

Material balances

Material balances:-

A material balance is nothing more than the application of the law of the conservation of mass: "Matter is neither created nor destroyed."

Although the conservation of mass is a simple concept, detailed explanations are required to enable you to be able to apply it to a full range of chemical engineering systems.

a. System.

The system **is mean any arbitrary portion of** or a whole process that you want to consider for analysis, such as a reactor, a section of a pipe. or an entire refinery by stating in words what the system is.

The second define the system by drawing the system boundary, namely a line that encloses the portion of the process that you want to analyze.

b. Closed system.

Closed system that is the system not enters nor leaves the vessel. That is, no material crosses-the system boundary.

Closed system. Changes can take place inside the system, **but for a closed system,** **((No mass exchange occurs with the surroundings)).**

هو النظام الذي لا يحدث تبادل للكتلة مع محيط.

c. Open system.

Open system: (also called a flow system) is the system that is material crosses the system boundary.

النظام المفتوح: (يسمى أيضاً نظام التدفق) هو النظام الذي تعبر المادة حدود النظام.

*****PROCESS CLASSIFICATION-:**

Accumulation: An increase or decrease in the material (e.g., mass or moles) in the system.

Batch process: A process in which material is neither added to nor removed from the process during its operation.

Closed system: A system that does not have material crossing the system boundary.

Component balance: A material balance on a single chemical component in a system.

Conservation or mass Matter is neither created nor destroyed overall.

Consumption: The depletion of a component in a system due to chemical reaction.

Continuous process: A process in which material enters and/or exist continuously.

Final condition: The amount of material (e.g., mass or moles) in the process at the end of the processing interval.

Flow system: An open system with material entering and/or leaving.

Generation: The appearance of a component in a system because of chemical reaction.

Initial condition: The amount of a material (e.g. mass or moles) in the process at the Beginning of the processing interval.

Input Material: (e.g., mass, moles) that enters the system.

Material balance: The balance equation that corresponds to the conservation of mass.

Negative accumulation: A depletion of material (usually mass or moles) in the system.

Open system: A system in which material crosses the system boundary.

Output: Material (e.g. mass, moles) that leaves the system.

Rate: Flow per unit.

Semi-batch process: A process in which material enters the system but product is not removed during operation.

Steady-state system: A system for which all the conditions (e.g., temperature, pressure, amount of material) remain constant with time.

System: Any arbitrary portion of or whole process that is considered for analysis.

System boundary: The closed line that encloses the portion of the process that is to be Analyzed.

Transient system: A system for which one or more of the conditions (e.g., temperature, pressure, amount of material) of the system vary with time. Also known as an unsteady-state system.

Unsteady-state system: A system for which one or more of the conditions (e.g., temperature, pressure, amount of material) of the system vary with time. Also known as a transient system.

Types of Material Balance Calculations:-

It is convenient to study material balance calculations by putting them in four separate section:-

- 1- Material balances without chemical reactions.
- 2- Material balances with chemical reactions.
- 3- Material balance on combustion processes.
- 4- Material balance on processes involving Recycle, Bypass, and purge streams.

$$IN - OUT + GEN. - CONS. = ACC. \quad \text{unsteady with reaction}$$

$$IN - OUT = ACC. \quad \text{unsteady without reaction}$$

$$IN = OUT \quad \text{steady stat without reaction}$$

The Strategy for Solving Problems:-

1. Read and understand the problem statement. 1. اقرأ وافهم السؤال جيدا (المشكلة).
2. Draw a sketch of the process and specify the system boundary. 2. ارسم مخططاً للعملية وحدد حدود النظام.
3. Place labels (symbols, numbers, and units) on the diagram for all of the known flows, materials, and compositions. For the unknown flows, materials, and compositions insert symbols and units. Add any other useful relations or information. 3. ضع ملصقات (الرموز والأرقام والوحدات) على الرسم البياني لجميع التيارات والمواد والتركيبات المعروفة. بالنسبة للتيارات والمواد والتركيبات غير المعروفة ، أدخل الرموز والوحدات أضف أي علاقات أو معلومات مفيدة أخرى.
4. Obtain any data you need to solve the problem, but are missing. 4. الحصول على أي بيانات تحتاجها لحل المشكلة ، وهي مفقودة.
5. Choose a basis. 5. اختر الأساس.
6. Determine the number of variables whose values are unknown (the *unknowns*). 6. تحديد عدد المتغيرات التي تكون قيمها غير معروفة (المجهولة).
7. Determine the number of independent equations and carry out a degrees of freedom analysis. 7. تحديد عدد المعادلات المستقلة وإجراء درجات الحرية لغرض التحليل.

موازنة مادة بدون تفاعل كيميائي وعلى جهاز واحد

الكمية الداخلة لكل مادة = كميتها الخارجة

$$IN = OUT$$

كمية بالوزن للمادة

$$wt \% = \frac{wt}{Total\ wt} \times 100$$

نسبة مئوية الوزنية

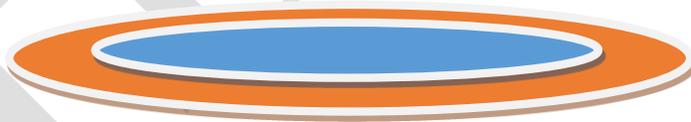
الوزن الكلي للخليط او المحلول (basis) قيمة خط

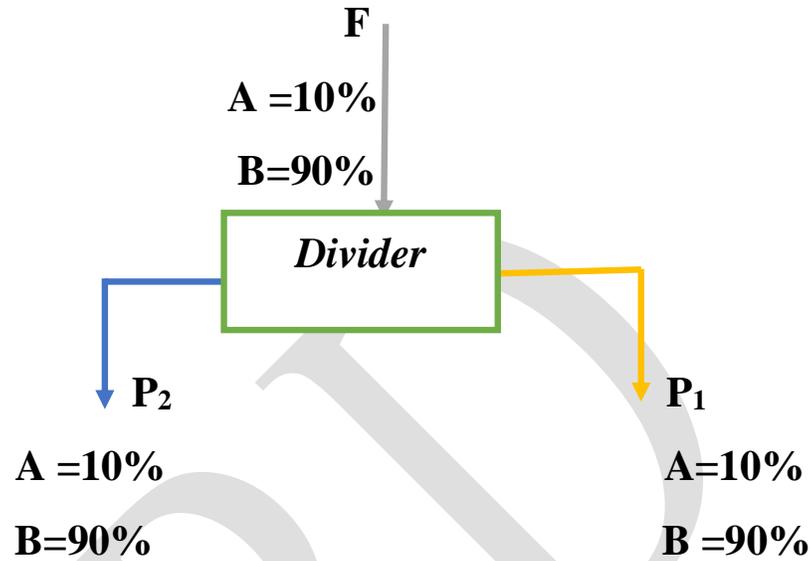
في حالة عدم اعطاء basis (لا وزن ولا حجم ولا مولات الخليط) يتم فرض Basis من قبل الطالب.

• يمكن عمل موازنات بقدر عدد المواد الموجودة بالجهاز بالاضافة الى

معادلة T.M.B تعني (TOTAL MATERIAL BALANCE)

يستفاد منها للتحقق من صحة الحل *Checking*



Equipment:-1// **divider:-****M.B. on A**

$$(10/100) * F = (10/100) * P_1 + (10/100) * P_2$$

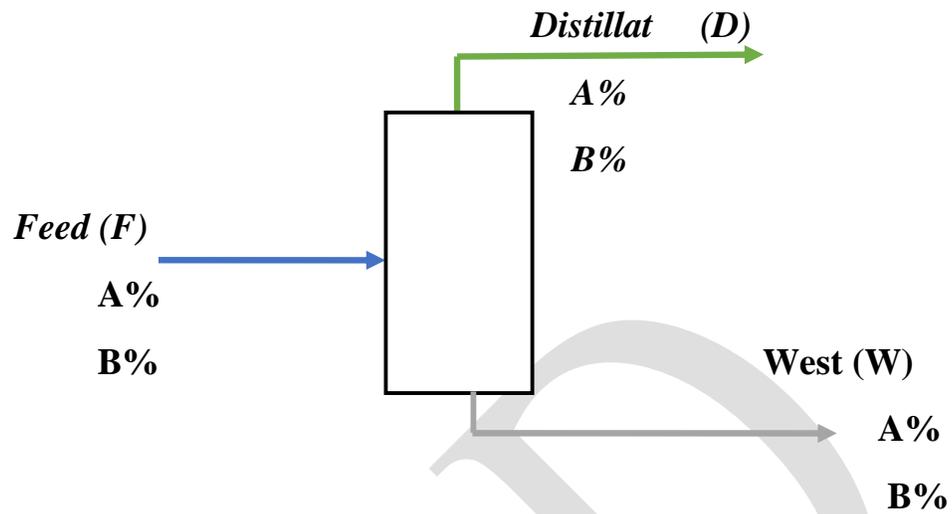
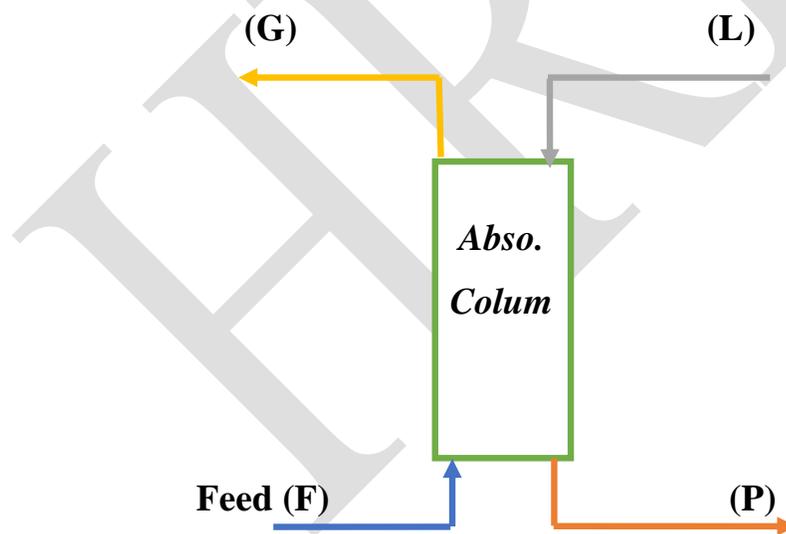
$$F = P_1 + P_2$$

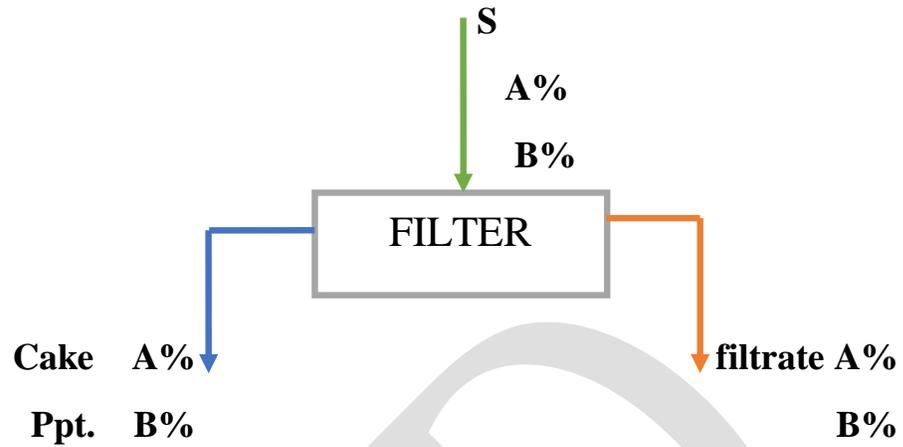
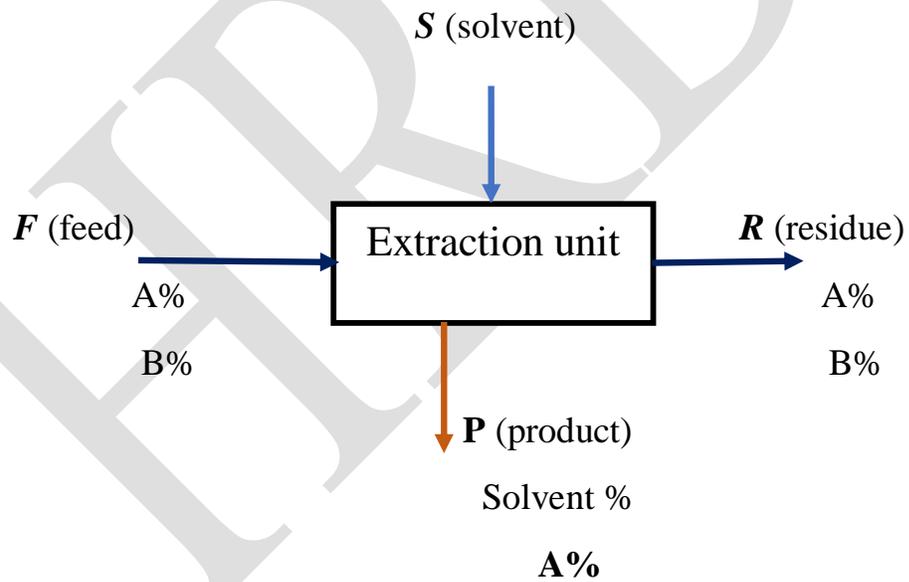
M.B. on B

$$(90/100) * F = (90/100) * P_1 + (90/100) * P_2$$

T.M.B.

$$F = P_1 + P_2$$

2// DISTILLATION:-3// Absorption

4// FILTER:-**5// Extraction unit**

Material balances without chemical reactions.

EXAMPLE 8.2:- Separation of Gases Using a Membrane:

Membranes represent a relatively new technology for the separation of gases. One use that has attracted attention is the separation of nitrogen and oxygen from air. Figure E8.2a illustrates a nano porous membrane that is made by coating a very thin layer of polymer on a porous graphite supporting layer. What is the composition of the waste stream if the waste stream amounts to 80% of the input stream?

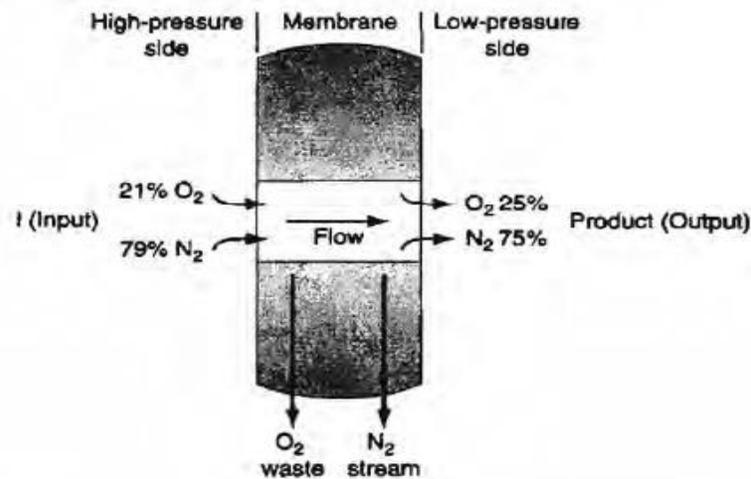


Figure E8.2a

Solution:-

Step 1

This is an open, steady-state process without chemical reaction. The system is the membrane as depicted in Figure E8.2. Let y_{O_2} be the mole fraction of oxygen as depicted in Figure E8.2) y_{N_2} be the mole fraction of nitrogen, and let n_{O_2} and n_{N_2} be the respective moles.

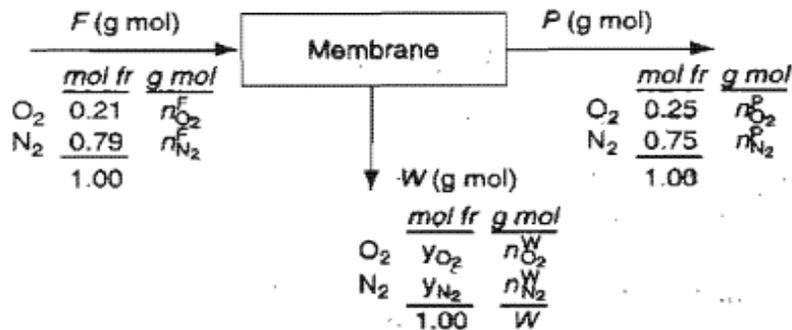


Figure E8.2b

Steps 2, 3, and 4

All of the data and symbols have been placed, in Figure E8.2b.

Step5

Pick a convenient basis.

Basis: 100 g mol. = F

A degree of freedom analysis that includes all of the variables comes next. You could either use moles or mole fractions as the unknowns.

Steps 6 and 7

Number of variables: 9

F, P, W and 6 n_i

Number of equations: 9

Basis: $F = 100$

$$\begin{aligned} \text{Specifications: } n_{\text{O}_2}^F &= 0.21(100) = 21 \\ n_{\text{N}_2}^F &= 0.79(100) = 79 \\ y_{\text{O}_2}^P &= n_{\text{O}_2}^P/P = 0.25 & n_{\text{O}_2}^P &= 0.25P \\ y_{\text{N}_2}^P &= n_{\text{N}_2}^P/P = 0.75 & n_{\text{N}_2}^P &= 0.75P \\ W &= 0.80(100) = 80 \end{aligned}$$

Material balances: O_2 and N_2

Implicit equations: $\sum n_i^W = W$ or $\sum y_j^W = 1$

The problem has zero degrees of freedom because of the way we have formulated the solution. Note that $n_{\text{O}_2}^F + n_{\text{N}_2}^F = F$ is a redundant equation because it repeats some of the specifications. Also, $n_{\text{O}_2}^P + n_{\text{N}_2}^P = P$ is redundant. Divide the equation by P to get $y_{\text{O}_2}^P + y_{\text{N}_2}^P = 1$, a relation that is equivalent to the sum of two of the specifications.

Step 8

If you introduce the known values into the species balances and implicit equation, you get three independent equations in three unknowns

	<i>In</i>	<i>Out</i>		<i>In</i>	<i>Out</i>
O_2 :	0.21 (100)	= 0.25P + $y_{\text{O}_2}^W$ (80)	or	0.21 (100)	= 0.25P + $n_{\text{O}_2}^W$
N_2 :	0.79 (100)	= 0.75P + $y_{\text{N}_2}^W$ (80)	or	0.79 (100)	= 0.75P + $n_{\text{N}_2}^W$
	1.00	= $y_{\text{O}_2}^W + y_{\text{N}_2}^W$	or	80	= $n_{\text{O}_2}^W + n_{\text{N}_2}^W$

Step 9

The solution of these equations is $n_{\text{O}_2}^W = 16$ and $n_{\text{N}_2}^W = 64$, or $y_{\text{O}_2}^W = 0.20$ and $y_{\text{N}_2}^W = 0.80$, and $P = 20$ g mol.

An alternate calculation involves the use of the total balance first in place of one component balance. The overall balance is easy to solve because

$$F = P + W \text{ or } 100 = P + 80$$

gives $P = 20$ straight off. Then, the oxygen balance would be

$$0.21(100) = 0.25(20) + n_{\text{O}_2}^W$$

from which you can get $n_{\text{O}_2}^W = 16$ g mol, and $n_{\text{N}_2}^W = 80 - 16 = 64$ g mol. Alternately, you could use the nitrogen balance to get the same result.

Step 10

Check. You can use the total balance as a check on the solution obtained from the two component balances

$$100 = 20 + 80 \text{ OK}$$

Material balances

Example 1:-

It is required to prepare 1250 kg of a solution composed of 12 wt. % ethanol and 88 wt. % water. Two solutions are available, the first contains 5 wt. % ethanol, and the second contains 25 wt. % ethanol. How much of each solution are mixed to prepare the desired solution?

Solution:

Basis: 1250 kg of M

1. Ethanol balance

$$A \left(\frac{5}{100} \right) + B \left(\frac{25}{100} \right) = M \left(\frac{12}{100} \right)$$

$$0.05 A + 0.25 B = 0.12(1250) = 150$$

$$A = \frac{150 - 0.25 B}{0.05} = 3000 - 5 B \quad \dots \dots \dots (1)$$

2. Water balance

$$0.95 A + 0.75 B = 0.88 M = 0.88(1250) = 1100 \quad \dots \dots \dots (2)$$

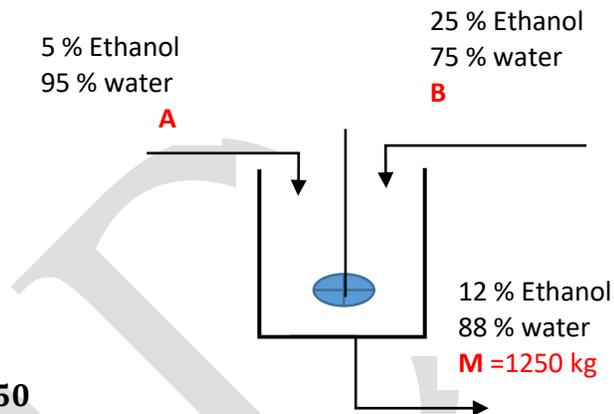
Sub. Eq. (1) in eq. (2)

$$0.95 (3000 - 5 B) + 0.75 B = 1100$$

$$2850 - 4.75 B + 0.75 B = 1100$$

$$4 B = 1750 \quad \rightarrow \quad B = 437.5 \text{ kg}$$

Sub. in eq. (1) $A = 3000 - 5(437.5) = 812.5 \text{ kg}$



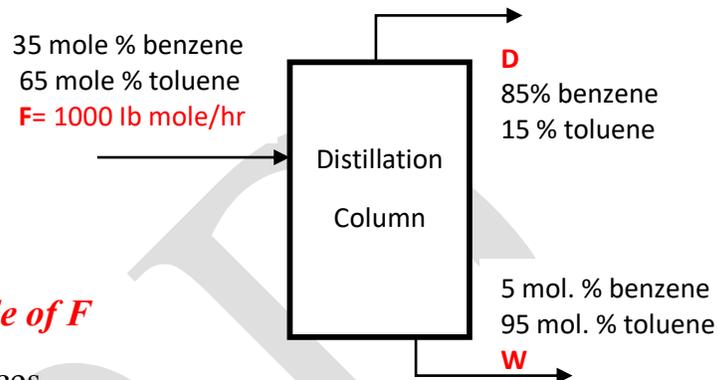
Chacking T. M. B.

$$\text{Input} = A + B = 437.5 + 812.5 = 1250 \text{ kg/hr}$$

$$\text{Output} = M = 1250 \text{ kg/hr}$$

Example 2:-

A binary mixture consists of 35% benzene and 65% toluene are continuously fed to the distillation column at rate of 1000 lb mole/hr. The distillate (top product) contains 85 mol. % benzene, whereas the residue (bottom product) contains 95 mol. % toluene. Calculate the quantities of distillate and residue obtained per hour.

Solution:

Basis: 1 hr. \equiv 1000 lb mole of F

1. Total material balances

$$F = D + W \rightarrow 1000 = D + W \dots \dots \dots (1)$$

2. Material balance on the benzene

$$F X_F = D X_D + W X_W$$

Where $X_F, X_D,$ and X_W are the mole fraction of benzene in the feed, distillate and bottom product respectively.

$$1000 \left(\frac{35}{100} \right) = D \left(\frac{85}{100} \right) + W \left(\frac{5}{100} \right)$$

$$350 = 0.85 D + 0.05 W \dots \dots \dots (2)$$

Sub. Eq. (1) in eq. (2)

$$350 = 0.85 D + 0.05 (1000 - D)$$

$$350 = 0.85 D + 50 - 0.05 D \rightarrow 300 = 0.8 D \rightarrow D = \frac{300}{0.8} = 375 \text{ lb mole/hr}$$

Sub. In eq. (1)

$$W = 1000 - 375 = 625 \text{ lb mole/hr}$$

Chacking toluene balance

$$\text{Toluene input} = F \left(\frac{65}{100} \right) = 650 \text{ lbmole}$$

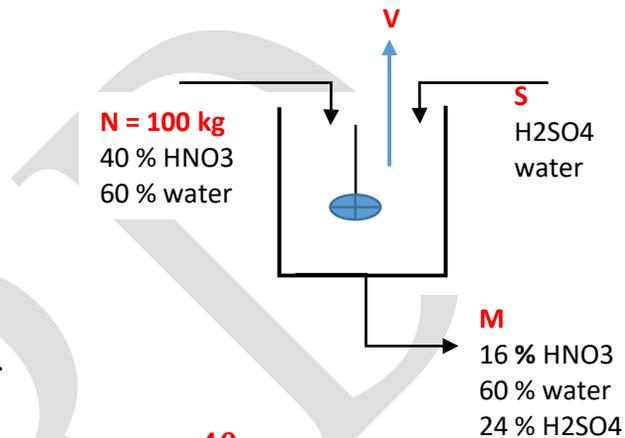
$$\begin{aligned} \text{Toluene output} &= D \left(\frac{15}{100} \right) + W \left(\frac{95}{100} \right) = 375(0.15) + 625(0.95) \\ &= 56.25 + 593.75 = 650 \text{ lb mole} \end{aligned}$$

Example 3:-

100 kg of nitric acid solution (N) containing 40 wt. % HNO_3 and 60 wt. % water are mixed with sulfuric acid solution (S). 25% of total water input are evaporated (V). The final mixture (M) contains 16 wt. % HNO_3 , 24wt. % H_2SO_4 and 60 wt. % water. Calculate:-

A// the quantities of the final mixture (M) and water vapor (V).

