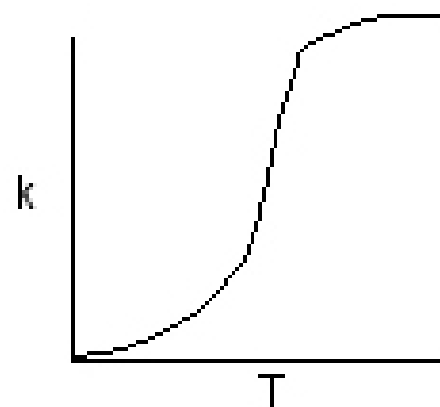
FOR THE TIME BEING $k = f(T)$ ENOUGH

This dependence is given by Arrhenius' equation

The reaction rate constant

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

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



E = activation energy (cal/mol) or J/mol

R = gas constant (cal/mol.K) or J/mol.K

T = Absolute temperature in K

A = frequency factor or pre-exponential factor

$$k \rightarrow 0$$

$$T \rightarrow 0$$

$$k \rightarrow A$$

$$T \rightarrow \infty$$



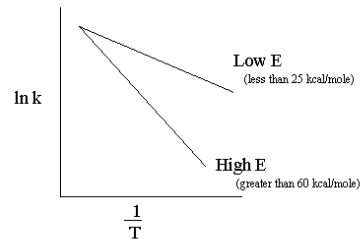
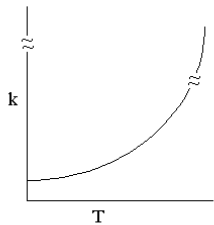
A little about Arrhenius

Svante August Arrhenius was born in Vik, Sweden in 1859. At age 25, he turned in his PhD thesis at the University of Uppsala, Sweden. His PhD examining committee did not think very highly of his thesis and rated it 4th class. His oral thesis defense did not fair much better as they rated it as only 3rd class. Arrhenius left Sweden for five years to work with Oswald, Boltzmann and Van't Hoff. In 1889 his interpretation of temperature-dependent equation by Van't Hoff led to the universal accepted Arrhenius equation for kinetic rate laws in chemistry.

He received the Nobel Prize in 1903. From 1905 until his death in 1927 he was director of Physical Chemistry at the Nobel Institute.

Activitation Energy

The activation energy is a measure of how temperature sensitive the reactor is. Reactions with large activation energies are very temperature sensitive.



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

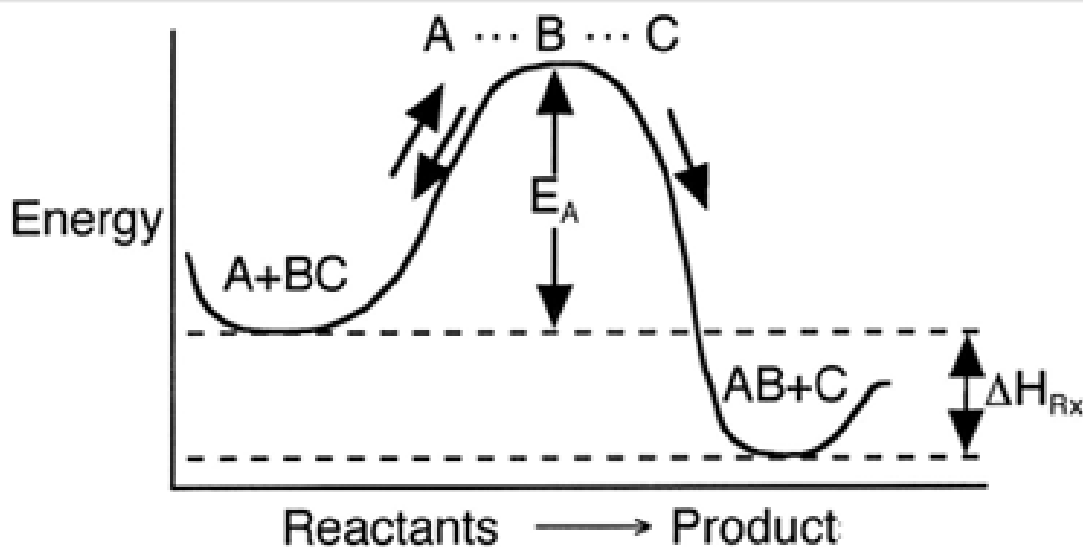
$$k_0 = Ae^{-E/RT_0}$$

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

$$k = k_0 \exp \left[\frac{E}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \right]$$

