

ChE 471 – LECTURE 1

1 Introduction to Chemical Reaction Engineering and Some Definitions

Whenever there is a change in the atomic content, or atomic configuration, of a molecule of a particular chemical species brought about by interaction with molecules of other chemical species, or due to an input of energy, a chemical reaction takes place! Such chemical transformations form the basis for manufacture of new chemicals, pharmaceuticals, fuels and materials and also occur in nature. Being able to conduct chemical reactions at controlled conditions with maximum selectivity, yield and energy efficiency, while minimizing the consequences to the environment, is one of the key tasks of chemical reaction engineering. The other is the development of quantitative understanding of the reactions in the natural environment and their interactions with the chemical species generated and/or released by man, and design of methods for pollution prevention and abatement. Finally, selecting appropriate reactions and executing them in a controlled fashion in production of specialty materials, pharmaceuticals, feed, food and a variety of consumer products is yet another task of chemical reaction engineering (CRE).

Chemical reaction engineering (CRE) is thought of as a blend of applied chemical kinetics and chemical thermodynamics by industrial chemists, who view it as a set of procedures by which one can determine how far a certain reaction can proceed (chemical equilibrium) and at what rate, depending on process conditions, can that final state be approached. Chemical engineers think of CRE as the subject of chemical reactor design, which, ideally, for important large-scale processes, requires them to master and follow the procedure specified below in steps a) through j).

- a) Establish reaction mechanism
- b) Collect rate data free of transport limitations.
- c) Correlate rate data by mathematical equation or otherwise.
- d) Formulate suitable models for reactor design and select reactor type (i.e. ideal flow pattern).
- e) Account for nonideality of real reactors and for the effect of physical transport processes.

- f) Select reactor size and operating conditions.
- g) Specify key reactor elements.
- h) Specify auxiliary equipment.
- i) Specify methods of control.
- j) Specify start-up and shut-down procedures.

Schematically, the body of knowledge and activities involved in reactor design are summarized in Figure 1.

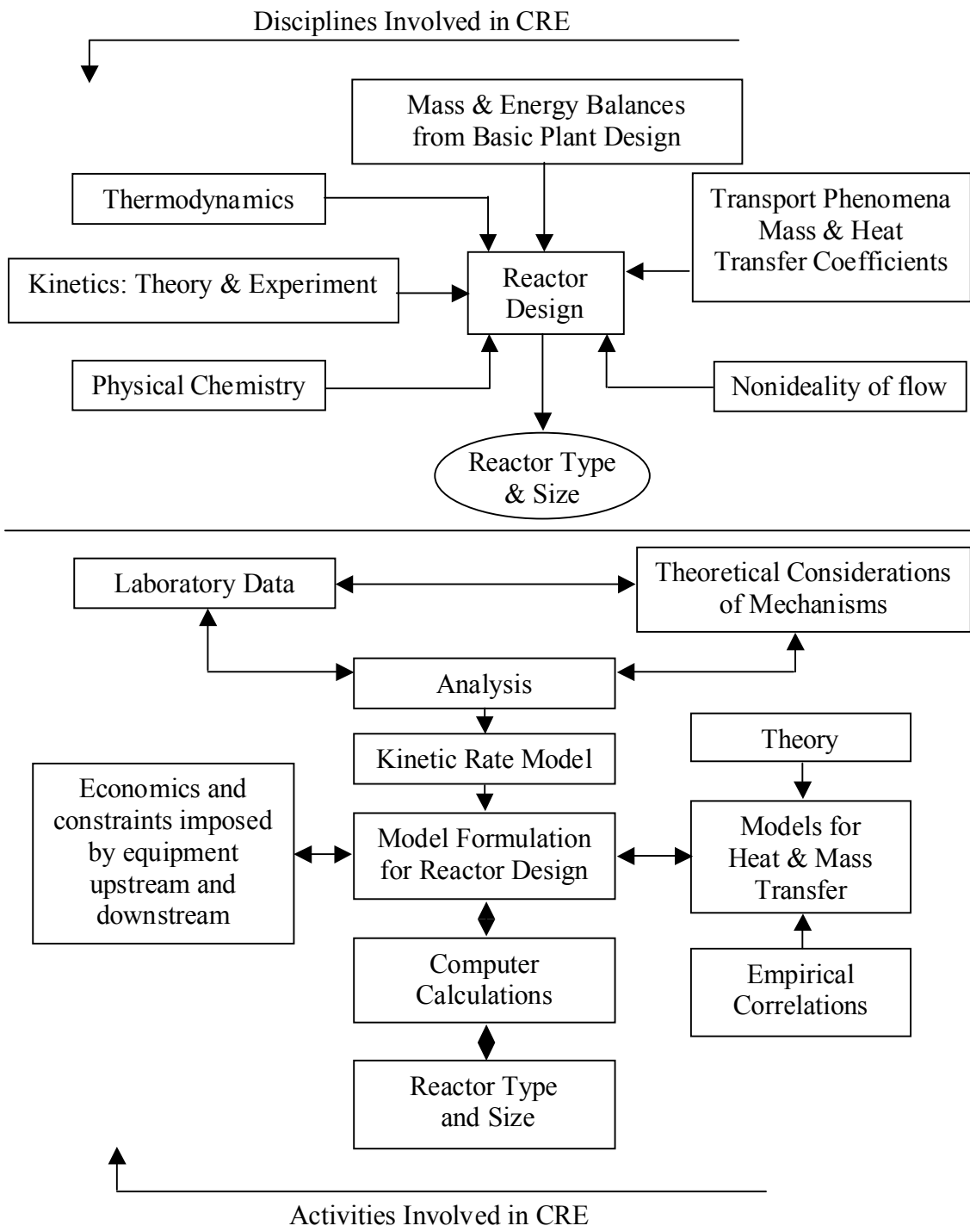


FIGURE 1: Disciplines and Activities Involved in CRE

We will now consider in turn some of the basic definitions needed for appropriate chemical reaction engineering analysis.

