PHARMACEUTICAL ENGINEERING

Unit Operations and Unit Processes

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**Introduction**

Every industrial chemical process is based on Unit Operations (physical treatment) and Unit Process (chemical treatment) to produce economically a desired product from specific raw materials. The raw materials are treated through physical steps to make it suitable for chemical reaction. So, knowledge of unit operations like ‘Mixing and agitation of liquid’ and ‘heat flow’ is very much necessary. The subject Unit Operations is based on fundamental laws, physicochemical principles. Unit Operations gives idea about science related to specific physical operation; different equipments-its design, material of construction and operation; and calculation of various physical parameters (mass flow, heat flow, mass balance, power and force etc.). Examples of Unit Operations are listed in Table 1.

<table>
<thead>
<tr>
<th>Table 1: List of some unit operations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat flow, Fluid flow</td>
</tr>
<tr>
<td>Mixing</td>
</tr>
<tr>
<td>Drying</td>
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<tr>
<td>Absorption</td>
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<td>Evaporation</td>
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<td>Adsorption</td>
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<td>Distillation</td>
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<td>Condensation</td>
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<tr>
<td>Crystallization</td>
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<td>Vaporization</td>
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<td>Leaching</td>
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<tr>
<td>Separation</td>
</tr>
<tr>
<td>Extraction</td>
</tr>
<tr>
<td>Sedimentation</td>
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<tr>
<td>Filtration</td>
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<tr>
<td>Crushing</td>
</tr>
</tbody>
</table>

After preparing raw materials by physical treatment, these undergo chemical conversion in a reactor. To perform chemical conversion basic knowledge of stoichiometry, reaction kinetics, thermodynamics, chemical equilibrium, energy balance and mass balance is necessary. Many alternatives may be proposed to design a reactor for a chemical process. One design may have low reactor cost, but the final materials leaving the unit need higher treatment cost while separating and purifying the desired product. Therefore, the economics of the overall process also play a vital role to select a suitable alternative design. Each chemical process consists of series of assembly that are organized systematically to achieve the goal. The physical and chemical steps in a process are set with the help of combined knowledge and experience of engineers, technologists and cost experts to produce a product.

The individual operations have some common phenomena and are based on the same scientific principles e.g. Heat transfer is the common phenomenon in evaporation, drying and crystallization. (Table 2)

A process designer designs a chemical process considering (1) efficiency of process and equipments (2) Safety with respect to the process, raw chemicals, finished products and long term effect on environment (3) financial viability of the products as demanded by the purchaser.

Following are some examples of physical processes:

(a) Sugar Manufacture:

Sugar cane crushing $\rightarrow$ sugar extraction $\rightarrow$ thickening of syrup $\rightarrow$

$\rightarrow$ evaporation of water $\rightarrow$ sugar crystallization $\rightarrow$ filtration $\rightarrow$ drying $\rightarrow$ screening $\rightarrow$ packing.
Table 2: Common Technique/Phenomenon

<table>
<thead>
<tr>
<th>Common Technique / Phenomenon</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Movement of Fluid</td>
<td>1. Fluid flow from one storage to reaction vessel.</td>
</tr>
<tr>
<td></td>
<td>2. Fluid flow involving heat transfer/exchange.</td>
</tr>
<tr>
<td></td>
<td>4. Fluidization (solid–liquid)</td>
</tr>
<tr>
<td></td>
<td>5. Filtration</td>
</tr>
<tr>
<td></td>
<td>6. Separation</td>
</tr>
<tr>
<td>Movement of Solid</td>
<td>1. Fluidization (solid–liquid)</td>
</tr>
<tr>
<td></td>
<td>2. Fluid bed drying</td>
</tr>
<tr>
<td></td>
<td>3. Settling</td>
</tr>
<tr>
<td></td>
<td>4. Blending of powder</td>
</tr>
<tr>
<td></td>
<td>5. Powder flow</td>
</tr>
<tr>
<td></td>
<td>6. Conveying</td>
</tr>
<tr>
<td>Mass Transfer</td>
<td>Drying, Evaporation, distillation, chemical reaction, diffusion, extraction, humidification, adsorption, chemical kinetics.</td>
</tr>
</tbody>
</table>

(b) Pharmaceutical Manufacture:
Formulation of chemicals, mixing, granulation → drying of granules→screening → pressing tablet → packaging.

(c) Salt Manufacture:
Brine transportation → evaporation → crystallization → drying → screening → conveying → packaging.

On the other hand conversion of starch to dextrose with the help of acid catalyst is a typical chemical reaction which involves transportation of raw materials, physical steps of mixing the reactants, heat transfer, reaction kinetics, fluid flow, separation of products, product purification, drying, screening, conveying and packaging.

In 'Pharmaceutical' curriculum, knowledge of 'unit operations' is very much relevant with respect to formulated drug products and basic drugs in Pharmaceutical Industry.

Because of the variety and complexity of modern processes, the 'process' had been classified for better understanding of the steps in detail. General flow chart exhibiting product formation has been shown in Fig.1. The figure shows the sequence of basic components generally used in a typical chemical process in which each block represents a stage in the overall process for producing a product from the raw materials. The design of the process involves selection, arrangement of the stages and the selection of specification and design of the equipment required to perform the stages.
Recycle of unreacted material

Stage 1

Stage 2

Stage 3

Stage 4

Stage 5

Stage 6

Stage 7

By products

Fig. 1: Flow sheet of a typical chemical process

Each stage may be simple or complex according to need of the process. Both theory and practice should be considered to yield designs for equipments that can be fabricated, assembled, operated and maintained.

**Unit Systems**

Knowledge of unit systems is very much necessary to express any physical quantity and to solve/calculate any problem based on physical data. A physical quantity is expressed with its magnitude and unit. For example: 6 feet, the unit (foot) tells us the type of a particular quantity / magnitude and it is this standard by which the quantity is measured. Magnitude or numerical value tells us how many units are needed to make that up to required quantity. For example, the statement that the height of a person is 6 feet; it means six '1–foot units' are required to cover the height of this person.

The official international system of units is the SI system (system international d' unite's), but older systems, particularly the centimeter gram–second (cgs) and foot–pound–second (fps) engineering gravitational systems, are still in use. Because of growing importance of the SI system in science and engineering, it becomes necessary to put effort on its universal adoption as the exclusive system for all engineering and science. The SI system covers the entire field of science and engineering including electromagnetic and illumination. The units are derivable from some basic equations with the help of arbitrarily chosen standards for mass, length, time, temperature, mole and arbitrarily chosen numerical values for the proportionality constants of the following basic equations.

\[ F = K_1 \frac{d}{dt} (m u) \ldots(1) \quad \text{Newton's second law of motion} \]

\[ F = K_2 \frac{m_a m_b}{r^2} \ldots(2) \quad \text{Newton's law of gravitation} \]

\[ Q_c = K_3 W_c \ldots(3) \quad \text{First law of thermodynamics} \]

\[ T = K_4 \lim_{\rho \to 0} \frac{PV}{m} \ldots(4) \quad \text{Equation relating absolute temperature, pressure and volume.} \]

\( F = \text{Force, } t = \text{time, } m = \text{mass, } m_a, m_b = \text{masses of two bodies, } u = \text{velocity,} \)

\( r = \text{distance, } W_c = \text{Work, } Q_c = \text{heat, } P = \text{pressure, } V = \text{Volume, } T=\text{Absolute} \)

\( \text{temperature, } K_1, K_2, K_3, K_4 = \text{proportionality factors} \)
These K values can be calculated if all the variables are measurable. Unit of K is derived from the units used for measuring the variables in the equation.

In SI system, \( K_1 = 1 \) and unit of force (F) is Newton (N) in equation (1)
\[
\therefore \text{IN} = 1 \text{ kg} \cdot \text{m/s}^2
\]

Similarly, in FPS system, 1 poundal is one unit force.
\[
\therefore 1 \text{ poundal} = 1 \text{ lb ft/s}^2 \ (K1 = 1)
\]

1 lb of mass experiences acceleration of 32.174 ft/s\(^2\) under gravitational force. Unit force cannot be defined if this value of acceleration due to gravity (g) is put in equation (1), considering \( K_1 = 1 \).

So, it is customary to use pound force instead of poundal and to use \( K_1 = \frac{1}{g_c} \). So equation (1) becomes, \( F = mg/g_c \) …(5)

g varies with latitude. But \( g_c \) is considered a constant, called 'Newton's law proportionality factor', since the ratio \( g/g_c \) can be taken as unity for all practical purposes. So, unit force (lb force, gm force) can be defined using unit mass. Numerical value of \( g_c \) approximately 32.174 that is average value of g.