Activation Energy

- ❑ Barrier to a reaction
- ❑ For any reaction to occur, the reactants must overcome an energy barrier or activation energy E_A

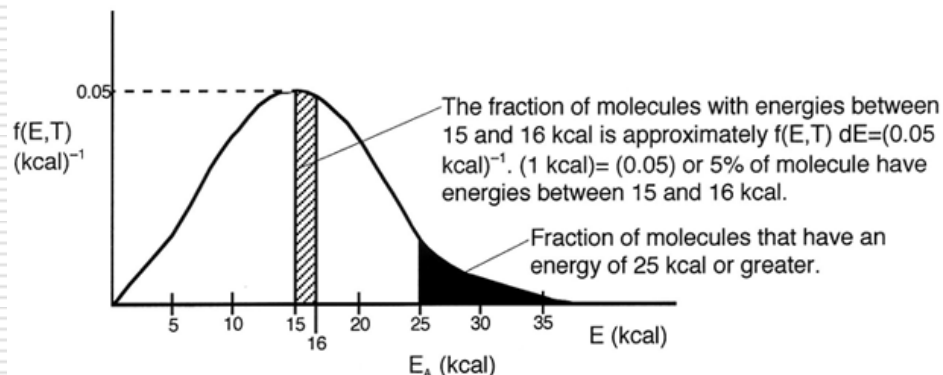


Activitation Energy

Why is there an Activation Energy?

- (1) the molecules need energy to distort or stretch their bonds in order to break them and to thus form new bonds
- (2) As the reacting molecules come close together they must overcome both steric and electron repulsion forces in order to react

Activitation Energy



AE additional info

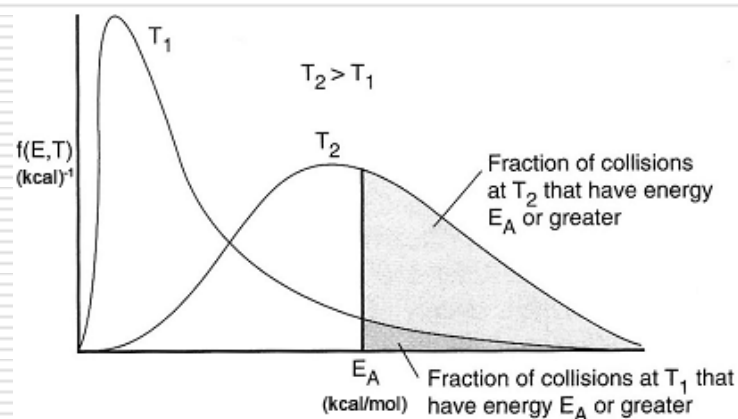
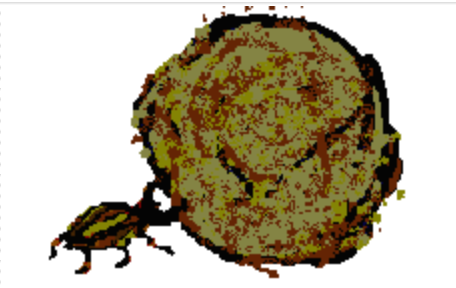


