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ONLINE COURSE WARE

SUBJECT NAME: CHEMICAL STOICHIOMETRY

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Lecture 1

Introduction about the subject: Details of unit and Dimension, Mathematical Expressions of small units and Derived units and their dimensional expressions**1.1.Introduction to Stoichiometry**

The term is derived from the Greek words stoicheion "element" and metron "measure". There are certain fundamental principles underlying all unit operations and unit processes. These can be broadly categorized into 4 groups. They are the material and energy balances and the laws of equilibrium and the rate processes. The quantitative relationship among reactants and products on the light of unit operation and unit processes is called stoichiometry.

1.2.Details of Units and Dimensions**1.2.1. Introduction**

Dimensions are our basic concepts of measurement such as length, time, mass, temperature and so on while **units** are the means of expressing the dimensions such as feet for length, second for time, gram for mass, etc.

Units used to designate magnitude of a dimension have evolved based on common usage and instruments available for measurement. Two major systems for measurement have been used: the English system, which was used primarily in industry, and the metric system, which was used in the sciences. The confusion that results from the use of various terms to represent the same dimension as led to the development of a common system of units that is proposed for use in both science and industry. The *System International d'Unites*(International System of Units) and the official international designation "SI" was adopted as a common system for measurement and mitigates the confusion.

1.2.2. Base Units of SI and Derived with Expressions

<i>Quantity</i>	<i>Unit</i>	<i>Symbol</i>	<i>Formula</i>
length	meter	m	
mass	kilogram	kg	
time	second	s	
electric current	ampere	A	
thermodynamic temperature	kelvin	K	
amount of substance	mole	mol	
luminous intensity	candela	c	
Frequency (of a periodic phenomenon)	Hertz	Hz	1/s
Force	Newton	N	kg m/s ²
Pressure, stress	Pascal	Pa	N/m ²
Energy, work, quantity of heat	Joule	J	N.m
Power	Watt	W	J/s
dynamic viscosity			Pa .s
surface tension			N/m
heat capacity, entropy			J/K
specific heat capacity, specific entropy			J/(kg.K)
molar energy			J/mol

The dimension of any physical quantity, whether base or derived, is a formula that defines how the numerical value of the quantity changes when the base unit sizes are changed. The dimension of a quantity does not by itself provide any information on the quantity's intrinsic nature. The same quantity (e.g. force) may have different dimensions in different systems of units, and quantities that are clearly physically different (e.g. work and torque) may have the same dimension.

Each of the derived units may be expressed in the form of the base units e.g. Heat capacity or entropy has a unit as,

$$\frac{\text{Joule}}{\text{Kelvin}} = \frac{\text{Newton} * \text{meter}}{\text{Kelvin}} = \frac{\text{kg} * \text{m} * \text{s}^{-2} * \text{m}}{\text{K}}$$

Here Newton (N) is expressed either as,

$$\frac{\text{kg} * \text{m}}{\text{s}^2}$$

or,

$$\text{kg} * \text{m} * \text{s}^{-2}$$

Expression of the derived units in terms of the base units is very important.

Lecture 2

Brief idea of Dimensional Analysis, Dimensionless Numbers and their significances.

2.1. Dimensionless Quantities

The use of dimensionless quantities arises from the principle of similarity. Equations that describe different systems having similar characteristics can be superimposed on each other to form a single expression suitable for all systems. Thus, if the physical characteristics of a fluid and the conditions that exist in an experiment are expressed in terms of dimensionless quantities, it will be possible to extrapolate results of an experiment to other fluids and other conditions. The principle of similarity makes it unnecessary to experimentally establish equations for heat transfer to each fluid. A general correlation equation will be suitable for all fluids. Following are some of the examples of dimensionless quantities,

Nusselt number (Nu): This expression involves the heat transfer coefficient (h), the characteristic dimension of the system (d), and the thermal conductivity of the fluid (k). This dimensionless expression may be considered as the ratio of the characteristic dimension of a system and the thickness of the boundary layer of fluid that would transmit heat by conduction at the same rate as that calculated using the heat transfer coefficient.

$$Nu = h \frac{d}{k}$$

Reynolds number (Re): This expression involves the characteristic dimension of the system (d), the velocity of the fluid (V), the density (ρ), and the viscosity (μ). It may be considered as the ratio of inertial forces to the frictional force.

$$Re = \frac{d V \rho}{\mu}$$

Prandtl number (Pr): This expression involves the specific heat (C_p), the viscosity (μ), and the thermal conductivity (k). It may be considered as the ratio of rate of momentum exchange between molecules and the rate of energy exchange between molecules that lead to the transfer of heat.

$$Pr = \frac{C_p \mu}{k}$$

2.2. Dimensional Analysis

The determination of the different dimensionless quantities involved in relationships between variables describing a system is done by a method called dimensional analysis. In dimensional analysis, an equation relating the various variables is first assumed, and by performing an analysis of the base dimensions of the variables to make the equation dimensionally consistent, specific groupings of the variables are formed.

Lecture 3

Details of Dimensionless Groups, Dimensional Analysis by Buckingham pi Theorem/Method.

3.1. Dimensionless Groups

A dimensionless group is a combination of dimensional or dimensionless quantities having zero overall dimensions. In a system of coherent units, it can therefore be represented by a pure number.

E.g. Reynolds Number which is expressed as

$$\text{Re} = \frac{d V \rho}{\mu}$$

has the following dimension for each of the quantities as

$$d = \text{m}$$

$$V = \text{m} \cdot \text{s}^{-1}$$

$$\rho = \text{kg} \cdot \text{m}^{-3}$$

$$\mu = \text{Pascal} \cdot \text{second} = (\text{Newton/Area}) \cdot \text{second} = \text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$$

thus, the dimension for Reynolds Number becomes dimensionless.

$$\text{Re} = \frac{\text{m} \cdot \text{m} \cdot \text{s}^{-1} \cdot \text{kg} \cdot \text{m}^{-3}}{\text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}} = \frac{\text{s}^{-1} \cdot \text{kg} \cdot \text{m}^{-1}}{\text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}}$$

➤ Problem

Try to investigate Nusselt and Prandtl number and see if they are truly dimensionless.

3.2. Dimensional Analysis by Buckingham pi Theorem/Method

When a complete relationship between dimensional physical quantities is expressed in dimensionless form, the number of independent quantities that appear in it is reduced from the original n to $n-k$, where k is the maximum number of the original n that are dimensionally independent.

The theorem derives its name from Buckingham's use of the symbol ' π ' for the dimensionless variables in his original 1914 paper. The π -theorem tells us that, because all complete physical equations must be dimensionally homogeneous, a restatement of any such equation in an appropriate dimensionless form will reduce the number of independent quantities in the problem by k . This can simplify the problem enormously, as will be evident from the example that follows. The π -theorem itself merely tells us the number of dimensionless quantities that affect the value of a particular dimensionless dependent variable. It does not tell us the forms of the dimensionless variables. That has to be discovered in some additional steps.

3.2. Steps to use the Buckingham pi Theorem/Method

Suppose we are interested in some particular physical quantity Q_0 that is a "dependent variable" in a well-defined physical process or event. By this we mean that, once all the quantities that define the particular processor event are specified, the value of Q_0 follows uniquely.

Step 1: The independent variables

The first and most important step in dimensional analysis is to identify a *complete* set of *independent* quantities $Q_1...Q_n$ that determine the value of Q_0 ,

$$Q_0 = f(Q_1, Q_2, \dots, Q_n) \quad (3.1)$$

A set $Q_1...Q_n$ is *complete* if, once the values of the members are specified, no other quantity can affect the value of Q_0 , and *independent* if the value of each member can be adjusted arbitrarily without affecting the value of any other member. Starting with a correct set $Q_1...Q_n$ is as important in dimensional analysis as it is in mathematical physics to start with the correct fundamental equations and boundary conditions. If the starting point is wrong, so is the answer. The relationship expressed symbolically in equation (3.1) is the result of the physical laws that govern the phenomenon of interest. It is our premise that its form must be such that, once the values $Q_1...Q_n$ are specified, the equality holds regardless of the sizes of the base units in terms of which the quantities are measured. The steps that follow derive the consequences of this premise.

Step 2: Dimensional considerations

Next we list the dimensions of the dependent variable Q_0 and the independent variables $Q_1...Q_n$. For example,

$$[Q_i] = L^{l_i} M^{m_i} t^{\tau_i} \quad (3.2)$$

where the exponents l_i , m_i and τ_i are dimensionless numbers that follow from each quantity's definition.

We now pick from the complete set of physically independent variables $Q_1...Q_n$ a *complete, dimensionally independent subset* $Q_1...Q_k$ ($k < n$), and express the dimension of each of the remaining independent variables $Q_{k+1}...Q_n$ and the dependent variable Q_0 as a product of powers of $Q_1...Q_k$. All physical quantities have dimensions which can be expressed as products of powers of the set of base dimensions. Alternatively, it is possible to express the dimension of one quantity as a product of powers of the dimensions of other quantities which are not necessarily base quantities. A subset $Q_1...Q_k$ of the set $Q_1...Q_n$ is *dimensionally independent* if none of its members has a dimension that can be expressed in terms of the dimensions of the remaining members. And *complete* if the dimensions of all the remaining quantities $Q_{k+1}...Q_n$ of the full set *can* be expressed in terms of the dimensions of the subset $Q_1...Q_k$.

Since equation (3.1) is dimensionally homogeneous, the dimension of the dependent variable Q_0 is also expressible in terms of the dimensions of $Q_1...Q_k$.

The dimensionally independent subset $Q_1...Q_k$ is picked by trial and error. Its members may be picked in different ways, but the *number* k of dimensionally independent quantities in the full set $Q_1...Q_n$ is unique to the set, and cannot exceed the number of base dimensions which appear in the dimensions the quantities in that set. For example, if the dimensions of $Q_1...Q_n$ involve only length, mass, and time, then $k < 3$. Having chosen a complete, dimensionally independent subset $Q_1...Q_k$, we express the dimensions of Q_0 and the remaining quantities $Q_{k+1}...Q_n$ in terms of the dimensions of $Q_1...Q_k$. These will have the form,

$$[Q_i] = [Q_1^{N_{i1}} Q_2^{N_{i2}} \dots Q_k^{N_{ik}}] \quad (3.3)$$

Equating the dimension given by equation (3.2) with that of equation (3.3), we obtain three equations,

$$l_i = \sum_{j=1}^k N_{ij} l_j \quad ; \quad m_i = \sum_{j=1}^k N_{ij} m_j \quad ; \quad \tau_i = \sum_{j=1}^k N_{ij} \tau_j \quad (3.4)$$

which can be solved for the three unknowns N_{i1} , N_{i2} , and N_{i3} .

Step 3: Dimensionless variables

We now define *dimensionless forms* of the n-k remaining independent variables by dividing each one with the product of powers of $Q_1...Q_k$ which has the same dimension,

$$\Pi_i = \frac{Q_{k+i}}{Q_1^{N(k+i)1} Q_2^{N(k+i)2} \dots Q_k^{N(k+i)k}} \quad (3.5)$$

where $i=1, 2, \dots, n-k$, and a dimensionless form of the dependent variable Q_0 ,

$$\Pi_0 = \frac{Q_0}{Q_1^{N_01} Q_2^{N_02} \dots Q_k^{N_0k}} \quad (3.6)$$

Step 4: Final Step

An alternative form of equation (3.1) is

$$\Pi_0 = f(Q_1, Q_2, \dots, Q_k; \Pi_1, \Pi_2, \dots, \Pi_{(n-k)}) \quad (3.7)$$

in which all quantities are dimensionless except $Q_1...Q_k$. The values of the dimensionless quantities are independent of the sizes of the base units.

The values of $Q_1...Q_k$, on the other hand, do depend on base unit size. They *cannot* be put into dimensionless form since they are (by definition) dimensionally independent of each other. From the principle that any physically meaningful equation must be dimensionally homogeneous, that is, valid independent of the sizes of the base units, it follows that $Q_1...Q_k$ must in fact be *absent* from equation (3.7), that is,

$$\Pi_0 = f(\Pi_1, \Pi_2, \dots, \Pi_{(n-k)}) \quad (3.8)$$

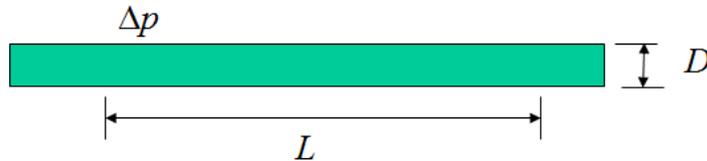
Lecture 4

Relevant Problems on Buckingham pi Theorem and their solutions.

▪ Problem

Using Buckingham Pi theorem, determine the dimensionless Π parameters involved in the problem of determining pressure drop along a straight horizontal circular pipe. Relevant flow parameters: Δp pressure drop, ρ density, V averaged velocity, μ viscosity, L pipe length, D pipe diameter. Therefore the pressure drop is a function of five variables

$$\Delta p = f_i(\rho, V, \mu, L, D)$$



Solution:

- Primary dimensions M(mass), L(length), t(time), and T(temperature).

Example: to describe the dimension of density ρ , we need M and L

$$[\rho] = [M/L^3], [\Delta p] = [F/A] = [ma/A] = [ML/t^2/L^2] = [M/(Lt^2)]$$

Similarly, $[\mu] = [M/(Lt)]$, $[V] = [L/t]$, $[L] = [L]$, $D = [L]$

Therefore, there are a total of three (3) primary dimensions involved: M, L, and t. We should be able to reduce the total number of the dimensional parameters to $(6-3)=3$.

- Now, we need to select a set of dimensional parameters that collectively they include all the primary dimensions. We will select three since we have three primary dimensions involved in the problem

We will select ρ , V and D for this example.

- Set up dimensionless Π groups by combining the parameters selected previously with the other parameters (such as Δp , μ and L in the present example), one at a time. Identify a total of $n-m$ dimensionless Π groups. You have to solve the dimensional equations to make sure all Π groups are dimensionless.

The first group: $\Pi_1 = \rho^a V^b D^c \Delta p$, a , b & c exponents are needed to non-dimensionalize the group. In order to be dimensionless:

$$\left[\frac{M}{L^3}\right]^a \left[\frac{L}{t}\right]^b [L]^c \left[\frac{M}{Lt^2}\right] = M^0 L^0 t^0$$

$$\text{So that } a + 1 = 0, -3a + b + c - 1 = 0 \text{ \& } b + 2 = 0$$

$$\text{Solved } a = -1, b = -2, c = 0.$$

$$\text{Therefore, the first } \Pi \text{ group is } \Pi_1 = \frac{\Delta p}{\rho V^2}$$

Use similar strategy, we can find the other two Π groups:

$$\Pi_2 = \frac{\mu}{\rho V D}, \quad \Pi_3 = \frac{L}{D}$$

The functional relationship can be written as

$$\Pi_1 = f_2(\Pi_2, \Pi_3) \text{ or } \frac{\Delta p}{\rho V^2} = f_2\left(\frac{\mu}{\rho V D}, \frac{L}{D}\right)$$

Therefore, the pressure drop in the pipe is a function of only two parameters: the Reynolds number and the ratio between its length and diameter.

- It can be understood that the pressure drop is linearly proportional to the length of the pipe. This has also been confirmed experimentally. Therefore:

$$\frac{\Delta p}{\rho V^2} = f_2\left(\text{Re}, \frac{L}{D}\right) = \frac{L}{D} f_3(\text{Re}), \text{ where } \text{Re} = \frac{\rho V D}{\mu}$$

Lecture 5

Conversion Factor; Conversion of Equation

5.1. Dimensional Equation

An equation that contains both numerals and their units is called a dimensional equation. The units in a dimensional equation are treated just like algebraic terms. All mathematical operations done on the numerals must also be done on their corresponding units. The numeral may be considered as a coefficient of an algebraic symbol represented by the unit.

Therefore, $(4\text{m})^2 = (4)^2(\text{m})^2 = 16\text{m}^2$

$$\& \left[5 \frac{\text{J}}{\text{kg K}} \right] (10 \text{ kg})(5\text{k}) = 5(10)(5) \left[\frac{\text{J kg K}}{\text{kg K}} \right] = 250 \text{ J}$$

Addition and subtraction of numerals and their units also follow the rules of algebra; that is, only like terms can be added or subtracted.

5.2. Conversion of Unit and Conversion factor

The conversion of units and symbols from one system to another often presents a troublesome operation in technical calculations. Most scientific units may be expressed in terms of simple dimensions, such as length, weight, time, temperature, and heat. In conversion, the unit is first expressed in terms of its simplest dimensions combined with the known numerical or symbolic value of the unit. Thus, the viscosity of a liquid is μ grams per second-centimeter in G.G.S System will be expressed in pounds per second-foot in the English system. One quantity is multiplied by a number of ratios termed conversion factors of equivalent values of combinations of time, distance and so on, to arrive at the final desired answer. Each of the dimensions is replaced separately by the dimensions of the desired system together with its corresponding conversion factor.

Thus, since $1 \text{ gram} = 0.002204 \text{ lb.}$ and $1 \text{ cm} = 0.0328 \text{ ft.}$

$$\mu \frac{\text{grams}}{(\text{sec})(\text{cm})} = \mu \frac{0.002204 \text{ lb}}{1 (\text{sec}) 0.0328 (\text{ft})} = 0.0670 \mu \frac{\text{lb}}{(\text{sec})(\text{ft})}$$

So as per the above equation 0.067 is the conversion factor when converting viscosity of liquid from grams per second-centimeter to pounds per second-foot.

5.3. Conversion of Dimensional Equation

Equations may be dimensionless (i.e., dimensionless groups are used in the equation). Examples of dimensionless groups are Reynolds number (Re), Nusselt number (Nu), Prandtl number (Pr), Fourier number (Fo), etc. An example of a dimensionless equation is the Dittus-Boelter equation for heat transfer coefficients in fluids flowing inside tubes:

$$\text{Nu} = 0.023 (\text{Re})^{0.8} (\text{Pr})^{0.3}$$

Because all terms are dimensionless, there is no need to change the equation regardless of what system of units is used in determining the values of the dimensionless groups. Dimensional equations result from empirical correlations (e.g., statistical analysis of experimental data). With dimensional equations, units must correspond to those used on the original data, and substitution of a different system of units will require a transformation of the equation.

▪ **Problem**

An equation for heat transfer coefficient between air flowing through a bed of solids and the solids is

$$h = 0.0128 G^{0.8}$$

where G is mass flux of air in lb/(ft² · h) and h is heat transfer coefficient in BTU/(h·ft²·F). Derive an equivalent equation in SI.

Solution

The dimensional equation is $\frac{BTU}{h \text{ ft}^2 F} = (\text{Conversion Factor}) * \left(\frac{lb}{h \text{ ft}^2}\right)^{0.8}$

An equation must be dimensionally consistent; therefore, the constant 0.0128 in the above equation must have units of

$$\frac{BTU}{h \text{ ft}^2 F} \left(\frac{lb}{h \text{ ft}^2}\right)^{-0.8} = \frac{BTU}{h^{0.2} \text{ ft}^{0.4} \text{ lb}^{0.8} F^{0.2}}$$

Converting the equation involves conversion of the coefficient. The equivalent SI unit for h=W/(m²K) and G = kg/(m² s). Thus, the coefficient will have units of J/(s^{0.2}m^{0.4}kg^{0.8}K).

The dimensionalequation for the conversion is

$$\begin{aligned} & \frac{J}{s^{0.2} m^{0.4} kg^{0.8} K} \\ = & (0.0128) \left[\frac{BTU}{h^{0.2} \text{ ft}^{0.4} \text{ lb}^{0.8} F^{0.2}} \cdot \frac{1054.8 \text{ J}}{BTU} \cdot \frac{\text{ft}^{0.4}}{(0.3048)^{0.4} m^{0.4}} \cdot \frac{h^{0.2}}{(3600)^{0.2} s^{0.2}} \cdot \frac{(2.2048)^{0.8} \text{ lb}^{0.8}}{kg^{0.8}} \cdot \frac{1.8 F}{K} \right] \end{aligned}$$

$$= 14.305$$

Therefore the converted equation is

$$h = 14.305G^{0.8}$$

Lecture 6

Elementary knowledge of solving Simultaneous Equations.

6.1. Solving Simultaneous Equations

Simultaneous equations are often encountered in problems involving material balances and multistage processes. The following methods are used:

- **Substitution**

If an expression for one of the variables is fairly simple, substitution is the easiest means of solving simultaneous equations. In a set of equations $x + 2y = 5$ and $2x - 2y = 3$, x may be expressed as a function of y in one equation and substituted into the other to yield an equation with a single unknown. Thus, $x = 5 - 2y$ and $2(5 - 2y) - 2y = 3$, giving a value of $y = 7/6$, and $x = 8/3$.

- **Elimination**

Variables may be eliminated either by subtraction or division. Division is used usually with geometric expressions, and elimination by subtraction is used with linear expressions. When subtraction is used, equations are multiplied by a factor such that the variable to be eliminated will have the same coefficient in two equations. Subtraction will then yield an equation having one less variable than the original two equations.

- **Determinants**

Coefficients of a system of linear equations may be set up in an array or matrix, and the matrices are resolved to determine the values of the variables. Solutions of a system of linear equations may be obtained using a spreadsheet program like Excel. For a system of three equations or more, setting up the matrix to solve the equations using Excel will be the fastest way to determine the values of the variables.

In a system of equations:

$$a_1x + b_1y + c_1z = d_1$$

$$a_2x + b_2y + c_2z = d_2$$

$$a_3x + b_3y + c_3z = d_3$$

The array of the coefficients is as follows:

$$\begin{vmatrix} a_1 & b_1 & c_1 & | & d_1 \\ a_2 & b_2 & c_2 & | & d_2 \\ a_3 & b_3 & c_3 & | & d_3 \end{vmatrix}$$

The values for x , y and z can be determined by the following method,

$$x = \frac{\begin{vmatrix} d_1 & b_1 & c_1 \\ d_2 & b_2 & c_2 \\ d_3 & b_3 & c_3 \end{vmatrix}}{\begin{vmatrix} a_1 & b_1 & c_1 \\ a_2 & b_2 & c_2 \\ a_3 & b_3 & c_3 \end{vmatrix}} \quad y = \frac{\begin{vmatrix} a_1 & d_1 & c_1 \\ a_2 & d_2 & c_2 \\ a_3 & d_3 & c_3 \end{vmatrix}}{\begin{vmatrix} a_1 & b_1 & c_1 \\ a_2 & b_2 & c_2 \\ a_3 & b_3 & c_3 \end{vmatrix}} \quad z = \frac{\begin{vmatrix} a_1 & b_1 & d_1 \\ a_2 & b_2 & d_2 \\ a_3 & b_3 & d_3 \end{vmatrix}}{\begin{vmatrix} a_1 & b_1 & c_1 \\ a_2 & b_2 & c_2 \\ a_3 & b_3 & c_3 \end{vmatrix}}$$

- **Graphical Method**

The graphical solution of linear simultaneous equations is the point of intersection found by drawing the two linear equations on the same axes. The point of intersection of the lines gives us the required solution.