1.1 Reaction Stoichiometry

Chemical reaction engineering analysis is much facilitated if reaction stoichiometry is well known. Reaction stoichiometry represents the application of the principle of conservation of mass to a particular reaction under consideration.

Single Reaction stoichiometry can always be written as:

$$\sum_{j=1}^s \nu_j A_j = 0$$

where the following designations and definitions are used:

A_j – chemical species j

ν_j - stoichiometric coefficient of j

s – total number of species

By Convention

$\nu_j > 0$ for products

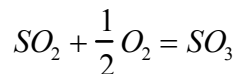
$\nu_j < 0$ for reactants

Equation (1), due to mass conservation, implies

$$\sum_{j=1}^s \nu_j M_j = 0 \quad (1-1a)$$

where M_j = molecular weight of species j .

For example, for sulfur dioxide oxidation, the stoichiometry and species designation can be written as:



e.g. $A_1 = SO_2, A_2 = O_2, A_3 = SO_3$

$$\nu_1 = -1, \nu_2 = -\frac{1}{2}, \nu_3 = 1$$

1.2 Progress of Reaction

1.2.1 Molar Extent

To monitor reaction progress we introduce the concept of (molar) extent of reaction, which for a batch system (no inlets and outlets) is defined by equation (1-2).

$$\frac{n_j - n_{j,o}}{\nu_j} = X \quad \text{Batch System} \quad (1-2)$$

$$n_j = n_{j0} + \nu_j X \quad (1-2a)$$

where

n_j – number of moles of species j, (mol)

n_{j0} – initial number of moles of j, (mol)

X – (molar) extent of reaction or degree of advancement (mol)

In a flow system at steady state

$$\frac{F_j - F_{j,o}}{\nu_j} = \dot{X} \quad \text{Flow System} \quad (1-3)$$

$$F_j = F_{j0} + \nu_j \dot{X} \quad \text{Steady state} \quad (1-3a)$$

F_j – molar flow rate of species j, (mol s⁻¹)

$F_{j,o}$ – molar flow rate of j in the feed, (mol s⁻¹)

\dot{X} – extent of reaction, (mol s⁻¹)

Reaction extent is an extensive measure of reaction progress (e.g. moles or moles/s). Often it is normalized based on mass or mass flow rate of the system, or made unitless by dividing it with total moles in the feed or total moles at conditions of interest. Clearly one should be careful as to how reaction extent is defined.

1.2.2 Fractional Conversion

In order to define another unitless measure of reaction progress it is necessary to introduce the concept of the limiting reactant first.

Limiting reactant is the reactant present in amount less than or equal to the amount required by stoichiometry for reaction completion

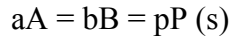
$$X_{\max} = \min_j \left\{ \frac{n_{j0}}{|\nu_j|} \right\} \quad (1-4a)$$

or

$$\dot{X}_{\max} = \min_j \left\{ \frac{F_{j0}}{(\nu_j)} \right\} \quad (1-4b)$$

Equation (1-4a) or (1-4b) identifies the limiting reactant, call it A, i.e. the reactant with the smallest ratio of the moles in the feed and the absolute value of its stoichiometric coefficient.

Alternative notation for reaction stoichiometry is often used as:



with a, b, p all positive. Clearly, $\nu_A = -a, \nu_B = -b, \nu_P = P$ establishes the link between eq (1-5) and eq (1-1).

Fractional conversion of limiting reactant A (e.g., j = A) is defined by

$$x_A = \frac{(\text{moles reacted})}{(\text{moles fed})} = \frac{n_{A0} - n_A}{n_{A0}} \quad \text{Batch} \quad (1-6a)$$

$$x_A = \frac{F_{A0} - F_A}{F_{A0}} \quad \text{Flow} \quad (1-6b)$$

The relations to molar extent are self evident.

$$\text{Number of moles reacted:} \quad n_{A0} x_A = (-\nu_A) X \quad (7a)$$

$$\text{Molar flow rate reacted:} \quad F_{A0} x_A = (-\nu_A) \dot{X} \quad (7b)$$

The relationship between molar quantities of any species, j, and those for the limiting reactant, A, using fractional conversion are:

$$n_j = n_{j0} + \frac{\nu_j}{\nu_A} (n_A - n_{A0}) \quad (1-8a) \quad F_j = F_{j0} + \frac{\nu_j}{\nu_A} (F_A - F_{A0}) \quad (1-8b)$$

This can be rewritten as:

$$n_j = n_{A0} \left[M_{j/A} + \frac{\nu_j}{(-\nu_A)} x_A \right] \quad (1-9a) \quad F_j = F_{A0} \left[M_{j/A} + \frac{\nu_j}{\nu_A} x_A \right] \quad (1-9b)$$

$$\text{where } M_{j/A} = C_{j0}/C_{A0} \quad (1-10)$$

1.3 Relationships between Reaction Progress and Measures of Composition

Neither molar extent nor fractional conversion are accessible by direct measurement. However, measures of the composition of the mixture e.g. mole fraction, molar concentration, etc., are readily accessible in direct measurement. It is then necessary to relate the changes in composition to measures of reaction progress as done below.