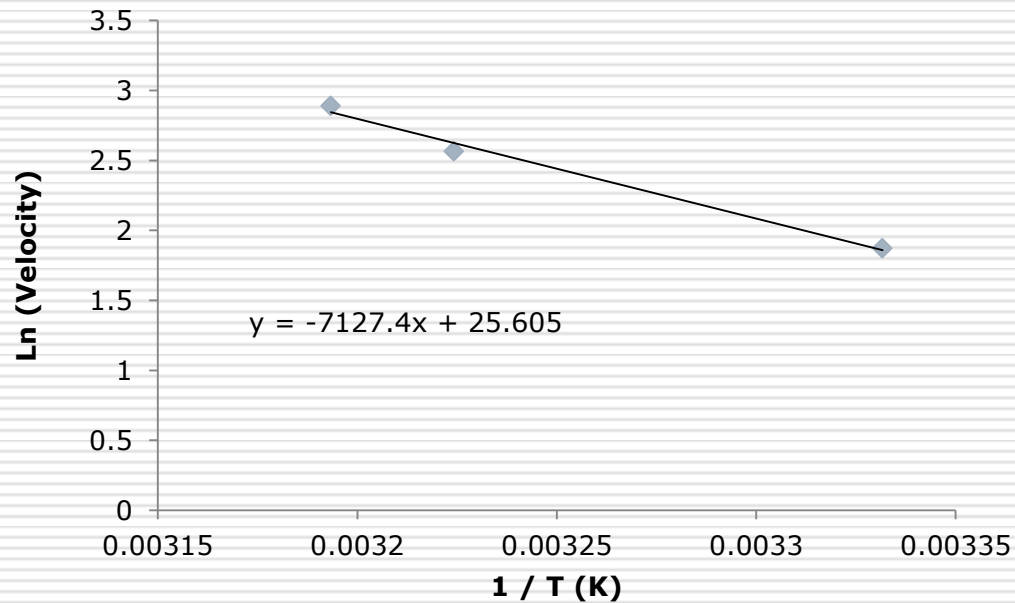
Figure 3-3 Energy distribution of reacting molecules.

Problem Time

Data on the tenebrionid beetle whose body mass is 3.3 g, show that it can push a 35 g ball of dung at 6.5 cm/s at 27 °C, 13 cm/s at 37 °C and 18 cm/s at 40 °C. How fast can it push dung at 41.5 °C?



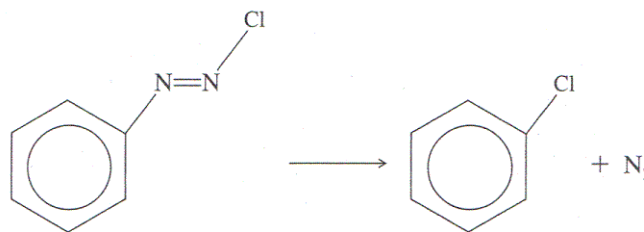
Problem Time



2.949436

19.09518

Problem Time



Calculate the activation energy for the decomposition of benzene diazonium chloride to give chlorobenzene and nitrogen

TABLE E3-1.1 DATA

$k \text{ (s}^{-1}\text{)}$	0.00043	0.00103	0.00180	0.00355	0.00717
$T \text{ (K)}$	313.0	319.0	323.0	328.0	333.0

So where are we? A Recap!!

Earlier we saw that if we had $-r_A$ as a function of X , $[-r_A = f(X)]$ we could size many reactors and reactor sequences and systems.

How do we obtain $-r_A = f(X)$?

We do this in two steps

1. Rate Law – Find the rate as a function of concentration,

$$-r_A = k \text{ fn } (C_A, C_B \dots)$$

2. Stoichiometry – Find the concentration as a function of conversion

$$C_A = g(X)$$

Stoichiometry: Batch reactor systems

	Initial (mol)	Change (mol)	Remaining mol
A	N_{A0}	$-N_{A0}X$	$N_A = N_{A0} - N_{A0}X$
B	N_{B0}	$-(b/a) N_{A0}X$	$N_B = N_{B0} - (b/a)N_{A0}X$
C	N_{C0}	$(c/a) N_{A0}X$	$N_C = N_{C0} + (c/a)N_{A0}X$
D	N_{D0}	$(d/a) N_{A0}X$	$N_D = N_{D0} + (d/a)N_{A0}X$
Inerts (I)	N_{I0}	*****	$N_I = N_{I0}$
Total	N_{T0}	$\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1$	$N_T = N_{T0} + \delta N_{A0}X$