Lecture 7

Different methods of solving simultaneous equations and relevant problems.

➤ Problem

Determine the values of x, y, and z in the following equations:

$$x + y + z = 100$$

$$0.8x + 0.62y + z = 65$$

$$0.89x + 0.14y = 20$$

$$\begin{bmatrix} 1 & 1 & 1 \\ 0.8 & 0.62 & 1 \\ 0.89 & 0.14 & 0 \end{bmatrix} \begin{bmatrix} 100 \\ 65 \\ 20 \end{bmatrix}$$

Solution

The array of the coefficients and constants is as follows

The matrix that consists of the coefficients of the variables will be the denominator of the three equations for x, y, and z.

$$\begin{array}{ccc} 1 & 1 & 1 \\ 0.8 & 0.62 & 1 \\ 0.89 & 0.14 & 0 \end{array} = 0.3102$$

The matrix (array B) that will be the numerator in the equation for x is

$$\begin{array}{ccc} 100 & 1 & 1 \\ 65 & 0.62 & 1 \\ 20 & 0.14 & 0 \end{array} = 2.7$$

Hence, $x = 2.7 / 0.3102 = 8.7$

Similarly we find $y = 87.5$ and $z = 3.8$.

➤ Problem

Calculate the value of τ and μ that would satisfy the following expressions:

$$\mu = 3.2(\tau)^{0.75}$$

$$\text{and, } 1.5\mu = 0.35(\tau)^{0.35}$$

Solution

μ is eliminated by division and from both the equations we get the following,

$$1/1.5 = (3.2 / 0.35)\tau^{0.75-0.35}$$

$$\tau = 0.00169$$

and, substituting the value of τ we find the value of μ as 0.02667

Lecture 8

Log-log and Semi-log expressions and graph paper; Small Problems and solutions related to Triangular Diagram; Graphical Differentiation & Integration.

8.1. Log-Log Graph

In science and engineering, a log–log graph or log–log plot is a two-dimensional graph of numerical data that uses logarithmic scales on both the horizontal and vertical axes. This is useful for determining power relationships. If a function of the form $y = ax^n$ is graphed on log–log paper, a straight line will be produced, with slope n and y -intercept $\log(a)$.

8.2. Semi-Log Graph

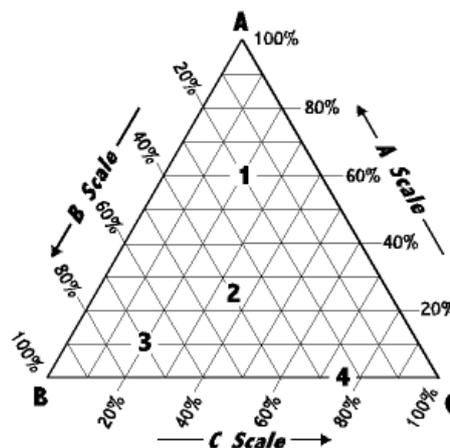
In a semi-log graph the y -axis is logarithmic, which means the separation between the ticks on the graph is proportional to the logarithm of numbers. The x -axis has a linear scale, which means the ticks are evenly spaced. These are required for representation of Power Law functions or Exponential functions.

8.3. Triangular Diagram

A ternary plot, ternary graph, triangle plot is a plot on three variables which sum to a constant. It graphically depicts the ratios of the three variables as positions in an equilateral triangle. It is used in physical chemistry, petrology, mineralogy, metallurgy, and other physical sciences to show the compositions of systems composed of three species.

All compositions, e.g., bulk compositions, liquid compositions and compositions of solid phases, on ternary diagrams are expressed in terms of the three end member components which define the system. These three components are located at the apexes of the triangle.

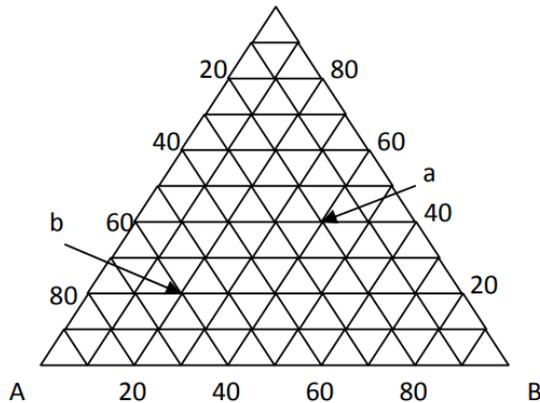
Each apex on the triangle representing the ternary system represents 100% of the component at that apex. The side of the triangle, directly opposite the apex, represents 0% of the apex component. Compositions of points which lie along the outside edge of the triangle are simply a mixture of the two components at each end of the tie line, with 0% of the third component.



➤ **Problem**

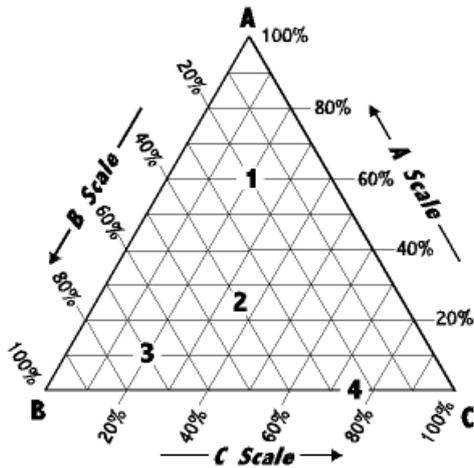
Sketch a composition triangle to represent composition of a ternary alloy and locate the alloys having following compositions (a) 20 %A, 40% B, 40%C (b) 60% A, 20% B, 20% C

Solution



➤ **Problem**

Determine the percent abundances for each of the following points.



Solution

1. 60% A | 20% B | 20% C = 100%
2. 25% A | 40% B | 35% C = 100%
3. 10% A | 70% B | 20% C = 100%
4. 0% A | 25% B | 75% C = 100%

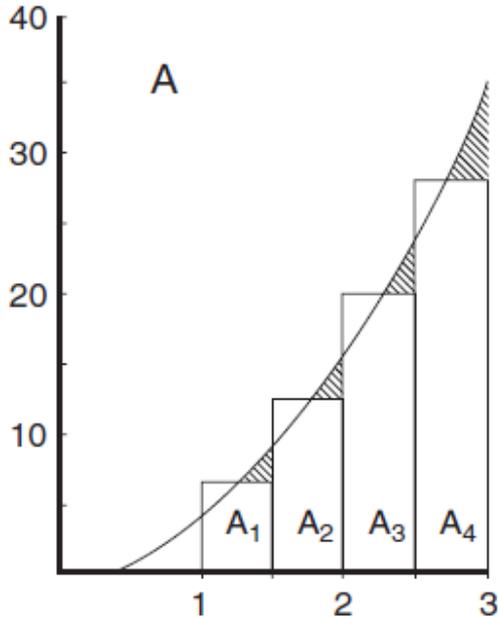
a. Graphical Differentiation

Often in applications one has a function $y = f(x)$ which is not given by a formula at all, but rather by drawing a smooth curve through points corresponding to a table of experimental data. Whenever the function $f(x)$ is given to you as a curve without any formula, you can find the derivative function using a graphical method. Namely, (1) divide up the domain of your function into regular intervals; (2) for each x which is an endpoint of an interval, look at the point over x on the curve; (3) put a small ruler along the curve at that point $(x, f(x))$ so that it just grazes the curve there (i.e., it is tangent to the curve there); (4) find the slope of the ruler, (5) tabulate the slopes obtained for all of the x values; (6) graph these values, drawing a smooth curve between them. The curve you draw is the derivative function.

b. Graphical Integration

Graphical integration is used when functions are so complex they cannot be integrated analytically. They are also used when numerical data are available, such as experimental results, and it is not possible to express the data in the form of an equation that can be integrated analytically. Graphical integration is a numerical technique used for evaluation of differential equations by the finite difference method. Three techniques for graphical integration will be shown. Each of these will be used to evaluate the area under a parabola, solved analytically in the preceding example.

A very popular technique that is used is called the Rectangular Rule as it is depicted below.



The domain under consideration is divided into a sequence of bars. The thickness of the bars represents an increment of x . The heights of the bars are set such that the shaded area within the curve that is outside the bar equals the area inside the bar that lies outside the curve. The increments may be unequal, but in the figure equal increments of 0.5 units are used. The heights of the bars are 6.5, 12.5, 20, and 28 for A_1, A_2, A_3 , and A_4 , respectively. The sum of the area increments is $0.5(6.5 + 12.5 + 20 + 28) = 33.5$

Lecture 1

Introductory Concepts of Material balance, Simplification of the general mass balance equation for steady and unsteady state processes

1. INTRODUCTORY CONCEPT OF MATERIAL BALANCE

Material balance calculation is an essential part of the solution of many complex chemical engineering problems. Material balance assists in the planning and design of processes, in the economic evaluation of the proposed and existing processes, in process control, and in process optimization. In chemical process industries, it is possible to produce a given end product from different raw materials. For an appropriate choice of a process, it is very essential to compute the material requirement for these different routes. A properly listed material balance enables one to estimate the material requirement for an existing process or for a process which is being planned. For instance, in the extraction of oil from oil seeds, it predicts the amount of solvent required for treating a given quantity of seeds. It can evaluate the quantity of water to be evaporated from an aqueous NaOH solution to produce a concentrated solution of given strength. Such information can be used in the design of equipment, in the search for alternative processes or in the evaluation of the economics of the process. Material balance can assist in the simulation of processes based on which certain financial decisions can be made. For existing processes, if direct measurements were made of the weight and compositions of various streams entering and leaving a process, and of the change in material inventory in the system, no material balance calculations would be necessary. As this is not always feasible, the calculation of unknown quantities will always be necessary. Thus, material balance can be used in the hourly and daily operating decisions to be made for running the process efficiently and economically.

1.1 BASIC MATERIAL BALANCE PRINCIPLES

Material balance is an expression of law of conservation of mass. The law of conservation of mass states that the mass can neither be created nor destroyed, but may undergo phase changes, i.e. transformation or transfer from one phase to another and also chemical changes. In an industrial process, material balance provides an exact accounting of all the materials that enter and leave and of the changes in the inventory of the material in the course of a given interval of time of operation.

The material balance for process with or without chemical reaction can be written in the following form

$$\begin{aligned} & \left[\begin{array}{c} \text{material input} \\ \text{to the system} \end{array} \right] - \left[\begin{array}{c} \text{material output} \\ \text{from the system} \end{array} \right] + \left[\begin{array}{c} \text{material generation} \\ \text{within the system} \end{array} \right] - \left[\begin{array}{c} \text{material consumption} \\ \text{within the system} \end{array} \right] \\ & = \left[\begin{array}{c} \text{accumulation of material} \\ \text{within the system} \end{array} \right] \end{aligned} \quad (9)$$

For material balance purposes, industrial processes may be classified as steady-state process or unsteady-state process and as batch or continuous processes. A steady-state process is one in which there is no change in conditions (Pressure, temperature, composition) or rates of flow with time at any given point in the system. All other processes are unsteady state process.

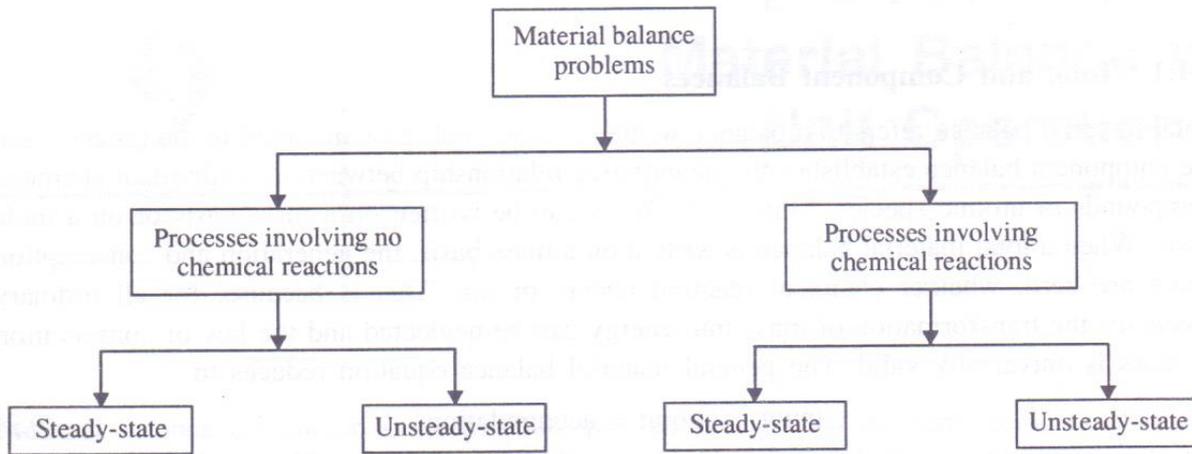


Fig. Classification of material balance problem

1.2 Batch and Continuous Processes

In a batch process, a given quantity of material is placed in a container and a change is made to occur by physical or chemical means. All batch processes are unsteady-state processes. In contrast, in a continuous process, feed streams are continuously fed to a piece of equipment and the products are continuously withdrawn. For example, consider a continuous nitration plant producing nitrobenzene. The reactant feed consists of benzene, nitric acid, sulphuric acid and water. The total mass of products obtained at the end of the nitration reaction will be equal to the mass of the feed, although the proportion of various components has changed as per chemical equilibrium. A continuous process may or may not be a steady-state process. For continuous and steady-state process the accumulation of material is zero. Then the material balance equation is

$$\text{input} = \text{output}$$

Lecture 2

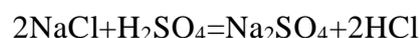
Procedure for material balance calculations

2. Steps to Follow in Material Balance Calculations

1. Draw a flow sheet of the entire process—each of the complex processes, such as those taking place within a reactor, drier, rectification column, evaporator, etc. being represented by a single block.
2. Write down the available quantitative information. The available information may include the flow rates of incoming and outgoing streams and their compositions.
3. Try to identify a substance which enters a process equipment through only one incoming stream and leaves through one outgoing stream. Such a substance is known as tie substance and knowledge of its percentage in the two streams establishes the ratio of the weights of the streams. Existence of a tie substance or key component is not essential. In complex problems, there may be more than one tie substance.
4. Select a suitable basis for calculation. For a batch process, the quantity of a substance present in the system may be taken as a basis. For a flow system, unit time may be taken as a basis.
5. If no chemical reaction takes place, material balance is computed on the basis of chemical compounds. Mass units are used.
6. If chemical reactions occur, material balance is computed with reference to chemical elements or radicals. Molar units are normally used.
7. Write the overall mass balance equations and the mass balance equations for each of the components in the entire process and around each piece of equipment.
8. The number of unknown quantities to be calculated cannot exceed the number of independent material balance equations; otherwise, the problem is indeterminate.
9. If the number of independent material balance equations exceeds the number of unknown quantities, one has to select certain equations. Usually, equations based on components forming a higher percentage of the total mass are selected.
10. For processes involving phase changes, phase equilibrium relations become important.

Prob. Estimate the consumption of 96% NaCl and 93% H₂SO₄ for the production of 500 kg of HCl if the conversion is 92%. Also calculate the amount of Na₂SO₄ produced during the process.

HCl is produced according to the reaction



Molecular masses of NaCl, H₂SO₄, Na₂SO₄, and HCl are 58.5, 98, 142 and 36.5, respectively.

Theoretical amount of NaCl required for the production of 500 kg of HCl

$$= (117.0/73) * 500 = 801.4 \text{ kg}$$

Since the reaction yield is 92% and the purity of NaCl is 96%, actual amount of NaCl required

$$801.4 / (0.92 * 0.96) = 907.4 \text{ kg}$$

Similarly, the consumption of H₂SO₄

$$(98/73) * (500 / (0.92 * 0.93)) = 784.5 \text{ kg}$$

Amount of Na₂SO₄ produced

$$(142 / 73) * 500 = 972.6 \text{ kg}$$

Lecture 3

Basic concept of Material balance without chemical Reactions, Crystallization

3. Material balance without chemical reactions

In chemical process industries, we employ a large number of chemical and physical operations for transforming matter from inexpensive raw materials to highly desired products. The physical operations are generally treated in chemical engineering parlance as unit operations. These involve the addition or removal of some form of energy in the contacting, transport, and conditioning of materials mainly by physical means. Unit operations in chemical engineering practice can be broadly classified as fluid flow operations, heat transfer operations, mass transfer operations and mechanical operations involving particle handling and conditioning. The mass transfer operations include various separation techniques such as distillation, gas absorption, liquid—liquid extraction, leaching, crystallization, adsorption, ion-exchange, humidification operations, drying, etc. Also included in this category are several membrane separations such as osmosis, reverse osmosis, dialysis, electro dialysis etc. Mechanical operations include size reduction operations, sedimentation filtration mixing and blending, centrifugation, etc.

Material balance calculations are very important in the design and analysis of various separation operations. There is hardly any process industry which does not require a preliminary treatment of the raw materials before they are taken to the vessels, and the final treatment of the products leaving the reaction units for their purification and separation, and removal of byproducts. Many separation techniques are employed to give definite properties to the products, to render the products in a form suitable for packaging and handling and to reduce the cost of transportation of the products. The material balance problems encountered in the separation operations are purely physical in nature, and no chemical conversions are involved.

3.1 Crystallization

Crystallization is the process in which solid particles are formed from liquid solution by evaporating and/or cooling of a saturated solution. Crystallization is important as a method of purification and the process is also important since a variety of materials is marketed in crystalline form. Tank crystallizers, agitated batch crystallizers, Swenson—Walker crystallizer, vacuum crystallizers and Krystal crystallizers are typical industrial equipment used for crystallization. Following figure shows a crystallizer of the circulating liquid type. The liquid is drawn through the tubes of a steam heated exchanger where it is heated to sufficiently high temperatures without evaporation. The heated liquid then flows into the vapour space where flash

evaporation occurs leading to the supersaturation of the solution. The supersaturated liquid is made to flow down through the downcomer and then up through the bed of crystals which grows in size. The saturated liquid leaving the bed joins the fresh feed solution before entering the heater.

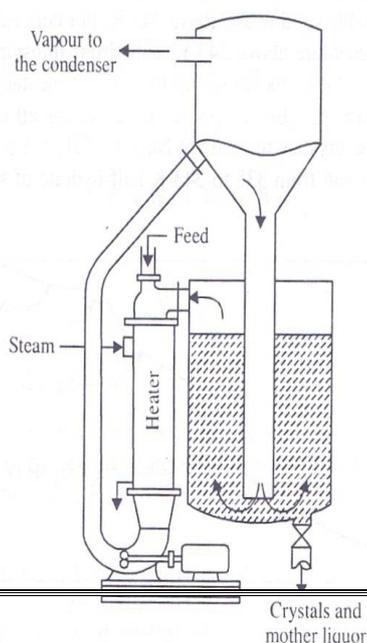
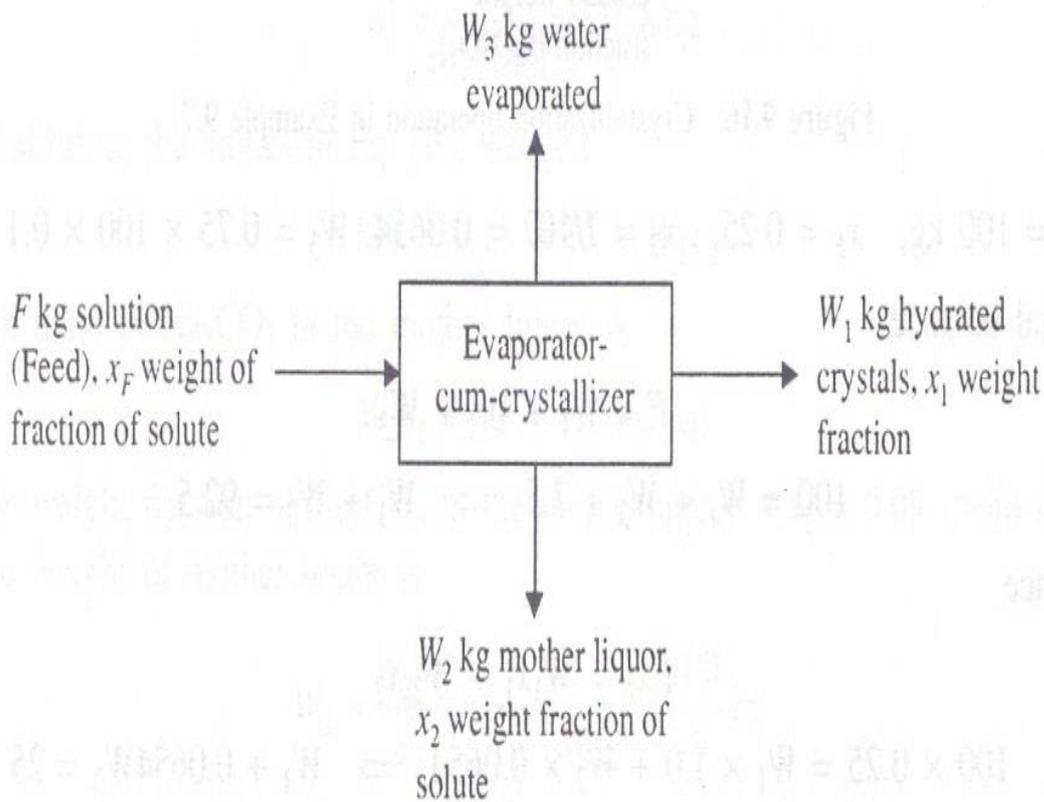


Fig. Evaporator crystallizer

In industrial crystallization processes, equilibrium is attained between the solution (mother liquor) and the crystals, and hence the mother liquor leaving the process is a saturated solution at the final temperature of crystallization. The yield of crystals can be calculated knowing the initial concentration of the solute, final temperature and the solubility at this temperature. The material balance calculations are straightforward when the solute crystals are anhydrous. Simple water and solute balances are sufficient. When the crystals are hydrated, some of the water in the solution is removed with the crystals as a hydrate.

Let W_1 kg of hydrated crystals are formed in which the weight fraction of solute is x_1 from F kg of solution containing x_F weight fraction of solute. Let x_2 be the solubility of the solute in weight fraction of solute, and W_2 and W_3 be the weights of mother liquor remaining after crystallization and the weight of water evaporated during crystallization operation (see Figure), respectively



The material balance for the crystallization operation yield the following equations: Total balance:

Solute balance

$$F = W_1 + W_2 + W_3$$

$$FX_F = W_1x_1 + W_2x_2$$

Solvent balance:

$$F(1-x_F) = W_1(1-x_1) + W_2(1-x_2) + W_3$$

Lecture 4

Basic concept of Material balance without chemical Reactions, Distillation

4. Distillation

Distillation is used to separate liquid mixtures into component parts by boiling and is one of the major operations in chemical and petroleum industries. The basic requirement for a separation by distillation is that the composition of the vapour be different from the composition of the liquid with which it is in equilibrium. Distillation differs from evaporation in that in the latter vapour produced on boiling is a pure fluid, whereas in the former all the components constituting the liquid will be present in the vapour but in different proportions. The vapour will be richer in the more volatile components compared to the liquid with which it is in equilibrium. The products obtained on distillation are commonly referred to as distillate (or top product), which is rich in more volatile components and residue (or bottom product), which is rich in less volatile components.