Unit of \( g_c \) is \( \frac{\text{lb}_{mass}}{\text{lb}_{force}} \times \frac{\text{ft}}{\text{s}^2} \); it is derived from equation (1)

'\( g_c \)' is very important in the conversion of unit of force. Conversion of x poundal to pound force unit is done as follows:

\[
x \text{ poundal} = x \frac{\text{lb}_{mass}}{\text{lb}_{force}} \times \frac{\text{ft}}{\text{s}^2}; \ \text{lb}_{mass} \text{ and lb}_{force} \text{ are written as lb}_m \text{ and lb}_f \text{ respectively.}
\]

or, \[
x \text{ poundal} = \frac{x}{32.2} \frac{\text{lb}_m}{\text{lb}_f} \times \frac{\text{ft}}{\text{s}^2} \times \frac{\text{lb}_f}{\text{lb}_m} \times \frac{s^2}{\text{ft}} = \frac{x}{32.2} \text{ lb}_f
\]

**Some examples of units:**

Convert \( \frac{\text{BTU}}{(\text{h})(\text{ft})(\circ\text{F})} \) to \( \frac{\text{g-cal}}{(\text{s})(\text{cm})(\circ\text{C})} \)

Conversion factors
1 BTU = 252 gm.cal; 1 ft = 30.48 cm;
1 h = 3600 s; 1\(^\circ\)F = \( \left( \frac{5}{9} \right) \circ\text{C} \)

\[
\frac{\text{BTU}}{(\text{h})(\text{ft})(\circ\text{F})} = \frac{252}{3600 \times 30.48 \times \frac{5}{9}} \frac{\text{gm.cal}}{\text{s}.\text{cm}.\circ\text{C}}
\]

\[
= 4.13385 \times 10^{-3} \frac{\text{gm.cal}}{\text{s}.\text{cm}.\circ\text{C}}
\]

\[
1 \frac{\text{g-cal}}{\text{s}.\text{cm}.\circ\text{C}} = 241.904 \approx 242 \frac{\text{BTU}}{\text{h}.\text{ft}.\circ\text{F}}
\]
Physical quantities are expressed in terms of primary and secondary units. Length, mass, time, heat and temperature are primary or fundamental units. Secondary units are expressed in terms of primary ones. The units of force, acceleration are secondary type.

Table 3: List of some physical quantities and their conversion units

<table>
<thead>
<tr>
<th>Quantity</th>
<th>To convert from</th>
<th>To</th>
<th>Multiply by</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy</td>
<td>BTU</td>
<td>kJ</td>
<td>1.05506</td>
</tr>
<tr>
<td>Specific enthalpy</td>
<td>BTU/lb</td>
<td>kJ/kg</td>
<td>2.326</td>
</tr>
<tr>
<td>Specific heat capacity</td>
<td>BTU/lb °F</td>
<td>kJ/kg °C</td>
<td>4.1868</td>
</tr>
<tr>
<td>Heat transfer coeff.</td>
<td>BTU/ft'h °F</td>
<td>W/m² °C</td>
<td>5.678</td>
</tr>
<tr>
<td>Viscosity</td>
<td>centipoise</td>
<td>kg/m.s</td>
<td>10⁻³</td>
</tr>
<tr>
<td>Surface tension</td>
<td>dyne/cm</td>
<td>N/m</td>
<td>10⁻³</td>
</tr>
<tr>
<td>Pressure</td>
<td>lb/ft²</td>
<td>N/m²</td>
<td>6.894 ×10⁹</td>
</tr>
<tr>
<td>Density</td>
<td>lb/ft³</td>
<td>kg/m³</td>
<td>16.0190</td>
</tr>
<tr>
<td>Volume</td>
<td>m³</td>
<td>gal (US)</td>
<td>264.17</td>
</tr>
</tbody>
</table>

1 US gallon = 0.84 imperial gallons (UK)

Material Balance
Mass balance or material balance is the expression of the conservation of mass that involves accounting of materials in a process. This age old mass balance concept is useful for assessing a process and sometimes improving management practices including waste reduction, on site tracking of toxic chemicals and transportation into and out of a facility. Moreover, material balance over a process helps to check performance against design, instrument calibration and to identify the source of material loss. It also helps to extend often the limited data available from the plant instrumentation. Therefore, a good understanding of material balance is necessary.

Einstein showed that mass and energy are equivalent. Energy can be converted into mass and mass into energy. The loss of mass associated with the production of energy is significant in nuclear reactions. In processes of nuclear fission and condensation the law of conservation of mass becomes invalid, but in ordinary industrial processes mass balance is highly practiced and it is accepted that energy and matter are to be separately conserved.

The conservation of mass can be written as:
Rate of flow of reactant into volume element = Rate of flow of reactant out of volume element + Rate of reactant removal by reaction within volume element + Rate of accumulation of reactant within volume element.

Material balance is carried over a certain element of volume. In steady state process i.e. continuous process, the accumulation will be zero. If there is no chemical reaction the steady state balance reduces to:
Rate of flow of reactant into volume element = Rate of flow of reactant out of volume element.

A mass balance can be written for individual elements, compounds and for total materials. Direct measurements of quantity of components of both entering and leaving streams in a process during a given time interval needs no calculation. Calculation of material balance is indispensable when direct measurement of one or more components is not possible. The measurements require knowledge of conservation of mass and of the standard units for expressing mass data, composition, concentration, flow rate of flowing streams in a process. If there is any change of physical or chemical properties of flowing streams, that must be accountable. Appropriate judgement must be exercised in selecting the methods for sampling, analysis and in choosing the frequency and duration of data acquisition of mass flows within a process.

Gross deviation from mass balance indicates that errors have been made in sampling and quantifying one or more mass balance components or else it needs some relevant information. So, precise evaluation is needed. In a mass balance operation, all chemical inputs to a manufacturing process and outputs from it and accumulations within are first identified and the masses are measured. The mass of inputs should be equal or closely approximate the mass of outputs plus accumulations.

The following step-by-step procedure helps to get efficient solution of material balance problems:
1. Draw a block diagram of the process to show significant steps by flow sheet diagram.
2. List all the available data. Indicate known quantities of the parameters on the block diagram.
3. List all the information.
4. Decide the system boundaries.
5. Write out all the chemical reactions involved for the main products and byproducts.
6. Note any other constraints if any, like azeotropes, phase equilibria, tie substances.
7. Check the number of conservation equations that can be written and compared with the number of unknowns. Decide the basis of calculation. The order of steps may vary according to need of the problem.

With simple problems, having only one or two recycle loops; the calculation can often be simplified by careful selection of the basis of calculation and the system boundaries. Following is an example of block diagram showing the main steps in the balanced process for the production of vinyl chloride (VC) from ethylene (C\textsubscript{2}H\textsubscript{4}). Each block represents a reactor and several other processing units (Fig.2).

**Block A. Chlorination**
C\textsubscript{2}H\textsubscript{4} + Cl\textsubscript{2} \rightarrow C\textsubscript{2}H\textsubscript{4}Cl\textsubscript{2} (di chloroethane, DCE)
Yield: based on ethylene 98%

**Block B. oxy hydrochlorination**
C\textsubscript{2}H\textsubscript{4} + 2HCl + 1/2 O\textsubscript{2} \rightarrow C\textsubscript{2}H\textsubscript{4}Cl\textsubscript{2} + H\textsubscript{2}O
Yield : based on ethylene 95%; on HCl 90%
Block C, Pyrolysis
\[ \text{C}_2\text{H}_4\text{Cl}_2 \rightarrow \text{C}_2\text{H}_3\text{Cl} \text{ (vinyl chloride)} + \text{HCl} \]
Yields: based on DCE 99%, on HCl 99.5%

X, Y, Z represent flow of ethylene to Block A, flow of ethylene to block B and flow of HCl in recycle loop.

In this problem flow of C\textsubscript{2}H\textsubscript{4} and DCE are unknown that can be calculated on the basis of the production rate of vinyl chloride with the help of algebraic method.

**Basis of Calculation:**
The initial step in tackling a mathematical problems starts with selection of a basis of calculation. This makes the solution of problem easier and simple. If the compositions of substances involved in a chemical reaction are given in weight percent, 100 pound or 100 gm of one of the substances entering or leaving system of a continuous process may be chosen as the basis of calculations and finally, the calculated values may be converted to other basis as per the desired statement of problem. A choice of basis is made before calculation depending upon desired information on parameters like time, mass, mole, volume (for gas), and batch (for batch process).

**Example:** Carbon dioxide is added at a rate of 10 lb/hr to an air stream and the air sample at the outlet shows 0.45% (v/v) CO\textsubscript{2} .Calculate the airflow rate. Normal content of CO\textsubscript{2} in air is 0.03% (v/v).

**Solution:** Inlet air contains 0.03% (v/v) CO\textsubscript{2}

- **Basis:** one hour
- Number of mole of CO\textsubscript{2} added to the air stream = mass of CO\textsubscript{2} / molecular weight of CO\textsubscript{2}
  \[ \text{CO}_2 = \frac{10}{44} = 0.2273 \text{ lb mole/hr} \]
- Let M lb mol/hr be the airflow rate, CO\textsubscript{2} being the tie component.
- Balance can be made on CO\textsubscript{2}, using the concept of ideal gas law, volume % = mole%
  \[ \text{CO}_2 \text{ in} = 0.0003M + 0.2273 \]
  \[ \text{CO}_2 \text{ out} = 0.0045M \]
By balancing CO$_2$, 0.0045M = 0.0003M + 0.2273  
∴ M = 54.119 lb mol/hr = 54.119 /29=1569.45 lb/hr

Molecular weight of air is 29.