Stoichiometry: Batch reactor systems

$$C_A = \frac{N_A}{V}$$



$$N_{A0}(1 - X) / V$$

$$\Theta_i = \frac{N_{i0}}{N_{A0}} = \frac{C_{i0}}{C_{A0}} = \frac{Y_{i0}}{Y_{A0}}$$

$$C_B = N_B / V$$



$$N_{B0} - (b/a)N_{A0}X / V$$

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

$$C_C = N_C / V$$



$$N_{C0} + (c/a)N_{A0}X / V$$

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

$$C_D = N_D / V$$



$$N_{D0} + (d/a)N_{A0}X / V$$

$$N_D = N_{A0} \left(\Theta_D + \frac{d}{a} X \right)$$

$$N_i = N_{A0} \Theta_i$$

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

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

Stoichiometry: Batch reactor systems

Write the rate law for the elementary liquid phase reaction solely in terms of conversion ($2A + B = C$). The feed to the batch reactor is equal molar A and B with $C_{A0} = 2 \text{ mol/dm}^3$ and $k_A = .01 \text{ (dm}^3/\text{mol)}^4\text{/s}$. What is the rate law? What is the concentration of A and B?

Hint

$$-r_a = k_a C_a^2 C_b$$

$$-r_a = C_{a0}^3 (1-X)^2 \left(\Theta_b - \frac{b}{a} X \right)$$

Stoichiometry: Flow systems

	Initial (mol)	Change (mol)	Remaining mol
A	F_{A0}	$-F_{A0}X$	$F_A = F_{A0} - F_{A0}X$
B	F_{B0}	$-(b/a) F_{A0}X$	$F_B = F_{B0} - (b/a)F_{A0}X$
C	F_{C0}	$(c/a) F_{A0}X$	$F_C = F_{C0} + (c/a)F_{A0}X$
D	F_{D0}	$(d/a) F_{A0}X$	$F_D = F_{D0} + (d/a)F_{A0}X$
Inerts (I)	F_{I0}	*****	$F_I = F_{I0}$
Total	F_{T0}	$\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1$	$F_T = F_{T0} + \delta F_{A0}X$

Stoichiometry: Flow systems

$$C_A = \frac{F_A}{v}$$



$$F_{A0}(1 - X) / V$$

$$\Theta_i = \frac{F_{i0}}{F_{A0}} = \frac{C_{i0}v_0}{C_{A0}v_0} = \frac{C_{i0}}{C_{A0}} = \frac{y_{i0}}{y_{A0}}$$

$$C_B = F_B / v$$



$$F_{B0} - (b/a)F_{A0}X / V$$

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

$$C_C = F_C / v$$



$$F_{C0} + (c/a)F_{A0}X / V$$

$$F_C = F_{A0} \left(\Theta_C + \frac{c}{a}X \right)$$

$$C_D = F_D / v$$



$$F_{D0} + (d/a)F_{A0}X / V$$

$$F_D = F_{A0} \left(\Theta_D + \frac{d}{a}X \right)$$

$$v = v_0$$

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

$$C_B = \frac{F_B}{v} = \frac{F_{A0}}{v_0} \left(\Theta_B - \frac{b}{a}X \right) = C_{A0} \left(\Theta_B - \frac{b}{a}X \right)$$

Stoichiometry: Flow systems (Gas Phase): Variable flow rate

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

with , $C_T = \frac{P}{ZRT}$, $F_T = C_T V$, $F_{T0} = C_{T0} V_0$, $C_{T0} = \frac{P_0}{Z_0 R T_0}$ Take ratio

$$v = v_0 \left(\frac{F_T}{F_{T0}} \right) \frac{T}{T_0} \frac{P_0}{P} \quad F_T = F_{T0} + F_{A0} \delta X$$