When a liquid mixture at a high temperature and pressure is subjected to a sudden reduction in pressure by passing through a valve, the liquid gets partially vaporized. The resulting liquid—vapour mixture is separated into the distillate and the bottom products as shown in Figure below. The process is known as *flash distillation* or *flash vaporization*. The flash distillation is an ideal single-stage operation in which the distillate and bottom products have equilibrium compositions. The products will have an appreciable difference in their compositions only if the volatilities of the constituents are appreciably different. Therefore, it is generally impossible to obtain pure products by a single-stage flash vaporization.

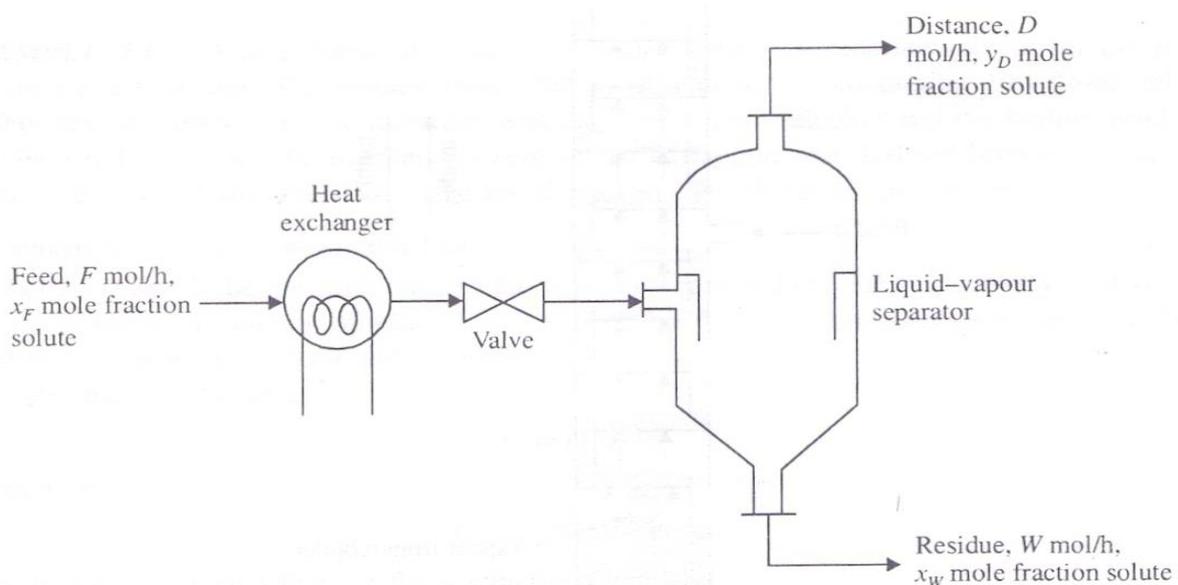


Fig. Equilibrium flash distillation

The vapour produced in a single-stage flashing operation can be enriched in the more volatile component by bringing it in contact with a liquid phase with which the vapour is not in equilibrium. The liquid phase known as *reflux* is obtained by condensing the vapour and recycling a part of the condensate. The distillation carried out in this fashion is known as *rectification* or *fractionation*. The fractionation can be carried out as a multi-stage operation in a plate column or as a continuous contact operation in a packed column. Distillation using a plate column is schematically represented in Figure below.

A fractionating column is a cylindrical vertical tower which is divided into a number of sections by means of plates or trays. Different designs for trays are available, the simplest one being a sieve tray. Sieve trays are flat plates with a large number of small perforations that permit upward flow of vapour. The liquid flows across the plate and run over an overflow weir through the downcomer in the plate to the plate below. The vapour issuing through the perforations provides turbulence in the pool of liquid present on the tray, thereby facilitating mass transfer on the plate. On each plate more volatile components are vaporized and transferred to the vapour and the less volatile components are condensed and transferred to the liquid. Thus, the vapour leaving the tray is richer in more volatile components than the vapour coming to that tray. The liquid leaving the tray is leaner in more volatile components compared to the liquid entering the tray, it is still capable of enriching the vapour coming to the lower plate.

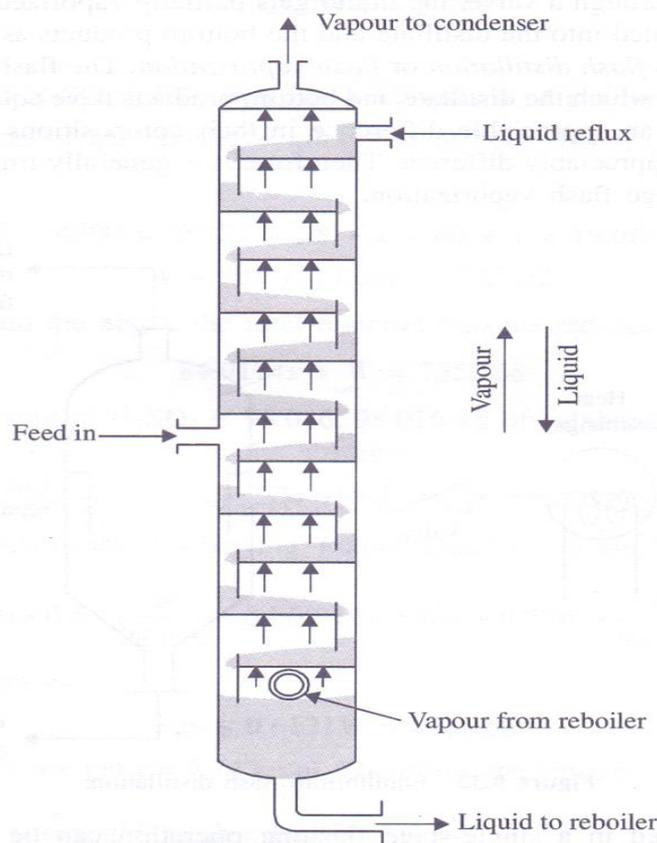


Fig. A plate column for fractionation.

In the fractionation column, the feed liquid is admitted almost centrally on the feed plate where it gets partially vaporized. The vapour flows upwards through the perforations and comes in contact with the liquid reflux on each plate. The vapour issuing from the top plate is taken to a condenser. The vapours are condensed by exchange of heat with a coolant, the most frequently used cooling medium being water. A part of the condensate is returned to the column as reflux and the other part is withdrawn as distillate or top product. The ratio of the moles of liquid recycled as reflux to the moles of distillate product is known as *reflux ratio*. The bottom of the column is equipped with a reboiler which receives the liquid flowing downwards from the feed plate and vaporizes it partially. The vapour so produced is sent back to the bottom plate. This vapour when comes in contact with the liquid flowing downwards strips away more volatile components from the liquid and as a result the bottom product can be made to be almost free of more volatile components. Steam is used as the heating medium in the reboiler. The liquid leaving the reboiler is collected as the residue or the bottom product.

Consider the distillation of a binary mixture of components A and B in which A is the more volatile component. Let F , D and W be the molar flow rates of the feed, distillate and residue respectively, and let x_F , x_D and x_W be their compositions expressed in terms of mole fractions of A. Considering the column as a whole, the total material balance and the component-A balance may be written as

$$F = D + W$$

$$Fx_F = Dx_D + Wx_W$$

Let R denotes the reflux ratio for the column, and let L be the reflux in kmol/h. Then, $L = RD$.

Lecture 5

Concept of Bypass, Recycle and Purging

5.1 Bypass

Bypass is employed mainly for effecting relatively small changes in a fluid stream. This is effectively achieved by introducing large changes in a small portion of the original stream and diverting the other portion without passing it through the unit accomplishing this change. The portion so diverted is known as the *bypass stream*. The stream that is passed through the process unit is later mixed with the bypassed stream to get the final desired change in the combined stream. For example, consider the air-conditioning practised in process industries to produce air of desired humidity. Air can be humidified or dehumidified by passing it through a spray chamber where water is sprayed into the air stream. An accurate control of the final humidity is possible by splitting the air stream into two parallel streams and subjecting one stream to the humidification or dehumidification operation described and bypassing the other stream around the humidifier or dehumidifier. The desired final mixture is obtained by combining the bypass stream with the conditioned air.

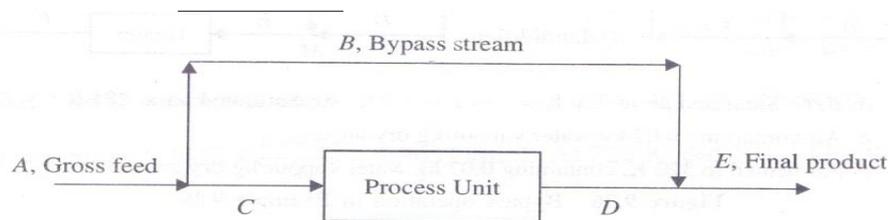


Fig. Bypass Operation

A portion of the gross feed stream (*A*) is diverted before entering the process unit and constitutes the bypass stream (*B*). The remaining portion (*C*) is passed through the unit and subjected to the necessary operation or process. The streams *A*, *B* and *C* have the same composition as well as other properties. The product stream leaving the processing unit (*D*) combines with the bypass stream and forms the final product (*E*) of desired properties.

5.2 Recycle

A system with recycle is one in which a stream leaving a processing unit is partly returned to the same unit for reprocessing or reusing. The recycling of the fluid stream in chemical processing practice to increase yields, to increase the purity, to enrich a product, to conserve heat, or to improve operations. A common example is the drying operation where a portion of the hot air leaving the drier is recycled to conserve heat or to reduce the rate of drying by controlling humidity of the air entering the drier. In a fractionating column, a part of the distillate is returned to the column as reflux to enrich the product. Many organic reactions do not give 100% yield of the desired product. In cases where the yield is low, the unreacted starting materials are separated from the product and sent back to the recycle streams and joins with a stream of reactants that enter the reactor. In ammonia synthesis, the gas mixture leaving the converter after recovery of ammonia is recycled through the converter.

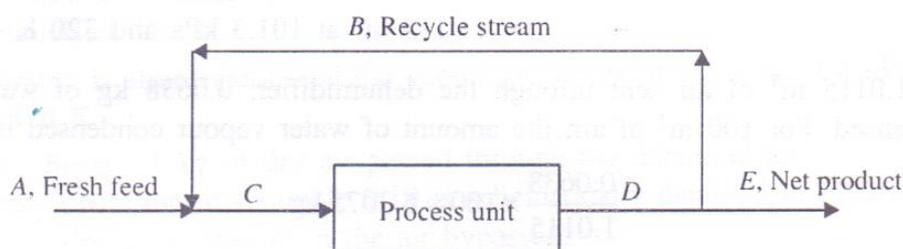


Fig. Recycle Operation

The recycling operation is schematically shown in fig below. The product stream D is split into two streams and one is recycled (B). The other stream is removed as the net product (E) from the operation. The physical properties and the chemical constitution of streams D , E and B may be same or different depending upon the operations that stream D has undergone before it is separated into streams E and B . The recycled stream combines with the fresh feed (A) and enters the unit as gross feed (C). The ratio of the quantity of a substance in the recycled stream to the quantity of the same substance in the fresh feed is known as the *recycle ratio*.

Two types of material balances may be written: (1) the overall material balance, in which the net feed material is equated to the net products, and (2) the once-through material balance, in which the gross feed is equated with the gross products. Material balances can be written for several different systems by the dashed envelopes 1, 2, and 3 as shown in Figure 9.37(b). Envelope 1 contains the entire process including the recycle stream, but the material balance over this will give no insight into the recycle stream. However, the balances written over envelopes 2 and 3 will contain recycle streams.

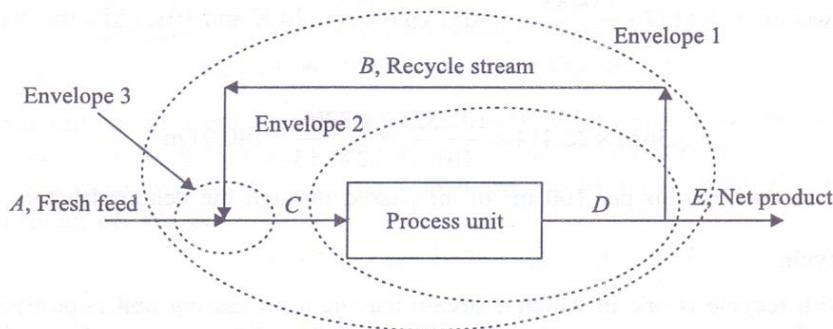


Fig. Material balance in Recycle Operation

5.3 Blowdown and Purge

A major limitation sometimes encountered in recycling operation is the gradual accumulation of inert materials or impurities in the recycled stock. The impurities may accumulate such a level that the process automatically comes to a stop. This difficulty can be overcome by bleeding off a fraction of the recycled stock. Similarly in processes involving chemical reaction employing recycle, if a small amount of a non-reactive material is present in the feed, it may be necessary to remove the non-reactive material in a purge stream to prevent its building-up above the maximum tolerable value. In the synthesis of ammonia from atmospheric nitrogen and hydrogen, the percentage conversion of a 1:3 mixture is 25% in a single pass through the reactor. The ammonia formed is removed by cooling and condensation under high pressures and the unconverted nitrogen and hydrogen are recirculated to the reactor. The methane present in the feed stream through the methanation reaction of hydrocarbon feed stock and argon coming from the atmospheric nitrogen enter the converter with the synthesis gas and accumulate in the gas stream entering the converter. The build-up of methane and argon beyond the permissible upper limit can be prevented by purging off a fraction of the recycled stream. In the manufacture of methanol from synthesis gas, purging is necessary to prevent the accumulation of methane.

In the electrolytic refining of copper employing the recycle of electrolyte, the accumulation of impurities is prevented by bleeding off a portion of the electrolyte and replacing the same with a fresh electrolyte. In the steam boiler using feed water containing dissolved solids, the solids would accumulate in the boiler, as steam is removed. Certain amounts of boiler contents are periodically removed as "blowdown" which, in principle, is analogous to purging operation.

If the impurity material is removed only through the purge stream, then the amount of inerts entering with the fresh feed should be equal to the amount of inerts in the purge. Let P be the amount of purge, and x_p be the composition of the inert in it, then

$$P x_p = F x_1$$

where F is the quantity of fresh feed and x_1 is its inert concentration.

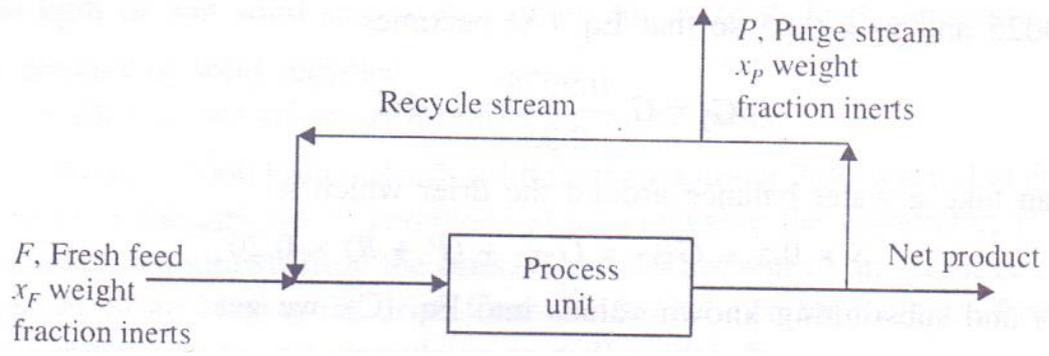


Fig.Purging Operation

Lecture 6

Concept of Material balance with chemical reaction: Combustion of solid, liquid and gaseous fuels

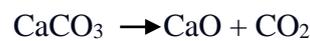
6. Material balance with chemical reaction

We have already seen that the general material balance equation can be written in the following form:

$$\begin{aligned} & \left[\begin{array}{c} \text{material input} \\ \text{to the system} \end{array} \right] - \left[\begin{array}{c} \text{material output} \\ \text{from the system} \end{array} \right] + \left[\begin{array}{c} \text{material generation} \\ \text{within the system} \end{array} \right] - \left[\begin{array}{c} \text{material consumption} \\ \text{within the system} \end{array} \right] \\ & = \left[\begin{array}{c} \text{accumulation of material} \\ \text{within the system} \end{array} \right] \end{aligned} \quad (9)$$

In the absence of generation and consumption of materials, the above equation reduces to input-output = accumulation

Under steady state, there is no accumulation and the terms on the right-hand sides of both the above equations reduce to zero. For processes with chemical conversion, the above equation is not universally valid. It is valid for the total material balance written on a mass basis, but not valid on a mole basis. Consider, for example, a process in which 1 kmol (100.09 kg) CaCO_3 is subjected to calcination reaction in a kiln. The following reaction takes place.



Assume that only 90% of the feed is converted. Then the quantities of the reactants and products in mass and molar units are given as follows:

Material	Input		Output	
	Mass (kg)	Moles (kmol)	Mass (kg)	Moles (kmol)
CaCO_3	100.09	1	10.01	0.1
CaO	0	0	50.47	0.9
CO_2	0	0	39.61	0.9
Total	100.09	1	100.09	1.9

6.1 COMBUSTION OF SOLID, LIQUID AND GASEOUS FUELS

The consumption of energy by chemical process industries is quite large in comparison with other industries. At present almost all the process energy requirement is met by the combustion of fossil fuels. The fossil fuels consist chiefly of carbon and hydrogen, with small amounts of oxygen, nitrogen, sulphur, mineral matter and moisture. The composition of the fuels varies widely depending upon the type and source of the fuels.

During combustion the chemical energy stored in the fuels is released as heat energy. The combustion process is the rapid chemical reaction of oxygen with materials and is used generally for the purpose of liberating heat energy. The combustion of coal, fuel oil or natural gas is the

main source of heat energy in process industries. The combustion process is generally carried out in furnaces and the heat liberated may be utilized for the production of steam for power generation and other heating purposes in the plant. Combustion calculations are carried out to relate quantities and composition of the fuel to those of the flue gas. In the following paragraphs some special terms used with reference to combustion calculations are discussed.

Theoretical oxygen is the oxygen required to burn all carbon in the fuel to carbon dioxide and all hydrogen to water. Oxygen required for combustion is supplied through air. To ensure complete combustion, usually more air is supplied than what is needed theoretically. If there is no adequate supply of air, incomplete combustion results, and carbon monoxide and free hydrogen will be present in the flue gases. *Excess oxygen* is the oxygen furnished through air in excess of the theoretical requirement of oxygen for the combustion. It is usually expressed as *percent excess oxygen*. Percent excess oxygen and percent excess air are the same. If oxygen is already present in the fuel, the percent excess oxygen is based on the *net oxygen*. Net oxygen is the total oxygen required for complete combustion minus the oxygen present **in** the fuel. Though a large percent excess air is preferred from the point of view of complete combustion, excess air supply is not without some problems. A large volume of gas in the furnace reduces the temperature attained on combustion and increases the loss of heat with the flue gas leaving the furnace.

6.1.1 Orsat Analysis

The Orsat analysis lists the composition of the flue gas on a dry basis. The Orsat apparatus measures the amount of CO_2 , CO and O_2 in a given sample of flue gas. The principle of measurement can be explained with the help of following Fig.

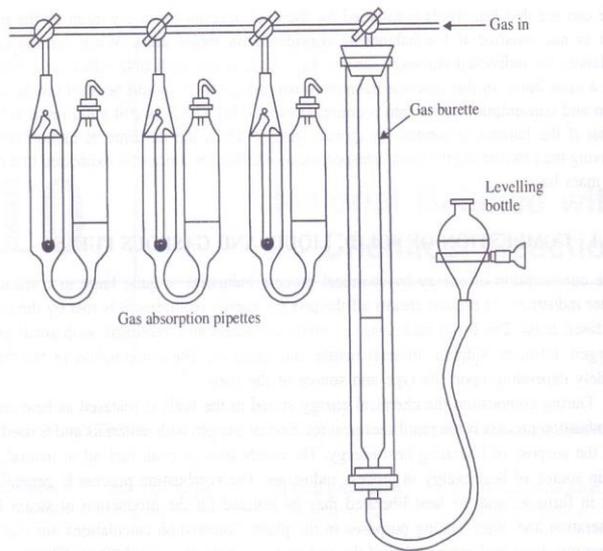


Fig. Orsat Apparatus

The Orsat apparatus consists of a gas measuring burette in which a 100-ml water saturated flue gas sample is initially taken. The gas from the burette can be passed through three absorption pipettes in succession. The CO_2 in the sample is absorbed by passing the gas through the pipette containing KOH solution. After ensuring the complete absorption of CO_2 , the volume change of

the gas is noted. The decrease in volume is the volume of CO, plus the water vapour it contained. The amount of oxygen in the flue gas sample is next found out by passing the gas through the second pipette which contains an oxygen-absorbing liquid such as alkaline pyrogallatesolution and by measuring the decrease in volume. Similarly, the CO content is measured by absorbing the gas in cuprous chloridesolution. The decrease in volume in each case measures the volume of CO₂, O₂, and CO respectively plus the water vapour associated with each of these gases. The ratio of the amount of water vapour associated with each gas to the amount of gas absorbed in each case is constant. This means that the decrease in volume in each case is equal to the volume percent of the gas on a dry basis. For example, assume that 100 mL of the gas sample contained 50 mL of CO₂, 10 mL of CO, 30 mL of O₂, and 10 mL of H₂O vapour. On absorbing CO₂, the decrease in volume would be $50 + 50 \times (10/90) = 55.56$ mL which is the percent of CO, in the gas on a water-free basis. Similarly, the concentrations of O₂, and CO are respectively 33.33% and 11.11%. The percent of nitrogen is found out by subtracting from 100 the sum of the percent concentrations of CO₂, CO and O₂.

The qualitative aspects of material balance in combustion process can be made clear with the help of the following Figure

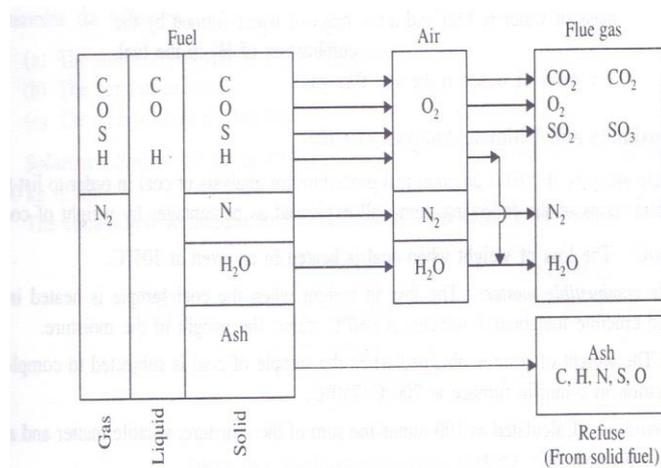


Fig: Material balance in combustion.