**Excess Reagent**

In most chemical reactions carried out in industry, the components are seldom fed to the reactor in exact stoichiometric proportions. A reagent may be supplied in excess of the amounts theoretically required for combination with the others in order to maximize the use of an expensive reagent or to ensure complete reaction of a reagent. As a result, the products contain some of the unreacted reactants. The amount of desired compound is determined by the amount of limiting reactant.

The percentage excess of any reactant is defined as the percentage ratio of the excess to the amount theoretically required by the stoichiometric equation for combination with the limiting reactant. So the 'Excess' refers to limiting reagent. The percentage excess reagent is expressed by the following:

\[
\text{Percentage excess} = \frac{\text{Quantity supplied} - \text{stoichiometric quantity}}{\text{stoichiometric quantity}} \times 100
\]

Complete reaction of the limiting material may not be achieved even in the presence of excess reagent. It happens due to insufficient time or opportunity for completion to the theoretically possible equilibrium. The degree of completion of a reaction is ordinarily expressed as the percentage of the limiting reacting material, which is converted or decomposed into other products. In case of 100% completion, outlet stream contains products and excess reactant.

**Example:** 20% excess air is supplied to a furnace burning natural gas (Methane 95% (v/v), Ethane 5% (v/v)). Calculate the moles of air required per mole of fuel.

Reactions:  
- CH$_4$ + 2O$_2$ → CO$_2$ + 2H$_2$O  
- C$_2$H$_6$ + 3.5 O$_2$ → 2CO$_2$ + 3 H$_2$O

**Solution:** Basis : We may use any number of mole of gas as basis, let us take 1000 mole of fuel gas, as the given composition is in volume percentage, stoichiometric moles of O$_2$ required = 950 x 2 + 50 x 3 = 2075  

with 20% excess, moles of O$_2$ required = 2075 x \( \frac{120}{100} \) = 2490

number of mole of air (21% O$_2$) = 2490 x \( \frac{100}{21} \) = 11857

Number of mole of air per mole fuel = 11857 / 1000 = 11.86

**Conversion and yield**

Conversion refers to the reactants and yield refers to the products formed. Conversion is a measure of the fraction of the reagent that converts due to reaction. Conversion is expressed by the following:

\[
\text{Conversion} = \frac{\text{Amount of reagent consumed}}{\text{amount supplied}}
\]
Yield = \frac{(\text{amount of reagent in feed stream}) - (\text{amount of reagent in product stream})}{(\text{amount in feed stream})}

This definition indicates the total conversion of the particular reagent to all products. The conversion of a particular reagent is often less than 100 percent in order to minimize by-product formation. If the conversion of a valuable reagent in a reaction process is appreciably less than 100 percent, the unreacted material is recycled.

Yield is a measure of the performance of a reactor or plant. Yield should be defined on clearly stated basis.

\[ \text{Yield} = \frac{\text{mole of product produced} \times \text{stoichiometric factor}}{\text{moles of reagent converted}} \]

Stoichiometric factor = Stoichiometric mole of reagent required per mol of product produced.

'Plant yield' is a measure of the overall performance of the plant and includes all chemical and physical losses.

\[ \text{Plant yield} = \frac{\text{mole of product produced} \times \text{stoichiometric factor}}{\text{mole of reagent fed to the process}} \]

When more than one reagent is used or product produced it is essential that the product and the reagent to which the yield value refers are clearly stated.

**Example:** Reaction: \[ \text{C}_2\text{H}_4 + \text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_5\text{OH} \]
\[ 2\text{C}_2\text{H}_5\text{OH} \rightarrow (\text{C}_2\text{H}_5)_2\text{O} + \text{H}_2\text{O} \]

Ethanol is produced by the hydrolysis of ethylene and diethyl ether is the by-product formed.

- \( \text{C}_2\text{H}_4, 55\% \)
- \( \text{Inert, 5\%} \)
- \( \text{H}_2\text{O, 40\%} \)

\[ \text{Reactor} \]

\[ \text{C}_2\text{H}_4 - 52.26\% \]
\[ \text{C}_2\text{H}_5\text{OH} - 5.49\% \]
\[ (\text{C}_2\text{H}_5)_2\text{O} - 0.16\% \]
\[ \text{H}_2\text{O} - 36.8\%, \text{ Inert - 5.28\%} \]

**Fig. 3:** Problem on yield of ethanol.

Calculate percentage of conversion of ethylene and the yield of ethanol and ether based on ethylene.

**Solution:** Basis: 100 moles of feed (Easier calculation on the basis feed components) Inert remains unchanged. So amounts of product components can be calculated on the basis of inert material’s amount.

Yield of product (ethanol) and byproduct are calculated on the basis of ethylene, not on water as water is relatively cheaper than ethylene. Water is fed in excess. Ethylene is the reagent.
### Feed stream components

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>55</td>
</tr>
<tr>
<td>Inert</td>
<td>5</td>
</tr>
<tr>
<td>Water</td>
<td>40</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
</tr>
</tbody>
</table>

### Product stream components

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>52.26</td>
</tr>
<tr>
<td>Ethanol</td>
<td>5.49</td>
</tr>
<tr>
<td>Ether</td>
<td>0.16</td>
</tr>
<tr>
<td>Water</td>
<td>36.81</td>
</tr>
<tr>
<td>Inert</td>
<td>5.28</td>
</tr>
</tbody>
</table>

**Basis of calculation**

- Ethylene $\frac{52.26}{5.28} \times 5 = 49.49$ mole
- Ethanol $\frac{5.49}{5.28} \times 5 = 5.2$ mole
- Ether $\frac{0.16}{5.28} \times (5) = 0.15$ mole
- Water $\frac{36.81}{5.28} \times 5 = 34.85$ mole
- Inert $\frac{5.28}{5.28} \times 5 = 5$ mole

Calculation is done with respect to quantity of inert.

**Amount ethylene converted** = Amount of reagent in feed stream - Amount of reagent in product stream = 55 - 49.49 = 5.51 mole

**Conversion** = \( \frac{\text{mole fed} - \text{mole out}}{\text{mole fed}} \times 100 \)

\[
= \frac{5.51}{55} \times 100 = 10\%
\]

**Yield of ethanol based on ethylene** = \( \left( \frac{5.2}{5.51} \times 1 \right) \times 100 = 94.4\% \)

Stoichiometric factor is 1.

**Yield of ether based on ethylene** = \( \left( \frac{0.15 \times 2}{5.5} \right) \times 100 = 5.45\% \)

Stoichiometric factor is 2, as 2 moles of ethylene produce 1 mol of ether.

### Problems on Material Balance

1. The composition of gas derived by the gasification of coal is, volume percentage: carbon dioxide 4, carbon monoxide 16, hydrogen 50, methane 15, ethane 3, and benzene 2, balance nitrogen. If the gas is burnt in a furnace with 20 per cent excess air, calculate:
   (a) The amount of air required per 100 kmol of gas
   (b) The amount of flue gas produced per 100 kmol of gas,
   (c) The composition of the flue gases, on a dry basis
   Assume complete combustion.

2. Ammonia is removed from a stream of air by absorption in water in a packed column. The air entering the column is at 760 mmHg pressure and 20°C. The air contains 5.0 per cent v/v ammonia. Only ammonia is absorbed in the column. If the flow rate of the ammonia air mixture to the column is 200 m³/s
and the stream leaving the column contains 0.05 per cent v/v ammonia, calculate:

(a) The flow rate of gas leaving the column.
(b) The mass of ammonia absorbed.
(c) The flow rate of water to the column, if the exit water contains 1% w/w ammonia.

3. Allyl alcohol can be produced by the hydrolysis of allyl chloride. Together with the main product, allyl alcohol, di-allyl ether is produced as a by-product. The conversion of allyl chloride is typically 97 per cent and the yield to alcohol 90 per cent, both on a molar basis. Assuming that there are no other significant side reactions, calculate masses of alcohol and ether produced, per 1000 kg of allyl chloride fed to the reactor.

**Energy Balance**

Energy balance is a mathematical or numerical expression of 'Conservation of energy' (also called first law of thermodynamics). Energy balance and mass balance are encountered often in the problems related to process design and operation. Principle of conservation of energy states that energy is indestructible, but can be transformed to other forms of energy and the total amount of energy entering any system must be exactly equal to that of leaving plus any accumulation within this system.

**Energy out = Energy in + generation – consumption – accumulation**

For steady state process the accumulation of both mass and energy will be zero. In mass balance, the total mass flow into a process unit is generally equal to the flow out at the steady-state except in biomass formation within a bioreactor where generation is concerned. In energy balance, the total enthalpy of the outlet streams will not be equal to that of the inlet streams if energy is generated (exothermic) or consumed (endothermic).