Molar Concentration of species j is the number of moles of j per unit volume of the system

$$C_j = \frac{n_j}{V} \quad (1-11a) \quad \text{or} \quad C_j = \frac{F_j}{Q} \quad (1-11b)$$

where

C_j – molar concentration of j, (mol/ m³)

V – volume of the batch system, (m³)

Q – volumetric flow rate in the steady flow system, (m³s⁻¹). Often volumetric flow rate is designated by \dot{V} or Q .

Total molar concentration then is:

$$C_{tot} = \frac{n_{tot}}{V} = \frac{N}{V} \quad (1-12a) \quad \text{or} \quad C_{tot} = \frac{F_{tot}}{Q} \quad (1-12b)$$

where

C_{tot} – total molar concentration of all species (mol m⁻³)

The total number of moles (or total molar flow rate) can then be expressed in terms of reaction extent.

$$N = n_{tot} = \sum_{j=1}^s n_j = n_{tot,o} + \sum_{j=1}^s \nu_j X \quad (1-13a)$$

$$F_{tot} = \sum_{j=1}^s F_j = F_{tot,o} + \sum_{j=1}^s \nu_j \dot{X} = F_{tot,o} \left[1 + \dot{X} \frac{\sum_{j=1}^s \nu_j}{F_{tot,o}} \right] \quad (1-13b)$$

The coefficient of expansion ε_A is defined by

$$\varepsilon_A = \frac{\text{(volume of the system at complete conversion of limiting reactant)} - \text{(Initial volume of the system)}}{\text{(Initial volume of the system)}} = \frac{V|_{x_A=1} - V|_{x_A=0}}{V|_{x_A=0}} \quad (1-14)$$

Thus we need an appropriate equation of state to relate the volume of the system, its temperature and pressure and total moles at complete conversion. At constant temperature, constant pressure conditions, the assumption that volume changes in liquids or solids caused by reaction are minimal is justified so that $V|_{x_A=1} = V|_{x_A=0}$ and $\varepsilon_A = 0$. For gases, if we can use the ideal gas equation of state, then:

$$PV = n_{tot} RT \quad (1-15)$$

At P, T constant it is clear that the volume, V, is directly proportional to the total number of moles in the system, n_{tot} . Therefore, equation (14) with the help of equation (13a) yields:

$$\varepsilon_A = \frac{n_{tot/x_A=1} - n_{tot/x_A=0}}{n_{tot/x_A=0}} = \frac{X_{max} \sum_{j=1}^s \nu_j}{n_{tot,o}} = y_{Ao} \frac{\sum_{j=1}^s \nu_j}{(-\nu_A)} \quad (1-16)$$

where y_{Ao} = mole fraction of limiting reactant in the feed.

The following relationship follows:

$$n_{tot} = n_{tot,o} \left(1 + \varepsilon_A \frac{X}{X_{max}} \right) = n_{tot,o} (1 + \varepsilon_A x_A) \quad (1-17a)$$

$$F_{tot} = F_{tot,o} \left(1 + \varepsilon_A \frac{\dot{X}}{X_{max}} \right) = F_{tot,o} (1 + \varepsilon_A x_A) \quad (1-17b)$$

Returning now to the definition of the molar concentration of species j by equation (1-11), we obtain the relation between molar concentration and reaction progress as shown below.

For liquids, assuming negligible change in volume due to reaction, and also for gas phase reactions conducted in a closed batch autoclave, equation (1-11a) yields a linear relation between molar concentration and reaction extent per unit volume or molar concentration and conversion.

$$C_j = C_{jo} + \nu_j \xi \quad (1-18) \quad \text{with} \quad \xi = \frac{X}{V} \quad \text{or} \quad \xi = \frac{\dot{X}}{Q} \quad (1-19)$$

$$C_j = C_{jo} + \frac{\nu_j}{(-\nu_A)} C_{Ao} x_A \quad (1-20)$$

For gases, assuming ideal gas mixture in a non-constant volume autoclave

$$C_j = \frac{T_o P}{T P_o} \frac{\left(C_{jo} + \frac{\nu_j X}{V_o} \right)}{\left(1 + \frac{\sum_{j=1}^s \nu_j}{N_o} X \right)} \quad (1-21)$$

or

$$C_j = C_{A,o} \frac{T_o P}{T P_o} \frac{\left(M_{j/A} + \frac{\nu_j}{(-\nu_A)} x_A \right)}{(1 + \varepsilon_A x_A)} \quad (1-21b)$$

Recall that the coefficient of expansion, ε_A is defined by equation (1-16) while

$y_{A,o}$ – mole fraction of A in initial mixture

T_o, P_o – initial temperature and pressure

T, P – temperature and pressure at the time (place) when (where) concentration is determined

N_o – initial total number of moles

$F_{tot,o}$ – total molar flow rate of the feed

$M_{j/A} = n_{j,o} / n_{A,o} = C_{j,o} / C_{A,o}$ – feed molar ratio of species j to limiting reactant A

In a flow system

$$C_j = C_{tot,p} \frac{T_o P}{T P_o} \frac{(F_{j,o} + \nu_j X)}{\left(F_{tot,o} + \sum_{j=1}^s \nu_j X \right)} \quad (1-22a)$$

$$C_j = C_{A,o} \frac{T_o P}{T P_o} \frac{\left(M_{j/A} + \nu_j x_A \right)}{(1 + \varepsilon_A x_A)} \quad (1-22b)$$

Subscript o refers now to the feed conditions.