B// the mass and composition (wt. %) of sulfuric acid solution(S).

Solution:

Basis: 100 kg of N

1. HNO_3 balance (**Tie component**).

$$N \left(\frac{40}{100} \right) = M \left(\frac{16}{100} \right) \rightarrow 100(0.4) = 0.16 M \rightarrow M = \frac{40}{0.16} = 250 \text{ kg}$$

2. H_2SO_4 balance.

Let x = wt. fraction of H_2SO_4 in (S), hence $(1-x)$ = wt. fraction of water

$$S X = M \left(\frac{24}{100} \right) = 250(0.24) = 60 \rightarrow SX = 60 \quad \dots \dots \dots (1)$$

3. **Water** balance.

$$\text{Water input} = N \left(\frac{60}{100} \right) + S(1 - x) = 60 + S - SX$$

$$\text{Water output in M} = \left(\frac{75}{100} \right) \text{ of water input}$$

$$\therefore 250(0.6) = 0.75(60 + S - SX) \quad \dots \dots \dots (2)$$

Sub. Eq. (1) in eq. (2)

$$150 = 0.75 (60 + S - 60) = 0.75 S \quad \rightarrow S = \frac{150}{0.75} = 200 \text{ kg} \quad \& \quad X = \frac{60}{200} = 0.3$$

S Consists of 30 % H_2SO_4 and 70 % Water

$$\text{Water Vapour (V)} = \frac{25}{100} \text{ of water input}$$

$$= 0.25 [60 + S (1 - x)] = 0.25 [60 + 200 (0.7)] = 50 \text{ kg}$$

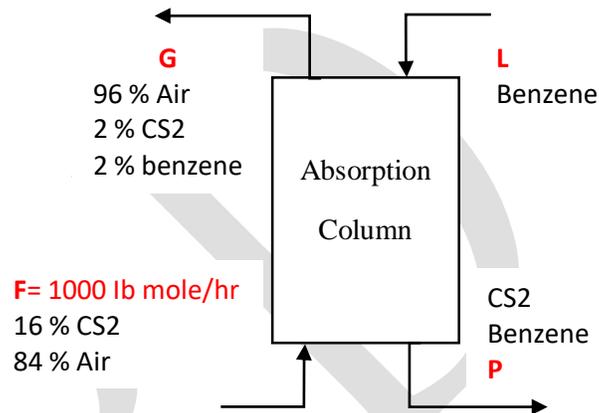
Chacking T. M. B.

$$\text{Input} = N + S = 100 + 200 = 300 \text{ kg}$$

$$\text{Output} = M + V = 250 + 50 = 300 \text{ kg}$$

Example 4:-

A gaseous mixture (F) consists of 16 mol. % CS₂ and 84 mol. % air are continuously fed to the absorption column at a rate of 1000 lb mole /hr. Most of CS₂ input are absorbed by liquid benzene (L) which fed to the top of the column. 1 % of benzene input are evaporated and out with the exit gas stream (G) which consists of 96 mol. % air, 2 mol. % CS₂ and 2mol. % benzene. The product liquid stream (P) consists of benzene and CS₂. Calculate the molal flow rates of (G), (L), (P) and the composition of (P).

Solution:

Basis: 1 hr. \equiv 1000 lb mole of F

1. Air balances (Tie component).

$$F \left(\frac{84}{100} \right) = G \left(\frac{96}{100} \right) \rightarrow 840 = 0.96G \rightarrow G = \left(\frac{840}{0.96} \right) = 875 \text{ lb mole/hr}$$

2. Benzene balances.

$$\text{benzene in G} = 875 \left(\frac{2}{100} \right) = 17.5 \text{ lb mole}$$

$$17.5 = 1\% \text{ of benzene input} = \frac{1}{100}(L) \rightarrow \therefore L = 17.5(100) = 1750 \text{ lb mole/hr}$$

$$\text{benzene in P} = 99\% \text{ of benzene input} = \frac{99}{100}(L) = 0.99(1750) = 1732.5 \text{ lb mole/hr}$$

Let x= mole fraction of benzene in (P)

$$P X = 1732.5 \quad \dots \dots \dots (1)$$

3. CS₂ balances.

$$F\left(\frac{16}{100}\right) = G\left(\frac{2}{100}\right) + P(1 - x)$$

$$1000(0.16) = 875(0.02) + P - PX \rightarrow 160 = 17.5 + P - 1732.5 \rightarrow P = 1875 \text{ lb mole/hr}$$

$$\text{Sub. in (1)} \quad \therefore X = \frac{1732.5}{1875} = 0.924 \text{ mole fraction of benzen in (P)}$$

Chacking T. M. B.

$$\text{Input} = F + L = 1000 + 1750 = 2750 \text{ lb mole/hr}$$

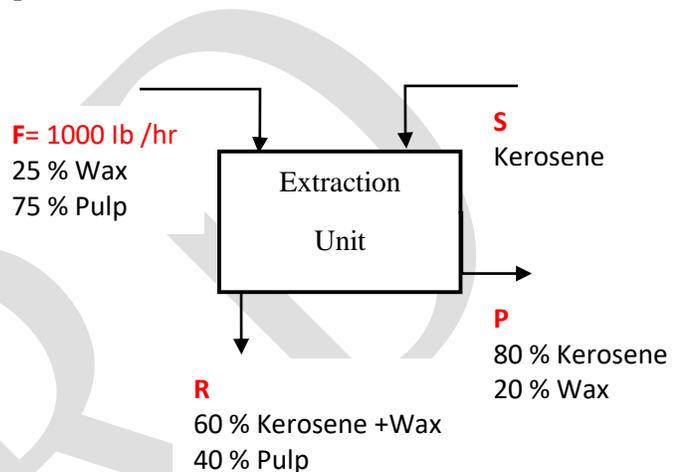
$$\text{Output} = G + p = 875 + 1875 = 2750 \text{ lb mole/hr}$$

Example 5:-

A waxed paper (F) containing 25 wt. % wax and 75 wt. % paper pulp are continuously fed at a rate of 1000 Ib/hr to a certain extraction unit in which 98% of the wax input to the unit are extracted by 37 °API kerosene (S). The extracted paper out from the extractor (R) contains 40 wt. % paper pulp, the remainder being kerosene and un-extracted wax. The product solution (P) consists of 80 % kerosene & 20 wt. % wax. Calculate:-

a// The flow rates of S, R and P. b// The composition of R.

c// Gallons of kerosene input to the unit per hour.

Solution:

Basis: 1 hr. \equiv 1000 Ib of F

a. Pulp balance (Tie component).

$$F \left(\frac{75}{100} \right) = R \left(\frac{40}{100} \right) \rightarrow 750 = 0.4R \rightarrow R = \left(\frac{750}{0.4} \right) = 1875 \text{ Ib/hr}$$

b. Wax balance

$$\text{Wax input} = 1000 \left(\frac{25}{100} \right) = 250 \text{ Ib}$$

$$\text{Wax in (P)} = 250 \left(\frac{98}{100} \right) = 245 = P \left(\frac{20}{100} \right) \rightarrow P = \frac{245}{0.2} = 1225 \text{ Ib/hr}$$

$$\text{Wax in (R)} = 250 \left(\frac{2}{100} \right) = 5 \text{ Ib}$$

c. Kerosene balance

$$(\text{Kerosene} + \text{Wax}) \text{ in R} = 1875 \left(\frac{60}{100} \right) = 1125 \text{ Ib}$$

$$(\text{Kerosene}) \text{ in R} = 1125 - 5 = 1120 \text{ Ib}$$

Composition of R: (Kerosene) = $\left(\frac{1120}{1875}\right) \times 100 = 59.73 \%$;

$$Wax = \frac{5}{1875} \times 100 = 0.27 \%$$

$$S = 1120 + P\left(\frac{80}{100}\right) \quad \rightarrow \quad S = 1120 + 1225(0.8) = 2100 \text{ Ib/hr}$$

Chacking T. M. B.

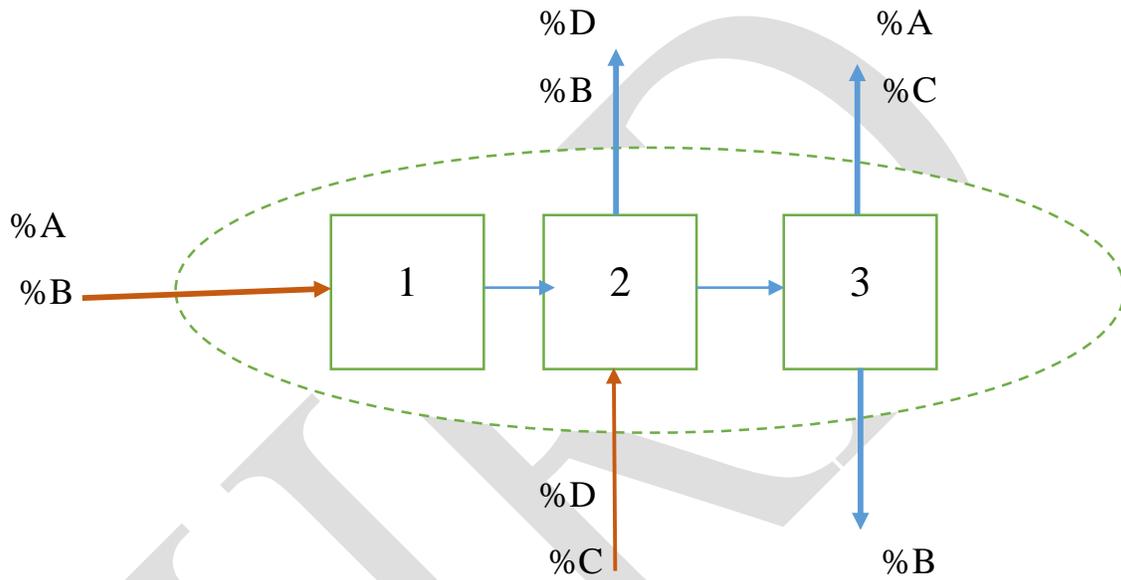
$$\text{Input} = F + S = 1000 + 2100 = 3100 \text{ Ib/hr}$$

$$\text{Output} = R + P = 1875 + 1225 = 3100 \text{ Ib/hr}$$

Material balance without chemical reaction on multi process.

$$\text{IN} = \text{OUT}$$

* اما يتم تقسيم كل جهاز على حدى أو تأخذ جميع الأجهزة كجهاز واحد فتسمى عملية الموازنة في هذه الحالة overall M. B.

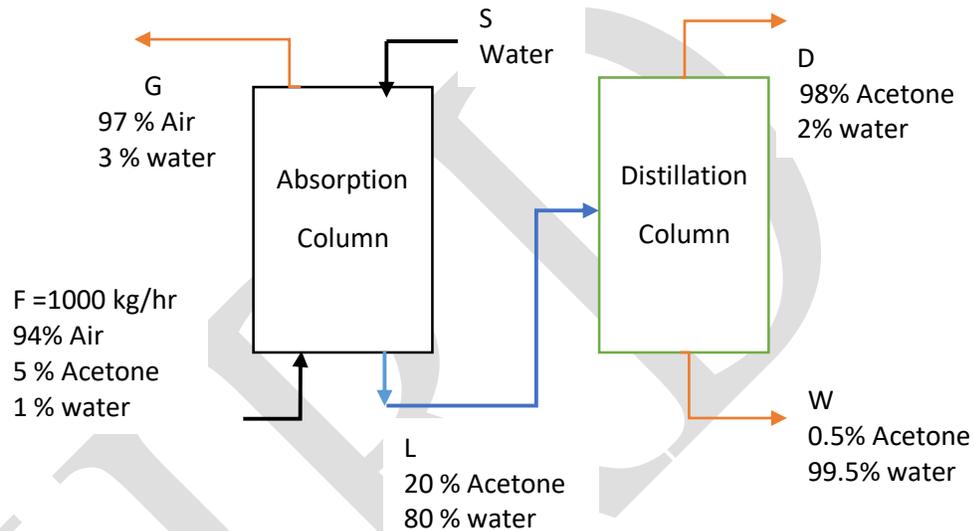


عند عمل الموازنة من نوع overall يتم اهمال الخطوط البينية

1. اذا كانت الخطوط البينية **معلومة** (كمية خط) او نسب المواد في ذلك الخط . يتم تقسيم كل جهاز على حدى.
2. اما اذا كانت الخطوط البينية **مجهولة** فنعمل موازنة من نوع overall M.B. دمج للأجهزة.

Example 6:-

Acetone can be recovered from a gaseous mixture by absorption followed by distillation. The feed gas (F) consists of 94 wt. % air, 5 wt. % acetone and 1 wt. % humidity (water) are continuously fed to the absorption column at rate of 1000 kg/hr. Water stream (S) enters the top of the column. The exit gases (G) consists of 97 wt. % air and 3 wt. % water. The exit liquid stream (L) enters the distillation column with composition of 20 wt. % acetone & 80 wt. % water. The top product (D) consists of 98 wt. % acetone, whereas the bottom product (W) consists 99.5 wt. % water. Calculate the flow rates of S, G, L, D and W.

Solution:-

Basis: 1 hr. \equiv 1000 kg of F

1. Material balances on Absorption Column

a. Air balances (**Tie component**).

$$F \left(\frac{94}{100} \right) = G \left(\frac{97}{100} \right) \rightarrow 940 = 0.97G \rightarrow G = \left(\frac{940}{0.97} \right) = 969 \text{ kg/hr}$$

b. Acetone balances (**Tie component**).

$$F \left(\frac{5}{100} \right) = L \left(\frac{20}{100} \right) \rightarrow 50 = 0.2L \rightarrow L = \left(\frac{50}{0.2} \right) = 250 \text{ kg/hr}$$

c. Water balances.

$$F \left(\frac{1}{100} \right) + S = L \left(\frac{80}{100} \right) + G \left(\frac{3}{100} \right)$$

$$10 + S = 250 (0.8) + 969 (0.03) \rightarrow S = 200 + 29 - 10 = 219 \text{ kg/hr}$$

Chacking T. M. B.

$$\text{Input} = F + S = 1000 + 219 = 1219 \text{ kg/hr}$$

$$\text{Output} = G + L = 969 + 250 = 1219 \text{ kg/hr}$$

2. Material balances on Distillation Column

a. **Total** Material balances $L = D + W \rightarrow 250 = D + W$

b. Acetone balances $L \left(\frac{20}{100} \right) = D \left(\frac{98}{100} \right) + W \left(\frac{0.5}{100} \right) \rightarrow D = 50 \text{ kg/hr}$

$$w = 200 \text{ kg/hr}$$

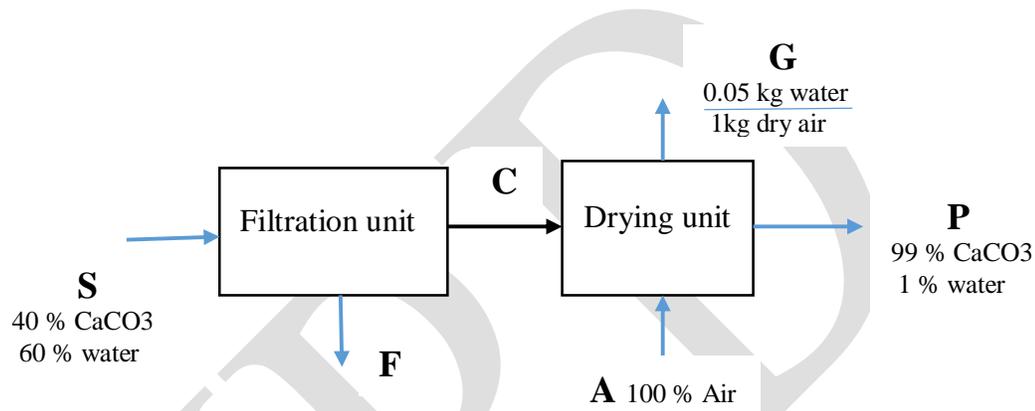
3. Final Chacking T. M. B. overall the process

$$\text{Input} = F + S = 1000 + 219 = 1219 \text{ kg/hr}$$

$$\text{Output} = G + D + W = 969 + 50 + 200 = 1219 \text{ kg/hr}$$

Example 7:-

A slurry (S) containing 40 wt. % CaCO_3 and 60 wt. % water are continuously fed at a rate of 1000 kg/hr to the filtration unit in which only 1 % of fine particles of CaCO_3 are passed through the filter cloth and out with the filtrate (F). The wet cake (C) are discharged in a continuous manner and input to the drying unit in which hot dry air (A) are passed over it, producing a product (P) consists of 99 wt. % CaCO_3 and 1 wt. % water. The exit air (G) contains 0.05 kg water/ 1kg dry air. The mass ratio between C and P = 1.1/1. Calculate the flow rates of F, C, A, P and the composition of the wet cake(C) and the filtrate (F).

**Solution:-**

Basis: 1 hr. \equiv 1000 kg of S

1- Material balances on the CaCO_3

$$\text{CaCO}_3 \text{ input} = S \left(\frac{40}{100} \right) = 1000 (0.4) = 400 \text{ kg}$$

$$\text{CaCO}_3 \text{ out with F} = 400 \left(\frac{1}{100} \right) = 4 \text{ kg}$$

$$\text{CaCO}_3 \text{ in P} = 400 - 4 = 396 = P \left(\frac{99}{100} \right) \rightarrow P = \frac{396}{0.99} = 400 \text{ kg}$$

$$\frac{C}{P} = \frac{1.1}{1} \rightarrow C = 1.1 (P) = 1.1 (400) = 440 \text{ kg/hr}$$

2- Material balances on Filtration unit

T. M. B. $S = C + F \rightarrow F = S - C = 1000 - 440 = 560 \text{ kg/hr}$

water in F = F - CaCO_3 in F = 560 - 4 = **556 kg**

Composition of F : $\text{Caco}_3 = \left(\frac{4}{560} \right) \times 100 = 0.7\%$, $\text{water} = \left(\frac{556}{560} \right) \times 100 = 99.3\%$

$$\text{CaCO}_3 \text{ in C} = \text{CaCO}_3 \text{ in S} - \text{CaCO}_3 \text{ in F} = 400 - 4 = 396 \text{ kg}$$

$$\text{water in C} = \text{C} - \text{CaCO}_3 \text{ in c} = 440 - 396 = 44 \text{ kg}$$

$$\text{Composition of C: CaCO}_3 = \left(\frac{396}{440}\right) \times 100 = 90\%, \text{ water} = \left(\frac{44}{440}\right) \times 100 = 10\%$$

3- Material balances on Drying unit

$$\text{water out with air} = \text{water in C} - \text{water in P} = 44 - 400\left(\frac{1}{100}\right) = 40 \text{ kg}$$

$$A = 40 \text{ kg water} \left(\frac{1 \text{ kg air}}{0.05 \text{ kg water}}\right) = 800 \frac{\text{kg}}{\text{hr}}, \text{ } \mathbf{G = A + 40 = 840 \text{ kg/hr}}$$

<u>H₂O</u>	<u>AIR</u>
0.05	1 KG
40	X

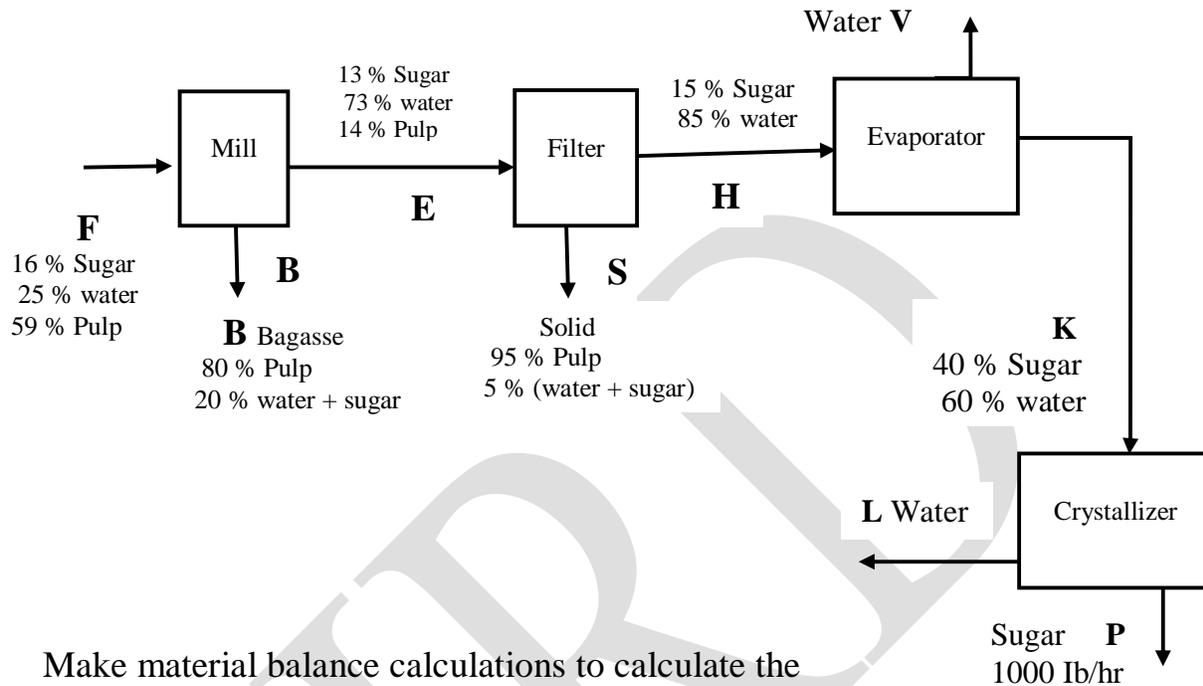
Chacking T. M. B. overall the process

$$\text{Input} = S + A = 1000 + 800 = 1800 \text{ kg/hr}$$

$$\text{Output} = F + P + G = 560 + 400 + 840 = 1800 \text{ kg/hr}$$

Example 8:-

The manufacture of sugar can be represented by the following block diagram:



Make material balance calculations to calculate the Flow rates and composition of all streams in the process.