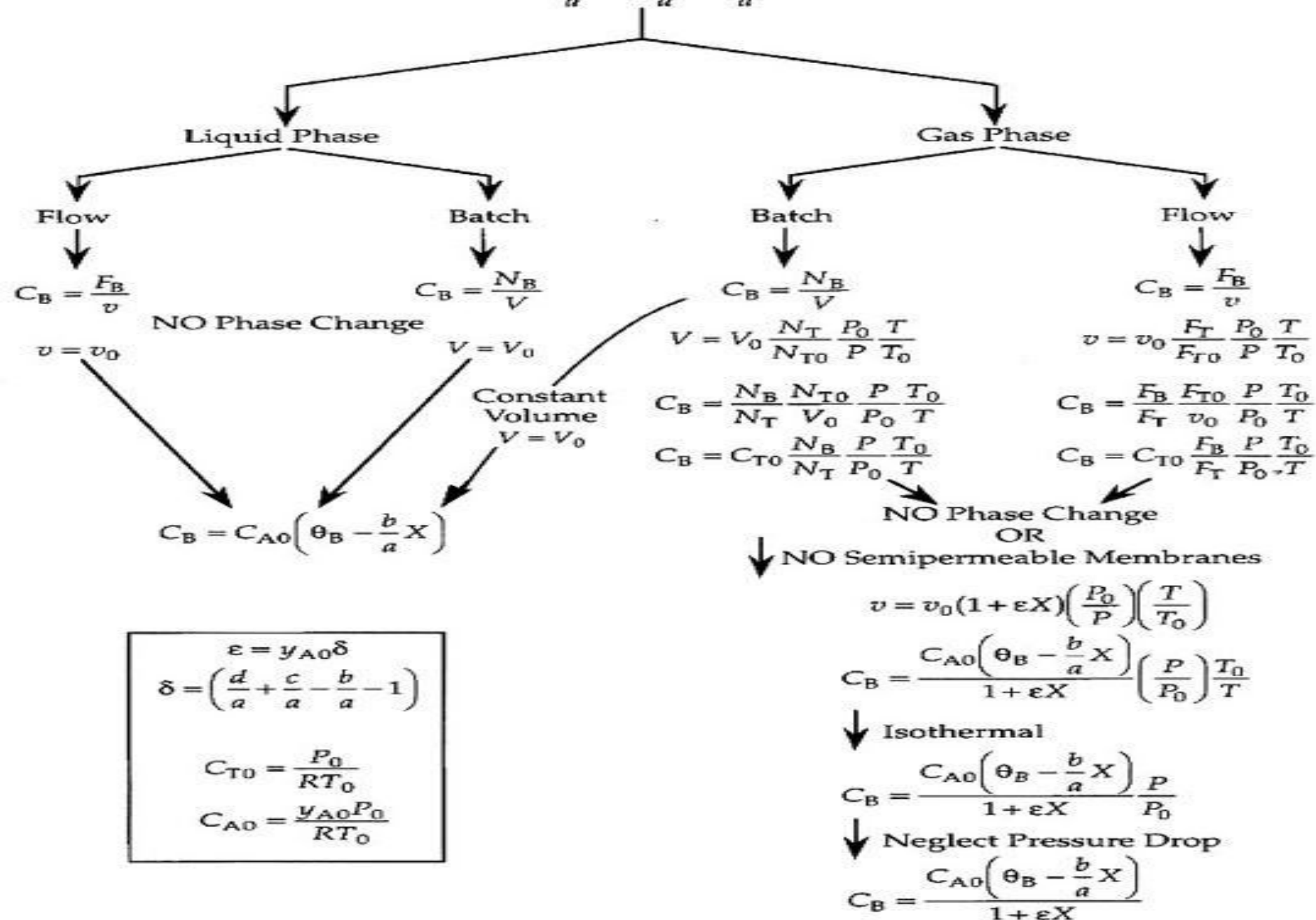
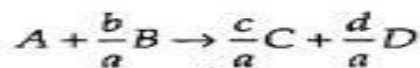
$$v = v_0 \left(\frac{F_{T0} + F_{A0} \delta X}{F_{T0}} \right) \frac{T}{T_0} \frac{P_0}{P}$$

$$v = v_0 \left(1 + \frac{F_{A0}}{F_{T0}} \delta X \right) \frac{T}{T_0} \frac{P_0}{P}$$

$$v = v_0 (1 + Y_{A0} \delta X) \frac{T}{T_0} \frac{P_0}{P}$$

$$v = v_0 (1 + \epsilon X) \frac{T}{T_0} \frac{P_0}{P}$$

DIY: What will C be as a f(X)?