The volumetric flow rate is given by:

$$Q = Q_o (1 + \varepsilon_A x_A) \frac{P_o T}{P T_o} \quad (1-23)$$

and total molar concentration is:

$$C_{tot} = C_{tot,o} \frac{T_o P}{T P_o} \quad (1-24)$$

Mole fraction of species j is:

$$y_j = \frac{C_j}{C_{tot}} = \frac{n_{j,o} + \nu_j X}{n_{tot,o} + X \sum \nu_j} = y_{A,o} \frac{M_{j/A} + \frac{\nu_j}{(-\nu_A)} x_A}{1 + \varepsilon_A x_A} \quad (1-25)$$

Mass Fraction, w_j

$$w_j = \frac{m_j}{m_{tot}} = w_{j0} + \nu_j M_j \xi' \quad \text{batch} \quad (1-26a)$$

$$w_j = \frac{\dot{m}_j}{\dot{m}_{tot}} = w_{j0} + \nu_j M_j \xi' \quad \text{flow} \quad (1-26b)$$

m_j, \dot{m}_j - mass of j or mass flow rate of j, (kg) or (kg/s)

M_j – molecular weight of j, (kg/ kmol)

The relationship between extent of reaction per unit mass or per unit volume is indicated below.

$$\xi' = \frac{X}{m_{tot}} = \frac{\xi}{\rho} = \frac{\dot{X}}{\dot{m}_{tot}} = \frac{\xi}{\rho} \quad (1-27)$$

1.4 **Rate of Reaction & Rate of Reaction of a Species**

Rate of reaction is defined as:

R_j = number of moles of species j formed by reaction per unit volume (or other unit measure of the reaction system) and per unit time (1-28)

R_j – rate of reaction of species j

$R_j > 0$ – j is a product, rate of formation is positive

$R_j < 0$ – j is a reactant, rate of formation is negative.

For a reactant j we can call $(-R_j) > 0$ the rate of disappearance which is positive. For a single reaction of stoichiometry :

$$\sum_{j=1}^s \nu_j A_j = 0$$

it follows that

$$\frac{R_j}{\nu_j} = r \quad \underline{R_j} = \nu_j r \quad (1-29)$$

where

r – intrinsic rate of reaction is always positive independent of species.

$R = f(T, C_j, P, \text{activity, etc.})$. Reaction rate is a function of temperature, composition, pressure, catalyst activity, etc. Empirically, whenever possible we try to represent the reaction rate as a product of a function of temperature, and a function of composition as

indicated by equation (1-30). It is known that the temperature dependence often (always for elementary reaction) can be described by one of the forms indicated by equation (1-31).

$$R = f_1(T), f_2(C_1) \quad (1-30)$$

$$f_1(T) = AT^m e^{-E/RT} \begin{cases} n = 0 \text{ Arrhenius form} \\ m = \frac{1}{2} \text{ Collision theory} \\ m = 1 \text{ Transition state theory} \end{cases} \quad (1-31)$$

The Arrhenius form is most commonly used.

$$f_1(T) = k_0 e^{-E/RT}$$

With

k_0 – frequency factor

E – activation energy (J/mol)

The dependence of the rate on concentrations is most often represented by a power law function. At constant temperature, the rate for an n -th order irreversible reaction ($K \gg 1$) then can be written as:

$$r = k C_1^{\alpha_1} C_2^{\alpha_2} \quad (1-32)$$

where

$k (=k_0 e^{-E/RT})$ – reaction rate constant [$(\text{kmol m}^{-3})^{1-n} \text{s}^{-1}$]

α_1, α_2 – reaction order with respect to reactant 1 and 2, respectively

$n = \alpha_1 + \alpha_2$ – overall reaction order

Let us consider the simplest n -th order rate form dependent on a single reactant A.

$$\underline{r = k C_A^n} \quad \text{with} \quad \underline{k = k_0 e^{-E/RT}} \quad (1-33)$$

The enclosed Figure 2 indicates the dependence of the rate on temperature at constant composition.