Solution:

Basis: 1000 Ib of F

1- Material balances on the Mill**a. Pulp balance**

$$F (0.59) = E (0.14) + B(0.86) \rightarrow 590 = 0.14E + 0.86 B \dots \dots \dots (1)$$

b. (Sugar +water) balance

$$F (0.41) = E (0.86) + B(0.2) \rightarrow 410 = 0.86 E + 0.2 B \dots \dots \dots (2)$$

Sub. Eq. (1) in (2)

$$410 = 0.2 \left(\frac{590 - 0.14 E}{0.8} \right) + 0.86 E \rightarrow 410 = 147.5 - 0.035 E + 0.86 E$$

$$0.825 E = 262.5 \rightarrow E = \left(\frac{262.5}{0.825} \right) = 318.2 \text{ lb}$$

Sub. In Eq. (1)

$$B = \left(\frac{590 - 0.14 E}{0.8} \right) = \left(\frac{590 - 0.14 (318.2)}{0.8} \right) = 681.8 \text{ lb}$$

Checking T. M. B.

$$\text{Input} = F = 1000$$

$$\text{Output} = E + B = 318.2 + 681.8 = 1000 \text{ lb}$$

c. Sugar balance

$$F (0.16) = E (0.13) + B X \quad X : \text{wt. fraction of sugar in } B$$

$$160 = 318.2 (0.13) + 681.8 X \rightarrow X = 0.174, \text{ Sugar in } B = 17.4 \text{ wt. \%}$$

d. Water balance

$$F (0.25) = E (0.73) + B y \quad y : \text{wt. fraction of water in } B$$

$$250 = 318.2 (0.73) + 681.8 y \rightarrow y = 0.026, \text{ Water in } B = 2.6 \text{ wt. \%}$$

$$\text{Checking } (X + y) = 0.174 + 0.026 = 0.20$$

2- Material balances on the Filter

a. Pulp balance

$$E (0.14) = S (0.95) \rightarrow 318.2 (0.14) = (0.95)S \rightarrow S = 46.9 \text{ lb}$$

b. (Sugar +water) balance

$$E (0.86) = S (0.05) + H \left(\frac{100}{100} \right) \rightarrow \therefore H = 318.2 (0.86) - 46.9(0.05)$$

$$\rightarrow H = 273.623 = 271.3$$

Chacking T. M. B.

$$\text{Input} = E = 318.2$$

$$\text{Output} = S + H = 46.9 + 271.3 = 318.2$$

c. Sugar balance

$$E (0.13) = H (0.15) + S X \quad X : \text{wt. fraction of sugar}$$

$$318.2 (0.13) = 271.3 (0.15) + 46.9 X \rightarrow 41.37 = 40.7 + 46.9X$$

$$\rightarrow X = 0.014, \quad \text{Sugar in } S = 1.4 \text{ wt. \%}$$

d. Water balance

$$E (0.73) = S y + H(0.85) \quad y : \text{wt. fraction of water}$$

$$318.2 (0.73) = 46.9 y + 271.3(0.85) \rightarrow 232.3 = 46.9y + 230.6$$

$$y = 0.036, \quad \text{water in } S = 3.6 \text{ wt. \%}$$

$$\text{Checking } (X + y) = 0.014 + 0.036 = 0.05$$

3- Material balances on the Evaporator**a. Sugar balance**

$$H (0.15) = K (0.4) \quad K = \frac{271.3 (0.15)}{0.4} = 101.4 \text{ Ib}$$

b. Water balance

$$H (0.85) = V + (0.6) K \rightarrow V = 271.3(0.85) - 0.6 (101.7) =$$

$$\rightarrow V = 230.6 - 61 = 169.6 \text{ Ib}$$

Chacking T. M. B.

$$\text{Input} = H = 271.6 \text{ Ib}$$

$$\text{Output} = V + K = 169.6 + 101.7 = 271.6 \text{ Ib}$$

4- Material balances on the Crystallizer**a. Water balance**

$$(0.6) K = L \quad \rightarrow \quad L = 101.7 (0.6) = 61 \text{ Ib}$$

b. Sugar balance

$$(0.4) K = P \quad \rightarrow \quad P = 101.7 (0.4) = 40.7 \text{ Ib}$$

Chacking T. M. B.

$$L + P = 61 + 40.7 = 101.7 \text{ Ib}$$

Final Chacking**Overall Material balance**

$$\text{Total input} = F = 1000 \text{ Ib}$$

$$\begin{aligned} \text{Total output} &= B + S + V + L + P \\ &= 681.8 + 46.9 + 169.6 + 61 + 40.7 = 1000 \text{ Ib} \end{aligned}$$

Change the basis to 1000 Ib of P								
F	B	E	S	H	V	K	L	P
1000	681.8	318.2	46.9	271.3	169.6	101.7	61	40.7
24.570	16752	7818	1152	6666	4167	2499	1499	1000

Material balances with chemical reactions.

Material balance with reaction:-

• موازنة مادة تفاعل كيميائي $A + B \rightarrow C + D$

• هذه هي موازنة كل مادة قبل السهم في المعادلة الكيميائية
($In = react + out$)

• هذه هي موازنة كل مادة بعد السهم في المعادلة الكيميائية.

$$In + product = out$$

• هذه هي موازنة كل مادة لابعد السهم ولاقبل السهم في المعادلة مثل
(عامل مساعد، Ash, impurities)

$$In = out$$

• لأيجاد: react

1. تعطى كمية مادة بعد السهم لغرض عمل المقارنة.

2. او تعطى $conv. = \frac{react}{in}$

3. او تعطى $degree\ of\ completion = \frac{react}{in}$

- The reaction goes to completion
- The reaction is completely conversion

$$In = react$$

- طريقة الحل:
- يجب ايجاد react حسب الطرق السابقة
- يتم عمل موازنات بقدر عدد المواد الموجودة بالجهاز مع الاخذ الاعتبار (موقع المادة) في المعادلة الكيمياوية.
- الحل يكون بالمولات ولكن

Checking

$$\text{Total mass (In)} = \text{Total mass (out)}$$

- الحل يكون اغلب الاحيان overall M.B. لان الخطوط البنينة غالبا ماتكون مجهولة.

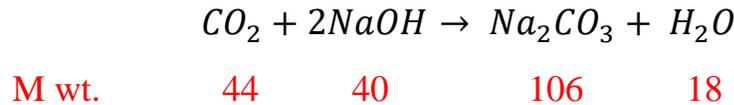


من المقارنة

من رسم الجهاز

Example 1:-

A gaseous mixture consists of 80 mol. % N_2 and 20 mol. % CO_2 are continuously fed to the absorption column in which CO_2 are completely absorbed by sodium hydroxide solution according to the following reaction:



The product liquid stream are left the bottom of the absorber at a rate of 1000 lb/hr with composition of 26.5 wt. % Na_2CO_3 , 4 wt. % NaOH and 69.5 wt. % H_2O . Pure nitrogen are out from the top of the column. **Calculate:**

- The mass flow rate and composition (wt. %) of NaOH solution.
- The mass flow rates of input & output gaseous stream.
- % excess and conversion of NaOH.

Solution:

Basis: 1 hr. \equiv 1000 lb. of product solution

a.

$$Na_2CO_3 \text{ produced} = 1000 \left(\frac{26.5}{100} \right) = 265 \text{ lb} \rightarrow \frac{265}{106} = 2.5 \text{ lb mole}$$

$$NaOH \text{ reacted} = 2.5 \left(\frac{2}{1} \right) = 5 \text{ lb mole} = 5 \times 40 = 200 \text{ lb}$$

$$NaOH \text{ output} = 1000 \left(\frac{4}{100} \right) = 40 \text{ lb}$$

NaOH	Na ₂ CO ₃
2	1
x	2.5

$$\therefore NaOH \text{ input} = 200 + 40 = 240 \text{ lb}$$

Similarly H_2O produced from reaction = 2.5 lb mole = 2.5(18) = 45 lb

$$H_2O \text{ output} = 1000 \left(\frac{69.5}{100} \right) = 695 \text{ lb}$$

$$\therefore H_2O \text{ input} = 695 - 45 = 650 \text{ lb}$$

$$\therefore NaOH \text{ solution input} = 240 + 650 = 890 \text{ lb/hr}$$

H ₂ O	Na ₂ CO ₃
1	1
x	2.5

$$NaOH = (240/890) \times 100 = 27\%$$

$$H_2O = (650/890) \times 100 = 73\%$$

b.

$$Na_2CO_3 \text{ produced} = 1000 \left(\frac{26.5}{100} \right) = 265 \text{ Ib} \rightarrow \frac{265}{106} = 2.5 \text{ Ib mole}$$

$$CO_2 \text{ reacted} = 2.5 \text{ Ib mole} = CO_2 \text{ input}$$

(since CO_2 are completely reaction)

$$N_2 \text{ input} = 2.5 \left(\frac{80}{20} \right) = 10 \text{ Ib mole}$$

$$\therefore \text{flow rate of feed gas} = 2.5 (44) + 10 (28) = 390 \text{ Ib /hr}$$

$$\text{flow rate of exit gas} = 10 (28) = 280 \text{ Ib/hr}$$

Chacking:

$$\text{Input} = 890 + 390 = 1280 \text{ Ib/hr}$$

$$\text{Output} = 1000 + 280 = 1280 \text{ Ib/hr}$$

c.

$$CO_2 \text{ input} = \text{quantity reacted} = 2.5 \left(\frac{1}{1} \right) = 2.5 \text{ Ib mole}$$

CO2	Na2CO3
1	1
X	2.5

$$NaOH \text{ input} = 240 \text{ Ib} = \frac{240}{40} = 6 \text{ Ib mole}$$

$$\% \text{ excess NaOH} = \frac{\text{input} - \text{theo.}}{\text{theo.}} \times 100 = \frac{6 - 5}{5} \times 100 = 20 \%$$

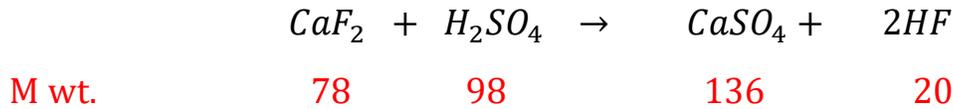
CO2	NaOH
1	2
2.5	X

$$\% \text{ Conversion OF NaOH} = \frac{\text{NaOH rected}}{\text{NaOH input}} \times 100 = \frac{5}{6} \times 100 = 83.3 \%$$

(DEPEND ON THE EXCESS)

Example 2:-

Hydrofluoric acid can be manufactured by treating crushed fluorite with an excess amount of sulfuric acid solution according to the:



The fluorite ore (F) contains 78 wt. % CaF_2 & 22 wt. % inert impurities. The acid solution (S) contains 95 wt. % H_2SO_4 . The reaction goes to completion and all HF and water are volatilized and separated as vapour (V) from residual sulfate cake (R) which contains 16 wt.% H_2SO_4 . On the basis of 1000 lb of the fluorite charged.

Calculate (a) the quantities of S, V, R and the composition of (v) & (R).
 (b) % excess of H_2SO_4 .

Solution:

Basis: 1000 lb. of F

a. CaF_2 input = $1000 \left(\frac{78}{100} \right) = 780 \text{ lb} = \frac{780}{78} = 10 \text{ lb mole} =$
quantity reacted since the reaction goes to completion

Impurities input = 220 lb = quantity output in (R)

CaSO_4 produced = $10 (136) = 1360 \text{ lb}$

$\therefore \text{CaSO}_4 + \text{Impurities} = 1360 + 220 = 1580 \text{ lb} = \text{R} \left(\frac{84}{100} \right)$

$\therefore \text{R} = \left(\frac{1580 \times 100}{84} \right) = 1881 \text{ lb}$

$\therefore \text{H}_2\text{SO}_4$ in R = $1881 \left(\frac{16}{100} \right) = 301 \text{ lb}$

Composition of (R).

Ca SO₄ = $(1360 / 1881) \times 100 = 72.3 \%$

Impurities = $(220/1881) \times 100 = 11.7\%$

H₂SO₄ = 16 %

$\therefore \text{H}_2\text{SO}_4$ input = H_2SO_4 reacted + H_2SO_4 unreacted S
 $= 10 (98) + 301 = 1281 = \text{S} \left(\frac{95}{100} \right) \rightarrow \text{S} = \frac{1281}{0.95} = 1348 \text{ lb}$

$$\text{Water input} = \text{water output with (V)} = 1348 \left(\frac{5}{100} \right) = 67 \text{ Ib}$$

$$\text{HF produced} = 10 \left(\frac{2}{1} \right) \times 20 = 400 \text{ Ib}$$

$$\therefore \text{vapour (V)} = 400 + 67 = 467 \text{ Ib}$$

Composition of (V).

$$\text{HF} = (400 / 467) \times 100 = 85.6 \%$$

$$\text{H}_2\text{O} = (67 / 467) \times 100 = 14.4\%$$

Chacking:

$$\text{Input} = F + S = 1000 + 1348 = \mathbf{2348 \text{ Ib}}$$

$$\text{Output} = R + V = 1881 + 467 = \mathbf{2348 \text{ Ib}}$$

b.

Composition of (V).

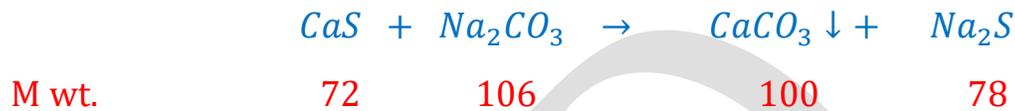
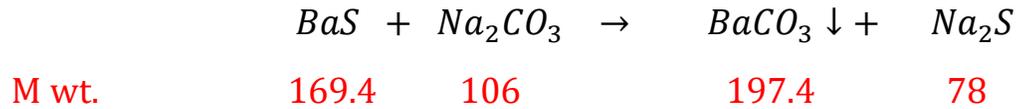
$$\text{H}_2\text{SO}_4 \text{ input} = 1281 \text{ Ib} = (1281 / 98) = 13.07$$

$$\text{CaF}_2 \text{ input} = 10 \text{ Ib mole}$$

$$\% \text{ excess } \text{H}_2\text{SO}_4 = \left(\frac{13.07 - 10}{10} \right) \times 100 = 30.7 \%$$

Example 3:-

A solution of barium and calcium sulfides (F) is treated with commercial soda ash (S) which consists of Na_2CO_3 and some impurities of CaCO_3 in order to produce barium carbonate according to the following reactions:



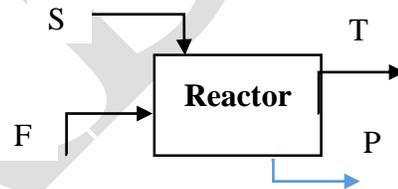
Reaction product are separated by filtration. The precipitate (P) contains 9.9 wt. % CaCO_3 & 90.1 wt. % BaCO_3 . The filtrate (T) contains 6.85 wt. % Na_2S , 2.25 wt. % Na_2CO_3 and 90.9 wt. % H_2O . The mass ratio between (P) & (T) is 16.45 Ib. / 100 Ib. Calculate the composition (wt. %) of (F) and (S).

Solution:

Basis: 1000 Ib. of T

\therefore mass of (P) = 164.5 Ib

P	T
16.45	100
x	1000



$$\begin{aligned} \text{BaCO}_3 \text{ produced from 1 st. reaction} &= 164.5 \left(\frac{90.1}{100} \right) = 148.2 \text{ Ib} \\ &= \frac{148.2}{197.4} = 0.751 \text{ Ibmole} \end{aligned}$$

$$\begin{aligned} \therefore \text{Na}_2\text{S produced from 1 st. reaction} &= 0.751 \text{ Ib mole} = \\ &0.751 (78) = 58.6 \text{ Ib} \end{aligned}$$

$$\text{Total Na}_2\text{S produced from both reactions} = 1000 \left(\frac{6.85}{100} \right) = 68.5 \text{ Ib}$$

$$\begin{aligned} \therefore \text{Na}_2\text{S produced from 2 nd reactions} &= 68.5 - 58.6 = 9.9 \text{ Ib} = \\ &\frac{9.9}{78} = 0.127 \text{ Ib mole} \end{aligned}$$

$$\begin{aligned} \therefore \text{Na}_2\text{CO}_3 \text{ reacted in both reactions} &= 0.751 + 0.127 = 0.878 \text{ Ibmole} \\ &= 0.878 \times 106 = 93.1 \text{ Ib} \end{aligned}$$

$$\text{Na}_2\text{CO}_3 \text{ unreacted} = 1000 \left(\frac{2.25}{100} \right) = 22.5 \text{ Ib}$$

$$\therefore \text{Na}_2\text{CO}_3 \text{ input} = 93.1 + 22.5 = 115.6 \text{ Ib}$$

CaCO_3 produced from 2 nd reactions = $0.127 (100) = 12.7 \text{ Ib}$

CaCO_3 output with (P) = $164.5 \left(\frac{9.9}{100}\right) = 16.3 \text{ Ib}$

CaCO_3 input with (S) = $16.3 - 12.7 = 3.6 \text{ Ib}$

$\therefore S = \text{Na}_2\text{CO}_3 \text{ input} + \text{CaCO}_3 \text{ input} \rightarrow S = 115.6 + 3.6 = 119.2 \text{ Ib}$

Composition of (S).

$$\text{Na}_2\text{CO}_3 = \frac{115.6}{119.2} \times 100 = 96.98 \%$$

$$\text{CaCO}_3 = \frac{3.6}{119.2} \times 100 = 3.02 \%$$

Similarly:-

BaS reacted = BaS input = $0.751 \text{ Ibmole} = 0.751 \times 169.4 = 127.2 \text{ Ib}$

CaS reacted = CaS input = $0.127 \text{ Ibmole} = 0.127 \times 72 = 9.1 \text{ Ib}$

H_2O input = H_2O output = $1000 \left(\frac{90.9}{100}\right) = 909 \text{ Ib}$

$\therefore F = \text{BaS}$ input + CaS input + H_2O input \rightarrow

$F = 127.2 + 9.1 + 909 = 1045.3 \text{ Ib}$

Composition of (F).

$\text{BaS} = (127.2 / 1045.3) \times 100 = 12.17 \%$

$\text{CaS} = (9.1 / 1045.3) \times 100 = 0.87 \%$

$\text{H}_2\text{O} = 86.96 \%$

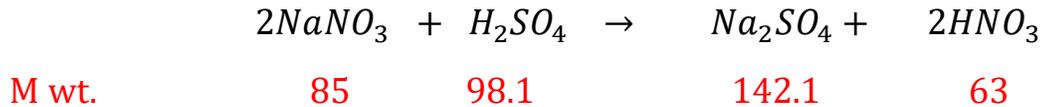
Chacking:

Input = F + S = 1045.3 + 119.2 = 1164.5 Ib

Output = T + P = 1000 + 164.5 = 1164.5 Ib

Example 4:-

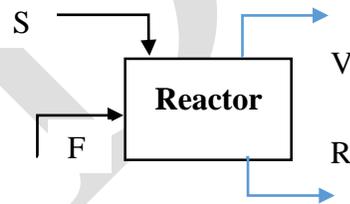
Nitric acid can be manufactured by treating pure sodium nitrate (F) with sulfuric acid solution (S) containing 95 wt. % H_2SO_4 according to the reactions:



Most of HNO_3 and H_2O are volatilized and separated as vapour (V) from residual niter cake (R) which contains 1.5 wt. % H_2O , 34 wt. % H_2SO_4 , Na_2SO_4 and 2 % of total HNO_3 produced from reaction. On the basis of 1000 lb of the (F), Calculate the quantities of S, V, R and the composition of (v) & (R).

Solution:

Basis: $F = 1000 \text{ lb}$.



since no quantity of $NaNO_3$ appears in V & R, thus all quantity input are reacted, i. e. the reaction goes to completion

$$\therefore NaNO_3 \text{ input} = NaNO_3 \text{ reacted} = \left(\frac{1000}{85}\right) = 11.765 \text{ lb mole}$$

$$\therefore HNO_3 \text{ produced} = 11.765 \text{ lb mole} = 11.765 (63) = 741 \text{ lb}$$

$$HNO_3 \text{ out with R} = 741 \left(\frac{2}{100}\right) = 14.8 \text{ lb}$$

$$HNO_3 \text{ out with V} = 741 - 14.8 = 726.2 \text{ lb}$$

$$\therefore Na_2SO_4 \text{ produced} = 11.765 \left(\frac{1}{2}\right) (142.1) = 835.9 \text{ lb}$$

$$(HNO_3 + Na_2SO_4) \text{ in R} = 14.8 + 835.9 = 850.7 \text{ lb} = R \left(\frac{64.5}{100}\right)$$

$$\therefore R = \left(\frac{850.7 \times 100}{64.5}\right) = 1318.9 \text{ lb}$$

$$\therefore H_2O \text{ in R} = 1318.9 \left(\frac{1.5}{100}\right) = 19.8 \text{ lb}$$

$$\therefore H_2SO_4 \text{ in R} = 1318.9 \left(\frac{34}{100}\right) = 448.4 \text{ lb}$$

Composition of (R).

$$Na_2SO_4 = \frac{835.9}{1318.9} \times 100 = 63.4 \%$$

$$HNO_3 = \frac{14.8}{1318.9} \times 100 = 1.1 \%$$

$$H_2O = 1.5 \%, \dots, H_2SO_4 = 34 \%$$

$$\therefore H_2SO_4 \text{ reacted} = 11.765 \left(\frac{1}{2}\right) (98.1) = 577 \text{ Ib}$$

$$\therefore H_2SO_4 \text{ input} = 448.4 + 577 = 1025.4 \text{ Ib} = S \left(\frac{95}{100}\right)$$

$$\therefore S = 1025.4 \left(\frac{100}{95}\right) = 1079.4 \text{ Ib}$$

$$\text{Water input} = 1079.4 \left(\frac{5}{100}\right) = 54 \text{ Ib} = \text{water output in R \& V}$$

$$\therefore \text{water in (V)} = 54 - 19.8 = 34.2 \text{ Ib}$$

$$\begin{aligned} \therefore V &= HNO_3 \text{ in V} + \text{water in V} \\ &= 726.2 + 34.2 = 760.4 \text{ Ib} \end{aligned}$$

Composition of (V).

$$HNO_3 = \frac{726.2}{760.4} \times 100 = 95.5 \%$$

$$H_2O = \frac{34.2}{760.4} \times 100 = 4.5 \%$$

Chacking:

$$\text{Input} = F + S = 1000 + 1079.4 = 2079.4 \text{ Ib}$$

$$\text{Output} = R + V = 1318.9 + 760.4 = 2079.3 \text{ Ib}$$

Material balances Involving Combustion

Introduction:

Combustion is one of the most industrial processes commonly used for heat generation. Fuels are burnt with oxygen, i.e air in such process to supply thermal energy to different industrial process units.

Hence, **combustion can be considered** as process in which **oxidation reaction** take place. It can be either “complete” or “incomplete”.

- **Combustion** is the reaction of a substance with **oxygen** with the associated **release of energy** and generation of product gases such as H₂O, CO₂, CO, and SO₂.
- Most **combustion processes** use **air** as the source of **oxygen**. For our purposes you can assume that air contains **79% N₂ and 21% O₂**.

Complete Combustion Process:-

If all carbon, hydrogen and sulphur of the fuel are converted to CO₂, H₂O and SO₂ respectively, the combustion is termed “Complete”.

Incomplete or Partial Combustion Process:-

If parts of the fuel remain unburned, or CO gaseous with product gases, the combustion is termed “incomplete” or “partial combustion”.

Note that

- The reaction of S with O₂ yield SO₂ and SO₃. Conversion of S to SO₃ requires specific conditions. Hence, it is customary to regard the conversion of all S to SO₃ as complete union for stoichiometric calculations.
- The quantity of heat produced from **complete combustion** of any fuel is **higher than** that produced from **incomplete combustion**. Theoretical quantity of oxygen required for any combustion process is **computed** on the assumption of **complete combustion**.

The three general constituents of any combustion process are 1- fuel 2- air and 3- the stack or flue gas. However, ash, or noncombustible material are included with solid fuel only.

1. FULE:-

The fuel used in power plant combustion furnaces may be solids, liquids, or gases.

A. Solid fuels: Principally **coal** is the most important classical and natural fuel. It consists of 1- elemental carbon; 2- complex hydrocarbons of unknown saturate consists of C, H, O, N, and S. 3- noncombustible matter that forms the ash.

B. Liquid fuel: Principally hydrocarbons obtained distillation of crude oil such as **gasoline, kerosene, diesel oil and fuel oil**. However, there is growing interest to use **alcohols obtained by fermentation** of grains as **liquid fuel**.

C. Gaseous fuel: Principally **natural gas** is an imported gaseous fuel. It consists of **80 -95 % CH₄** the remainder being **ethane, propane** and small quantities of other gases. However, **light hydrocarbons** obtained from petroleum or coal treatment such as procedure gas, blast-furnace gas and refinery gas are examples of synthetic gaseous fuels. **Acetylene and hydrogen can be also used as fuel** but their production are relatively expensive.

2. Air:

Air is **the source of oxygen** in most combustion processes for obvious economic reasons. Air has the following composition:

Mol. %	Mol. %	Mol. %	Mol. %
N ₂ = 78.03	O ₂ = 20.99	Ar = 0.94	CO ₂ = 0.03
H ₂ , He, Ne, Kr, Xe. = 0.01 mol%			
Total = 100 %			
Average molecular weight = 29.0			
The volume of 1 lbmole under 77 °F & 1 atm. is equal to 392 ft³			

However, combustion calculators are usually carried out with composition of **79% N₂ and 21% O₂** to simplify such calculations.