Energy balance is carried out to know the energy needed in heating / cooling and supplying power in a process. 'Energy balance' exhibits a pattern of usage and suggests areas for conservation and savings. Energy can exist in many forms making 'energy balance' more complex than mass balance, such as potential energy, kinetic energy, flow energy, heating energy, mechanical energy, electrical energy etc. **Total energy is conserved as per the law of conservation of energy.**

<table>
<thead>
<tr>
<th>Table 4: Potential Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>External Form</strong></td>
</tr>
<tr>
<td>It is attributed due to relative position / height of matter above datum point ((z)). It is quantified by, ( \frac{gz}{g_c} )</td>
</tr>
</tbody>
</table>
Table 5: Kinetic Energy

<table>
<thead>
<tr>
<th>External Form</th>
<th>Internal Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>It is attributed due to motion of matter and quantified by ( \frac{1}{2} \frac{u^2}{g_c} ) per unit mass; ( u ) is the average velocity of the stream.</td>
<td>It is attributed due to presence, relative position, and movement of molecules, atoms, and subatomic units. The translational, rotational and vibrational motion of the atoms, electrons, contributes it.</td>
</tr>
</tbody>
</table>

The kinetic portion of total 'internal energy' is determined by the temperature of the substance and by its molecular structure. The remainder of the internal energy remains as potential energy due to attractive and repulsive forces between molecules, atoms. All translational energy disappears at temperature absolute zero, but energy is reserved as potential energy. 'Absolute Zero', temperature as reference is used to calculate kinetic part of internal energy \( (U = f(T)) \). The total internal energy of a substance cannot be determined.

Flow energy (PV) often appears in flow process. It is external form of energy and determined by the product of pressure and volume. Another form of external energy is surface energy, which is often encountered in making of emulsion. Heat energy is the energy in transition under the influence of temperature difference (\( \Delta t \)). When heat flows from a source (hot) to a receiver (cold) body, it is stored as internal energy and so, internal energy of receiver is enhanced.

Another form of energy in transition is work. Work done is manifestation of the transition of one form of energy into another. When a force \( (F) \) acts on a body through a distance, work is expressed by, \( w = \int_0^x F \, dx \) where \( x, \ell \) = distance,

Work is considered negative when it is done on a system by its surrounding. It is positive when work is done by the system on its surrounding. When work is done due to change in pressure or volume, \( w = \int_1^2 P \, dv; \) \( P = \) pressure, pascal

\( v = \) volume per unit mass, \( m^3/kg \)

Following figure illustrates energy balance in a steady state process

![Energy Balance Diagram](image)

**Fig. 4: Energy balance.**
P is pressure, \( V \) is volume, \( \bar{u} \) is the average velocity, \( z \) is the distance from datum plane, \( g \) is the acceleration due to gravity and \( g_c \) is gravitational constant.

For unit mass of material, following energy balance equation can be written, covering both flow process (steady state) and nonflow or batch process (unsteady state).

\[
U_1 + P_1 V_1 + \frac{\bar{u}_1^2}{2g_c} + z_1 \frac{g}{g_c} + Q + \Delta E = U_2 + P_2 V_2 + \frac{\bar{u}_2^2}{2g_c} + z_2 \frac{g}{g_c} + W
\]

In the above expression \( Q \) is the heat transferred to the system and \( W \) is the work done by the system. \( \Delta E \) is the special terminology used for batch process only, where terms like \( U, PV, \frac{\bar{u}^2}{2g_c}, \frac{zg}{g_c} \) will not appear in the equation, since all these terms are accounted in \( \Delta E \). \( \Delta E \) represents the change in energy content of the system as a result of any change in inventory (temperature, composition) of the system.

\[
\Delta E = U_2' + \frac{z_2'g}{g_c} + \frac{\bar{u}_2'^2}{2g_c} - \left( U_1' + \frac{z_1'g}{g_c} + \frac{\bar{u}_1'^2}{2g_c} \right)
\]

\[
\left( U_2' - U_1' \right) + \left( z_2' - z_1' \right) \frac{g}{g_c} + \frac{\left( \bar{u}_2'^2 - \bar{u}_1'^2 \right)}{2g_c}
\]

Prime sign is used for batch process.

In chemical processes (continuous or flow), the kinetic and potential energy terms are usually small compared to heat and work terms, so these can be omitted from the generalised equation. Here, \( \Delta E = 0 \). Therefore, we can write

\[
Q - W = (U_2 + P_2 V_2) - (U_1 + P_1 V_1)
\]

or \( Q - W = H_2 - H_1 \)

Here, \( H (= U + PV) \) is the enthalpy that is function of temperature and pressures. Enthalpy can be calculated by specific and latent heat. The above equation helps to estimate heating and cooling requirements of various unit operations involved in chemical processes.

In nonflow process, we may write,

\[
Q - W = \Delta E.
\]

Considering changes in potential energy and kinetic energy due to stirring negligible, the above equation can be simplified to

\[
Q - W = (U_2' - U_1')
\]

We know that,
\[
W = P \Delta V
\]
At constant volume, \( W = 0 \)
\[
\therefore Q = U_2' - U_1' = \Delta U = \text{Change in internal energy}
\]
At constant pressure, if work of expansion is performed against pressure (P)
\( W = PV'_2 - PV'_1 \), putting this equation in the earlier equation obtained in non flow
process, we get
\[ Q - W = (U'_2 - U'_1) \]
Or, \( Q = W + (U'_2 - U'_1) = PV'_2 - PV'_1 + (U'_2 - U'_1) \)
\[ \therefore Q = \left( U'_2 + PV'_2 \right) - \left( U'_1 + PV'_1 \right) = H'_2 - H'_1 = \Delta H \]
Therefore, heat added to the system at constant volume changes internal energy and
heat added to the system at constant pressure changes enthalpy of the system.

**Units used in energy balance**
(a) erg (dyne cm), Joule (10⁷ erg), Newton–meter (Joule), foot–pound or pound force
(32.174 poundal), foot poundal.
(b) gm–calorie, kilogram calorie, British Thermal Unit (BTU), Centigrade heat unit
(CHU) or pound calorie.

Thermochemical gram calorie
\[ = 4.184 \text{ absolute Joule} \]
I. T. gm calorie
\[ = 4.18605 \text{ International Joule} \]
\[ = 4.18674 \text{ Absolute Joule} \]
1(I. T. g–Cal) /gm = 9/5 BTU/lb
1 BTU = 252 g – cal = 5/5 CHU.

**Example:** One hundred pound of pure C is burnt to CO₂ using dry air (79% N₂, 21%
O₂) theoretically necessary to supply O₂ for combustion. The air and C enters the
burner at 18°C and the product gases leave at 2000°C. The burner is operated at a
constant pressure of 760 mm of Hg. Calculate the amount of heat unaccounted for.
When 1 lb mole of C combined with 1 lb mole of O₂ at atmospheric pressure and
18°C, 169250 BTU is evolved.

Mean heat capacity of CO₂ and N₂ in the temperature range (18–2000°C) at constant
pressure are 23.45 BTU / lb mole – °C and 14.38 BTU / lb mole °C respectively.

**Solution:**
Amount of C = 100/12 = 8.34 lb mole
Amount of O₂ necessary = 8.34 lb mole
Amount of Air necessary = 8.34 × \( \frac{100}{21} \) = 39.7 lb mole
Amount of CO₂ in product = 8.34 lb mole
Amount of N₂ in outlet stream= Amount of N₂ in inlet stream= 0.79 × 39.7 = 31.36 lb
mole
N₂ is tie substance.
Heat Balance of Input
Sensible heat of air, carbon at 18\(^\circ\)C is taken as zero energy level. Potential heat energy content of C in conversion of \(\text{CO}_2\) = \(8.34 \times 169250 = 1411545\) BTU
Heat input = 1411545BTU

Heat Balance of Output
Total sensible heat in gases = \(8.34 \times 23.45 (2000 - 18) + 31.36 \times 14.38 (2000 - 18)\) = 1281422 BTU
Total heat energy = 1281422+ unaccounted for losses
\(\therefore\) 1411545= 1281422+ unaccounted for loss.
Heat unaccounted for losses = 130123 BTU.

Ideal gas law
Ideal gas law is a useful relationship among pressure, volume, mass and temperature that has been utilized in many practical problems: in solvent recovery system, ammonia recovery from air–ammonia mixture, humidification, drying and combustion etc.

Although real gas or vapour does not follow accurately ideal gas law, but ideal gas law is sufficiently useful at ordinary temperature and pressure in many engineering calculations.

Ideal gas law is expressed by \(PV = nRT\),
Where, \(P = \) pressure, \(V = \) volume, \(T = \) Absolute temperature, \(n = \) number of moles of gas.
\(R = \) Gas constant (equal for all gases) = \(8.314.47 \text{ J} / \text{ kg mole / } ^\circ\text{K}\)
\(\quad = 1.9873 \text{ cal/gm mole / } ^\circ\text{K}\)
\(\quad = 82.056 \text{ cm}^3\text{–atm} / \text{ gm mole / } ^\circ\text{K}\)

Ideal gas law is based on some assumptions of kinetic theory:
- Gas molecules behave like elastic spheres and these are free to move and collide with each other and surrounding wall randomly.
- No change in kinetic energy during collision.
- Energy due to intermolecular force of attraction is negligible in comparison to kinetic energy.
- Number of molecules per unit volume in space is constant.