In combustion process there are three streams: the fuel, the air supply and the flue gas. Sometimes, as in the case of solid fuels, a refuse stream, which is constituted by the mineral matter present in the fuel, and unburned fuel constituents also will be present. The material balances on the various elements can be written in order to establish the quantitative relationship between different streams.

The masses of the fuel burned and the flue gases produced can be related by a *carbon balance*. All the carbon in the flue gas (such as in CO₂, CO, soot, etc.) comes from the fuel, since CO, in the air is negligible. The amount of refuse formed may be obtained by making an *inert material balance (ash balance)* around the furnace. The key component relating the solid fuel and the furnace refuse is the ash. All the ash in the fuel leaves the furnace with the refuse. Some of the carbon charged in the solid fuel remains unburned and leaves with the refuse. An ash balance and a refuse analysis would be necessary to determine the fraction of carbon charged that is unburned. The nitrogen in the fuel plus that in the air equals the nitrogen in the flue gas. Thus the *nitrogen balance* can be used to find out the amount of air that was supplied per unit mass of the flue gas. On combustion, the hydrogen in the fuel becomes water and it leaves with the flue gas. The total water present in the flue gas is made up of water produced by the combustion of

hydrogen with oxygen plus the moisture present in the fuel and air. The *oxygen balance* can thus be made to determine the amount of hydrogen in the fuel. This gives

moles of oxygen used for burning H, = moles of O₂, in the fuel and air — moles of
oxygen in the dry flue gas as CO₂, SO₂, CO, O₂, etc.

Knowing that one mole of oxygen is equivalent to two moles of hydrogen, we can determine the moles of hydrogen in the fuel that have combined with oxygen to form water. Since the flue gas analysis is reported on a dry basis, it is necessary that the amount of water in the flue gas be known to find the volume of wet flue gas. This is done by taking a *water balance* around the furnace, i.e.

mass of water in fuel and air + mass of water formed by the
combustion of H₂ in the fuel = mass of water in the wet flue gas

6.1.2 Proximate and Ultimate Analysis of Coal

The proximate analysis of coal is an empirical procedure for analysis of coal in order to list the composition in terms of the following items, all expressed as percentages by weight of coal:

- *Moisture*: The loss of weight when coal is heated in an oven at 105°C.
- *Volatile combustible matter*: The loss in weight when the coal sample is heated in a covered crucible for about 7 minutes at 950°C minus the weight of the moisture.
- *Ash*: The weight of residue obtained when the sample of coal is subjected to complete combustion in a muffle furnace at 700°C-750°C.
- *Fixed carbon*: Calculated as 100 minus the sum of the moisture, volatile matter and ash already obtained, i.e.

$$FC = 100 - (M + VCM + A)$$

where *FC*, *M*, *VCM* and *A* are the percentages of fixed carbon, moisture, volatile combustible matter and ash respectively. Due to the environmental problems associated with the combustion of sulphur, it is now required to report the percentage by weight of sulphur also in the proximate analysis.

The ultimate analysis of coal gives the composition as the percentage by weight of the various elements such as C, H, N, O, S, etc. and the ash. The ultimate analysis provides the necessary data required for material balance in the combustion of coal. The analysis is carried out by elaborate and standard chemical techniques. The carbon dioxide, water and sulphur dioxide formed by burning coal in a sufficient supply of oxygen determine respectively the amounts of carbon, hydrogen and sulphur in coal. Carbon dioxide and water are absorbed in suitable solvents and sulphur dioxide in lead chromate. The nitrogen in the coal is determined by the Kjeldahl method. The percentage of oxygen in the coal is found out by subtracting the percentages of all other constituents from 100.

The hydrogen reported in the ultimate analysis includes the hydrogen in the volatile matter and the hydrogen in the moisture present in coal. The carbon reported in the ultimate analysis includes the fixed carbon and the carbon present in the volatile matter. The volatile matter contains complex organic substances made up of C, H, O, N and S. The fixed carbon is the combustible residue of tar and coke resulting from the pyrolysis reaction at 950°C. Oxygen and total hydrogen may be reported in the ultimate analysis, or the oxygen may be reported as equivalent "combined water" in which case, the remaining hydrogen is the available hydrogen or net hydrogen. The available hydrogen is the only hydrogen that requires oxygen from the air for combustion.

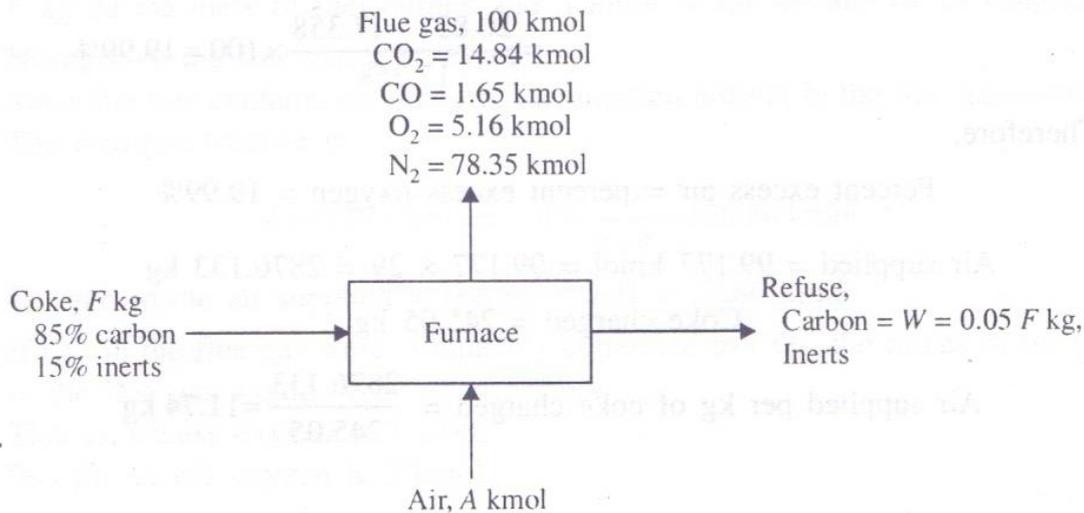
Lecture 7

Mathematical problem based on Material balance with chemical reaction

Prob. 1. Hydrogen-free coke containing 85% (weight) carbon and the rest inert materials is burned in a furnace. It is found that during combustion 5% of the coke charged is lost unburned. The flue gas analysis shows 14.84% CO₂, 1.65% CO, 5.16% O, and 78.35% N₂. The flue gas leaves the furnace at 500 K and 100 kPa. Calculate the following:

- i) The percent excess air on the basis of complete combustion of coke
- ii) The weight of air supplied per kg of coke charged
- iii) The volume of flue gas per kg of coke charged
- iv) The composition of the refuse from the furnace

Solution Basis: 100 kmol flue gas



Let F kg be the mass of coke charged and W kg be the mass of coke left unburned per 100 kmol flue gas produced. $W = 0.05 F$.

The amount of coke charged to the burner to obtain 100 kmol flue gas can be obtained by taking a carbon balance.

Carbon present in the flue gas = carbon in CO₂ + carbon in CO

$$= 14.84 + 1.65 = 16.49 \text{ kmol} = 16.49 \times 12 = 197.88 \text{ kg Carbon in the coke charged} = F \times 0.85 \text{ kg}$$

$$\text{Carbon in the unburned coke} = W \times 0.85 = 0.05F \times 0.85$$

Carbon balance:

$$F \times 0.85 = 0.05F \times 0.85 + 197.88$$

Solving the above equation, we get, $F = 245.05 \text{ kg}$

- i) Let A kmol air is supplied for combustion. Since the nitrogen in the flue gas is coming from the air supplied, a nitrogen balance gives

$$A \times 0.79 = 78.35$$

or $A = 99.177 \text{ kmol}$

Thus,

$$\text{Oxygen supplied} = A \times 0.21 = 99.177 \times 0.21 = 20.827 \text{ kmol}$$

Theoretical oxygen requirement is calculated as the moles of oxygen required for the complete conversion of carbon in the coke charged to CO_2 . That is,

$$\text{Theoretical requirement of oxygen} = \frac{245.05 \times 0.85}{12} = 17.358 \text{ kmol}$$

$$\text{Percent excess of oxygen} = \frac{\text{excessoxygen}}{\text{theoreticaloxygen}} \times 100$$

$$= \frac{20.827 - 17.358}{17.358} \times 100 = 19.99\%$$

Therefore, Percent excess air = percent excess oxygen = 19.99%

ii) $\text{Air supplied} = 99.177 \text{ kmol} = 99.177 \times 29 = 2876.133 \text{ kg}$

$$\text{Coke charged} = 245.05 \text{ kg}$$

$$\text{Air supplied per kg of coke charged} = \frac{2876.133}{245.05} = 11.74 \text{ kg}$$

iii) For 100 kmol flue gas, 245.05 kg of coke is charged. Therefore, the volume of flue gas at 500 K and 100 kPa is

$$\frac{100}{245.05} \times 22.414 \times \frac{101.325}{100} \times \frac{500}{273.13} = 16.96 \text{ m}^3$$

iv) The refuse from the furnace is made up of inerts in the coke charged and the unburned carbon. Therefore, the total weight of refuse is:

$$\text{carbon in the refuse} = F \times 0.05 \times 0.85 = 10.41 \text{ kg}$$

$$\text{inerts in the refuse} = F \times 0.15 = 36.76 \text{ kg}$$

Therefore, the total weight of refuse is

$$36.76 + 10.41 = 47.17 \text{ kg}$$

Composition of refuse is

$$\text{Carbon} = \frac{10.41}{47.17} \times 100 = 22.07\%$$

$$\text{Inerts} = \frac{36.76}{47.17} \times 100 = 77.93\%$$

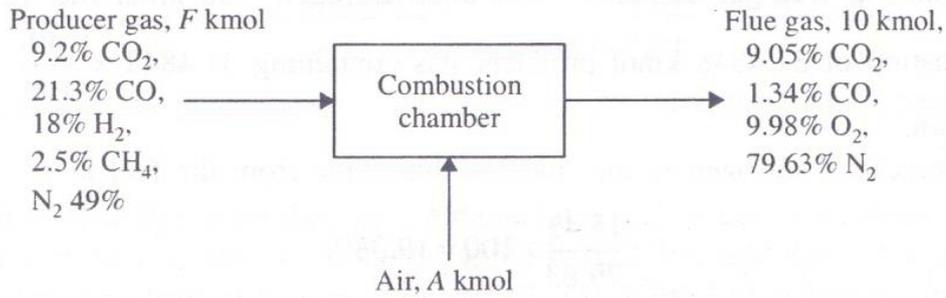
Prob. 2. A producer gas contains 9.2% CO_2 , 21.3% CO , 18% H_2 , 2.5% CH_4 , and the rest N_2 . It is burned with an excess supply of air. The flue gas analysed 9.05% CO_2 , 1.34% CO , 9.98% O_2 and 79.63% N_2 . Determine the following:

i) The volumetric ratio of air supplied to the fuel burned

ii) The percent excess air supplied

iii) The percent of nitrogen in the flue gas that came from the fuel.

Solution Basis: 100 moles of flue gas



Let F moles of fuel be burned with A moles of air to obtain 100 moles of dry flue gas.

Carbon balance:

$$\begin{aligned} \text{carbon in the fuel burned} &= \text{carbon in the flue gas as CO, and CO} \\ 0.092F + 0.213F + 0.025F &= 9.05 + 1.34 = 10.39 \text{ kmol} \end{aligned}$$

Therefore, the moles of fuel burned to produce 100 kmol flue gas, $F = 31.4848$ kmol.

Air supplied for the combustion may be obtained by a nitrogen balance. Nitrogen in the flue gas is the sum of the nitrogen present in the fuel and that in the air. The mole percentage of nitrogen in the producer gas = $100 - 21.3 - 9.2 - 2.5 - 18.0 = 49\%$.

Nitrogen balance:

$$\text{nitrogen from the fuel} + \text{nitrogen in the air} = \text{nitrogen in the flue gas}$$

$$31.4848 \times 0.49 + A \times 0.79 = 79.63$$

Solving this we get $A = 81.2689$ kmol

i) The molar ratio of air to fuel is $= \frac{81.2689}{31.4848} = 2.58$, which is the same as the volumetric ratio of air to fuel.

ii) The percent excess of oxygen supplied can be calculated as

$$\text{percent excess} = \frac{\text{oxygen excess}}{\text{theoretical requirement}} \times 100$$

The flue gases contain 9.98 kmol oxygen. The amount of oxygen that would have been present in the flue gas had the combustion were complete would be less than this by the amount of oxygen required by CO present in the flue gas for its combustion to CO_2 .

That is

$$\text{Excess oxygen} = 9.98 - 0.5 \times 1.34 = 9.31 \text{ kmol}$$

$$\begin{aligned} \text{Theoretical requirement of oxygen} &= \text{oxygen supplied} - \text{oxygen excess} \\ &= 81.2689 \times 0.21 - 9.31 = 7.76 \text{ kmol} \end{aligned}$$

Percent excess of air = percent excess of oxygen

$$\frac{9.31}{7.76} \times 100 = 120\%$$

iii) 100 kmol of flue gas contains 79.63 kmol nitrogen. 100 kmol fuel results from the combustion of 31.4848 kmol producer gas containing $31.4848 \times \frac{49}{100} = 15.43$ kmol nitrogen.

The percent of nitrogen in the flue gas that came from the fuel is

$$\frac{15.43}{79.63} \times 100 = 19.38\%$$

Lecture 8

Material Balance with recycle, bypass and purge streams

8.1 Recycle Operation

The recycle, bypass and purging operations have been discussed with emphasis on processes with no chemical reactions, where we have seen the advantages and areas of applications of these operations. In processes involving chemical reactions, recycle is generally employed to increase the yield. Many organic reactions do not give 100% yield of the desired product. In cases where the yield is low, the unreacted starting materials are separated from the product and sent back to the reactor as a recycle stream as shown in below Figure. Unreacted material is separated from the reactor products and fed back and joins with a stream of fresh reactants, and the combined stream then enters the reactor. In ammonia synthesis, the gas mixture leaving the converter after recovery of ammonia is recycled through the converter.

In processes involving chemical reactions, the recycle process necessitates the specification of two types of conversions: the *overall conversion* and the *single-pass conversion*. The overall conversion is the fraction of the reactant in the fresh feed that is reacted considering the overall process.

$$\text{Overall conversion} = \frac{\text{moles of reactant in the fresh feed} - \text{moles of reactant in the product from the overall process}}{\text{moles of reactant in the fresh feed}}$$

$$= \frac{\text{moles of reactant in stream A} - \text{moles of reactant in stream E}}{\text{moles of reactant in stream A}}$$

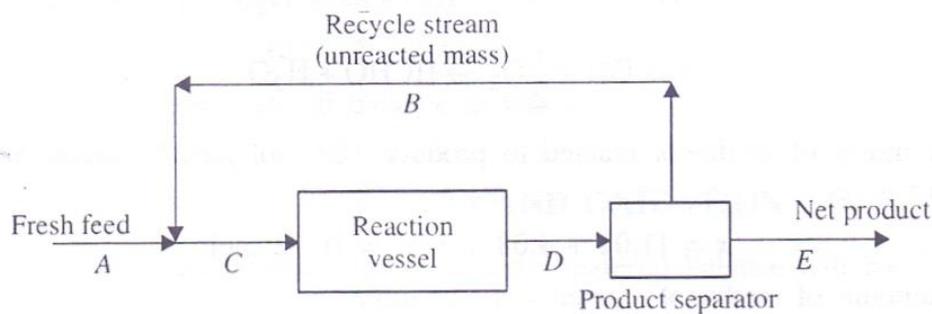


Fig. Recycle in processes with chemical reaction

Consider a chemical reaction $A + B \rightarrow C$ being carried out in a unit shown in below figure where the single-pass conversion of A is 25%. Assume that the reactants are present in stoichiometric proportions in the fresh feed. What is the amount recycled per 100 moles of fresh feed?

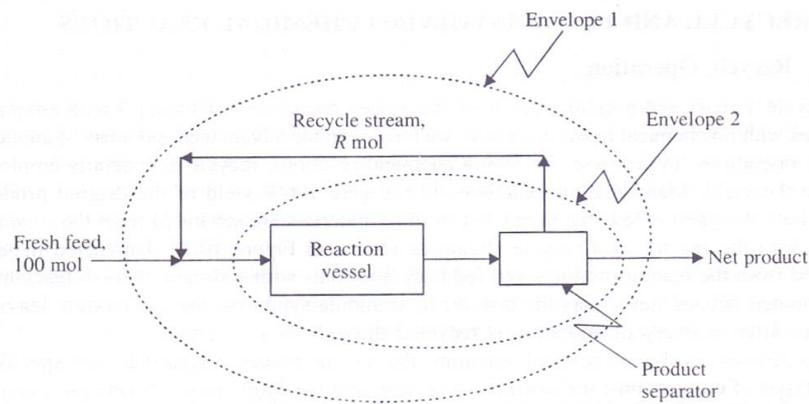


Fig. Recycle in processes with chemical reaction

Taking an A -balance or $A + B$ balance for the overall unit (envelope 1) will not give us any information on the recycle. Consider envelope 2 that encompasses the reactor and the separator in which the recycle is separated from the reaction products, and take a material balance for

$A + B$ assuming that R moles are recycled per 100 moles of fresh feed. For a steady-state material balance for processes with chemical reaction, the general material balance can be written as

material in = material out + material consumed due to chemical reaction Since the moles entering the reactor is $100 + R$, we get

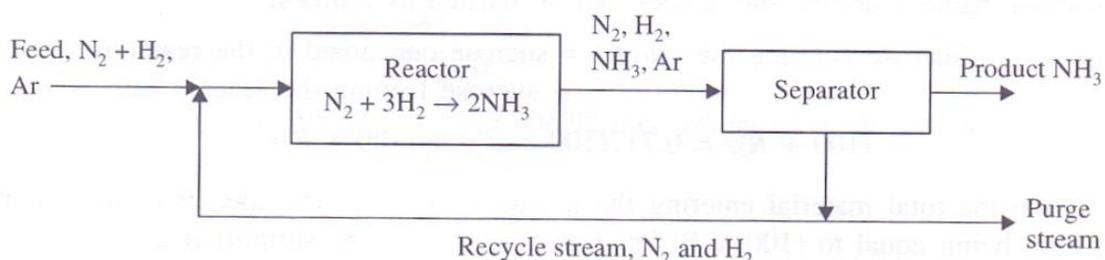
$$100 + R = (100 + R)0.25 + R$$

which gives $R = 300$ moles.

8.2 Purging Operation

In some recycling operations purging will be necessary to prevent the accumulation of inerts and non-reacting materials in the feed stream entering the reactor. In the absence of purging, the non-reactive material present in the feed stream builds up beyond the maximum tolerable value. For example, in the synthesis of ammonia from atmospheric nitrogen and hydrogen, the percentage conversion of a 1:3 mixture is 25% in a single pass through the reactor. The unconverted nitrogen and hydrogen constitutes the recycle stream in which methane and argon are present as impurities. The buildup of methane and argon beyond the permissible upper limit can be prevented by bleeding off a fraction of the recycled stream. The same is the case with the manufacture of methanol from synthesis gas where purging is necessary to prevent the accumulation of methane.

Under steady-state conditions, loss of inert in the purge = rate of feed of inerts into the system



The concentration of inerts in the purge stream is equal to the concentration of inerts in the recycle stream at the point where the purge is carried out. Thus, the quantity purged off can be evaluated as

$$\text{purge} = \frac{\text{feed rate} \times \text{mole fraction of inerts in the feed}}{\text{mole fraction of inerts in the recycle}}$$

Energy is defined as the capacity of a physical system to perform work. However, it's important to keep in mind that just because energy exists, that doesn't mean it's necessarily available to do work.

- **Units of energy:** The SI unit of energy is the joule (J) or newton-meter (N * m)

Different forms of energy:

Energy exists in several forms such as heat, kinetic or mechanical energy, light, potential energy, and electrical energy.

- **Heat** - Heat or thermal energy is energy from the movement of atoms or molecules. It may be considered as energy relating to temperature.
- **Kinetic Energy** - A system's kinetic energy is associated with directed motion (e.g. translation, rotation) of the system. Translation refers to straight line motion. The kinetic energy E_k of a moving object of mass m and travelling with speed u is given by,

$$E_k = \frac{1}{2} mu^2$$

u is measured relative to a frame of reference that defines what is "stationary". E_k has units of energy, m of mass, and u of length/time.

- **Potential Energy** - Potential energy of a system is due to the position of the system in a potential field. There are various forms of potential energy, but only gravitational potential energy will be considered in this course. The gravitational potential energy of an object of mass m at an elevation z in a gravitational field, relative to its gravitational potential energy at a reference elevation z_0 , is given by,

$$E_p = mg (z-z_0)$$

The quantity g is the gravitational acceleration that defines the strength of the gravitational field. Often, the earth's surface is used as the reference and assigned $z_0 = 0$, in which case mgz represents the gravitational potential energy of the object relative to its potential energy if it rested on the earth's surface. E_p has units of energy, m of mass, g of length/time², and z of length.

- **Mechanical Energy** - Mechanical energy is the sum of the kinetic and potential energy of a body.
- **Light** - Photons are a form of energy.
- **Electrical Energy** - This is energy from the movement of charged particles, such as protons, electrons, or ions.
- **Magnetic Energy** - This form of energy results from a magnetic field.
- **Chemical Energy** - Chemical energy is released or absorbed by chemical reactions. It is produced by breaking or forming chemical bonds between atoms and molecules.

- **Nuclear Energy** - This is energy from interactions with the protons and neutrons of an atom. Typically this relates to the strong force. Examples are energy released by fission and fusion.

Internal Energy: The internal energy of a system is identified with the random, disordered motion of molecules; the total (internal) energy in a system includes potential and kinetic energy. This is contrast to external energy which is a function of the sample with respect to the outside environment (e.g. kinetic energy if the sample is moving or potential energy if the sample is at a height from the ground etc). The symbol for Internal Energy Change is ΔE .