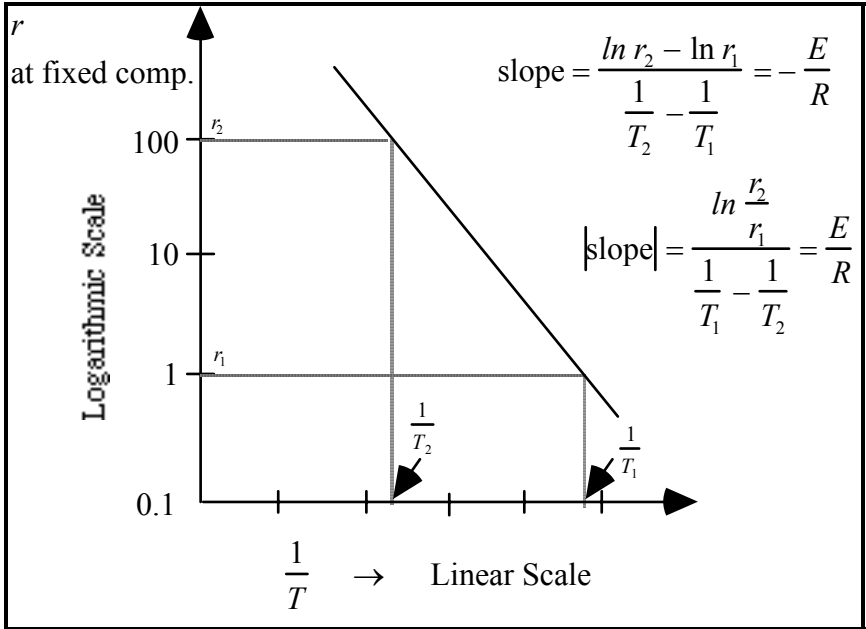


FIGURE 2: Arrhenius Plot for an n-th Order Reaction

A 25°C temperature rise raises the rate 10 fold for a process with an activation energy of 20 k cal. It raises the rate 1,000 times for a process with activation energy of 60 k cal. To get the corresponding increases in the rate for $n = 1$ (first order process) we would have to increase the reactant concentration (or pressure) by ten or thousand times, respectively. For a second order process one would have to increase the concentration (pressure) by a factor of 3.2 and 32 in order to get the corresponding increases in the rate. Clearly, the rate of reaction is much more sensitive to temperature than to composition (in most cases).

For a reversible reaction $\sum_{j=1}^s \nu_j A_j = 0$, an n-th order rate form at constant temperature can be written as:

$$r = k_1 C_1^{\alpha_1} C_2^{\alpha_2} - k_2 C_3^{\beta_3} C_4^{\beta_4} \quad (1-34)$$

Order of forward reaction $n_f = \alpha_1 + \alpha_2$

Order of reverse (backward) reaction $n_b = \beta_3 + \beta_4$

At equilibrium $r = 0$, so that

$$\frac{k_1}{k_2} = \left(\frac{C_3^{\beta_3} C_4^{\beta_4}}{C_1^{\alpha_1} C_2^{\alpha_2}} \right)_{eq} = K_c^p \quad (1-35)$$

with $p = 1/s$ where s is an integer and represents the stoichiometric number of the rate limiting step.

K_c – the equilibrium constant (in concentration units) is given by the following generalized product of reactant and product concentrations:

$$K_c = \left(C_3^{\nu_3} C_4^{\nu_4} / C_1^{-\nu_1} C_2^{-\nu_2} \right)_{eq} = \left(C_1^{\nu_1} C_2^{\nu_2} C_3^{\nu_3} C_4^{\nu_4} \right)_{eq} = \prod_{j=1}^{s=4} (C_j^{\nu_j})_{eq} \quad (1-36)$$

The thermodynamic equilibrium constant $K = \prod_{j=1}^s a_j^{\nu_j}$ is related to the Gibbs free energy

change for the reaction

$$-\Delta G_R^o = RT \ln K \quad \Delta G_R^o = \sum_{j=1}^s \nu_j \Delta G_{f_j}^o \quad (1-37)$$

a_j – equilibrium activity of species j

ΔG_R^o - standard Gibbs free energy change of reaction.

The following relationship holds for gas systems that follow ideal gas law:

$$K = K_p P_o^{-\sum_{j=1}^s \nu_j} = K_c (P_o)^{-\sum_{j=1}^s \nu_j} (RT)^{\sum_{j=1}^s \nu_j} \quad (1-38)$$

where

$P_o = 1$ atm, most frequently

Now if the Arrhenius form holds for the rate constants

$$k_1 = k_{10} e^{-E_1/RT} \quad k_2 = k_{20} e^{-E_2/RT} \quad (1-39)$$

then

$$E_1 - E_2 = \frac{\Delta H_R^o}{s} \quad (1-40)$$

where

$$\Delta H_R^o = \sum_{j=1}^s \nu_j \Delta H_{f_j}^o \quad \text{- standard heat of reaction} \quad (1-41)$$

The needed $\Delta H_{f_j}^o, \Delta G_{f_j}^o$ - heat of formation and free enthalpy of formation, respectively, are tabulated for all species.

Langmuir-Hinshelwood (Hougen-Watson) Rate Form

Quite frequently the rate form cannot be represented by a product of a rate constant, that has an Arrhenius or similar exponential dependence on temperature, and a power law function of concentrations. In other words the n-th order rate form does not hold. Sometimes a Langmuir Hinshelwood or Hougen-Watson rate form is suggested by theory or found to fit experimental data. A sample L-H rate form is given below.

$$r = \frac{k \prod_{j=1}^S C_j^{\alpha_j}}{\prod_{i=1}^R (K_i + C_i)^{\beta_i}} \quad (1-42)$$

In this case

- the order of reaction cannot be defined uniquely
- an activation energy cannot be defined uniquely

For example, if the L-H rate form is as shown below

$$r = \frac{k_o e^{-E_1/RT} C_A}{K_o e^{\frac{\Delta E}{RT}} + C_A} \quad (1-43)$$

- at low T, high pressure \rightarrow apparent order = 0
- at high T, low pressure \rightarrow apparent order = 1
- at low T $\rightarrow E_{\text{apparent}} = E_1$
- at high T $\rightarrow E_{\text{apparent}} = E_1 - \Delta E$

This is illustrated in Figure 3.