Total translational kinetic energy possessed by one mole of gas is determined by temperature.

Based on the above assumptions the following equation may be derived from the principles of mechanics:
\[PV = n \times \frac{2}{3} \times N \left(\frac{1}{2}mu^2\right) = nRT\]
\[PV = n \times \frac{2}{3} \times \text{x kinetic energy possessed by a mole} = nRT\]
\(n = \) number of mole
\(N = \) Avogadro's number
\(u = \) Average velocity of gas molecule.
When a real gas expands, it has to overcome force of attraction at the expense of its own internal energy.

Let us suppose, pressure of a gas ($P_1$) is changed to $P_2$ so that volume expands from $V_1$ to $V_2$. Now energy due to $P_1V_1$ is not exactly same as $P_2V_2$, since gas spends its own internal energy during expansion in order to overcome intermolecular force of attraction.

At standard condition, volume of ideal gas is 22.4 litres per gm mole or 359 cubic feet per pound mole or 22.4 cubic meter per kg mole. But real gas has volume less than 22.4 litre per kg mole at N.T.P.

Real gas deviates from ideal gas law at high pressure due to compression, so compressibility factor $(Z = \frac{PV}{RT})$ must be introduced. For ideal gas behavior this factor is unity. At standard condition, following specifications are followed.

| Table 6 |
|-----------------|----------|----------|
| Volume / Mole   | Temperature | Pressure |
| 22400 cm$^3$    | 273.15 °K  | 1 atm or 760 mm of Hg |
| 359 cu ft       | 491.69 °R  | 29.92 inch of Hg or 14.7 p.s.i. |

Gas law holding the relationship among mass, pressure, temperature and volume of gaseous substance, often is desired to calculate any one unknown quantity of the above mentioned variables when others are specified with the help of well known Boyles' law and Charles law expression:

$$\frac{P_1V_1}{T_1} = nR = \frac{P_2V_2}{T_2}$$

$$\therefore V_2 = V_1 \times \frac{P_1}{P_2} \times \frac{T_2}{T_1}$$

1, 2 indicate initial and final conditions.

If one condition refers to N.T.P., number of moles ($n$) can be determined on the basis of volume occupied at standard condition.

Let $V_1$ cu ft. changes to $V_2$ cu ft. at standard condition due to changes of pressure and temperature.

Now, $n = \frac{V_2}{359}$; $n$ can also be calculated also if $P_1$, $V_1$ and $T_1$ are known

$P_1V_1 = nRT_1$, unit of $R$ should be consistent with $P$, $V$ and $T$.

When volume of gas expands from $V_1$ to $V_2$ due to changes in pressure or temperature, the ratio $\frac{P_1}{P_2} > 1$ and $\frac{T_2}{T_1} > 1$

When volume of gas decreases from $V_1$ to $V_2$ due to changes in pressure or temperature, the ratio $\frac{P_1}{P_2}$ is $< 1$ and $\frac{T_2}{T_1}$ is $< 1$. 
Gaseous Mixtures
Problem encountered in many practical situations like 'vapor recovery by condensation', scrubbing of ammonia from air–ammonia mixture', fuel gas production by combustion' etc. ‘gases produced in chemical reaction' often deal with mixture of gaseous substances.

In a mixture of different gas molecules, the total pressure is equal to the sum of the pressures (partial) exerted by the molecules of each component gas.

“Dalton's law of partial pressures states that the total pressure exerted by a mixture of ideal gases may be considered to be the sum of the pressures that would be exerted by each of the ideal gases if it alone were present and occupied the total volume”.

“Amagat's law of partial volumes, which states that, in a mixture of ideal gases, each gas can be considered to occupy the fraction of the total volume equal to its own mole fraction and to be at the total pressure of the mixture”.

Ideal gas law is applicable at low pressure, high temperature corresponding to large molal volumes.

Let us consider three gas components (a, b, c) are confined in a volume V at temp T. According to Dalton's law of partial pressure, the following equations can be written:

\[ p_a = \frac{n_aRT}{V} \quad \text{(1)}; \quad p_b = \frac{n_bRT}{V} \quad \text{(2)}; \quad p_c = \frac{n_cRT}{V} \quad \text{(3)} \]

Total pressure = P

\[ P = p_a + p_b + p_c = (n_a + n_b + n_c) \frac{RT}{V} \quad \therefore P = \frac{nRT}{V} \quad \text{(4)} \]

\( n_a, n_b, n_c \) are the number of moles of a, b, c respectively.

Dividing (1) by (4)

\[ \frac{p_a}{P} = \frac{n_a}{n} = N_a = \text{mole fraction of a} \quad ; \quad n \text{ is the sum of number of moles of a, b and c.} \]

Similarly, we get \( \frac{p_b}{P} = \frac{n_b}{n} \) and \( \frac{p_c}{P} = \frac{n_c}{n} \)

\( \therefore \text{Pressure } \% = \text{mole } \% \)

According to Amagat's law, it can be written that

\[ PV_a = n_aRT \quad \text{(5)} \quad PV_b = n_bRT \quad \text{(6)} \quad PV_c = n_cRT \quad \text{(7)} \]

\( v_a, v_b, v_c \) are pure component volumes at pressure P, temperature T.

\[ \therefore P(V_a + V_b + V_c) = (n_a + n_b + n_c)RT \]

or, \( PV = nRT \quad \text{(8)} \)

Dividing (5) by (8), we get

\[ \frac{V_a}{V} = \frac{n_a}{n} = N_a \quad ; \quad V \text{ is the sum of the volume of a, b and c.} \]

Similarly, we get \( \frac{V_b}{V} = \frac{n_b}{n} \) and \( \frac{V_c}{V} = \frac{n_c}{n} \)

\( \therefore \text{Volume } \% = \text{mole } \% \).
Combining Dalton's law of partial pressure and Amagat's law of partial volume, the following expression can be written:

\[ \text{pressure \%} = \text{mole \%} = \text{volume \%} \]

This expression is widely used in solving problems of gaseous system.

**Problem on gas laws**

1. It is desired to construct a drier for removing 100 lb of water from wet granules per hour. Air is supplied to the drying chamber at 151°F at atmospheric pressure (humidity of air 8.35 x 10^{-3} lb mole / lb mole. If the air leaves the drier at temperature of 95°F at atmospheric pressure (humidity of air = 30 x 10^{-3} lb mole / lb mole), calculate the volume of air at the initial conditions that must be supplied per hour.

**Solution:**

**Basis: 1 hr.**

In tablet manufacturing by wet granulation method, drier is indispensable equipment and humidity of air is a serious parameter to be considered both for drying operation and designing of drier.

Let us know about the definition of humidity

Molal humidity is defined as

\[ \text{molal humidity} = \frac{\text{number of moles of moisture}}{\text{number of moles of moisture free gas}} \]

Number of moles of moisture to be removed from wet material = \frac{100}{18} lb mole

From humidity data –

\[ \frac{\text{Number of mole of moisture removed}}{\text{Number of mole of moisture free air}} = (30 - 8.35) \times 10^{-3} \text{ lb/mole.} \]

= 0.02165 lb mole/lb mole

So we can write,

\[ \left( \frac{100}{18} \right) \text{ lb mole of moisture is removed from} \left( \frac{100}{18} \right) / 0.02165 \text{ lb mole of moisture free air. Therefore, 256.6076 lb mole of moisture free air enters the drier.} \]

Volume of inlet air \( V_1 \) can be calculated by using **ideal gas law**.

\[ 760 \times V_1 = \frac{760 \times 256.6076 \times 359}{(459.6+151)} \]

or \( V_1 = 114421.83 \text{ cu ft} \)

(349 cu ft is the volume of 1 mole at standard conditions).

**Answer:** 114421 cu ft (approx.) of air is supplied per hour to remove 100 lb of moisture from wet material.

Following is another example of application of gas law.

2. A combustion gas at temperature of 210.6°C and pressure of 1 atm is humidified.

The gas leaves the humidifier at 94.93°C and a pressure of 1 atm.

**Table 7: Composition (mole %) of gas**

<table>
<thead>
<tr>
<th>Component</th>
<th>Inlet gas</th>
<th>Outlet gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>79.2</td>
<td>48.3</td>
</tr>
<tr>
<td>Oxygen</td>
<td>7.2</td>
<td>4.4</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>13.6</td>
<td>8.3</td>
</tr>
<tr>
<td>Water</td>
<td>0</td>
<td>39</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100</strong></td>
<td><strong>100</strong></td>
</tr>
</tbody>
</table>
Calculate (a) weight of water evaporated per 100 cu ft of inlet gas (b) volume of gas leaving the humidifier per 100 cu ft of inlet gas.