Figure

Expressing concentration as a function of conversion.

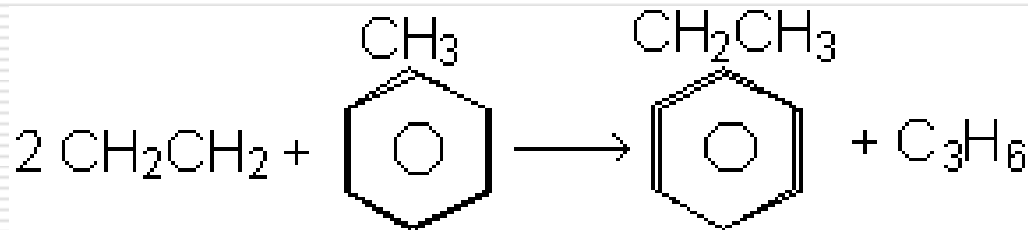
Try a Problem!! Smile..

1. For the gas phase reaction, $2A + B \rightarrow C$, what is δ and ε ? The feed is equimolar in A & B.
2. What is the volume of a gas for a variable volume batch reaction?



Problem!!

1. Let us consider the production of ethyl benzene



The gas feed consists of 25% toluene and 75% ethylene. Set up a stoichiometric table to determine the concentrations of each of the reacting species and then to write the rate of reaction solely as a function of conversion. Assume the reaction is elementary with . The entering pressure is 8.2 atm and the entering temperature is 227 °C and the reaction takes place isothermally with no pressure drop.

Problem!!Hint

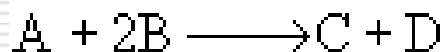
1. What is the basis of your calculation?
2. What are the entering concentrations of ethylene and toluene?

$$C_{A0} = y_{A0} C_{T0} = y_{A0} \frac{P_0}{RT_0}$$

3. What are ε and δ ?
4. Write the row in the stoichiometric table for ethylene & Toluene?
5. Form the entire table including total flowrates?
6. Write the volumetric flowrates in terms of conversion?
7. Write the concentration of ethylene and propylene in terms of conversion?
8. Write the disappearance of A as a function of conversion
9. What is the relative rate of ethylene?

Problem!!Solution

1. The stoichiometric ratio is one toluene to two ethylene (1/2). However, the feed is one toluene to three ethylene (1/3) and there is not sufficient toluene to consume all the ethylene. Therefore toluene is the limiting reactant and thus the basis of calculation
2. Let A = toluene, B = ethylene, C = ethyl benzene and D = propylene



$$C_{A0} = y_{A0} C_{T0} = y_{A0} \frac{P_0}{RT_0}$$

$$C_{T0} = \frac{P_0}{RT_0} = 0.2 \frac{\text{mol}}{\text{dm}^3}$$

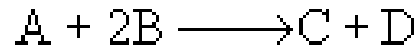
$$= 0.25 \left(\frac{8.2 \text{ atm}}{0.082 \frac{\text{atm} \cdot \text{dm}^3}{\text{mol} \cdot \text{K}}} \right) (500\text{K}) = (0.25) \left(0.2 \frac{\text{mol}}{\text{dm}^3} \right) = 0.05 \frac{\text{mol}}{\text{dm}^3}$$

$$C_{B0} = y_{B0} C_{T0} = (0.75) 0.20 \frac{\text{mol}}{\text{dm}^3} = 0.15 \frac{\text{mol}}{\text{dm}^3}$$

Problem!!Solution (3,4)

3. Since toluene, i.e. A, is the limiting reactant and has a stoichiometric coefficient of 1

$$y_{A0} = 0.25$$



$$\delta = (1 + 1 - 1 - 2) = -1$$

$$\varepsilon = y_{A0}\delta = (0.25)(-1) = -0.25$$

Species	Symbol	Entering	Change	Leaving
Toluene	A	F_{A0}	$\diamond F_{A0}X$	$F_A = F_{A0}(1 \diamond X)$