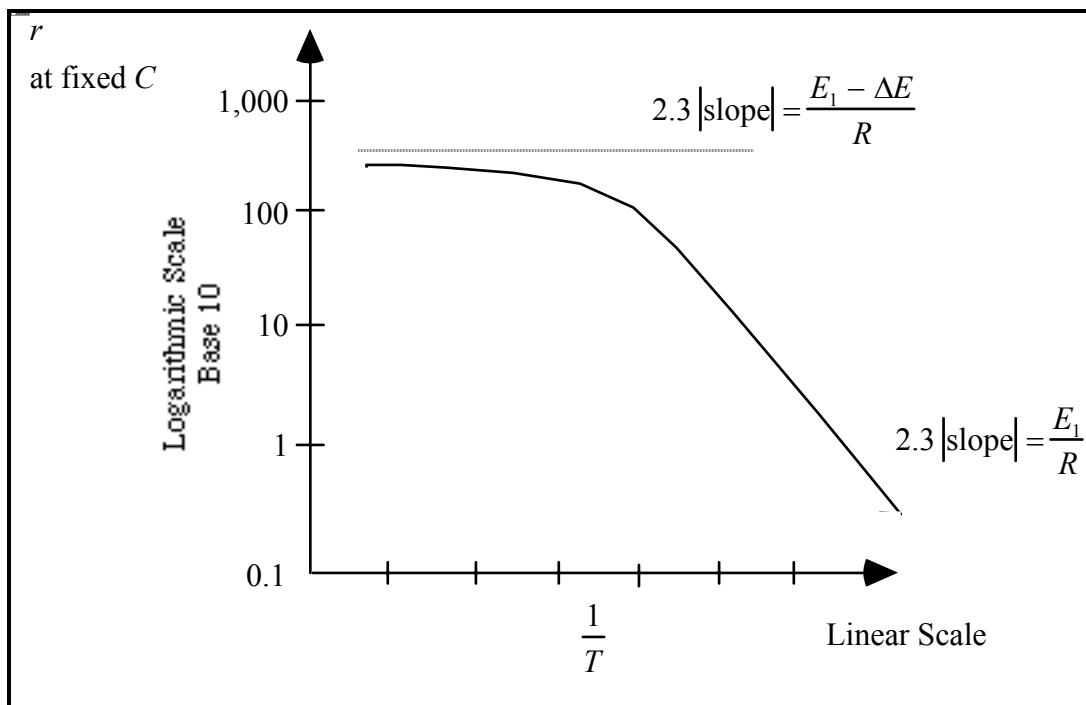


FIGURE 3: Arrhenius Plot for the L-H Reaction

A word of caution about the value of the rate constant is in order.

Given $2A + 1B = 2P$ and $r = 0.2 C_A^\alpha C_B^\beta$ at some specified temperature T , the rate of disappearance of A is given by

$$-R_A = 0.2 \times 2 C_A^\alpha C_B^\beta$$

Hence, the rate constant for A at the same conditions is 0.4. This is sometimes overlooked because often it is not clearly stated which rate or rate constant is reported. Such errors should be carefully avoided.

Conversion of units come into play when relationship between rates based on various unit measures of the system are required. Often rates expressed per unit area or unit mass are used in heterogeneous systems.

$$(\text{rate of reaction}) = \frac{(\text{change in the number of moles of species } j \text{ caused by reaction})}{(\text{stoichiometric coefficient of } j)(\text{unit measure of the system})(\text{time})}$$

$$r \left(\frac{\text{kmol}}{\text{m}^3 \text{ reaction mixture s}} \right) \quad \varepsilon_b \left(\frac{\text{m}^3 \text{ fluid}}{\text{m}^3 \text{ bed}} \right) - \text{porosity of the bed}$$

$$r' \left(\frac{\text{kmol}}{\text{kg catalyst s}} \right) \quad S_g \left(\frac{\text{m}^2}{\text{kg}} \right) - \text{catalyst total area}$$

$$r'' \left(\frac{\text{kmol}}{\text{m}^2 \text{ catalyst total area s}} \right) \quad S_{ex} \left(\frac{\text{m}^2}{\text{kg}} \right) - \text{catalyst external}$$

$$r^{iv} \left(\frac{\text{kmol}}{\text{m}^3 \text{ packed bed s}} \right) \quad \rho_b \left(\frac{\text{kg}}{\text{m}^3 \text{ bed}} \right) - \text{bulk density}$$

$$r^v \left(\frac{\text{kmol}}{\text{m}^3 \text{ catalyst s}} \right) \quad \rho_p \left(\frac{\text{kg}}{\text{m}^3 \text{ catalyst}} \right) - \text{catalyst density}$$

The relationships among these rates are:

$$\Rightarrow r^{iv} = r'' S_g \rho_b = r' \rho_b = r \varepsilon_b = r''' S_{ex} \rho_b = r^v \frac{\rho_b}{\rho_p} \Leftarrow \quad (1-45)$$

1.5 Multiple Reactions

Our treatment presented above for a single reaction can readily be extended to multiple reactions.

$$\sum_{j=1}^S \nu_{ij} A_j = 0 \quad i = 1, 2 \dots R \quad (1-46)$$

where

S – total number of chemical species.

R – total number of independent reactions.

Stoichiometric requirements yield:

$$n_j = n_{j,o} + \sum_{i=1}^R \nu_{ij} X_i \quad \text{batch} \quad (1-47a)$$

$$F_j = F_{j,o} + \sum_{i=1}^R \nu_{ij} \dot{X}_i \quad \text{flow system} \quad (1-47b)$$

where X_i is the molar extent of the i -th reaction.