**Solution**

**Basis:** 1 gm – mole of inlet / entering gas

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole fraction</th>
<th>number of mole</th>
<th>Volume of mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>0.792 gm mole</td>
<td>(nₐ)</td>
<td>Vₐ</td>
</tr>
<tr>
<td>O₂</td>
<td>0.072 gm mole</td>
<td>(n₉)</td>
<td>V₉</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.136 gm mole</td>
<td>(n₃)</td>
<td>V₃</td>
</tr>
<tr>
<td>Total</td>
<td>1 gm mole</td>
<td>N</td>
<td>V</td>
</tr>
</tbody>
</table>

Now, volume of inlet gas (V) at initial conditions is calculated with the help of 'Amagat's law' equation

\[
\frac{V}{P} = \frac{1 \times 82.06 \times (273 + 210.6)}{RT} = 39684.22 \text{ c.c.} = 1.401435 \text{ cu ft} \approx 1.401 \text{ cu ft.}
\]

Let x be the number of mole of water added to entering air during humidification.

\[\frac{x}{x + 1} \times 100 = 39 \quad \text{or} \quad x = 0.6393 \text{ gm mole} \]

\[= \frac{0.6393 \times 18}{453.6} = 0.025369 \text{ lb} \]

453.6 gm = 1 lb, Molecular weight of water is 18

for, 1.401 cu ft of entering air 0.025369 lb of water is needed

100 cu ft of entering air \[\frac{0.025369 \times 100}{1.401} \approx 1.81 \text{ lb} \]

Number of mole of outlet / leaving gas per 1 gm mole of inlet gas is (1+0.6393)

Volume of leaving gas

\[= \frac{1.6393 \times 82.06 \times (273 + 94.93)}{1} = 49494.296 \text{ c.c.} \approx 1.7478 \text{ cu ft} \]

For 1.401 cu ft of inlet gas, volume of outlet gas = 1.7478 cu ft.

For 100 cu ft of inlet gas, volume of outlet gas = \[\left(\frac{1.7478}{1.401}\right) \times 100 \approx 124.75 \text{ cu ft.} \]

**Answer:** Weight of water evaporated during humidification of gas and volume of gas leaving the humidifier per 100 cu ft of entering gas are respectively 1.81 lb. (approx.) and 125 cu.ft (approx.)

**Problem**

Pure methane gas (CH₄) is completely burnt with air. Excess air is not considered here. The mixture of gases leaving the combustion chamber is passed through a condenser where 30 lb of water is condensed. Calculate the following:

a.(i) Composition of mixture of gases leaving the condenser.
(ii) Mole fraction of nitrogen in the gas mixture leaving the condenser.
(iii) The average molecular weight of the mixture of gases leaving the condenser.
(iv) The partial pressure of moisture that exists with the leaving gases at total pressure of 18 psia.

b. How much amount of water is condensed if mole fraction of nitrogen in the gas mixture leaving the condenser is 0.8?

**Dimensional analysis**

Dimensional analysis is a conceptual tool often applied in Engineering and Science to attack a complicated problem for which no formal mathematical equation could be derived. It is often the basis of mathematical models of real situation. This method is intermediate between formal mathematical development and completely empirical method. Dimensionless groups are generated after analysis of variables involved in a phenomenon by dimensional analysis method. Fluid flow when analyzed, Reynolds number is generated.

Problems of this type are specifically found in fluid flow, heat flow, powder flow and diffusional operations. In empirical method, effect of each independent variable on dependent variable is studied by systematically varying that variable while keeping rest of the variables constant. The drawbacks of this method are that the procedure is lengthy and laborious and difficult to organize the results to a useful correlation for further calculation and the correlation is usually not dimensionally homogeneous.

Engineers and physicists often utilize ‘Dimensional analysis method’ to develop relationships among variables of physical quantities that are involved in a particular phenomenon. There are two ways in dimensional analysis method.

1. Raleighs method of indices (Algebraic summation method)
2. Buckingham method (dimensional groups can be shown as zero power of a group of variables).

Dimensional analysis is an algebraic treatment of the symbols for units considered independently of magnitude. This method rapidly simplifies the task of fitting experimental data to derive a dimensionally homogeneous equation.

Dimensional analysis of a particular problem is made complete by knowing entire physics of the situation that reveals all possible variables involved in that problem and related basic laws. In this method, many variables are assembled in a group that is dimensionless. Dimensionally homogeneous equation consists of more than one dimensionless group. However, it does not give numerical equation. These groups may carry exponents of any magnitude, not necessarily whole numbers but a pure number of dimensionless.

Numerical values of exponents, proportionality constant are determined by putting experimental data in that correlation. The final correlation helps to find value of unknown variable if other values of variables / physical quantities are known. Any system of units (fps, cgs, SI) may be used to calculate numerical value of dimensionless groups. For example, Reynolds group or number, \(N_R = \frac{Du}{\mu}\); it is used in fluid flow,

Where, \(D = \) diameter of pipe  
\(u = \) Velocity of fluid
e = Density of fluid
µ = Viscosity of fluid.

Value of \( N_{Re} \) would be same irrespective of system of units.

Now, \( N_{Re} \) is found dimensionless putting cgs and fps system of units

\[
N_{Re} = \frac{Du\rho}{\mu} = \frac{cm \times cm/s \times gm/cm^3}{gm/cm.s} = 1 \quad \text{or} \quad N_{Re} = \frac{ft \times \frac{ft}{s} \times lb}{lb/ft.s} = 1
\]

This method is advantageous in checking the consistency of the units in equations, in converting units and in scale up of data obtained in sample experiments to predict the performance of full–scale equipment, in reducing number of independent variables.

This is based on concept of dimension and dimensional formulas.

Following steps are followed in Raleigh's method of indices.

**Step–1.** All the variables / parameters (dependent and independent) are entered as a function in a correlation.

**Step–2.** (a) Independent variables are assigned exponents, (b) all the variables are expressed with their respective standard dimensions (Mass – M, Length – L, Time – θ).

**Step–3.** The sums of the exponents relating to any given dimension (Mass, for example) must be same on both sides of the equation. So, algebraic equations are obtained by balancing exponents.

**Step–4.** The above equations are solved to obtain simplified value or expression of one exponent in terms of others.

**Step–5.** Exponents obtained in Step–4 are put in Step–2.

**Step–6.** Variables are assembled in-groups in such a way, that these are found as dimensionless groups.

Finally these groups are entered in an equation, which is dimensionally homogeneous. Following is an example of dimensional analysis method:

Dimensional analysis of variables involved in mass transfer of fluid flow operation.
From the mechanism of mass transfer it can be expected that the mass transfer coefficient, \( K_c \) would depend on the diffusivity, \( D_v \) and on other controlling variables like velocity, \( u \); viscosity, \( µ \); density, \( ρ \) of fluid flowing through a pipe and linear dimension, \( D \).

\[
K_c = f(D_v, D, u, \mu, \rho)
\]

or, \( K_c = A D_v^a D^b u^c \mu^d \rho^e \) \( \ldots(1) \)

\( K_c \) – Standard dimension – L/θ

\( D_v \) – Standard dimension – L^2/θ

\( D \) – Standard dimension, L

\( u \) – Standard dimension, L/θ

\( \mu \) – Standard dimension, M/Lθ
\[ \rho - \text{Standard dimension, } M/L^3 \]

Equation (1) may be written as

\[
\frac{L}{\theta} = A \left( \frac{L}{\theta} \right)^a L^b \left( \frac{M}{L^2} \right)^c \left( \frac{M}{L^2} \right)^d \left( \frac{M}{L^2} \right)^e
\]

A is proportionality constant and \( a, b, c, d \) and \( e \) are exponents.

Now, balancing exponents of \( M, L, \theta \) we get the following equations

\[
\begin{align*}
0 &= d + e \quad \text{...}(2) \\
1 &= 2a + b + c - d - 3e \quad \text{...}(3) \\
1 &= a + c + d \quad \text{...}(4)
\end{align*}
\]

From equation (2), \(-d = e\).

From equation (3), we get

\[
1 = a + b + a + c - d + 3d
\]

or, \( 1 = a + b + (a + c + d) + d \)

or, \( 1 = a + b + 1 + d \)

or, \( a + b = -d = e \)

From equation (4), we get

\[
d = 1 - (a + c)
\]

or, \( e = a + c - 1 \)

Since \( a + b = -d \)

\[
\therefore b = -a - d = -a - (1 - a - c)
\]

or, \( b = c - 1 \)

Now the exponents are arranged serially.