Theoretical air or (theoretical oxygen):

It is the quantity of air (or oxygen) required to burn the fuel completely according to the stoichiometric requirement so that all C, H, and S are converted to CO₂, H₂O and SO₂ respectively.

Excess Air (or excess oxygen):

In actual practice, theoretical air is not sufficient to get complete combustion, hence, excess amount of air is usually supplied. It is defined as following

$$\text{excess air} = \text{actual air input} - \text{theoretical amount of air}$$

$$\% \text{ excess air} = \frac{\text{excess air}}{\text{theoretical air}} \times 100 = \frac{\text{actual input} - \text{theoretical air}}{\text{theoretical air}} \times 100$$

% excess air may be also computed as:

$$\% \text{ excess air} = \frac{\text{actual O}_2 \text{ input} - \text{theoretical O}_2}{\text{theoretical O}_2} \times 100$$

It is important to note that heat losses through the fuel gases increases with increasing % excess air, hence, it is better to choose the optimum value of % excess air depending type of the fuel as given in the following table.

Excess air for fuels	
Fuels	% Excess air
Solids	25 to 60
Liquids	15 to 35
Gases	10 to 20

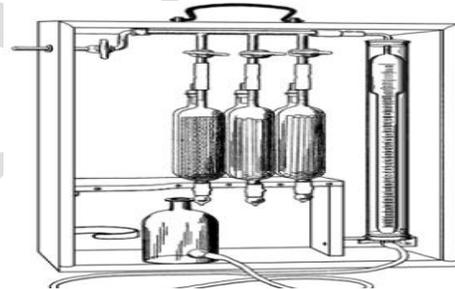
3 Stack or flue Gases::

The product gases where are proceed from combustion reactions including the water vapour is known as the “stack or flue gas” since it leaves the combustion chamber and has been evolved to the atmosphere through the stack. Normally, flue gases contain CO₂, CO, O₂, N₂, and H₂O.

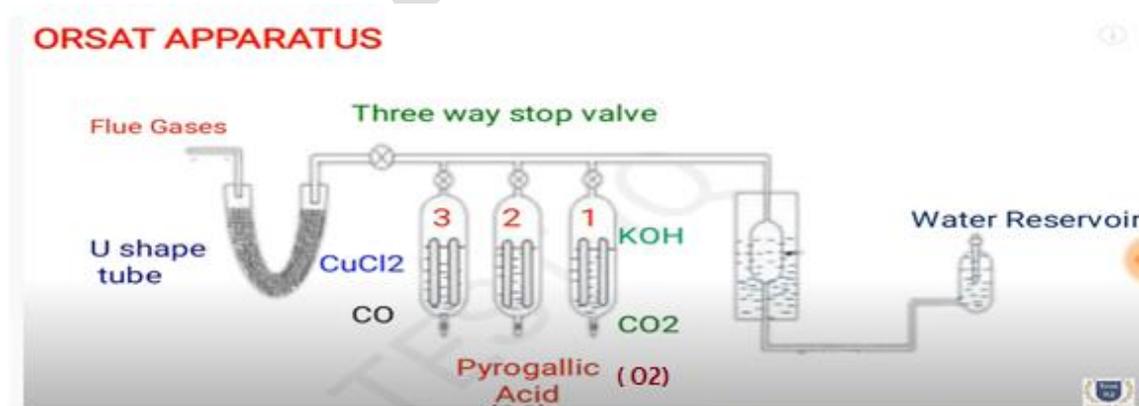
The most common method used for flue gas analyses is by “Orsat analyses” The Orsat apparatus was originally patent in 1873 by Orsat, and was modify later by a number of investigators. It is based on passing measured volume (usually 100 Cm³) of a dry sample of a flue gas on a series of absorbents and successively measured the reduction in volume of sample.

Note: water vapour does not appear in the Orsat analysis since it is eliminated from the flue gas before analysis measurements, hence analysis by this method is on “dry basis”

Flue or stack gas analysis (Wet basis)				
CO ₂	CO	O ₂	N ₂	H ₂ O
Dry flue gas Orsat analysis or (dry basis)				
CO ₂	CO	O ₂	N ₂	



Schematic diagram of Orsat analysis and analysis procedure are as follow:



Special terms:

1. **Flue or stack gas:** All the gases resulting from combustion process **including** the **water vapor**, sometimes known as a wet basis.
2. **Orsat analysis or dry basis:** All the gases resulting from combustion process **not including the water vapor**. Orsat analysis refers to a type of gas analysis apparatus in which the volumes of the respective gases are measured over and in equilibrium with water; hence each component is saturated with water vapor. The net result of the analysis is to eliminate water as a component being measured (show Figure 10.4).
3. **Complete combustion:** the complete reaction of the hydrocarbon fuel producing CO₂, SO₂, and H₂O.
4. **Partial combustion:** the combustion of the fuel producing at least some CO. Because CO itself can react with oxygen, the production of CO in a combustion process does not produce as much energy as it would if only CO₂ were produced.
5. **Theoretical air (or theoretical oxygen):** The minimum amount of air (or oxygen) required to be brought into the process for complete combustion. Sometimes this quantity is called the required air (or oxygen).
6. **Excess air (or excess oxygen):** In line with the definition of excess reactant given in Chapter 9, excess air (or oxygen) would be the amount of air (or oxygen) in excess of that required for complete combustion as defined in (5).

Note: The calculated amount of excess air does not depend on how much material is actually burned but what is possible to be burned. Even if only partial combustion takes place, as, for example, C burning to both CO and CO₂, the excess air (or oxygen) is computed as if the process of combustion went to completion and produced only CO₂.

The percent excess air is identical to the percent excess O₂:

$$\% \text{ excess air} = \frac{\text{excess air}}{\text{required air}} \times 100 = \frac{\text{excess O}_2 / 0.21}{\text{required O}_2 / 0.21} \times 100 \quad \dots \dots \dots (1)$$

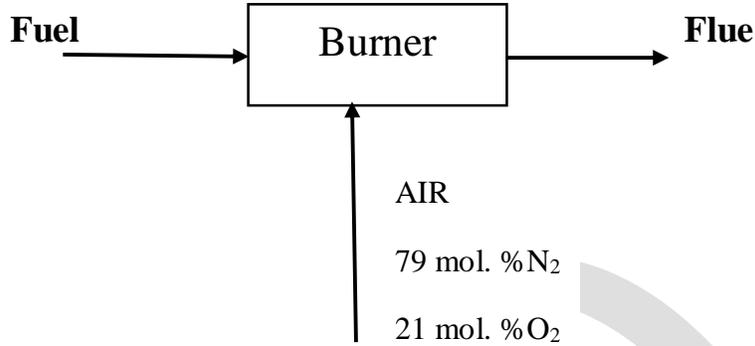
$$\text{excess air} = \text{excess O}_2 \times \frac{1}{0.21}$$

O ₂	AIR
Excess O ₂	excess air
0.21	1

Note that the ratio 1/0.21 of air to O₂ cancels out in Equation (1) Percent excess air may also be computed as

$$\% \text{ excess air} = \frac{\text{O}_2 \text{ entering process} - \text{O}_2 \text{ required}}{\text{O}_2 \text{ required}} \times 100 \quad \dots \dots \dots (2)$$

$$\text{OR} \quad \% \text{ excess air} = \frac{\text{excess O}_2}{\text{O}_2 \text{ entering} - \text{excess O}_2} \times 100 \quad \dots \dots \dots (3)$$

الاحتراق :- ((Combustion)) Material balance

: Wet flue gas, stock gas, flue

كل الغازات الخارجة من الاحتراق **H₂O** , **Co** , **O₂** , **N₂** , **So₂** , **Ash, impurities**

: Orsate analysis, dry flue gas

كل الغازات الخارجة من الاحتراق **ولكن بدون H₂O**

$$\% \text{ excess} = \frac{\text{In} - \text{theo.}}{\text{theo.}} \times 100$$

- ❖ **Theo.** الكمية النظرية الواجب توفيرها من O₂ لحرق الوقود بشكل كامل.
- ❖ **Theo.** يمكن ايجاده من المقارنة (in مع in) فقط في معادلة الاحتراق التام.

Example 11.1 Excess Air

Fuels for motor vehicles other than gasoline are being eyed because they generate lower levels of pollutants than does gasoline. Compressed propane has been suggested as a source of economic power for vehicles. Suppose that in a test 20 kg of C₃H₈ is burned with 400 kg of air to produce 44 kg of CO₂ and 12 kg of CO. What was the percent excess air?

Solution:

This is a problem involving the following reaction (is the reaction equation correctly balanced?)



Basis: 20 kg of C₃H₈

Since the percentage of excess air is based on the complete combustion of C₃H₈ to CO₂ and H₂O, the fact that combustion is not complete has no influence on the definition of "excess air". The required O₂ is

$$\frac{20 \text{ kg C}_3\text{H}_8}{44.09 \text{ kg C}_3\text{H}_8} \left| \frac{1 \text{ kg mol. C}_3\text{H}_8}{1 \text{ kg mol. C}_3\text{H}_8} \right| \left| \frac{5 \text{ kg mol. O}_2}{1 \text{ kg mol. C}_3\text{H}_8} \right| = 2.27 \text{ kg mol. O}_2$$

C ₃ H ₈	O ₂
1	5
0.453	X

The entering O₂ is

$$\frac{400 \text{ kg air}}{29 \text{ kg air}} \left| \frac{1 \text{ kg mol. air}}{100 \text{ kg mol. air}} \right| \left| \frac{21 \text{ kg mol. O}_2}{100 \text{ kg mol. air}} \right| = 2.90 \text{ kg mol. O}_2$$

Air	O ₂
100	21
20	X

The percentage excess air is

$$\frac{\text{excess O}_2}{\text{required O}_2} \times 100 = \frac{\text{entering O}_2 - \text{required O}_2}{\text{required O}_2} \times 100$$

$$\% \text{ excess air} = \frac{2.90 \text{ kg mol O}_2 - 2.27 \text{ kg mol O}_2}{2.27 \text{ kg mol O}_2} \times 100 = 28 \%$$

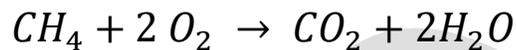
Example 11.2

Methane is completely burned with 26 % excess air. Calculate:

A// the Orsat analysis of the flue gas.

B// the molal ratio of water vapour to the dry flue gas, and.

C// the molal ratio of air to methane.

Solution:

Basis: 100 lb mole of CH₄

$$\therefore \text{Theo. } O_2 = 200 \text{ lb mole}$$

$$\text{excess } O_2 = 200 \left(\frac{26}{100} \right) = 52 \text{ lb mole}$$

$$\text{Actual } O_2 \text{ input} = 252 \text{ lb mole}$$

$$N_2 \text{ input} = 252 \text{ } O_2 \left(\frac{79 \text{ } N_2}{21 \text{ } O_2} \right) = 948 \text{ lb mole}$$

$$CH_4 \text{ reacted} = CH_4 \text{ input} = 100 \text{ lb mole}$$

$$O_2 \text{ reacted} = 100 (2) = 200 \text{ lb mole}$$

$$CO_2 \text{ Produced} = 100 = 100 \text{ lb mole}$$

$$H_2O \text{ Produced} = 200 = 200 \text{ lb mole}$$

$$O_2 \text{ unreacted} = 52 \text{ lb mole}$$

CH ₄	O ₂
1	2
100	X

N ₂	O ₂
79	21
X	254

Orsat analysis		
CO ₂	100	9.1%
O ₂	52	4.7 %
N ₂	948	86.2 %
	1100	100 %

$$\left(\frac{\text{Water vap.}}{\text{dry flue gas}} \right) = \frac{200}{1100} = \frac{2}{11} = 0.182:1 = \frac{18.2 \text{ mol } H_2O}{100 \text{ mol dry flue gas}}$$

$$\text{Air input} = 252 \text{ } O_2 + 948 \text{ } N_2 = 1200 \text{ lb mole}$$

$$\frac{\text{Air}}{CH_4} = \frac{1200}{100} = 12 : 1$$

Example 11.3

A gaseous fuel composed of 80 mol. % CH₄, 10 mol. % H₂, 10 mol. % N₂ is burned with 40 % excess air. 80 % of the carbon burned goes to CO₂, the rest convert to CO, and all hydrogen are converted to H₂O. Calculate: A// the molal ratio of air input to the fuel burned. B// Orsat analysis of the flue gas, and C// molal ratio of water vapour to the dry flue gas.

Solution:

Basis: 100 lb mole of the fuel.

CH₄ = 80 lb mole	H₂ = 10 lb mole	N₂ = 10 lb mole
------------------------------------	-----------------------------------	-----------------------------------

$CH_4 + 2 O_2 \rightarrow CO_2 + 2H_2O$ 80	Theoretically assumed complete combustion
$H_2 + 1/2 O_2 \rightarrow H_2O$ 10	

$$\therefore \text{Theoretical } O_2 \text{ required} = 80(2) + 10 \left(\frac{1}{2}\right) = 165 \text{ lb mole}$$

$$\text{excess } O_2 = 165 \left(\frac{40}{100}\right) = 66 \text{ lb mole}$$

$$\text{Actual } O_2 \text{ input} = 165 + 66 = 231 \text{ lb mole}$$

$$\text{Air input} = 231 \left(\frac{100}{21}\right) = 1100 \text{ lb mole}$$

$$\therefore \frac{\text{Air}}{\text{Fuel}} = \frac{1100}{100} = 11 : 1$$

<u>Air</u>	<u>O₂</u>
100	21
X	231

$$N_2 \text{ input with Fuel} + N_2 \text{ input with Air} = N_2 \text{ output}$$

$$N_2 \text{ output} = 10 + 1100 \left(\frac{79}{100}\right) = 869 \text{ lb. mole}$$

<u>Air</u>	<u>N₂</u>
100	79
1100	X

$CH_4 + 2 O_2 \rightarrow CO_2 + 2H_2O$ 64	Actual reaction $CH_4 \text{ goes to } CO_2 = 80 \left(\frac{80}{100} \right) = 64 \text{ lb. mole}$
$CH_4 + 3/2 O_2 \rightarrow CO + 2H_2O$ 16	$CH_4 \text{ goes to } CO = 80 \left(\frac{20}{100} \right) = 16 \text{ lb. mole}$
$H_2 + 1/2 O_2 \rightarrow H_2O$ 10	

$$\therefore CO_2 \text{ Produced} = 64 \text{ lb mole}$$

$$CO \text{ Produced} = 16 \text{ lb mole}$$

$$\therefore H_2O \text{ Produced} = 64(2) + 16(2) + 10 = 170 \text{ lb mole}$$

$$\therefore O_2 \text{ reacted} = 64(2) + 16(1.5) + 10\left(\frac{1}{2}\right) = 157 \text{ lb mole}$$

$$O_2 \text{ output} = O_2 \text{ input} - O_2 \text{ reacted} = 231 - 157 = 74 \text{ lb mole}$$

Orsat analysis		
Component	Ib. mole	Mol. %
CO ₂	64	6.2%
CO	16	1.5 %
N ₂	879	85.1 %
O ₂	74	7.2
Total	1033	100 %

$$\frac{H_2O}{\text{Dry flue gas}} = \frac{170}{1033} = \frac{0.165 \text{ mol } H_2O}{\text{mol dry flue gas}}$$

Example 11.4

A liquid fuel consists of 36 mol. % Pentane (C_5H_{12}) and 64 mol. % Hexane (C_6H_{14}) is burned with 20 % excess air. 80 % of the carbon goes to CO_2 and 20 % goes to CO . Calculate the Orsat analysis of the stack gas and the molal ratio of water vapour to the dry flue gas.

Solution:

Basis: 100 lb mole of the fuel.

$C_5H_{12} = 36$ lb mole	$C_6H_{14} = 64$ lb mole
$C_5H_{12} + 8 O_2 \rightarrow 5 CO_2 + 6H_2O$ 36	Theoretically assumed complete combustion
$C_6H_{14} + 9.5 O_2 \rightarrow 6 CO_2 + 7H_2O$ 64	

$$\therefore \text{Theoretical } O_2 \text{ required} = 36(8) + 64(9.5) = 896 \text{ lb mole}$$

$$\text{excess } O_2 = 896 \left(\frac{20}{100} \right) = 179 \text{ lb mole}$$

$$\text{Actual } O_2 \text{ input} = 896 + 179 = 1075 \text{ lb mole}$$

$$N_2 \text{ input} = 1075 O_2 \left(\frac{79 N_2}{21 O_2} \right) = 4044 \text{ lb mole} = N_2 \text{ output}$$

$$\therefore \text{Air input} = 1075 + 4044 = 5119 \text{ lb mole}$$

Method 1

$C_5H_{12} + 8 O_2 \rightarrow 5 CO_2 + 6H_2O$ $36 \left(\frac{80}{100} \right) = 28.8 \text{ lb mole}$	Actual reaction
$C_5H_{12} + 5.5 O_2 \rightarrow 5 CO + 6H_2O$ $36 \left(\frac{20}{100} \right) = 7.2 \text{ lb mole}$	
$C_6H_{14} + 9.5 O_2 \rightarrow 6 CO_2 + 7H_2O$ $64 \left(\frac{80}{100} \right) = 51.2 \text{ lb mole}$	
$C_6H_{14} + 6.5 O_2 \rightarrow 6 CO + 7H_2O$	

$$64 \left(\frac{20}{100} \right) = 12.8 \text{ lb mole}$$

$$\therefore \text{CO}_2 \text{ Produced} = 5(28.8) + 6(51.2) = 451 \text{ lb mole}$$

$$\text{CO Produced} = 5(7.2) + 6(12.8) = 113 \text{ lb mole}$$

$$\begin{aligned} \therefore \text{H}_2\text{O Produced} &= 6(28.2 + 7.2) + 7(51.2 + 12.8) = 216 + 447 \\ &= 664 \text{ lb. mole} \end{aligned}$$

$$\begin{aligned} \therefore \text{O}_2 \text{ reacted} &= 8(28.8) + 5.5(7.2) + 9.5(51.2 + 6.5(12.8)) \\ &= 230.4 + 39.6 + 486.4 + 83.2 = 840 \text{ lb. mole} \end{aligned}$$

$$\text{O}_2 \text{ output} = 1075 - 840 = 235 \text{ lb mole}$$

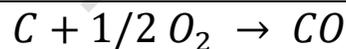
$$\frac{\text{H}_2\text{O}}{\text{Dry flue gas}} = \frac{664}{4843} = \frac{0.137 \text{ mol H}_2\text{O}}{\text{mol dry flue gas}}$$

Method 2

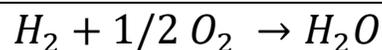
Component	Ib. mole	Ib. mole C	Ib. mole H ₂
C ₅ H ₁₂	36	5 X 36 = 180	6 X 36 = 216
C ₆ H ₁₄	64	6 X 64 = 384	7 X 64 = 448
Total	100	564	664



$$564 \left(\frac{80}{100} \right) = 451 \text{ lb mole}$$



$$564 \left(\frac{20}{100} \right) = 113 \text{ lb mole}$$



664

$$\therefore \text{CO}_2 \text{ Produced} = 451 \text{ lb mole}$$

$$\text{CO Produced} = 113 \text{ lb mole}$$

$\therefore H_2O \text{ Produced} = 664 \text{ lb. mole}$

$\therefore O_2 \text{ reacted} = 451 + \frac{113}{2} + \frac{664}{2} = 840 \text{ lb. mole}$

Orsat analysis		
Component	lb. mole	Mol. %
CO₂	451	9.31%
CO	113	2.34 %
N₂	4044	82.5 %
O₂	235	4.89
Total	4843	100 %

Example 11.5

A fuel composed of carbon and hydrogen is burned with dry air. The Orsat analysis of the flue gas are as follow: CO₂ 5.4 %, O₂ 7.7 %, N₂ 86.9 %. Calculate:

A// Ib mole of air used per 100 Ib. mole of the dry flue gas. B// % excess air?

C// Ib mole of H₂O used per 100 Ib. mole of the dry flue gas.

D//The mass ratio of carbon to hydrogen the fuel and

E//Ib. mole of the flue gas produced from burning 1 Ib. of the fuel.

Solution:

A// **Basis: 100 Ib mole of dry flue gas**

CO ₂ = 5.4 Ib mole	O ₂ = 7.7 Ib mole	N ₂ = 86.9 Ib mole
-------------------------------	------------------------------	-------------------------------

$$N_2 \text{ input} = N_2 \text{ output} = 86.9 \text{ Ib mole}$$

$$\text{Actual } O_2 \text{ input} = 86.9 N_2 \left(\frac{21 O_2}{79 N_2} \right) = 23.1 \text{ Ib mole}$$

$$\therefore \text{Air input} = 86.9 + 23.1 = 110 \text{ Ib mole}$$

i. e. 110 Ib mole air / 100 Ib mole dry flue gas

<u>N₂</u>	<u>O₂</u>
79	21
86.9	X

B//

∴ Since no quantity of CO in the flue gas, hence these is complete combustion

i. e. Theoretical O₂ = O₂ reacted

$$\text{i. e. Theoretical } O_2 = O_2 \text{ input} - O_2 \text{ output} = 23.1 - 7.7 = 15.4 \text{ Ib mole}$$

$$\% \text{ excess} = \frac{O_2 \text{ In} - O_2 \text{ theo.}}{O_2 \text{ theo.}} \times 100 = \frac{23.1 - 15.4}{15.4} \times 100 = 50 \%$$

C//

 O_2 reacted with C = 5.4 lb mole O_2 reacted with H_2 = 15.4 – 5.4 = 10 lb mole $\therefore H_2$ in the fuel = 10(2) = 20 lb mole H_2O Produced = 20 lb mole \rightarrow i. e. 20 lb mole/100 lb mole dry flue gas

D//

$$\text{i. e. carbon/hydrogen } \left(\frac{W}{W}\right) \text{ ratio} = \left(\frac{5.4 \times 12}{20 \times 2}\right) = \left(\frac{64.8}{40}\right) = 1.62$$

E//

mass of fuel = mass of C + mass of H

$$\text{mass of fuel} = 64.8 + 40 = 104.8 \text{ lb}$$

$$\text{mole of flue gas} = 100 + 20 = 120 \text{ lb mole}$$

$$\text{mole flue gas/lb fuel} = \left(\frac{120}{104.8}\right) = 1.145 \frac{\text{lb mol flue gas}}{\text{lb fuel}}$$

<u>lb fuel</u>	<u>lb. mole flue gas</u>
104.8	120
1	x

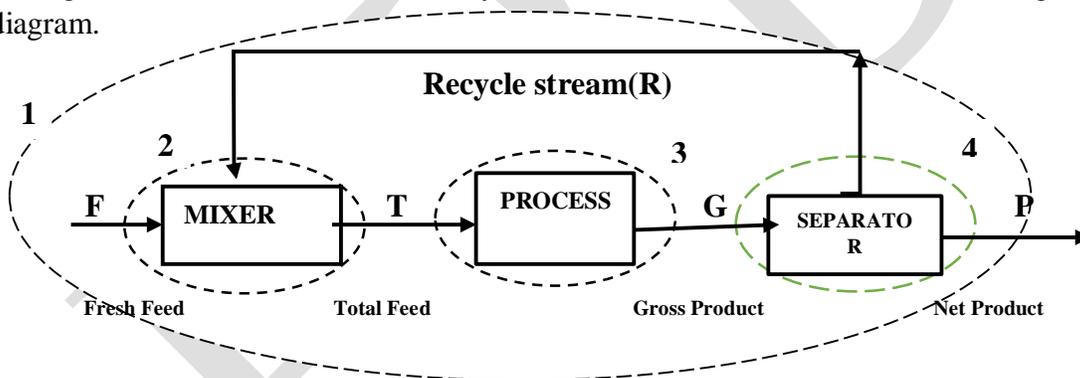
Material balance on processes involving Recycle, by pass and purge streams

Introduction:

Recycle, by pass and purge streams are commonly used in the design of chemical processes around the reaction units (reactors) as well as in unit operations such as drying, distillation and extraction units. **Typical materials balance calculations on processes** involving such streams are given in this section.

(A): Recycle Stream:

It is part of the product stream (either of similar or different composition) that is separated and returned to mix again with inlet stream (fresh feed) for economic considerations .The gross product (G) leaving the process is commonly separated by suitable separation technique such as distillation, filtration, extractionetc. into the net product (P) and the recycle stream (R); whereas the total feed (T) input to the process is made up by mixing the fresh feed (F and the recycle stream (R) as shown in the following block diagram.