Rate of Reaction of species j is now obtained by summing the rate of reaction of j in each reaction.

$$R_j = \sum_{i=1}^R \nu_{ij} r_i \quad (1-48a) \text{ so that } \underline{R} = \underline{\nu} \underline{r} \quad \underline{r} = \underline{\underline{\underline{\nu}}}^{-1} \underline{R} \quad (1-49b)$$

R_j - rate of reaction of species j

r_i - rate of i -th reaction

Given a set of R reactions among S chemical species one should determine first the R independent reactions by examining the rank of the matrix of stoichiometric coefficients

$$R = \text{rank } \nu = \text{rank} [\nu_{ij}] \quad (1-49)$$

The rank of the matrix of stoichiometric coefficients gives the number of independent reactions.

If the rank is determined by the Gauss-Jordan procedure then the set of independent reactions is readily picked from it.

In a reaction system of S chemical species with R independent reactions we need to monitor the change in composition of R species only. The composition of the remaining $S-R$ species is given by the $S-R$ invariants of the system. This implies that we need to know only the rates of R reactions, the rates of all species can then be obtained.

If we have selected $j = 1, 2, \dots, R$ species, then the rates of these species, R_j for $j = 1, 2, \dots, R$, are given in terms of the rates $r_i, i = 1, 2, 3, \dots, R$ for the R reactions. In matrix form this is stated below:

$$\begin{matrix} \underline{R} \\ (R \times 1) \end{matrix} = \begin{matrix} \underline{\nu} \\ (R \times R) \end{matrix} \begin{matrix} \underline{r} \\ (R \times 1) \end{matrix} \quad (1-50)$$

Solve for the R rates of reaction, $r_i, i = 1, 2, \dots, R$

$$\underline{r} = (\underline{\underline{\underline{\nu}}})^{-1} \underline{R} \quad (1-51)$$

Then solve for the remaining rates of $S-R$ chemical species $R_j, j = R + 1, \dots, S$

$$R_j = \sum_{i=1}^R \frac{\Delta_{ij}}{\Delta} R_i = \sum_{i=1}^R \frac{\Delta_{ij}}{\Delta} R_i \quad (1-52)$$

$$\Delta = \det \begin{pmatrix} \nu_{11} \nu_{12} \cdots \nu_{1i} \cdots \nu_{1R} \\ \nu_{21} \nu_{22} \cdots \nu_{2i} \cdots \nu_{2R} \\ \nu_{R1} \nu_{R2} \cdots \nu_{Ri} \cdots \nu_{RR} \end{pmatrix} \quad (1-53)$$

$$\Delta_{ij} = \det \begin{pmatrix} \nu_{11} \nu_{12} \cdots \nu_{ij} \cdots \nu_{1R} \\ \nu_{21} \nu_{22} \cdots \nu_{2j} \cdots \nu_{2R} \\ \nu_{R1} \nu_{R2} \cdots \nu_{Rj} \cdots \nu_{RR} \end{pmatrix} \quad (1-54)$$

Similarly

$$F_j = F_{j,o} + \sum_{i=1}^R \frac{\Delta_{ij}}{\Delta} (F_i - F_{i,o}) \quad j = R+1, R+2, \dots, S \quad (1-55a)$$

$$n_j = n_{j,o} + \sum_{i=1}^R \frac{\Delta_{ij}}{\Delta} (n_i - n_{i,o}) \quad j = R+1, \dots, S \quad (1-55b)$$

To understand fully what this means and how it works consider the following system of $R=3$ reactions among $S=4$ species



and let

$$A_1 = C, A_2 = O_2, A_3 = CO, A_4 = CO_2 \text{ so that } S = 4.$$

First show that there are only two independent reactions $R=2$ (this is rather evident here as the sum of (56a) and (56b) yields (56c)!). Choose the first two reactions and first two species to apply eq (50) and eq (51) to. Then solve for the rates of CO and CO₂ in terms of the rates of C and O₂ using eq (52).

1.5.1 Change in composition in multiple reactions due to reaction, (temperature and pressure change)

The formulas for a single reaction can readily be extended as shown below.

Molar flow rate (total)

$$F_{tot} = F_{tot,o} + \sum_{j=1}^S \sum_{i=1}^R \nu_{ij} \dot{X}_i = F_{tot,o} + \sum_{i=1}^R \bar{\nu}_i \dot{X}_i \quad (1-57)$$

$$\bar{\nu}_i = \sum_{j=1}^S \nu_{ij} \quad (1-58)$$

Total molar concentration (ideal gas mixture)

$$C_{tot} = \frac{P}{RT} \quad C_{tot,o} = \frac{P_o}{RT_o} \quad (1-59)$$

$$QC_{tot} = Q_o C_{tot,o} \left[1 + \frac{\sum_{i=1}^R \bar{\nu}_i \dot{X}_i}{F_{tot,o}} \right] \quad (1-60)$$

Volumetric Flow Rate

$$Q = Q_o \frac{P_o T}{P T_o} \left[1 + \frac{\sum_{i=1}^R \bar{\nu}_i \dot{X}_i}{F_{tot,o}} \right] \quad (1-61)$$

Molar Concentration

$$C_{tot,o} \frac{P T_o}{P_o T} \frac{F_{jo} + \sum_{i=1}^R \nu_{ij} \dot{X}_i}{\sum_{j=1}^S \left(F_{jo} + \sum_{i=1}^R \nu_{ij} \dot{X}_i \right)} \quad (1-62)$$

$$C_{tot} = C_{tot,o} \frac{P T_o}{P_o T} \quad (1-63)$$

Mole Fraction

$$y_j = \frac{F_{jo} + \sum_{i=1}^R \nu_{ij} \dot{X}_i}{F_{tot,o} + \sum_{i=1}^R \bar{\nu}_i \dot{X}_i} \quad (1-64)$$

Mass Fraction

$$w_j = w_{jo} + \sum_{i=1}^R \nu_{ij} \xi_i'' M_j \quad ; \quad \xi_i'' = \frac{\dot{X}_i}{\dot{m}_{tot}} \quad (1-65)$$

Thus, for gas-phase reactions in order to get a linear set of equations between measures of composition and reaction mass fractions should be used.

Additional terminology often used when dealing with multiple reactions is as follows:

Point (relative) yield

$$y\left(\frac{P}{A}\right) = \frac{R_P}{-R_A} = \frac{\text{(rate of production of P)}}{\text{(rate of disappearance of A)}} \quad (1-66)$$

Overall (relative) yield

$$Y\left(\frac{P}{A}\right) = \frac{F_P - F_{Po}}{F_{Ao} - F_A} = \frac{\text{(moles of product P formed)}}{\text{(moles of A consumed)}} \quad (1-67)$$

Overall Operational Yield

$$\bar{Y}\left(\frac{P}{A}\right) = \frac{F_P - F_{Po}}{F_{Ao}} = \frac{\text{(moles of product P formed)}}{\text{(moles of A fed to the system)}} \quad (1-68)$$

Suggested Exercises

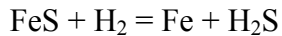
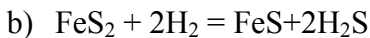
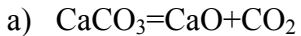
1.6 Other Extensions

The definitions introduced in this chapter were used to describe a single or multiple reactions in homogeneous, single phase system that was operated either as a batch or in continuous steady state mode. Extensions can readily be made to semi-batch systems, or to multiphase systems. In the spirit of lifetime learning you should do well to think as to how you could accomplish this. Discuss it among yourselves.

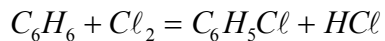
- a) Express the following reaction systems in the form

$$\sum_{j=1}^S \nu_{ij} A_j = 0 \quad i = 1, 2, \dots, R$$

and identify all A_j , ν_{ij} , R & S



- 2 For the reaction

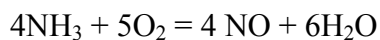


and the feed rate of

$$F_{C_6H_6,0} = 1 \frac{\text{kmol}}{\text{s}} \quad F_{Cl_2,0} = 0.5 \text{ kmol/s}$$

- a) find the limiting reactant
b) Find the molar flow rates at the outlet of all species at 90% conversion of the limiting reactant.

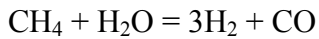
- 3 Consider the following reaction at atmospheric pressure (constant pressure) and temperature of 700 K



Feed: 10% (mole) NH_3 , 1-% O_2 , 80% N_2 Conversion of limiting reactant 0.95. Feed rate $F_{\text{tot},0} = 0.01 \text{ kmol/s}$.

- find the limiting reactant
- calculate molar flow rates at the exit
- calculate molar concentrations at the exit.

4 Consider steam reforming of natural gas



At 1300 K, $P = 10 \text{ atm}$. Assume both temperature and pressure are constant.

Feed: 0.01 kmol CH_4/s , 0.02 kmol $\text{H}_2\text{O}/\text{s}$.

Conversion of limiting reactant 85%.

Calculate

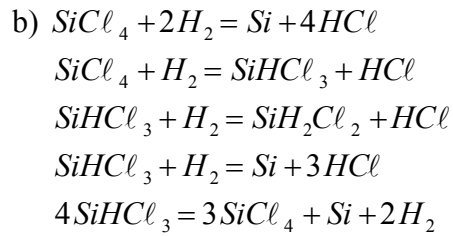
- Q/Q_0 the ratio of exit and feed volumetric flow rate
- Molar concentrations of all components at the exit
- Mole fractions at the exit
- Mass functions at the exit

5. The rate of reaction of SO_3 at a given set of conditions is found to be $0.02 \text{ (kmol/m}^3 \text{ reactor s)}$

- Find the rates of reaction of SO_2 and O_2 and the equivalent rate of reaction.
- If catalyst bulk density is $1.2 \text{ (g/cm}^3\text{)}$, catalyst pellet density is $2.1 \text{ (g/cm}^3\text{)}$, catalyst total surface area is $S_g = 80 \text{ (m}^2/\text{g)}$, find the rate of reaction expressed per
 - unit volume reaction mixture
 - unit volume of catalyst
 - unit catalyst area
 - unit catalyst mass

6. Find the number of independent reactions and all the invariants for the system:

- $\text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3\text{H}_2$
 $2\text{CH}_4 + 3\text{O}_2 = 2 \text{CO} + 4\text{H}_2\text{O}$
 $2\text{CO} + \text{O}_2 = 2\text{CO}_2$



7. Suppose that we are conducting reactions described by 6b) at 1400 K and $P = 1$ atm.

The feed rate is at 600 K, 1 atm and consists of 10% (mole), $SiCl_4$, 20% $SiHCl_3$ and 80% H_2 .

- a) Calculate the equilibrium composition at reaction conditions,
 c) Calculate the ratio of molar flow rate at equilibrium and inlet conditions for each species and for total moles.
-