\( a, c - 1, c, 1 - a - c, a + c - 1 \)

Putting the above exponents in equation (1), we get

\[
K_c = AD^a D^{c-1} (u)^c (\mu)^{1-a-c} (\rho)^{a+c-1}
\]

or,

\[
K_c = A \left( \frac{D\mu}{\mu} \right)^c \left( \frac{\mu}{D\rho} \right)^{1-a-c} \left( \frac{\mu}{D\rho} \right)^{a+c-1}
\]

Both L.H.S. and R.H.S. are divided by \( u \)

or,

\[
\frac{K_c}{u} = A \left( \frac{D\mu}{\mu} \right)^c \left( \frac{\mu}{D\rho} \right)^{1-a-c} \left( \frac{\mu}{D\rho} \right)^{a+c-1}
\]

Both L.H.S. and R.H.S. are multiplied by \( \left( \frac{D\mu}{\mu} \right) \times \left( \frac{\mu}{pD_v} \right) \)
or,
\[
\frac{KcD}{D_v} = A\left(\frac{\text{Dup}}{\mu}\right)^{b+1}\left(\frac{\mu}{\rho D_v}\right)^{1-a}
\]

Therefore, we get 3 groups which are known as Sherwood number, \(N_{sh}\left(\frac{KcD}{D_v}\right)\); Reynolds number, \(N_{Re}\left(\frac{\text{Dup}}{\mu}\right)\); Schmidt number, \(N_{Sc}\left(\frac{\mu}{\rho D_v}\right)\)

These groups are found dimensionless by putting respective units.

\[
N_{sh} \left(\frac{KcD}{D_v}\right) = \frac{\text{cm/s.cm}}{\text{cm}^2/\text{s}}
\]
\[
N_{Re} \left(\frac{\text{Dup}}{\mu}\right) = \frac{\text{cm*cm/s.gm/cm}}{\text{gm/cm3/s}}
\]
\[
N_{sc} = \frac{\mu}{\rho D_v} = \frac{\text{gm/cm/s}}{\langle\text{gm/cm}^3\rangle \cdot \text{cm}^2/\text{s}}
\]

Total number of variables is 6.

Total number of standard dimension is 3 (M, L, θ).

Total number of dimensionless groups is 6 – 3 = 3.

The numerical values of A, are determined with the help of experimental data.

Thus, dimensionless correlation is developed by dimensional analysis method. Here, M, L, θ are the standard dimensions used for primary physical quantities. Secondary physical quantities are expressed by dimensional formulas; for example, for Force, \(F\) \(\text{ML}/\theta^2\) used.

In the mixing of liquid, some factors like speed of impellor (n), diameter of impellor (Da), Newton's law proportionality factor (gc), acceleration due to gravity (g) viscosity (μ) and density of fluid (ρ) and shape factors control power (P) delivered by

the impeller. By applying dimensional analysis, power number \(N_p\), \(\left(\frac{P_{gc}}{\rho n^2 Da^2 \frac{\gamma}{\mu}}\right)\) is expressed as function of Reynolds number, \(N_{Re}\left(\frac{n Da^2 \rho}{\mu}\right)\) and Froude number \(N_{Fr}\left(\frac{n^2 Da}{g}\right)\) while ignoring shape factors.

Following are some other examples of dimensionless groups.

Fannings friction factor, \(f\); Nusselt number, \(N_{Nu}\), Prandtl number, \(N_{Pr}\) .
**Reynolds number** (\( \text{Du} / \mu \)) is a measure of type of fluid flow (laminar, turbulent) through a tubular pathway. This expression is different in mixing of liquid (\( N_{\text{Re}} = nD_a^2 \rho / \mu \)), here velocity term is proportional to \( nD_a \) where
\( n \) is the r.p.m. of the impellor and \( D_a \) is the diameter of impellor.

**Froude number** is a measure of the ratio of the inertial stress to the gravitational force per unit area acting on the fluid.

**Nusselt number** (\( N_{\text{nus}} = hD/k = D/x \)) is the ratio of the tube diameter to the equivalent thickness (\( x \)) of the laminar layer. This number has application in heat transfer phenomenon. \( h \) is the heat transfer coefficient (BTU/ft\(^2\)-h-°F) and \( k \) is the thermal conductivity (BTU/ft-h-°F).

**Prandtle number** is a measure of momentum diffusivity relative to that of the thermal diffusivity. Its numerical value depends on temperature, pressure of fluid.

**Power number** is proportional to the ratio of the drag force acting on a unit area of the impellor and the inertial stress.

Fannings friction factor is defined as the ratio of the wall shear stress to the product of the density and velocity head.

**Different types of Graph plotting**

Graph plotting is done on graphical sheets in many ways, along its axes so that plotted data at various location of sheet are displayed. This may help in many ways –

- Exhibit relative position / location of various data that represent one variable with respect to another variable.
- Develop correlation between variables.
- Extrapolation of curve to find unknown data.

There are different types of plotting system. So, various types of graph papers with axes of different types of graduation are available, such as

1. Cartesian graph papers in which both the axes are graduated evenly or linearly.
2. Semi logarithmic graph paper and logarithmic graph paper or log–log graph paper.
3. Triangular diagrams or ternary plotting.

In semi logarithmic graph paper one axis is graduated with logarithmic value and another axis is graduated linearly. In log–log paper both the axes are graduated with logarithmic value. So, logarithmic scale is not uniform. Presentation of data on a logarithmic scale can be helpful when the data covers a large range of values. Before the advent of computer graphics, logarithmic graph paper was a basic scientific tool.

Logarithmic graph plotting reduces the tedious task of converting a good number of physical quantities to its log value as required by the correlation. It was difficult to locate a point specifically when log values of data were very small and negative and data range is comparatively wide.

There are numerous exponential equations such as first order rate equation, microbial growth equation, cell death kinetics and nutrient degradation kinetics equation etc.
One famous equation known as Arrhenius equation, \( K = Ae^{-\frac{E_a}{RT}} \) can be used for explaining method of semi logarithmic graph plotting. The above equation can be written as:

\[
\log_{10} K = -\frac{E_a}{2.303RT} + \ln A \; ; \text{This is straight-line equation.}
\]

Now, suppose we want to determine unknown quantity \( E_a \) (energy of activation). Therefore, data obtained for the reaction rate constant, \( K \) and the reciprocal of temperature \( (1/T) \) are plotted on y axis (log–scale) and on x axis (linear scale) respectively.

\[ -\frac{E_a}{2.303R} = \text{Slope of the straight line} \]

\[
\frac{\log y_2 - \log y_1}{x_2 - x_1} = \frac{\log \left( \frac{y_2}{y_1} \right)}{x_2 - x_1}
\]

where \((x_1, y_1)\) and \((x_2, y_2)\) are the co–ordinates of two points on the straight line and \( R \) is gas constant.

Average value of \( E_a \) is determined with the help of at least three pairs of co–ordinates of points that exist on different parts of straight line. 'A' is determined by putting '\( E_a \)' value and any co–ordinate of point that lie on the straight line, in Arrhenius equation.

Another equation used for Non–Newtonian flow, \( F^N = \mu G \) can be written as,

\[ \log G = N \log F - \log \mu \]

Where, \( F \) = shear stress, \( G \) = Rate of shear strain, \( \mu \) = Co efficient of viscosity of fluid, \( N \) is exponent.

In the above equation, both the variables \((F, G)\) are expressed in log form. Then \( \mu \) can be determined by plotting data of \( F \) on x-axis and data of \( G \) on y-axis of log–log graph paper. Here, both the axes are graduated according to logarithmic scale. When the plot appears as straight line slope is determined by the following expression:

\[ N = \text{slope} = \frac{\log y_2 - \log y_1}{\log x_2 - \log x_1} = \frac{\log \left( \frac{y_2}{y_1} \right)}{\log \left( \frac{x_2}{x_1} \right)} \]

Putting the average value of \( N \) and co–ordinate value of a point on the equation of straight line, '\( \mu \)' is determined.

Logarithmic scale can be developed along the axes according to values of \( \log_{10} x \) \((x = 1 \text{ to } 10)\). A network of lines is then ruled onto the paper based on the non–linear scales of antilogarithm. That is, antilogarithmic values (anti \( \log_{10} x = x \), for example, it is written as 1,2,3…...) are shown on the axes. The same style of graduation is repeated after one such cycle \((x=1 \text{ to } 10)\) is completed. Each cycle has 9 nonlinear divisions. Each division is further graduated into smaller divisions. End of one cycle is 10 times the starting value of this cycle. Axis is graduated according to data range. Following is an example of axis graduation:

\[
\begin{align*}
0.1 & , 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, (1), 2, 3, 4, 5, 6, 7, 8, 9, (10), 20, 30, 40, 50, 60, 70, 80, 90, (100); 
\end{align*}
\]
Here, value (1), (10), (100) indicate end of cycle or starting of next cycle. Numerous data can be plotted easily and directly on graph paper without converting these to corresponding logarithmic values. The only disadvantage of the logarithmic plot is that the scales normally used cannot be read too closely, but in most cases points can be plotted with accuracy comparable to the accuracy of ordinary engineering data. An advantage of log–log plotting is that deviations of point from a curve of a given distance represent deviation of a constant percent of the total value of the variable at that point, irrespective of the part of the plot in which it exists.

Following is an example of log–log plotting of two variables (x, y).

\[ y = kx^n \] – this is a correlation between x and y and k and n are constants.

<table>
<thead>
<tr>
<th>x</th>
<th>3.4</th>
<th>4.5</th>
<th>5.5</th>
<th>5.9</th>
<th>7</th>
<th>7.55</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>y</td>
<td>30.3</td>
<td>55</td>
<td>75</td>
<td>93.5</td>
<td>137</td>
<td>175</td>
<td>280</td>
</tr>
</tbody>
</table>

The data are plotted on the log log sheet and the straight–line curve is obtained.