Energy on a smaller scale

- Internal energy includes energy on a microscopic scale
- It is the sum of all the microscopic energies such as:
 - i. translational kinetic energy
 - ii. vibrational and rotational kinetic energy
 - iii. potential energy from intermolecular forces

3.2.GeneralEnergy Balance Equation:

$$\left\{ \begin{array}{l} \text{energy in through} \\ \text{system boundaries} \end{array} \right\} - \left\{ \begin{array}{l} \text{energy out through} \\ \text{system boundaries} \end{array} \right\} = \left\{ \begin{array}{l} \text{energy accumulated} \\ \text{within the system} \end{array} \right\}$$

$$\Sigma E_R = \Sigma E_P + \Sigma E_W + \Sigma E_L + \Sigma E_S$$

Where,

$$\Sigma E_R = E_{R1} + E_{R2} + E_{R3} + \dots = \text{Total Energy Entering}$$

$$\Sigma E_P = E_{P1} + E_{P2} + E_{P3} + \dots = \text{Total Energy Leaving with Products}$$

$$\Sigma E_W = E_{W1} + E_{W2} + E_{W3} + \dots = \text{Total Energy Leaving with Waste Materials}$$

$$\Sigma E_L = E_{L1} + E_{L2} + E_{L3} + \dots = \text{Total Energy Lost to Surroundings}$$

$$\Sigma E_S = E_{S1} + E_{S2} + E_{S3} + \dots = \text{Total Energy Stored}$$

Lecture 2

Explanation and derivation of some terms related to energy balance

3.3.1.Enthalpy:

Enthalpy, the sum of the internal energy and the product of the pressure and volume of a thermodynamic system. Enthalpy is an energy-like property or state function—it has the dimensions of energy (and is thus measured in units of joules or ergs), and its value is determined entirely by the temperature, pressure, and composition of the system and not by its history. In symbols, the enthalpy, H , equals the sum of the internal energy, E , and the product of the pressure, P , and volume, V , of the system: $H = E + PV$.

Enthalpy change: According to the law of energy conservation, the change in internal energy is equal to the heat transferred to, less the work done by, the system. If the only work done is a change of volume at constant pressure, the enthalpy change is exactly equal to the heat transferred to the system. When energy needs to be added to a material to change its phase from a liquid to a gas, that amount of energy is called the enthalpy (or latent heat) of vaporization and is expressed in units of joules per mole. Other phase transitions have similar associated enthalpy changes, such as the enthalpy (or latent heat) of fusion for changes from a solid to a liquid. As with other energy functions, it is neither convenient nor necessary to determine absolute values of enthalpy. For each substance, the zero-enthalpy state can be some convenient reference state.

3.3.2. Heat Capacity:

The heat capacity of a defined system is the amount of heat (usually expressed in calories, kilocalories, or joules) needed to raise the system's temperature by one degree (usually expressed in Celsius or Kelvin). It is expressed in units of thermal energy per degree temperature. To aid in the analysis of systems having certain specific dimensions, molar heat capacity and specific heat capacity can be used. To measure the heat capacity of a reaction, a calorimeter must be used. Bomb calorimeters are used for constant volume heat capacities, although a coffee-cup calorimeter is sufficient for a constant pressure heat capacity.

- **Molar Heat Capacity:** The amount of heat needed to increase the temperature of one mole of a substance by one degree is the molar heat capacity. It is expressed in joules per moles per degrees Celsius (or Kelvin). For example, the molar heat capacity of lead is 26.65 Joules/Moles⁰C , which means that it takes 26.65 Joules of heat to raise 1 mole of lead by °C.
- **Specific Heat Capacity:** The amount of heat needed to increase the temperature of one gram of a substance by one degree is the specific heat capacity. It is expressed in joules per gram per degree Celsius, Joules/Grams°C. Because the specific heat of lead is 0.128 Joules/Grams°C , it 0.128 Joules of heat is required to raise one gram of lead by one °C.
- **Quantity of Heat:** The quantity of heat is a measurement of the amount of heat is present. The formula of quantity of heat, q , is equal to the mass of substance, m , multiplied with the specific heat and the change in temperature, ΔT . When the mass of substance is multiplied with the specific heat the product is equal to heat capacity, which is donated as C .

$$Q = \Delta T \times C \times m$$

Heat capacity, C , can never be negative for a mass or a substance and the specific heat of a substance can never be negative. Thus, if the change in temperature is negative, the initial temperature is more than the final temperature, then quantity of heat must be negative, for a negative number multiplied by a positive number equals a negative number. When the quantity of

heat is negative heat the system is depleted of its heat; however, if the quantity of heat is positive then the system gains heat.

3.3.3. Latent Heat and Sensible Heat:

Latent heat is the energy absorbed by or released from a substance during a phase change from a gas to a liquid or a solid or vice versa. If a substance is changing from a solid to a liquid, for example, the substance needs to absorb energy from the surrounding environment in order to spread out the molecules into a larger, more fluid volume. If the substance is changing from something with lower density, like a gas, to a phase with higher density like a liquid, the substance gives off energy as the molecules come closer together and lose energy from motion and vibration.

Sensible heat is the energy required to change the temperature of a substance with no phase change. The temperature change can come from the absorption of sunlight by the soil or the air itself. Or it can come from contact with the warmer air caused by release of latent heat (by direct conduction). Energy moves through the atmosphere using both latent and sensible heat acting on the atmosphere to drive the movement of air molecules which create wind and vertical motions.

- **Specific Latent Heat:** There are two types of specific latent heat: vaporization and fusion. The specific latent heat of vaporization is defined as the quantity of heat energy that is necessary to raise one unit of weight (pounds or grams) with no change of temperature in the surroundings. Like the name implies, this specific latent heat quantifies the transfer of energy when a substance's state changes from liquid to gas or from gas to liquid. On the other hand, the specific heat of fusion is the quantity of heat that is necessary to raise one unit of weight without any change in temperature. This specific latent heat quantifies the transfer of energy when a substance's state changes from a solid to a liquid or from a liquid to a solid. Two formulas has be derived from this property:

$$Q=m \times L \text{ and thus } L=Q/m$$

When, Q = the amount of heat increase or decrease as the state changes,

m = the mass of the substance present, and

L = the specific latent heat for that substance.

Lecture 3

Energy Balance without chemical reaction

3.4. Closed System and Open System:

A closed system is a physical system that doesn't exchange any matter or energy with its surroundings, and isn't subject to any force whose source is external to the system.

An open system is a system that freely exchanges energy and matter with its surroundings. For instance, when you are boiling soup in an open saucepan on a stove, energy and matter are being transferred to the surroundings through steam. The saucepan is an open system because it allows for the transfer of matter (for example adding spices in the saucepan) and for the transfer of energy (for example heating the saucepan and allowing steam to leave the saucepan).

3.5.1. Energy balance for a non-flow system (without chemical reaction):

In a non-flow process, where no stream of material enters or leaves a system during the course of an operation, the potential energy, kinetic energy and flow energy (work) terms of the stream do not come into play.

$$Q = \Delta E + W,$$

For a non-flow process at constant volume, $W=0$,

Therefore, $Q = \Delta E$

For a non-flow process at constant pressure, $W = P\Delta V$,

Where, P= pressure, V= Volume

Therefore, $Q = \Delta E + P\Delta V = \Delta (E + PV) = \Delta H$, ΔH = Change in enthalpy

3.5.2. Energy balance for a flow system (without chemical reaction):

In a flow system, the heat added is equal to the gain in kinetic energy, potential energy and enthalpy of the system and work done by the system.

$$Q = \Delta K_E + \Delta P_E + \Delta H + W_S$$

Where, K_E = Kinetic energy

P_E = Potential energy

W_S = Work done by the system

For, most industries flow process such as the operation of boilers, chemical reactors, absorbers, distillation columns or heat exchangers, the kinetic energy, potential energy and work terms are negligible or cancel out and heat added to the system is equals the increase in enthalpy.

Therefore, $Q = \Delta H$

Lecture 4

Energy Balance with chemical reaction

3.6. Energy Balance without chemical reaction:

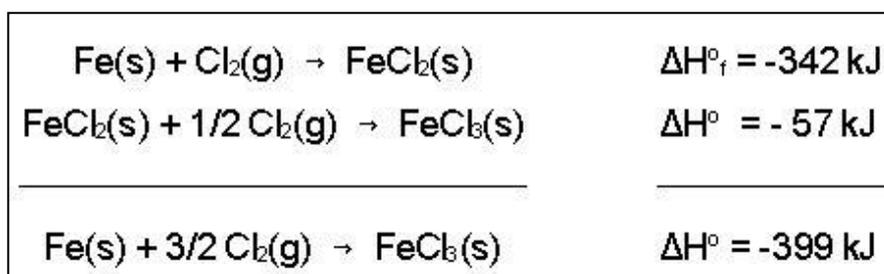
Reactions are either endothermic or exothermic.

The change in enthalpy of a system is dependent on the initial and final states of the system and is independent of the path in which the change of state is brought about. At a given temperature and pressure the amount of energy required to decompose a compound into its elements equals the energy evolved in formation of that compound of the elements.

3.6.1. Hess's law: If a process can be written as the sum of several steps, the enthalpy change of the process equals the sum of the enthalpy changes of the individual steps.

- If we know the enthalpy changes of a series of reactions that add up to give an overall reaction, we add these enthalpy changes to determine the enthalpy change of the overall reaction.

Using the enthalpy change for the reaction of Fe with Cl₂ to give FeCl₂ and the enthalpy change for the reaction of FeCl₂ with Cl₂ to give FeCl₃, we can determine the enthalpy change for the reaction of Fe with Cl₂ to give FeCl₃.



- If we know the standard enthalpies of formation, ΔH_f° , of the reactants and products of a reaction we can calculate the enthalpy change of the reaction using the following shorthand version of Hess's law:

$$\Delta H^\circ = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants})$$

Heat of Reaction: The Heat of Reaction (also known as Enthalpy of Reaction) is the change in the enthalpy of a chemical reaction that occurs at a constant pressure. It is a thermodynamic unit of measurement useful for calculating the amount of energy per mole either released or produced in a reaction. Since enthalpy is derived from pressure, volume, and internal energy, all of which are state functions, enthalpy is also a state function.

Heat of Formation: The heat released or absorbed (enthalpy change) during the formation of a pure substance from its elements, at constant pressure and usually denoted by ΔH_f .

Heat of Combustion: The calorific value is the total energy released as heat when a substance undergoes complete combustion with oxygen under standard conditions. The chemical reaction is typically a hydrocarbon or other organic molecule reacting with oxygen to form carbon dioxide and water and release heat. It may be expressed with the quantities:

- energy/mole of fuel (kJ/mol)
- energy/mass of fuel
- energy/volume of the fuel

1.6.2. Heat of reaction at constant pressure and constant volume:

For constant volume process,

$Q_v = \Delta H_v = \Delta E_v$, where, Q_v = absorption of heat at constant volume

For constant pressure process,

$$Q_p = \Delta H_p = \Delta E_p + P\Delta V$$

Therefore,

$$Q_p - Q_v = (\Delta E_p - \Delta E_v) + P\Delta V$$

For a system in which the reactants and products are gases, behaving ideally, the change in internal energy is unaffected by the pressure.

$$\text{So, } \Delta E_p = \Delta E_v$$

In case of ideal gases,

$$P\Delta V = P\Delta V_g = RT \Delta n_g, \text{ Where, } \Delta n_g \text{ is the change in the moles of gaseous components}$$

Now, we can conclude from the above equations,

$$Q_p = Q_v + \Delta n_g RT$$

For exothermic reactions where heat is evolved,

$$Q_p = Q_v - \Delta n_g RT$$

Lecture 5

Heat Capacity and Enthalpy Calculation Procedures

3.7. Heat capacity (C): It describes the amount of heat required to change the temperature of a substance:

- $C = \frac{dQ}{dT}$

By definition, the heat capacity of water at 15°C is 1 cal K⁻¹ g⁻¹ or 18 cal K⁻¹ mol⁻¹ (i.e., the heat required to heat 1 gram of water from 14.5 to 15.5°C is 1 calorie).

Heat capacities of solids approach zero as absolute zero is approached:

- $\lim_{T \rightarrow 0} C = 0$

The heat capacity is written with a subscript P or V depending on whether it obtains for constant pressure C_P or constant volume C_V.

As an aside,

- $C_P = C_V + TV\alpha^2/\beta$

where α and β are the expansivity and compressibility--for solids the difference between C_P and C_V is minimal and can be ignored as a first approximation. For gases, C_P = C_V + R, and is quite significant.

Heat capacities are measured by calorimetry and often fit by a function of the form:

- $C_P = a + bT + cT^{-2} + dT^{-0.5}$

but there are other expansions for the heat capacity involving more or fewer terms. Below are some examples of heat capacities of minerals. Note how silicates have a nearly constant heat capacity of ~1 J K⁻¹ g⁻¹ above 400K.

3.8. Enthalpy Calculation from heat capacity: We have already talked about the familiar concept of heat as energy.

Let's define another measure of energy called enthalpy H--a kind of measure of the thermal energy of a crystal. As we will see below,

- $dH = dQ + VdP$

Recall that we interpreted

- $dE = dQ - PdV$

to mean that the internal energy change is the heat change minus the energy lost to relaxation of the crystal. Thus,

- $dH = dQ + VdP$

means that the enthalpy change is the heat change plus the energy the crystal gains by virtue of not being allowed to expand.

Enthalpy includes the vibrational and bonding energy at absolute zero H₀[°], plus the energy required to increase temperature:

- $H = H_0^\circ + \int_{T_{ref}}^T C_P dT$

i.e., we can find the enthalpy change ΔH produced by changing temperature by integrating the heat capacity C_P :

- $\Delta H = \int_{T_1}^{T_2} C_P dT$

1.9. How to integrate the heat capacity (to determine change in enthalpy ΔH):

- $\int_{T_1}^{T_2} C_P dT = \int_{T_1}^{T_2} (a + bT + cT^{-2} + dT^{-0.5})$
- $= aT + bT^2/2 - c/T + 2dT^{0.5}$

and is evaluated as

- $= a(T_2 - T_1) + b(T_2^2 - T_1^2)/2 - c/(T_2^{-1} - T_1^{-1}) + 2d(T_2^{0.5} - T_1^{0.5})$

How to integrate the heat capacity divided by T (to determine entropy S):

- $\int_{T_1}^{T_2} \frac{C_P}{T} dT = \int_{T_1}^{T_2} (a/T + b + cT^{-3} + dT^{-1.5})$
- $= a \ln T + bT - cT^{-2}/2 - 2dT^{-0.5}$

and is evaluated as

- $a(\ln T_2 - \ln T_1) + b(T_2 - T_1) - c(T_2^{-2} - T_1^{-2})/2 - 2d(T_2^{-0.5} - T_1^{-0.5})$

3.10. Kopp's Rule:

When experimental data are lacking, Kopp's rule may be used for making rough estimation of the heat capacity of solids. Kopp's rule predicts that the heat capacity of a solid compound at room temperature is approximately equal to the sum of the heat capacities of individual elements. The atomic heat capacity values of some elements are given below:

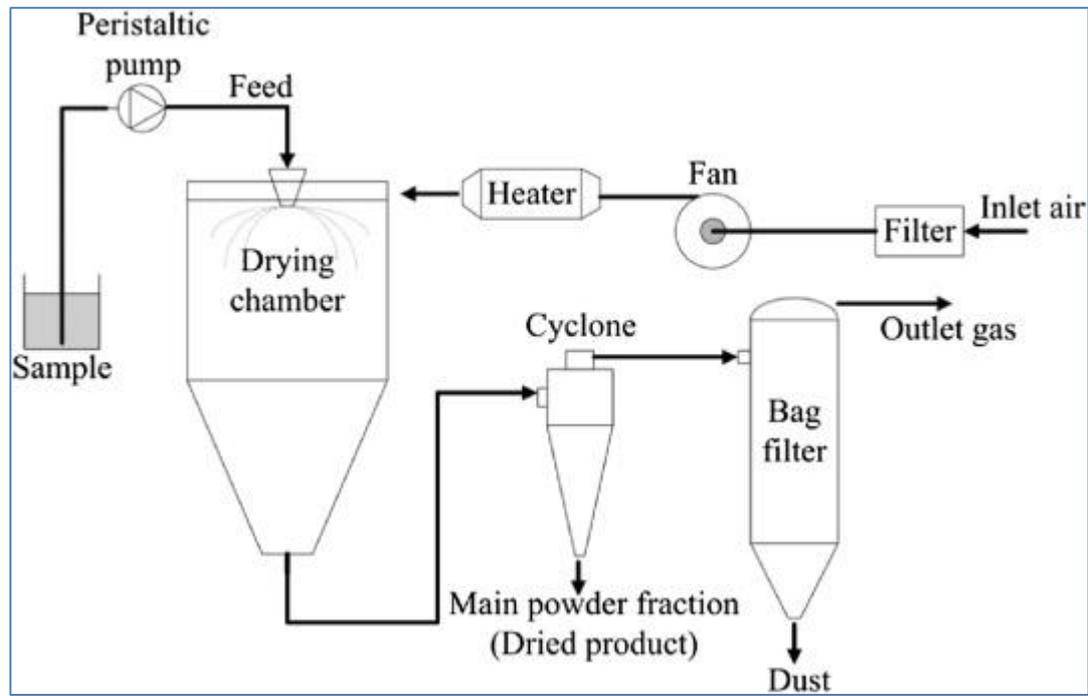
Atomic heat capacity values for using Kopp's rule (Heat capacity at 293K, J/gm-atom K)

Elements	Solids	Liquids
Carbon	7.5	11.7
Hydrogen	9.6	18.0
Boron	11.3	19.7
Silicon	15.9	24.3
Oxygen	16.8	25.1
Fluorine	20.9	29.3
Phosphorus and sulphur	22.6	31.0
All others	25.96	33.5

Lecture 6

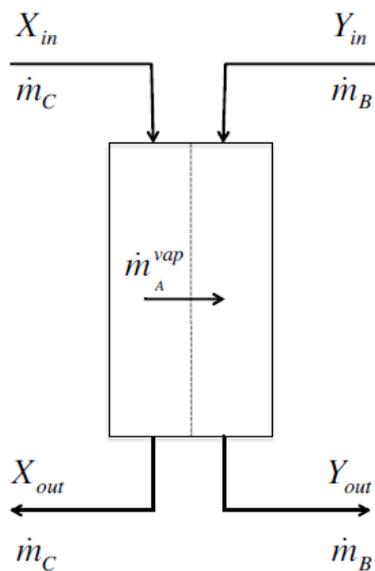
Enthalpy calculation procedures of spray dryer

3.11. Enthalpy calculation procedures of spray dryer:



Schematic diagram of spray drier

Mass and enthalpy balance



A ... solvent
B ... dry gas
C ... dry solids

assumptions:
1) non-volatile solids
2) non-condensable gas

moisture content in solids $X = \frac{m_A}{m_C}$

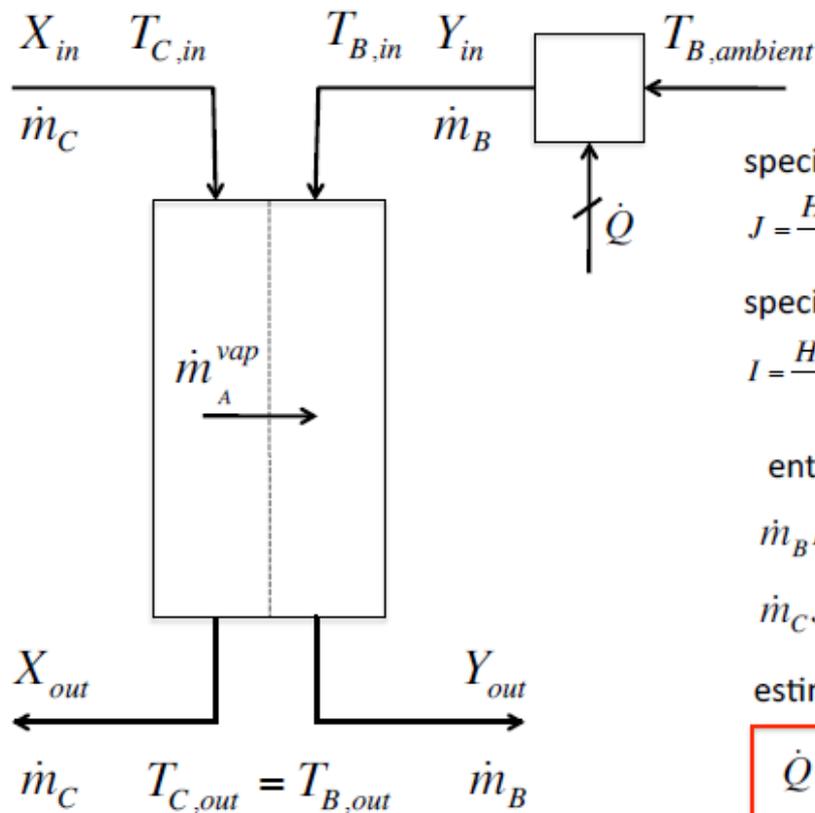
moisture content of gas $Y = \frac{m_A}{m_B}$

moisture mass balance:

$$\dot{m}_C (X_{in} - X_{out}) = \dot{m}_B (Y_{out} - Y_{in}) = \dot{m}_A^{vap}$$

⇒ evaporation rate \dot{m}_A^{vap}
⇒ gas consumption \dot{m}_B

Mass and enthalpy balance



assumption:
isenthalpic drying

specific enthalpy of wet solids

$$J = \frac{H_A + H_C}{m_C} = (Xc_{p,A} + c_{p,C})T$$

specific enthalpy of wet gas

$$I = \frac{H_A + H_B}{m_B} = (Yc_{pg,A} + c_{p,B})T + Y\Delta h_{vap,A}$$

enthalpy balances:

$$\dot{m}_B I_{in} = \dot{Q} + \dot{m}_B I_{ambient}$$

$$\dot{m}_C J_{in} + \dot{m}_B I_{in} = \dot{m}_C J_{out} + \dot{m}_B I_{out}$$

estimate of minimum heating duty

$$\dot{Q} = \dot{m}_A^{vap} \Delta h_{vap,A}$$

Lecture 7

Change in enthalpy due to temperature change

3.12.1. Some terminology related to enthalpy change:

- **Standard heat of combustion:** When the reaction under consideration is a combustion reaction, the heat of reaction is known as heat of combustion. The heat of combustion of a substance is the heat of reaction when a substance is oxidized with molecular oxygen. The standard heat of combustion at temperature T is the enthalpy change when the substance at its standard state and temperature T, undergoes combustion, yielding products also at their standard state and temperature T.
- **Standard heat of formation:** The heat released or absorbed (enthalpy change) during the formation of a pure substance from its elements, at constant pressure and usually denoted by ΔH_f .
When reactants and products are at their standard states, the heat of formation is called standard heat of formation. The enthalpy of formation of the elements is taken as zero.
- **Adiabatic reaction:** If no heat is added to the system from the surroundings or no heat is removed from the system during reaction, the reaction can be termed as an adiabatic reaction. This condition can be achieved by insulating the reaction vessel.
In the case of combustion or explosions, the heat is generated so rapidly that it is generally impossible to transfer the heat away, and as a consequence the adiabatic conditions are achieved.
- **Adiabatic reaction temperature:** When the products get heated up utilizing the heat liberated during the reaction, the temperature attained is termed the temperature of reaction. In the case of adiabatic reactions, this temperature is adiabatic reaction temperature.
- **Adiabatic flame temperature:** When a fuel is burned in air or in oxygen under adiabatic conditions the heat of reaction is the heat of combustion and the temperature attained by the system is known as adiabatic flame temperature.

Assuming that, the enthalpy of cooling the reactants from temperature T_1 to 298 K by ΔH_1 and the enthalpy of heating the products from 298 to T, the adiabatic flame temperature by ΔH_2 , we can write that,

$$\Delta H = \Delta H_1 + \Delta H_{298}^0 + \Delta H_2$$

Where, ΔH = difference between enthalpy of products and the enthalpy of the reactants

For, adiabatic reaction, $\Delta H = 0$

Therefore, $\Delta H_2 = -\Delta H_1 - \Delta H_{298}^0$

3.12.2. Kirchhoff's Law:

Kirchhoff's Law describes the enthalpy of a reaction's variation with temperature changes. In general, enthalpy of any substance increases with temperature, which means both the products and the reactants' enthalpies increase. The overall enthalpy of the reaction will change if the increase in the enthalpy of products and reactants is different.

At constant pressure, the heat capacity is equal to change in enthalpy divided by the change in temperature.

$$C_p = \Delta H / \Delta T \dots\dots\dots(i)$$

$$H_{T_f} = H_{T_i} + \int_{T_i}^{T_f} C_p dT \dots\dots\dots(ii)$$

If the heat capacity is temperature independent over the temperature range, then Equation (i) can be approximated as

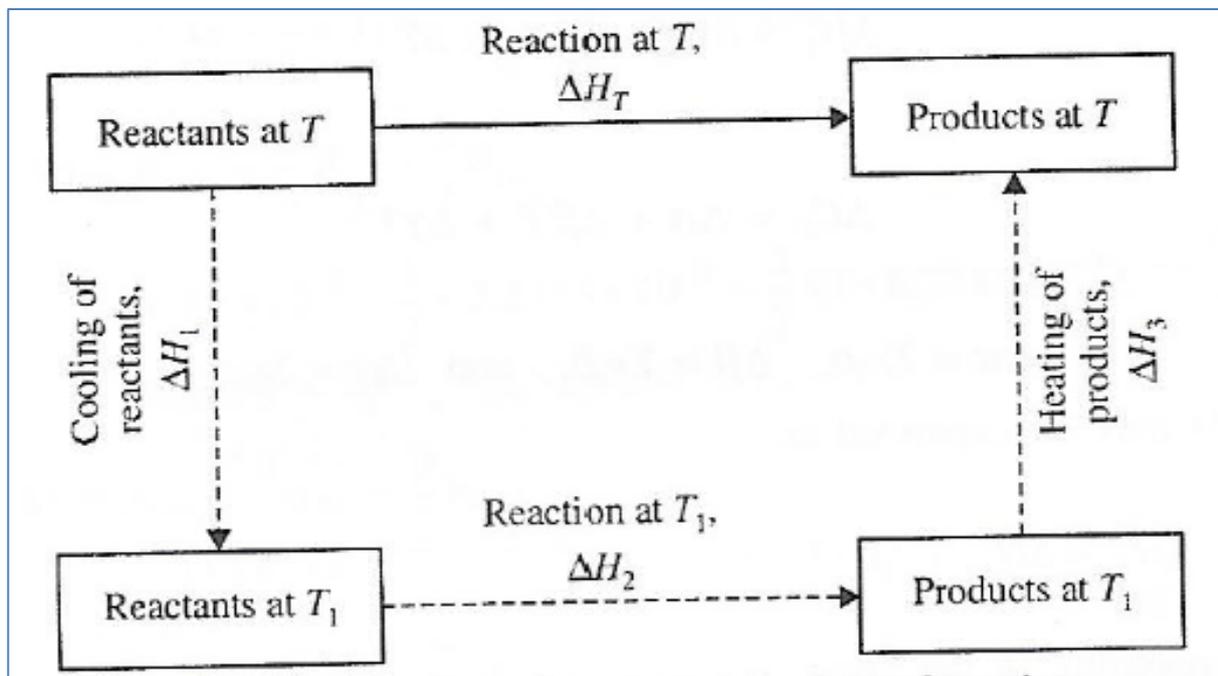
$$H_{T_f} = H_{T_i} + C_p(T_f - T_i) \dots\dots\dots(iii)$$

Where,

- C_p is the (assumed constant) heat capacity and
- H_{T_i} and H_{T_f} are the enthalpy at the respective temperatures.

Kirchhoff Law can only be applied to small temperature changes, (<100 K) because over a larger temperature change, the heat capacity is not constant. There are many biochemical applications because it allows us to predict enthalpy changes at other temperatures by using standard enthalpy data.

3.12.3. Effect of temperature on standard heat of reaction:



Consider the reaction



Here, a, b, c and d are stoichiometric coefficient.

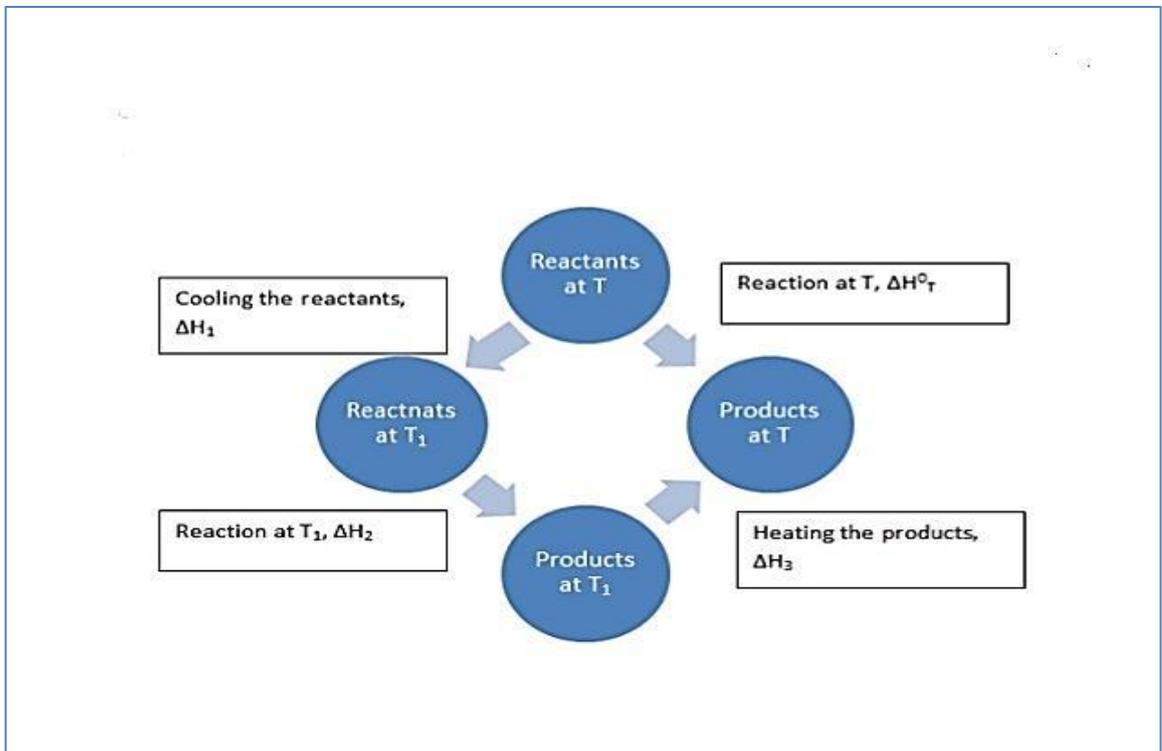
This reaction may be written as

$$cC + dD - aA - bB = 0, \text{ in which } -a, -b, c, d \text{ are called stoichiometric numbers}$$

Denoting the stoichiometric numbers of the species taking part in a chemical reaction by v_i , a chemical reaction in general may be represented by

$$\sum_i v_i A_i = 0 \dots \dots \dots (i)$$

The actual reaction occurring at temperature T, for which the standard heat of reaction is ΔH^0_T ,



The reactants are cooled from temperature T to T₁.

The enthalpy change for this step is

$$\Delta H_1 = \sum_{\text{Reactants}} \int_T^{T_1} n_i C_{p,i} dT = \sum_{\text{Reactants}} \int_T^{T_1} v_i C_{p,i} dT \dots \dots (2)$$

This reaction is allowed to occur at temperature T₁.

The enthalpy change is, $\Delta H_2 = \Delta H^0_{T_1} \dots \dots \dots (3)$

The temperature of the product is raised from T1 to T in this step.

So, the enthalpy change is

$$\Delta H_3 = \sum_{Products} \int_{T_1}^T n_i C_P, dT = \sum_{Products} \int_{T_1}^T v_i C_P, \dots \dots \dots (4)$$

The standard heat of reaction at temperature T, is obtained by adding the preceding three equations, that is

$$\Delta H^0_T = \Delta H_1 + \Delta H_2 + \Delta H_3 = \sum_{Reactants} \int_{T_1}^T v_i C_P, dT + \Delta H^0_{T_1} + \sum_{Products} \int_{T_1}^T v_i C_P,$$

The above result can be written as.

$$\Delta H^0_T = \Delta H^0_{T_1} + \int_{T_1}^T (\sum v_i C_P, i) dT \dots \dots \dots (5)$$

The summation in the above equation is overall species taking part in a reaction. Let the heat capacity of the substances be represented by following equation,

$$C_P = \alpha + \beta T + \gamma T^2 \dots \dots \dots (6)$$

Utilising equation (6), equation (5) can be written as

$$\Delta H^0_T = \Delta H^0_{T_1} + \int_{T_1}^T \Delta C_P dT \dots \dots \dots (7)$$

$$\text{Where, } \Delta C_P = \Delta \alpha + (\Delta \beta) + (\Delta \gamma)^2 \dots \dots \dots (8)$$

$$\text{And, } \Delta \alpha = \sum v_i \alpha, \Delta \beta = \sum v_i \beta, \Delta \gamma = \sum v_i \gamma \dots \dots \dots (9)$$

Equation (5) may be expanded as

$$\Delta H^0_T = \Delta H^0_{T_1} (T - T_1) + (1/2) \Delta \beta (T^2 - T_1^2) + (1/3) (\Delta \gamma) (T^3 - T_1^3) \dots \dots \dots (10)$$

The constants appearing in the above equation can be grouped together to a single constant

$\Delta H'$, so that we have,

$$\Delta H^0_T = \Delta H' + \Delta \alpha T + (\Delta \beta / 2) T^2 + \Delta \gamma / 3 T^3 \dots \dots \dots (11)$$

The constant $\Delta H'$ in the above equation can be evaluated if the heat of reaction at a single temperature is known. Equation (11) can be used for the evaluation of the standard heat of reaction at any temperature T.

Lecture 8

Energy-balance equation for cell culture and fermentation processes

3.13. Energy balance in cell culture and fermentation process:

- In fermentations, the heat of reaction so dominates the energy balance that small enthalpy effects due to sensible heat change and heats of mixing can generally be ignored.
- In this section we incorporate these observations into a simplified energy balance equation for cell processes.
- Changes in heats of mixing of input and output solutes are generally negligible.
- The overall change in enthalpy due to sensible heat is also small.
- Usually, heat of reaction, latent heat of phase change and shaft work are the only energy effects worth considering in fermentation energy balances.
- Evaporation is the most likely phase change in fermenter operation; if evaporation is controlled then latent heat effects can also be ignored.
- Per cubic meter of fermentation broth, metabolic reactions typically generate (5 – 20) kJ heat per second for growth on carbohydrate, and up to 60 kJ/s for growth on hydrocarbon substrates.
- By way of comparison, in aerobic cultures sparged with dry air, evaporation of the fermentation broth removes only about $0.5 \text{ kJ s}^{-1} \text{ m}^{-3}$ as latent heat.
- Energy input due to shaft work varies between 0.5 and $5 \text{ kJ s}^{-1} \text{ m}^{-3}$ in large-scale vessels and $10\text{-}20 \text{ kJ s}^{-1} \text{ m}^{-3}$ in small vessels.
- Sensible heats and heats of mixing are generally several orders of magnitude smaller.
- For cell processes, we can simplify energy balance calculations by substituting expressions for heat of reaction and latent heat for the first two terms of Eq. (1).

$$\sum_{\text{input streams}} (Mh) - \sum_{\text{output stream}} (Mh) - Q + W_s = 0 \dots \dots \dots (1),$$

Where M is mass and h is specific enthalpy

- ΔH_{rxn} (heat of reaction) is the difference between product and reactant enthalpies.

$$\Delta H_{\text{rxn}} = \sum_{\text{product}} (Mh) - \sum_{\text{reactant}} (Mh) \dots \dots \dots (2)$$

- As the products are contained in the output flow and the reactants in the input, ΔH_{rxn} is nearly equal to the difference in enthalpy between input and output streams.
- If evaporation is also significant, the enthalpy of vapor leaving the system will be greater than that of liquid entering by $M\Delta h$, where M is the mass of liquid evaporated and Δh is the latent heat of vaporization.
- The energy-balance equation can be modified as follows:

$$-\Delta H_{rxn} - M_v h_v - Q + W_s = 0 \dots\dots\dots(3)$$

- Eq. (5.26) applies even if some proportion of the reactants remains unconverted or if there are components in the system which do not react.
- At steady state, any material added to the system that does not participate in reaction must leave in the output stream; ignoring enthalpy effects due to change in temperature or solution and unless the material volatilizes, the enthalpy of unreacted material in the output stream must be equal to its inlet enthalpy.
- As sensible heat effects are considered negligible, the difference between ΔH°_{rxn} and ΔH_{rxn} at the reaction temperature can be ignored.
- It must be emphasised that Eq. (3) is greatly simplified and may not be applicable to single-enzyme conversions.

Lecture 1

Enthalpy of heat of mixing

4.1. Heat of mixing:

The environment of a molecule in a solution is different from that in the pure state. Since the energy of interaction between like molecules is different from that between unlike molecules, the energy of a solution is different from the sum of the energies of its constituents. This difference between the energy of the solution and the energy of the constituents leads to the absorption or evolution of heat during the mixing process. The heat of mixing (or the enthalpy change of mixing) is the enthalpy change when pure species are mixed at constant pressure and temperature to form one mole (or unit mass) of solution.

4.1.2. Enthalpy of a binary process:

For a binary mixture,

$$\Delta H = H - (x_1 H_1 - x_2 H_2) \dots \dots \dots (i)$$

Where, x_1 and x_2 are the mole fractions of components 1 and 2 in the solution.

H_1 and H_2 are enthalpies of the pure constituents.

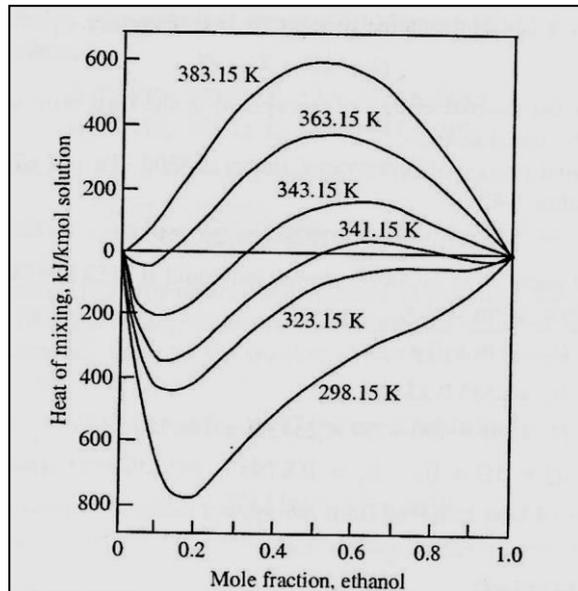
So, heat of mixing at the given concentration, the enthalpy of the solution is,

$$H = (x_1 H_1 + x_2 H_2) + \Delta H \dots \dots \dots (ii)$$

When solids or gases are dissolved in liquids, the accompanying enthalpy change is usually measured as heats of solution,

$$\Delta H_s = \frac{\Delta H}{x_1} \dots \dots \dots (iii)$$

where ΔH_s is the heat of solution per mole of solute (component 1)



Heat of mixing of ethanol in water

Problem: Caustic soda is concentrated from 10% to 50% in a single effect-evaporator. The feed at 305 K enters at a rate of 1000 kg/h. The concentrated solution leaves the evaporator at 380 K and the vapour leaves at 373.15 K. Determine the heat to be supplied in the evaporator. The mean heat capacity applicable to the solutions are 3.67 kJ/kg K for the feed and 3.34 kJ/kg K for the product. The heat of solution of 10% and 50% NaOH solution at 298 K are, respectively -42.85 kJ/mol and -25.89 kJ/mol. The latent heat of vaporization of water at 298 K is 2442.5 kJ/kg and the mean heat capacity of water vapour is 1.884 kJ/kg K.

Solution:

Basis: 1000 kg/h of 10% NaOH solution

The product is 50% NaOH solution.

Let P be the weight of the product.

$$\text{NaOH balance: } 0.5P = 0.1 \times 1000$$

Therefore, $P = 200$ kg/hr.

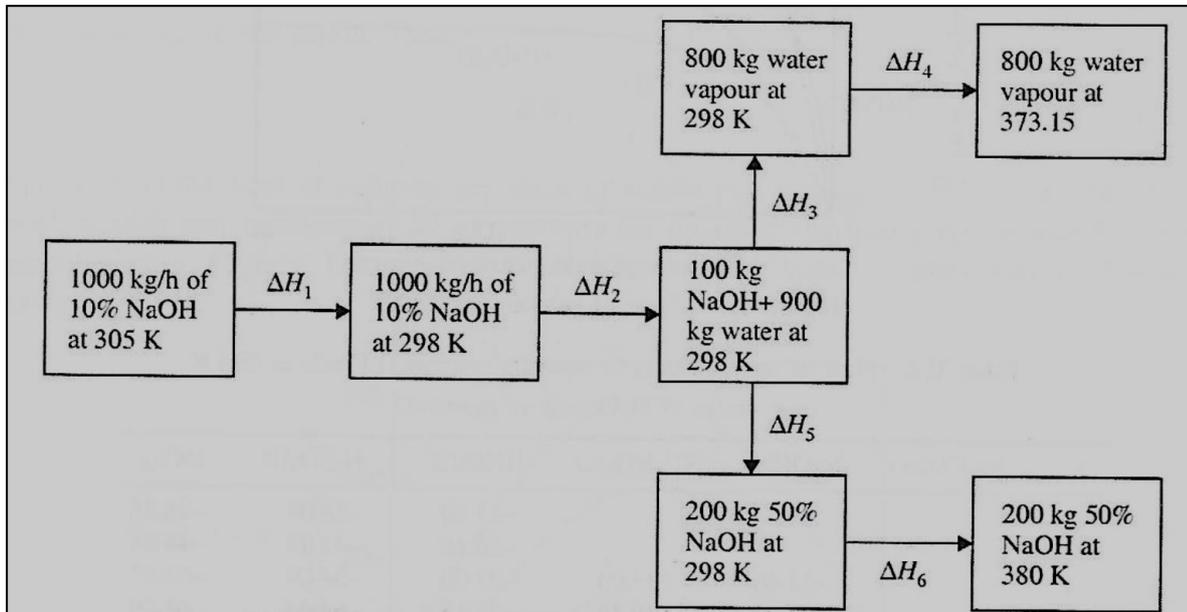
Let W be the quantity of water vaporized. Then the total material balance gives

$$1000 = P + W$$

The amount of water vaporized,

$$W = 1000 - 200 = 800 \text{ kg/h}$$

The process can be assumed to take place along the paths shown in figure below:



Step 1. Cooling 1000 kg/h of 10% solution from 305 K to 298 K.

$$\Delta H_1 = 1000 \times 3.67 \times (298 - 305) = -25\,690 \text{ kJ}$$

Step 2. Separation of the solution into the pure constituents at 298 K. The enthalpy change in this step is the negative of the heat of solution. The heat of solution is -42.85 kJ/mol . The number of moles of NaOH in the solution is

$$100/40 = 2.5 \text{ kmol} = 2500 \text{ mol}$$

$$\Delta H_2 = (-42.85 \times 2500) = 107\,125 \text{ kJ}$$

Step 3. 800 kg of water at 298 K is converted to water vapour at 298 K.

$$\Delta H_3 = 2442.5 \times 800 = 1\,954\,000 \text{ kJ}$$

Step 4. Water vapour at 298 K is heated to 373.15 K.

$$\Delta H_4 = 800 \times 1.884 \times (373.15 - 298) = 113\,266 \text{ kJ}$$

Step 5. Formation of 200 kg of 50% NaOH solution at 298 K.

$$\Delta H_5 = 2500 \times (-25.89) = 64\,725 \text{ kJ}$$

Step 6. Heating the solution from 298 K to 380 K.

$$\Delta H_6 = 200 \times 3.34 \times (380 - 298) = 54\,776 \text{ kJ}$$

The enthalpy change accompanying the complete process is,

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6$$

$$= -25\,690 + 107\,125 + 1\,954\,000 + 113\,266 - 64\,725 + 54\,776$$

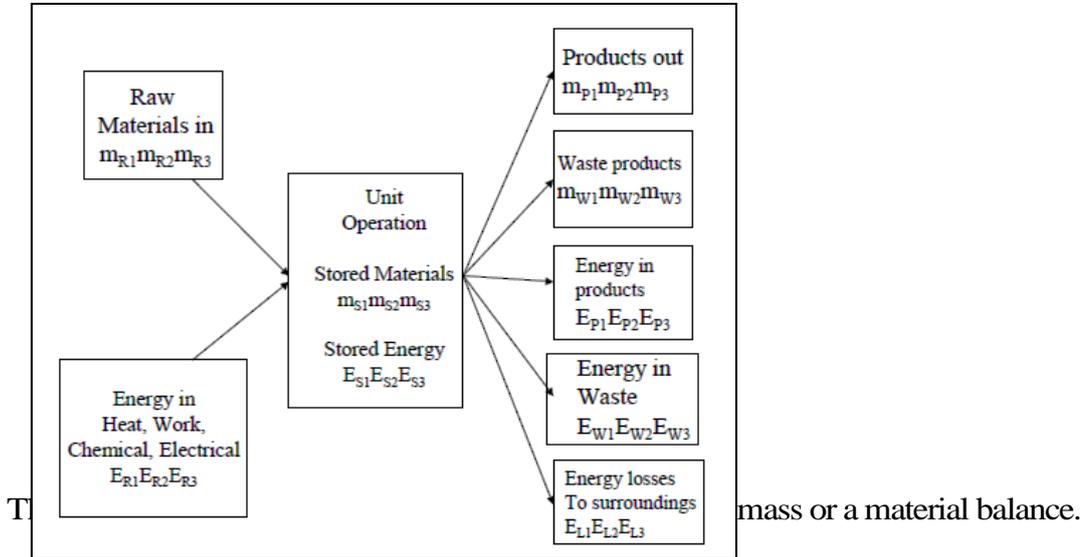
$$= 2\,138\,752 \text{ kJ}$$

Lecture 2

Materials and Energy Balance

4.2. Basic principle of material and energy balance:

If the unit operation, whatever its nature is seen as a whole it may be represented diagrammatically as a box, as shown in figure below. The mass and energy going into the box must balance with the mass and energy coming out.



$$\text{Mass In} = \text{Mass Out} + \text{Mass Stored}$$

$$\text{Raw Materials} = \text{Products} + \text{Wastes} + \text{Stored Materials.}$$

$$\sum m_R = \sum m_P + \sum m_W + \sum m_S$$

(where Σ denotes the sum of all terms).

$$\sum m_R = \sum m_{R1} + \sum m_{R2} + \sum m_{R3} = \text{Total Raw Materials}$$

$$\sum m_P = \sum m_{P1} + \sum m_{P2} + \sum m_{P3} = \text{Total Products.}$$

$$\sum m_W = \sum m_{W1} + \sum m_{W2} + \sum m_{W3} = \text{Total Waste Products}$$

$$\sum m_S = \sum m_{S1} + \sum m_{S2} + \sum m_{S3} = \text{Total Stored Products.}$$

If there are no chemical changes occurring in the plant, the law of conservation of mass will apply also to each component, so that for component A:

$$m_{A \text{ in entering materials}} = m_A \text{ in the exit materials} + m_A \text{ stored in plant.}$$

For example, in a plant that is producing sugar, if the total quantity of sugar going into the plant is not equaled by the total of the purified sugar and the sugar in the waste liquors, then there is something wrong. Sugar is either being burned (chemically changed) or accumulating in the plant or else it is going unnoticed down the drain somewhere. In this case:

$$M_A = (m_{AP} + m_{AW} + m_{AU}), \quad m_{AU} = \text{unknown loss which need to be identified}$$

Now:

$$\text{Raw Materials} = \text{Products} + \text{Waste Products} + \text{Stored Products} + \text{Losses}$$

Where, Losses are the unidentified materials.

Just as mass is conserved, so is energy conserved in food-processing operations. The energy coming into a unit operation can be balanced with the energy coming out and the energy stored.

Energy In = Energy Out + Energy Stored

$$\sum E_R = \sum E_P + \sum E_W + \sum E_L + \sum E_S$$

Where,

$$\sum E_R = E_{R1} + E_{R2} + E_{R3} + \dots = \text{Total Energy Entering}$$

$$\sum E_P = E_{P1} + E_{P2} + E_{P3} + \dots = \text{Total Energy Leaving with Products}$$

$$\sum E_W = E_{W1} + E_{W2} + E_{W3} + \dots = \text{Total Energy Leaving with Waste Materials}$$

$$\sum E_L = E_{L1} + E_{L2} + E_{L3} + \dots = \text{Total Energy Lost to Surroundings}$$

$$\sum E_S = E_{S1} + E_{S2} + E_{S3} + \dots = \text{Total Energy Stored}$$

Energy balances are often complicated because forms of energy can be interconverted, for example mechanical energy to heat energy, but overall the quantities must balance.

Lecture 3

Application of Stoichiometry: Stoichiometry of microbial growth and product formation

4.3.1. Elemental balance:

A material balance on biological reactions can easily be written when the compositions of substrates, products, and cellular material are known. Usually, electron—proton balances are required in addition to elemental balances to determine the stoichiometric coefficients in bioreactions. Accurate determination of the composition of cellular material is a major problem. A typical cellular composition can be represented as $\text{CH}_{1.8}\text{O}_{0.5}\text{N}_{0.2}$. One mole of biological material is defined as the amount containing 1 gram atom of carbon, such as $\text{CH}_{\alpha}\text{O}_{\beta}\text{N}_{\delta}$.

4.3.2. Degree of reduction:

In more complex reactions, as in the formation of extracellular products, an additional stoichiometric coefficient is added, requiring more information. Also, elemental balances provide no insight into the energetics of a reaction. Consequently, the concept of degree of reduction has been developed and used for proton—electron balances in bioreactors. The degree of reduction, γ , for organic compounds may be defined as the number of equivalents of available electrons per gram atom C. The available electrons are those that would be transferred to oxygen upon oxidation of a compound to CO_2 , H_2O , and NH_3 . The degrees of reduction for some key elements are C = 4, H = 1, N = -3, O = -2, P = 5, and S = 6. The degree of reduction of any element in a compound is equal to the valence of this element. For example, 4 is the valence of carbon in CO_2 and -3 is the valence of N in NH_3 .

$$\text{Methane (CH}_4\text{): } 1(4)+4(1)= 8, \gamma= 8/1 = 8$$

$$\text{Glucose (C}_6\text{H}_{12}\text{O}_6\text{): } 6(4) + 12(1) + 6(-2) = 24, \gamma = 24/6 = 4$$

$$\text{Ethanol (C}_2\text{H}_5\text{OH): } 2(4) + 6(1) + 1(-2) = 12, \gamma= 12/2 = 6$$

A high degree of reduction indicates a low degree of oxidation.

Considering the aerobic production of a single extracellular product,



Where CH_mO_n represents 1 mole of carbohydrate and $\text{CH}_{\alpha}\text{O}_{\beta}\text{N}_{\delta}$ stands for 1 mole of cellular material. Simple elemental balances on C, H, O, and N yield the following equations:

$$\text{C: } 1=c+e$$

$$\text{H: } m+3b = c\alpha + 2d$$

$$\text{O: } n+2a=c\beta+d+2e \quad \text{(ii)}$$

$$\text{N: } b = c\delta$$

The respiratory quotient (RQ) is

$$\text{RQ} = e/a \quad \text{(iii)}$$

Equations ii and iii constitute five equations for five unknowns a , b , c , d , and e . With a measured value of RQ, these equations can be solved to determine the stoichiometric coefficients.

$$\gamma_b = 4 + \alpha - 2\beta - 3\delta \dots \dots \dots (iv)$$

$$\gamma_p = 4 + x - 2y - 3z \dots \dots \dots (v)$$

(For CO₂, H₂O, and NH₃ the degree of reduction is zero.)

Equation (ii) can lead to elemental balances on C, H, O, and N, an available electron balance, an energy balance, and a total mass balance. Of the equations, only five will be independent. If all the equations are written, then the extra equations can be used to check the consistency of an experimental data set. Because the amount of water formed or used in such reactions is difficult to determine and water is present in great excess, the hydrogen and oxygen and oxygen balances are difficult to use. For such a data set, we would typically choose a carbon, a nitrogen, and an available-electron balance. Thus,

$$c + d + f = 1 \dots \dots \dots (vi)$$

$$c\delta + dz = b \dots \dots \dots (vii)$$

$$c\gamma_b + d\gamma_p = \gamma_s - 4a \dots \dots \dots (viii)$$

With partial experimental data, it is possible to solve this set of equation. Measurement of RQ and a yield coefficient would, for example, allow the calculation of the remaining coefficients. It should be noted that the coefficient, c , is $Y_{x/S}$ (on a molar basis) and d is $Y_{p/S}$ (also on a molar basis).

An energy balance for aerobic growth is

$$Q_0 c \gamma_b + Q_0 d \gamma_p = Q_0 \gamma_s - Q_0 4a \dots \dots \dots (ix)$$

If Q_0 , the heat evolved per equivalent of available electrons transferred to oxygen, is constant in equation (ix) is not independent of eq. (viii). Recall that an observed regularity is 26.95 Kcal/gmequivalent of available electrons transferred to oxygen, which allows the prediction of heat evolution based on estimates of oxygen consumption.

Equations (viii) and (ix) also allow estimates of the fractional allocation of available electrons or energy for an organic substrate. Equation (viii) can be rewritten as

$$1 = c \gamma_b / \gamma_s + d \gamma_p / \gamma_s + 4a / \gamma_s \dots \dots \dots (xa)$$

$$1 = \xi_b + \xi_p + \epsilon \dots \dots \dots (xb)$$

Where,

ϵ = the fraction of available electrons in the organic substrate that is transferred to oxygen

ξ_b = the fraction of available electrons that is incorporated into biomass,

ξ_p = fraction of available electrons that is incorporated into extracellular products.

Lecture 4

Problem related to stoichiometry of microbial growth and product formation

4.3.3. Problem: Assume that experimental measurements for a certain organism have shown that cells can convert two-thirds (wt/wt) of the substrate carbon (alkane or glucose) to biomass.

a) Calculate the stoichiometric coefficients for the following biological reactions:



b) Calculate the yield coefficients $Y_{x/s}$ (g dw cell/g substrate), Y_{x/O_2} (g dw cell/g O_2) for both reactions. Comment on the differences.

Solution:

a) For hexadecane,

amount of carbon in 1 mole of substrate = $16(12) = 192$ g amount of carbon

converted to biomass = $192(2/3) = 128$ g

Then, $128 = c(4.4)(12)$; $c = 2.42$

Amount of carbon converted to $CO_2 = 192 - 128 = 64$ g

$$64 = e(12), \quad e = 5.33$$

The nitrogen balance yields

$$14b = c(0.86)(14)$$

$$b = (2.42)(0.86) = 2.085$$

The hydrogen balance is

$$34(1) + 3b = 7.3c + 2d$$

$$d = 12.43$$

The oxygen balance yields

$$2a(16) = 1.2c(16) + 2e(16) + d(16)$$

$$a = 12.427$$

For glucose.

amount of carbon in 1 mole of substrate = 72 g

amount of carbon converted to biomass = $72(2/3) = 48$ g

Then, $48 = 4.4c(12)$; $c = 0.909$.

The amount of carbon converted to $CO_2 = 72 - 48 = 24$ g

$$24 = 12e; \quad e = 2$$

The nitrogen balance yields

$$14b = 0.86c(14)$$

$$b = 0.782$$

The hydrogen balance is

$$12 + 3b = 7.3c + 2d$$

$$d = 3.854$$

The oxygen balance yields

$$6(16) + 2(16)a = 1.2(16)c + 2(16)e + 16d$$

$$a = 1.473$$

b) For hexadecane,

$$Y_{X/S} = \frac{2.42(\text{MW})_{\text{biomass}}}{(\text{MW})_{\text{substrate}}}$$

$$Y_{X/S} = \frac{2.42(91.34)}{226} = 0.98 \text{ gdw cells/g substrate}$$

$$Y_{X/O_2} = \frac{2.42(\text{MW})_{\text{biomass}}}{12.43(\text{MW})_{O_2}}$$

$$Y_{X/O_2} = \frac{2.42(91.34)}{(12.43)(32)} = 0.557 \text{ gdw cells/g } O_2$$

For glucose,

$$Y_{X/S} = \frac{(0.909)(91.34)}{180} = 0.461 \text{ gdw cells/g substrate}$$

$$Y_{X/O_2} = \frac{(0.909)(91.34)}{(1.473)(32)} = 1.76 \text{ gdw cells/g } O_2$$

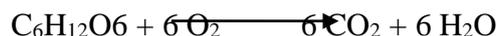
The growth yield on more reduced substrate (hexadecane) is higher than that on partially oxidized substrate (glucose), assuming that two-thirds of all the entering carbon is incorporated in cellular structures. However, the oxygen yield on glucose is higher than that on the hexadecane, since glucose is partially oxidized.

Lecture 5

Theoretical prediction of yield coefficient

4.3.4. Theoretical prediction of yield coefficient:

In aerobic fermentations, the growth yield per available electron in oxygen molecules is approximately 3.14 ± 0.11 gdw cells/electron when ammonia is used as the nitrogen source. The number of available electrons per oxygen molecule (O_2) is four. When the number of oxygen molecules per mole of substrate consumed is known, the growth yield coefficient, $Y_{x/s}$, can easily be calculated. Consider the aerobic catabolism of glucose.



The total number of available electrons in 1 mole of glucose is 24. The cellular yield per available electron is $Y_{x/s} = 24(3.14) = 76$ gdw cells/mol.

The predicted growth yield coefficient is $Y_{x/s} = 76/180 = 0.4$ gdw cells/g glucose.

Most measured values of $Y_{x/s}$ for aerobic growth on glucose are 0.38 to 0.51 g/g .

The ATP yield ($Y_{x/ATP}$) in many anaerobic fermentations is approximately 10.5 ± 2 gdw cells/mol ATP. In aerobic fermentations, this yield varies between 6 and 29. When the energy yield of a metabolic pathway is known (N moles of ATP produced per gram of substrate consumed), the growth yield $Y_{x/s}$ can be calculated using the following equation:

$$Y_{x/s} = Y_{x/ATP} N$$

Problem: Estimate the theoretical growth and product yield coefficients for ethanol fermentation by *S. cerevisiae* as described by the following overall reaction:



Solution:

Since, $Y_{x/ATP} \approx 10.5$ gdw/mol ATP and since glycolysis yields 2 ATP/mol of glucose in yeast,

$$Y_{x/s} \approx 10.5 \text{gdw/mol ATP} * 2 \text{ moles ATP/ 180 gm glucose}$$

Or,

$$Y_{x/s} \approx 0.117 \text{ gdw/g glucose}$$

For complete conversion of glucose to ethanol by the yeast pathway, the maximal yield would be

$$Y_{p/s} = 2 (46)/180 = 0.51 \text{ gm ethanol/ gm glucose}$$

While, for CO_2 the maximum yield is

$$Y_{CO_2/s} = 2(44/180) = 0.49 \text{ g ethanol /g glucose}$$

In practice, these maximal yields are not obtained. The product yields are about 90% to 95%

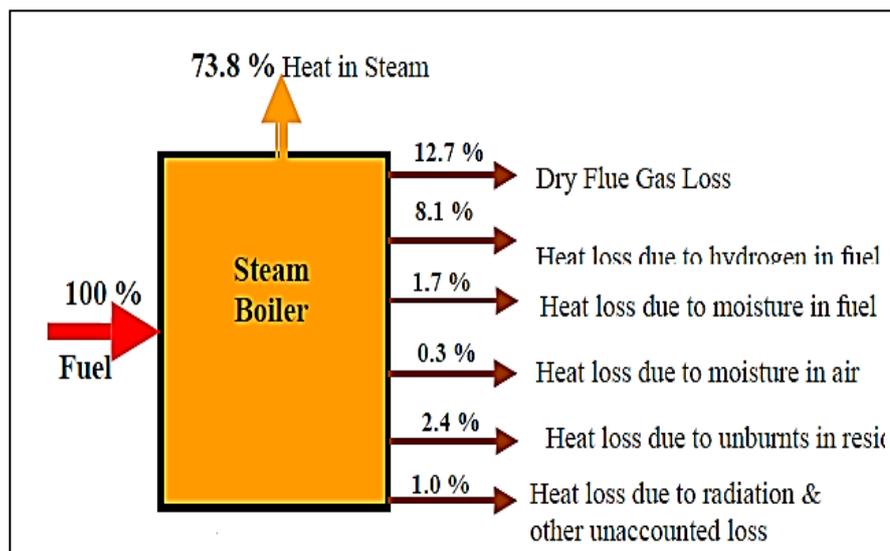
of the maximal values, because the glucose is converted into biomass and other metabolic by-products (e.g., glycerol or acetate).

Lecture 6

Applications of Mass and Energy Balance

4.4.1. Heat Balance in a Boiler:

A heat balance is an attempt to balance the total energy entering a system (e.g boiler) against that leaving the system in different forms. The following figure illustrates the heat balance and different losses occurring while generating steam.



4.4.2. Problem related to refrigeration load:

Problem: It is desired to freeze 10,000 loaves of bread each weighing 0.75 kg from an initial room temperature of 18°C to a final temperature of -18°C. The bread-freezing operation is to be carried out in an air-blast freezing tunnel. It is found that the fan motors are rated at a total of 80 horsepower and measurements suggest that they are operating at around 90% of their rating, under which conditions their manufacturer's data claims a motor efficiency of 86%. If 1 ton of refrigeration is 3.52 kW, estimate the maximum refrigeration load imposed by this freezing installation assuming (a) that fans and motors are all within the freezing tunnel insulation and (b) the fans but not their motors are in the tunnel. The heat-loss rate from the tunnel to the ambient air has been found to be 6.3 kW.

Solution:Extraction rate from freezing bread (maximum)= 104 kW

Fan rated horsepower = 80

Now, 0.746 kW = 1 horsepower and the motor is operating at 90% of rating,

And so (fan + motor) power = $(80 \times 0.9) \times 0.746 = 53.7$ kW

(a) With motors + fans in tunnel

Heat load from fans + motors = 53.7 kW

Heat load from ambient = 6.3 kW

Total heat load = $(104 + 53.7 + 6.3)$ kW = 164 kW
= 46 tons of refrigeration

(b) With motors outside, the motor inefficiency = $(1 - 0.86)$ does not impose a load on the refrigeration

Total heat load= $(104 + [0.86 \times 53.7] + 6.3)$
= 156 kW
= 44.5 tons of refrigeration

In practice, material and energy balances are often combined as the same stoichiometric information is needed for both.

Lecture 7

Problems Related Industrial Stoichiometry

4.5.1. Problem: Ammonia is produced by the following reaction :



In a commercial process for ammonia production, the feed to an adiabatic reactor contains 1 kmol/s of nitrogen and stoichiometric amounts of hydrogen at 700 K. What is the maximum allowable conversion in the reactor, if the adiabatic temperature rise across the reactor should not exceed 100 K.

Assume the feed and product streams to be ideal gas mixtures. The heat of reaction at 700 K for the above reaction is calculated to be -94.2 kJ/mol. The mean molar heat capacities in the range of 700-800 K are 0.03, 0.0289, and 0.0492 kJ/mol K for nitrogen, hydrogen and ammonia, respectively.

Solution:

Basis: Feed consisting of 1 kmol/s nitrogen and 3 kmol/s hydrogen

Let, x be the fraction of nitrogen converted. Since the heat of reaction at 700 K is 94.2 kJ/mol, the heat liberated by the reaction is $-94.2 \times 10^3 x$ kJ. The product stream consists of $2x$ kmol NH_3 , $(1 - x)$ kmol N_2 , and $3(1 - x)$ kmol hydrogen. When the temperature of the product stream rises by 100 K, the heat utilized is

$$(1 - x) \times 0.03 \times 10^3 \times 100 + 3(1 - x) \times 0.0289 \times 10^3 \times 100 + 2x \times 0.0492 \times 10^3 \times 100 \text{ kJ} \\ = 11.67 \times 10^3 - 1.83 \times 10^3 x \text{ kJ}$$

Since, the reaction is adiabatic, the only heat available for raising the temperature of the products is the heat liberated by the reaction which is $94.2 \times 10^3 x$ kJ. Therefore,

$$11.67 \times 10^3 - 1.83 \times 10^3 x = 94.2 \times 10^3 x$$

On solving this equation, we get $x = 0.1215$. It means that the maximum conversion for nitrogen should be 12.15 % if the temperature rise permitted is 100 K.

4.5.2. Problem: Hydrogen gas is burned in an adiabatic reactor with two times the theoretical quantity of air, both air and hydrogen being at 298 K initially. What will be the temperature of the reaction products? The standard heat of formation of gaseous water is -241.826 kJ/mol. The heat capacities (kJ/kmol K) of the gases are given below:

Water vapour: $C_p = 30.475 + 9.652 \times 10^{-3}T + 1.189 \times 10^{-6}T^2$

Nitrogen: $C_p = 27.034 + 5.815 \times 10^{-3}T - 0.2889 \times 10^{-6}T^2$

Oxygen: $C_p = 25.611 + 13.260 \times 10^{-3}T - 4.2077 \times 10^{-6}T^2$

Solution:

Basis: 1 kmol hydrogen burned. The theoretical requirement of oxygen is 0.5 kmol.

The amount of oxygen supplied = $2 \times 0.5 = 1$ mol

The amount of air supplied = $1 \times 100/21 = 4.762$ kmol

The amount of nitrogen in the air supplied = $4.762 - 1 = 3.762$ kmol

Reactants: Hydrogen = 1 kmol, Air = 4.762 kmol

Products: Water vapour = 1 kmol, Oxygen = $1 - 0.5 = 0.5$ kmol, Nitrogen = 3.762 kmol

Let T be the temperature attained.

$$\begin{aligned} \text{Then } \Delta H_2 &= \int_{298}^T \left[\begin{aligned} &1 \times (30.475 + 9.652 \times 10^{-3}T + 1.189 \times 10^{-6}T^2) \\ &+ 0.5 \times (27.034 + 5.815 \times 10^{-3}T - 0.2889 \times 10^{-6}T^2) \\ &+ 3.762 \times (25.611 + 13.260 \times 10^{-3}T - 4.2077 \times 10^{-6}T^2) \end{aligned} \right] dT \\ &= \int_{298}^T (140.34 + 62.444 \times 10^{-3}T - 14.785 \times 10^{-6}T^2) dT \\ &= 140.34(T - 298) + \frac{62.444 \times 10^{-3}}{2} (T^2 - 298^2) - \frac{14.785 \times 10^{-6}}{3} (T^3 - 298^3) \\ &= 140.34T + 31.222 \times 10^{-3}T^2 - 4.928 \times 10^{-6}T^3 - 44\,463.54 \text{ kJ} \end{aligned}$$

The standard heat of reaction at 298 K, $\Delta H^0_{298} = -241.826 \times 10^3$ kJ

Therefore,

$$\Delta H_2 = -\Delta H_1 - \Delta H^0_{298}$$

Since, $\Delta H_1 = 0$,

We have

$$140.34T + 31.222 \times 10^{-3}T^2 - 4.928 \times 10^{-6}T^3 - 44\,463.54 = 241.826 \times 10^3 \text{ kJ}$$

On solving this equation, we get $T = 1609.8$ K.

Lecture 8

Problems Related Industrial Stoichiometry: Problems Related Flue Gas

4.5.3. Problem:

The composition of a sample of bituminous coal by weight is found to be 75% C, 5% H₂, 12% O₂, 3% N₂, 1% S and 4% ash. Calculate (i) the minimum volume of air at N.T.P. necessary for the complete combustion of 1 kg of the coal and (ii) the composition of the dry flue gases, by volume, if 20% excess air be supplied.

Solution:

Basis: 1 kg of coal

		Weight of element, kg	Weight of O ₂ needed, kg	Weight of dry flue gas, kg
C	—	0.75	$0.75(32/12) = 2.0$	$0.75(44/12) = 2.75(\text{CO}_2)$
H ₂	—	0.05	$0.05(16/2) = 0.4$	—
O ₂	—	0.12	—	—
N ₂	—	0.03	—	0.03 + that from air (N ₂)
S	—	0.01	$0.01(32/32) = 0.01$	$0.01(64/32) = 0.02(\text{SO}_2)$
Ash	—	0.04	—	—
Total	—	1.00	2.41	2.80 + N₂ from air

Assume that air contains 23% O₂, and 77% N₂ by weight and has a molecular weight of 28.8 a.m.u.

Weight of O₂ to be supplied

= Weight of O₂ needed for combustion – weight of O₂ present in coal

= $2.41 - 0.12 = 2.29$ kg

Weight of air needed for combustion = $2.29/0.23 = 9.96$ kg

Since, 22.4 m³ of air at N.T.P. weighs 28.8 kg, the minimum volume of air at N.T.P.

Necessary for the complete combustion of 1 kg of coal = $(22.4/28.8)9.96 = 7.75$ m³.

As 20% excess air is supplied, the weight of air supplied = $1.20(9.96) = 11.95$ kg

Weight of N₂ supplied with air = $11.95(0.77) = 9.20$ kg

Weight of N₂ present in coal = 0.03 kg

Total weight of N₂ present in flue gas = 9.23 kg

Weight of O₂ present in flue gas (due to excess air)

= $11.95(0.23) - 2.29 = 0.46$ kg

Weights of the various constituents of the dry flue gas are,

CO₂ = 2.75 kg

SO₂ = 0.02 kg

N₂ = 9.23 kg

O₂ = 0.46 kg

Moles of the gases present in the flue gas are

CO₂ : $2.75/44 = 0.0625$

$$\text{SO}_2 : 0.02/64 = 0.0003$$

$$\text{N}_2 : 9.23/28 = 0.3296$$

$$\text{O}_2 : 0.46/32 = 0.0144$$

$$\text{Total} = 0.4068$$

Mole-fractions of the gases present are:

$$\text{CO}_2 : 0.1536; \quad \text{SO}_2 : 0.0007; \quad \text{N}_2 : 0.8102; \quad \text{O}_2 : 0.0354$$

Composition of the dry flue gases by volume is:

$$\text{CO}_2 : 15.36\%; \quad \text{SO}_2 : 0.07\%; \quad \text{N}_2 : 81.02\%; \quad \text{O}_2 : 3.54\%$$

4.5.3. Problem:

A sample of coal has 80% C, 5% H₂, 0.5% S, and 14.5% ash. Calculate theoretical quantity of air necessary for the combustion of 1 kg of coal. Find the composition of the flue gas by weight and by volume if 25% excess air is supplied.

Solution:

Basis: 1 kg of coal

<i>Constituent (kg)</i>	<i>Oxygen needed (kg)</i>	<i>Flue gas (kg)</i>
C = 0.80	0.80(32/12) = 2.133	CO ₂ = 0.8 (44/12) = 2.93
H ₂ = 0.05	0.05 (16/2) = 0.4	H ₂ O = 0.05 (18/2) = 0.45
S = 0.005	0.005 (32/32) = 0.005	SO ₂ = 0.005 (64/32) = 0.01
Ash = 0.145	O ₂ from excess air
		N ₂ from air

$$\text{Weight of O}_2 \text{ to be supplied} = 2.538 \text{ kg}$$

$$\text{Weight of air needed for combustion} = 2.538 (100/23) = 11.04 \text{ kg}$$

$$\text{As 25\% excess air is supplied, its weight} = 1.25(11.04) = 13.8 \text{ kg}$$

The flue gas contains:

$$\text{N}_2 = 13.8 (0.77) = 10.63 \text{ kg} = 0.380 \text{ kmol}$$

$$\text{O}_2 = (13.8 - 11.04) (0.23) = 0.64 \text{ kg} = 0.020 \text{ kmol}$$

$$\text{CO}_2 = 2.93 \text{ kg} = 0.067 \text{ kmol}$$

$$\text{H}_2\text{O} = 0.45 \text{ kg} = 0.025 \text{ kmol}$$

$$\text{SO}_2 = 0.01 \text{ kg} = 0.00016 \text{ kmol}$$

$$\text{Total} = 14.66 \text{ kg} = 0.49216 \text{ kmol}$$

Percentages by weight of the gases present in flue gas

$$\text{N}_2 : (10.63/14.66) 100 = 72.51\%$$

$$\text{O}_2 : (0.64/ 14.66) 100 = 4.37\%$$

$$\text{CO}_2: (2.93/14.66) 100 = 19.99\%$$

$$\text{H}_2\text{O} : (0.45/14.66) 100 = 3.07\%$$

$$\text{SO}_2 : (0.01/14.66)100 = 0.07\%$$

Percentages by volume of the gases present in flue gas:

$$\text{N}_2 : (0.380/0.49126)100 = 77.21\%$$

$$\text{O}_2 : (0.020/0.49126) 100= 4.06\%$$

$$\text{CO}_2 : (0.067/0.49126) 100 = 13.61\%$$

$$\text{H}_2\text{O} = (0.025/0.49216)100 = 5.08\%$$

$$\text{SO}_2= (0.00016/0.49216)100 = 0.03\%$$

Question Bank

Multiple Choice Question (MCQ)

1. Choose the correct alternative of the following (Any ten)

(i) An aqueous solution contains 19% NH_3 , 65.6% NH_4NO_3 and 6.0% urea (by mass). The available nitrogen content in solution will be

(a) 4.141%; (b) .41415; (c) 41.41 %; (d) none of these

(ii) The number of atoms of oxygen present in 500gm oxygen is

(a) 9.41×10^{23} ; (b) $.941 \times 10^{23}$; (c) 94.10×10^{23} ; (d) 941×10^{23}

(iii) The Molal Humidity to Absolute Humidity conversion factor is - (a) 0.72; (b) 0.52; (c) 0.62; (d) 0.064.

(iv) Slope of straight line in the Semi log Plot can be expressed as

(a) $(Y_2 - Y_1) / (\log X_2 - \log X_1)$; (b) $(\log Y_2 - \log Y_1) / (X_2 - X_1)$; (c) $(Y_2 - Y_1) / (X_2 - X_1)$; (d) None of these

(v) By Passing of stream (fluid) is applied to (a) Packed Tower; (b) Humidifier ; (c) Air conditioner; (d) None of these.

(vi) Graphical integration is more accurate when using - (a) Rectangular rule; (b) Trapezoidal rule; (c) Simpson's rule; (d) None of these.

(vii) Standard enthalpy of reaction is measured at - (a) 303°K and 10KPa; (b) 303°K and 100 KPa; (c) 298°K and 1atm; (d) all of these.

(viii) Specific heat of water is

(a) 2093.4J/kg.k, (b) 4186.8J/kg.k, (c) 1J/kg.k, (d) 0.5J/Kg.k

(ix) In steady state process (a) Input > Output ; (b) Input < Output ; (c) Input=Output;

(d) Input \leq Output

(x) Froude Number is the ratio of

(a) Inertial force to viscous force; (b) Pressure force to inertia force; (c) inertial force to surface tension force; (d) inertial force to gravitational force

(xi) Growth Stoichiometry of a microbial cell mass depends upon stoichiometric balances of (a) Carbon, (b) Hydrogen, (c) Nitrogen and Oxygen, (d) All of these

(xii) The volumetric flow rate of kerosene in a cylindrical pipe is 75 gallon/minute where the density of kerosene is 0.8 kg/dm^3 . The mass flow rate of kerosene is 45.46kg/s ; (b) 4.546kg/s ; (c) 454.6kg/s; (d) .4546kg/s

(xiii) Standard enthalpy of reaction is measured at - (a) 303°K and 10KPa; (b) 303°K and 100 KPa; (c) 298°K and 1atm; (d) all of these.

(ii) Specific heat of water is

(a) 2093.4J/kg.k, (b) 4186.8J/kg.k, (c) 1J/kg.k, (d) 0.5J/Kg.k

(xiv) Among the following processes, which is not energy intensive?

(a) Physical process (b) Chemical process (c) Biological process (d) Adiabatic process

(iv) Energy transferred as a result of any driving force other than temperature difference is

(a) Internal energy (b) Kinetic energy (c) Potential energy (d) Work

(xv) Which of the following is not a reason of occurrence of change in enthalpy?

(a) Temperature change (b) Change of phase (c) Mixing or solution (d) None

(xvi) The property of solution components dependant on temperature and concentration of mixture is

- (a) Heat of reaction (b) latent heat of sublimation(c) heat of mixing (d) heat of combustion
 (xvii) Which of the following is a state function?
 (a) Temperature (b) pressure(c) density (d) enthalpy

Short Question (SQ)

2. The equation for heat transfer to or from a stream of gas flowing in turbulent motion is as follows

$$h = \frac{16.6 \text{ CpG}^{0.8}}{D^{0.2}}$$

Where Cp in BTU/lb⁰F; D in inch and G in lb/sec.ft². Find an equivalent expression in S.I system. 5

3. How Triangular diagram is utilized in liq-liq extraction process? Differentiate between Graphical differentiation and Graphical Integration Process. 3+2=5

4. If 35000 kg of whole milk containing 4% fat is to be separated in a 6 hour period into skim milk with 0.45% fat and cream with 45% fat, what are the flow rates of the two output streams from a continuous centrifuge which accomplishes this separation? 5

5. In a textile mill a double effect evaporator system concentrates weak liquor containing 4 % (by mass) caustic soda to produce a lye containing 25% solid (by mass). Calculate the evaporation of water per 100kg feed in the evaporator. 5

6. A drier is feed with raw cabbage to reduce the moisture content from 80% to 15%.the product leaving the drier is entered to an oven which further brings down the moisture to 2%. If the drier can handle 1000kg of raw cabbage per day, calculate (a) the weight of dried cabbage leaving the drier and oven per day; (b) the percentage of the original water that is removed in the drier and the oven. 5

7. Dry neem leaves were subjected to extraction with supercritical carbondioxide at 200 bar and 60⁰C (333k). Dry leaves are analyzed to contain 0.46% α-tocopherol and 0.01% β-carotene. The extract is found to contain 15.5% α-tocopherol and 0.41% β-carotene. All percentages are by mass. If β-carotene content of the leached residue is nil, calculate (a) by mass of extract phase per kg of dry leaves and (b) % recovery of α-tocopherol. 5

8.The frictional pressure drop(ΔP) for the flow of a fluid through a long straight round pipe depends upon the length(l), diameter(d) , the average fluid velocity(u), the density(ρ) and the viscosity(μ) of the fluid. Use the Buckingham pi method to make a dimensional analysis of the system. 5

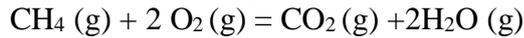
9. What is sensible heat and what is latent heat? What do you mean by energy balance? 2+2+1=5

10. When 16 gm of CuSO_4 were dissolved in 384 gm of water, the temperature rose by 3.95°C . Determine the enthalpy of formation of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ from anhydrous salt and water, if the enthalpy of solution of the crystal hydrate is 11.7 kJ/mol . And the specific heat of the solution is 4.18 kJ/(kg.K) . 5

11. A sample of dry flue gas has the following composition by volume : CO_2 13.4%; N_2 80.5% and O_2 6.1%. Calculate the excess air supplied. 5

12. What is enthalpy?

Calculate the change in enthalpy Δ for the reaction



The enthalpies of formation are:

$\text{CH}_4 (\text{g})$	-74.9 kJ/mol
$\text{CO}_2 (\text{g})$	-393.5 kJ/mol
$\text{H}_2\text{O} (\text{l})$	-241.8 kJ/mol

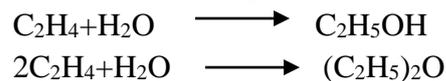
5

13. What do you understand by adiabatic reaction, adiabatic reaction temperature, and adiabatic flame temperature? 2+1+2=5

Long answer type questions (LQ)

14. (a) Define Limiting reactant, excess reactant, conversion, selectivity and yield of a chemical process.

(b) In the vapor phase hydration of ethylene to ethanol, diethyl ether is obtained as a byproduct represented by the following chemical reaction



A feed mixture consisting of 60% C_2H_4 , 3% inerts and 37% H_2O is sent to the reactor. The products analyzed as 53.89% C_2H_4 , 14.37% $\text{C}_2\text{H}_5\text{OH}$, 1.80 % $(\text{C}_2\text{H}_5)_2\text{O}$, 26.35% H_2O and 3.59% inerts. Calculate the conversion of C_2H_4 , yield of $\text{C}_2\text{H}_5\text{OH}$ and $(\text{C}_2\text{H}_5)_2\text{O}$ based on C_2H_4 . 5+10

15. (a) The spent acid from a Nitrating process containing 35% H_2SO_4 , 35% HNO_3 , and 30% H_2O by weight. This acid is to be strengthened by the addition of conc. H_2SO_4 containing 95% H_2SO_4 and conc. HNO_3 containing 76% HNO_3 . The strengthened mixed acid is to contain 40% H_2SO_4 and 42% HNO_3 . Calculate the quantity of spent acid and the concentrated acids that should be mixed together to yield 1000kg of the desired mixed acid.

(b) Estimate the consumption of 96% NaCl and 93% H_2SO_4 for the Production of 600kg HCl if the conversion is 95%. Also calculate the amount of Na_2SO_4 Produced during the Process. HCl is produced according to the reaction.

$2\text{NaCl} + \text{H}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + 2\text{HCl}$. Molecular weight of NaCl , H_2SO_4 , Na_2SO_4 and HCl are 58.5, 98, 142 and 36.5 respectively. 5+10

16. (a) A solution of $K_2Cr_2O_7$ in water contains 15% $K_2Cr_2O_7$ by weight. 1000kg of this solution is evaporated to remove some amount of water. The remaining solution is cooled to $20^\circ C$. If the yield of crystal is 80%, calculate the amount of water evaporated. Solubility of $K_2Cr_2O_7$ at $20^\circ C$ is 114.7 kg per 1000kg of water.

(b) HNO_3 is produced by treating $NaNO_3$ with 95% H_2SO_4 . The resulting nitre cake contains 34% H_2SO_4 and 1.5% H_2O . 2% of the HNO_3 formed remains in the cake. The reaction is complete. Calculate the following:

(i) The weight of nitre cake per 100kg of $NaNO_3$

(ii) The composition of nitre cake

(iii) The weight of aqueous H_2SO_4 used

(iv) The weight of HNO_3 and H_2O distilled from the nitre cake for 100 kg of $NaNO_3$

7+8

17. (a) A mixture of acetone vapour and nitrogen gas at 101.3kPa and 295 K contains acetone vapour to the extent that it exerts a partial pressure of 15kPa. The vapour pressure of acetone at 295K is 26.36 kPa. Determine the following:

(i) The weight fraction of acetone in the mixture

(ii) The absolute humidity

(iii) The molal humidity

(iv) The molal saturation humidity

(v) The absolute saturation humidity

(b) An aqueous solution of methanol containing 20% (weight) methanol is to be separated into a distillate product containing 97% (weight) methanol and a bottom product containing 2 % (weight) methanol. For treating 100kg of feed with a reflux ratio of 3.5 on a weight basis, calculate the following:

(a) The amount of distillate and bottom products

(b) The amount of vapour condensed in the condenser per kg of distillate

(c) The amount of vapour condensed in the condenser per kg of feed

5+10

18. (a) A mixture containing 30% acetone and 70% chloroform is extracted with a mixed solvent containing acetic acid and water. The two immiscible phases—the raffinate and extract phases—that result after extraction had the following analysis:

Extract: Acetone 7.0%; chloroform 3.0%; acetic acid 30% and water 60%

Raffinate: Acetone 20.0%; chloroform 67.0%; acetic acid 10% and water 3%

Now for the basis of 100kg of the mixture extracted determine the following:

(i) The composition of the mixed solvent on weight basis

(ii) The quantities of the raffinate and extract phases

(iii) The amount of mixed solvent used

(b) Ammonia is recovered from a gas mixture containing 25 % (volume) carbon dioxide and 75% (volume) ammonia by scrubbing with water. Assuming that carbon dioxide is insoluble in water, determine the percent ammonia in the entering gas that is absorbed if the gas leaving the scrubber analyzes 35% ammonia.

10+5

19. (a) A producer gas contains 9.2% CO₂, 21.3% CO, 18% H₂, 2.5% CH₄ and the rest N₂. It is burned with an excess supply of air. The flue gas analyzed 9.05% CO₂, 1.34% CO, 9.98% O₂ and 79.63% N₂. Determine the following:

- (i) The volumetric ratio of air supplied to the fuel burned
 - (ii) The percent excess air supplied
 - (iii) The percent of nitrogen in the flue gas that came from the fuel
- (b) Define cinder and gangue

13+2

20. Propane is dehydrogenated to form propylene in a catalytic reactor by the following chemical reaction



The process is to be designed for a 95% overall conversion of propane. The reaction products are separated into two streams: the first, which contains H₂, C₃H₆ and 0.555% of the C₃H₈ that leaves the reactor, is taken off as product; the second stream which contains the balance of the unreacted propane and 5% of propylene in the product stream, is recycled to the reactor. Determine the following:

- (i) Composition of the product
- (ii) Recycle ratio
- (iii) Single pass conversion

5+5+5

21. For the reaction $\text{A} \longrightarrow \text{B}$ takes place in a catalytic converter, the fresh feed of A contains 0.5% of inerts by volume. 60% conversion of A per pass is obtained. The concentration of inerts going into the converter must be held at 2% by volume. Assuming all streams are ideal gases and the process is at steady state determine

- (i) How many moles need to be recycled per mole of total feed to the converter?
- (ii) How many moles need to be purged?
- (iii) What is the overall conversion of A?

5+5+5

22. (a) Define the respiratory quotient and yield coefficients of an aerobic fermentation reaction.

(b) The experimental measurement for a yeast strain *Saccharomyces cerevisiae* have shown that cells can convert two thirds (wt/wt) of the substrate carbon (alkane or glucose) to biomass in the following biochemical reactions



Determine the following

- (i) Stoichiometric coefficients for both these reactions
- (ii) Yield coefficients for both these reactions

3+12

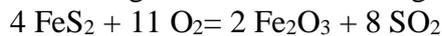
23. a) Caustic soda is concentrated from 10% to 50% in a single effect evaporator. The feed at 305 K enters at a rate of 1000 kg/hr. The concentrated solution leaves the evaporator at 380 K and the vapour leaves at 373.15 K. Determine the heat to be supplied in the evaporator. The mean heat capacity applicable to the solution is 3.67 kJ/kg K for the feed and 3.34 kJ/kg K for the product. The heat of solution of 10% and 50% NaOH solution at 298 K are, -42.85 kJ/mol and -25.89 kJ/mol respectively. The latent heat of vaporization of water at 298 K is

2442.5 kJ/kg and the mean heat capacity of water vapour is 1.884 kJ/kg K.

b) Calculate the enthalpy change for 1 mol of a gas when it is heated from 400 K to 1500K at 1 atm pressure given that the mean specific heat of the gas at the reference temperature of 273K are 35 kJ/kmol K at 400 K and 50 kJ/kmol K at 1500 K. 12+3

24. a) Explain Hess's Law.

b) In a sulfuric acid plant, sulphur dioxide is obtained by the roasting of iron pyrites containing 80% FeS₂ and 20% gangue. Iron reacts with oxygen according to the reaction:

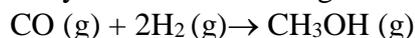


The cinder formed on the combustion analyzes 5 % FeS₂. Determine the standard heat of reaction per kg of ore, given the following standard heat of formation values at 298K, are FeS₂ (S) = - 178.02 kJ/mol; Fe₂O₃ (S) = - 822.71 kJ/mol and SO₂ (g) = -296.9 kJ/mol.

c) Pure CO is mixed with 100% excess air and completely burned at constant pressure. The reactants are originally at 400 K. Determine the heat added or removed if the products leave at 600 K. The standard heat of reaction at 298K is 282.99 kJ/ mol CO burned. The mean specific heats applicable in the temperature range of this problem are 29.10, 29.70, 29.10 and 41.45 J/ (mol.K) respectively for CO, O₂, N₂ and CO₂.

2+8+5

25. Methanol is synthesized according to the following reaction:



The standard heats of formation at 298 K are -110.6 kJ/mol for CO and -238.64 kJ/mol for methanol (l). The latent heat of vaporization of methanol at 298 K is 37.98 kJ/mol. The specific heats (J/ mol.K) are given by:

$$C_p (\text{CH}_3\text{OH}) = 18.382 + 101.564 \times 10^{-3} T - 28.683 \times 10^{-6} T^2$$

$$C_p (\text{CO}) = 28.068 + 4.631 \times 10^{-3} T - 2.5773 \times 10^{-4} T^{-2}$$

$$C_p (\text{H}_2) = 27.012 + 3.509 \times 10^{-3} T + 6.9006 \times 10^{-4} T^{-2}$$

Calculate the standard heat of reaction at 1073 K.

15

26. a) A spherical storage tank of 3 m in diameter is half-filled with 12500 kg of an organic liquid at 7000 kPa. If the total internal energy in the tank is 5.3×10^6 kJ, what is the specific enthalpy of the fluid tank?

b) 1000kg/h of a thermic fluid, to be used as heat transfer medium, is being indirectly heated in a heater from 380K to 550 K. Calculate the heat load on the heater in kW. The heat capacity equation for the thermic fluid is

$$C_p = 1.436 + 2.18 \times 10^{-3} T$$

Where, C_p is in kJ/(kg.K) and T is in K

C) Calculate the values of ΔH_{298}^0 for the reactions in the transformation of glucose in an organism



ii) $C_6H_{12}O_6(s) + 6O_2(g) = 6CO_2(g) + 6H_2O(l)$
 Which of the reactions supplies more energy to the organism?
 The standard enthalpies of formation are:

$C_6H_{12}O_6(s)$	-1273.0 kJ/mol
$C_2H_5OH(l)$	-277.6 kJ/mol
$CO_2(g)$	-393.5kJ/mol
$H_2O(l)$	-285.8 kJ/mol

5+5+5

27. a) Showing the different steps, stoichiometrically represent the effect of temperature on the heat of reaction.

b) Ammonia is synthesized according to the following reaction:



The specific heats of the components are represented by

$$C_p = \alpha + \beta T + \gamma T^2$$

Where C_p is in J/ (mol K) and the constants α, β, γ are:

Molecules	α	β	γ
N_2	27.31	5.2335×10^{-3}	-4.1868×10^{-9}
H_2	29.09	-8.374×10^{-4}	2.0139×10^{-6}
NH_3	25.48	36.89×10^{-3}	-6.305×10^{-6}

Determine the heat of reaction at 700 K.

7.5+7.5

28. a) Explain Copp's rule with example.

b) Determine the heat capacity of $Na_2SO_4 \cdot 10H_2O$ at room temperature using Copp's rule. The atomic heat capacity of the elements (J/g.atm.k) are 26.04 for Na, 22.6 for S, 16.8 for O, and 9.6 for H. Compare the result with the experimental value of the heat capacity of 592.2 J/mol.K.

c) Calculate the heat requirement for an air drier that uses 2000 ft³ / min of air at 1 atm and 170°F if ambient air at 70°F is heated to 170°F for use in the process.

[C_{pm} is constant at 0.241 BTU/(lb. °F) up to 200°F for air]

2.5+5+7.5