The recycle ratio; sometimes **called reflux ratio**, is widely used in recycle calculations. It is the ratio between the amount of recycle to that of the net product, i.e. $\left(\frac{R}{P}\right)$.

Material balance calculations can be made around (1) the entire process, (2) the mixing unit (3) the process only, and (4) separation unit.

The sequence of calculation steps depends on the data given in the problem.

***Note:** that the quantity of net product **depends only** on the charged once at the starting period of working the process and remains circulated inside the process with constant flow rate and composition under **steady state condition** and it is fixed according to economic considerations

Some of important aims and applications of recycling operation are as follow.

1. To recovery and avoid wastage of catalyst and unconverted substances for processes involving chemical reactions of lower percent conversion of reactants.

لاستعادة وتجنب إهدار العامل المساعد والمواد غير المتحوّلة

2. To utilize the heat being lost in the outgoing stream such as recycling part of the hot wet air that leaves the drying unit to mix with the fresh feed of add dry air.

الاستفادة من الحرارة المفقودة في التيار الخارج

3. To maintain the required conditions to perform the process **with higher efficiency** such as recycling part of the top product in **rectification distillation** from the top of the column with vapour from the bottom of the column in order to separate the components by gas liquid mass transfer operation.

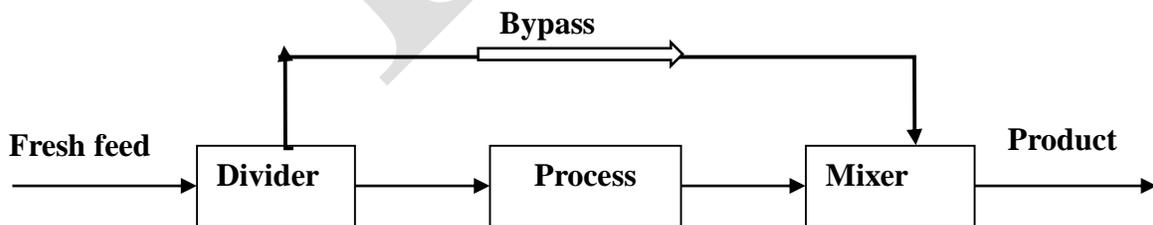
Reflux ratio $\left(\frac{R}{D}\right)$ is the most important parameter in the design of distillation column so that the cost is directly dependent on this parameter.

للحفاظ على الشروط المطلوبة لأداء العملية بكفاءة أعلى

4. To dilute the fresh feed such as recycling part of filtrate that leaves filtrations unit to mix with fresh slurry since it is difficult to handle slurry with high solid concentration and the filter will operate more properly with recycle.
5. To improve the selectivity of the desired product.

(B) By pass Stream:

It is a **fraction** of the **fresh feed** that **skips** once or **more stages** of the process and goes directly to another stage in parallel with other fraction of the feed that passes through the process as shown in the following block diagram. This arrangement is used when it is desired **to make a relatively small change** in the feed stream or **to control the composition of product** at desired value.



Some of important applications of bypass stream are as follow

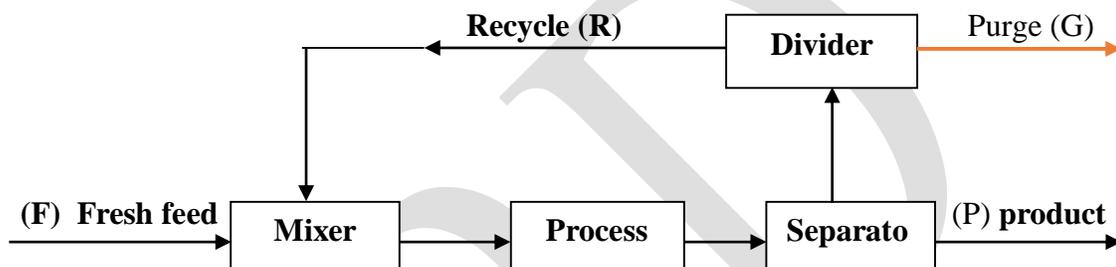
1. Pumping of liquid from a storage tank by **a more efficient pump** of high horsepower to a small process unit at **desired lower flow rate**.
2. Dissolution of caustic soda in water by a two steps process to the very high heat of dissolution.

3. Separation of mixtures by a more efficient distillation column, so that a bypass stream is used to control the composition of the final product at the desired value.

(C) Purge stream:

It is fraction of the recycle stream (**with the same composition**) that is removed out the process **to prevent accumulation of inert materials** (that are not involve in the reaction) in the recycle stream so that the quantity of inert input with the fresh feed is equal to that output with purge stream as shown in the following block diagram .

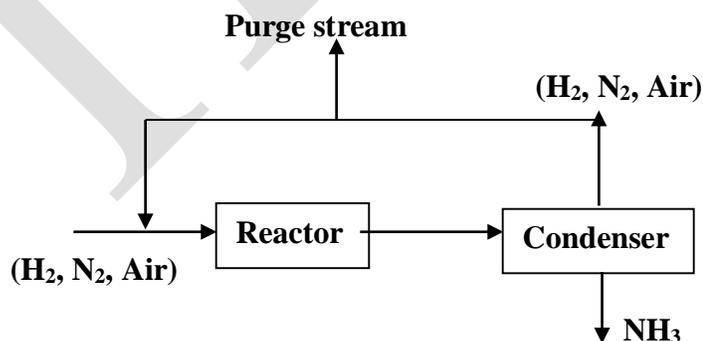
شكر اش



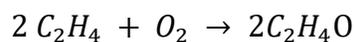
F (wt. fraction of inert in F) = G (wt. fraction of inert in G) = R (wt. fraction of inert in R)

[Since: G & R have the same composition]

The important example of application of purge stream is in the production of ammonia from gaseous mixture of N₂ & H₂ containing some impurities of argon as shown in the following block diagram.



Similarly, purge stream is used in the process of **acetaldehyde** production by oxidation of ethylene according to the reaction:



The feed to the process consists of ethylene and air and conversion of C_2H_4 is about 50 %, hence, nitrogen input with air must be removed by purge stream in order to return unreacted C_2H_4 as a recycle stream.

Recycle, by pass and Purge Streams

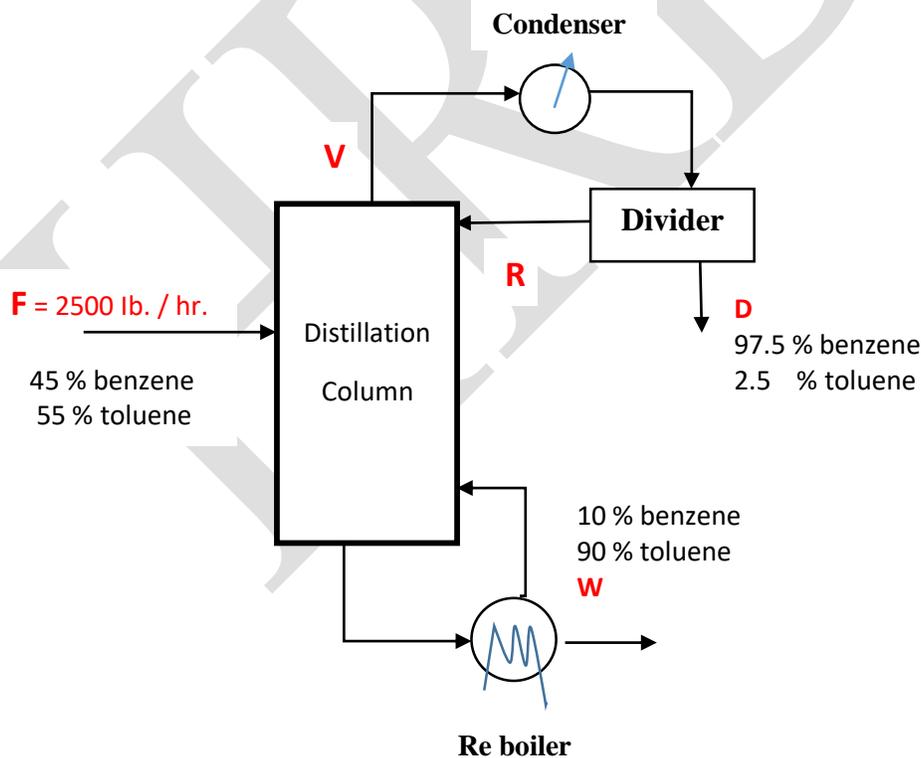
Example 1:

A binary mixture consists of 45 Wt.% benzene and 55 Wt.% toluene are continuously fed to distillation column at a rate of 2500 lb / hr .The Top product contains 97.5 Wt.% benzene, whereas the bottom product contains 90 Wt.% toluene The column operate with reflux ratio of 2.5.

Calculate: A// the top & bottom products produced per hour

B// the recycle stream and the vapor input to the condenser per hour

Solution:



A// **Basis: 1 hr. \equiv 2500 lb. of F**

1- Material balance overall the process

$$T.M.B \quad F = D + W \quad \rightarrow \quad D + W = 2500 \quad \dots \dots \dots (1)$$

Benzene balance

$$F X_F = D X_D + W X_W$$

$$2500 (0.45) = D (0.975) + W(0.1) \rightarrow 1125 = 0.975 D + 0.1 W \quad \dots\dots (2)$$

(Sub. 1 in 2)

$$1125 = 0.975 D + 0.1 (2500 - D)$$

$$875 = 0.875 D \rightarrow D = \frac{875}{0.875} = 1000 \text{ lb/hr}$$

(Sub. in 1)

$$W = 2500 - 1000 = 1500 \text{ lb/hr}$$

Checking

Toluene balance:

$$\text{Toluene input} = F \left(\frac{55}{100} \right) = 2500 (0.55) = 1375 \text{ lb}$$

$$\text{Toluene output} = D \left(\frac{2.5}{100} \right) + W \left(\frac{90}{100} \right) = 1000(0.025) + 1500(0.9) = 1375 \text{ lb}$$

B// 2. Material balance on Divider

$$T.M.B \quad V = R + D \quad \dots\dots\dots (3)$$

$$\text{Reflux ratio} = \frac{R}{D} = 2.5 \rightarrow \therefore R = 2.5 D = 2.5 (1000) = 2500 \text{ lb/hr}$$

(Sub. in 3)

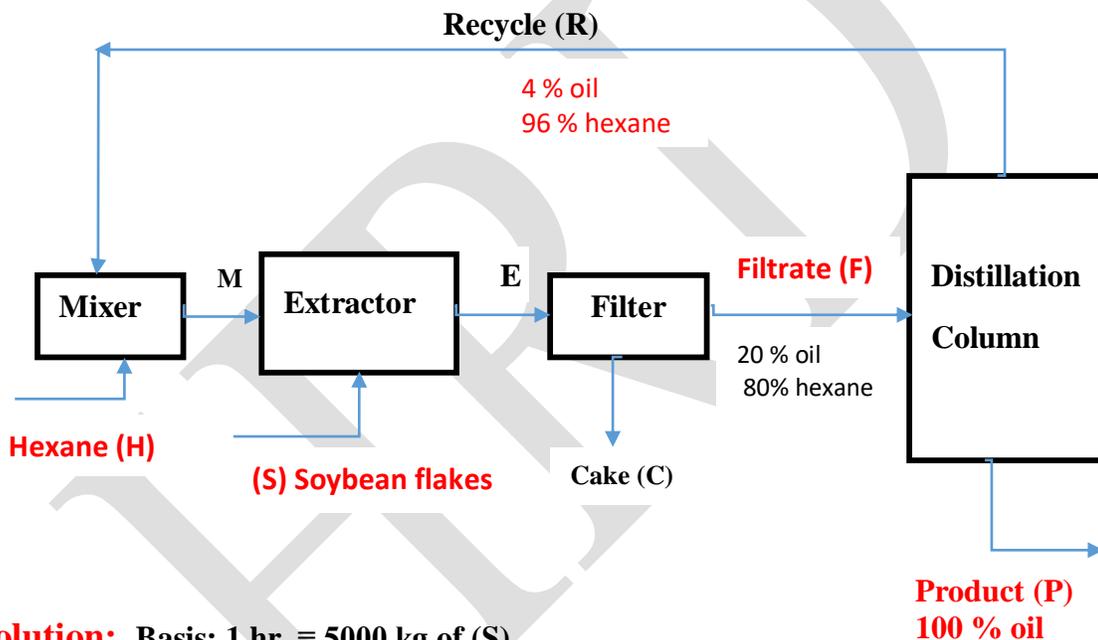
$$V = 2500 + 1000 = 3500 \text{ lb/hr}$$

Example 2:

Soybean slakes (S) containing 19 wt.% oil & 81 wt.% solids are continuously fed at rate of 5000 kg /hr. to the vegetable oil production process in which soybean oil are extracted by hence as show in the following block diagram

The filter cake (C) contains 90 wt. % solids & 10 wt. % liquid of hexane +oil of the same composition of the filtrate (F). **Calculate:**

- The flow rates in kg/hr. of all streams of the process and the composition of (M) & (E).
- Yield of the process



Solution: Basis: 1 hr. \equiv 5000 kg of (S)

1. Material balance overall the process

- solid balance

$$S \left(\frac{81}{100} \right) = C \left(\frac{90}{100} \right)$$

$$5000 (0.81) = 0.9 C \rightarrow C = 4500 \text{ Kg/hr}$$

- hexane balance

$$H = C \left(\frac{8}{100} \right) \rightarrow H = 4500 \left(\frac{8}{100} \right) = 360 \text{ kg/hr}$$

Calc. the composition of (C)

Basis 100kg of C

Solid in C = 90 kg

Liquid in C = 10 kg

% of liq. = 20 % oil & 80 % hexane

Oil = 10 (20/100) = 2 kg

Hexane = 10 (80/100) = 8 kg

i.e. 2% oil & 8% hexane and 90% solid

(c) oil balance

$$S \left(\frac{19}{100} \right) = P + C \left(\frac{2}{100} \right) \rightarrow P = 950 - 90 = 860 \frac{\text{kg}}{\text{hr}}$$

Checking:

$$\text{input} = S + H = 5000 + 360 = 5360 \text{ kg/hr}$$

$$\text{output} = C + P = 4500 + 860 = 5360 \text{ kg/hr}$$

$$\text{Yield} = \frac{\text{Product}}{\text{Feed}} = \frac{860 \text{ kg Oil}}{5000 \text{ kg Soybean}} = 0.172 \text{ kgoil /kg soybean}$$

2. Material balance on distillation

a. Oil balance

$$0.2 F = P + 0.04 R = 860 + 0.04R \dots \dots \dots (1)$$

b. Hexane balance

$$0.8 F = 0.96 R \dots \dots \dots (2)$$

(Sub. 1 in 2)

$$R = 4300 \text{ kg/hr and } F = 5160 \text{ kg/hr}$$

3. Material balance on Mixer

$$M = R + H \rightarrow M = 4300 + 360 = 4660 \text{ kg/hr}$$

Composition of M

$$\text{Oil} = \left(\frac{4300 (0.04)}{4660} \right) \times 100 = 3.69 \%$$

$$\text{Hexane} = \left(\frac{360 + 4300 (0.96)}{4660} \right) \times 100 = 96.31 \%$$

4. Material balance on Extractor

$$E = M + S \rightarrow E = 4660 + 5000 = 9660 \text{ kg/hr}$$

Oil in E	172+ 950 = 1122 kg 0.04 R + oil in S= 1122 Kg	11.6%
Hexane in E	4488 kg 0.96 R + H =	46.5%
Solid in E	4050 kg Soild in S	41.9%
Total	9660 kg	100 %

5. Final checking (material balance on filter)

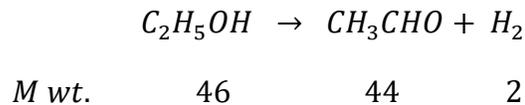
Checking:

$$\text{input} = E = 9660 \text{ kg/hr}$$

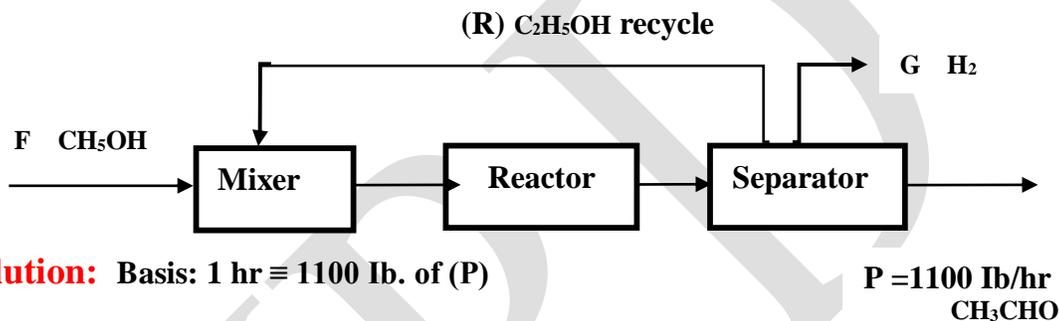
$$\text{output} = F + C = 5160 + 4500 = 9660 \text{ kg/hr}$$

Example 3:

Acetaldehyde (CH_3CHO) is produced at rate of 1100 lb/hr (P) by catalytic dehydrogenation of ethanol:



It is found that 80% of ethanol input to the reactor are converted, and the rest are completely recycled. Calculate the mass flow rate of fresh ethanol (F), recycle stream (R), and hydrogen evolved (G).



Solution: Basis: 1 hr \equiv 1100 lb. of (P)

$$\text{CH}_3\text{CHO produced} = \frac{1100}{44} = 25 \text{ lbmole}$$

$$\text{H}_2 \text{ Produced} = 25 \text{ lbmole} \quad \rightarrow \quad G = 25 (2) = 50 \text{ lb/hr}$$

$$\text{C}_2\text{H}_5\text{OH reacted} = 25 \text{ lbmole} \quad \rightarrow \quad F = 25 (46) = 1150 \text{ lb/hr}$$

(Since no quantity of $\text{C}_2\text{H}_5\text{OH}$ out from the process hence all quantity input are reacted)

Checking T.M.B. overall the process

input = F = 1150 lb
output = P + G = 1100 + 50 = 1150 lb

$$\text{Conversion of } \text{C}_2\text{H}_5\text{OH produced} = \frac{\text{C}_2\text{H}_5\text{OH reacted}}{\text{C}_2\text{H}_5\text{OH input to the reactor}}$$

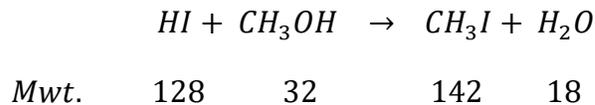
$$\frac{80}{100} = \frac{1150}{1150 + R} \rightarrow 1150 = 0.8 (1150) + 0.8R \rightarrow R = \frac{1150 - 920}{0.8} = 287.5 \text{ lb/hr}$$

Checking:

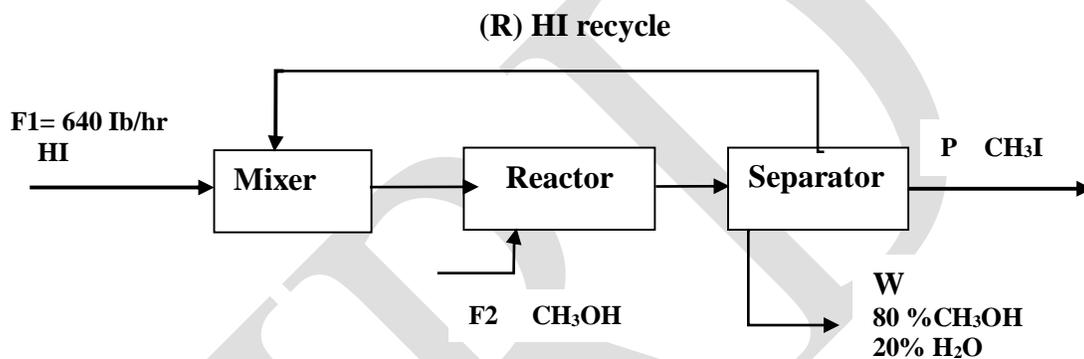
Ethanol input to the reactor = F + R = 1150 + 287.5 = 1437.5 lb
Ethanol reacted = 1437.5(80/100) = 1150 lb. = F
Ethanol un reacted = 1437.5 (20/100) = 287.5 lb.= R

Example 4:

Methyl iodide is produced by adding HI to an excess amount of methanol according to the following reaction:



Fresh HI are fed to process at a rate of 640 lb / hr (F1). The degree of completion of the reaction a 40 %. Calculate: the flow rates of streams (P), (W), (F2) and (R) shown in the following block diagram.

**Solution:**

A// **Basis: 1 hr. \equiv 640 lb. of F1**

1- Material balance overall the process

$$\text{HI input} = \frac{640}{128} = 5 \text{ lb mole} = \text{HI reacted}$$

(Since no quantity of HI out from the process)

$$\text{CH}_3\text{I Produced} = 5 (142) = 710 \text{ lb/hr} = p$$

$$\text{H}_2\text{O Produced} = 5 (18) = 90 \frac{\text{lb}}{\text{hr}} = W \left(\frac{20}{100} \right) \rightarrow W = \left(\frac{90}{0.2} \right) = 450 \text{ lb/hr}$$

$$\text{CH}_3\text{OH output in W} = 450 \left(\frac{80}{100} \right) = 360 \text{ lb}$$

$$\text{CH}_3\text{OH input} = \text{CH}_3\text{OH reacted} + \text{CH}_3\text{OH unreacted}$$

$$F2 = 5 (32) + 360 \rightarrow F2 = 160 + 360 = 520 \text{ lb/hr}$$

Checking:

$$\text{input} = F1 + F2 = 640 + 520 = 1160 \text{ Ib}$$

$$\text{output} = P + W = 710 + 450 = 1160 \text{ Ib}$$

$$\xi_{CH_3OH}^{max} = \frac{16.25}{1} = 16.25$$

$$\xi_{HI}^{max} = \frac{5}{1} = 5$$

Hence: HI is The Limiting reactant and CH₃OH is the excess reactant.

$$\text{degree of completion} = \frac{HI \text{ reacted}}{HI \text{ input to the reactor}}$$

$$\frac{40}{100} = \frac{640}{640 + R} \rightarrow 256 + 0.4R = 640 \rightarrow R = 960 \text{ Ib/hr}$$

Checking

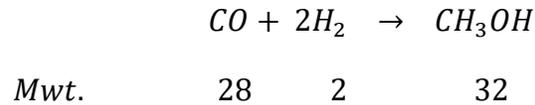
$$HI \text{ input to the reactor} = F1 + R = 640 + 960 = 1600 \text{ Ib}$$

$$HI \text{ reacted} = 1600 \left(\frac{40}{100} \right) = 640 \text{ Ib} = F1$$

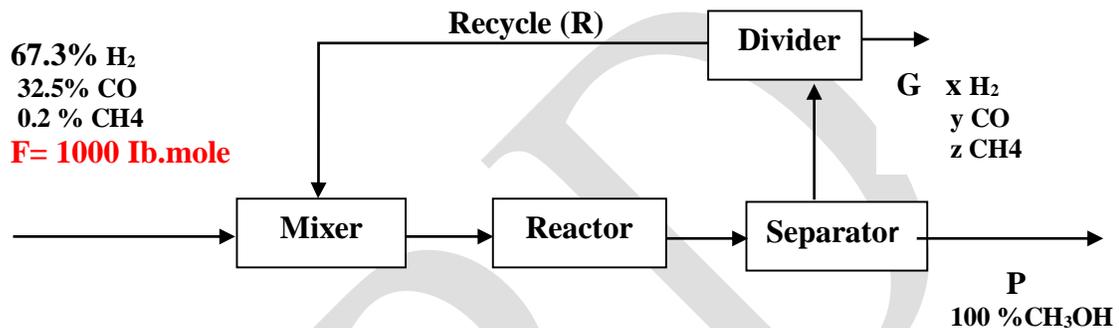
$$HI \text{ unreacted} = 1600 \left(\frac{60}{100} \right) = 960 \text{ Ib} = R$$

Example 5:

Methanol can be produced according to the following reaction:



A gaseous mixture (F) consists of 67.3 mol. % H₂, 32.5 mol. % CO, and 0.2 mol. % CH₄ are fed at a rate of 1000 lb. mole/hr. to the process shown in the following block diagram.



Since CH₄ is not involved in the reaction, hence a purge stream (G) is used to maintain the composition of CH₄ in the recycle stream as 3.2 mol. %. If the conversion of CO = 18%. Calculate the flow rates of (P), (G), (R) and the composition of (R).

Solution:

Basis: 1 hr. \equiv 1000 lbmole of F

Let x, y, z = mole fraction of H₂, CO and CH₄ in (R) & (G) respectively.

Note: that (R) and (G) have the same composition since the stream out from the separator is separated to (R) & (G) by divider.

$$\therefore z = 0.032$$

CH₄ balance over all process

$$1000 \left(\frac{0.2}{100} \right) = G (0.032) \rightarrow G = \left(\frac{2}{0.032} \right) = 62.5 \text{ lbmol./hr}$$

H₂ reacted = H₂ input – H₂ output

$$H_2 \text{ reacted} = 1000 \left(\frac{67.3}{100} \right) - G (X) = 673 - 62.5 X \dots \dots \dots (1)$$

CO reacted = CO input – CO output

$$\text{CO reacted} = 1000 \left(\frac{32.5}{100} \right) - G(y) = 325 - 62.5y \dots \dots \dots (2)$$

Since H_2 reacted is **twice** CO reacted hence:

Note: **G & P ≠ F**

$$673 - 62.5X = 2(325 - 62.5y) = 650 - 125y$$

Why???

$$\therefore X = \left(\frac{23 + 125Y}{62.5} \right) = 0.368 + 2y \dots \dots \dots (3)$$

$$x + y + z = 1 \rightarrow x + y = 1 - z = 0.968 \dots \dots \dots (4)$$

$$\text{Sub. 3 in (4)} \quad 0.368 + 2y + y = 0.968 \rightarrow y = \frac{0.968 - 0.368}{3} = 0.2$$

$$\text{Sub. in 3} \quad X = 0.368 + 2(0.2) = 0.768$$

$$\text{CH}_3\text{OH Produced} = \text{CO reacted} = 325 - 62.5y = 312.5 \text{ lbmol/hr} = (P)$$

$$\text{Conversion of CO} = \frac{18}{100} = \frac{\text{CO reacted}}{\text{CO input}} = \frac{312.5}{0.2R + 325}$$

$$\therefore 312.5 = 0.036R + 58.5 \rightarrow R = \frac{254}{0.036} = 7055.6 \text{ lbmol/hr}$$

Composition of R		
H ₂	x = 0.768	76.8 %
CO	y = 0.20	20.0 %
CH ₄	Z = 0.032	3.2 %
Total	1	100 %

Ideal and Real gases

Introduction:

This chapter deals with the pressure – volume –temperature (P-V-T) relationships for ideal and real gaseous behavior of pure components and mixtures of gases.

These relation are of importance in all calculation involve gases such as energy balance, combustion, thermodynamics and design of pressure vessels Etc.

It is convenient to study relationships of gases by putting them in four separate sections:-

1. Ideal gas law.
2. Ideal gas mixtures.
3. Real gas relationships.
4. Real gas mixtures.

1- Ideal gas law

The ideal gas can be defined as that gas in which the average distance between the molecules is great enough that the intermolecular forces are **negligible**, and the volume of gas molecules is **very small compared with the total volume** of the gas and can be neglected.

An ideal gas is an imaginary gas that obeys certain simple law known as “ideal gas law “. The behavior of any real gas such as H₂, O₂, CO₂etc. approaches that of an ideal gas at low pressure and high temperatures. Thus, the ideal gas law can be used for simplicity in many engineering calculations at low pressure (up to 3 - 4 atm.) since it gives incorrect result at higher pressures and lower temperatures.

❖ Ideal gas law was developed from the work of many scientist as follow:

A// Boyle law

Robert Boyle (1627 - 1691), an English chemist. In 1662 found that the volume of a certain quantity of an ideal gas is **inversely proportional** to the absolute pressure at constant temperature.

Hence for one mole of an ideal gas, $\bar{V} \propto \frac{1}{P}$

$$P \bar{V} = K_1 \quad \text{at constant } T \quad \dots \dots \dots (1)$$

$$\text{Where } \bar{V} = \text{molar volume} = \frac{V}{n} ; K_1 \text{ is constant}$$

Table 13.1: Pressure-Volume Data		
Pressure (atm)	Volume (mL)	$P \times V = k$ (atm·mL)
0.5	1000	500
0.625	800	500
1.0	500	500
2.0	250	500
5.0	100	500
8.0	62.5	500
10.0	50	500

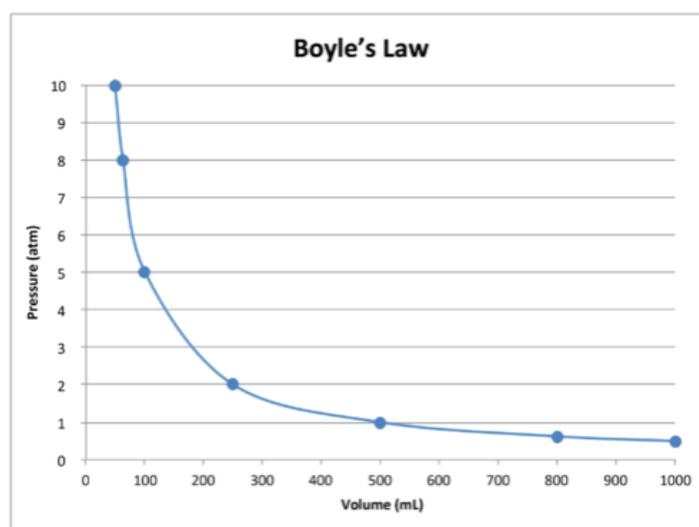


Figure 13.1: The pressure of a gas decreases as the volume increases, making Boyle's law an inverse relationship.

B// Charles and Gay-Lussac law

In 1787, they demonstrated that the volume of a certain quantity of an ideal gas varies directly with absolute temperature at constant pressure.

Hence for one mole of an ideal gas, $\vec{V} \propto T$

$$\text{i. e. } \vec{V} = K_2 T \quad \text{OR} \quad \frac{\vec{V}}{T} = K_2 \quad \text{at constant } P \quad \dots \dots \dots (2)$$

Where K_2 is constant

Combination of eq. 1 & 2 gives $\frac{P \vec{V}}{T} = R \dots \dots \dots (3)$

Where R is a constant

Table 13.2: Temperature-Volume Data

Temperature (K)	Volume (mL)	$\frac{\vec{V}}{T} = K$
50	20	0.40
100	40	0.40
150	60	0.40
200	80	0.40
300	120	0.40
500	200	0.40
1000	400	0.40

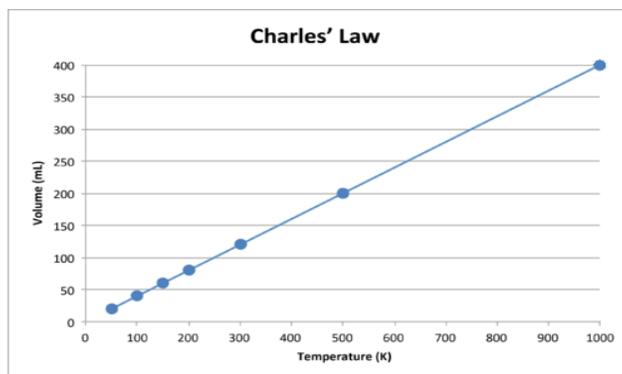


Figure 13.2: The volume of a gas increases as the Kelvin temperature increases.

C// Avogadro Hypothesis

In 1811, Avogadro proposed his famous hypothesis that “equal volumes of different gases contain the same number of molecules under the **same condition of temperature and pressure**. This means that molar volumes (\bar{V}) of all gases of ideal behavior are equal at the same temperature & pressure.

Thus, the constant (R) is the same for all gases. It is known “the universal gas constant”.

The ideal gas law usually put in the form:

$$P V = n R T \quad \dots \dots \dots (4)$$

Where:

p = absolute pressure of the gas

V = total volume occupied by the gas

n = number of moles of the gas

R = ideal (universal) gas constant in appropriate units

T = absolute temperature of the gas

Several arbitrarily specified standard states (usually known as standard conditions, or S.C. or S.T.P. for standard temperature and pressure) of temperature and pressure have specified for gases by custom.

TABLE 13.3 Common Standard Conditions for the Ideal Gas

System	T	P	\bar{V}
SI	273.15 K	101.325 kPa	22.415 m ³ /kg mol
American engineering	491.67 °R (32°F)	1 atm. (14.7 psia)	359.05 ft ³ /lb mol

EXAMPLE 13.1 Use of Standard Conditions to Calculate Volume from Mass

Calculate volume, in cubic meters, occupied by 40 kg of CO₂ at standard conditions assuming CO₂ acts as an ideal gas.

Solution

Basis: 40 kg of CO₂

$$\frac{40 \text{ kg CO}_2}{44 \text{ kg CO}_2} \left| \frac{1 \text{ kg mol CO}_2}{1 \text{ kg mol CO}_2} \right| \frac{22.42 \text{ m}^3 \text{ CO}_2}{1 \text{ kg mol CO}_2} = 20.4 \text{ m}^3 \text{ CO}_2 \text{ at S.C.}$$

Notice in this problem how the information that 22.42 m³, at S.C. = 1 kg mol is applied to transform a known number of moles into an equivalent number of cubic meters. An alternate way to calculate the volume at standard conditions is to use, Equation (4).

EXAMPLE 13.2 Calculation of R Using the Standard Conditions

Find the value for universal constant R to match the following combination of units: For 1 g mol. of ideal gas when the pressure in atm. the volume is in cm³, and the temperature is in K.

Solution

The following values are the ones to use (along with their units). At standard conditions:

$$p = 1 \text{ atm}$$

$$\hat{V} = 22,415 \text{ cm}^3/\text{g mol}$$

$$T = 273.15 \text{ K}$$

$$R = \frac{p\hat{V}}{T} = \frac{1 \text{ atm}}{273.15 \text{ K}} \left| \frac{22,415 \text{ cm}^3}{1 \text{ g mol}} \right| = 82.06 \frac{(\text{cm}^3)(\text{atm})}{(\text{K})(\text{g mol})}$$

The values of (R) in different units are as follow:

$82.06 \text{ atm. cm}^3 / \text{g mol. K}$	$10.73 \text{ psia. ft}^3 / \text{lb mol. } ^\circ\text{R}$
$0.08206 \text{ atm. liter} / \text{g mol. K}$	$0.73 \text{ atm. ft}^3 / \text{lb mol. } ^\circ\text{R}$
$8.314 \text{ J} / \text{mol. K}$	$1545 \text{ ft. lb}_f / \text{lb mol. } ^\circ\text{R}$
$83.14 \text{ cm}^3 \text{ bar} / \text{g mol. K}$	$21.9 \text{ in Hg. ft}^3 / \text{lb mol. } ^\circ\text{R}$
$1.987 \text{ cal} / \text{g mol. K}$	$1.987 \text{ Btu} / \text{lb mol. } ^\circ\text{R}$

If a specific quantity of an ideal gas is **changed from condition** (1) to condition (2), then:

$$P_1 V_1 = n R T_1 \quad \dots \dots \dots (5)$$

$$P_2 V_2 = n R T_2 \quad \dots \dots \dots (6)$$

Hence,

$$\left(\frac{P_1}{P_2}\right) \left(\frac{V_1}{V_2}\right) = \left(\frac{T_1}{T_2}\right) \quad \dots \dots \dots (7)$$

❖ Volumetric & molar flow rate of ideal gas:

The relationship between volumetric flow rate and molar flow rate for ideal gas can be derived from equation 4:

$$P \left(\frac{V}{\theta}\right) = \left(\frac{n}{\theta}\right) R T$$

i. e. Volumetric flow rate = molar flow rate $\left(\frac{R T}{P}\right) \dots \dots \dots (8)$

$$\left(\frac{V}{\theta}\right) = \left(\frac{n}{\theta}\right) \left(\frac{R T}{P}\right) \dots \dots \dots (8)$$

❖ Density & specific gravity of ideal gas:

Density of ideal gas can be estimated at any temperature and pressure from ideal gas law:

$$PV = nRT \rightarrow PV = \left(\frac{\text{mass}}{M_{wt}}\right)RT$$

$$\therefore \rho = \frac{\text{mass}}{V} = \left(\frac{P M_{wt}}{RT}\right) \dots \dots \dots (9)$$

- The specific gravity (Spg) of a gas is estimated with **reference to air** either at the same condition of the gas or at the standard condition (0 °C & 1 atm.).
- The spg of ideal gas compared to air at the **same condition** can be directly estimated from ideal gas law:

$$Spg = \left(\frac{\rho_{gas}}{\rho_{air}}\right)_{P,T} = \frac{\left(\frac{P M_{wt}}{RT}\right)_{gas}}{\left(\frac{P M_{wt}}{RT}\right)_{air}} = \frac{M_{wt_{gas}}}{29} \dots \dots \dots (10)$$

Note: Eq. (10) is true for ideal gas only compared to air at the **same P&T**.

EXAMPLE 13.1

Find the numerical value of the universal gas constant (R) in the following units:

(A) $\text{atm. ft}^3 / \text{lb mol. K}$ (B) $\text{J} / \text{mol. K}$ (C) $\text{ft. lb}_f / \text{lb mol. } ^\circ\text{R}$

Solution:-

(A) at S.C. $P = 1 \text{ atm.}$, $T = 273 \text{ K}$, $\bar{V} = 359 \text{ ft}^3 / \text{lb mol}$

$$R = \frac{P \bar{V}}{T} = \frac{1 \text{ atm.} \times 359 \text{ ft}^3 / \text{lb mol}}{273 \text{ K}} = 1.3145 \text{ atm. ft}^3 / \text{lb mol. K}$$

(B) at S.C. $P = 1 \text{ atm.} = 101.3 \text{ kpa} = 101300 \frac{\text{N}}{\text{m}^2}$, $T = 273 \text{ K}$

$$\bar{V} = 22.415 \frac{\text{liter}}{\text{mol}} \times \frac{\text{m}^3}{1000 \text{ liter}} = 0.022415 \frac{\text{m}^3}{\text{mol}}$$

$$R = \frac{P \bar{V}}{T} = \frac{101300 \frac{N}{m^2} \times 0.022415 \frac{m^3}{mol}}{273 \text{ k}} = 8.314 \text{ J/mol.K}$$

(C) at S.C. $P = 14.7 \frac{lb_f}{in^2} \times \frac{144 \text{ in}^2}{ft^2} = 216.8 \frac{lb_f}{ft^2}$, $T = 273 \text{ K}$

$$R = \frac{P \bar{V}}{T} = \frac{216.8 \frac{lb_f}{ft^2} \times 359 \text{ ft}^3 / \text{lb mol}}{492 \text{ }^\circ\text{R}} = 1545 \text{ ft. lb}_f / \text{lb mol. }^\circ\text{R}$$

EXAMPLE 13.2

60 gm of a paraffinic gas fills a 20 liters vessel at 32 °C and 22 psig. What is the molecular formula of the gas? Given that:- $R = 0.082 \text{ atm. l./g mol.K}$

Solution:-

$$T = 32 + 273 = 305 \text{ k}$$

$$P_{abs} = P_{gage} + P_{atm} = 22 + 14.7 = 36.7 \text{ Psia} \times \frac{1 \text{ atm.}}{14.7 \text{ Psi}} = 2.5 \text{ atm}$$

$$P V = n R T = \left(\frac{\text{mass}}{M_{wt}} \right) R T$$

$$\begin{aligned} \therefore M_{wt} &= \frac{\text{mass} \times R \times T}{P V} = \frac{60 \text{ gm} \times 0.082 \frac{\text{atm.l}}{\text{g mole k}} \times 305 \text{ k}}{2.5 \text{ atm} \times 20 \text{ l}} \\ &= 30 \frac{\text{gm}}{\text{g mole}} \end{aligned}$$

The chemical formula of paraffinic is $C_n H_{2n+2}$

$$\therefore 12(n) + 1(2n + 2) = 30 \quad \rightarrow \quad 14n = 28 \quad \rightarrow$$

$$n = 2 \quad \text{i.e. the gas is } C_2 H_6 \quad \text{(ethane)}$$

Example 3:

Ten cubic feet of air at 70 F and 1.0 atm are heated to 600 F and compressed to 2.50 atm. What is the volume occupied by the gas in state? It's final state?

Ans.

Since $n_1 = n_2$ (the number of moles of the gas does not change), and assuming ideal gas (since low pressure), heater

$$P_1 V_1 = n_1 R T_1 \quad \text{and} \quad P_2 V_2 = n_2 R T_2$$

$$T_1 = 70 + 460 = 530 \text{ }^\circ\text{R} \quad T_2 = 600 + 460 = 1060 \text{ }^\circ\text{R}$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \rightarrow \left(\frac{P_1}{P_2}\right) \left(\frac{V_1}{V_2}\right) = \frac{T_1}{T_2} \quad \dots \dots \text{(Eq. 7)}$$

$$V_2 = \frac{V_1 P_1 T_2}{P_2 T_1} = \frac{10 \text{ ft}^3 \times 1 \text{ atm} \times 1060 \text{ }^\circ\text{R}}{2.5 \text{ atm} \times 530 \text{ }^\circ\text{R}} = 8.0 \text{ ft}^3$$

Example 4:

An: ideal paraffinic gas fills a 200 liters vessel at 25 °C 175 psig. The specific gravity of the gas referred to air at the same conditions=2.0

What is the gas and its mass in gm.?

Ans.

$$SPg = \frac{(M \text{ wt})_{\text{gas}}}{29} \rightarrow (M \text{ wt})_{\text{gas}} = 2 (29) = 58$$

$$12n = 1(2n + 2) = 58 \rightarrow n = \frac{56}{14} = 4 \text{ The gas is } C_4H_{10} \text{ butane}$$

$$PV = nRT$$

$$P = 17.5 + 14.7 = 32.2 \text{ psia} \times \frac{1 \text{ atm}}{14.7} = 2.19 \text{ atm}$$

$$T = 273 + 25 = 298 \text{ K}$$

$$n = \frac{pv}{RT} = \frac{2.19 \text{ atm} (200 \text{ liters})}{0.08206 (\text{atm.l}) / (\text{gm.mole.k}) (298 \text{ K})} = 17.91 \text{ mol.}$$

$$\therefore \text{Mass} = \text{No. of mole} \times \text{Mwt.} = 17.91 \times 58 = 1039 \text{ gm}$$

2- Ideal Gas Mixtures:

In gaseous mixture each component contributes its share to the pressure and volume of the mixture which is **proportional to its mole fraction in the mixture**.

Two basic terms are widely used in calculation of gaseous mixtures:

❖ Partial pressure (p)

It is the pressure exerted by each component of a gaseous mixture if it occupies alone the total volume of the mixture at the **same temperature**.

❖ Partial Volume (v)

It is the volume occupied by each component of a gaseous mixture if it exists alone under the total pressure of the mixture at the **same temperature**.

❖ Dalton's law of Partial pressures:

This law states that the total pressure of ideal gas mixture is equal to the **sum of partial pressures of component**.

$$P = p_A + p_B + p_C + \dots \dots \dots \text{etc.}$$

i. e.

$$P = \sum_{i=1}^n p_i \dots \dots \dots (11)$$

Where:-

P: total pressure of the mixture.

p: partial pressure of component (i).

The relationship between (P) & (p_i) can be derived from ideal gas law:

Let N: total number of moles of mixture.

n_A n_B n_C : moles of component A, B, C respectively.

V: total volume of the mixture.

$$\therefore N = n_A + n_B + n_C$$

$$\text{For gas mixture: } P V = N R T \dots \dots \dots (*)$$

$$\text{For component A: } P_A V = n_A R T \dots \dots \dots (a)$$

$$\text{For component B: } P_B V = n_B R T \dots \dots \dots (b)$$

$$\text{For component C: } P_C V = n_C R T \dots \dots \dots (c)$$

Divide each of equation (a), (b), (c) by equation (*) gives:

$$\left(\frac{p_A V}{P V}\right) = \left(\frac{n_A R T}{N R T}\right) \rightarrow \left(\frac{p_A}{P}\right) = \left(\frac{n_A}{N}\right) = y_A \text{ i.e. mole fraction of component A}$$

$$\therefore p_A = P y_A$$

$$\text{In general } p_i = P y_i \dots \dots \dots (12)$$

That is the partial pressure of any component in an ideal gas mixture is equal to the mole fraction of that component times the total pressure.

❖ **Amagat's law of Partial volumes:**

This law states that the total volume of ideal gas mixture is equal to **the sum of partial volumes of component**.

$$V = v_A + v_B + v_C + \dots \dots \dots \text{etc.}$$

i.e.

$$V = \sum_{i=1}^n v_i \dots \dots \dots (13)$$

Where:-

V: total volume of the mixture

v_i : partial volume of component (i).

The relationship between (V) & (v_i) can be derived from ideal gas law:

Let P: total Pressure of the mixture.

$$\therefore \text{For gas mixture: } P V = N R T \dots \dots \dots (*)$$

$$\text{For component A: } P v_A = n_A R T \dots \dots \dots (a)$$

$$\text{For component B: } P v_B = n_B R T \dots \dots \dots (b)$$

$$\text{For component C: } P v_C = n_C R T \dots \dots \dots (c)$$

Divide each of equation (a), (b), (c) by equation (*) gives:

$$\left(\frac{P v_A}{P V}\right) = \left(\frac{n_A R T}{N R T}\right) \rightarrow \left(\frac{v_A}{V}\right) = \left(\frac{n_A}{N}\right)$$

$$= y_A \text{ i.e. mole fraction of component A}$$

$$\therefore v_A = V y_A$$

$$\text{In general } v_i = V y_i \dots \dots \dots (14)$$

That is the partial volume of any component in an ideal gaseous mixture is equal to the mole fraction of that component times the total volume.

$$\therefore \left(\frac{v_i}{V} \right) = y_i$$

For ideal gas, volume fraction = mole fraction

EXAMPLE 13.5

A tank containing a quantity of nitrogen at 100 °F, 1.6 lb of CH₄ are added. So that the partial pressure of N₂= 48 psia and that of CH₄=12 psia. If the temperature remains constant at 100 °F and if it is assumed ideal behavior of gases.

Calculate A// Composition of the mixture, B// mass of nitrogen originally presented in the tank, C// volume of the tank, and D// partial volumes of N₂ and CH₄.

Solution:

A//

$$P = \sum_{i=1}^n p_i = 48 + 12 = 60 \text{ psia}$$

$$y_{N_2} = \left(\frac{p_{N_2}}{P_{tot}} \right) = \frac{48}{60} = 0.8 \quad ; \quad y_{CH_4} = \left(\frac{p_{CH_4}}{P_{tot}} \right) = \frac{12}{60} = 0.2$$

The mixture consists of 80 mol % N₂ & 20 mol% CH₄

B//

$$\text{No. of mole CH}_4 = \frac{\text{mass}}{M_{wt}} = \left(\frac{1.6}{16} \right) = 0.1 \text{ lb mole}$$

$$\therefore \text{mole of mixture} = 0.1 \left(\frac{100}{20} \right) = 0.5 \text{ lb mole} \rightarrow \therefore \text{mol N}_2 = 0.5 \left(\frac{80}{100} \right) = 0.4 \text{ lb mole}$$

$$\therefore \text{mass of N}_2 = 0.4(28) = 11.2 \text{ lb}$$

C//

$$\therefore V_{tot} = \frac{nRT}{P_{tot}} = \frac{0.5 \text{ lb mole} \times 10.73 \frac{\text{psia} \cdot \text{ft}^3}{\text{lb mole} \cdot ^\circ\text{R}} \times 560 ^\circ\text{R}}{60 \text{ psia}} = 50 \text{ ft}^3$$

$$\therefore v_{N_2} = V_{tot} y_{N_2} = 50 (0.8) = 40 \text{ ft}^3$$

$$\therefore v_{CH_4} = V_{tot} y_{CH_4} = 50 (0.2) = 10 \text{ ft}^3$$

EXAMPLE 13.6

A tank containing 0.15 lb mole of nitrogen at 100 °F & 20 Psia. A quantity of hot paraffinic gas are added to the tank. The partial pressure of N₂ after mixing=21 psia, and that of the paraffinic gas=14 psia. The specific gravity of the mixture referred to air at the same conditions= 0.8. Assuming ideal behavior of gases.

Calculate (a) Volume of the tank, (b) lb moles of the paraffinic gas added, (c) Final temperature of the mixture and (d) Identify the paraffinic gas.

Ans

(a) For N₂ only before addition of the paraffinic gas = $PV = nRT$

$$V = \frac{nRT}{P} = \frac{\quad}{20 \text{ psia}} = 45 \text{ ft}^3$$

(b) $p_{tot} = \Sigma p_i = 21 + 14 = 35 \text{ psia}$

$$y_{N_2} = \frac{p_{N_2}}{p_{tot}} = \frac{21}{35} = 0.6 ; y_{CH_4} = \frac{n_{N_2}}{n_{tot}} = \frac{0.15}{n_{tot}} = 0.6 \quad n_{tot} = \frac{0.15}{0.6} = 0.25 \text{ lb mole}$$

$$\therefore \text{mole of paraffinic gas} = 0.25 - 0.15 = 0.1 \text{ lb mole} \rightarrow y_p = \frac{0.1}{0.25} = 0.4$$

$$(c) T = \frac{PV}{nR} = \frac{35 (45)}{0.25 (10.73)} = 527 \text{ }^\circ\text{R} = 127^\circ\text{F} \quad \text{Final temperature of mixture}$$

$$(d) Spg = \frac{M_{mix}}{29} = 0.8 \rightarrow M_{mix} 29 (0.8) = 23.2$$

$$23.2 = M_{N_2} y_{N_2} + M_p y_p = 28 (0.6) + M_p (0.4)$$

$$M_p = \frac{23.2 - 16.8}{0.4} = \frac{6.4}{0.4} = 16$$

$$\therefore C_n H_{2n+2} \quad 12(n) + 1(2n + 2) = 16 \rightarrow n = 1$$

; i. e the gas is methane (CH₄)

Example7:

Two similar tanks connected by a valve which is initially closed. The first tank contains 0.1 lb. mole of N_2 at 30psia and 100°F. The second tank contains CO_2 at 220°F. When the valve connecting the tanks is opened and the gases are completely mixed, it is found that the partial pressure of $N_2 = 16.8$ psia and that of $CO_2 = 25.2$ psia. Assuming ideal gaseous behavior, calculate: (a) volume of each tank in (ft^3), (b) lb. mole of CO_2 in the second tank, (c) the reading of the pressure gauge of the second tank before opening the valve, (d) the final temperature in (°F) of the mixture after opening the valve, and (e) the partial volume of N_2 and CO_2 .

Ans.

$$(a) V_1 = \frac{n_{N_2}RT}{P} = \frac{0.1(10.73)(560)}{30} = 20 ft^3 = V_2 \text{ (since the tanks are similar)}$$

$$(b) P_{tot} = \sum p_i = 16.8 + 25.2 = 42 \text{ psia}$$

$$y_{N_2} = \frac{P_{N_2}}{P_{tot}} = 0.4 \text{ lb. mole}$$

$$y_{N_2} = \frac{n_{N_2}}{n_{tot}} \Rightarrow n_{tot} = \frac{0.1}{0.4} = 0.25 \text{ lb. mole}$$

$$n_{CO_2} = 0.25 - 0.1 = 0.15 \text{ lb. mole}$$

$$y_{CO_2} = \frac{n_{CO_2}}{n_{tot}} = \frac{0.15}{0.25} = 0.6$$

$$(c) \text{ For 2 not tank before mixing } p = \frac{n_{CO_2}}{V} = \frac{0.15(10.73)(680)}{20} = 54.7 \text{ psia}$$

$$p_{gag} = p_{abs} - p_{atm} = 54.7 - 14.7 = 40 \text{ psig the reading of pressure gauge.}$$

$$(d) \text{ After opening the valve, } v_{tot} = v_1 + v_2 = 40 ft^3$$

$$T = \frac{p_{tot}v_{tot}}{n_{tot}R} = \frac{42(40)}{(0.25)(10.73)} = 626.3 \text{ } ^\circ R \Rightarrow T = 166.3 \text{ } ^\circ F$$

$$(e) v_{N_2} = v_{tot}y_{N_2} = 40(0.4) = 16 ft^3$$

$$v_{CO_2} = v_{tot}y_{CO_2} = 40(0.6) = 24 ft^3$$

❖ Critical state and critical constants:

It is the state at which no distinction between liquid and vapour and the specific properties such as density, viscosity, heat capacity...etc. of the gas and liquid phases of the substance become identical. At this point there is only one phase neither liquid nor gaseous but it is known as critical state. The critical state of any substance is described by three constant quantities known as “critical constants”. These constants are defined as follow:

A// Critical Temperature (T_c)

It is the highest temperature at which liquid and vapour of a pure materials can exist in equilibrium. Any gas cannot be liquefied under any applied pressure unless it is cooled below its critical temperature.

B// Critical pressure (P_c)

It is the highest pressure at which liquid and vapour of a pure material can exist in equilibrium.

C// Critical volume (\bar{V}_c)

It is the volume occupied by one mole of the substance at the critical state.it is expressed either in $\text{cm}^3/\text{gm mole}$ or in $\text{ft}^3/\text{lb mole}$

Values of T_c , P_c , and \bar{V}_c for various substances are shown in the following Tables.

Critical constants are commonly used in relationships of real gas and many other thermodynamic concepts and calculations.

Reduced Conditions and reduced parameters

These are conditions of the gas expressed mathematically in terms of its, Critical conditions by three dimensionless quantities. These quantities are:

(a) Reduced temperature $T_r = \frac{T}{T_c}$

(b) Reduced pressure $P_r = \frac{P}{P_c}$

(c) Reduced volume $\bar{V}_r = \frac{\bar{V}}{\bar{V}_c}$

For H₂ and He only

$$T_r = \frac{T}{T_c + 8 \text{ K}}$$

$$P_r = \frac{P}{P_c + 8 \text{ atm}}$$

Some of real gas relationships involve reduced parameters rather than critical constant of the gas.

TABLE 16.5

The experimental critical constants of various substances.

Species	T_c/K	P_c/bar	P_c/atm	$\bar{V}_c/L \cdot \text{mol}^{-1}$	$P_c \bar{V}_c / RT_c$
Helium	5.1950	2.2750	2.2452	0.05780	0.30443
Neon	44.415	26.555	26.208	0.04170	0.29986
Argon	150.95	49.288	48.643	0.07530	0.29571
Krypton	210.55	56.618	55.878	0.09220	0.29819
Hydrogen	32.938	12.838	12.670	0.06500	0.30470
Nitrogen	126.20	34.000	33.555	0.09010	0.29195
Oxygen	154.58	50.427	50.768	0.07640	0.29975
Carbon monoxide	132.85	34.935	34.478	0.09310	0.29445
Chlorine	416.9	79.91	78.87	0.1237	0.28517
Carbon dioxide	304.14	73.843	72.877	0.09400	0.27443
Water	647.126	220.55	217.66	0.05595	0.2295
Ammonia	405.30	111.30	109.84	0.07250	0.23945
Methane	190.53	45.980	45.379	0.09900	0.28735
Ethane	305.34	48.714	48.077	0.1480	0.28399
Ethene	282.35	50.422	49.763	0.1290	0.27707
Propane	369.85	42.477	41.922	0.2030	0.28041
Butane	425.16	37.960	37.464	0.2550	0.27383
2-Methylpropane	407.85	36.400	35.924	0.2630	0.28231
Pentane	469.69	33.643	33.203	0.3040	0.26189
Benzene	561.75	48.758	48.120	0.2560	0.26724

Van der Waals Constants

Gas	a ($\text{bar}\cdot\text{L}^2/\text{mol}^2$)	a ($\text{atm}\cdot\text{L}^2/\text{mol}^2$)	b (L/mol)
CH ₄	2.303	2.273	0.0431
CO ₂	3.658	3.610	0.0429
Cl ₂	6.343	6.260	0.0542
NH ₃	4.225	4.170	0.0371
H ₂ O	5.537	5.465	0.0305
Xe	4.192	4.137	0.0516
CCl ₄	20.01	19.75	0.1281
O ₂	1.382	1.363	0.0319
N ₂	1.370	1.351	0.0387
Kr	5.193	5.121	0.0106
Ar	1.355	1.336	0.0320
CO	1.472	1.452	0.0395
H ₂ S	4.544	4.481	0.0434
NO	1.370	1.351	0.0387
N ₂ O	3.852	3.799	0.0444
NO ₂	5.36	5.29	0.0443
SO ₂	6.865	6.770	0.0568
HF	9.565	9.431	0.0739
HCl	3.700	3.648	0.0406
HBr	4.500	4.437	0.0442
HI	6.309	6.221	0.0530

Reference: *CRC Handbook of Chemistry and Physics*, 2007

(3) Real Gas Relationships

Most gases can be assumed to Act as ideal gases at room Temperature and pressure.

The difference between the actual value of $P\bar{V}$ and that calculated from ideal gas law at any temperature clearly increases with increasing pressure as shown in the following figure.

Thus, real gas relations must be used rather than ideal gas law to compute P-V-T values of a gas at higher pressures (more than 3-4atm.)

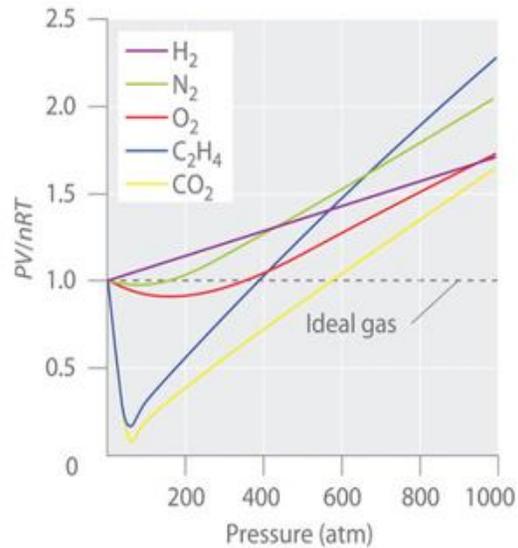


Figure 13.3: Deviation of real gases from the ideal Gas law at high pressure.

Two mathematical methods are commonly used for prediction real gas properties:

(a) Equations of State:

These are empirical relations involve two or more coefficients which relate pressure, volume, and temperature of a pure real gas (or mixtures). These equations were proposed to fit a large mass of experimental data and also to permit accurate interpolation between experimental data points. The following table lists a few of the commonly used equations of state from among the hundreds that have been proposed.

Only one of these equations (van der waal's equation) is used in computational problems in this stage of study since it is the simplest and most well known than others. However, applications of other equations of state in computational problems are involved in the contents of thermodynamics -2nd year.

They provide a continuous function to facilitate calculation of physical properties based on differentiation and integration of p-V-T relationships. Finally, they provide a point of departure for the treatment of the properties of mixtures.

Some of the advantages of using an equation of state versus other prediction methods are:

- 1. Values of p-V-T can be predicted with reasonable error in regions where no data exist.*
- 2. Only a few values of coefficients are needed in the equation to be able to predict gas properties versus collecting large amounts of data by experiment.*
- 3. The equations can be manipulated on a computer whereas graphics methods cannot.*

Some disadvantages are:

1. The form of an equation is hard to change to fit new data.
2. Inconsistencies may exist between equations for p-V-T and equations for other physical properties.
3. Usually the equation is quite complicated and may not be easy to solve for p, V or T because of its nonlinearity

If you plan to use a specific equation of state such as one of those listed in Table 15.1, you have numerous choices, no one of which win consistently give the best results.

❖ **Van der Waals Equations:**

In this equation, the effect of the attractive forces among the molecules, and also the effect of the volume occupied by the molecules themselves were taken into account and included in the ideal gas law by adding the term $\left(\frac{n^2 a}{V^2}\right)$ to the pressure and subtracting the term (n b) from the volume. Thus, the equation was put in the following forms:

$$\left(P + \frac{n^2 a}{V^2}\right) (V - n b) = n R T \quad \dots \dots \dots (15)$$

OR

$$P = \left(\frac{R T}{V - b}\right) - \left(\frac{a}{V^2}\right) \quad \dots \dots \dots (16)$$

Where (a) and (b) are van der waals constants which can be estimated from the critical constant according to the following relationships:

$$a = \left(\frac{27 R^2 T_c^2}{64 P_c}\right) \quad ; ; ; ; ; ; ; ; ; \quad b = \left(\frac{R T_c}{8 P_c}\right) \quad \dots \dots \dots (17)$$

If T_c is taken in (K) and P_c in (atm), then $R = 1.3145 \left(\frac{\text{atm} \cdot \text{ft}^3}{\text{lb mole} \cdot \text{K}}\right)$. The value of (a) & (b) for most substances are listed in the preceding table.

TABLE 15.1 Examples of Equations of State (for 1 g mole)*

van der Waals:	Soave-Redlich-Kwong (SRK equation):
$\left(p + \frac{a}{\hat{V}^2}\right)(\hat{V} - b) = RT$	$p = \frac{RT}{\hat{V} - b} - \frac{a'\lambda}{\hat{V}(\hat{V} + b)}$
$a = \left(\frac{27}{64}\right) \frac{R^2 T_c^2}{p_c}$	$a' = \frac{0.42748 R^2 T_c^2}{p_c}$
$b = \left(\frac{1}{8}\right) \frac{RT_c}{p_c}$	$b = \frac{0.08664 RT_c}{p_c}$
Peng-Robinson (PR equation):	$\lambda = [1 + \kappa(1 - T_r^{1/2})]^2$
$p = \frac{RT}{\hat{V} - b} - \frac{a\alpha}{\hat{V}(\hat{V} + b) + b(\hat{V} - b)}$	$\kappa = (0.480 + 1.574\omega - 0.176\omega^2)$
$a = 0.45724 \left(\frac{R^2 T_c^2}{p_c}\right)$	Redlich-Kwong (RK equation):
$b = 0.07780 \left(\frac{RT_c}{p_c}\right)$	$p = \frac{RT}{(\hat{V} - b)} - \frac{a}{T^{1/2} \hat{V}(\hat{V} + b)}$
$\alpha = [1 + \kappa(1 - T_r^{1/2})]^2$	$a = 0.42748 \frac{R^2 T_c^{2.5}}{p_c}$
$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2$	$b = 0.08664 \frac{RT_c}{p_c}$
Benedict-Webb-Rubin (BWR equation):	Kammerlingh-Onnes (a virial equation):
$p\hat{V} = RT + \frac{\beta}{\hat{V}} + \frac{\sigma}{\hat{V}^2} + \frac{\eta}{\hat{V}^4} + \frac{\omega}{\hat{V}^5}$	$p\hat{V} = RT \left(1 + \frac{B}{\hat{V}} + \frac{C}{\hat{V}^2} + \dots\right)$
$\beta = RTB_0 - A_0 - \frac{C^0}{T^2}$	Holborn (a virial equation):
$\sigma = bRT - a + \frac{c}{T^2} \exp\left(-\frac{\gamma}{\hat{V}^2}\right)$	$p\hat{V} = RT(1 + B'p + C'p^2 + \dots)$
$\eta = cy \exp\left(-\frac{\gamma}{\hat{V}^2}\right)$	
$\omega = a\alpha$	

* T_c and p_c are explained in Chapter 14; \hat{V} is the specific volume; ω is the acentric factor.

B// Law of corresponding states or (Compressibility Factor Method):

This law states that “all gases have the same reduced volume at the same reduced temperature & pressure and have similar deviation from ideal gas law”.

A convenient way of expressing this deviation is by introducing a dimensionless factor (**Z**) known as “compressibility factor” to the ideal gas law:

$$P V = Z n R T \quad \dots \dots \dots (18)$$

Hence the compressibility factor (**Z**) accounts for non-ideal behavior. The deviation of (**Z**) from unity is an indication to the degree of non-ideality of the gas since $Z=1$ for ideal gas.

The compressibility factor is function of the reduced temperature and pressure of the gas

$$i. e. \quad Z = f (P_r, T_r) \quad \dots \dots \dots (19)$$

The compressibility factor (**Z**) is commonly & easily estimated graphically from a” generalized compressibility chart “from (P_r & T_r). this chart was constructed assuming $Z_C = 0.27$.

Where (Z_C) is the compressibility factor at the critical point. It is defined as:

$$Z_C = \left(\frac{P_C \bar{V}_C}{R T_C} \right) \quad \dots \dots \dots (20)$$

It is important to note that Z_C for most substances are ranged between 0.23 to 0.30, and more than 60 % of substances have Z_C between 0.26 – 0.28 with average value of 0.27.

The accuracy of this method depends on the deviation of Z_C of the substance from this value (0.27). However, another parameter termed as “acentric factor (ω)” can be included for more accurate estimation of (**Z**) but calculation becomes heavy. The generalized chart yields quite reasonable value for engineering purposes.

Some references add another helpful parameter to the generalized compressibility chart. This parameter is “the ideal reduced volume” ($V_{r i}$) which is defined as:

$$V_{r i} = \frac{\bar{V}}{\bar{V}_{C i}}$$

Where: ($\bar{V}_{C i}$) is ideal critical volume, i.e. $\bar{V}_{C i} = \frac{R T_C}{P_C}$

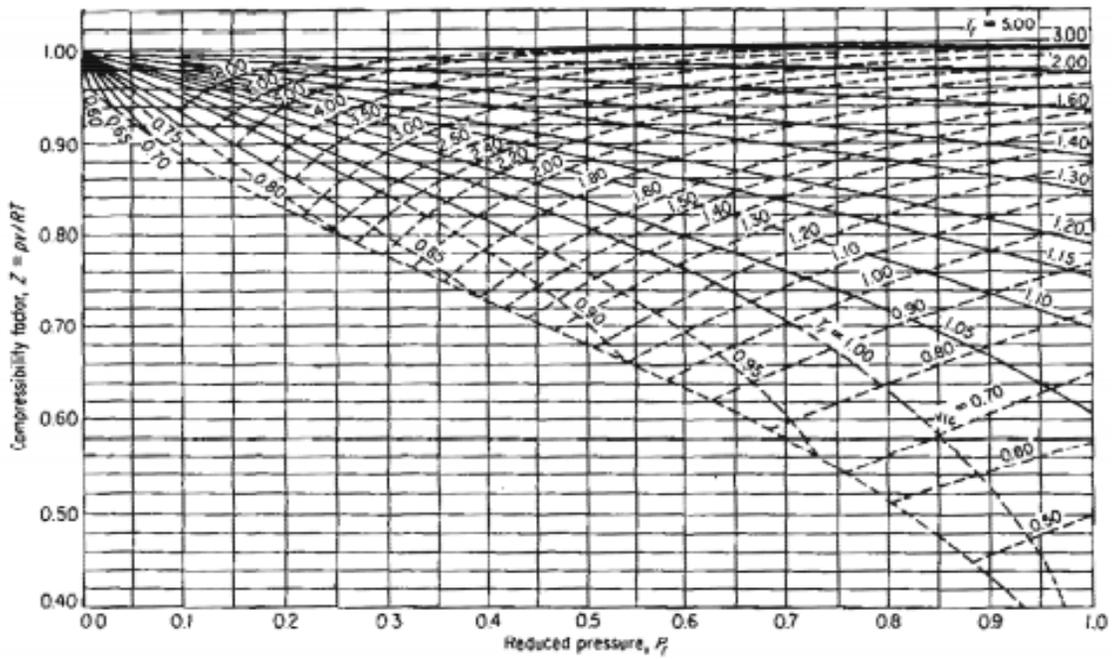


Figure 14.4a Generalized compressibility chart for lower pressures showing z as a function of p_r , T_r and $V_{r,r}$

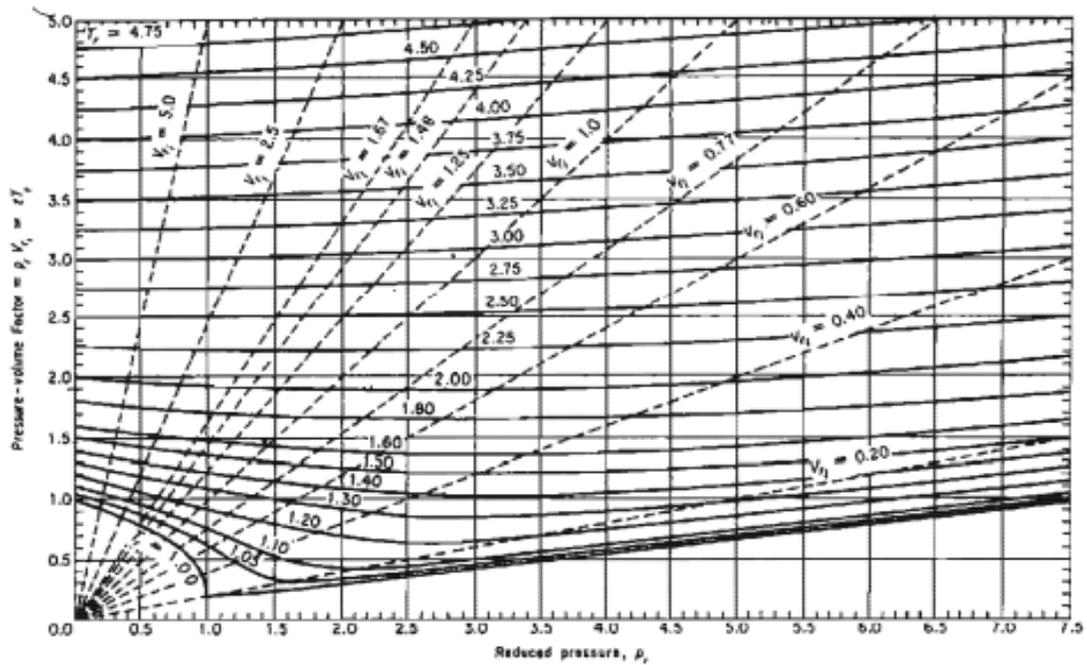


Figure 14.4b Generalized compressibility chart for higher values of p_r

4- Real Gas Mixtures:

The same relationships and for pure real gas can be used for real gaseous mixtures with special techniques for calculating the coefficients involved in these equation.

A// Van der waals Equation:

This equation can be used for real gas mixtures. Van der waals constants of the mixture (a_{mix} & b_{mix}) are estimated from those of pure components as follow:

$$a_{mix}^{1/2} = a_A^{1/2} y_A + a_B^{1/2} y_B + a_C^{1/2} y_C + \dots$$

And

$$b_{mix} = b_A y_A + b_B y_B + b_C y_C + \dots$$

Then,

$$\left(P + \frac{n^2 a_{mix}}{V^2} \right) (V - n b_{mix}) = n R T \quad \dots \dots \dots (22)$$

B// Compressibility Factor Method:

This method can be used for ideal gas mixture so that:

$$P V = Z_m n R T \quad \dots \dots \dots (23)$$

Where Z_m is the mean “Compressibility Factor for the mixture”

Methods were proposed for estimation Z_m (Dalton’s, Amagat’s and Kay’s methods). However, **kay’s method** is both simple and reasonably accurate than others. It is based an estimation Z_m from the “pseudocritical constant of mixture” (P_{cm} & T_{cm}).

Where:

$$P_{cm} = P_{CA} y_A + P_{CB} y_B + P_{CC} y_C + \dots \quad \dots \dots \dots (24)$$

And

$$T_{cm} = T_{CA} y_A + T_{CB} y_B + T_{CC} y_C + \dots \quad \dots \dots \dots (25)$$

The reduced parameter for the mixture can be estimated from (P_{cm} & T_{cm}):

$$P_{rm} = \frac{P}{P_{cm}} \quad \& \quad T_{rm} = \frac{T}{T_{cm}} \quad \dots \dots \dots (26)$$

Then

$$i.e. \quad Z_m = f (P_{rm}, T_{rm}) \quad \dots \dots \dots (27)$$

Example 11:

A pressure vessel with volume of 131 ft³ contains ethane (C₂H₆) at 360 psia and 90 °F. Calculate the mass in pounds of ethane in this vessel.

Solution:

Since, ethane present under very high pressure, hence it is considered as real gas. Calculation according to the compressibility factor method are follow.

From table $P_C = 48.8 \text{ atm.}$ $T_C = 305.2 \text{ k}$ *Given or get from table*

$$T = 90 + 460 = 550 \text{ }^\circ\text{R} \left(\frac{1 \text{ k}}{1.8 \text{ R}} \right) = 305.5 \text{ k}$$

$$\left\{ P_r = \frac{P}{P_C} = \frac{360 \text{ Psi}}{48.8 \text{ atm.}} \times \frac{\text{atm.}}{14.7 \text{ psi}} = 0.5 \quad \& \quad T_r = \frac{T}{T_C} = \frac{305.5}{305.2} = 1.0 \right\} Z = 0.8 \text{ from chart}$$

$$n = \left(\frac{P V}{Z R T} \right) = \frac{360 \text{ psia} (131 \text{ ft}^3)}{0.8 \left(10.73 \frac{\text{psia ft}^3}{\text{lb mol } ^\circ\text{R}} \right) (550 \text{ }^\circ\text{R})} = 10 \text{ lb mole}$$

$$\therefore \text{mass} = n \times M_{wt} = 10 (30) = 300 \text{ lb}$$

Example 12:

A pressure vessel with volume of 131 ft³ contains 300 lb of ethane (C₂H₆) at 90 °F. Calculate the pressure in psia by **Vander waals equation**. Given that M_{wt} of C₂H₆ = 30

Solution: From table $P_C = 48.8 \text{ atm.}$ $T_C = 305.2 \text{ k}$ *Given or get from table*

$$a = \left(\frac{27 R^2 T_C^2}{64 P_C} \right) = \frac{27 (1.3145)^2 (305.5)^2}{64 (48.8)} = 1391 \text{ atm} \left(\frac{\text{ft}^3}{\text{lb mole}} \right)^2$$

$$b = \left(\frac{R T_C}{8 P_C} \right) = \frac{1.3145 \frac{\text{atm. ft}^3}{\text{lb mole k}} (305.5 \text{ k})}{8 (48.8 \text{ atm.})} = 1.028$$

$$\left(P + \frac{n^2 a}{V^2} \right) (V - n b) = n R T$$

$$\left(P + \frac{10^2 (1391)}{131^2} \right) (131 - 10 (1.028)) = 10 \text{ lb mole} \left(0.73 \frac{\text{atm. ft}^3}{\text{lb mole } ^\circ\text{R}} \right) (550 \text{ }^\circ\text{R})$$

$$(P + 8.106) (131 - 10.28) = 4015 \quad \rightarrow \rightarrow \quad 120.72 P = 3036.4$$

$$P = 25.15 \text{ atm} \left(\frac{14.7 \text{ psi}}{1 \text{ atm.}} \right) = 370 \text{ psia}$$

Example 13:

66 lb of propane are contained in vessel with volume of 11 ft³ at 170 °C. Calculate the pressure in the vessel using compressibility factor method.

Solution: Method (1)

$$n = \frac{\text{mass}}{M_{wt}} = \frac{66}{44} = 1.5 \text{ lb mole}$$

$$T = 170 + 273 = 443 \text{ k}$$

For propane $P_C = 42 \text{ atm.}$ $T_C = 369.9 \text{ k}$ *Given or get from table*

$$P_r = \frac{P}{P_C} = \frac{P}{42} \quad \& \quad T_r = \frac{T}{T_C} = \frac{443}{369.9} = 1.2$$

Solve by trial & error			
P assume	Pr	Z	$P_{calc.} = \left(\frac{Z n R T}{V} \right)$
42	1.0	0.8	$P_{calc.} = \frac{0.8 (1.5)(1.1345)(443)}{11} = 63.5$
55	1.3	0.73	58
56.5	1.35	0.72	57.2
56.8			P = 56.8

Solution: Method (2)

Use ideal reduced volume (\bar{V}_{ri})

$$\bar{V} = \frac{V}{n} = \frac{11}{1.5} = 7.33 \frac{\text{ft}^3}{\text{lb mole}}$$

$$\bar{V}_{Ci} = \frac{R T_C}{P_C} = \frac{(1.3145)(369.9)}{42} = 11.58 \frac{\text{ft}^3}{\text{lb mole}}$$

$$\bar{V}_{ri} = \frac{\bar{V}}{\bar{V}_{Ci}} = \frac{7.33}{11.58} = 0.63$$

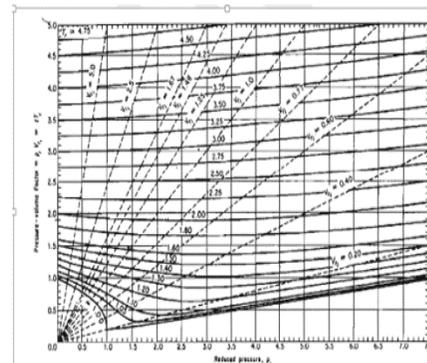


Figure 14.4b Generalized compressibility chart for higher values of p_r .

From intersection between (\bar{V}_{ri}) & T_r we get $P_r = 1.3 = \frac{P}{P_C}$ from fig. (F)

$$\therefore P = 1.3 (P_C) = 1.3 (42) = 54.6 \text{ atm.}$$

Example 14:

3.5 kg of oxygen are contained in tank of 27.8 liter under 70 atm. What is the temperature?

Solution:

From table $P_c = 49.7 \text{ atm}$. $T_c = 154.3 \text{ k}$ *Given or get from table*

$$n = \frac{\text{mass}}{M_{wt}} = \frac{3.5}{32} = 0.109 \text{ kg mole}$$

$$\bar{V} = \frac{V}{n} = \frac{27.8 \text{ liter}}{0.109 \text{ kg mol}} \times \frac{\text{m}^3}{1000 \text{ liter}} = 0.255 \frac{\text{m}^3}{\text{kg mole}}$$

Method (1)

$$\bar{V}_{ci} = \frac{R T_c}{P_c} = \frac{(0.08206) (154.3 \text{ k})}{49.7} = 0.255 \frac{\text{m}^3}{\text{kg mole}}$$

$$\bar{V}_{ri} = \frac{\bar{V}}{\bar{V}_{ci}} = \frac{0.255}{0.255} = 1.0 \rightarrow P_r = \frac{P}{P_c} = \frac{70}{49.7} = 1.4$$

From intersection between (\bar{V}_{ri}) & P_r we get $T_r = 1.6 = \frac{T}{T_c}$ from fig. (F)

$$\therefore T = (T_r) \times (T_c) = 1.6 (154.3) = 247 \text{ K} = -26^\circ \text{C}$$

OR it can be solved by trial & error as in example13

$$\text{For Oxygen } a = \left(\frac{27 R^2 T_c^2}{64 P_c} \right) = \frac{27 (0.08206)^2 (154.3)^2}{64 (49.7)} = 1.361 \text{ atm} \left(\frac{\text{m}^3}{\text{kg mole}} \right)^2$$

$$b = \left(\frac{R T_c}{8 P_c} \right) = \frac{0.08206 \frac{\text{atm. m}^3}{\text{kg mole k}} (154.3 \text{ k})}{8 (49.7 \text{ atm.})} = 0.0318 \frac{\text{m}^3}{\text{kg mole}}$$

$$\left(P + \frac{n^2 a}{V^2} \right) (V - n b) = n R T$$

$$\left(70 + \frac{(0.109)^2 (1361)}{(0.0278)^2} \right) (0.0278 - 0.109 (0.0318)) = 0.109 (0.08206) T$$

$$(70 + 20.92) (0.0243) = 0.00394 T \rightarrow T = \frac{90.92 \times 0.0243}{0.00394} = 247 \text{ K} = -26^\circ \text{C}$$

Example 15:

Fifty pounds of propane (C₃H₈) are contained in cylinder at 223 °F under 665 psig. Calculate the volume of the cylinder use Van der waals equation.

Solution:

$$P = 665 + 14.7 = 679.7 \text{ psia} \times \frac{\text{atm.}}{14.7 \text{ psia}} = 46.2 \text{ atm.} \rightarrow T = 223 + 460 = 683^\circ\text{R}$$

$$\text{Form table } a = 2374 \text{ atm} \left(\frac{\text{ft}^3}{\text{lb mole}} \right)^2 ; \quad b = 1.446 \frac{\text{ft}^3}{\text{lb mole}}$$

$$n = \frac{\text{mass}}{M_{wt}} = \frac{50}{44} = 1.136 \text{ lb mole}$$

$$\left(P + \frac{n^2 a}{V^2} \right) (V - n b) = n R T$$

$$\left(46.2 + \frac{(1.136)^2 (2374)}{(V)^2} \right) (V - 1.136 (1.446)) = 1.136 (0.73) (683)$$

$$\left(46.2 + \frac{(3064)}{V^2} \right) (V - 1.643) = 566.4$$

$$46.2 V + \frac{(3064)}{V} - 75.9 - \frac{5034}{V^2} - 566.4 = 0$$

$$46.2 V^3 - 642.3 V^2 + 3064 V - 5034 = 0 \quad \text{Multiply } V^2$$

$$V^3 - 13.9 V^2 + 66.3 V - 109 = 0 \quad \text{divide by 46.2}$$

This equation can be solved by Newton's method according to the following equ.

$$V_{n+1} = V_n - \frac{f(V_n)}{f'(V_n)}$$

$$\text{Where } f(V) = V^3 - 13.9 V^2 + 66.3 V - 109 \quad \dots \dots \dots (1)$$

$$\text{and } f'(V) = 3V^2 - 27.8 V + 66.3 \quad \dots \dots \dots (2)$$

$$V_0 \text{ as the first trial can be estimated from ideal gas law } V_0 = \frac{n R T}{P}$$

$$V_0 = \frac{n R T}{P} = \frac{1.136 \times 0.73 \times 683}{46.2} = 12.26 \text{ ft}^3$$

$$\text{From equ. (1) } f(V_0) = (12.26)^3 - 13.9 (12.26)^2 + 66.3 (12.26) - 109 = 457.3$$

$$f'(V_0) = 3(12.26)^2 - 27.8 (12.26) + 66.3 = 176$$

$$V_1 = V_0 - \frac{f(V_0)}{f'(V_0)} = 12.26 - \frac{457.3}{176.4} = 12.26 - 2.59 = 9.67 \text{ ft}^3$$

for next trial $V_1 = 9.67$, $f(V_1) = 136.3$, $f'(V_1) = 78 \Rightarrow V_2 = 7.92 \text{ ft}^3$

Similarity $V_3, V_4 \dots \dots \dots$ are calculated till the final solution $(V_n) = 5 \text{ ft}^3$

$$\begin{aligned} \text{Check } f(V_5) &= (5)^3 - 13.9(5)^2 + 66.3(5) - 109 = \dots \dots \dots \\ &= 125 - 347.5 + 331.5 - 109 = 0 \end{aligned}$$

Hence $V_n = V_{n-1}$

Example 16:

A gaseous mixture consists of 20 mol % CH₄ and 80 mol % C₂H₄ at 735 psia and 70 °C. Calculate the molar volume in ft³/lb mole by

(A) ideal gas law , (B) kay's method , (C) Van der waal's equation

Solution:**A// ideal gas law.**

$$T = 70 + 273 = 343 \text{ k} \quad \text{or} \quad T = 70 (1.8) + 32 = 158 \text{ }^\circ\text{F} = 618 \text{ }^\circ\text{R}$$

$$\therefore V = \frac{n R T}{P} = \frac{(1) \times (10.73) \times (618)}{735} = 9.0 \text{ ft}^3$$

B// kay's method.

Solve by kay's method.					
Component	Tc, k	Pc, atm	y	y Tc	y Pc
CH ₄	191.1	45.8	0.2	38.2	9.2
C ₂ H ₄	282.8	50.7	0.8	226.2	40.6
				$T_{cm} = 264.4$	$P_{cm} = 49.8$

$$P_r = \frac{P}{P_{cm}} = \frac{735}{49.8 \times 14.7} = 1.0 \quad \& \quad T_r = \frac{T}{T_{cm}} = \frac{343}{264.4} = 1.3$$

From chart $Z_m = 0.85$

$$\therefore V = \frac{Z_m n R T}{P} = (0.85) \times (9) = 7.65 \text{ ft}^3$$

C// Van der waals Method:

$$a_{mix}^{1/2} = 0.2 (581.2)^{1/2} + 0.8 (1150)^{1/2} = 31.95 \quad \rightarrow \quad a_{mix} = 1021 \text{ atm} \left(\frac{\text{ft}^3}{\text{lb mol}} \right)^2$$

And

$$b_{mix} = 0.2 (0.6855) + 0.8 (0.9165) = 0.870 \quad \frac{\text{ft}^3}{\text{lb mol}}$$

Then use Newton's method to calculate (V) as in example 15

$$f(V) = V^3 + 9.9 V^2 + 20.4 V = 0 \quad \rightarrow \quad V = 7.5 \text{ ft}^3$$

Ideal and Real gases

Introduction:

This chapter deals with the pressure – volume –temperature (P-V-T) relationships for ideal and real gaseous behavior of pure components and mixtures of gases.

These relation are of importance in all calculation involve gases such as energy balance, combustion, thermodynamics and design of pressure vessels Etc.

It is convenient to study relationships of gases by putting them in four separate sections:-

1. Ideal gas law.
2. Ideal gas mixtures.
3. Real gas relationships.
4. Real gas mixtures.

1- Ideal gas law

The ideal gas can be defined as that gas in which the average distance between the molecules is great enough that the intermolecular forces are **negligible**, and the volume of gas molecules is **very small compared with the total volume** of the gas and can be neglected.

An ideal gas is an imaginary gas that obeys certain simple law known as “ideal gas law “. The behavior of any real gas such as H₂, O₂, CO₂etc. approaches that of an ideal gas at low pressure and high temperatures. Thus, the ideal gas law can be used for simplicity in many engineering calculations at low pressure (up to 3 - 4 atm.) since it gives incorrect result at higher pressures and lower temperatures.

❖ Ideal gas law was developed from the work of many scientist as follow:

A// Boyle law

Robert Boyle (1627 - 1691), an English chemist. In 1662 found that the volume of a certain quantity of an ideal gas is **inversely proportional** to the absolute pressure at constant temperature.

Hence for one mole of an ideal gas, $\bar{V} \propto \frac{1}{P}$

$$P \bar{V} = K_1 \quad \text{at constant } T \quad \dots \dots \dots (1)$$

$$\text{Where } \bar{V} = \text{molar volume} = \frac{V}{n} ; K_1 \text{ is constant}$$

Pressure (atm)	Volume (mL)	$P \times V = k$ (atm·mL)
0.5	1000	500
0.625	800	500
1.0	500	500
2.0	250	500
5.0	100	500
8.0	62.5	500
10.0	50	500

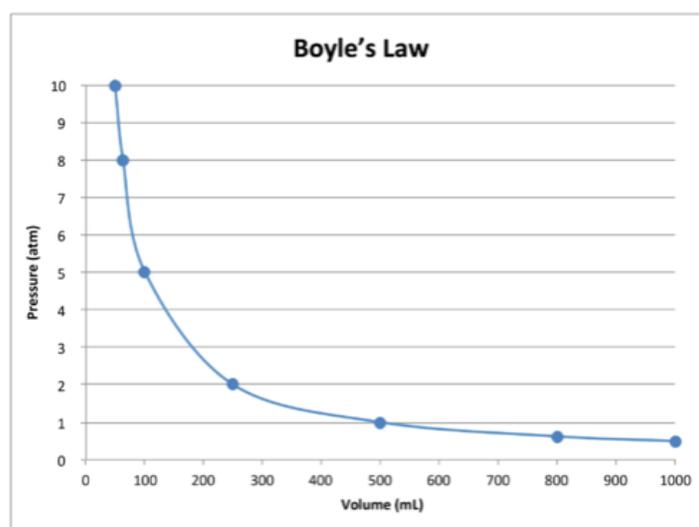


Figure 13.1: The pressure of a gas decreases as the volume increases, making Boyle's law an inverse relationship.

B// Charles and Gay-Lussac law

In 1787, they demonstrated that the volume of a certain quantity of an ideal gas varies directly with absolute temperature at constant pressure.

Hence for one mole of an ideal gas, $\vec{V} \propto T$

$$\text{i. e. } \vec{V} = K_2 T \quad \text{OR} \quad \frac{\vec{V}}{T} = K_2 \quad \text{at constant } P \quad \dots \dots \dots (2)$$

Where K_2 is constant

Combination of eq. 1 & 2 gives $\frac{P \vec{V}}{T} = R \dots \dots \dots (3)$

Where R is a constant

Table 13.2: Temperature-Volume Data

Temperature (K)	Volume (mL)	$\frac{\vec{V}}{T} = K$
50	20	0.40
100	40	0.40
150	60	0.40
200	80	0.40
300	120	0.40
500	200	0.40
1000	400	0.40

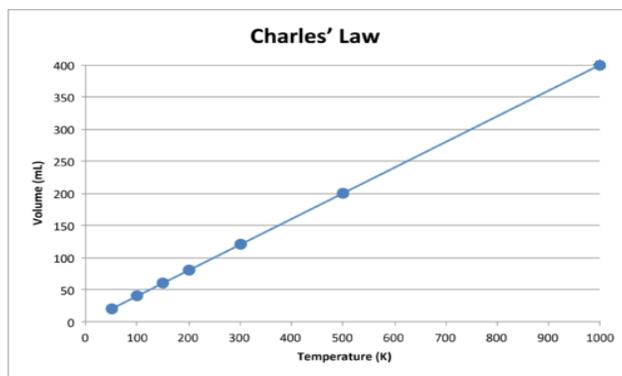


Figure 13.2: The volume of a gas increases as the Kelvin temperature increases.

C// Avogadro Hypothesis

In 1811, Avogadro proposed his famous hypothesis that “equal volumes of different gases contain the same number of molecules under the **same condition of temperature and pressure**. This means that molar volumes (\bar{V}) of all gases of ideal behavior are equal at the same temperature & pressure.

Thus, the constant (R) is the same for all gases. It is known “the universal gas constant”.

The ideal gas law usually put in the form:

$$P V = n R T \quad \dots \dots \dots (4)$$

Where:

p = absolute pressure of the gas

V = total volume occupied by the gas

n = number of moles of the gas

R = ideal (universal) gas constant in appropriate units

T = absolute temperature of the gas

Several arbitrarily specified standard states (usually known as standard conditions, or S.C. or S.T.P. for standard temperature and pressure) of temperature and pressure have specified for gases by custom.

TABLE 13.3 Common Standard Conditions for the Ideal Gas

System	T	P	\bar{V}
SI	273.15 K	101.325 kPa	22.415 m ³ /kg mol
American engineering	491.67 °R (32°F)	1 atm. (14.7 psia)	359.05 ft ³ /lb mol

EXAMPLE 13.1 Use of Standard Conditions to Calculate Volume from Mass

Calculate volume, in cubic meters, occupied by 40 kg of CO₂ at standard conditions assuming CO₂ acts as an ideal gas.

Solution

Basis: 40 kg of CO₂

$$\frac{40 \text{ kg CO}_2}{44 \text{ kg CO}_2} \left| \frac{1 \text{ kg mol CO}_2}{1 \text{ kg mol CO}_2} \right| \frac{22.42 \text{ m}^3 \text{ CO}_2}{1 \text{ kg mol CO}_2} = 20.4 \text{ m}^3 \text{ CO}_2 \text{ at S.C.}$$

Notice in this problem how the information that 22.42 m³, at S.C. = 1 kg mol is applied to transform a known number of moles into an equivalent number of cubic meters. An alternate way to calculate the volume at standard conditions is to use, Equation (4).

EXAMPLE 13.2 Calculation of R Using the Standard Conditions

Find the value for universal constant R to match the following combination of units: For 1 g mol. of ideal gas when the pressure in atm. the volume is in cm³, and the temperature is in K.

Solution

The following values are the ones to use (along with their units). At standard conditions:

$$p = 1 \text{ atm}$$

$$\hat{V} = 22,415 \text{ cm}^3/\text{g mol}$$

$$T = 273.15 \text{ K}$$

$$R = \frac{p\hat{V}}{T} = \frac{1 \text{ atm}}{273.15 \text{ K}} \left| \frac{22,415 \text{ cm}^3}{1 \text{ g mol}} \right| = 82.06 \frac{(\text{cm}^3)(\text{atm})}{(\text{K})(\text{g mol})}$$

The values of (R) in different units are as follow:

$82.06 \text{ atm. cm}^3 / \text{g mol. K}$	$10.73 \text{ psia. ft}^3 / \text{lb mol. } ^\circ\text{R}$
$0.08206 \text{ atm. liter} / \text{g mol. K}$	$0.73 \text{ atm. ft}^3 / \text{lb mol. } ^\circ\text{R}$
$8.314 \text{ J} / \text{mol. K}$	$1545 \text{ ft. lb}_f / \text{lb mol. } ^\circ\text{R}$
$83.14 \text{ cm}^3 \text{ bar} / \text{g mol. K}$	$21.9 \text{ in Hg. ft}^3 / \text{lb mol. } ^\circ\text{R}$
$1.987 \text{ cal} / \text{g mol. K}$	$1.987 \text{ Btu} / \text{lb mol. } ^\circ\text{R}$

If a specific quantity of an ideal gas is changed from condition (1) to condition (2), then:

$$P_1 V_1 = n R T_1 \quad \dots \dots \dots (5)$$

$$P_2 V_2 = n R T_2 \quad \dots \dots \dots (6)$$

Hence,

$$\left(\frac{P_1}{P_2}\right) \left(\frac{V_1}{V_2}\right) = \left(\frac{T_1}{T_2}\right) \quad \dots \dots \dots (7)$$

❖ Volumetric & molar flow rate of ideal gas:

The relationship between volumetric flow rate and molar flow rate for ideal gas can be derived from equation 4:

$$P \left(\frac{V}{\theta}\right) = \left(\frac{n}{\theta}\right) RT$$

i. e. Volumetric flow rate = molar flow rate $\left(\frac{RT}{P}\right) \dots \dots \dots (8)$

$$\left(\frac{V}{\theta}\right) = \left(\frac{n}{\theta}\right) \left(\frac{RT}{P}\right) \dots \dots \dots (8)$$

❖ Density & specific gravity of ideal gas:

Density of ideal gas can be estimated at any temperature and pressure from ideal gas law:

$$P V = n R T \rightarrow P V = \left(\frac{\text{mass}}{M_{wt}} \right) R T$$

$$\therefore \rho = \frac{\text{mass}}{V} = \left(\frac{P M_{wt}}{R T} \right) \dots \dots \dots (9)$$

- The specific gravity (Spg) of a gas is estimated with reference to air either at the same condition of the gas or at the standard condition (0 °C & 1 atm.).
- The spg of ideal gas compared to air at the same condition can be directly estimated from ideal gas law:

$$Spg = \left(\frac{\rho_{gas}}{\rho_{air}} \right)_{P,T} = \frac{\left(\frac{P M_{wt}}{R T} \right)_{gas}}{\left(\frac{P M_{wt}}{R T} \right)_{air}} = \frac{M_{wt_{gas}}}{29} \dots \dots \dots (10)$$

Note: Eq. (10) is true for ideal gas only compared to air at the same P&T.

EXAMPLE 13.4

60 gm of a paraffinic gas fills a 20 liters vessel at 32 °C and 22 psig. What is the molecular formula of the gas? Given that:- $R = 0.082 \text{ atm. l./g mol.K}$

Solution:-

$$T = 32 + 273 = 305 \text{ k}$$

$$P_{abs} = P_{gage} + P_{atm} = 22 + 14.7 = 36.7 \text{ Psia} \times \frac{1 \text{ atm.}}{14.7 \text{ Psi}} = 2.5 \text{ atm}$$

$$P V = n R T = \left(\frac{\text{mass}}{M_{wt}} \right) R T$$

$$\therefore M_{wt} = \frac{\text{mass} \times R \times T}{P V} = \frac{60 \text{ gm} \times 0.082 \frac{\text{atm.l}}{\text{g mole k}} \times 305 \text{ k}}{2.5 \text{ atm} \times 20 \text{ l}}$$

$$= 30 \frac{\text{gm}}{\text{g mole}}$$

The chemical formula of paraffinic is $C_n H_{2n+2}$

$$\therefore 12(n) + 1(2n + 2) = 30 \rightarrow 14n = 28 \rightarrow$$

$$n = 2 \quad \text{i.e. the gas is } C_2 H_6$$

(ethane)