Problem!!Solution (6)

$$\left[\begin{array}{l} [F_T = F_{T0} + \delta F_{A0} X] \\ \delta = -1, F_{T0} = 4F_{A0} \\ F_T = 4F_{A0} - F_{A0} X \end{array} \right]$$

Species	Symbol	Entering	Change	Leaving
Toluene	A	F_{A0}	$-F_{A0}X$	$F_A = F_{A0}(1-X)$
Ethylene	B	$F_B = 3F_{A0}$	$-2F_{A0}X$	$F_B = F_{A0}(3-2X)$
Ethyl benzene	C	0	$F_C = F_{A0}X$	$+F_{A0}X$
Propylene	D	0	$+F_{A0}X$	$F_D = F_{A0}X$
Total		$F_{T0} = 4F_{A0}$		$F_T = 4F_{A0} - F_{A0}X$

Problem!!Solution (7, 8)

$$v = v_o(1 + \varepsilon X) \frac{P_0}{P} \frac{T}{T_0}$$

$$\varepsilon = y_{A0} \delta = (0.25)(1 + 1 - 1 - 2) = -0.25$$

$$v = v_o(1 - 0.25X)$$

$$C_A = \frac{F_A}{v}$$



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

$$C_A = \frac{0.05(1-X)}{1-0.25X}$$

$$C_B = \frac{F_B}{v} = \frac{F_{A0}(3-2X)}{v_o(1+\varepsilon X)} = C_{A0} \frac{(3-2X)}{(1-0.25X)}$$

Problem!!Solution (9)

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

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

$$C_B = C_{A0} \frac{(3-2X)}{(1+\varepsilon X)}, \quad \varepsilon = -0.25$$

$$-r_A = k C_{A0}^3 \frac{(1-X)(3-2X)^2}{(1-0.25X)^3}$$

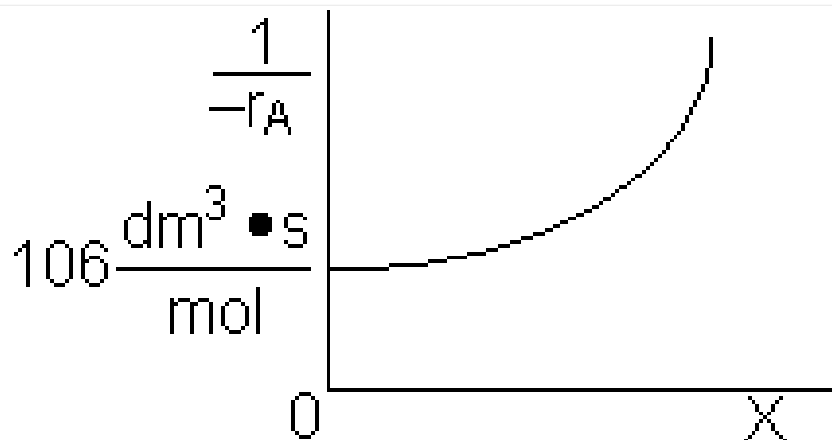
$$k C_{A0}^3 = y_{A0}^3 k C_{T0}^3 = (0.25)^3 \left(\frac{2 \times 10^{-1}}{s} \right) \left(\frac{\text{mol}}{\text{dm}^3} \right)$$

$$k C_{A0}^3 = y_{A0}^3 k C_{T0}^3 = (0.25)^3 \left(\frac{2 \times 10^{-1}}{s} \right) \left(\frac{\text{mol}}{\text{dm}^3} \right)$$

$$= \frac{3.13 \times 10^{-3}}{s} \left(\frac{\text{mol}}{\text{dm}^3} \right)$$

$$-r_A = \frac{3.13 \times 10^{-3}}{s} \left(\frac{\text{mol}}{\text{dm}^3} \right) \frac{(1-X)(3-2X)^2}{(1-0.25X)^3}$$

Problem!!Solution (10)



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

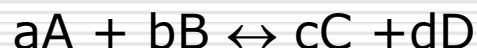
$$-r_B = 2r_A$$

$$-r_B = 2(-r_A)$$

$$= 2 \left(\frac{3.13 \times 10^{-4} \left(\frac{\text{mol}}{\text{dm}^3} \right)}{\text{s}} \right) \frac{(1-X)(3-X)^2}{(1-0.25X)^3}$$

$$-r_B = \frac{6.26 \times 10^{-4} \left(\frac{\text{mol}}{\text{dm}^3} \right)}{\text{s}} \frac{(1-X)(3-X)^2}{(1-0.25X)^3}$$

Reversible reactions



$$\text{rate}_{\text{net}} = \text{rate}_{\text{forward}} - \text{rate}_{\text{reverse}}$$

At equilibrium, $\text{rate}_{\text{net}} = 0$ and the rate law must reduce to an equation that is thermodynamically consistent with the equilibrium constant for the reaction.

Consider the exothermic, heterogeneous reaction



At low temperature, the rate law for the disappearance of A is

Reversible reactions

At low temperature, the rate law for the disappearance of A is

$$-r'_A = \frac{k_A P_A P_B}{1 + K_A P_A}$$

At high temperature, the exothermic reaction is significantly reversible:

What is the corresponding rate law?



Reversible reactions

(C \rightarrow A + B) is

$$r'_{Arev} = \frac{k_{-A}P_C}{1 + K_A P_A}$$

$$r_A = r_{A_{net}} = r_{A_{for}} + r_{A_{rev}}$$

$$K_P = \frac{P_{C_e}}{P_{A_e}P_{B_e}} = \frac{k_A}{k_{-A}}$$

$$r_A = \frac{-k_A P_A P_B}{1 + K_A P_A} + \frac{k_{-A} P_C}{1 + K_A P_A}$$

$$-r_A = \frac{k_A P_A P_B}{1 + K_A P_A} - \frac{k_{-A} P_C}{1 + K_A P_A} = \frac{k_A P_A P_B - k_{-A} P_C}{1 + K_A P_A}$$

$$-r'_A = \frac{k_A}{1 + K_A P_A} \left(P_A P_B - \frac{P_C}{K_P} \right)$$

Reversible reactions

Does this rate law satisfy our requirement that, at equilibrium, it must reduce to an equation that is thermodynamically consistent with K_p ?

for a reaction at equilibrium: $K_p = \frac{P_{C_e}}{P_{A_e} P_{B_e}}$

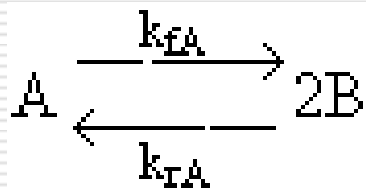
At equilibrium, $r_{\text{net}} = 0$,

$$-r_A \cong 0 = \frac{k_A}{1 + K_A P_{A_e}} \left(P_{A_e} P_{B_e} - \frac{P_{C_e}}{K_p} \right)$$

$$K_p = \frac{P_{C_e}}{P_{A_e} P_{B_e}}$$

Reversible reactions

Write the rate law for the elementary reaction



Here k_{fA} and k_{rA} are the forward and reverse specific reaction rates both defined with respect to A.

What is the rate of reaction?

Sample Problem (Constant volume batch reactor)



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

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

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

$$C_{Ae} = C_{A0} (1 - X_e)$$

$$(C_{A0} = 0.2 \text{ mol/dm}^3 \text{ and } K_C = 100 \text{ dm}^3/\text{mol})$$

$$C_{Be} = C_{A0} \left(\frac{1}{2} X_e \right)$$

$$100 = \frac{X_e}{2(0.2)(1 - X_e)^2}$$

$$X_e = 0.83$$

Objective Assessment of Chapter

- 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 or conversion
- Write $-r_A$ solely as a function of conversion given the rate law and then entering concentration

Beliefs are what divide people.
Doubt unites them.

Peter Ustinov