![Plotting on log-log graph paper](image)

Average slope (n) is found as 0.4713.
The data cannot be extrapolated to determine the intercept, where x = 1 goes far beyond the scale of plot. By putting n = 0.4713 and any co–ordinate (170, 7.8) in the equation, K is found as 0.693.

**Graphical Integration**

Graphical Integration is sorted when no mathematical correlation helps to determine one of the variables when a variable changes with respect to another. The addition or integration of small changes (dy) in dependent variable with respect to small change (dx) in independent variable gives the value of total change in y within some limits. From the first principle of integral calculus, we know the value of a definite integral is the area bound by the curve of f(x) vs. x, the ordinates at x = x_a and x = x_b and x axis.

\[ \int_{x_a}^{x_b} f(x)dx = \int_{y_a}^{y_b} f'(x)dx \] …(1) \( f'(x) \) is the derivative of original function, \( y = f(x) \)
If the derivative \( f'(x) \) is very simple type i.e. \( y = x^3 \) or \( \frac{dy}{dx} = \frac{x^4}{4} \), it can be integrated by analytical method of integration.

There are equations that cannot be integrated so easily. For example: Rayleigh's equation in differential distillation,

\[
\int_{w_0}^{w_1} \frac{dW}{W} = \ln \frac{W_0}{W_1} = \int_{x_0}^{x_1} \frac{dx}{(y-x)} ; \quad W_0 \text{ and } W_1 \text{ are the initial and final weight in moles respectively and } x \text{ and } y \text{ are the liquid and vapor composition of the component respectively.}
\]

In the above equation, right hand side can be integrated graphically with the help equilibrium data \((x, y)\) and \(x_0, x_1\). Though, \(x\) and \(y\) are related with each other but there is no mathematical correlation between \(x\) and \(y\) so that it can be integrated by analytical method of integration, therefore the area under the correlating curve \((1/(y-x))\) vs. \(x\) within limits \(x_0, x_1\) are measured. Right hand side \((1/(y-x))\) \((dx)\) gives area concept. So, numerical value of area may be taken same as integral value. The area under the curve within the limits may be determined by dividing the area into a number of rectangular strips and adding area of all rectangles. Each of these may not be perfect rectangle due to nonlinearly of curve.

Each rectangular, strip is made a perfect 'rectangle' in such a way the area of a triangle excluded due to new rectangle formation is approximately equal to the area of new triangle included in the rectangle above the curve. Area of each rectangle is calculated by multiplying its height and width and then all the areas are added to get the desired value of integral. Following example will help undergraduate students to understand the method of graphical integration.

A given variable \(z\) is a function of the two variable \(x\) and \(y\) such that \(z = \int_{x_0}^{x_1} ydx\).

Integrate the function over the range from \(x = 0.2\) to \(x = 0.4\) by graphical method.

<table>
<thead>
<tr>
<th>Table 10</th>
</tr>
</thead>
<tbody>
<tr>
<td>(x)</td>
</tr>
<tr>
<td>(y)</td>
</tr>
</tbody>
</table>

Solution:
Following steps to be followed:
1. Plot the curve \(y\) vs. \(x\).
2. Draw vertical lines at \(x = 0.2\) and \(x = 0.4\) intersecting the above curve.
3. Split the area under the curve, vertical lines and axis into number of rectangles with width, \(dx = 0.05\).
4. Draw a vertical dotted line through the mid point of each width that intersects the curve at a point. Through this point of intersection, draw a short horizontal line along each width. Now, a perfect rectangle informed. Height of each rectangle is tabulated in a column.
Table 11

<table>
<thead>
<tr>
<th>Rectangle</th>
<th>Width of rectangle</th>
<th>Height of rectangle</th>
<th>Area of rectangle</th>
<th>Total area = cumulative area</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.05</td>
<td>0.715</td>
<td>0.03575</td>
<td>0.03575</td>
</tr>
<tr>
<td>b</td>
<td>0.05</td>
<td>0.760</td>
<td>0.03800</td>
<td>0.07375</td>
</tr>
<tr>
<td>c</td>
<td>0.05</td>
<td>0.745</td>
<td>0.03725</td>
<td>0.1110</td>
</tr>
<tr>
<td>d</td>
<td>0.05</td>
<td>0.650</td>
<td>0.0325</td>
<td>0.1435</td>
</tr>
</tbody>
</table>

Therefore, \( Z = 0.1418 \)

Fig. 6: Plot for Graphical Integration

**Graphical differentiation**

When two variables \((x, y)\) are simply related with each other and then differentiation \(\left(\frac{dy}{dx}\right)\) can be done easily by analytical method. If it is not so, then it can be done with the help of mathematical correlation. If it is not so, then it can be done by graphical method with the help of experimental data. First, a histogram like plot is made relating finite derivative \(\left(\frac{\Delta y}{\Delta x}\right)\) against \(x\), where width of each rectangle is \(\Delta x\) and height is \(\Delta y/\Delta x\). Finite derivative \(\left(\frac{\Delta y}{\Delta x}\right)\) is calculated with the help of experimental data \((x, y)\). A particular \(\Delta y\) value is constant for particular range \(\Delta x\). \(\Delta x\) is not infinitesimally small value. Infinite derivative value \(\left(\frac{dy}{dx}\right)\) at any value of \(x\) can be obtained by drawing a curve that connects all the mid points of range \((\Delta x)\) corresponding to each \(\Delta y/\Delta x\) value. Now derivative \(dy/dx\) at any value of \(x\) can be obtained with the help this curve.

**Ternary Plot**

The ternary plot or triangular diagram is a specialization of bary centric plot for three variables. It graphically depicts the ratios of three proportions. It is often used in petrology, mineralogy and other physical sciences to show the relative composition of
soils and rocks, but it can be more generally applied to any system of three components.

Pharmaceutical formulation often deals with multicomponent liquid system, which may not appear homogeneous as desired if composition is not properly formulated. This can be achieved by altering composition of chemicals. This needs a trial. This kind of plotting is useful in extraction problems also. Ternary diagram and plotting of three component system help to determine amount of solvent needed to extract a component from another solvent. Let us suppose two component A and B are soluble with each other and we want to add to a certain quantity of C. After addition of C, the liquid may be found as heterogeneous or homogeneous system depending upon the respective amounts of A, B and C. It needs time consuming trial to prepare desired system. It is better to make a graphical chart. This can be done by a method known as Ternary plotting or plotting in triangular diagram. Different compositions are prepared first and its homogeneity or heterogeneity is observed and then a curve is plotted within this triangle. The curve is a boundary between homogeneous composition and heterogeneous compositions. Once the plot is ready, composition is selected according to the need of the formulation.

<table>
<thead>
<tr>
<th>Table 12</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
</tr>
<tr>
<td>B</td>
</tr>
<tr>
<td>C</td>
</tr>
</tbody>
</table>

In dealing with three component systems, compositions may be represented by points within a triangle, each point representing one unique composition. While an equilateral triangle is frequently used but a triangle of any shape may be employed.

In a ternary plot, each variable (a, b, c) is represented as 1 (as fraction) or 100 (as %) when it exists as single component. Therefore, if composition (%) of two variables (a, b) are known in the system (a, b, c), then c can be easily determined. Each base or side of the triangle represents a proportion of 0% of a particular component, with the point (apex) of the triangle opposite to that base represents a proportion of 100% of that component in the system (a/b/c). As a proportion increases in any one of the samples, representing point moves from base towards its apex up to increased proportion. Now, a straight line passing through this point intersects another line passing through the point corresponding to another variable's proportion.

The point of intersection represents composition of a, b and c in that particular sample. In this way, point is located within a triangle.

Following figure illustrates triangular or ternary plot of 3 component system (a, b, c). A graphical plot is made with the help of following compositions.
Fig. 7: Ternary plot of a three component system

In the above figure, each apex represents 100% of a component. The apex (A) of above triangle represents 100% of component ‘a’. Points on the line opposite to an apex contain none of the material corresponding to the apex. So, the points on the line B–C have no component of ‘a’. Each edge represents binary composition of two components; for example, line A–B represents compositions of mixture of A and B. The closer a point is towards apex A, the more of the component ‘a’ in the mixture. The mole % component ‘a’ at C is zero. The lines a’, b’, c’ are parallel to the edges of the triangle and intersect at the point P. P represents the composition (a – 40%, b – 30%, c – 30%) of a 3 component system that is presented in the above table by encircled data. The mole fraction of ‘a’ at P is given by the following expression:

\[
\frac{\text{The perpendicular distance from line B – C to line a - a'}}{\text{The perpendicular distance from line B – C to A}} = \frac{c}{ca} = 0.4/1=0.4
\]

Aaa’ and ABC are similar triangles.

The zone under the curve (Fig.7) represents some physical characteristics of the system. This type of curve is exhibited in liquid – liquid extraction .When composition falls within the curved area, two solvent phases (extract and raffinate) separate out. So, the composition is selected in such a way that liquid phases can be separated out after extraction is over.

References: