Subject: MATERIAL AND ENERGY BALANCE

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3rd Semester

Department of Chemical Engineering

References:

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Book1: RM Felder and RW Rousseau, "Elementary Principles of Chemical Processes" 4th edition, John Wiley & Sons, 2011.

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UNITS AND DIMENSIONS

1.1 In a multiple effect evaporator system, the second effect is maintained under vacuum of 475 torr (mmHg). Find the absolute pressure in kPa.

solution: The relationship between absolute pressure and vacuum is

Absolute Pressure = atmospheric pressure - vacuum

$= 760 - 475 = 285$ torr (mmHg)

$$\text{Absolute pressure} = 285 (\text{mmHg}) \times \left(\frac{101.325}{760}\right)\left(\frac{\text{kPa}}{\text{mmHg}}\right)$$

$= 38$ kPa

1.2 A force of 20 kgf is applied on a piston of diameter 5 cm. Find the pressure exerted on the piston in kPa.

Sol:

$$P = \frac{F}{A}$$

$$A = \frac{\pi}{4} d^2 = \frac{\pi}{4}(5)^2 = 19.635\ \text{cm}^2$$

$$F = 20\ \text{kgf}$$

$$P = \frac{20}{19.635} = 1.018\ \text{kgf/cm}^2$$

$$P = 1.018 \left(\frac{\text{kgf}}{\text{cm}^2}\right) \times \frac{101.325}{1.033227}\left(\frac{\text{kPa}}{\text{kgf/cm}^2}\right)$$

$= 99.89$ kPa

1.3 Convert a pressure of 2 atm to mmHg.

Sol: Basis: 2 atm pressure.

Conversion factor between atm and mmHg is:

1 atm = 760 mmHg ∴ 2 atm = ?

$$\text{Pressure} = 2(\text{atm}) \times \left(\frac{760}{1}\right)\left(\frac{\text{mmHg}}{\text{atm}}\right)$$

$= 1520$ mmHg

1.4 Convert a volumetric flow rate of $2\ m^3/s$ to l/s.

Sol: Basis: volumetric flow rate of $2\ m^3/s$.

Relationship between volume in m^3 and volume in l is

$$1\ m^3 = 1000\ l$$

$$\therefore \text{Volumetric flow rate} = 2\ (m^3/s) \times \left(\frac{1000}{1}\right)(l/m^3)$$

$$= 2000\ l/s$$

BASIC CHEMICAL CALCULATIONS

Gram atom: It is used to specify the amounts of chemical elements. It is defined as the mass in grams of an element which is numerically equal to its atomic weight.

$$\text{Gram atoms of an element} = \frac{\text{Weight in grams}}{\text{Atomic weight}}$$

$$\therefore \text{Gram atoms of an element A} = \frac{\text{Weight in grams of A}}{\text{Atomic weight of A}}$$

Gram mole: It is used to specify the amounts of chemical compounds. It is defined as the mass in grams of a substance that is equal numerically to its molecular weight.

$$\therefore \text{Gram moles of compound B} = \frac{\text{Weight in grams of B}}{\text{Molecular weight of B}}$$

2.1 Calculate the kilogram atoms of carbon which weight 36 kg.

Sol: Basis: 36 kg carbon.

Atomic weight of carbon = 12

$$\therefore \text{katom of carbon} = \frac{\text{Weight in kg of carbon}}{\text{Atomic weight of carbon}} = \frac{36}{12} = 3$$

2.2 Find molecular weight of (i) H_2SO_4, (ii) Na_2CO_3 and (iii) $KMnO_4$.

Sol: Atomic weights: H = 1, S = 32 and O = 16

Molecular weight of $H_2SO_4 = 2\times1 + 1\times32 + 4\times16 = 98$

Atomic weights: Na = 23, C = 12 and O = 16

Molecular weight of $Na_2CO_3 = 2 \times 23 + 1 \times 12 + 3 \times 16 = 106$

Atomic weights : K = 39, Mn = 5 and O = 16

Molecular weight of $KMnO_4 = 1 \times 39 + 1 \times 55 + 4 \times 16 = 158$

2.3 Convert 88 kg of carbon dioxide into its amount in molar units.

Sol: Basis : 88 kg of carbon dioxide.

Molecular formula of carbon dioxide = CO_2

Atomic weights : C = 12 and O = 16

Molecular weight of $CO_2 = 1 \times 12 + 2 \times 16 = 44$

$$\text{kmol of } CO_2 = \frac{\text{kg of } CO_2}{\text{Molecular weight of } CO_2} = \frac{88}{44} = 2$$

$\therefore$ 88 kg of CO_2 = 2 kmol CO_2

2.4 Convert ~~49g~~ 499 g of $CuSO_4 \cdot 5H_2O$ into moles.

Sol: Basis : 499 g of $CuSO_4 \cdot 5H_2O$.

Atomic weights : Cu = 63.5, S = 32, O = 16 and H = 1

Molecular weight of $CuSO_4 \cdot 5H_2O = 1 \times 63.5 + 1 \times 32 + 4 \times 16 + 5(2 \times 1 + 1 \times 16) = 249.5$

$$\text{Moles of } CuSO_4 \cdot 5H_2O = \frac{499}{249.5} = 2 \text{ mol}$$

2.5 Find moles of K_2CO_3 that will contain 117 kg of K.

Sol: Basis : 117 kg of K.

Atomic weight of K = 39

$$\text{Atoms of K} = \frac{117}{39} = 3 \text{ katom}$$

Each mole of K_2CO_3 contains 2 atom of K

2 atom of K ≡ 1 mole of K_2CO_3

2 katom of K ≡ 1 kmol of K_2CO_3

$\therefore$ Moles of $K_2CO_3 = \frac{1}{2} \times 3 = 1.5$ kmol

Equivalent weight of an element or a compound is defined as the ratio of the atomic weight or molecular weight to its valence. The valence of an element or a compound depends on the number of hydroxyl ions(OH^-) donated or the hydrogen ions(H^+) accepted for each atomic weight or molecular weight.

$$\therefore \text{Equivalent weight} = \frac{\text{Molecular weight}}{\text{Valence}}$$

Normality :

$$\text{Normality(N)} = \frac{\text{gram-equivalents of solute}}{\text{Volume of solution in litre}}$$

Molarity :

$$\text{Molarity(M)} = \frac{\text{gram moles of solute}}{\text{Volume of Solution in litre}}$$

Molality :

$$\text{Molality} = \frac{\text{gram moles of solute}}{\text{Mass of solvent in kg}}$$

$$\underline{\text{Concentration}(g/L) =} \text{Normality} \times \text{Equivalent weight}$$

2.6 Find the equivalent weights of (1) HCl, (2) NaOH, (3) Na_2CO_3 and (4) H_2SO_4.

Sol: (1) HCl :

Molecular weight of HCl $= 1\times1+1\times35.5 = 36.5$

valence of HCl = 1

$\therefore$ Equivalent weight of HCl $= \frac{36.5}{1} = 36.5$

(2) NaOH :

Molecular weight of NaOH $= 1\times23+1\times16+1\times1 = 40$

Valence of NaOH = 1

$\therefore$ Equivalent weight of NaOH $= \frac{40}{1} = 40$

(3) Na_2CO_3 :

Molecular weight of $Na_2CO_3 = 2\times23+1\times12+3\times16 = 106$

Valence of $Na_2CO_3 = 2$

$\therefore$ Equivalent weight of $Na_2CO_3 = \frac{106}{2} = 53$

(4) H_2SO_4 :

Molecular weight of $H_2SO_4 = 2\times1+1\times32+4\times16 = 98$

Valence of $H_2SO_4 = 2$

$\therefore$ Equivalent weight of $H_2SO_4 = \frac{98}{2} = 49$

2.7. A solution of caustic soda contains 20% NaOH by weight. Taking density of the solution as 1.196 kg/l find the normality, molarity and molality of the solution.

Sol: Basis : 100kg of solution.

The solution contains 20kg NaOH and 80kg water (solvent)

Density of the solution = 1.196 kg/l

Volume of the solution $= \frac{100}{1.196} = 83.62\,l$

Moles of NaOH in the solution $= \frac{20}{40} = 0.5$ kmol $= 500$ mol

$\therefore$ Molarity (M) of the solution $= \frac{\text{gram moles of NaOH}}{\text{Volume of solution in litre}}$

$$= \frac{500}{83.52} = 5.98$$

for NaOH since valence = 1, we have

Equivalent weight = Molecular weight

$\therefore$ Normality (N) = Molarity (M) = 5.98

$$\text{Molality} = \frac{\text{gram moles of NaOH}}{\text{kg of solvent}}$$

$$= \frac{500}{80} = 6.25 \text{ mol/kg}$$

2.8. A solution of H_2SO_4 has a molarity of 11.24 and molality of 94. Calculate the density of the solution.

Sol: Basis : 1 litre of the solution.

Molarity = 11.24 and Molality = 94

Now, $\text{molarity} = \frac{\text{gram moles of } H_2SO_4}{\text{volume of the solution}}$

$\therefore \quad 11.24 = \frac{\text{gram moles of } H_2SO_4}{1}$

$\therefore$ Moles of H_2SO_4 = 11.24 × 1 = 11.24 mol

Amount of H_2SO_4 in the solution = 11.24 × 98 = 1101.52 g
= 1.101 kg

Molality = mol H_2SO_4/kg of solvent

$\therefore$ Amount of the solvent = $\frac{11.24}{94}$ = 0.1195 kg

Amount of the solution = 1.101 + 0.1195 = 1.2205 kg

Density of the solution = $\frac{1.2205}{1}$ = 1.2205 kg/l

2.9 Do the following conversions:

(a) 294 g/l H_2SO_4 to normality

(b) 5N H_3PO_4 to g/l. (c) 54.75 g/l HCl to molarity

(d) 3M K_2SO_4 to g/l. and (e) 4.8 mg/ml $CaCl_2$ to normality

Sol: (a) 294 g/l H_2SO_4 to normality:

Basis: 1 litre of solution

H_2SO_4 in the solution = 294 g

Gram equivalents of H_2SO_4 = $\frac{294}{49}$ = 6 g eq

$\therefore$ Normality = $\frac{6}{1}$ = 6 N

(b) 5N H_3PO_4 to g/l:

Molecular weight of H_3PO_4 = 98

valence of H_3PO_4 = 3

Equivalent weight of H_3PO_4 = $\frac{98}{3}$ = 32.67

$\therefore$ Concentration in grams per litre of the solution = Normality × Equivalent weight

Concentration of the solution = 5 × 32.67 = 163.35 g/l

(C) 54.75g/l Hcl to molarity:

Basis : 1 l of Hcl solution.

Amount of Hcl in it = 54.75g

∴ Moles of Hcl = $\frac{54.75}{36.5}$ = 1.5 mol

∴ Molarity = $\frac{1.5}{1}$ = 1.5 M

(d) 3M K_2SO_4 to g/L :

Basis : 1 L of Solution

Moles of K_2SO_4 = 3×1 = 3 mol

Molecular weight of K_2SO_4 = 174

Amount of K_2SO_4 = 3×174 = 522 g

∴ concentration of the Solution = $\frac{522}{1}$ = 522 g/l

(e) 4.8 mg/ml $CaCl_2$ to normality :

Basis : 1 l of the solution

4.8 mg/ml $CaCl_2$ = 4.8 g/L $CaCl_2$

$CaCl_2$ in the solution = 4.8 g

Molecular weight of $CaCl_2$ = 111

Equivalent weight of $CaCl_2$ = $\frac{111}{2}$ = 55.5

∴ gram equivalents of $CaCl_2$ = $\frac{48}{55.5}$ = 0.0865

∴ Normality = $\frac{0.0865}{1}$ = 0.0865 N

2.10 An aqueous solution of K_2CO_3 is Prepared by dissolving 43 kg of K_2CO_3 in 100 kg of water at 293 K (20°C). Calculate the molarity, normality and molality of the solution. Density of the solution is 1.3 kg/L.

sol: Basis: 43 kg of K_2CO_3 and 100 kg of water.

weight of K_2CO_3 solution = 43+100 = 143 kg

volume of the solution = $\frac{143}{1.3}$ = 110 l

Molecular weight of K_2CO_3 = 138

∴ Equivalent weight of K_2CO_3 = $\frac{138}{2}$ = 69

∴ Moles of K_2CO_3 in the solution $= \frac{43}{138} = 0.3116$ kmol $=$ 311.6 mol

Molarity of the solution $\frac{311.6}{110} = 2.832M$

Gram equivalents of $K_2CO_3 = \frac{43 \times 10^3}{69} = 623.19$ g eq

Normality of the solution $= \frac{623.19}{110} = 5.665N$

Molality of the solution $= \frac{311.6}{100} = 0.3116$

Weight Percent:

$$\therefore \text{weight \% of } A = \frac{\text{weight of } A}{\text{Total weight of system}} \times 100$$

$$= \frac{W_A}{W} \times 100$$

volume percent:

$$\therefore \text{volume \% of } A = \frac{\text{Pure component volume of } A}{\text{Total volume of system}} \times 100$$

$$= \frac{V_A}{V} \times 100$$

Mole Percent:

$$\therefore \text{Mole \% of } A = \frac{\text{Moles of } A}{\text{Total moles of system}} \times 100$$

$$= \frac{\frac{W_A}{M_A}}{\frac{W_A}{M_A} + \frac{W_B}{M_B}} \times 100$$

Mole fraction:

∴ for a binary system of A and B:

$$\text{mole fraction of } A = \frac{\text{Moles of } A}{\text{Total moles of system}}$$

$$x_A = \frac{\frac{W_A}{M_A}}{\frac{W_A}{M_A} + \frac{W_B}{M_B}}$$

$$x_B = \frac{\frac{M_B}{W_B}}{\frac{W_A}{M_A} + \frac{W_B}{M_B}}$$

Mole % of A = Mole fraction of A × 100

$$\sum_{i=1}^{n} x_i = 1.0$$

Weight fraction:

$$\text{Weight fraction of } A = \frac{\text{Weight of } A}{\text{Total weight of system}}$$

weight % of A = weight fraction of A × 100

2.11 An aqueous solution of Sodium chloride is prepared by dissolving 25 kg of Sodium chloride in 100 kg of water. Determine (a) weight % and (b) mole % composition of solution.

Sol: **Basis**: 25 kg of Sodium chloride and 100 kg of water.

Amount of the solution = 25 + 100 = 125 kg

Weight % Nacl in the solution $= \frac{\text{kg of NaCl}}{\text{kg of the solution}} \times 100$

$= \frac{25}{125} \times 100 = 20$

weight % H_2O = 100 − weight % of Nacl
= 100 − 20 = 80

Molecular weight of NaCl = 58.5, Molecular weight of $H_2O = 18$

∴ Moles of NaCl $= \frac{25}{58.5} = 0.427$ kmol

Moles of $H_2O = \frac{100}{18} = 5.56$ kmol

Total moles of the Solution = 0.427 + 5.56 = 5.987 kmol

Mole % Nacl in the solution $= \frac{\text{kmol NaCl}}{\text{kmol solution}} \times 100$

$= \frac{0.427}{5.987} \times 100 = 7.13$

Mole % H_2O in the solution = 100 − Mole % of Nacl
= 100 − 7.13 = 92.87

2.12 What will be % Na_2O Content of lye containing 73% (by weight) Caustic soda?

Sol: <u>Basis</u> : 100 kg of lye.
It contains 73 kg of caustic soda (NaOH).

$2\,NaOH = Na_2O + H_2O$

Molecular weight of NaOH = 40, Molecular weight of $Na_2O = 62$

$2\,NaOH \rightarrow N_2O + H_2O$

The relationship between NaOH and N_2O on the molar basis is

2 kmol NaOH ≡ 1 kmol Na_2O

$80\,kg\ NaOH \equiv 62\,kg\ Na_2O$ … on weight basis

$\therefore$ Amount of Na_2O in the lye $= \frac{62}{80} \times 73 = 56.575\,kg$

weight % Na_2O in the lye $= \frac{56.575}{100} \times 100 = 56.575$

2.13 A sample of caustic soda flakes contains 74.6% Na_2O by weight. Determine the purity of the flakes of caustic soda flakes.

Sol: Basis: 100 kg of caustic soda flakes.

It contains 74.6 kg of Na_2O.

$2NaOH = Na_2O + H_2O$

$2\,kmol$ of $NaOH \equiv 1\,kmol$ of Na_2O

$80\,kg$ of $NaOH \equiv 62\,kg$ of Na_2O

Amount of NaOH in the flakes $= \frac{80}{62} \times 74.6 = 96.26\,kg$

% Purity of the flakes $= \frac{kg\,NaOH}{kg\,flakes} \times 100 = \frac{96.26}{100} \times 100$

$= 96.26$

2.14 A sample of water contains 2000 ppm solids. Express the concentration of solids in the sample in weight percent.

Sol: Basis: 10^6 kg of sample of water.

solids in the water = 2000 ppm

$\therefore$ Amount of solids in the water $= \frac{2000}{10^6} \times 10^6 = 2000\,kg$

weight % of solids $= \frac{2000}{10^6} \times 100 = 0.20$

Ideal Gas Law:

$PV = constant$

$PV = nRT$

Partial Pressure: The partial pressure of a component gas that is present in a gas mixture is the pressure that would be exerted by that component gas if it alone were present in the same volume and at the same temperature.

Dalton's Law: It states that the total Pressure exerted by a gaseous mixture is equal to the sum of the Partial Pressures of the component gases present in the gas mixture. Thus, it expresses the additive nature of Partial Pressures.

Mathematically, $P = P_A + P_B + P_C + \cdots$

where P is the total Pressure and P_A, P_B and P_C etc. are the Partial Pressures of the component gases A, B, C, etc. respectively.

Average Molecular weight of gas Mixture.

DENSITY OF GAS MIXTURE

$$\rho_{mix} = \text{Density of gas mixture} = \frac{\text{Mass (weight)}}{\text{volume}}$$

$$\text{Specific gravity of a gas} = \frac{\text{Density of the gas}}{\text{Density of air at the same T and P}}$$

$$= \frac{\text{Molecular weight of the gas}}{\text{Molecular weight of air}}$$

Raoult's and Henry's Laws: The approximate relationships that govern the distribution of a substance between gas and liquid phases are Raoult's and Henry's laws which give reasonably accurate results in many cases.

consider a component 'A' contained in a gas-liquid system in equilibrium at temperature T and pressure P.

Let P_A° be the vapour pressure of Pure liquid 'A'.

Let x_A be the ~~vap~~ mole fraction of A in the liquid phase and y_A be the mole fraction of 'A' in the vapour phase.

Let P_A be the equilibrium Partial Pressure of A in the vapour phase.

Vapour Pressure:

The vapour pressure of a liquid is defined as the absolute pressure at which the liquid and its vapour are in equilibrium at a given temperature. Pure water exerts the vapour pressure of 101.325 kPa (760 torr) at 373.15 K (100°c).

The vapour pressure of a liquid at a given temperature is the pressure exerted by the vapour in equilibrium with the liquid at that temperature.

Raoult's Law:

$$P_A = P_A^0 x_A$$

$$y_A = P_A/P = P_A^0 x_A/P$$

Henry's Law:

$$x_A = \frac{1}{H_A} P_A$$

$$P_A = x_A H_A$$

2.15 Calculate the volume occupied by 20 kg of chlorine gas at a Pressure of 100 kPa and 298 K (25°c).

Sol: Basis: 20 kg Cl_2 gas.

Moles of Cl_2 gas $= \frac{20}{71} = 0.2817$ kmol

The ideal gas equation is

$$PV = nRT$$

$$\therefore \quad V = \frac{nRT}{P}$$

where, $n = 0.2817$ kmol, $T = 298$ K, $P = 100$ kPa, $R = 8.3145$ m³·kPa/(kmol·K)

$$\text{volume, } V = \frac{0.2817 \times 8.3451 \times 298}{100} = 6.98 \text{ m}^3$$

2.16. A gas mixture contains 0.274 kmol of Hcl, 0.337 kmol of N_2 and 0.089 kmol of O_2. Calculate (a) Average molecular weight of gas and (b) Volume occupied by this mixture at 405.3 kPa and 303 K (30°C).

Sol: **Basis**: Gas mixture Containing 0.274 kmol Hcl, 0.337 kmol N_2 and 0.089 kmol O_2.

Total moles of the gas mixture = 0.274 + 0.337 + 0.089 = 0.7 kmol

Mole fraction of Hcl $(x_{Hcl}) = \frac{0.274}{0.7} = 0.391$

Mole fraction of N_2 $(x_{N_2}) = \frac{0.337}{0.7} = 0.481$

Mole fraction of O_2 $(x_{O_2}) = \frac{0.089}{0.7} = 0.127$

Molecular weight of Hcl $= M_{Hcl} = 36.5$, Molecular weight of $N_2 = M_{N_2} = 28$

Molecular weight of $O_2 = M_{O_2} = 32$

$$M_{avg} = \Sigma M_i x_i$$
$$= M_{Hcl} \cdot x_{Hcl} + M_{N_2} \cdot x_{N_2} + M_{O_2} \cdot x_{O_2}$$
$$= 36.5 \times 0.391 + 28 \times 0.481 + 32 \times 0.127$$

$\therefore M_{avg} = 31.80$

2.17. A mixture of CH_4 and C_2H_6 has an average molecular weight of 22.4. Find mole % CH_4 and C_2H_6 in the mixture.

Sol: **Basis**: Average molecular weight of 22.4 of gas mixture.

Let x_{CH_4} and $x_{C_2H_6}$ be the mole fractions of CH_4 and C_2H_6 respectively.

$$M_{avg} = \Sigma M_i x_i$$

$$M_{avg} = M_{CH_4} \cdot x_{CH_4} + M_{C_2H_6} \cdot x_{C_2H_6}$$

∴ $$22.4 = 16 x_{CH_4} + 30 x_{C_2H_6}$$

$$\Sigma x_i = 1$$

$$x_{CH_4} + x_{C_2H_6} = 1$$

∴ $$x_{C_2H_6} = 1 - x_{CH_4}$$

Substituting for $x_{C_2H_6}$ from Equation (3) into Equation (1) and solving for x_{CH_4} gives

$$22.4 = 16 x_{CH_4} + 30\left(1 - x_{CH_4}\right)$$

∴ $$x_{CH_4} = 0.543$$

$$x_{C_2H_6} = 1 - 0.543 = 0.457$$

Mole % of CH_4 = Mole fraction of $CH_4 \times 100 = 0.543 \times 100 =$ 54.30

Mole % of $C_2H_6 = 0.457 \times 100 = 45.70$

2.16 Assuming air to contain 79% N_2 and 21% O_2 by volume, calculate the density of air at NTP.

Sol: Basis: Air containing 21% O_2 and 79% N_2 by volume.

For ideal gases, mole % = volume %

∴ Mole % of $N_2 = 79$, Mole % of $O_2 = 21$

mole fraction of N_2 $(x_{N_2}) = \dfrac{\text{Mole \% of } N_2}{100} = \dfrac{79}{100} = 0.79$

Mole fraction of $(x_{O_2}) = \dfrac{\text{Mole \% of } O_2}{100} = \dfrac{21}{100} = 0.21$

$$M_{avg} = M_{N_2} \cdot x_{N_2} + M_{O_2} \cdot x_{O_2}$$
$$= 28 \times 0.79 + 82 \times 0.21 = 28.84$$

The density of a gas mixture (air) is given by

$$\rho = \frac{PM_{avg}}{RT}$$

Where, $M_{avg} = 28.84$, $T = 273K$, $P = 101.325\ kPa$, $R = 8.3145\ lm^3.kPa/(kmol.K)$

$$\rho = \frac{101.325 \times 28.84}{8.31451 \times 273} = 1.2874\ kg/m^3$$

Density of air $= 1.2874\ kg/m^3$

2.19 A mixture of CH_4 and C_2H_6 has density $1.0\ kg/m^3$ at 273K (0 °C) and 101.325 kPa pressure. Calculate the mole % and weight % of CH_4 and C_2H_6 in the mixture.

Sol: **Basis**: $1\ kg/m^3$ density of gas mixture at 273 K and 101.325 kPa.

The density of a gas mixture is given by

$$\rho = \frac{PM_{avg}}{RT}$$

$$\therefore \quad M_{avg} = \rho.\frac{RT}{P}$$

where, $\rho = 1\ kg/m^3$, $T = 273K$, $P = 101.325\ kPa$, $R = 8.31451\ m^3.kPa/(kmol.K)$

$$\therefore M_{avg} = 1 \times \frac{8.31451 \times 273}{101.325} = 22.4$$

Let x_{CH_4} and $x_{C_2H_6}$ be the mole fractions of CH_4 and C_2H_6 respectively.

For our case, M_{avg} is: $M_{avg} = \Sigma M_i x_i = M_{CH_4} \cdot x_{CH_4} + M_{C_2H_6} \cdot x_{C_2H_6}$

$$\therefore \quad 22.4 = 16\,x_{CH_4} + 30\,x_{C_2H_6}$$

$$\Sigma x_i = 1$$

$$x_{CH_4} + x_{C_2H_6} = 1$$

$$\therefore \quad x_{C_2H_6} = 1 - x_{CH_4}$$

Substituting $x_{C_2H_6}$ from Equation(3) into Equation(1) and solving for x_{CH_4}, we get

$$22.4 = 16x_{CH_4} + 30(1 - x_{CH_4})$$

$$\therefore \quad x_{CH_4} = 0.543$$

$$x_{C_2H_6} = 1 - 0.543 = 0.457$$

Mole % of $CH_4 = x_{CH_4} \times 100 = 0.543 \times 100 = 54.3$

Mole % of $C_2H_6 = x_{C_2H_6} \times 100 = 0.457 \times 100 = 45.7$

weight of CH_4 in 1 kmol mixture $= 0.543 \times 16 = 8.69$kg

weight of C_2H_6 in 1 kmol mixture $= 0.457 \times 30 = 13.71$kg

weight of gass mixture = 22.4kg

weight % of CH_4 in the mixture $= \frac{8.69}{22.4} \times 100 = 38.8$

weight % of C_2H_6 in the mixture $= 100 - 38.8 = 61.2$

Psychrometry

Dry bulb temperature (DBT): The temperature measured by a bare thermometer or thermocouple is called the dry bulb temperature.

Wet bulb temperature (WBT): The temperature measured by a thermometer or thermocouple with a wet wick covering the bulb, under equilibrium condition, is called the wet bulb temperature

Absolute humidity (n_v):

$$[n_v] = \left[\frac{y_A}{y_B}\right] = \frac{P_A}{P_B} = \left[\frac{P_v}{P - P_v}\right] = \frac{\text{moles of A}}{\text{moles of B}}$$

$$n_v = [n_v] \times \left[\frac{M_A}{M_B}\right] = \left[\frac{P_v}{P-P_v}\right] \times \left[\frac{M_A}{M_B}\right] = \frac{\text{mass of } A}{\text{mass of } B}$$

Relative humidity or relative saturation ($y_r\%$):

Relative Saturation $= y_r\ \% = \frac{P_v}{P_s} \times 100$

Percentage Saturation or percentage absolute humidity (y_p):

Percentage saturation $= y_p\ \% = \frac{n_v}{n_s} \times 100$

Dew Point: This is the temperature at which a vapour-gas mixture becomes saturated when cooled at constant total pressure out of contact with a liquid. The moment the temperature is reduced below the dew point, the vapour will condense as a liquid dew.

20. On a particular day in solapur, the dry bulb temperature and dew point of ambient air were found to be 302 K (29°c) and 291 K (18°c) respectively. Barometer reads 100 kPa. Calculate:

(a) the absolute molal humidity, (b) the absolute humidity,
(c) the % RH, (d) the % Saturation.

Data: Vapour pressure of water at 291 K = 2.0624 kPa.
Vapour pressure of water at 302 K = 4.004 kPa.

Solution: Basis: Air-water vapour mixture with DB = 302 K and DP = 291 K.

At DP, Partial pressure of water in air is equal to the vapour pressure of water.

P_A = Partial pressure of water vapour in air = 2.0624 kPa
P = total pressure = 100 kPa

Absolute molal humidity, $H_m = \frac{P_A}{P - P_A} = \frac{2.0624}{100 - 2.0624}$

$= 0.02106 \frac{\text{kmol water vapour}}{\text{kmol dry air}}$

Molecular weight of H_2O = 18, molecular weight of air = 29

Absolute humidity, $H = H_m \times \frac{\text{Molecular weight of } H_2O}{\text{Molecular weight of air}}$

$= 0.02106 \times \frac{18}{29}$

$= 0.0131 \frac{\text{kg water vapour}}{\text{kg dry air}}$

At saturation, DB = WB = DP = 302K

vapour pressure at saturation, i.e., at 302K = P_S = 4.004 kPa

$\% RH = \frac{P_A}{P_S} \times 100 = \frac{2.0624}{4.004} \times 100 = 51.51$

saturation humidity, $H_S = \left[\frac{P_S}{P - P_S}\right] \frac{\text{Molecular weight of } H_2O}{\text{Molecular weight of air}}$

$\therefore \quad H_S = \left[\frac{4.004}{100 - 4.004}\right] \times \frac{18}{29}$

$= 0.02589 \frac{\text{kg water vapour}}{\text{kg dry air}}$

$\%$ saturation $= \frac{H}{H_S} \times 100 = \frac{0.0131}{0.02589} \times 100 = 50.60$

21 A mixture of acetone vapour and nitrogen contains 15.8% acetone by volume. Calculate the relative and percent saturation of the mixture at a temperature of 293K (20°c) and a pressure of 101.325 kPa.

Data: Vapour pressure of acetone at 293K = 24.638 kPa.

Sol: Basis: 1 mol of acetone-nitrogen mixture.

Mole % acetone = Volume % acetone = 15.8

mole fraction of acetone in the mixture $(y) = \frac{15.8}{100} = 0.158$

Total Pressure(P) = 101.325 kPa

Partial Pressure of acetone(P_A) = $y \cdot P$

$= 0.158 \times 101.325 = 16.009$ kPa

vapour pressure of acetone at 293K(P_s) = 24.638 kPa

% relative saturation $= \frac{P_A}{P_s} \times 100$

$= \frac{16.009}{24.638} \times 100 = 64.98$

Moles of acetone per mole nitrogen in the gas mixture(H_m)

$= \frac{0.158}{1-0.158} = 0.1876$

consider one mole of saturated mixture at 293 K (20°c) and 101.325 kPa.

$\therefore$ $\begin{pmatrix}\text{volume \% acetone} \\ \text{in saturated mixture}\end{pmatrix} = \begin{pmatrix}\text{Pressure \% acetone} \\ \text{in saturated mixture}\end{pmatrix}$

$\therefore$ volume % acetone $= \frac{24.638}{101.325} \times 100 = 24.31$

mole % acetone in the saturated mixture = volume % acetone = 24.31

Acetone in the saturated mixture $= \frac{24.31}{100} \times 1 = 0.2431$ mol

Nitrogen in the saturated mixture = 1 − 0.2431 = 0.7569 mol

Moles of acetone per mole nitrogen in the saturated mixture (H_{ms}) $= \frac{0.2431}{0.7569} = 0.3212$

% saturation $= \frac{H_m}{H_{ms}} \times 100$

$= \frac{0.1876}{0.3212} \times 100 = 58.40$

22. A gas mixture containing benzene vapour is saturated at 101.325 kPa and 323 K (50°c). calculate the absolute humidity if the other component of the mixture is (a) nitrogen and (b) carbon dioxide.

Data: vapour pressure of benzene at 323 k = 36.664 kPa.

Sol: Basis: Gas mixture at 101.325 kPa and 323 K.

(a) Nitrogen and benzene vapour mixture:

Molecular weight of $N_2 = 28$, molecular weight of $C_6H_6 = 78$

As the mixture is saturated at 323k, the partial pressure of benzene is equal to vapour pressure of benzene at 323 k.

$\therefore$ $P_A = 36.664$ kPa

$P = 101.325$ kPa

$$H_m = \frac{P_A}{P - P_A} = \frac{36.664}{101.325 - 36.664}$$

$$= 0.567 \frac{\text{kmol benzene vapour}}{\text{kmol nitrogen}}$$

$$\text{Absolute humidity, } H = H_m \times \frac{\text{Molecular weight of } C_6H_6}{\text{Molecular weight of } N_2}$$

$$= 0.567 \times \frac{78}{28}$$

$$= 1.579 \frac{\text{kg benzene}}{\text{kg nitrogen}}$$

(b) carbon dioxide - benzene vapour mixture:

Molecular weight of $CO_2 = 44$,

$P_A = 36.664$ kPa,

$P = 101.325$ kPa,

$$H_m = \frac{P_A}{P - P_A} = \frac{36.664}{101.325 - 36.664},$$

$$= 0.567 \frac{\text{kmol benzene vapour}}{\text{kmol carbon dioxide}}$$

Absolute humidity,

$$H = H_m \times \frac{\text{molecular weight of } C_6H_6}{\text{Molecular weight of } CO_2}$$

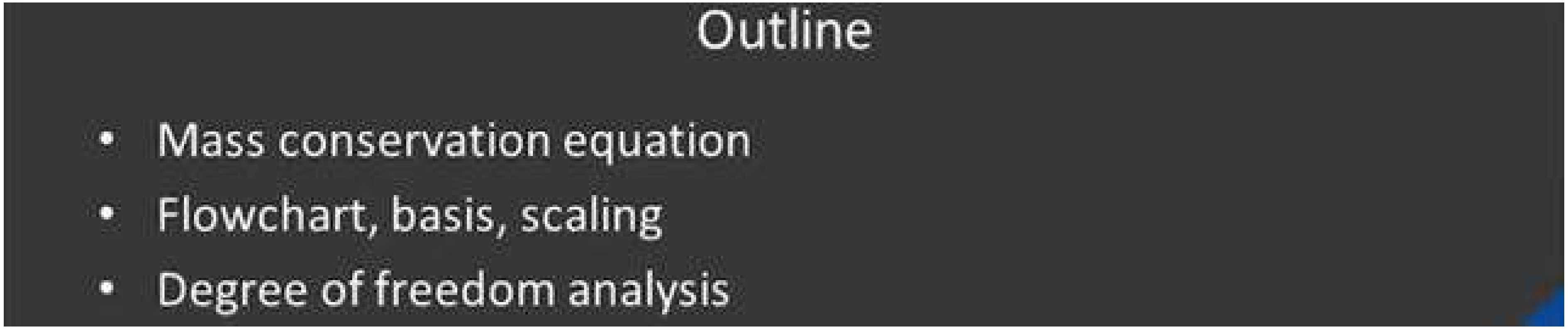
$$= 0.567 \times \frac{78}{44}$$

$$= 1.005 \frac{\text{kg benzene}}{\text{kg carbon dioxide}}$$

MODULE2: MASS BALANCE WITHOUT CHEMICAL REACTION

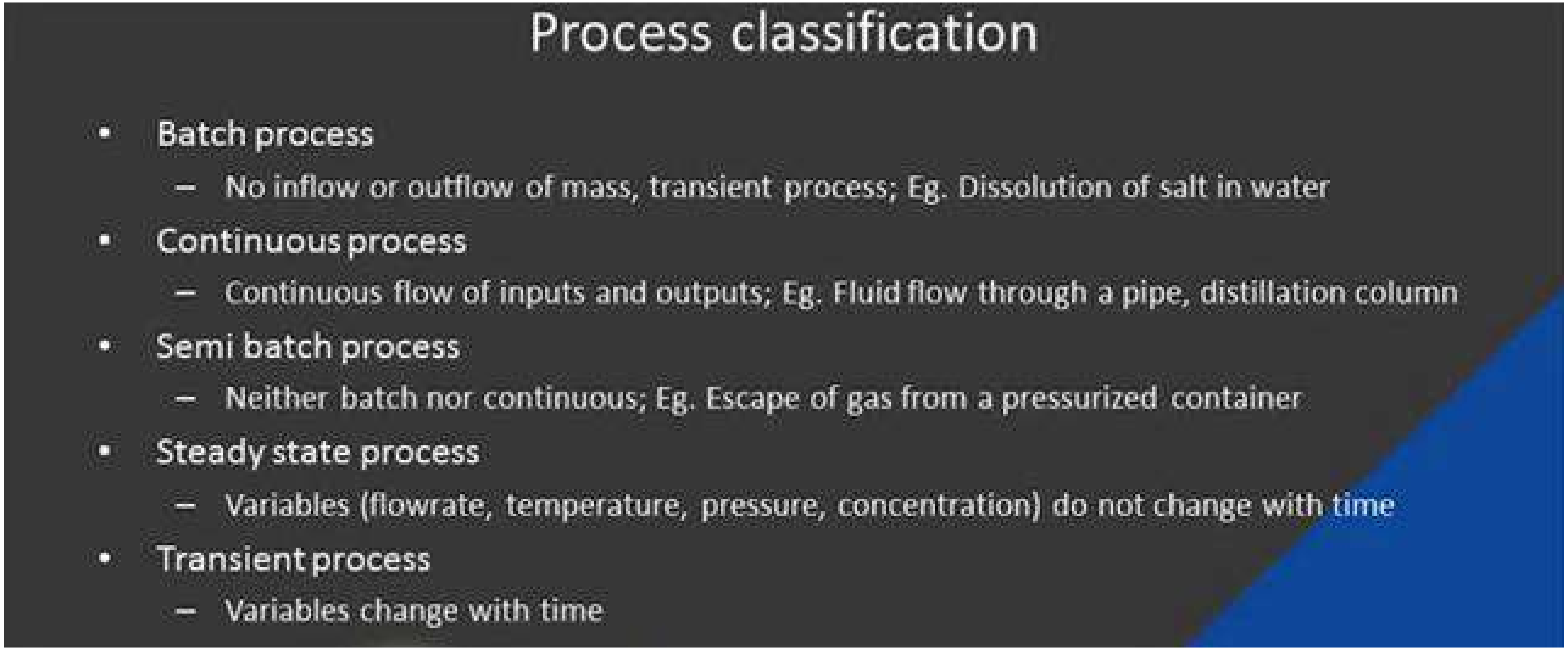
References:

https://www.youtube.com/watch?v=zzCI9V-kPcg
https://www.youtube.com/watch?v=PYaE3qV-G8U
https://www.youtube.com/watch?v=KU_b_nas7Nk
https://www.youtube.com/watch?v=4bY6f8U_42c
Book: RM Felder and RW Rousseau, “Elementary Principles of Chemical Processes” 4th edition, John Wiley & Sons, 2011.



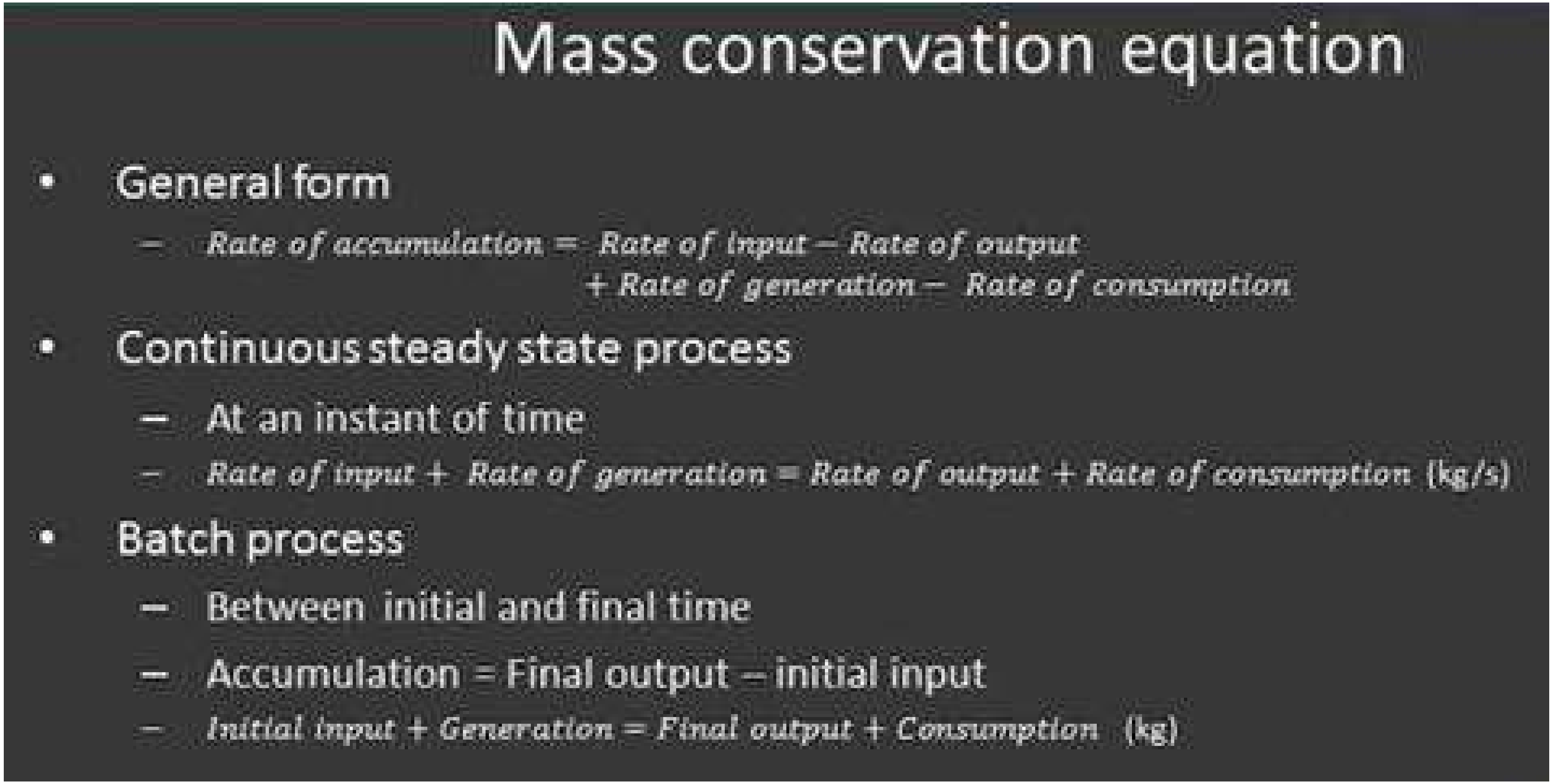
Outline

- Mass conservation equation
- Flowchart, basis, scaling
- Degree of freedom analysis



Process classification

- Batch process
  - No inflow or outflow of mass, transient process; Eg. Dissolution of salt in water
- Continuous process
  - Continuous flow of inputs and outputs; Eg. Fluid flow through a pipe, distillation column
- Semi batch process
  - Neither batch nor continuous; Eg. Escape of gas from a pressurized container
- Steady state process
  - Variables (flowrate, temperature, pressure, concentration) do not change with time
- Transient process
  - Variables change with time



Mass conservation equation

- General form
  - $\text{Rate of accumulation} = \text{Rate of input} - \text{Rate of output} + \text{Rate of generation} - \text{Rate of consumption}$
- Continuous steady state process
  - At an instant of time
  - $\text{Rate of input} + \text{Rate of generation} = \text{Rate of output} + \text{Rate of consumption}$ (kg/s)
- Batch process
  - Between initial and final time
  - Accumulation = Final output – initial input
  - $\text{Initial input} + \text{Generation} = \text{Final output} + \text{Consumption}$ (kg)

Outline

- Mass conservation equation
- Flowchart, basis, scaling
- Degree of freedom analysis

Flowchart or Flowsheet

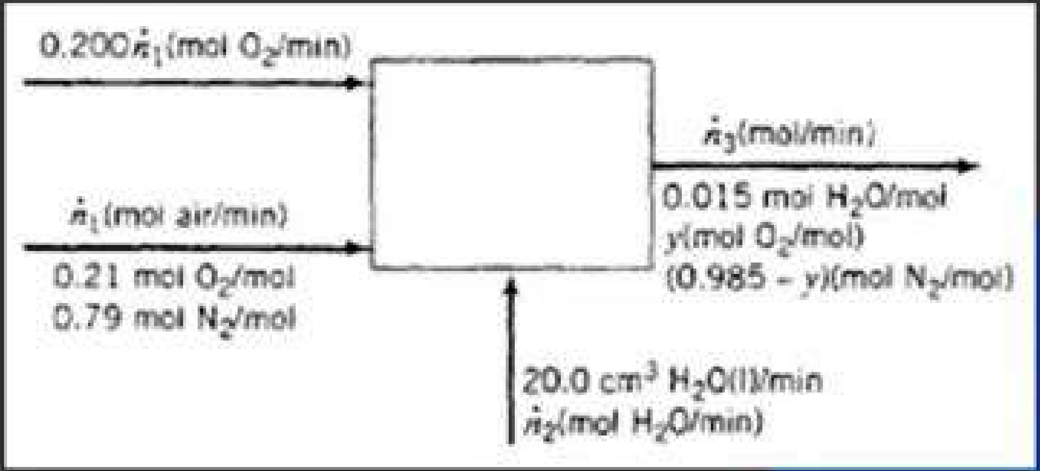
An experiment requires humid air enriched in oxygen. Three input streams are fed into an evaporation chamber to produce an output stream with the desired composition.

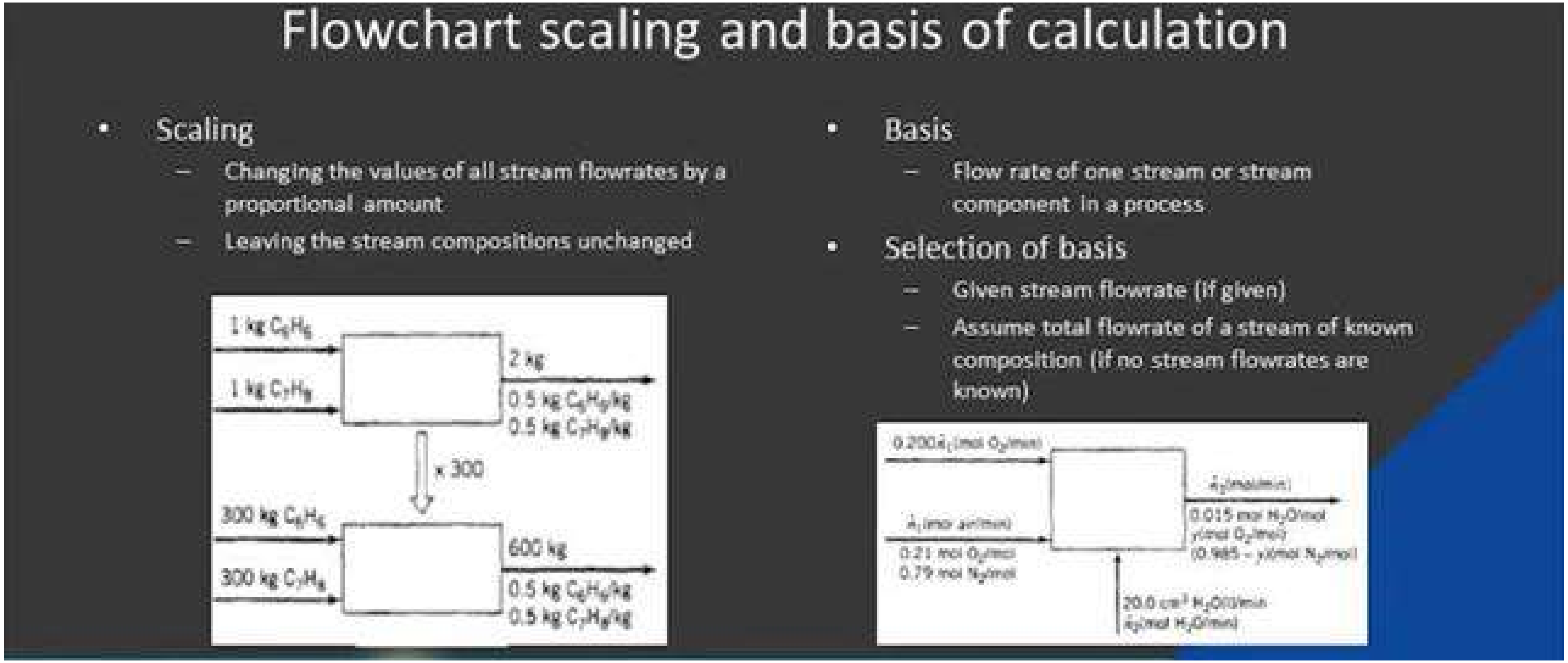
A: Liquid water, fed at a rate of 20.0 cm^3/min

B: Air (21 mole% O_2 , the balance N_2)

C: Pure oxygen, with a molar flow rate one-fifth of the molar flow rate of stream B

The output gas is found to contain 1.5 mole% water.

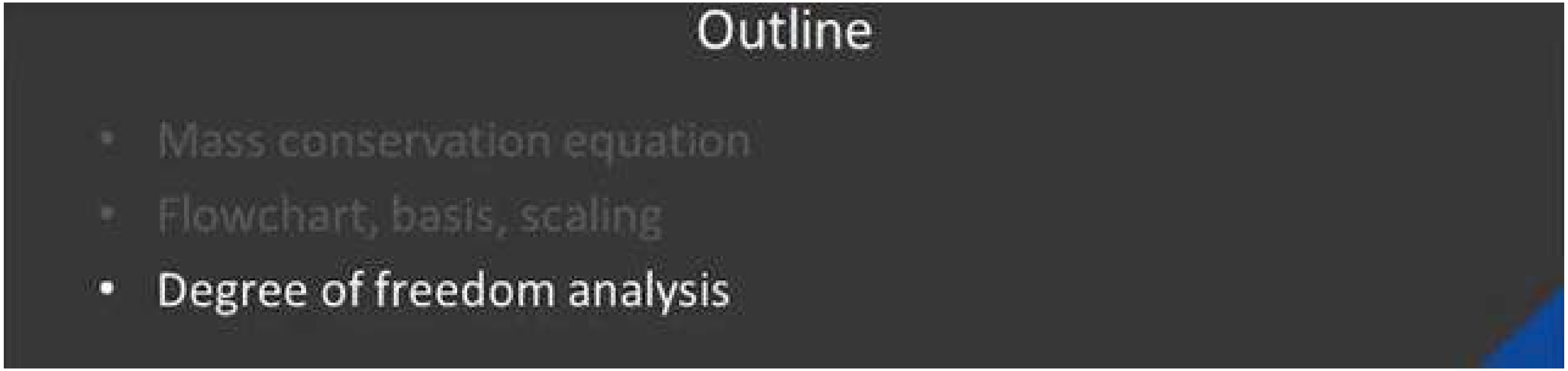




Flowchart scaling and basis of calculation

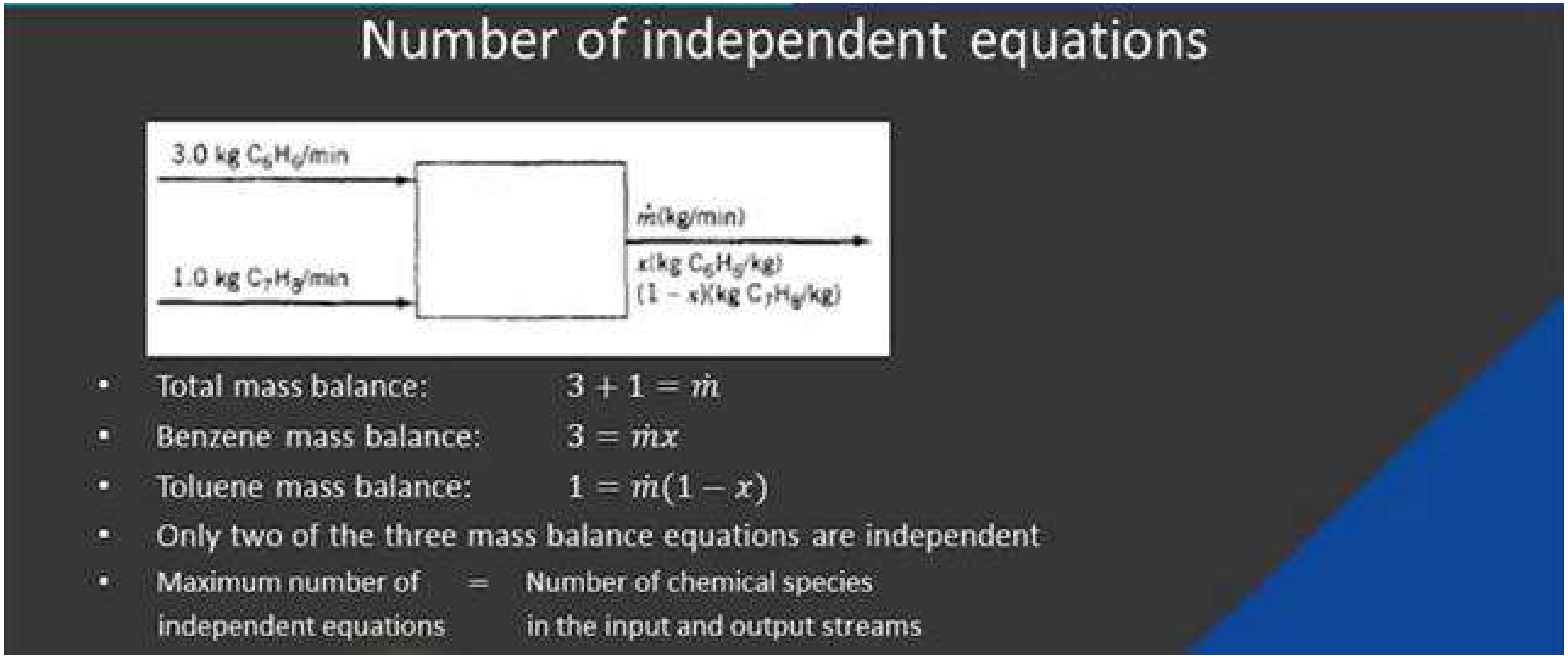
- Scaling
  - Changing the values of all stream flowrates by a proportional amount
  - Leaving the stream compositions unchanged

- Basis
  - Flow rate of one stream or stream component in a process
- Selection of basis
  - Given stream flowrate (if given)
  - Assume total flowrate of a stream of known composition (if no stream flowrates are known)



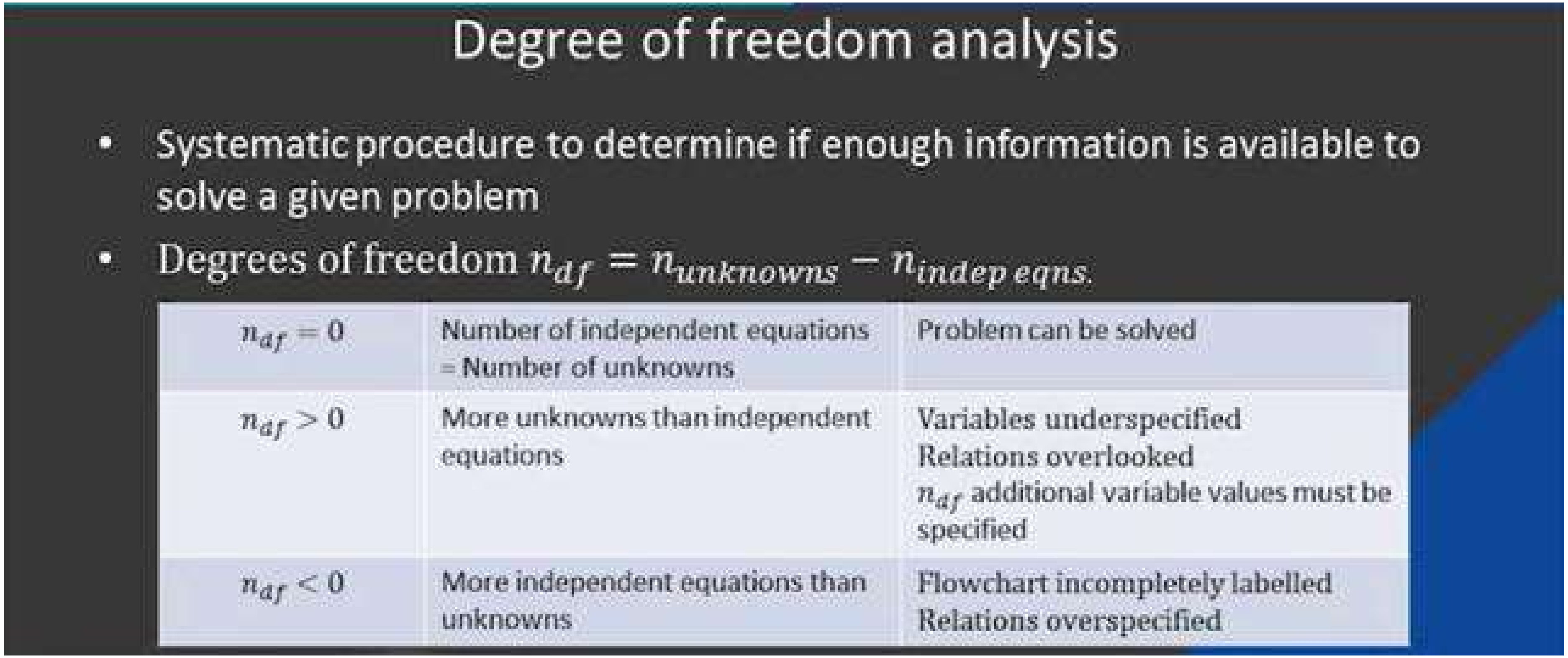
Outline

- Mass conservation equation
- Flowchart, basis, scaling
- Degree of freedom analysis



Number of independent equations

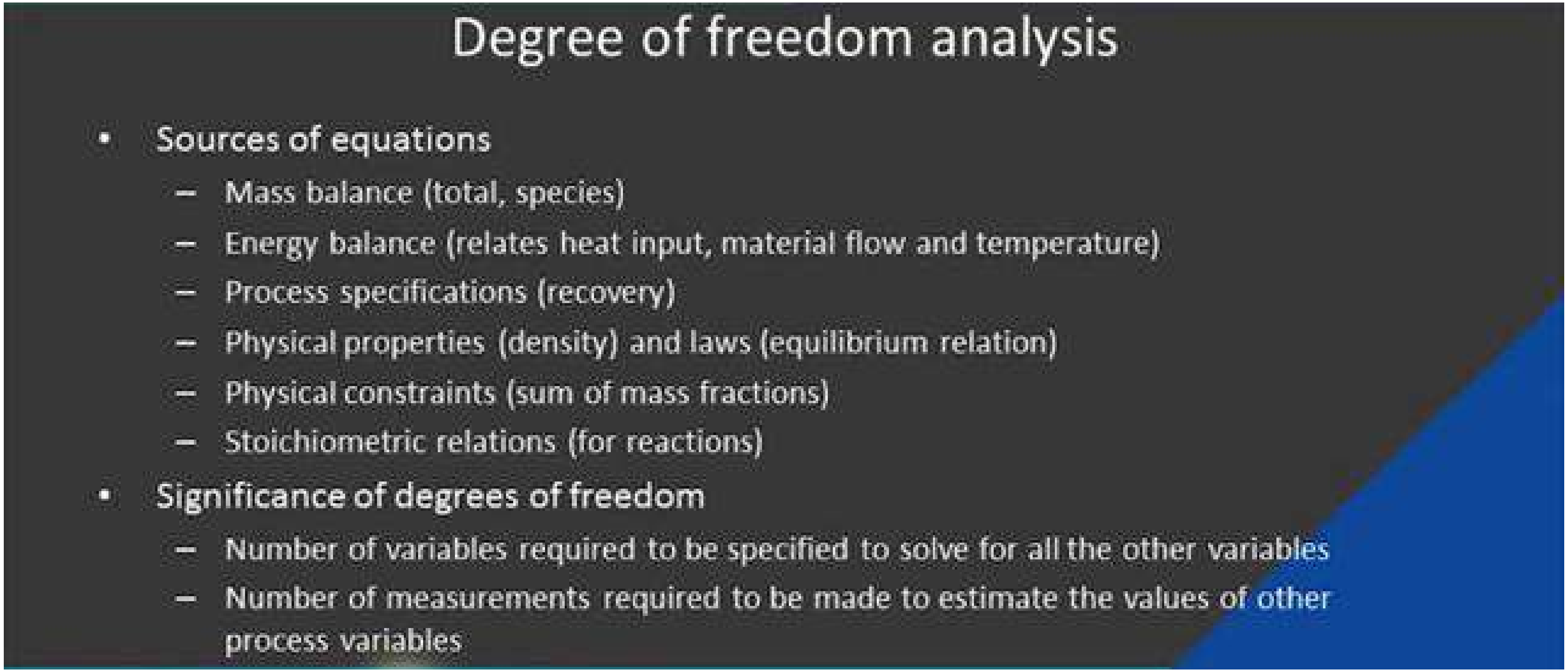
- Total mass balance: $3 + 1 = \dot{m}$
- Benzene mass balance: $3 = \dot{m}x$
- Toluene mass balance: $1 = \dot{m}(1 - x)$
- Only two of the three mass balance equations are independent
- Maximum number of independent equations = Number of chemical species in the input and output streams



Degree of freedom analysis

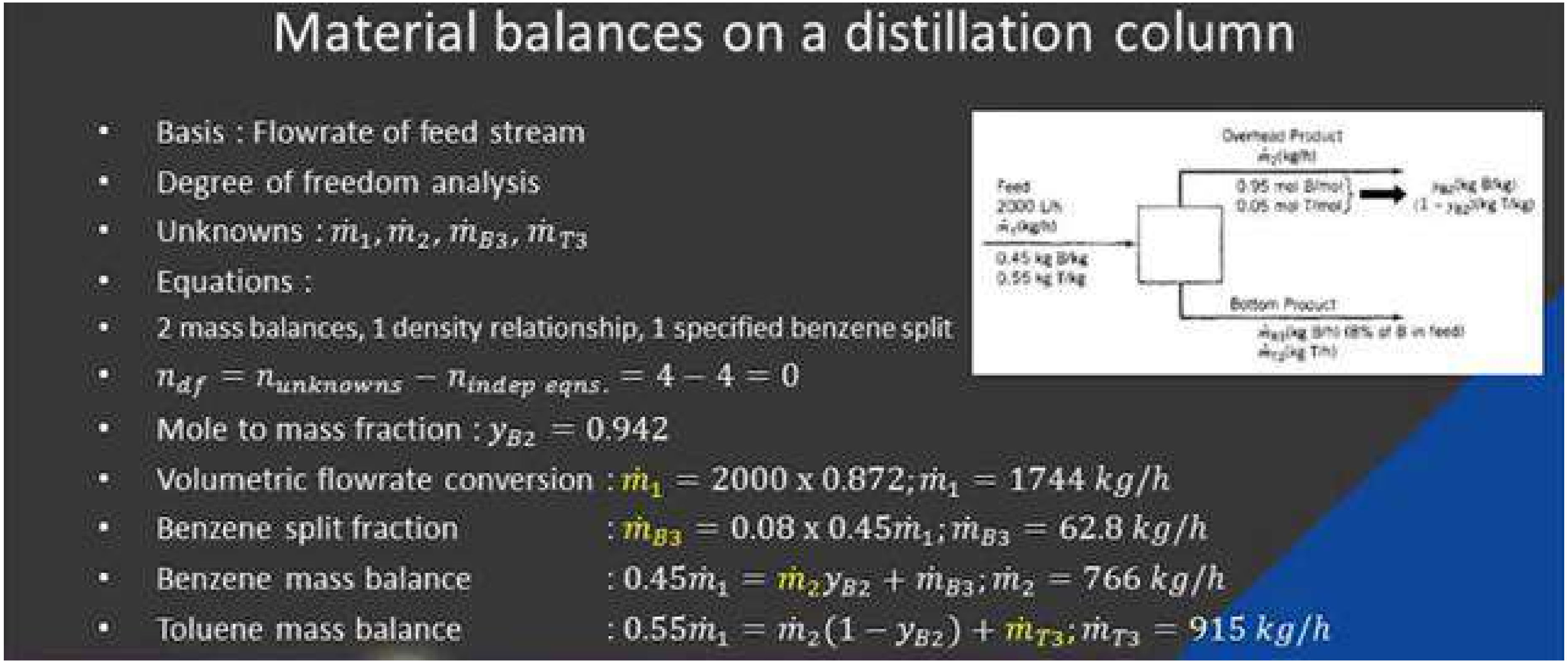
- Systematic procedure to determine if enough information is available to solve a given problem
- Degrees of freedom $n_{df} = n_{unknowns} - n_{indep\ eqns.}$

$n_{df} = 0$	Number of independent equations = Number of unknowns	Problem can be solved
$n_{df} > 0$	More unknowns than independent equations	Variables underspecified Relations overlooked n_{df} additional variable values must be specified
$n_{df} < 0$	More independent equations than unknowns	Flowchart incompletely labelled Relations overspecified



Degree of freedom analysis

- Sources of equations
    - Mass balance (total, species)
    - Energy balance (relates heat input, material flow and temperature)
    - Process specifications (recovery)
    - Physical properties (density) and laws (equilibrium relation)
    - Physical constraints (sum of mass fractions)
    - Stoichiometric relations (for reactions)
- Significance of degrees of freedom
    - Number of variables required to be specified to solve for all the other variables
    - Number of measurements required to be made to estimate the values of other process variables



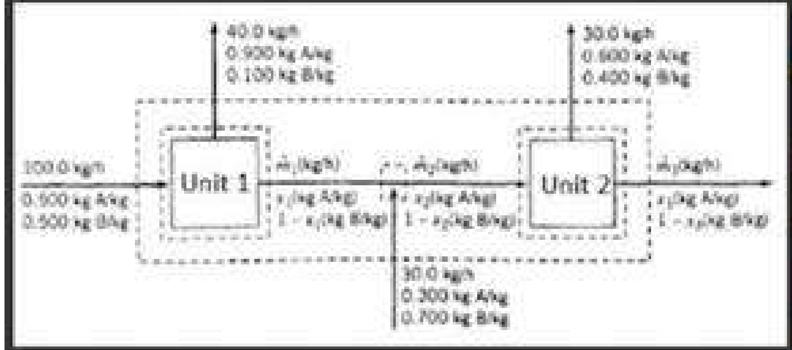
Material balances on a distillation column

- Basis : Flowrate of feed stream
- Degree of freedom analysis
- Unknowns : $\dot{m}_1, \dot{m}_2, \dot{m}_{B3}, \dot{m}_{T3}$
- Equations :
- 2 mass balances, 1 density relationship, 1 specified benzene split
- $n_{df} = n_{unknowns} - n_{indep\ eqns.} = 4 - 4 = 0$
- Mole to mass fraction : $y_{B2} = 0.942$
- Volumetric flowrate conversion : $\dot{m}_1 = 2000 \text{ x } 0.872; \dot{m}_1 = 1744\ kg/h$
- Benzene split fraction : $\dot{m}_{B3} = 0.08 \text{ x } 0.45\dot{m}_1; \dot{m}_{B3} = 62.8\ kg/h$
- Benzene mass balance : $0.45\dot{m}_1 = \dot{m}_2 y_{B2} + \dot{m}_{B3}; \dot{m}_2 = 766\ kg/h$
- Toluene mass balance : $0.55\dot{m}_1 = \dot{m}_2(1 - y_{B2}) + \dot{m}_{T3}; \dot{m}_{T3} = 915\ kg/h$

Two unit process

Flowchart

Basis : All given flowrates

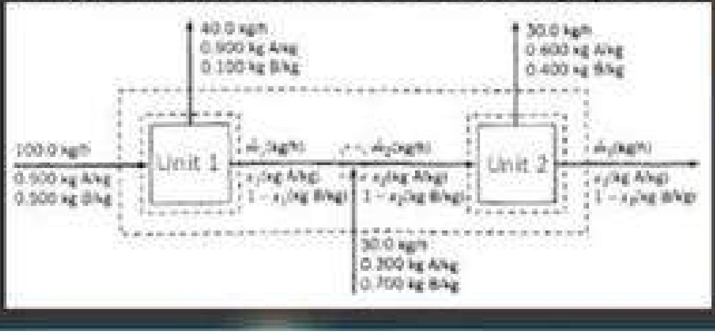


Degree of freedom analysis

	Unit 1	Mixing point	Unit 2	Overall process
Unknowns	2 ($\dot{m}_1, x_1$)	4 ($\dot{m}_1, x_1, \dot{m}_2, x_2$) 2 ($\dot{m}_2, x_2$)	4 ($\dot{m}_2, x_2, \dot{m}_3, x_3$)	2 ($\dot{m}_3, x_3$)
Equations	2 mass balances	2 mass balances	2 mass balances	2 mass balances
n_{df}	0	2 0	2	0
Sequence	Second	Third		First

Two unit process

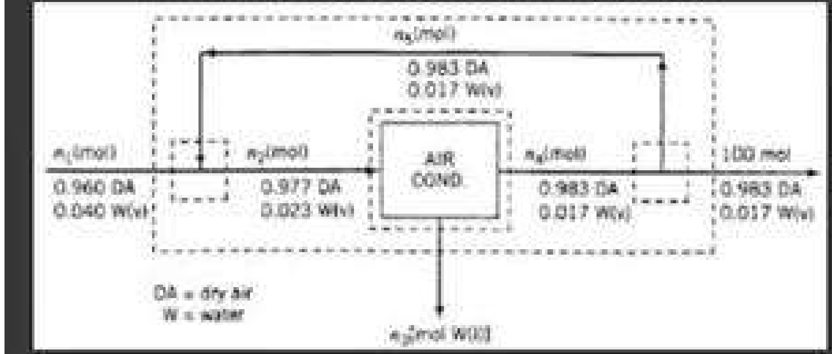
- Overall total mass balance : $100 + 30 = 40 + 30 + \dot{m}_3; \dot{m}_3 = 60\ kg/h$
- Overall species A mass balance : $100x0.5 + 30x0.3 = 40x0.9 + 30x0.6 + \dot{m}_3 x_3; x_3 = 0.00833$
- Unit I total mass balance : $100 = 40 + \dot{m}_1; \dot{m}_1 = 60\ kg/h$
- Unit I species A mass balance : $100x0.5 = 40x0.9 + \dot{m}_1 x_1; x_1 = 0.233$
- Mixing point total mass balance : $\dot{m}_1 + 30 = \dot{m}_2; \dot{m}_2 = 90\ kg/h$
- Mixing point species A mass balance : $\dot{m}_1 x_1 + 30x0.3 = \dot{m}_2 x_2; x_2 = 0.255$



	Unit 1	Mixing point	Unit 2	Overall process
Unknowns	2 ($\dot{m}_1, x_1$)	4 ($\dot{m}_1, x_1, \dot{m}_2, x_2$) 2 ($\dot{m}_2, x_2$)	4 ($\dot{m}_2, x_2, \dot{m}_3, x_3$)	2 ($\dot{m}_3, x_3$)
Equations	2 mass balances	2 mass balances	2 mass balances	2 mass balances
n_{df}	0	2 0	2	0
Sequence	Second	Third		First

Recycle and bypass

- Recovery of unconsumed reactants, reflux in a distillation column, circulation of a working fluid
- Material balance on an air conditioner with recycle
- Basis : Moles of air leaving the process

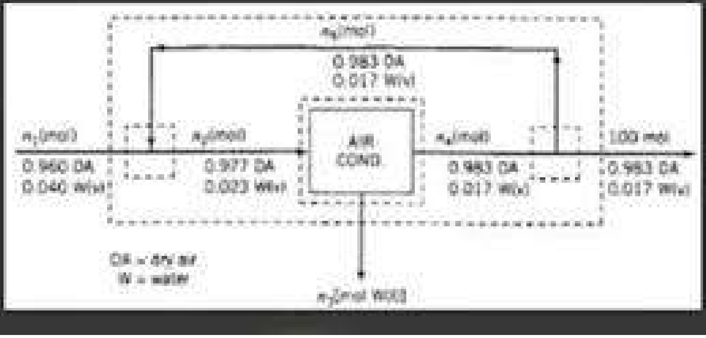


	Mixing point	Air conditioner	Splitting point	Overall process
Unknowns	3 (n_1, n_2, n_5) 2 (n_2, n_5)	3 (n_2, n_3, n_4) 2 (n_2, n_4)	2 (n_4, n_5)	2 (n_1, n_3)
Equations	2 mass balances	2 mass balances	1 mass balance	2 mass balances
n_{df}	1 0	1 0	1	0
Sequence	Second	Third		First

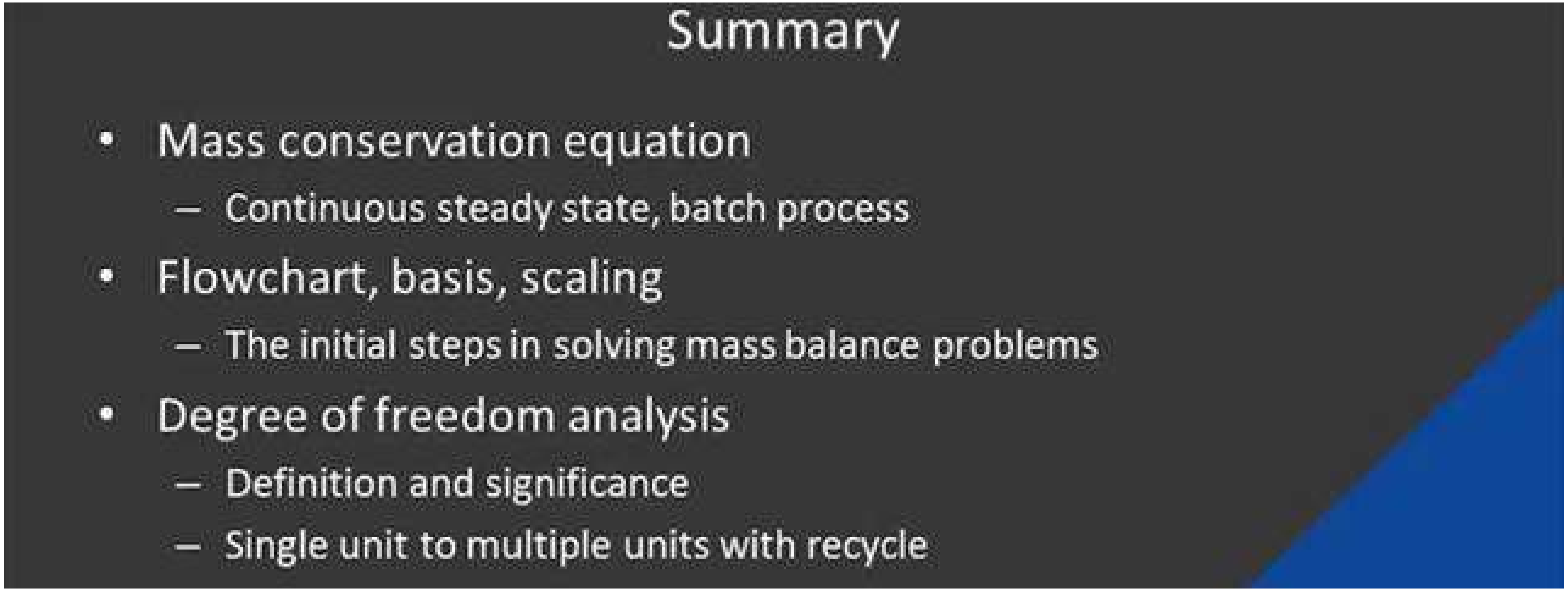
Recycle and bypass

- Overall dry air mass balance : $n_1 x0.96 = 100x0.983; n_1 = 102.4\,mol$
- Overall total mass balance : $n_1 = n_3 + 100; n_3 = 2.4\,mol$
- Mixing point total mass balance : $n_1 + n_5 = n_2;$
- Mixing point water mass balance : $n_1 x0.04 + n_5 x0.017 = n_2 x0.023;$

$$n_2 = 392.5\,mol; n_5 = 290\,mol$$



	Mixing point	Air conditioner	Splitting point	Overall process
Unknowns	3 (n_1, n_2, n_5) 2 (n_2, n_5)	3 (n_2, n_3, n_4) 2 (n_2, n_4)	2 (n_4, n_5)	2 (n_1, n_3)
Equations	2 mass balances	2 mass balances	1 mass balance	2 mass balances
n_{df}	1 0	1 0	1	0
Sequence	Second	Third		First



Summary

- Mass conservation equation
  - Continuous steady state, batch process
- Flowchart, basis, scaling
  - The initial steps in solving mass balance problems
- Degree of freedom analysis
  - Definition and significance
  - Single unit to multiple units with recycle

EXAMPLE 9.1 Coal contains 85% carbon and 15% ash. The cinder formed in the combustion of coal contains 80% ash and 20% carbon. Determine the weight of cinder formed by the combustion of 100 kg of coal and the percent of fuel value that is lost.

Solution *Basis*: 100 kg of coal (refer to Figure 9.3)

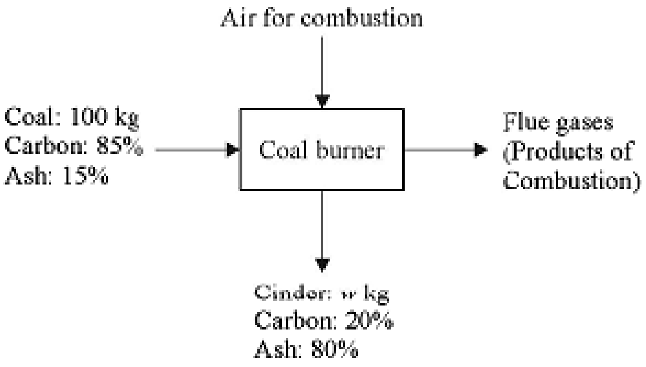


Figure 9.3 Combustion of coal (Example 9.1).

Ash enters the system in a single stream, that is, with the coal fired. It leaves the system in a single stream without any change, with the cinder formed by the combustion. Therefore, ash can be used as a key component for getting the quantity of cinder formed.

The weight of ash entering the system is

$$\frac{15}{100} \times 100 = 15 \text{ kg}$$

Let w be the weight of cinder formed.

The weight of ash leaving is

$$w \times \frac{80}{100} \text{ kg}$$

Taking an ash balance, we get

$$15 = w \times \left(\frac{80}{100}\right) \qquad \Rightarrow \qquad w = 18.75 \text{ kg}$$

Hence, 18.75 kg cinder is formed by the combustion of 100 kg coal.

Since 20% of cinder is carbon, weight of carbon that is lost unburned when 100 kg of coal is charged is equal to (20/100) × 18.75 = 3.75 kg. As the coal originally contained 85 kg of carbon, the percent fuel value that is lost in the cinder is

$$(3.75/85) \times 100 = 4.41\%$$

EXAMPLE 9.2 Wood containing 40% moisture is dried to 5% moisture. What mass of water in kilograms is evaporated per kg of dry wood?

Solution *Basis*: 1 kg of dry wood in the feed to the drier (Figure 9.4)

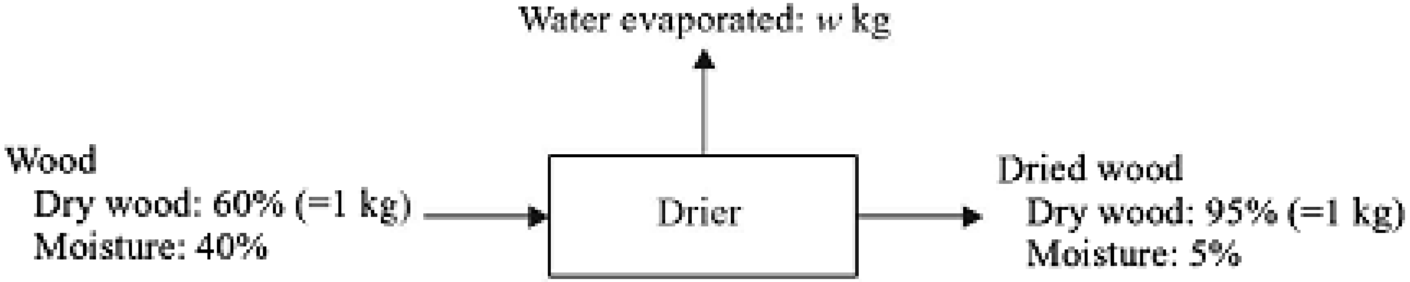


Figure 9.4 Drying of wood (Example 9.2).

The entering material contains 40/60 = 2/3 kg water per kg dry wood and the leaving material contains 5/95 kg water per kg dry wood. If *w* be the weight of water evaporated, then water balance about the drier yields

$$1\times\frac{40}{60}=w+\frac{5}{95} \quad\Rightarrow\quad w=\frac{40}{60}-\frac{5}{95}=0.614\ \text{kg}$$

The amount of water evaporated per kg dry wood is 0.614 kg.

If we were required to find the amount of water evaporated per kilogram of wet wood entering the drier, the basis of 1 kg of dry wood could still be chosen for solving the problem. Knowing that 1 kg of dry wood is associated with 100/60 kg of wet wood, the water evaporated per kg of wet material is

$$0.614\times\frac{60}{100}=0.368\ \text{kg}$$

EXAMPLE 9.3 The liquid effluent from a processing unit is discharged into a stream. The flow rate and BOD of the stream before the discharge point are respectively 6 m^3/s and 3×10^{-5} g/L. The measurements made immediately below the discharge point indicated a BOD of 5×10^{-3} g/L. If the plant discharges the effluents at a rate of 16×10^3 m^3/day, what is the BOD of the effluent from the plant? (Note: Biochemical Oxygen Demand, BOD, is a measure of the oxygen utilized by microorganisms during the oxidation of organic materials. BOD is a direct measure of oxygen requirement and is directly proportional to the amount of organic waste which has to be broken down.)

Solution *Basis*: One hour of operation (Figure 9.5)

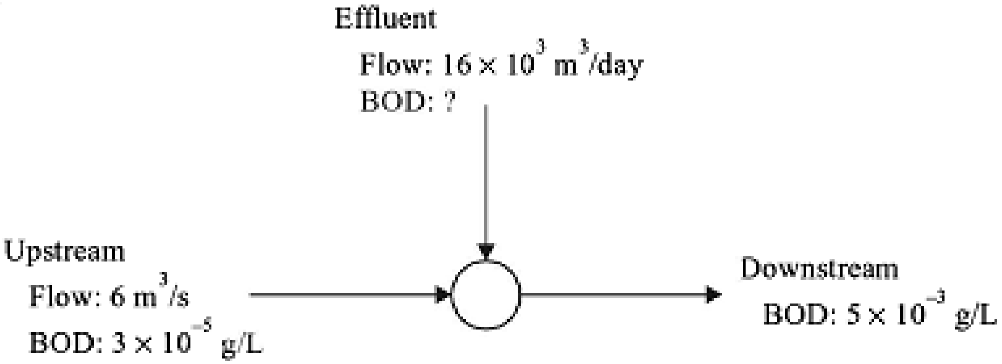


Figure 9.5 Effluent discharge (Example 9.3).

The rate of discharge of effluent is

$$\frac{16 \times 10^3}{24} = 666.67 \text{ m}^3/\text{h} \quad (= 666.67 \times 10^3 \text{ L/h})$$

Let x be the BOD expressed in g/L. Consider the BOD balance at the point where the discharge from the plant joins the stream.

$$6 \times 10^3 \times 3600 \times 3 \times 10^{-5} + 666.67 \times 10^3 x = (21600 + 666.67) \times 10^3 \times 5 \times 10^{-3}$$

Solving this we get $x = 0.1660$. Hence, the BOD of the effluents = 0.1660 g/L.

EXAMPLE 9.4 In the azeotropic distillation of an ethanol–water solution, a feed mixture containing 95.6% alcohol is mixed with pure benzene and distilled. The benzene forms a ternary azeotrope with alcohol–water with a composition of 74.1% benzene, 7.4% water and 18.5% alcohol, which is distilled over as the overhead product. Absolute alcohol is obtained as the residue product. Determine the quantity of benzene required for producing 100 kg of absolute alcohol.

Solution Let us first try to solve this problem by the direct and most obvious method, i.e. by taking a basis of 100 kg of absolute alcohol product.

Basis: 100 kg of absolute alcohol

Let the feed be F kg of the mixture of 95.6% alcohol and pure benzene. The overhead product is D kg and the bottom is W kg. Here W = 100 kg. Let the weight fractions of alcohol, water and benzene in the feed be respectively $w_{F,a}$, $w_{F,w}$ and $w_{F,b}$.

We can now formulate the balance equations. The overall material balance is

$$F = D + W \quad \Rightarrow \quad F = D + 100 \tag{A}$$

Alcohol balance:

$$Fw_{F,a} = 0.185D + W \quad \Rightarrow \quad Fw_{F,a} = 0.185D + 100 \tag{B}$$

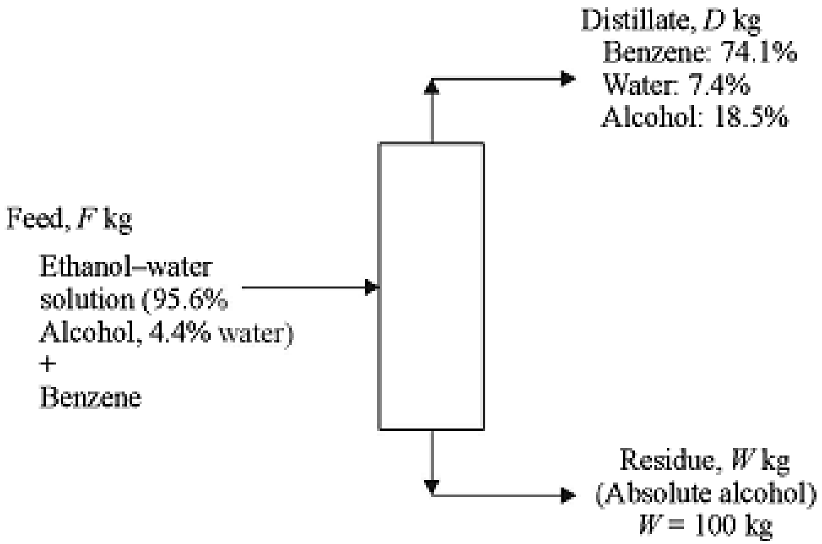


Figure 9.7 Distillation (Example 9.4).

Water balance:

$$Fw_{F,w} = 0.074D \tag{C}$$

Benzene balance:

$$Fw_{F,b} = 0.741D \tag{D}$$

Since the sum of the weight fractions is unity, we have

$$w_{F,a} + w_{F,w} + w_{F,b} = 1 \tag{E}$$

Examination of Eqs. (A) through (E) reveals that not all of them are independent. Combining together Eqs. (B) through (E) gives Eq. (A). Thus we have only four independent equations—Eqs. (B) through (E)—in five unknown quantities. Since the feed is formed from 95.6% alcohol, the weight fractions $w_{F,a}$ and $w_{F,w}$ are related as

$$\frac{w_{F,a}}{w_{F,w}} = \frac{95.6}{4.4} = 21.7273 \quad \Rightarrow \quad w_{F,a} = 21.7273w_{F,w} \tag{F}$$

Since the weight fractions of alcohol and water in the feed are interrelated as given by Eq. (F), the number of independent variables to be determined reduces to four. These four variables can be determined by the solution of the four equations. Combining Eqs. (B), (C) and (F), we get $D = 70.28$ kg. Using this in Eq. (D), the amount of benzene in the feed = $Fw_{F,b}$ = 52.08 kg.

The problem can be solved more easily by taking a basis of 100 kg of distillate.

Basis: 100 kg of overhead product

D = 100 kg. Choose water as the key component. Let x be the weight of 95.6% alcohol in the feed. Then, water balance gives

$$\frac{4.4}{100}x = 7.4 \quad \Rightarrow \quad x = 168.1818 \text{ kg}$$

The amount of absolute alcohol is obtained from alcohol balance.

$$168.1818 \times 0.956 = 18.5 + W$$

$$W = 168.1818 \times 0.956 - 18.5 = 142.28 \text{ kg}$$

When 142.28 kg of absolute alcohol is produced, benzene used is 74.1 kg. Therefore, for 100 kg of absolute alcohol, benzene required is

$$\left(\frac{74.1}{142.28}\right)100 = 52.08 \text{ kg}$$

9.1.7 Steps for Solving Material Balance Problems

We can summarize the various points we made above into the following step-by-step procedure for the solution of material balance problems.

1. Read the entire problem carefully.
2. Draw a sketch of the equipment/unit.
3. Label the flow of each stream and associated composition with symbols.
4. List all the available data on composition and stream flows in the picture. Calculate additional compositions from the given data as necessary.
5. Establish the key component or tie element.
6. Select a suitable basis for calculation.
7. With the chosen basis, write the overall material balance and the individual balances for the components.
8. Before attempting to solve, check whether the number of unknowns and the number of equations formulated are equal. The number of unknown quantities cannot exceed the number of independent material balance equations. Otherwise, the problem is indeterminate. If the number of independent equations exceeds the number of unknown quantities, the choice of the equations to be used for solving the problem is left to your judgement.
9. Solve the equations.
10. Check the answers by substituting them, or at least some of them into the material balances.

EXAMPLE 9.5 1000 kg of mixed acid of composition 40% H_2SO_4, 45% HNO_3 and 15% H_2O is to be produced by strengthening waste acid of composition 30% H_2SO_4, 36% HNO_3 and 34% H_2O by weight. Concentrated sulphuric acid of strength 95% and concentrated nitric acid containing 80% acid are available for this purpose. How many kilograms of spent acid and concentrated acids are to be mixed together?

Solution Let W kg of waste acid, S kg of concentrated sulphuric acid and N kg of concentrated nitric acid are mixed together to produce M kg of mixed acid. The streams in quantities and compositions are indicated in Figure 9.8.

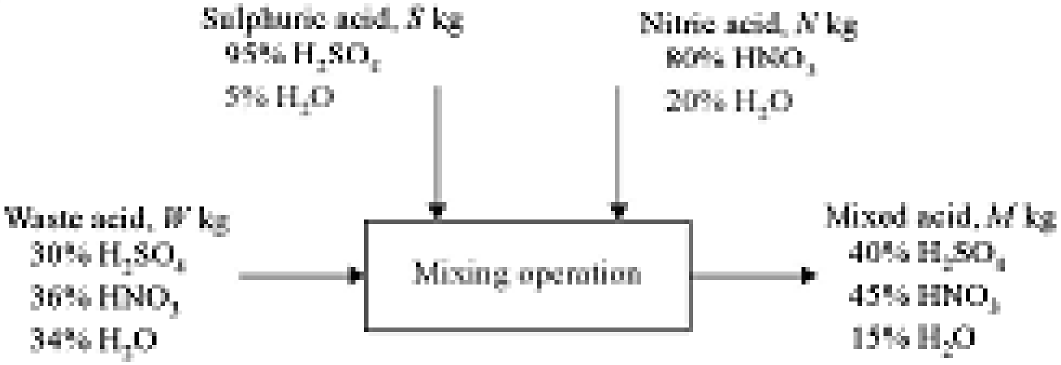


Figure 9.8 Fortification of waste acid (Example 9.5).

Basis: 1000 kg of mixed acid. $M = 1000$ kg.

We can write four material balance equations—one total material balance, three component balances, one each for H_2SO_4, HNO_3 and H_2O.

Total material balance:

$$W + S + N = 1000 \tag{A}$$

H_2SO_4 balance:

$$0.3W + 0.95S = 0.4 \times 1000 \tag{B}$$

HNO_3 balance:

$$0.36W + 0.8N = 0.45 \times 1000 \tag{C}$$

H_2O balance:

$$0.34W = 0.05S + 0.20N = 0.15 \times 1000 \tag{D}$$

There are only three independent material balance equations as Eq. (D) can be obtained by adding together Eqs. (B) and (C) and subtracting the sum from Eq. (A). The number of unknown quantities is three. They are W, S and N. Equations (A), (B) and (C) are solved simultaneously to determine the quantities W, S and N. We get $W = 70.22$ kg, $S = 398.88$ kg, $N = 530.90$ kg.

Quantities to be mixed are:

Waste acid = 70.22 kg

Concentrated H_2SO_4 = 398.88 kg

Concentrated HNO_3 = 530.90 kg

9.2.1 Evaporation

Evaporation is used in industries for concentrating aqueous solutions by vaporizing the solvent water and removing it as vapour. Typical industrial applications of evaporation include concentration of cane-sugar juice in a sugar factory, concentration of ammonium sulphate in a fertilizer unit, and concentration of spent soap *lye* to produce glycerine in a soap industry. Depending upon the mode of providing heat energy to the liquid being concentrated, evaporators fall into different types. Evaporators heated by direct fire, evaporators with heating medium in jackets and steam heated tubular evaporators are common in industries. Among the tubular evaporators, short-tube vertical evaporators, long-tube evaporators, climbing film and falling film evaporators, etc. are some industrially important ones in use. A schematic sketch of a standard short-tube evaporator is shown in Figure 9.9.

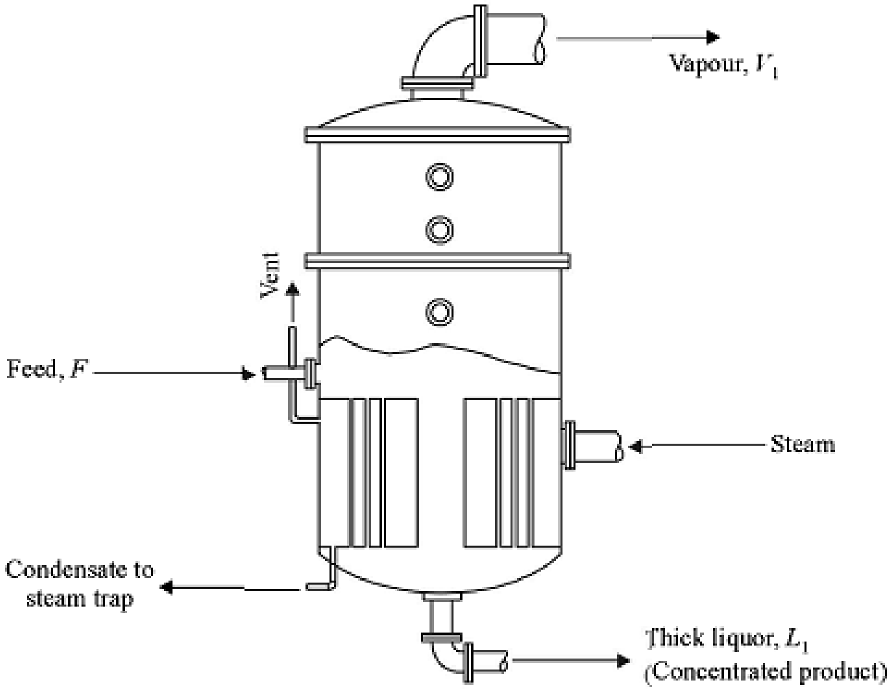


Figure 9.9 Schematic sketch of a short-tube vertical evaporator.

The feed solution is admitted as shown. The solution flows up through the inside of the tubes and is heated by steam condensing in the steam chest, outside the tubes. The heat liberated by the condensing steam is transferred through the tubes to the liquid. The vapour space of the evaporator is maintained at a lower pressure. When the temperature of the liquid reaches the boiling point of the solution at this reduced pressure, the liquid boils. The vapour generated is taken out through the vapour outlet which is condensed and discarded. The concentrated solution known as *thick liquor* is withdrawn as product from the bottom of the evaporator.

Let F be the feed rate in kg/h and x_F be the mass fraction of the solute in the feed. Let the thick liquor be withdrawn at a rate of L_1 kg/h and the concentration of the solute in the final product be x_1. Let V_1 be the quantity of vapour produced in kg/h. The overall material balance can be written as

$$F = V_1 + L_1$$

Since the vapour produced is free of solute, the solute balance gives

$$Fx_F = L_1x_1$$

Simultaneous solution of these two equations provide answer to the material balance problems on single-effect evaporators.

In a single-effect evaporator, with one kilogram of steam condensing in the steam chest, roughly only one kilogram of vapour is produced. The cost of steam consumption is therefore the major cost of operation of the evaporator unit. To reduce the steam consumption, several evaporators can be connected in series to form a multiple-effect evaporator system. The vapour produced in the first effect is used as the heating medium in the second effect and the vapour from the second is the heating medium for the third and so on. Thus by one kilogram of steam condensing in the first effect, approximately N kilograms of vapour can be produced, where N is the number of effects provided. A triple-effect forward-feed evaporator is shown in Figure 9.10.

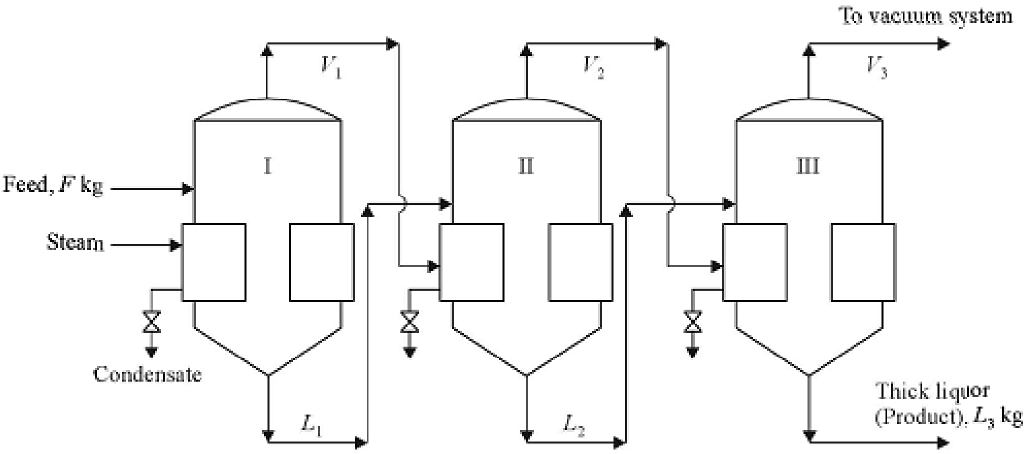


Figure 9.10 Forward-feed triple effect evaporator.

The overall material balance for a triple-effect evaporator is

$$F = V_1 + V_2 + V_3 + L_3$$

where V_1, V_2, and V_3 are the amounts of vapour produced in the first, second and third effect respectively, in kg/h, and L_3 is the product rate in kg/h. Let x_1, x_2, and x_3 be the concentration of the liquid leaving each effect. The solute balance for the combined system is

$$Fx_F = L_3x_3$$

The following solute balance equations can be written for each effect.

$$Fx_F = L_1x_1$$

$$L_1x_1 = L_2x_2$$

$$L_2x_2 = L_3x_3$$

The total material balance for individual effects are

$$F = V_1 + L_1$$
$$L_1 = V_2 + L_2$$
$$L_2 = V_3 + L_3$$

EXAMPLE 9.6 A triple effect evaporator (Figure 9.11) is used to concentrate 1000 kg of aqueous solution from a concentration of 20% solute to 80% solute. Assuming an equal amount of vaporization in each effect, calculate the composition and weight of the solution entering the second and third effects.

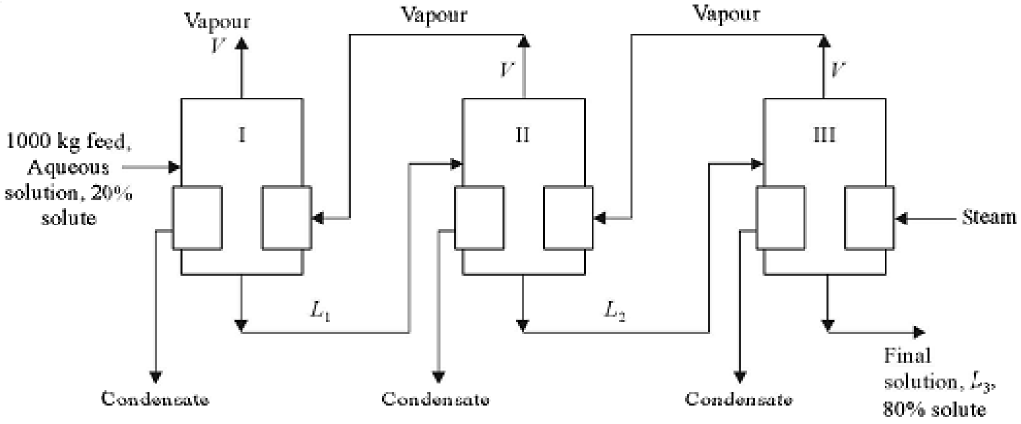


Figure 9.11 Triple effect evaporator for Example 9.6.

Solution *Basis:* 1000 kg feed to the first effect

Let L_1, L_2 and L_3 be the rate at which the concentrated solution is leaving each effect, x_1, x_2 and x_3 respectively be the concentrations of solute in these effects. Let V be the amount of vapour produced in each effect. Consider the combined system consisting of all the three effects. The total material balance yields

$$1000 = 3V + L_3 \tag{A}$$

The solute balance is

$$1000 \times 0.2 = L_3x_3$$
$$200 = 0.8L_3 \tag{B}$$

Solving Eqs. (A) and (B), we get $L_3 = 250$ kg and $V = 250$ kg.

Now we can write the material balance equation for the first effect.

Total balance:

$$1000 = L_1 + V = L_1 + 250 \tag{C}$$

Solute balance:

$$1000 \times 0.2 = L_1x_1 \tag{D}$$

From Eq. (C), $L_1 = 750$ kg. Substituting this in Eq. (D), we get $x_1 = 0.2667$.

For the second effect, the corresponding equations are

$$L_1 = L_2 + V \quad \Rightarrow \quad 750 = L_2 + 250 \qquad \text{(E)}$$

$$L_1x_1 = L_2x_2 \quad \Rightarrow \quad 750 \times 0.2667 = L_2x_2 \qquad \text{(F)}$$

From Eqs. (E) and (F), we get $L_2 = 500$ kg and $x_2 = 0.4$.

The results of material balance calculation for the triple-effect evaporator system are summarized as follows:

Effect	*Feed* (kg)	*Products* (kg)		*Liquid concentration* (%)	
		Liquid	*Vapour*	*Feed*	*product*
I	1000	750	250	20	26.67
II	750	500	250	26.67	40
III	500	250	250	40	80

9.2.2 Crystallization

Crystallization is the process in which solid particles are formed from liquid solution by evaporating and/or cooling of a saturated solution. Crystallization is important as a separation and purification technique as well as a means of marketing materials in crystalline form. Tank crystallizers, agitated batch crystallizers, Swenson–Walker crystallizer, vacuum crystallizers and Krystal crystallizers are typical industrial equipment used for crystallization. Figure 9.12 shows a crystallizer of the circulating liquid type. The liquid is drawn through the tubes of a steam

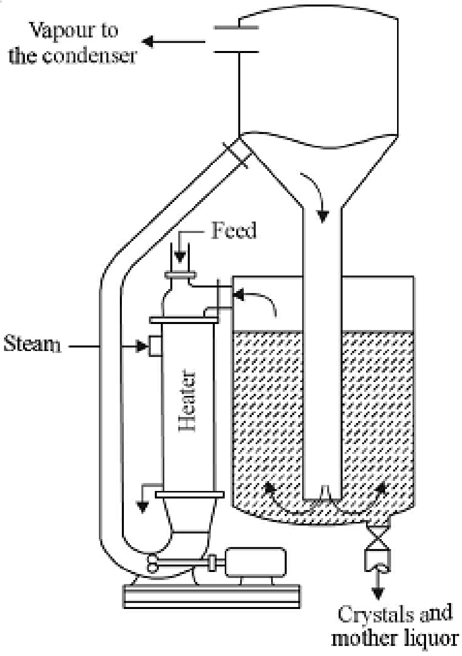


Figure 9.12 Evaporator crystallizer.

heated exchanger where it is heated to sufficiently high temperatures without evaporation. The heated liquid then flows into the vapour space where flash evaporation occurs leading to the supersaturation of the solution. The supersaturated liquid is made to flow down through the downcomer and then up through the bed of crystals which grows in size. The saturated liquid leaving the bed joins the fresh feed solution before entering the heater.

Crystallization occurs when the solution is concentrated and usually cooled until the solute concentration becomes greater than its solubility at that temperature. Equilibrium is said to be attained when the solution is saturated.

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

Let W_1 kg of hydrated crystals are formed in which the weight fraction of solute is x_1 from F kg of solution containing x_F weight fraction of solute. Let x_2 be the solubility of the solute in weight fraction of solute, and W_2 and W_3 be the weights of mother liquor remaining after crystallization and the weight of water evaporated during crystallization operation (see Figure 9.13), respectively.

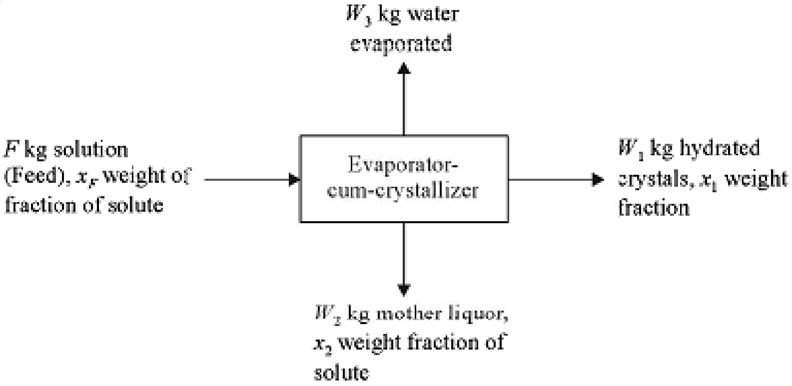


Figure 9.13 Crystallization operation.

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

Total balance:

$$F = W_1 + W_2 + W_3$$

Solute balance:

$$Fx_F = W_1x_1 + W_2x_2$$

Solvent balance:

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

EXAMPLE 9.7 A crystallizer is charged with 100 kg of a solution containing 25% $Ba(NO_3)_2$ in water. On cooling 10% of the original water present evaporates. Calculate the yield of crystals when the solution is cooled to 283 K. The solubility at 283 K is 7.0 kg $Ba(NO_3)_2$/100 kg total water.

Solution *Basis:* 100 kg of feed solution

Let W_1 be the weight of crystals, F the weight of feed, and x_F weight fraction of solute in the feed. Let x_2 be the solubility of the solute in weight fraction of solute, and W_2 and W_3 be the weights of mother liquor remaining after crystallisation and the weight of water evaporated during crystallization operation (see Figure 9.14).

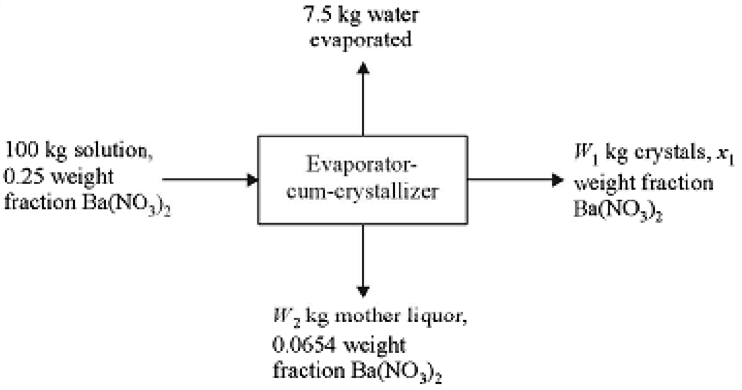


Figure 9.14 Crystallization operation in Example 9.7.

$$F = 100 \text{ kg}, \quad x_F = 0.25, \quad x_2 = 7/107 = 0.0654, \; W_3 = 0.75 \times 100 \times 0.1 = 7.5 \text{ kg}$$

Total material balance

$$F = W_1 + W_2 + W_3$$

That is,

$$100 = W_1 + W_2 + 7.5 \quad \Rightarrow \quad W_1 + W_2 = 92.5 \tag{A}$$

Solute balance

$$Fx_F = W_1x_1 + W_2 x_2$$

$$100 \times 0.25 = W_1 \times 1.0 + W_2 \times 0.0654 \quad \Rightarrow \quad W_1 + 0.0654W_2 = 25 \tag{B}$$

Solving Eqs. (A) and (B) simultaneously, we get $W_1 = 20.28$ kg.

EXAMPLE 9.8 An aqueous solution of Na_2CO_3 contains 15% carbonate by weight. 80% of the carbonate is recovered as $Na_2CO_3 \cdot 10H_2O$ by evaporation of water and subsequent cooling to 278 K. The solubility of Na_2CO_3 at 278 K is 9.0% (weight). On the basis of 100 kg of solution treated, determine the following:

(a) The quantity of crystals formed
(b) The amount of water evaporated

Solution *Basis:* 100 kg solution treated

See Figure 9.13. Let W_1 be the weight of hydrated crystals, x_1 the weight fraction of Na_2CO_3 in the crystals, F the weight of feed and x_F the weight fraction of Na_2CO_3 in the feed. Let x_2 be the solubility of Na_2CO_3 in weight fraction Na_2CO_3, and W_2 and W_3 be the weights of mother liquor remaining after crystallization and the weight of water evaporated during crystallization operation.

Total material balance:

$$F = W_1 + W_2 + W_3 \tag{A}$$

Na_2CO_3 balance:

$$Fx_F = W_1x_1 + W_2x_2 \tag{B}$$

Here F = 100 kg, x_F = 0.15, the molecular weight of Na_2CO_3 = 106 and the molecular weight of $Na_2CO_3 \cdot 10H_2O$ = 286.

(a) The weight fraction of Na_2CO_3 in the crystals is

$$x_1 = \frac{106}{286} = 0.3706$$

The mass of Na_2CO_3 recovered in the crystals is

$$W_1x_1 = 0.8Fx_F = 0.8 \times 100 \times 0.15 = 12 \text{ kg}$$

Therefore, the quantity of crystals formed is

$$W_1 = \frac{12}{0.3706} = 32.28 \text{ kg}$$

(b) Substituting the values in Eq. (B), we get,

$$100 \times 0.15 = 12 + W_2x_2$$

The mass of Na_2CO_3 in the mother liquor is

$$W_2x_2 = 15 - 12 = 3 \text{ kg}$$

The weight fraction of Na_2CO_3 in the mother liquor = x_2 = 0.09 (from solubility)

The weight of mother liquor is

$$W_2 = \frac{W_2x_2}{x_2} = \frac{3}{x_2} = \frac{3}{0.09} = \frac{100}{3} \text{ kg}$$

From Eq. (A), we get

$$W_3 = F - (W_1 + W_2)$$

$$= 100 - (32.38 + 33.33) = 34.29 \text{ kg}$$

Hence, the amount of water evaporated = 34.29 kg

EXAMPLE 9.9 An aqueous solution containing 60% $Na_2S_2O_3$ and 1% soluble impurities is diluted with water and fed to a crystallizer where it is cooled in order to crystallize $Na_2S_2O_3 \cdot 5H_2O$. The crystals carry 0.05 kg of solution (excluding impurities) per kg of crystals. The free water present in the adhering solution is removed on drying the crystals. The final dried product contains not more than 0.1% impurity. The solubility of the pentahydrate is 1.5 kg $Na_2S_2O_3{\cdot}5H_2O$/kg free water. On the basis of 100 kg of 60% solution, calculate the following:

(a) The amount of water in kilograms added before cooling
(b) The amount of crystals formed
(c) The percentage recovery of the $Na_2S_2O_3$ in the dried hydrated crystals

Solution *Basis:* 100 kg 60% solution

Refer to Figure 9.15. Let W kg pure water is added to the original solution. W_1, W_2 and W_3 are the weights of $Na_2S_2O_3{\cdot}5H_2O$ crystallized, the mother liquor obtained and the solution carried away by the crystals, respectively. The impurities present in the feed get dissolved in the free water and is present in the products in association with W_2 kg mother liquor and W_3 kg adhering solution. When the crystals are dried, the impurities in the adhering solution gets deposited on the crystals, the concentration of which in the final dried crystals being limited to 0.1%.

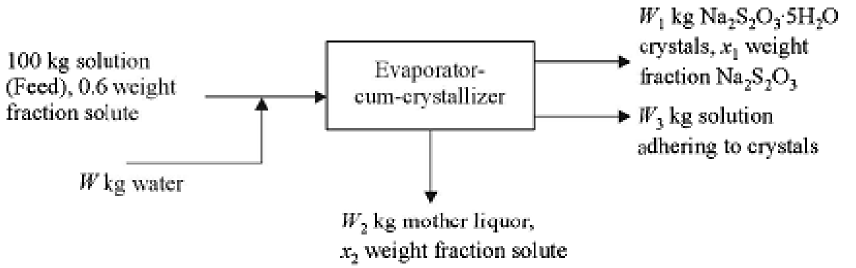


Figure 9.15 Crystallization operation in Example 9.9.

The molecular weight of $Na_2S_2O_3$ = 158 and the molecular weight of $Na_2S_2O_3{\cdot}5H_2O$ = 248. Since no water is lost by evaporation, all the free water present in the combined feed will be present in the mother liquor. 60 kg of anhydrous salt forms $60 \times \dfrac{248}{158} = 94.117$ kg of pentahydrate, the free water present in the system is $100 + W - 1 - 94.177 = W + 4.823$ kg. Therefore, the concentration of impurity in the mother liquor is $x_1 = \dfrac{1}{W + 4.823}$ kg of impurity/kg of free water. Now consider the material balance over the crystallizer.

Total (impurities-free) balance:

$$100 - 1 + W = W_1 + W_2 + W_3$$

That is,

$$W_1 + W_2 + W_3 - W = 99 \qquad \text{(A)}$$

$Na_2S_2O_3$ balance:

$$60 = \left(W_1 + W_2 \times \frac{1.5}{2.5} + W_3 \times \frac{1.5}{2.5}\right) \times \frac{158}{248}$$

which simplifies as

$$W_1 + 0.6W_2 + 0.6W_3 = 94.177 \qquad \text{(B)}$$

Since each kilogram of crystals carry 0.05 kg solution, $W_3 = 0.05W_1$. Substituting this in Eqs. (A) and (B), we get

$$1.05W_1 + W_2 - W = 99 \tag{C}$$

$$1.03W_1 + 0.6W_2 = 94.177 \tag{D}$$

Impurity in the adhering solution is

$$W_3 \times \frac{1}{2.5} \times \frac{1}{W + 4.823}\ \text{kg}$$

Substituting $W_3 = 0.05W_1$, the amount of impurity in the adhering solution is

$$\frac{0.05W_1}{2.5(W + 4.823)}\ \text{kg}$$

However, this should not be more than 0.1% of the final weight of crystals. The final weight of impurity-free crystals is

$$W_1 + W_3\,\frac{1.5}{2.5} = W_1 + 0.05W_1\,\frac{1.5}{2.5} = 1.03W_1$$

Therefore,

$$\frac{\text{weight of impurities in the crystals}}{\text{weight of pure crystals}} = 0.001$$

$$= \frac{0.05W_1/2.5(W + 4.823)}{1.03W_1} = \frac{0.0194}{W + 4.823}$$

Solving the above equation, we get $W = 14.577$ kg. Substituting this in Eq. (C), we get

$$1.05W_1 + W_2 = 113.577 \tag{E}$$

Solving Eqs. (D) and (E), we get $W_1 = 65.08$ kg, $W_2 = 45.25$ kg and, $W_3 = 0.05W_1 = 45.25$ kg

(a) The amount of water added before cooling = 14.58 kg.

(b) The amount of $Na_2S_2O_3{\cdot}5H_2O$ crystals formed = 65.08 kg

(c) $Na_2S_2O_3$ in the adhering solution gets deposited on the crystals on drying. Therefore, total anhydrous $Na_2S_2O_3$ produced

$$W_1 \times \frac{158}{248} + W_3 \times \frac{1.5}{2.5} \times \frac{158}{248} = 42.701\ \text{g}$$

The percentage recovery of $Na_2S_2O_3$ = $\dfrac{42.70}{60} \times 100 = 71.2\%$

9.2.3 Leaching

Leaching is the separation of the components of a solid mixture by selectively dissolving the soluble components of the solid in a liquid solvent. Recovery of minerals from naturally occurring ores, oils from oilseeds, tannin from wood barks, vitamins and pharmaceutical products from plant leaves and roots, sugar from sugar beets, etc. are some of the industrial applications of leaching. A Bollman extractor (Figure 9.16) is a typical industrial unit used for leaching oil from seeds.

Solids are moved in perforated baskets attached to a chain conveyor. As the solids move downwards, solvent (half miscella) moves in parallel flow. The perforations on the basket permit passage of liquid from basket to basket. The strong solution of oil (full miscella) collects at the bottom and is removed. The leaching is completed when the solids move upward countercurrent to the fresh solvent which is admitted at the top as shown in the figure.

Consider a leaching operation such as the recovery of oil from oilseeds by treating with an organic solvent like hexane. Let C be the component that is being transferred from the solid phase to the liquid phase. The inert insoluble components in the feed is denoted as B. A is the solvent used for leaching. In the present example, A is hexane, B is insoluble materials in the feed, and C is oil. The streams entering and leaving a leaching unit are shown in Figure 9.17. After the solute has been transferred into the liquid, the mixture is allowed to settle. On settling, a clear solution known as *overflow* (R) containing the solute C dissolved in the solvent and an *underflow* which is a slurry of leached solids B suspended in the solution (E) that is not removed as overflow are obtained.

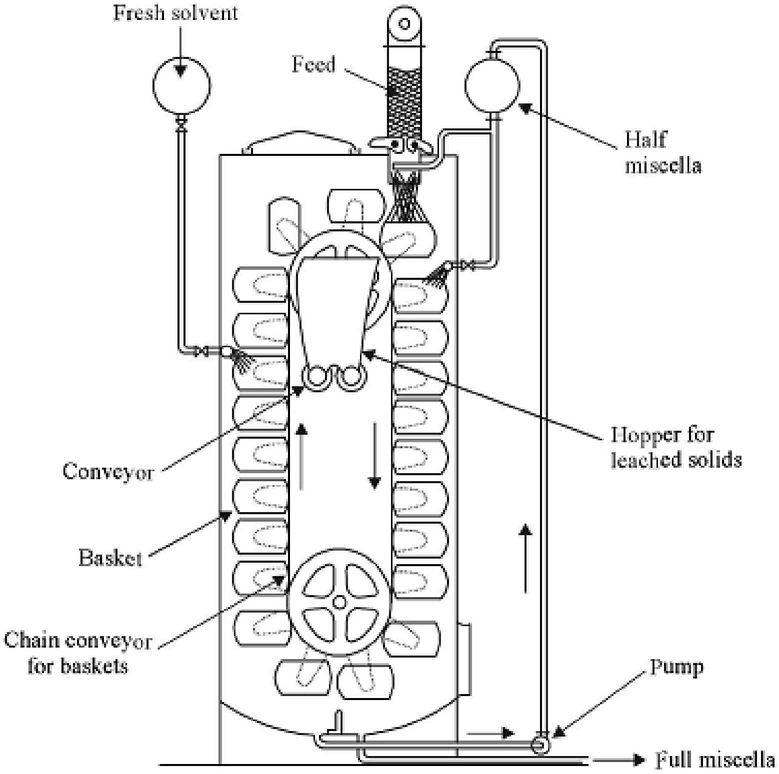


Figure 9.16 Bollman extractor.

Feed is a mixture of B kg inert solids and F kg solute. S is the mass of solvent added. The overflow is R kg solution consisting of A and C. Underflow is B kg inert solids suspended in E kg clear solution. Concentration of inert material in any stream can be represented as weight ratio of B on B-free basis and is denoted by N. Concentration of solute is represented as the weight ratio of solute on B-free basis. x represents solute concentration in overflow solution and y represents solute concentration in underflow solution. Thus, x and y are calculated as the ratio of C to $(A + C)$ in a mixture and N is calculated as the ratio of B to $(A + C)$ in the mixture. For the leaching system shown in Figure 9.17, we can write the inert balance as

$$B = N_F F = NE$$

where N_F and N are the inert concentration in the feed and underflow on an inert-free basis. The solution $(A + C)$ balance can be written as

$$F + S = E + R$$

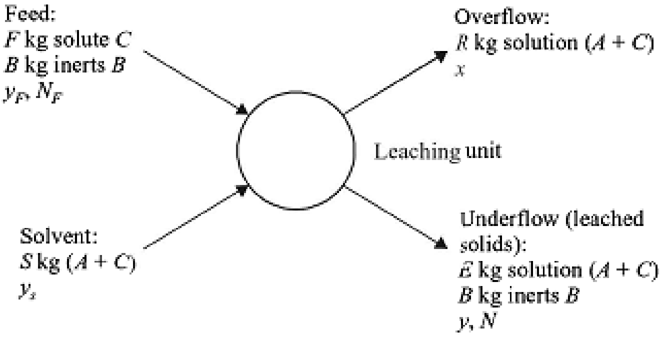


Figure 9.17 Streams in a leaching operation.

The component-C (solute) balance is

$$Fy_F + Sy_S = Ey + Rx$$

EXAMPLE 9.10 A tannery extracts certain wood barks which contains 40% tannin, 5% moisture, 23% soluble non-tannin materials and the rest insoluble lignin. The residue removed from the extraction tanks contain 50% water, 3% tannin and 1% soluble non-tannin materials. What percent of the original tannin remains unextracted?

Solution *Basis:* 100 kg of bark

The feed to the leaching unit contains 100 – 40 – 5 – 23 = 32 kg of lignin. Since lignin is insoluble in the solvent used for leaching, all this will be present in the residue. Therefore, lignin can be treated as the key component for material balance. Let the residue left after the leaching operation be W kg. The weight percent of lignin in the residue = 100 – 50 – 3 – 1 = 46%. Take a balance on the key component lignin:

$$32 = W \times 0.46$$

which gives

$$W = \frac{32}{0.46} = 69.57 \text{ kg}$$

Since the residue contains 3% unextracted tannin, the percentage of the tannin in the bark that is unextracted is

$$\frac{69.57 \times 0.03}{100 \times 0.40} \times 100 = 5.2\% .$$

EXAMPLE 9.11 Oilseeds containing 49% oils, 40% pulp, 3% mineral salts and the rest moisture are leached with hexane as the solvent. The underflow from the leaching operation contains 25% hexane, 2.5% salts, 15% oil and 7.5% moisture. The overflow contains 25% oil which is distilled to recover the entire hexane in pure form leaving behind the oil, water and salt. The underflow is subjected to steam distillation which recovers 95% hexane. For treating 100 kg seeds, calculate the following:

(a) The kilograms of hexane used
(b) The percent of hexane used that is recovered from the underflow
(c) Percent recovery of oil

Solution *Basis:* 100 kg oil seeds charged to the leaching unit

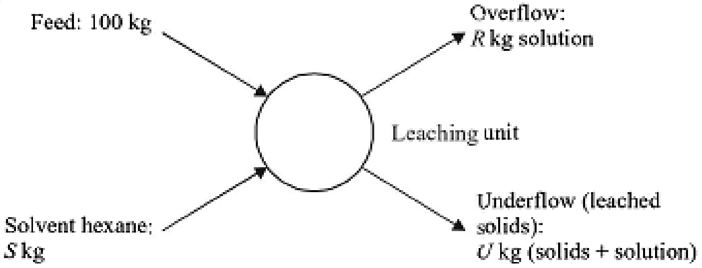


Figure 9.18 Streams in a leaching operation.

See Figure 9.18. Let S be the kilograms of hexane used for leaching. The underflow from the operation contains all the insoluble pulp present in the feed in addition to the unextracted oil, salt and moisture. Hexane dissolves some oil, salt and moisture. A portion of this solution is adhering with the insoluble solids in the underflow and let U be the combined weight of the underflow solids and solution adhering to it. The other portion forms the clear solution (R).

(a) Total balance:

$$100 + S = U + R \tag{A}$$

The feed contains 49 kg of oil, oil concentration in the underflow is 15% and that in the overflow is 25%. Hence, the oil balance:

$$49 = U \times 0.15 + R \times 0.25 \tag{B}$$

The feed contains 40 kg of pulp. The percentage of pulp in the underflow is 100 − 25 − 15 − 2.5 − 7.5 = 50%. Therefore, the inert balance:

$$40 = 0.5U \tag{C}$$

The insoluble pulp is the tie element in this problem as it is entering in a single stream and leaves as a single stream. The inert balance [Eq. (C)] gives

$$U = 80 \text{ kg}$$

Substituting $U = 80$ kg in Eq. (B), we get

$$R = 148 \text{ kg}$$

Substituting U and R in Eq. (A), we get $S = 128$ kg. Thus the amount of solvent used for extraction = 128 kg.

(b) The hexane in the underflow = $0.25U = 20$ kg. The amount of hexane recovered by steam distillation is $0.95 \times 20 = 19$ kg. This constitutes only

$$\frac{19}{128} \times 100 = 14.84\%$$

(c) Oil recovered in the clear solution is

$$\frac{37}{49} \times 100 = 75.51\%$$

9.2.4 Adsorption

Components of a gas or liquid mixture can be adsorbed on the surface of a solid adsorbent. Two types of adsorption phenomena exist: *physical adsorption* occurring due to the intermolecular forces and *chemisorption* occurring due to the chemical interaction between the solid and the fluid. Physical adsorption is utilized as a separation method. The solid used for adsorption is known as *adsorbent*, and the fluid adsorbed on the surface is the *adsorbate*. The adsorption of organic vapours on activated charcoal, decolourization of cane-sugar solution by adsorbing the colouring matter on activated carbon, drying of gases by adsorbing water on silica gel, etc. are examples to cite a few. The adsorbed constituent can be removed from the solid and thereby separation can be completed and the adsorbent regenerated for further use. Fuller's earth, activated clays, activated charcoal, bone char, bauxite, alumina, silica gel, etc. are some important adsorbents. Adsorption of a fluid on the surface of a solid occurs till equilibrium is attained. The adsorption equilibrium is a relationship between the concentration of solute in the fluid and the quantity adsorbed per unit weight of adsorbent. This relationship for a constant temperature is known as *adsorption isotherm*.

9.2.5 Drying

Drying is usually one of the last operations in a process industry. Drying operation is unavoidable and an integral part of the process in industries such as paper industries, whereas it is done in other processes to reduce the cost of transportation of the product, to give some useful properties to the product like the free flowing nature of salt, and to prepare the product in a form that is suitable for handling and use. In drying, a wet solid or slurry is contacted with dry gas (usually air or flue gas) so that water is vaporized from the solid and is carried away by the gas. When the vapour pressure exerted by the moisture in the solid equals the partial pressure of water in the gas exposed to the solid, the solid is said to have attained its *equilibrium moisture content*, and drying stops. Depending upon the characteristics of the solid being dried, several types of driers are in common use. Tray driers (for pasty materials and lumpy solids), rotary driers (for granular and free flowing solids), freeze driers (for foodstuffs and pharmaceuticals) and spray driers (for slurries and pastes) are typical driers in use. The continuous driers are smaller in size in relation to the quantity being dried, and the dried product has a uniform moisture content. A rotary continuous drier is shown in Figure 9.19 and a general flow diagram is shown in Figure 9.20.

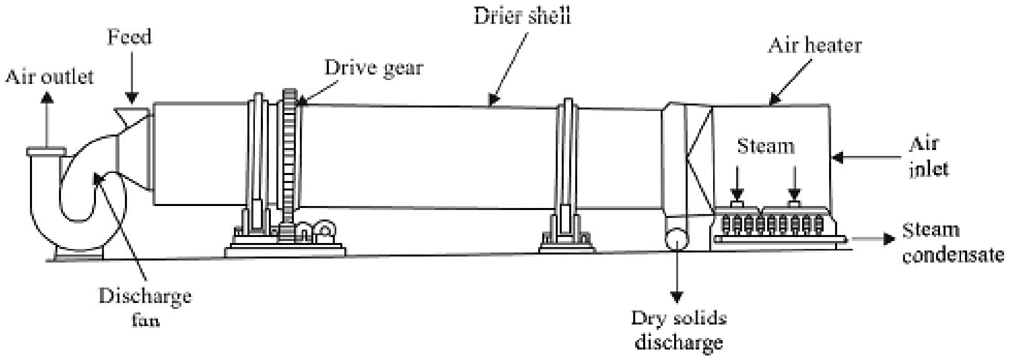


Figure 9.19 Counter-current direct heated rotary drier.

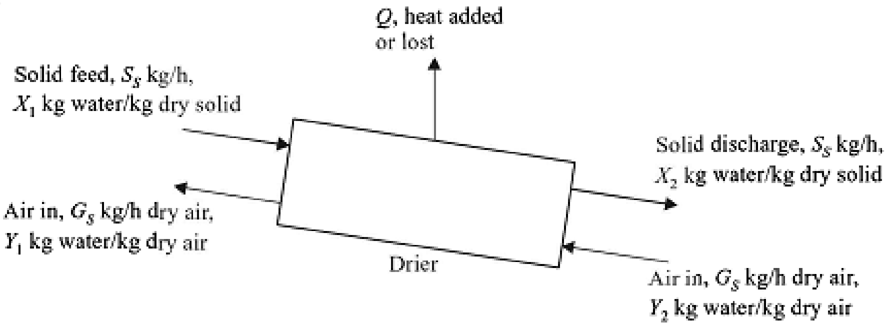


Figure 9.20 Continuous counter-current drying.

The drier is a long cylinder installed at a slight inclination with the floor to facilitate the free flow of the material to be dried that is introduced at one end. The cylinder is made to rotate at a very low speed. The drying gas, which may be hot air or dry flue gas is admitted at the other end, flows counter current to the solid, the gas being pulled through the drier by means of exhaust fans.

Let S_S kg/h be the mass flow rate of dry solid in the wet material admitted to the drier and let it be dried from an initial moisture content of X_1 to a final moisture content of X_2, the moisture content being expressed as kilograms of moisture per kilogram of dry solid. The gas flow rate is G_S kilograms of dry gas per hour and it receives the moisture evaporated from the solid. The humidity of the gas stream increases from Y_2 to Y_1 kg moisture per kilogram of dry gas. A moisture balance on the drier yields

$$S_S(X_1 - X_2) = G_S(Y_1 - Y_2)$$

EXAMPLE 9.12 A drier is fed with wet solid to reduce the moisture content from 80% to 15%. The product leaving the drier is admitted into an oven which further brings down the moisture to 2%. If the drier can handle 1000 kg of wet solid per day, calculate

(a) The weight of products leaving the drier and the oven per day
(b) The percentage of the original water that is removed in the drier and the oven

Solution *Basis:* 1000 kg of wet solid admitted to the drier

Let V_1 kg and V_2 kg be the amount of water removed in the drier and the oven respectively. Let x_1 and x_2 be the weight fraction of moisture in the solid leaving the drier and the oven respectively. Let F be the amount of wet material fed to the drier and x_F be the moisture content in the feed. The total material balance for the drier is

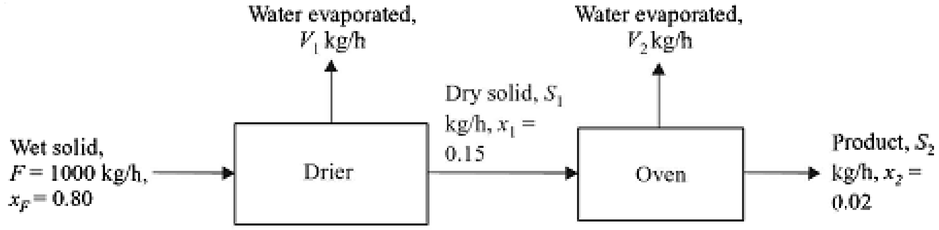


Figure 9.21 Drying operation in Example 9.12.

$$F = S_1 + V_1 \tag{A}$$

The corresponding moisture-free solid balance is

$$F(1 - x_F) = S_1(1 - x_1) \tag{B}$$

Similarly for the oven we can write

$$S_1 = S_2 + V_2 \tag{C}$$

$$S_1(1 - x_1) = S_2(1 - x_2) \tag{D}$$

Here, $F = 1000$ kg, $x_F = 0.80$, $x_1 = 0.15$ and $x_2 = 0.02$. Equations (B) and (D) are balances for the tie element—moisture free solid—and substituting the given values, they give $S_1 = 235.29$ kg and $S_2 = 204.08$ kg.

Substituting the value of S_1 in Eq. (A), we get $V_1 = 764.71$ kg.

Substituting the values of S_1 and S_2 in Eq. (C), we get $V_2 = 31.21$ kg.

(a) The weight of products leaving the drier = $S_1 = 235.29$ kg.
The weight of products leaving the oven = $S_2 = 204.08$ kg.

(b) The percentage of original water that is removed in the drier is

$$\frac{V_1}{Fx_F} \times 100 = \frac{764.71}{800} \times 100 = 95.6\%$$

The percentage of original water that is removed in the oven is

$$\frac{V_2}{Fx_F} \times 100 = \frac{31.21}{800} \times 100 = 3.90\%$$

EXAMPLE 9.13 Air at 101.3 kPa enters an adiabatic drier at 87.5°C with a dew point of 20°C and leaves at 70% humidity. Wet paper enters the drier with 25% moisture and leaves with 5% moisture. Determine the following:

(a) Water evaporated in kilograms per 100 cubic metres of air entering
(b) Finished product in kilograms per 100 cubic metres of air entering.

Solution The operation is schematically represented as shown in Figure 9.22.

The drying air enters with a dry-bulb temperature of 87.5°C and a dew point of 20°C. From the humidity charts for the air–water system at 101.3 kPa, we can see that these conditions correspond to a humidity of 0.015 kg water/kg dry air (Y_2). In an adiabatic drier, air absorbs moisture from the wet solid, and the humidity and temperature of the air change along the adiabatic cooling line passing through the point on the psychrometric chart that represents the condition of the inlet air. By moving along the adiabatic cooling line to 70% saturation, we see that the final humidity of the drying air (Y_1) is 0.035 kg water/kg dry air.

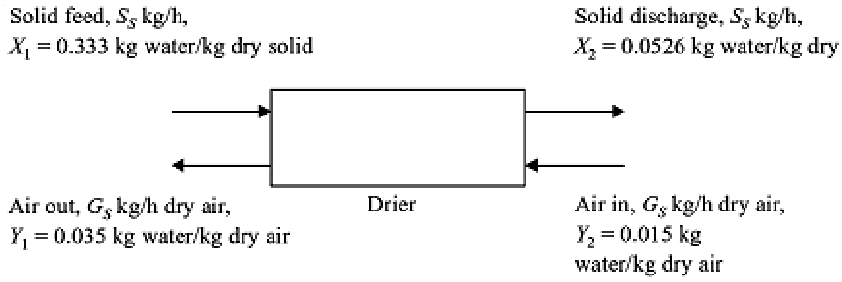


Figure 9.22 Drying in Example 9.13.

Since the amount of dry solid present in the product stream remains the same as that in the feed stream, and the amount of dry air present in the gas stream also remains constant, it is better to do the material balance on a dry basis. Let S_S kg/h be the mass flow rate of dry solid in the wet material admitted to the drier and it is dried from an initial moisture content of X_1 to a final moisture content of X_2 on a dry basis.

$$X_1 = \frac{25}{75} = 0.333 \text{ kg water/kg dry solid}$$

$$X_2 = \frac{5}{95} = 0.0526 \text{ kg water/kg dry solid}$$

Basis: 1 kg of dry air passed through the drier

The moisture balance for the drier is

$$S_S X_1 + Y_2 = S_S X_2 + Y_1$$

$$S_S (X_1 - X_2) = Y_1 - Y_2 \quad \Rightarrow \quad S_S = \frac{Y_1 - Y_2}{X_1 - X_2}$$

$$= \frac{0.035 - 0.015}{0.333 - 0.0526} = 0.0713 \text{ kg of dry solid}$$

That is, with 1 kg of dry air and accompanying water, the moisture associated with 0.0713 kg of dry solid can be reduced by the desired extent.

(a) 100 m^3 air enters the drier at 101.3 kPa and 87.5°C (360.65 K).
Moles of wet air entering the drier is

$$\frac{100}{22.414} \times \frac{101.3}{101.325} \times \frac{273.15}{360.65} = 3.3782 \text{ kmol}$$

Moisture content in the air admitted = 0.015 kg water/kg dry air, i.e.

$$\frac{0.015}{1} \times \frac{29}{18} = 0.0242 \text{ kmol water/kmol dry air}$$

Moles of dry air present in 100 m^3 of air admitted is

$$3.3782 \times \frac{1}{1 + 0.0242} = 3.2984 \text{ kmol}$$

Mass of dry air is $3.2984 \times 29 = 95.65$ kg

Since the moisture content of the air increases from 0.015 kg water/kg dry air to 0.035 kg water per kg dry air, the total moisture evaporated is

$$95.65(0.035 - 0.015) = 1.913 \text{ kg}$$

(b) Since 1 kg of dry air is needed for treating 0.0713 kg of dry solids, 95.65 kg of dry air can treat $0.0713 \times 95.65 = 6.82$ kg of dry solid. Since the product contains 0.0526 kg of moisture per kg of dry solid, the quantity of finished product is

$$6.82 \times \frac{1.0526}{1} = 7.18 \text{ kg}$$

9.2.6 Liquid–Liquid Extraction

The process of separation of the components of a liquid mixture by treating with an immiscible liquid solvent in which the constituents are differently soluble is known as *liquid–liquid extraction*. The liquid–liquid extraction operation involves bringing the feed liquid in intimate contact with an immiscible or partially miscible solvent, allowing the solute to get distributed between the phases and finally allowing the phases to separate from each other. The resulting solvent-rich phase is called the *extract* and the residual solution from which the solute is extracted is known as the *raffinate*. The mutually insoluble extract and raffinate phases are then separated from one another by settling and gravity separation. For example, aqueous acetic acid solution is mixed with isopropyl ether solvent in order to extract the acid into the ether phase. A single-stage extraction operation may be represented as shown in Figure 9.23.

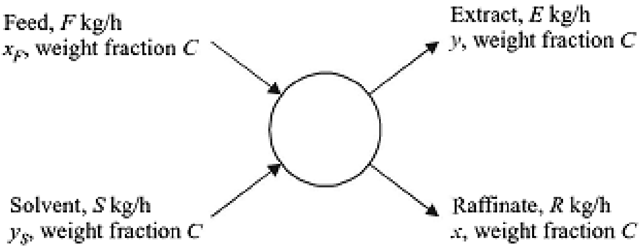


Figure 9.23 Extraction operation.

Consider a simple case in liquid–liquid extraction in which solute C to be extracted is present in the feed in association with solvent A. A solvent B is used for extraction of C from the feed. B is either insoluble in A or is partially miscible with A. When the solvent is contacted with the feed, the solute gets transferred to the solvent. The products leaving the extraction unit are an A-rich phase known as raffinate and a B-rich phase known as extract. The solute C will be present in the raffinate and extract phases. If A and B are partially miscible, traces of B will be present in the raffinate and traces of A will be present in the extract. In a most general extraction operation, therefore, we have to deal with ternary mixtures as raffinate and extract phases. Denoting the weight fraction of solute in the raffinate and extract phases by x and y respectively, that in the feed and solvent by x_F and y_S respectively, and the mass flow rates of feed, solvent, raffinate and extract phases by F, S, R and E respectively, the total material balance and component-C balance can be written as

$$F + S = E + R$$

$$Fx_F + Sy_S = Ey + Rx$$

Gravity settlers, mixer-settler cascades, sieve-tray columns, packed columns, spray towers, rotating-disk contactors, etc. are the common types of extraction equipment. Figure 9.24 shows a rotating-disk extractor schematically.

For good mass transfer rates, one liquid should be thoroughly dispersed in the other and the liquid dispersion is facilitated in rotating-disk contactors by mechanical means. The mechanical agitation is provided by high-speed rotating disks.

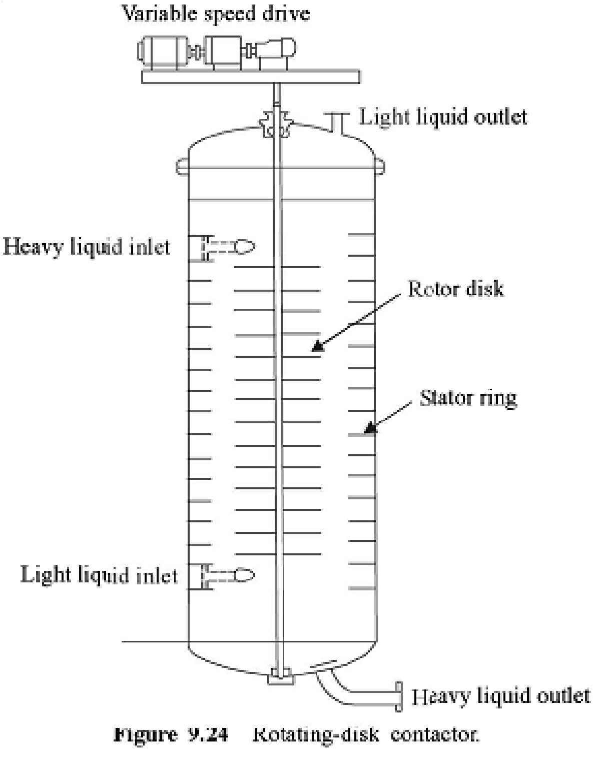


Figure 9.24 Rotating-disk contactor.

EXAMPLE 9.14 Isopropyl alcohol and water can be separated by extraction with ethylene tetrachloride (C_2Cl_4). 100 kg of a solution containing 30% (weight) isopropyl alcohol and the rest water is mixed with the solvent ethylene tetrachloride. After extraction, the raffinate phase analyzed 71% water, 28.1% isopropyl alcohol and 0.9% ethylene tetrachloride. The extract phase analyzed 94% ethylene tetrachloride, 5.2% isopropyl alcohol and the rest water. Calculate the following:

(a) The amount of solvent
(b) The quantities of raffinate and extract phases
(c) The percent extraction of isopropyl alcohol

Solution *Basis:* 100 kg of feed

The extraction operation is schematically represented in Figure 9.25.

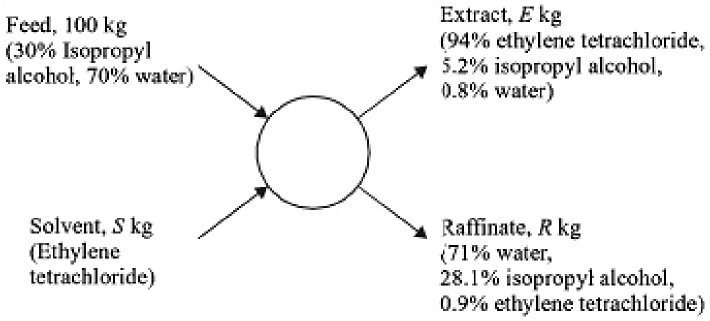


Figure 9.25 Extraction operation in Example 9.14.

Let R kg be the amount of raffinate (water-rich phase) and E kg be the amount of extract (solvent-rich phase). Let x_A, x_B and x_C be the weight fractions of water, ethylene tetrachloride and isopropyl alcohol, respectively, in the raffinate. Let y_A, y_B and y_C the corresponding values in the extract. Let S be the amount of solvent used.

Total balance:

$$R + E = 100 + S \tag{A}$$

Isopropyl alcohol balance:

$$0.281R + 0.052E = 30 \tag{B}$$

Ethylene tetrachloride balance:

$$0.009R + 0.94E = S \tag{C}$$

Simultaneous solution of the above equations gives $S = 45.10$, $E = 47.04$ and $R = 98.06$.

(a) The amount of solvent used = S = 45.10 kg.
(b) The amount of extract = 47.04 kg; the amount of raffinate = 98.06 kg.
(c) The amount of isopropyl alcohol extracted is

$$Ey_c = 47.04 \times 0.052 = 2.45 \text{ kg}$$

The percent extraction of isopropyl alcohol is

$$\frac{2.45}{30} \times 100 = 8.17\%$$

9.2.7 Absorption

In absorption, soluble constituents of a gas mixture are separated by absorbing in a suitable liquid solvent. The reverse process—the removal of certain constituents of a liquid mixture by contacting with a gas phase—is known as *desorption* or *stripping*. Ammonia is absorbed from a mixture of ammonia and air by contacting the gas with water in equipment known as *absorption columns*. Benzene vapours present in coke-oven gases can be absorbed in hydrocarbon oils and hydrogen sulphide can be absorbed from gas mixtures using ethanolamine solutions. The essential difference between absorption and distillation is that in absorption, the liquid phase used for effecting separation is a foreign substance introduced as a solvent whereas in distillation, the vapour and liquid phases are produced from the feed material by boiling.

The rate at which a gaseous constituent of a mixture is absorbed in a liquid depends upon the equilibrium solubility of the gas in the liquid at the given temperature, which in turn depends upon the partial pressure of the gas in the mixture. For example, the equilibrium solubility of ammonia in water is 25% (weight) ammonia for a partial pressure of 30.3 kPa at 293 K and 46.9 kPa at 303 K. Therefore, if a gas mixture with a partial pressure of ammonia greater than 30.3 kPa is in contact with a 25% aqueous ammonia solution at 293 K, ammonia will be absorbed in the liquid.

As absorption is a gas–liquid contact operation like distillation, the equipment for absorption and distillation are similar. Plate towers and packed columns are commonly employed for gas absorption and distillation operations. A packed column for gas absorption is shown in Figure 9.26.

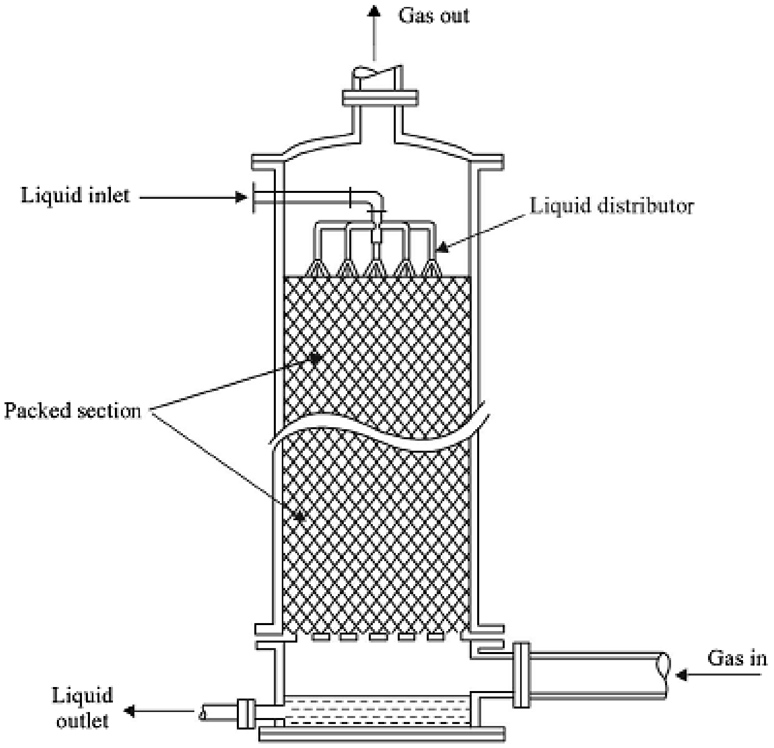


Figure 9.26 Packed bed absorption column.

Packed columns are vertical columns filled with some packing materials. Tower packings are devices of large surfaces, low weight per unit volume, and they provide a large free cross section for flow of fluids. Random packings such as Raschig rings, Lessing rings, Berl saddles, Intalox saddles, etc. and regular packings such as wood grids, stacked Raschig rings, etc. are used for this purpose. The liquid is distributed over and trickles down through the packing. Gas is admitted from the bottom and flows counter-current to the liquid. The gas is in contact with the liquid throughout the column unlike in a plate column where the gas is in contact with the liquid only intermittently. The mass transfer occurs and compositions of the gas and liquid change continuously in a packed column.

Consider absorption of solute A from a gas mixture into a liquid solvent. Let G and L represent the flow rate of the gas and liquid in kmol/h, and x and y the mole fraction of A in the liquid and gas, respectively. The flow rates as well as the concentrations vary throughout the column. The conditions at the bottom of the column are represented by suffix 1 and conditions at the top of the column are indicated by suffix 2. Then the total material balance for the column is

$$G_1 + L_2 = G_2 + L_1$$

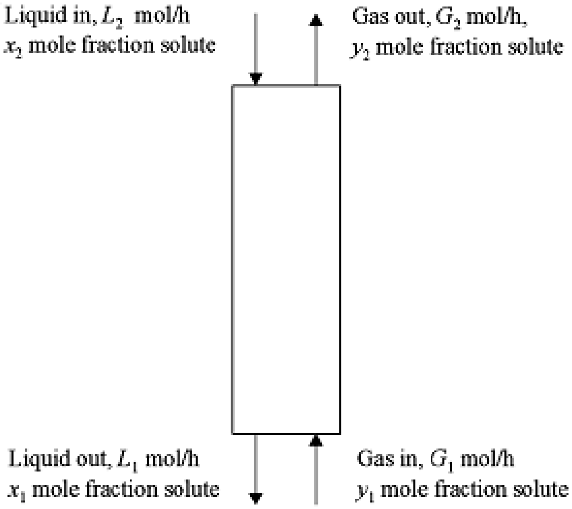


Figure 9.27 Absorption operation.

The solute balance is

$$G_1y_1 + L_2x_2 = G_2y_2 + L_1x_1 \tag{9.7}$$

The material balance can be written in another way if the flow rates and compositions are expressed on a solute-free basis. In an absorption operation though the total flow rate of gas decreases from G_1 to G_2 due to absorption of A, the flow rate of non-diffusing gas is unaltered and let this be G_S kmol/h. Similarly, while the molar flow rate of the liquid phase increases from L_2 to L_1 the flow rate of pure solvent is constant at, say, L_S kmol/h. Let X and Y represent the mole ratio of solute in the liquid and gas respectively. Then

$$X = \frac{\text{moles of } A \text{ in the liquid}}{\text{moles of solvent}} = \frac{x}{1-x}$$

$$Y = \frac{\text{moles of } A \text{ in the gas}}{\text{moles of solute free gas}} = \frac{y}{1-y}$$

The number of moles of solute present in a gas stream can be determined as the product of G_S and Y, and the number of moles of solute in a liquid stream can be obtained as the product of L_S and X. Thus,

$$G_1 y_1 = G_S Y_1 \quad \text{and} \quad G_2 y_2 = G_S Y_2$$

$$L_1 x_1 = L_S X_1 \quad \text{and} \quad L_2 x_2 = L_S X_2$$

where X_1 and X_2 are the mole ratio of solutes in the liquid at the bottom and top of the column, and Y_1 and Y_2 are the mole ratio of solute in the gas stream at the inlet and the exit of the gas. Substituting these values in Eq. (9.7) we get,

$$G_S (Y_1 - Y_2) = L_S (X_1 - X_2) \tag{9.8}$$

EXAMPLE 9.15 Acetone is recovered from an acetone-air mixture containing 25% (volume) acetone by scrubbing with water. Assuming that air is insoluble in water, determine the percent of acetone in the entering gas that is absorbed if the gas leaving the scrubber analyzes 5% acetone.

Solution *Basis:* 100 kmol gas admitted to the absorption column

Let G_1 and G_2 be the molar flow rate of the gas at the inlet and the exit of the absorber respectively, and y_1 be the mole fraction of acetone at the inlet and y_2 that at the exit (Figure 9.28). The air being insoluble in water, the entire quantity of air in the entering stream will appear in the gas stream leaving the absorber. An air balance therefore leads to

$$G_1(1 - y_1) = G_2(1 - y_2) \quad \Rightarrow \quad 100 \times 0.75 = G_2 \times 0.95$$

Therefore, $G_2 = 78.95$ kmol

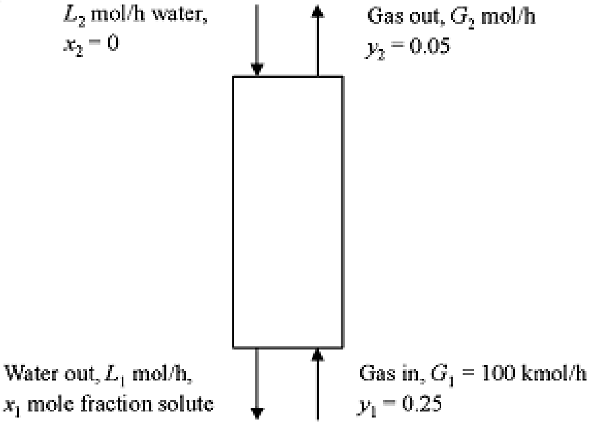


Figure 9.28 Absorption operation in Example 9.15.

The amount of acetone in the gas leaving is

$$G_2y_2 = 78.95 \times 0.05 = 3.9475 \text{ kmol}$$

The amount of acetone in the gas entering is

$$G_1y_1 = 100 \times 0.25 = 25 \text{ kmol}$$

Acetone absorbed is

$$\frac{25 - 3.9475}{25} \times 100 = 84.21\%$$

EXAMPLE 9.16 A gas mixture consisting of 65% N_2 and 35% SO_3 by volume is admitted to an absorption column at a rate of 4500 kg/h. It is contacted with a stream of 50% H_2SO_4 flowing counter-current to the gas stream at a rate of 5000 kg/h. The gases leave at 101.3 kPa. Water lost with the exit gases exerts a partial pressure of 25.0 kPa. If the concentrated acid leaving the bottom of the column contained 75.0% H_2SO_4, what percent of the entering SO_3 is absorbed and converted to acid?

Solution *Basis:* One hour operation

The absorption operation of this example is shown schematically in Figure 9.29.

The average molecular weight of gas entering the column = 0.65 × 28 + 0.35 × 80 = 46.2.

The molar flow rate of gases entering the absorber is

$$\frac{4500}{46.2} = 97.40 \text{ kmol/h}$$

Therefore, the moles of nitrogen entering is

$$97.4 \times 0.65 = 63.31 \text{ kmol}$$

$$\text{Moles of } SO_3 \text{ entering} = 97.4 \times 0.35 = 34.09 \text{ kmol}$$

Let W kg be the mass of 75% H_2SO_4 produced and x be the moles of SO_3 that leaves with the exit gases unabsorbed.

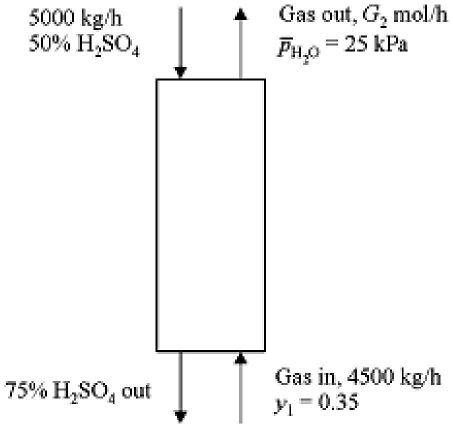


Figure 9.29 Absorption operation of Example 9.16.

Since no nitrogen is absorbed, the gases leaving will contain 63.31 kmol nitrogen, x kmol SO_3 and water vapour, which exerts a partial pressure of 25 kPa. Let y be the moles of water vapour present in the gases. Then

$$\frac{25}{101.3} = \frac{y}{63.31 + x + y}$$

which means that

$$y = 0.32765x + 20.744 \qquad \text{(A)}$$

Total balance:

Kilograms of H_2SO_4 (50%) entering + kilograms of gas mixture entering
= kilograms of gas leaving + kilograms of con. H_2SO_4 (75%) leaving

That is,

$$5000 + 4500 = (63.31 \times 28 + x \times 80 + y \times 18.016) + W$$

$$\Rightarrow \qquad W + 80x + 18.016y = 7727.32$$

Substituting Eq. (A) into the above the total material balance reduces to

$$84.9174x + W = 7352.68 \qquad \text{(B)}$$

Since the molecular weight of H_2SO_4 is 98.016, 98.016 kg of sulphuric acid contains 80 kg of SO_3. Now consider an SO_3-balance for the absorber:

Kilograms of SO_3 entering with 50% H_2SO_4 + kilograms of SO_3 in the feed gas
= kilograms of SO_3 in the gas leaving + kilograms SO_3 in the 75% H_2SO_4 leaving

$$5000 \times 0.5 \times \frac{80}{98.016} + 34.09 \times 80 = 80x + 0.75W \times \frac{80}{98.016}$$

The above equation reduces to

$$80x + 0.6121W = 4767.68 \qquad \text{(C)}$$

Solving Eqs. (B) and (C), we get $x = 9.74$ kmol. Therefore, the amount of SO_3 absorbed = $34.09 - 9.74 = 24.35$ kmol.

The percent of SO_3 that is absorbed is

$$\frac{24.35}{34.09} \times 100 = 71.43\%$$

9.2.8 Distillation

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

When a liquid mixture at a high temperature and pressure is subjected to a sudden reduction in pressure by passing through a valve, the liquid gets partially vaporized. The resulting liquid–vapour mixture is separated into the distillate and the bottom products as shown in Figure 9.30. The process is known as *flash distillation* or *flash vaporization*. The flash distillation is an ideal single-stage operation in which the distillate and bottom products have equilibrium compositions. The products will have an appreciable difference in their compositions only if the volatilities of the constituents are appreciably different. Therefore, it is generally impossible to obtain pure products by a single-stage flash vaporization.

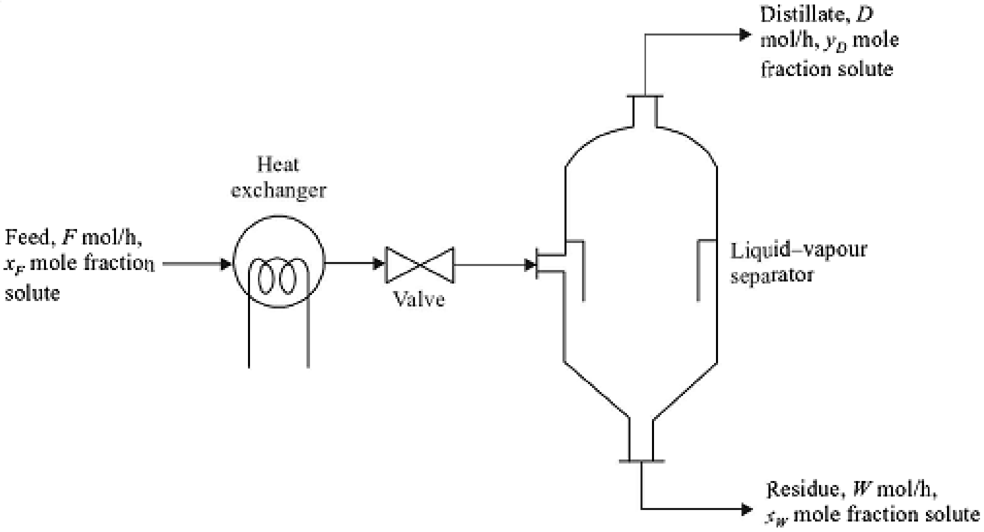


Figure 9.30 Equilibrium flash distillation.

The vapour produced in a single-stage flashing operation can be enriched in the more volatile component by bringing it in contact with a liquid phase with which the vapour is not in equilibrium. The liquid phase known as *reflux* is obtained by condensing the vapour and recycling a part of the condensate. The distillation carried out in this fashion is known as *rectification* or *fractionation*. The fractionation can be carried out as a multi-stage operation in a plate column or as a continuous contact operation in a packed column. Distillation using a plate column is schematically represented in Figure 9.31.

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

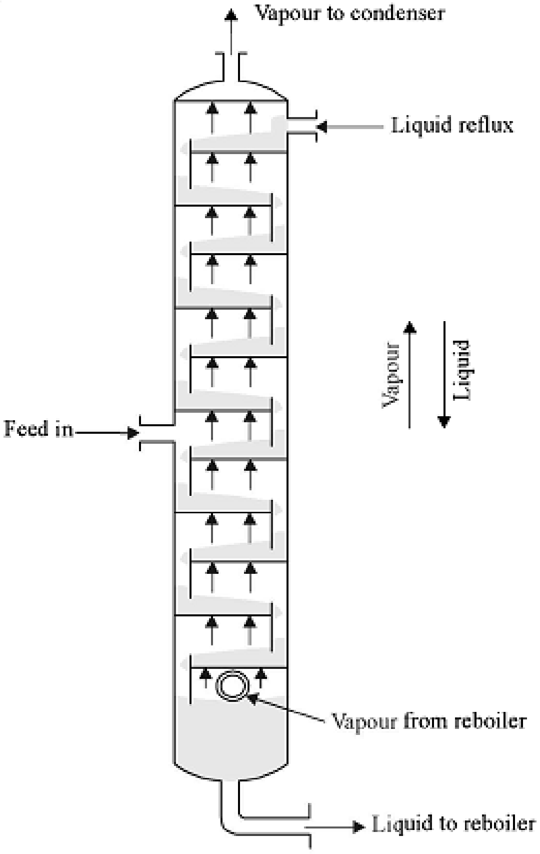


Figure 9.31 A plate column for fractionation.

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

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

$$F = D + W \tag{9.9}$$

$$Fx_F = Dx_D + Wx_W \tag{9.10}$$

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

EXAMPLE 9.17 A continuous distillation column is used to regenerate solvent for use in a solvent extraction unit. The column treats 200 kmol/h of a feed containing 10% (mol) ethyl alcohol and the rest water. The overhead product is 89% (mol) alcohol and the bottom product is 0.3% (mol) alcohol. The overhead is sent to the extraction unit and the bottom is wasted. What is the daily requirement of make-up alcohol in the solvent extraction unit?

Solution *Basis:* 200 kmol/h feed

Let F, D and W be the flow rates of the feed, distillate and residue respectively, and x_F, x_D and x_W be the mole fraction of ethanol in the feed, distillate and residue respectively. F = 200 kmol/h, $x_F = 0.10$, $x_D = 0.89$ and $x_W = 0.003$.

The total material balance:

$$F = D + W$$

Alcohol balance:

$$Fx_F = Dx_D + Wx_W$$

Substituting the given values in these equations, we get

$$D + W = 200$$

$$0.89D + 0.003W = 200 \times 0.10 = 20$$

Solving the above equations, we get $D = 21.87$ kmol and $W = 178.13$ kmol.

$$\begin{aligned}\text{Alcohol wasted} &= \text{alcohol present in the residue}\\ &= Wx_W = 178.13 \times 0.003 = 0.5344 \text{ kmol/h}\end{aligned}$$

Therefore, the make-up alcohol required per day = 0.5344 × 24 × 46 = 589.98 kg

EXAMPLE 9.18 An aqueous solution of methanol containing 20% (weight) methanol is to be separated into a distillate product containing 97% (weight) methanol and a bottom product containing 2% (weight) methanol. For treating 100 kg of feed with a reflux ratio of 3.5 on a weight basis, calculate the following:

(a) The amounts of distillate and bottom products
(b) The amount of vapour condensed in the condenser per kg of distillate
(c) The amount of vapour condensed in the condenser per kg of feed.

Note: The reflux ratio is defined as the ratio of the amount of condensate recycled to the amount of condensate withdrawn as distillate product.

Solution *Basis:* 100 kg feed

The distillation operation of this example is represented schematically in Figure 9.32.

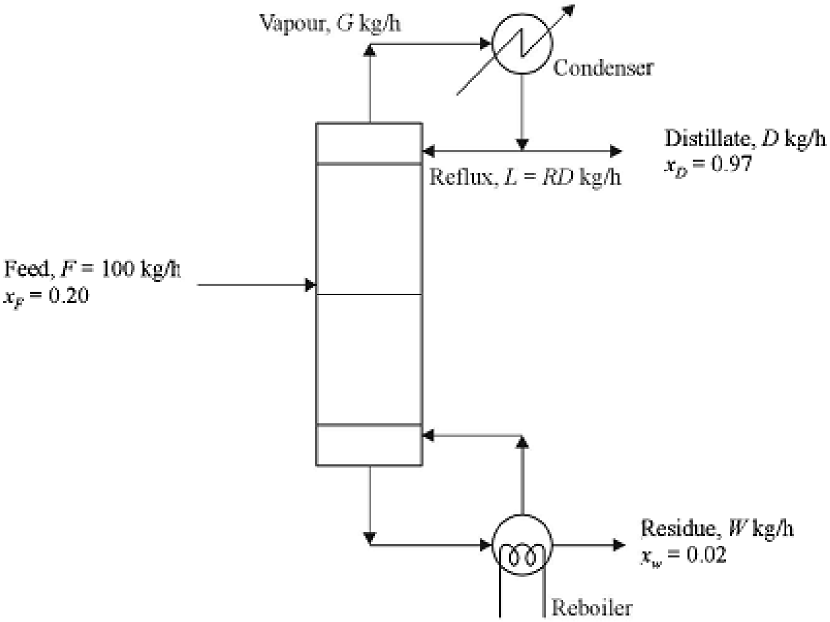


Figure 9.32 Distillation operation of Example 9.18.

(a) The total material balance:

$$F = D + W$$

Alcohol balance:

$$Fx_F = Dx_D + Wx_W$$

Substitute $x_F = 0.20$, $x_D = 0.97$ and $x_w = 0.02$ in Eq. (9.10) and eliminate W using Eq. (9.9), we get

$$0.20F = 0.97D + 0.02(F - D)$$

Put $F = 100$ and solve the above equation for D. We get $D = 18.95$ kg/h. Putting values of F and D in Eq. (9.9), we get $W = 81.05$ kg/h.

(b) Take a total material balance around the condenser.

$$G = L + D$$

Since the reflux ratio $R = 3.5$, the reflux $L = RD = 3.5D$, and the above equation gives, $G = 4.5D$. For 1 kg distillate product, the amount of vapour condensed, $G = 4.5$ kg.

(c) For one kg of feed, the distillate obtained is $D = 0.1895$ kg [from part (a)]. Therefore, the amount of vapour condensed per kg of feed is

$$4.5 \times 0.1895 = 0.853 \text{ kg}$$

Module3: Mass Balances with Chemical Reactions

REFERENCES

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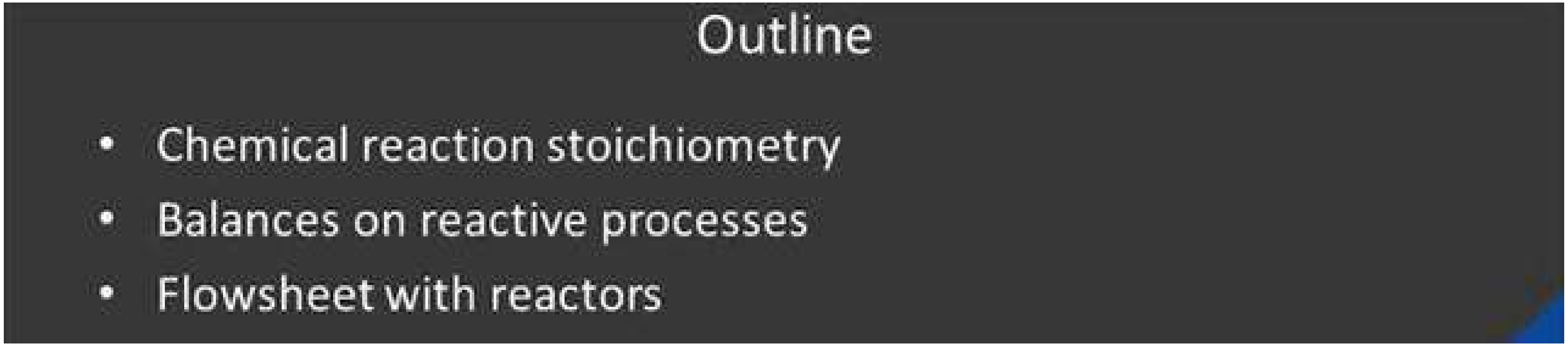
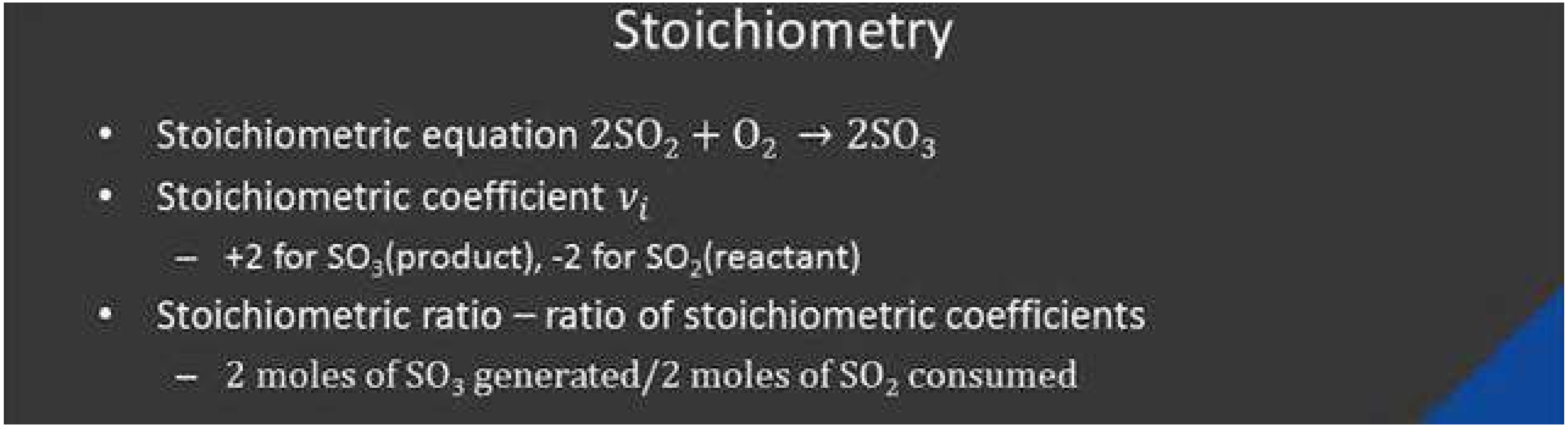
BOOK: KV Narayanan and B Lakshmikutty, “Stoichiometry and Process Calculations” 2nd edition, 2016.



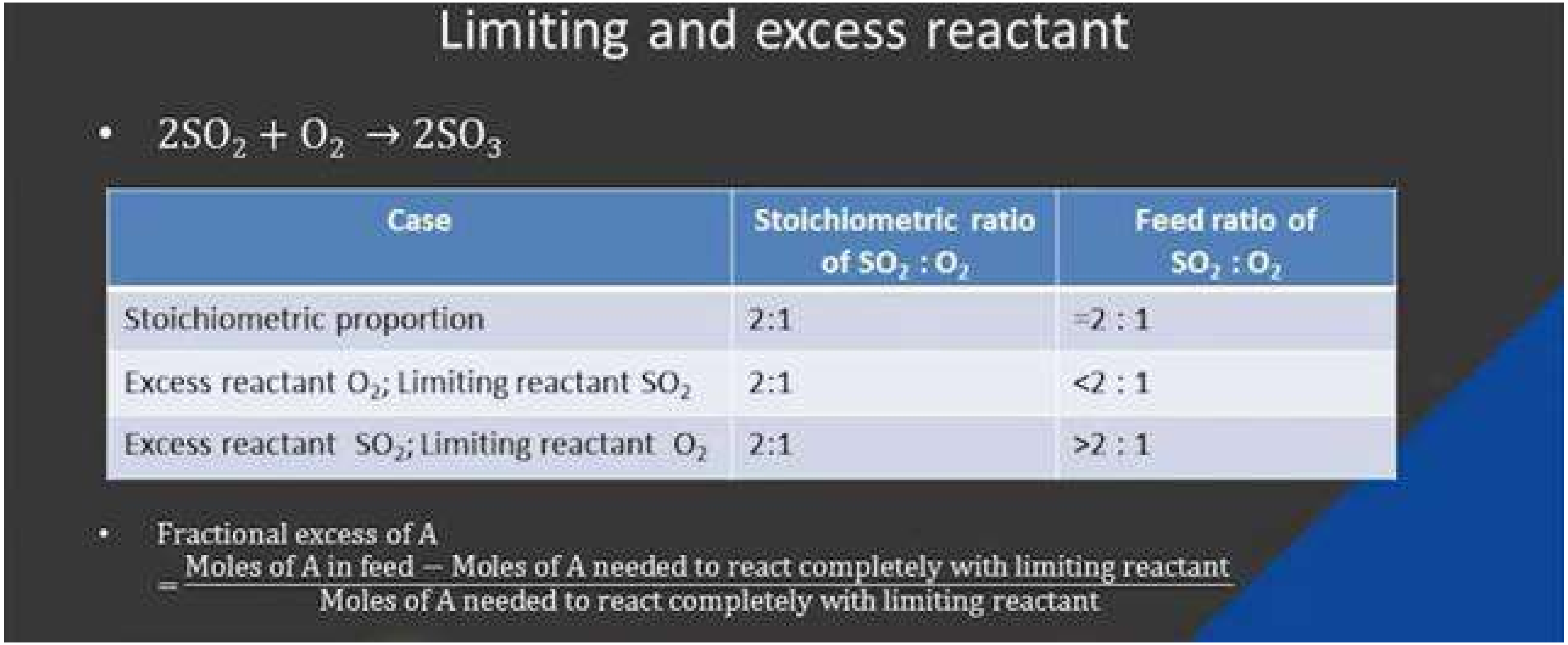
Outline

- Chemical reaction stoichiometry
- Balances on reactive processes
- Flowsheet with reactors



Stoichiometry

- Stoichiometric equation $2SO_2 + O_2 \rightarrow 2SO_3$
- Stoichiometric coefficient ν_i
  - +2 for SO_3(product), -2 for SO_2(reactant)
- Stoichiometric ratio – ratio of stoichiometric coefficients
  - $2 \text{ moles of } SO_3 \text{ generated}/2 \text{ moles of } SO_2 \text{ consumed}$



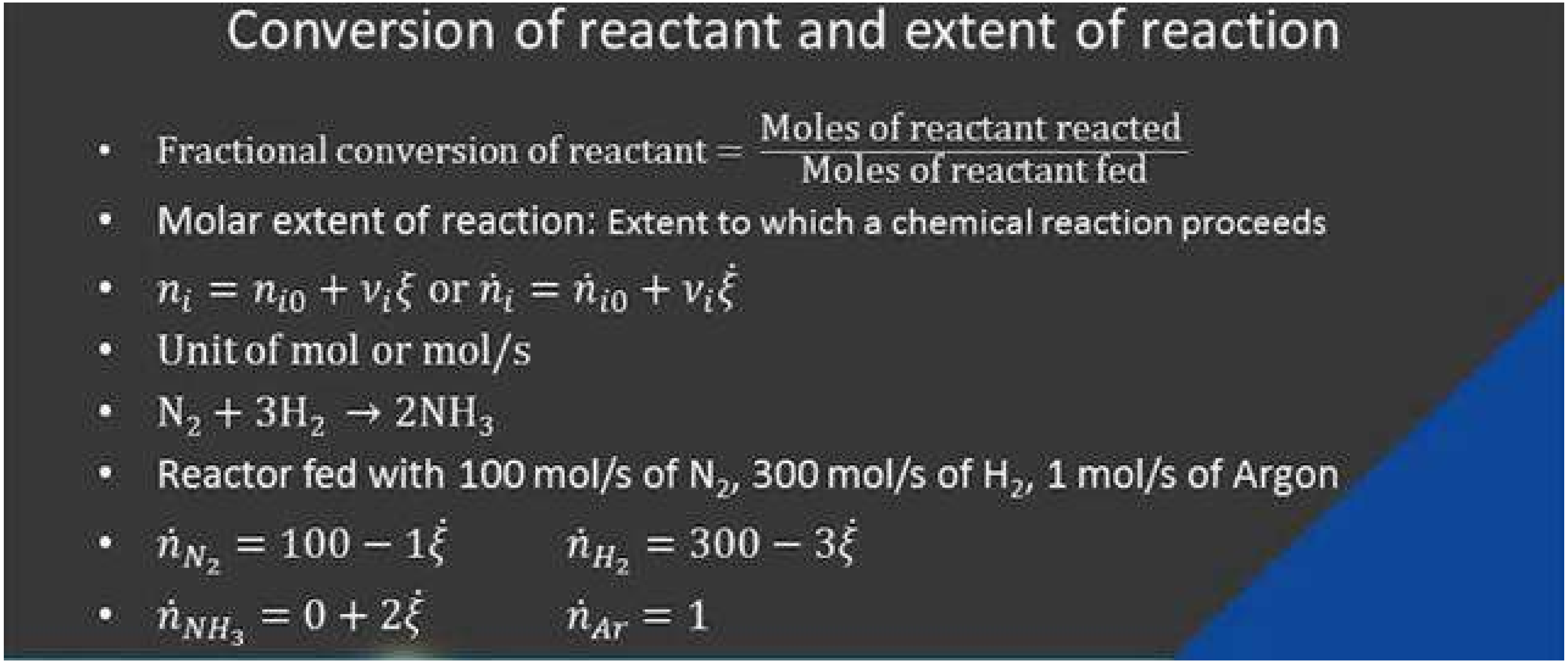
Limiting and excess reactant

- $2SO_2 + O_2 \rightarrow 2SO_3$

Case	Stoichiometric ratio of $SO_2 : O_2$	Feed ratio of $SO_2 : O_2$
Stoichiometric proportion	2:1	=2 : 1
Excess reactant O_2; Limiting reactant SO_2	2:1	<2 : 1
Excess reactant SO_2; Limiting reactant O_2	2:1	>2 : 1

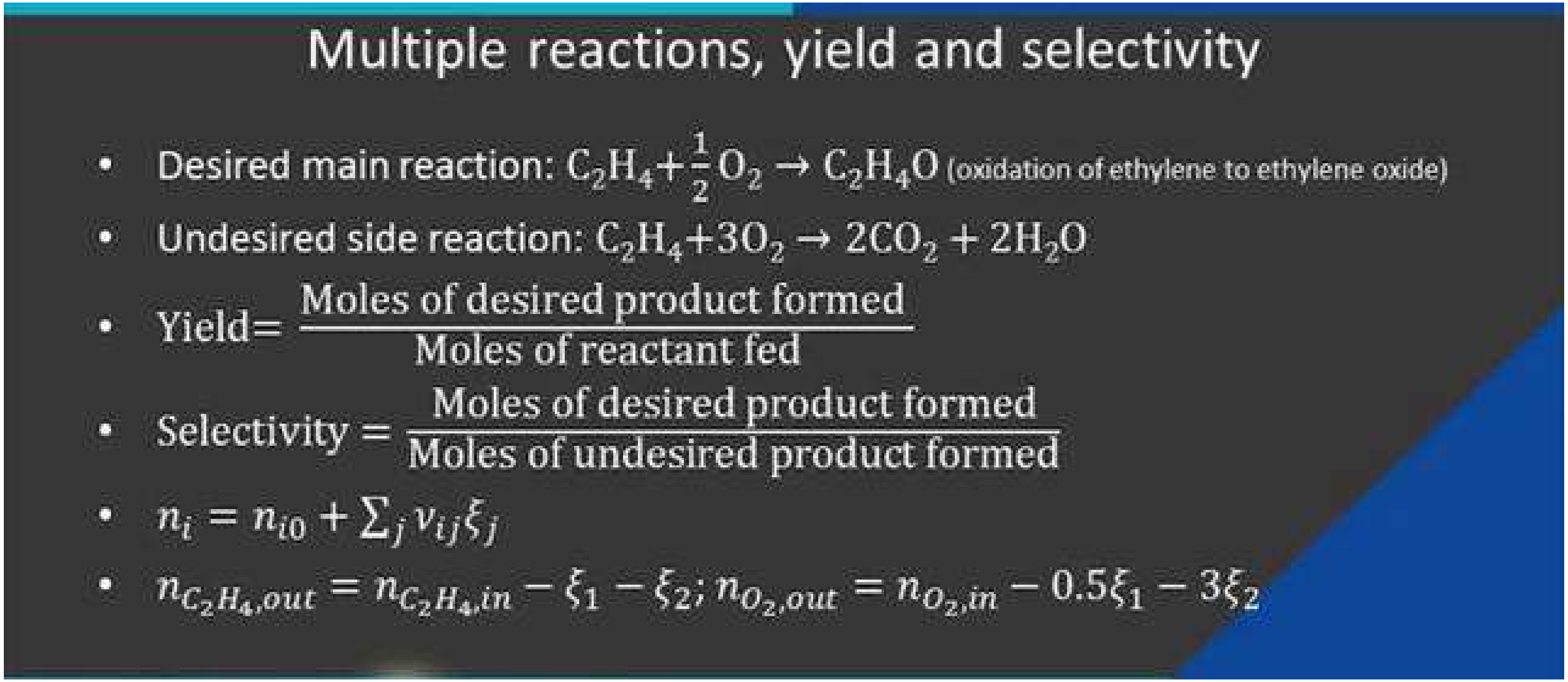
- Fractional excess of A

$$= \frac{\text{Moles of A in feed} - \text{Moles of A needed to react completely with limiting reactant}}{\text{Moles of A needed to react completely with limiting reactant}}$$



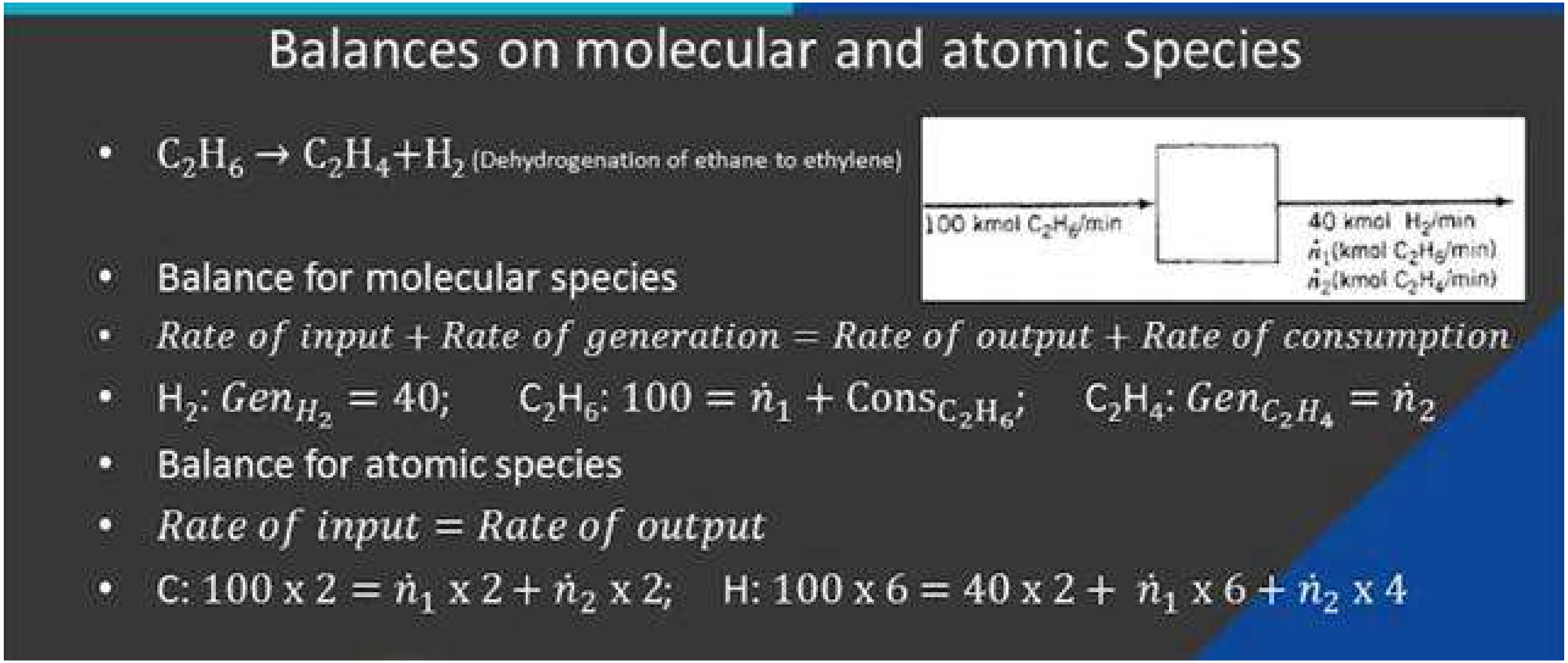
Conversion of reactant and extent of reaction

- Fractional conversion of reactant $= \frac{\text{Moles of reactant reacted}}{\text{Moles of reactant fed}}$
- Molar extent of reaction: Extent to which a chemical reaction proceeds
- $n_i = n_{i0} + \nu_i \xi$ or $\dot{n}_i = \dot{n}_{i0} + \nu_i \dot{\xi}$
- Unit of mol or mol/s
- $N_2 + 3H_2 \rightarrow 2NH_3$
- Reactor fed with 100 mol/s of N_2, 300 mol/s of H_2, 1 mol/s of Argon
- $\dot{n}_{N_2} = 100 - 1\dot{\xi}$ $\qquad$ $\dot{n}_{H_2} = 300 - 3\dot{\xi}$
- $\dot{n}_{NH_3} = 0 + 2\dot{\xi}$ $\qquad$ $\dot{n}_{Ar} = 1$



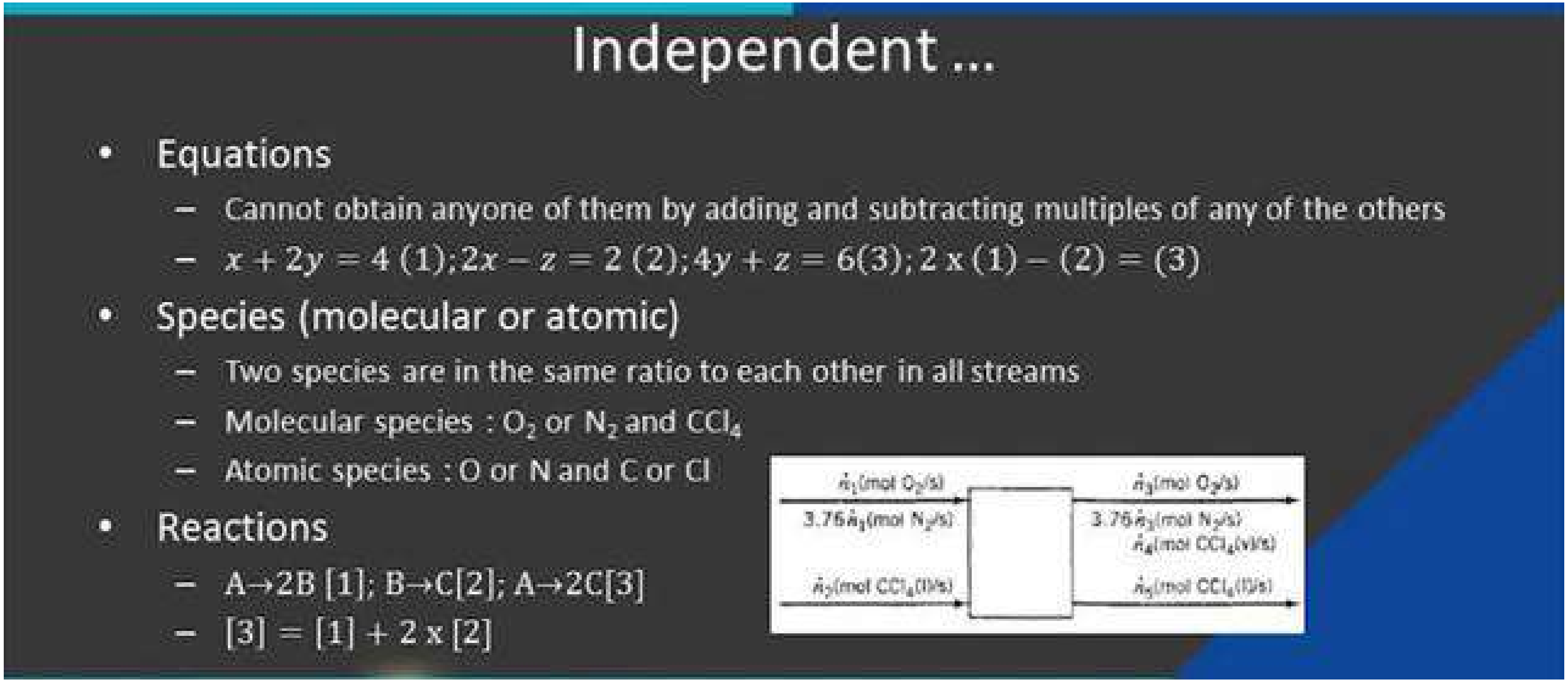
Multiple reactions, yield and selectivity

- Desired main reaction: $C_2H_4+\frac{1}{2}O_2 \rightarrow C_2H_4O$ (oxidation of ethylene to ethylene oxide)
- Undesired side reaction: $C_2H_4+3O_2 \rightarrow 2CO_2+2H_2O$
- $\text{Yield}=\dfrac{\text{Moles of desired product formed}}{\text{Moles of reactant fed}}$
- $\text{Selectivity}=\dfrac{\text{Moles of desired product formed}}{\text{Moles of undesired product formed}}$
- $n_i = n_{i0} + \sum_j \nu_{ij}\xi_j$
- $n_{C_2H_4,out} = n_{C_2H_4,in} - \xi_1 - \xi_2; n_{O_2,out} = n_{O_2,in} - 0.5\xi_1 - 3\xi_2$



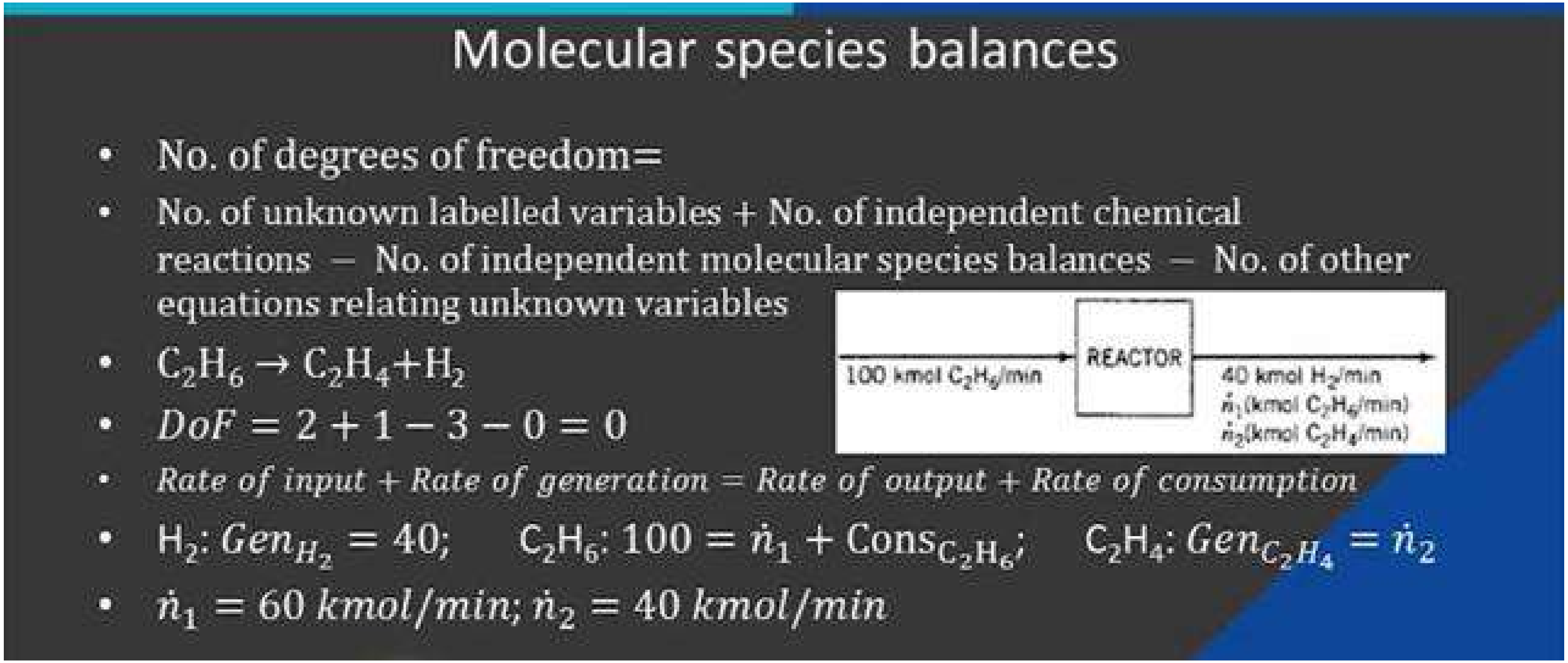
Balances on molecular and atomic Species

- $C_2H_6 \rightarrow C_2H_4 + H_2$ (Dehydrogenation of ethane to ethylene)
- Balance for molecular species
- $Rate\ of\ input + Rate\ of\ generation = Rate\ of\ output + Rate\ of\ consumption$
- H_2: $Gen_{H_2} = 40$; C_2H_6: $100 = \dot{n}_1 + \mathrm{Cons}_{C_2H_6}$; C_2H_4: $Gen_{C_2H_4} = \dot{n}_2$
- Balance for atomic species
- $Rate\ of\ input = Rate\ of\ output$
- C: $100 \text{ x } 2 = \dot{n}_1 \text{ x } 2 + \dot{n}_2 \text{ x } 2$; H: $100 \text{ x } 6 = 40 \text{ x } 2 + \dot{n}_1 \text{ x } 6 + \dot{n}_2 \text{ x } 4$



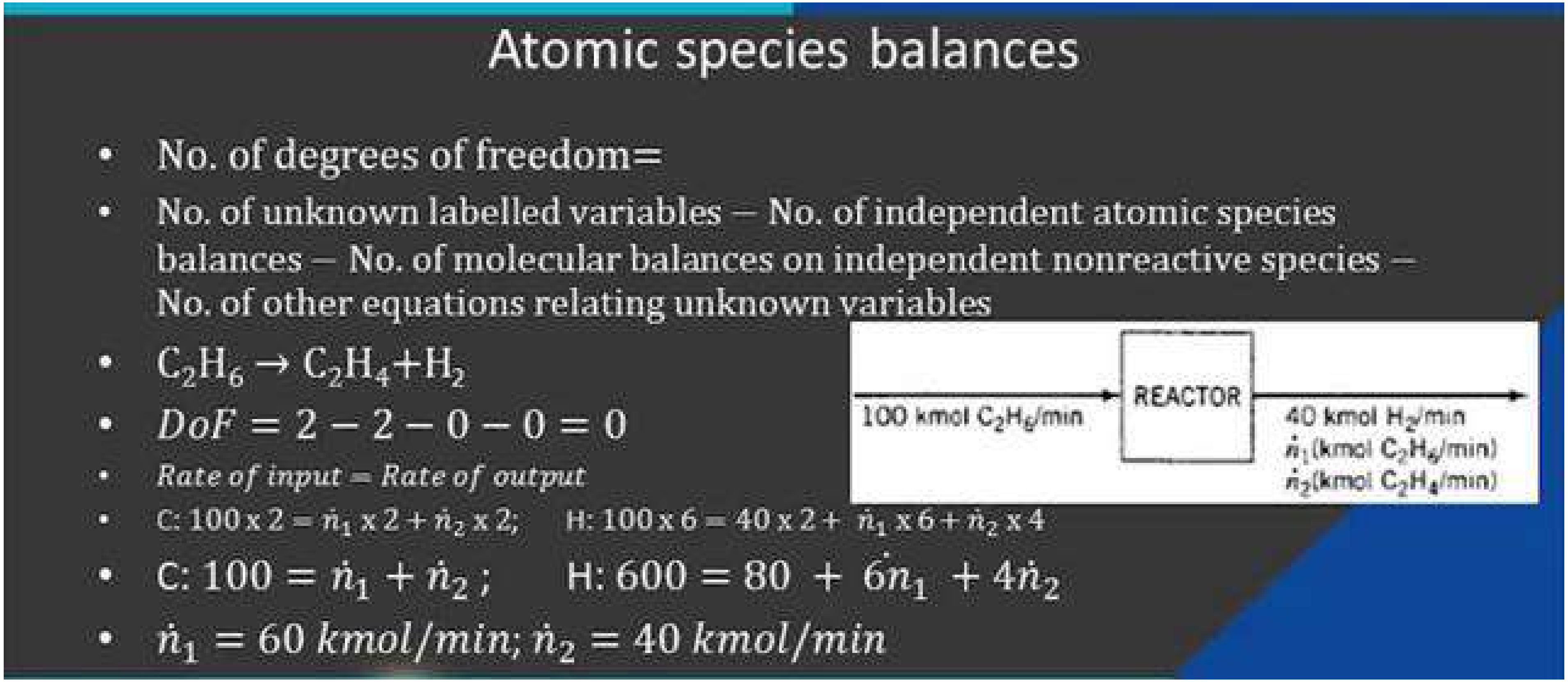
Independent …

- Equations
  - Cannot obtain anyone of them by adding and subtracting multiples of any of the others
  - $x + 2y = 4$ (1); $2x - z = 2$ (2); $4y + z = 6$ (3); 2 x (1) – (2) = (3)
- Species (molecular or atomic)
  - Two species are in the same ratio to each other in all streams
  - Molecular species : O_2 or N_2 and CCl_4
  - Atomic species : O or N and C or Cl
- Reactions
  - A→2B [1]; B→C[2]; A→2C[3]
  - [3] = [1] + 2 x [2]



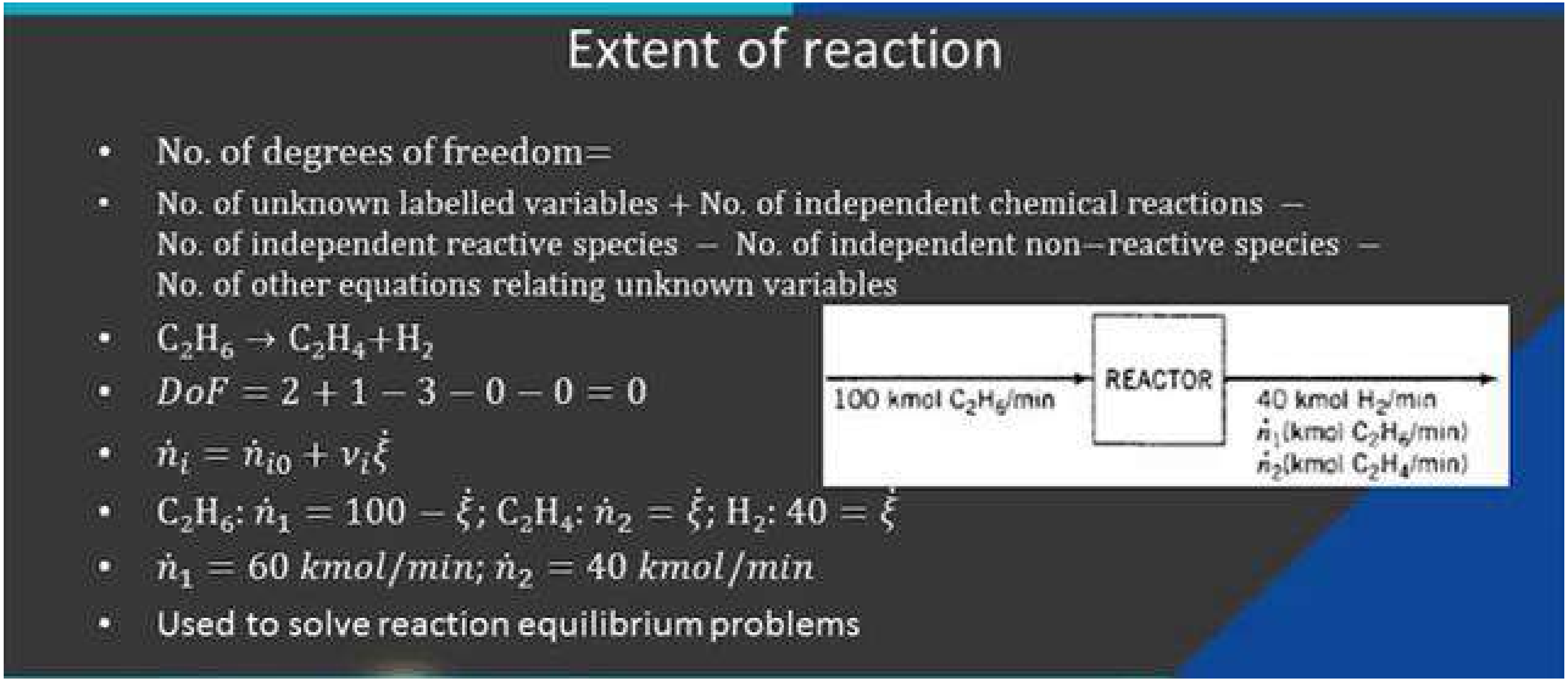
Molecular species balances

- No. of degrees of freedom=
- No. of unknown labelled variables + No. of independent chemical reactions − No. of independent molecular species balances − No. of other equations relating unknown variables
- $C_2H_6 \rightarrow C_2H_4 + H_2$
- $DoF = 2 + 1 - 3 - 0 = 0$
- $Rate\ of\ input + Rate\ of\ generation = Rate\ of\ output + Rate\ of\ consumption$
- H_2: $Gen_{H_2} = 40$; C_2H_6: $100 = \dot{n}_1 + \mathrm{Cons}_{C_2H_6}$; C_2H_4: $Gen_{C_2H_4} = \dot{n}_2$
- $\dot{n}_1 = 60\ kmol/min;\ \dot{n}_2 = 40\ kmol/min$



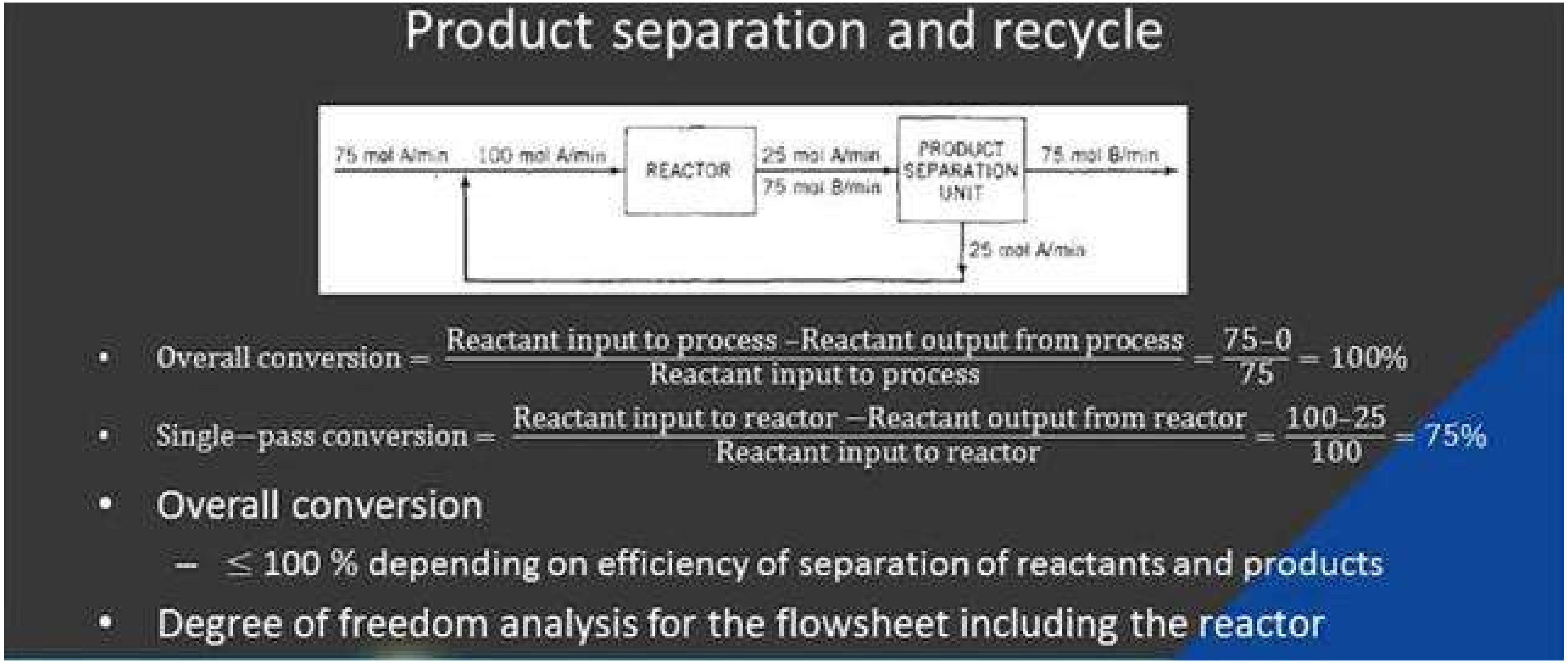
Atomic species balances

- No. of degrees of freedom=
- No. of unknown labelled variables – No. of independent atomic species balances – No. of molecular balances on independent nonreactive species – No. of other equations relating unknown variables
- $C_2H_6 \rightarrow C_2H_4 + H_2$
- $DoF = 2 - 2 - 0 - 0 = 0$
- $Rate\ of\ input = Rate\ of\ output$
- C: $100 \times 2 = \dot{n}_1 \times 2 + \dot{n}_2 \times 2$; H: $100 \times 6 = 40 \times 2 + \dot{n}_1 \times 6 + \dot{n}_2 \times 4$
- C: $100 = \dot{n}_1 + \dot{n}_2$; H: $600 = 80 + 6\dot{n}_1 + 4\dot{n}_2$
- $\dot{n}_1 = 60\ kmol/min; \dot{n}_2 = 40\ kmol/min$



Extent of reaction

- No. of degrees of freedom=
- No. of unknown labelled variables + No. of independent chemical reactions − No. of independent reactive species − No. of independent non−reactive species − No. of other equations relating unknown variables
- $C_2H_6 \rightarrow C_2H_4 + H_2$
- $DoF = 2 + 1 - 3 - 0 - 0 = 0$
- $\dot{n}_i = \dot{n}_{i0} + v_i \dot{\xi}$
- C_2H_6: $\dot{n}_1 = 100 - \dot{\xi}$; C_2H_4: $\dot{n}_2 = \dot{\xi}$; H_2: $40 = \dot{\xi}$
- $\dot{n}_1 = 60\ kmol/min;\ \dot{n}_2 = 40\ kmol/min$
- Used to solve reaction equilibrium problems

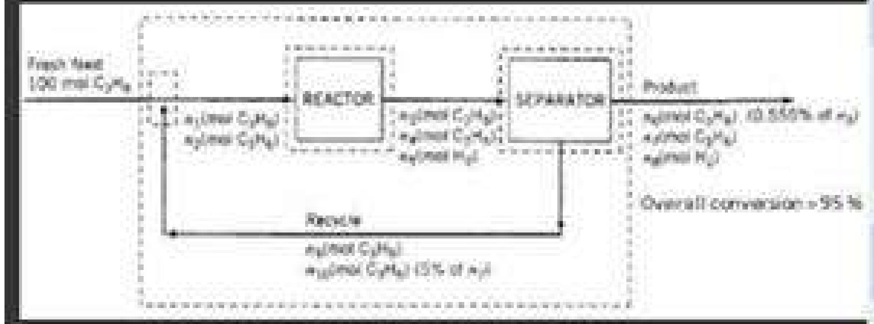


Product separation and recycle

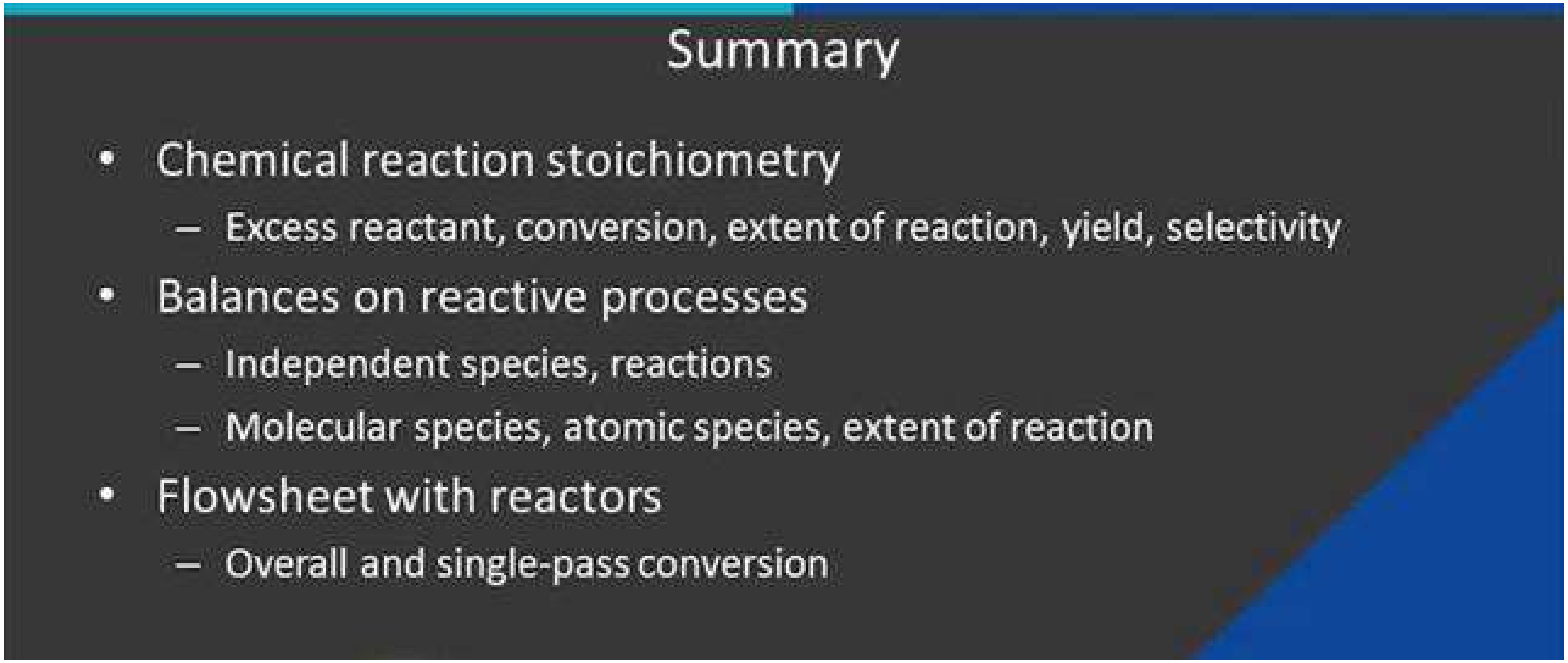
- $\text{Overall conversion} = \dfrac{\text{Reactant input to process} - \text{Reactant output from process}}{\text{Reactant input to process}} = \dfrac{75-0}{75} = 100\%$
- $\text{Single}-\text{pass conversion} = \dfrac{\text{Reactant input to reactor} - \text{Reactant output from reactor}}{\text{Reactant input to reactor}} = \dfrac{100-25}{100} = 75\%$
- Overall conversion
  - – $\leq$ 100 % depending on efficiency of separation of reactants and products
- Degree of freedom analysis for the flowsheet including the reactor

Product separation and recycle

- Dehydrogenation of propane $C_3H_8 \rightarrow C_3H_6 + H_2$
- Basis: 100 mol of feed



	Mixing point	Reactor	Separator	Overall
Unknowns	4 (n_1 n_2 n_9 n_{10}) 2 (n_1 n_2)	5 (n_1 to n_5) 2 (n_1 n_2)	8 (n_3 to n_{10}) 5 (n_3 n_4 n_5 n_9 n_{10})	3 (n_6 n_7 n_8)
Equations	2 molecular species balances	2 atomic species balances	3 molecular species balances + 2 additional relations	2 atomic species balances + 1 additional relation
n_{df}	2 0	3 0	3 0	0
Sequence	Third	Third	Second	First
Moles	n_1 = 995, n_2 = 4.75 Recycle ratio = 9	Single pass conversion 9.6%	n_3 = 900, n_4 = 99.75 n_5 = 95, n_9 = 895, n_{10} = 4.75	n_6 = 5 n_7 = 95, n_8 = 95



Summary

- Chemical reaction stoichiometry
  - Excess reactant, conversion, extent of reaction, yield, selectivity
- Balances on reactive processes
  - Independent species, reactions
  - Molecular species, atomic species, extent of reaction
- Flowsheet with reactors
  - Overall and single-pass conversion

EXAMPLE 10.1 Propane is burned with excess air to ensure complete combustion. If 55 kg of CO_2 and 15 kg of CO are obtained when propane is completely burned with 500 kg air, determine the following:

(a) The mass of propane burnt (in kilograms)
(b) The percent excess air
(c) The composition of flue gas

Solution *Basis:* 55 kg of CO_2 and 15 kg of CO obtained by burning propane with 500 kg of air

The combustion of propane in this example is schematically represented in Figure 10.3.

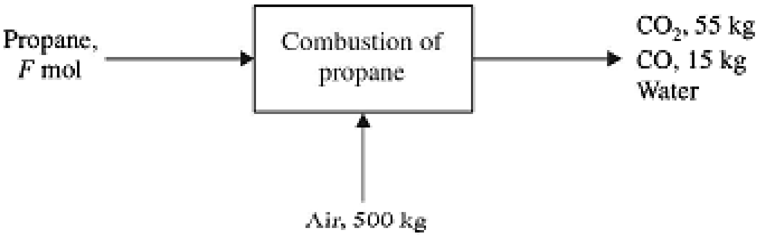


Figure 10.3 Combustion of propane (Example 10.1).

The molecular weight of CO_2 is 44 and the molecular weight of CO is 28. Therefore,

$$\text{Moles of } CO_2 \text{ in the flue gas} = \frac{55}{44} = 1.25 \text{ kmol}$$

$$\text{Moles of CO in the flue gas} = \frac{15}{28} = 0.5357 \text{ kmol}$$

$$\text{Air supplied} = \frac{500}{29} = 17.24 \text{ kmol}$$

(a) Let F be the moles of propane burned. It can be calculated by a carbon balance:

moles of carbon in the inlet gas = moles of carbon in the exit gases

Since one mole of propane contains three moles of carbon, the carbon balance gives

$$3F = 1.25 + 0.5357 \tag{A}$$

Therefore, the moles of propane burned $F = 0.5952$ kmol.

$$\begin{aligned}\text{Mass of propane burned} &= 0.5952 \times \text{molecular weight of propane}\\ &= 0.5952 \times 44.064 = 26.23 \text{ kg}\end{aligned}$$

(b) One mole propane requires 5 moles of oxygen for complete combustion:

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O \tag{B}$$

Theoretical oxygen requirement is

$$0.5952 \times 5 = 2.976 \text{ kmol}$$

Theoretical requirement of air is

$$\frac{100}{21}\times 2.976 = 14.17 \text{ kmol}$$

$$\text{Percent excess of air} = \frac{\text{excess air}}{\text{thoretical air}}\times 100 = \frac{\text{air supplied} - \text{theoretical air}}{\text{theoretical air}}\times 100$$

$$= \frac{17.24 - 14.17}{14.17}\times 100 = 21.67\%$$

(c) The products of combustion contains CO_2, CO, O_2, N_2, and H_2O vapour produced on combustion. The reactions that occur are as follows:

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O \qquad \text{(C)}$$

$$C_3H_8 + \tfrac{7}{2}O_2 \rightarrow 3CO + 4H_2O \qquad \text{(D)}$$

When 0.5952 kmol propane is burnt, 0.5952 × 4 = 2.3808 kmol water is produced. The moles of oxygen present in the combustion gases can be determined by an oxygen balance:

O_2 in the air supplied = O_2 present in the flue gas as CO_2, CO and H_2O
+ unburned oxygen

That is,

$$17.24\times\frac{21}{100} = 1.25 + 0.5357\times 0.5 + 2.3808\times 0.5 + \text{unburned } O_2$$

Therefore, the amount of free oxygen present in the flue gas is

$$17.24\times\frac{21}{100} - (1.25 + 0.5357\times 0.5 + 2.3808\times 0.5) = 0.9122 \text{ kmol}$$

[Alternatively the moles of oxygen in the flue gas can be obtained by considering the reaction in steps. With every 3 mol CO_2 formed according to reaction *C*, 5 mol oxygen is consumed, and with every 3 mol CO formed according to reaction *D* 3.5 mol oxygen is consumed. Thus,

$$\text{moles of oxygen consumed by reaction } C = 1.25\times\frac{5}{3} = 2.0833 \text{ kmol}$$

Therefore,

$$\text{moles of oxygen consumed by reaction } D = 0.5357\times\frac{3.5}{3} = 0.6250 \text{ kmol}$$

$$\text{total moles of oxygen consumed} = 2.0823 + 0.6250 = 2.7083 \text{ kmol}$$

$$\text{moles of oxygen supplied} = 17.24 \times 0.21 = 3.6204 \text{ kmol}$$

Moles of free oxygen present in the flue gas by an oxygen balance is equal to the moles of oxygen supplied minus the moles of oxygen consumed. Therefore, moles of free oxygen = 3.6204 – 2.7083 = 0.9121 kmol]

The entire nitrogen in the air supplied will appear in the flue gas. Therefore, flue gas contains 17.24 × 0.79 = 13.6196 kmol. The composition of the flue gas can now be calculated as shown in the table below.

Constituent	*The number of moles in the flue gas*	*Percent composition, (mol%)*
CO_2	1.25	$\frac{1.25}{18.6983}\times 100 = 6.69\%$
CO	0.5357	$\frac{0.5357}{18.6983}\times 100 = 2.87\%$
O_2	0.9122	$\frac{0.9122}{18.6983}\times 100 = 4.88\%$
N_2	13.6196	$\frac{13.6196}{18.6983}\times 100 = 72.84\%$
H_2O	2.3808	$\frac{2.3808}{18.6983}\times 100 = 12.72\%$
Total	18.6983	100

EXAMPLE 10.2 Hydrogen-free coke containing 85% (weight) carbon and the rest inert materials is burned in a furnace. It is found that during combustion 5% of the coke charged is lost unburned. The flue gas analysis shows 14.84% CO_2, 1.65% CO, 5.16% O_2 and 78.35% N_2. The flue gas leaves the furnace at 500 K and 100 kPa. Calculate the following:

(a) The percent excess air on the basis of complete combustion of coke
(b) The weight of air supplied per kg of coke charged
(c) The volume of flue gas per kg of coke charged
(d) The composition of the refuse from the furnace

Solution *Basis:* 100 kmol flue gas

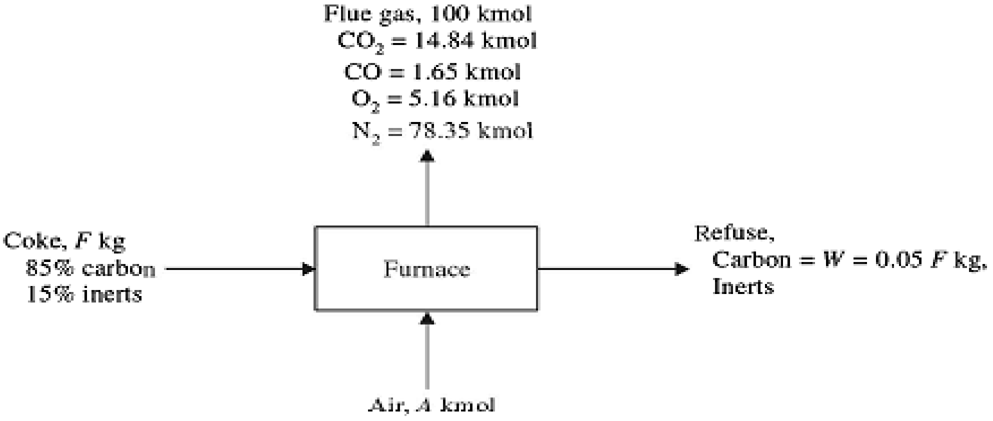


Figure 10.4 Combustion of coke (Example 10.2).

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

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

$$\text{Carbon present in the flue gas} = \text{carbon in } CO_2 + \text{carbon in CO}$$
$$= 14.84 + 1.65 = 16.49 \text{ kmol} = 16.49 \times 12 = 197.88 \text{ kg}$$

$$\text{Carbon in the coke charged} = F \times 0.85 \text{ kg}$$

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

Carbon balance:

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

Solving the above equation, we get

$$F = \frac{197.88}{0.95 \times 0.85} = 245.05 \text{ kg}$$

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

$$A \times 0.79 = 78.35$$

or

$$A = 99.177 \text{ kmol}$$

Thus,

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

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

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

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

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

Therefore,

$$\text{Percent excess air} = \text{percent excess oxygen} = 19.99\%$$

(b)

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

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

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

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

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

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

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

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

Therefore, the total weight of refuse is

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

Composition of refuse is

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

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

EXAMPLE 10.3 A fuel oil containing 70% carbon by weight and the rest combustible hydrogen and moisture is burned with excess air. The flue gas analyzed 9% CO_2, 2% CO, 3% O_2 and 86% N_2. Determine the following:

(a) The percentage of excess air
(b) The ratio of carbon to combustible hydrogen in the fuel on a weight basis
(c) The ratio of carbon to total hydrogen in the fuel on a weight basis
(d) The percentages of combustible hydrogen and moisture in the fuel
(e) The mass of moisture present in the flue gas per kg of oil burned

Solution *Basis:* 100 kmol flue gas

Carbon content in the flue gas = carbon in CO_2 and CO = 11 kmol

Let F kg be the mass of fuel burned and A kmol be the amount of air supplied.

(a) Nitrogen in the flue gas = 86 kmol

Since the fuel contains no nitrogen, the nitrogen present in the flue gas comes from air. The nitrogen balance is

$$A\times 0.79 = 86 \;\Rightarrow\; A=\frac{86}{0.79}=108.86\ \text{kmol}$$

Oxygen in the air supplied = 108.86 × 0.21 = 22.86 kmol

If CO in the flue gas were completely converted to CO_2, the moles of oxygen present in the flue gas would be 3 − 1 = 2 kmol.

That is, excess oxygen is 2 kmol.

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

$$= \frac{2}{22.86 - 2} \times 100 = 9.59\%$$

(b) The combustible hydrogen in the fuel is determined from the quantity of oxygen that is consumed by the net hydrogen in the formation of water. Of the 22.86 moles of oxygen supplied, the oxygen that is accounted in the flue gas as CO_2, CO or excess oxygen is only 9 + 1 + 3 = 13 kmol. The difference has been utilized by the net hydrogen in the formation of water. That is, the oxygen balance is

Oxygen in the air supplied = oxygen accounted in the flue
gas as CO_2, CO or excess oxygen
+ oxygen consumed by the net hydrogen

The amount of oxygen consumed by net hydrogen is

$$22.86 - 13 = 9.86 \text{ kmol}$$

Therefore, the net hydrogen burned is

$$2 \times 9.86 = 19.72 \text{ kmol} = 39.76 \text{ kg}$$

The mass of carbon burned is

$$9 + 2 = 11 \text{ kmol} = 132 \text{ kg}$$

The ratio of carbon to net hydrogen in the fuel is

$$\frac{132}{39.76} = 3.32:1$$

(c) For 1 kg of net hydrogen in the fuel, carbon present is 3.32 kg. Let x kg be the mass of moisture present in the fuel for every kilogram of net hydrogen present. It is given that the weight percentage of carbon in the fuel is 70%. Therefore,

$$0.7 = \frac{3.32}{(1 + 3.32 + x)}$$

which on solving gives $x = 0.423$ kg.
The mass of hydrogen present in 0.423 kg of moisture is

$$0.423 \times \frac{2.016}{18.016} = 0.047 \text{ kg}$$

Therefore,

$$\text{Total hydrogen present} = 0.047 + 1 = 1.047 \text{ kg}$$

The ratio of carbon to total hydrogen is

$$\frac{3.32}{1.047} = 3.17:1$$

(d) Carbon = 3.32 kg; combustible hydrogen = 1.0 kg and moisture = 0.423 kg. The percentage composition by weight is

$$\text{net hydrogen} = \frac{1.00}{(1+3.32+0.423)}\times 100 = \frac{1.00}{4.743}\times 100 = 21.08\%$$

$$\text{moisture} = \frac{0.423}{4.743}\times 100 = 8.92\%$$

(e) Since the fuel contains 70% carbon, 21.08% net hydrogen and 8.92% moisture, the products of combustion when 100 kg of fuel is burned will contain

$$8.92 + \frac{18.016}{2.016}\times 21.08 = 197.3\ \text{kg}$$

The mass of moisture in the flue gas per kg of fuel burned = 1.973 kg.

EXAMPLE 10.4 A producer gas contains 9.2% CO_2, 21.3% CO, 18% H_2, 2.5% CH_4, and the rest N_2. It is burned with an excess supply of air. The flue gas analysed 9.05% CO_2, 1.34% CO, 9.98% O_2 and 79.63% N_2. Determine the following:

(a) The volumetric ratio of air supplied to the fuel burned
(b) The percent excess air supplied
(c) The percent of nitrogen in the flue gas that came from the fuel.

Solution *Basis:* 100 moles of flue gas

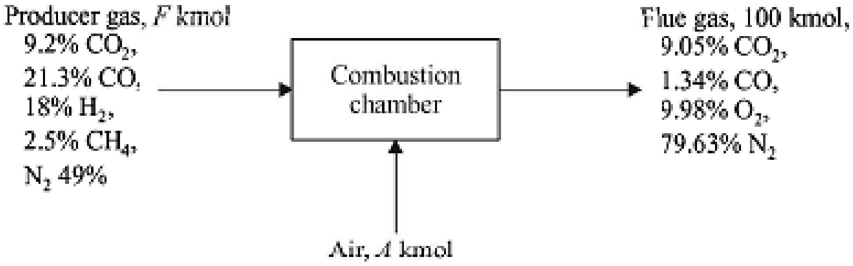


Figure 10.5 Combustion of producer gas (Example 10.4).

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

Carbon balance:

carbon in the fuel burned = carbon in the flue gas as CO_2 and CO

$$0.092F + 0.213F + 0.025F = 9.05 + 1.34 = 10.39\ \text{kmol}$$

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

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

Nitrogen balance:

nitrogen from the fuel + nitrogen in the air = nitrogen in the flue gas

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

Solving this we get $A = 81.2689$ kmol.

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

(b) The percent excess of oxygen supplied can be calculated as

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

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

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

$$\text{Theoretical requirement of oxygen} = \text{oxygen supplied} - \text{oxygen excess}$$

$$= 81.2689 \times 0.21 - 9.31 = 7.76 \text{ kmol}$$

Percent excess of air = percent excess of oxygen

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

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

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

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

Note: Consider the calculation of percent excess air in part (b). Instead of calculating the theoretical requirement of oxygen as the difference between the oxygen supplied and oxygen present in excess, the theoretical requirement of oxygen can be computed as the oxygen required for complete combustion of the various constituents of the fuel based on the fuel analysis. Ideally both calculations should give the same result. Here, let us calculate the oxygen required by 31.4848 kmol producer gas. The producer gas contains 21.3% CO, 18% H_2 and 2.5% CH_4.

$$CO + \frac{1}{2}O_2 \rightarrow CO_2$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$

$$\text{Oxygen required by CO} = 0.5 \times 21.3 = 10.65 \text{ kmol}$$

$$\text{Oxygen required by methane} = 2 \times 2.5 = 5.0 \text{ kmol}$$

$$\text{Oxygen required by hydrogen} = 0.5 \times 18 = 9 \text{ kmol}$$

Theoretical requirement of oxygen is

$$\frac{(10.65 + 5.0 + 9.0)}{100} \times 31.4848 = 7.76 \text{ kmol}$$

The value obtained is equal to the theoretical requirement already calculated in part (b) on the basis of the flue gas analysis. This will rarely be the case in many practical situations. Though the composition of the products of combustion is a unique function of the composition of the fuel and the air-fuel ratio employed, since the flue gas analysis and the fuel analysis are done by two independent measurements, these data are rarely consistent. Any inconsistency in these measurements may lead to difference in the values calculated for theoretical air requirement by different methods. For example, try the following problem:

Producer gas containing 5.3% CO_2, 21.1% CO, 15.3% H_2, 1.0% CH_4, and 57.3% N_2 is burned in a furnace in an excess supply of air. The flue gas contains 14.1% CO_2, 2.3% O_2 and 83.6% N_2. Find the percent excess air.

Calculate the percent excess air by the following three different formulae:

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

$$\text{Percent excess} = \frac{\text{excess oxygen}}{\text{oxygen supplied} - \text{excess oxygen}} \times 100$$

$$\text{Percent excess} = \frac{\text{oxygen supplied} - \text{theoretical oxygen}}{\text{theoretical oxygen}} \times 100$$

and you will see that the percent excess air calculated by these different formulae are not the same.

10.2 OXIDATION OF SULPHUR COMPOUNDS AND RELATED PROCESSES

Sulphur is one of the raw materials for the production of sulphuric acid. It is available as elemental sulphur or as sulphide ores such as pyrites. Combustion of sulphur or sulphide ores is carried out for producing sulphur dioxide. Some sulphur trioxide is also formed during combustion. It is usually impossible to eliminate completely the formation of sulphur trioxide. Usually, about 2–10 % of the sulphur burned is converted to trioxide.

$$S + O_2 \rightarrow SO_2$$

$$2S + 3O_2 \rightarrow 2SO_3$$

In the combustion gas analysis, the SO_3 content will not be given since it is removed from the gas as H_2SO_4 before the analysis. However, its concentration in the gas can be determined from the moles of oxygen supplied for combustion, which in turn is calculated from the nitrogen content of the gas, and the oxygen that is accounted for in the SO_3-free gas. The difference between the oxygen supplied and the oxygen accounted for in the product gas is the oxygen that is consumed for the formation of SO_3.

When iron pyrites is burned in air the following reactions occur:

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$
$$4FeS_2 + 15O_2 \rightarrow 2Fe_2O_3 + 8SO_3$$

Since the percent of SO_3 is not reported in the burner gas analysis, it has to be determined by the quantity of oxygen unaccounted for in the analysis. The oxygen equivalent of nitrogen in the burner gas gives the amount of oxygen supplied through air. Subtracting from this the oxygen consumed for the formation of SO_2 and the excess oxygen present in the burner gas, we get the oxygen that is unaccounted. The moles of SO_3 formed with this oxygen can be calculated. It is probable that some of the SO_3 that is formed gets adsorbed in the solid refuse known as *cinder* formed on combustion. Analysis of the cinder is necessary to determine the fraction of the SO_3 formed that is adsorbed in it. The cinder is made up of Fe_2O_3 formed during the reaction, the unburned sulphides, and the incombustible materials known as *gangue*.

Assume that the burner gas analyzes 5% SO_2 and 10% oxygen, the rest being nitrogen. The number of moles of oxygen supplied is obtained from the moles of nitrogen in the burner gas. For a basis of 100 moles of the burner gas, the number of moles of oxygen supplied is $85 \times \frac{21}{79} = 22.595$ mol. The amount of oxygen consumed for the formation of 5 moles of SO_2 is, according to the chemical reaction given above, $5 \times \frac{11}{8} = 6.875$ mol. Therefore, the amount of oxygen unaccounted for is $22.595 - 6.875 - 10 = 5.72$ mol. Since according to the reaction equation, 15 moles of O_2 is required for the formation of 8 moles of SO_3, the moles of SO_3 formed is $5.72 \times \frac{8}{15} = 3.05$ mol. Not all this SO_3 may be present in the burner gas. A part may get adsorbed on the cinder. The quantity adsorbed is to be measured by analysis of the cinder, and by subtracting this quantity from the total SO_3 produced, the SO_3 in the burner gas can be determined.

In the contact process for the manufacture of sulphuric acid, SO_2 is converted to SO_3 in series of vessels known as *converters*.

$$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$$

For completing the conversion of SO_2 to SO_3, secondary air supply may be necessary in the converters. The SO_3 leaving the converters is absorbed in concentrated sulphuric acid by admitting the gas at the bottom of an absorption column packed with ceramic packings. 98.5 to 99% acid is used as absorption solvent, and it is fed at the top and flows counter-current to the gas. Usually a 20% *oleum* product is obtained as the concentrated solution leaving the absorption tower. (Oleum is SO_3 dissolved in H_2SO_4. One hundred kilograms of 20% oleum contains 20 kg SO_3 dissolved in 80 kg of H_2SO_4.)

EXAMPLE 10.7 Find the Orsat analysis of the burner gas when pure sulphur is burned with 20% excess air. Of the sulphur burned, 5% is converted to SO_3 and the rest to SO_2.

Solution *Basis:* 1 kg-atom sulphur burned

$$S + O_2 \rightarrow SO_2$$

Theoretical requirement of oxygen = 1 kmol
Oxygen supplied = 1.2 kmol

$$\text{Nitrogen in the air supplied} = 1.2 \times \frac{79}{21} = 4.514 \text{ kmol}$$

Since only 95% is converted to SO_2, SO_2 produced is 0.95 kmol. Therefore,

$$SO_3 \text{ produced} = 0.05 \text{ kmol}$$

$$\text{Oxygen consumed} = 0.95 + \frac{3}{2} \times 0.05 = 1.025 \text{ kmol}$$

Therefore,

$$\text{Oxygen remaining} = 1.2 - 1.025 = 0.175 \text{ kmol}$$

The burner gas contains:

Component	kmol	*Mole%*	*Mole% on SO_3-free basis*
SO_2	0.95	$\frac{0.95}{5.689} \times 100 = 16.70$	$\frac{0.95}{5.689 - 0.05} \times 100 = 16.85$
SO_3	0.05	$\frac{0.05}{5.689} \times 100 = 0.88$	
O_2	0.175	$\frac{0.175}{5.689} \times 100 = 3.08$	$\frac{0.175}{5.689 - 0.05} \times 100 = 3.10$
N_2	4.514	$\frac{4.514}{5.689} \times 100 = 79.34$	$\frac{4.514}{5.689 - 0.05} \times 100 = 80.05$
Total	5.689		

The results in the last column gives the Orsat analysis of the burner gas.

EXAMPLE 10.8 In a sulphuric acid plant, pyrites containing 50% (weight) sulphur is burned to give SO_2 which is subsequently converted to SO_3 in a converter. The analysis of the burner gas shows 9.5% SO_2 and 7.0% oxygen. The cinder is analysed and it is found that it contains 2.5% sulphur as SO_3. Assuming that all the sulphur in the feed is burned, calculate the following:

(a) The weight of pyrites burned per 100 kmol SO_3-free burner gas
(b) The weight of cinder obtained per 100 kmol SO_3-free burner gas
(c) The percent of the sulphur in the charge that is lost in the cinder
(d) The percent of sulphur charged that is there in the burner gas as SO_3

Solution *Basis:* 100 kmol SO_3-free burner gas
The amount of nitrogen present in the burner gas is

$$100 - (9.5 + 7.0) = 83.5 \text{ kmol}$$

Since the nitrogen in the burner gas is that present in the air supplied for combustion, the amount of oxygen supplied is

$$83.5\times\frac{21}{79}=22.20\text{ kmol}$$

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$

$$4FeS_2 + 15O_2 \rightarrow 2Fe_2O_3 + 8SO_3$$

With every 8 kmol SO_2 in the burner gas, 2 kmol Fe_2O_3 is produced accounting for 3 mol of oxygen. Therefore the total moles of oxygen accounted for = Moles of oxygen in the burner gas + Moles of oxygen in the cinder as Fe_2O_3. This is equal to

$$9.5 + 7.0 + 9.5 \times \frac{3}{8} = 20.06 \text{ kmol}$$

The amount of oxygen unaccounted = 22.20 – 20.06 = 2.14 kmol.

2.14 kmol oxygen is consumed by sulphur in the pyrites for the formation of SO_3. As 15 mol oxygen is required for 8 mol SO_3, the total SO_3 formed is

$$2.14\times\frac{8}{15}=1.14\text{ kmol}$$

(a) Total S burned = 9.5 + 1.14 = 10.64 kmol = 10.64 × 32.064 = 341.16 kg
This constitutes 50% of the pyrites burned. The total pyrites burned is

$$\frac{341.16}{0.5}=682.32\text{ kg}$$

(b) 10.64 kmol sulphur is equivalent to $\frac{10.64}{2}$ = 5.32 kmol FeS_2. Since the molecular weight of FeS_2 is 119.975, the mass of FeS_2 present in the ore is

$$5.32 \times 119.975 = 638.27 \text{ kg}$$

Weight of gangue = weight of pyrites burned – weight of FeS_2 in the ore

$$= 682.32 - 638.27 = 44.05 \text{ kg}$$

5.32 kmol FeS_2 on combustion will produce

$$5.32 \times \frac{1}{2} = 2.66 \text{ kmol } Fe_2O_3$$

Therefore, the mass of Fe_2O_3 in the cinder is

$$2.66 \times 159.694 = 424.79 \text{ kg}$$

The cinder contains 2.5% sulphur as SO_3. That is, 100 kg of cinder contains

$$\frac{2.5}{32.064} = 0.078 \text{ kmol S or } 0.078 \text{ kmol } SO_3.$$

SO_3 present in 100 kg of cinder is

$$0.078 \times 80.064 = 6.245 \text{ kg}$$

The Fe_2O_3 and gangue together constitutes 100 – 6.245 = 93.755% of the total weight of cinder.

Let x be the weight of cinder. Then,

$$0.937\,55x = 424.79 + 44.05 \quad \text{or} \quad x = 500.07 \text{ kg}$$

Hence, the weight of cinder produced = 500.07 kg.

(c) Since 100 kg of cinder contains 0.078 kmol sulphur, the total amount of sulphur lost in the cinder is

$$500.07 \times \frac{0.078}{100} = 0.3901 \text{ kmol sulphur.}$$

The total amount of sulphur burned is 10.64 kmol.

Percent of total S burned that is lost in the cinder is

$$\frac{0.3901}{10.64} \times 100 = 3.67\%$$

(d) The mass of SO_3 present in the cinder is

$$500.07 \times \frac{6.245}{100} = 31.23 \text{ kg}$$

31.23 kg of SO_3 is equivalent to 0.3904 kmol SO_3. That is 0.3904 kmol SO_3 gets adsorbed in the cinder. Since the total amount of SO_3 formed is 1.14 kmol, the amount of SO_3 present in the burner gas is

$$1.14 - 0.3904 = 0.7496 \text{ kmol}$$

Therefore, the percent of S charged that is present as SO_3 in the burner gas is

$$\frac{0.7496}{10.64} \times 100 = 7.05\%$$

10.3 CARBON DIOXIDE FROM LIMESTONE

The processes analyzed in this section are based on limestone as the raw material and are important in the lime and cement industries. Lime, sold as quicklime consists of 90% calcium oxide and 0–5% magnesia. Lime is produced by the calcination of limestone in lime kilns (rotary kilns are preferred for large production rates) where the carbonates of calcium and magnesium are converted to the respective oxides, and carbon dioxide is obtained as a by-product. The reactions occurring are the following:

$$CaCO_3 + C + O_2 \rightarrow CaO + 2CO_2$$
$$MgCO_3 + C + O_2 \rightarrow MgO + 2CO_2$$

As the suitability of lime for any particular use depends on its composition, it is frequently necessary to regulate the rate of supply and composition of the charge to the calciner. The material balance calculations are necessary for achieving this as well as for estimating the amount of CO_2 obtained as the by-product. Carbon dioxide is used in food industries as a refrigerant and in carbonated beverages. Also, it is an important fire-extinguisher and a raw material for many products.

The amount of lime produced per unit weight of fuel charged is known as the *fuel ratio*, which can be readily evaluated from the analysis of kiln gas provided the analysis of fuel and limestone are known. If the fuel ratio is specified, the composition of the product can be estimated by the material balance. The following examples illustrate the calculations generally encountered in the calcination of limestone.

EXAMPLE 10.10 Limestone mixed with coke is being burnt in a kiln. An average analysis of the limestone is $CaCO_3 = 84.5\%$, $MgCO_3 = 11.5\%$ and the rest inerts. The coke contains 76.0% carbon, 21% ash and 3% moisture. The calcination of $CaCO_3$ is only 95% complete and that of $MgCO_3$ is 90%. The carbon in the coke is completely burnt to CO_2. The kiln is fed with one kg of coke per 5 kg of limestone. Calculate the weight percent of CaO in the product leaving the kiln. Assume that the moisture in the feed is completely vaporized.

Solution *Basis:* A charge consisting of 5 kg of limestone and 1 kg of coke

The limestone charged as feed consists of the following constituents:

$$CaCO_3 = 5 \times 0.845 = 4.225 \text{ kg} = \frac{4.225}{100.09} = 0.0422 \text{ kmol}$$

$$MgCO_3 = 5 \times 0.115 = 0.575 \text{ kg} = \frac{0.575}{84.312} = 6.82 \times 10^{-3} \text{ kmol}$$

$$\text{Inerts} = 5 \times 0.04 = 0.2 \text{ kg}$$

The coke charged contains the following constituents:

$$\text{Carbon} = 0.76\ \text{kg} = \frac{0.76}{12} = 0.0633\ \text{kmol}$$

$$\text{Water} = 0.03\ \text{kg} = \frac{0.03}{18.016} = 1.665 \times 10^{-3}\ \text{kmol}$$

$$\text{Ash} = 0.21\ \text{kg}$$

The reactions occurring are as follows:

$$CaCO_3 + C + O_2 \rightarrow CaO + 2CO_2$$

$$MgCO_3 + C + O_2 \rightarrow MgO + 2CO_2$$

The product contains CaO, MgO, unconverted $CaCO_3$ and $MgCO_3$, inerts and ash

$$CaO = 0.95 \times 0.0422 = 0.0401\ \text{kmol} = 0.0401 \times 56.08 = 2.2482\ \text{kg}$$

$$MgO = 0.90 \times 6.82 \times 10^{-3} = 6.138 \times 10^{-3}\ \text{kmol} = 6.138 \times 10^{-3} \times 40.312 = 0.2474\ \text{kg}$$

$$CaCO_3 = 0.05 \times 4.225 = 0.2113\ \text{kg}$$

$$MgCO_3 = 0.10 \times 0.575 = 0.0575\ \text{kg}$$

$$\text{Inerts} = 0.2\ \text{kg}$$

$$\text{Ash} = 0.21\ \text{kg}$$

The total weight of product is

$$2.2482 + 0.2474 + 0.2113 + 0.0575 + 0.2 + 0.21 = 3.1744\ \text{kg}$$

The weight percent of CaO in the product leaving the kiln is

$$\frac{2.2482}{3.1744} \times 100 = 70.82\%$$

EXAMPLE 10.11 Pure CO_2 may be prepared by treating limestone with aqueous H_2SO_4. The limestone used contained $CaCO_3$ and $MgCO_3$, the remainder being inert insoluble materials. The acid used contained 12% H_2SO_4 by weight. The residue from the process had the following composition—$CaSO_4$: 9.00%, $MgSO_4$: 5.00%, H_2SO_4: 1.2%, inerts: 0.50%, CO_2: 0.2% and H_2O: 84.10%. During the process, the mass was warmed, and CO_2 and H_2O vapour were removed. Calculate the following:

(a) The analysis of limestone used
(b) The percentage excess of acid used
(c) The mass of water vaporized and removed per 100 kg of limestone
(d) The mass of CO_2 obtained per 100 kg of limestone

Solution *Basis:* 100 kg of residue
Molecular weight of $CaSO_4$ = 136.144 and molecular weight of $MgSO_4$ = 120.376
The amount of $CaSO_4$ present in the residue is

$$9.00\ \text{kg} = \frac{9.00}{136.144} = 0.0661\ \text{kmol}$$

The amount of $MgSO_4$ present in the residue is

$$5.00\text{ kg} = \frac{5.00}{120.376} = 0.0415\text{ kmol}$$

(a)
$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2$$

$$MgCO_3 + H_2SO_4 \rightarrow MgSO_4 + H_2O + CO_2$$

The mass of $CaCO_3$ burned to produce 0.0661 kmol $CaSO_4$ is

$$0.0661\text{ kmol} = 0.0661 \times 100.08 = 6.6153\text{ kg}$$

The mass of $MgCO_3$ burned to produce 0.0415 kmol $MgSO_4$ is

$$0.0415\text{ kmol} = 0.0415 \times 84.312 = 3.4989\text{ kg}$$

Therefore, the limestone used has the following analysis:

Constituent	*Mass* (kg)	*Weight* %
$CaCO_3$	6.6153	$\frac{6.6153}{10.6142} \times 100 = 62.32$
$MgCO_3$	3.4989	$\frac{3.4989}{10.6142} \times 100 = 32.96$
Inerts	0.50	$(100 - 62.32 - 32.96) = 4.72$
Total	10.6142	

(b) The amount of H_2SO_4 required by $CaCO_3$ and $MgCO_3$ for complete reaction is

$$(0.0661 + 0.0415) = 0.1076\text{ kmol} = 10.5534\text{ kg}$$

The mass of excess H_2SO_4 present in the refuse is 1.2 kg.

$$\text{Percent excess acid supplied} = \frac{1.2}{10.5534} \times 100 = 11.37\%$$

(c)
$$\text{Total sulphuric acid supplied} = 10.5534 + 1.2 = 11.7534\text{ kg}$$

Since the acid used is 12% sulphuric acid, the mass of water entering the process is

$$\frac{11.7534}{0.12} \times 0.88 = 86.1916\text{ kg}$$

The amount of water produced in the reaction is

$$0.1076 \times 18.016 = 1.9385\text{ kg}$$

$$\text{Total water present} = 86.1916 + 1.9385 = 88.1301\text{ kg}$$

Since 100 kg of residue contains 84.10 kg of water, the mass of water vaporized is

$$88.1301 - 84.10 = 4.0301\text{ kg}$$

This is the amount of water vaporized per 10.6142 kg of limestone.
The amount of water vaporized per 100 kg of limestone is

$$\frac{4.0301}{10.6142} \times 100 = 37.97\text{ kg}$$

(d) The amount of CO_2 produced per 100 kg of residue is

$$0.1076 \text{ kmol} = 0.1076 \times 44 = 4.7344 \text{ kg}$$

The amount of CO_2 released per 100 kg of residue is

$$4.7344 - 0.20 = 4.5344 \text{ kg}$$

Therefore, the amount of CO_2 released per 100 kg of limestone is

$$\frac{4.5344}{10.6142} \times 100 = 42.72 \text{ kg}$$

13

Energy Balance
Thermochemistry

Thermochemistry plays a very significant role in the design and analysis of chemical processes. Energy balances in processes involving chemical reactions are important in the design of process reactors for carrying out industrial reactions under specified conditions. A chemical engineer should be able to make accurate estimates of energy requirements for carrying out chemical processes and the energy changes involved in various stages of the process. The enthalpy changes involved in chemical reactions, the influence of temperature on the enthalpy changes of chemical reactions and the methods for the evaluation of the heat of reaction are important for process calculations and these are discussed in the following sections.

13.1 HEAT EFFECTS ACCOMPANYING CHEMICAL REACTIONS

Energy changes are involved in the course of a chemical reaction; heat is either absorbed or evolved during the reaction. The reactions in which heat is absorbed are called *endothermic reactions* and those in which heat is evolved are called *exothermic reactions*. Knowledge of the heat effects accompanying chemical reactions and the influence of the operating parameters on these energy changes is essential for the proper design and operation of reaction vessels.

13.1.1 The Standard Heat of Reaction

By heat of reaction we mean the change in enthalpy of the system for the reaction proceeding at constant temperature. It is the difference between the enthalpy of products and the enthalpy of reactants and is denoted by ΔH. Thus, positive values of ΔH indicate increase in the enthalpy and therefore represent endothermic reactions and, negative values of ΔH mean decrease in enthalpy and therefore refer to exothermic reactions.

$$\Delta H_r = \Sigma H_P - \Sigma H_R \tag{13.1}$$

where ΔH_r is the heat of reaction and H_P and H_R are the enthalpies of the products and reactants respectively. To complete the definition of the heat of reaction, it is necessary to specify the conditions of every product and reactant involved in the reaction.

The *standard heat of reaction* is the enthalpy change accompanying a reaction when both the reactants and products are at their standard states at constant temperature T. It is represented by the symbol ΔH_T^0, the superscript '0' indicating that the heat of reaction refers to the standard conditions. By convention, the standard heats of reaction are reported at a temperature of 298 K and are represented by ΔH_{298}^0. The standard state is specified by specifying the pressure, composition and the state of aggregation, or the physical state of the species. By convention, the standard state pressure is one standard atmosphere. The choice of one bar as the standard state pressure is now widely accepted. The species are assumed to be pure components in the standard state. The physical state of the components are: for gases, the pure substances in the ideal gas state at 1 bar; for solids and liquids, the pure substances in the solid or liquid state respectively at 1 bar.

For example, consider the following reaction:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H_{298}^0 = -890 \text{ kJ}$$

This equation means 1 mole of methane in the form of pure methane gas at 1 bar reacts completely with 2 moles of pure oxygen gas at 1 bar to produce one mole of pure CO_2 gas and 2 moles of pure liquid water at 1 bar, all the substances being at 298 K. Since the heat of reaction is negative, the above equation says that 890 kJ heat is liberated in the reaction. In the reaction

$$2C(s) + O_2(g) \rightarrow 2CO(g) \qquad \Delta H_{298}^0 = -221.2 \text{ kJ}$$

2 mol solid carbon reacts with 1 mol gaseous oxygen both at their standard state of 1 bar giving 2 mol gaseous carbon monoxide also at the standard state of 1 bar, the temperature being kept constant at 298 K. During this reaction 221.2 kJ of heat is liberated.

The heat evolved or absorbed in a chemical reaction corresponds to the stoichiometric numbers of the reacting species as given in the chemical equation. For example, when the above reaction is written as follows, the standard heat of reaction is just half of the value in the previous equation:

$$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g) \qquad \Delta H_{298}^0 = -110.6 \text{ kJ}$$

In the absence of chemical equation, the reported values of heat of reaction should clearly mention the basis as given below:

$$\Delta H_r^0 = -110.6 \text{ kJ per mol CO}$$

In the case of *incomplete reactions*, the heat of reaction is to be calculated considering only the quantity of reactants actually consumed or the quantity of the products actually formed in the reaction. Suppose that the heat liberated on the combustion of 12 kg of carbon is to be calculated. We have seen that on complete combustion, the heat liberated is 110.6×10^3 kJ. If only 50% carbon is reacted, the heat liberated will be $0.5 \times (110.6 \times 10^3)$ kJ.

EXAMPLE 13.1 A gas mixture analyzing 20% (mol) CO, 30% (mol) H_2 and 50% (mol) N_2 is completely burned in air. The following heat of reaction data are available:

$$CO(g) + \frac{1}{2}O_2(g) \to CO_2(g) \qquad \Delta H_r^0 = -282.91 \text{ kJ/mol}$$

$$H_2(g) + \frac{1}{2}O_2(g) \to H_2O(g) \qquad \Delta H_r^0 = -241.83 \text{ kJ/mol}$$

(a) Determine the amount of heat liberated on the complete combustion of 100 mol of the gas mixture.

(b) If only 90% of the CO and 80% of the H_2 react, how much heat is liberated on the combustion of 100 mol of the mixture?

Solution *Basis:* 100 mol gas mixture burned

(a) The heats of reactions are negative, indicating that heat is liberated during the reaction. According to the stoichiometric equation, 1 mol CO on combustion liberates 282.91 kJ of heat. The number of moles of CO present is 20 mol. Therefore, the amount of heat liberated on combustion of CO = 20 × 282.91 kJ = 5658.2. Similarly, the amount of heat liberated on combustion of 30 mol hydrogen = 30 × 241.83 kJ = 7254.9 kJ. Therefore, the total amount of heat liberated is

$$5658.2 + 7254.9 = 12913.1 \text{ kJ}$$

(b) The number of moles of CO reacted is

$$0.9 \times 20 = 18 \text{ mol}$$

The number of moles of hydrogen reacted is

$$0.8 \times 30 = 24 \text{ mol}$$

The total amount of heat liberated is

$$18 \times 282.91 + 24 \times 241.83 = 10{,}896.3 \text{ kJ}$$

13.1.2 The Standard Heat of Combustion

When the reaction under consideration is a combustion reaction, the heat of reaction is known as *heat of combustion*. The heat of combustion of a substance is the heat of reaction when a substance is oxidized with molecular oxygen. The standard heat of combustion at temperature T is the enthalpy change when the substance at its standard state and temperature T, undergoes combustion, yielding products also at their standard state and temperature T. In the following reaction, the standard heat of combustion of liquid acetaldehyde at 298 K, $\Delta H_{c,298}^0$, is −1168.12 kJ/kmol.

$$CH_3CHO\ (l) + \frac{5}{2}O_2(g) \to 2CO_2(g) + 2H_2O\ (l) \qquad \Delta H_{c,298}^0 = -1168.12 \text{ kJ}$$

(*Note:* The heat of combustion values are reported on the basis that water formed is in the liquid state.)

The heat of combustion is usually expressed per mole of the substance reacted. The negative of the heat of combustion of a fuel is frequently referred to as its *heating value*. This is the energy exchanged with the surroundings when the unit mass of fuel is burnt in oxygen. The heat of combustion of a fuel is a negative quantity, whereas the heating value is positive. When water formed during combustion is in the liquid state, the energy liberated will be more than the energy liberated when the combustion products contain water in the vapour state. The heating value in the former is known as *higher heating value* or *gross heating value*, and that in the latter is known as *lower heating value* or *net heating value*. Unless otherwise stated, the heating value reported along with the fuel analysis is the gross heating value since this is the one that is usually determined using a calorimeter.

The gross heating value of coal can be calculated using the Dülong formula:

$$\text{Heating value (kJ/kg of coal)} = 338.2w_C + 1442.8w_{H(net)} + 94.2w_S$$

where w_C, w_S, $w_{H(net)}$ are, respectively, the weight percentage of carbon, sulphur and net hydrogen. The net hydrogen

$$w_{H(net)} = w_H - \frac{w_O}{8}$$

where w_O is the weight percentage of oxygen and w_H is the weight percentage of hydrogen.

13.1.3 The Standard Heat of Formation

The heat of formation is the heat evolved or absorbed in the formation of one mole of a substance from its constituent elements or the change in enthalpy accompanying the formation of one mole of a substance from the constituent elements is termed the *heat of formation*. When the reactants and products are at their standard states, the heat of formation is called *standard heat of formation*. The enthalpy of formation of the elements is taken as zero. The standard heat of formation of carbon monoxide gas at 298 K, $\Delta H^0_{f,298}$, is -110.6 kJ/mol. The standard heat of formation at 298 K for methyl chloride is -81.923 kJ/mol. These statements are equivalent to the following equations:

$$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g) \qquad \Delta H^0_{f,298} = -110.6 \text{ kJ}$$

$$C(s) + \frac{3}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightarrow CH_3Cl(g) \qquad \Delta H^0_{f,298} = -81.923 \text{ kJ}$$

The standard heat of formation of sulphuric acid is given by the equation

$$H_2(g) + S(s) + 2O_2(g) \rightarrow H_2SO_4(l), \qquad \Delta H^0_{f,298} = -811.86 \text{ kJ}$$

which means that when one mole sulphuric acid is formed from its constituent elements all at 298 K and a pressure of one bar, 811.86 kJ heat is evolved.

Standard heats of formation and combustion data for certain compounds are given in Appendix (Table A.2).

13.1.4 Hess's Law of Constant Heat Summation

Heat of reaction represents the difference between the enthalpy of products and the enthalpy of reactants. Enthalpy as we know, is a state function and the heat of reaction, therefore, depends only on the initial and final states, no matter how this change is carried out. *The net heat evolved or absorbed in a chemical reaction is the same whether the reaction takes place in a single step or in a series of steps*. This is known as *Hess's law*. This law permits us to treat all thermochemical equations as algebraic equations. Using this, we can calculate the heat of formation of a compound from a series of reactions not involving the direct formation of the compound from its elements. For example, the heat of formation of a compound can be calculated if the heat of combustion data of all the species involved in the formation reaction are known. Similarly, if the data on the heat of formation of all the substances taking part in a chemical reaction are available, the heat of reaction may be readily calculated.

Hess's law permits us to estimate accurately the heat of formation of compounds that are difficult to determine experimentally. For example, the heat of formation of $CaCO_3(s)$ can be estimated to be -1207.8 kJ, given the following heat of reaction data:

$$Ca(s) + \frac{1}{2}O_2(g) \rightarrow CaO(s) \qquad \Delta H^0 = -635.8 \text{ kJ}$$

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H^0 = -393.8 \text{ kJ}$$

$$CaO(s) + CO_2(g) \rightarrow CaCO_3 \qquad \Delta H^0 = -178.2 \text{ kJ}$$

Adding the above three equations together gives

$$Ca(s) + C(s) + \frac{3}{2}O_2(g) \rightarrow CaCO_3(s)$$

$$\Delta H^0 = -635.8 + (-393.8) + (-178.2) = -1207.8 \text{ kJ}$$

Heat of reaction from heat of combustion or heat of formation data: The heat of reaction may be calculated as the difference between the algebraic sum of the heat of combustion of the reactants and the algebraic sum of the heat of combustion of products.

$$\Delta H^0 = \sum_{\text{Reactants}} \Delta H_c^0 - \sum_{\text{Products}} \Delta H_c^0 \tag{13.2}$$

It can also be shown that the standard heat of reaction is the difference between the algebraic sum of the standard heat of formation of products and that of the reactants.

$$\Delta H^0 = \sum_{\text{Products}} \Delta H_f^0 - \sum_{\text{Reactants}} \Delta H_f^0 \tag{13.3}$$

EXAMPLE 13.2 The heat of combustion of methane, carbon and hydrogen are -890.4 kJ/mol, -393.51 kJ/mol and -285.84 kJ/mol respectively. Calculate the heat of formation of methane.

Solution The desired reaction is

$$C(s) + 2H_2(g) \rightarrow CH_4(g) \qquad \Delta H_f^0 = ?$$

The heat of reaction (in this case, the heat of formation) can be calculated either by using the Hess's law or by using Eq. (13.2) directly.

Using Hess's law: Since the heat of combustion data are available, the following combustion reactions may be written:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H^0 = -890.4 \text{ kJ} \qquad (A)$$

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H^0 = -393.51 \text{ kJ} \qquad (B)$$

$$H_2(g) + \frac{1}{2}O_2(l) \rightarrow H_2O(l) \qquad \Delta H^0 = -285.84 \text{ kJ} \qquad (C)$$

Multiply Eq. (C) by 2 and add the result to Eq. (B) and subtract Eq. (A) from the sum. The result is the desired reaction. That is, Eq. (B) + 2 × Eq. (C) – Eq. (A) gives

$$C(s) + 2H_2(g) \rightarrow CH_4(g)$$

The same algebraic operations are to be carried out on the respective heat of reactions. By Hess's law, the heat of desired reaction is

$$\Delta H^0\ (B) + 2\Delta H^0\ (C) - \Delta H^0\ (A) = -393.51 + 2(-285.84) - (-890.4) = -74.79 \text{ kJ}$$

Using Eq. (13.2): Heat of reaction can be calculated from heat of combustion data using Eq. (13.2). The heat of reaction is the sum of the heat of combustion of all the reactants in the desired reaction minus the sum of the heat of combustion of all the products of the desired reaction. Here the reactants are one mole of carbon and two moles hydrogen, and the product is one mole of methane. Therefore, the heat of reaction is

$$1 \times (-393.51) + 2 \times (-285.84) - (-890.4) = -74.79 \text{ kJ}$$

Therefore, the heat of formation of methane is – 74.79 kJ.

EXAMPLE 13.3 Coal having the following analysis on a weight basis has a gross heating value of 29 000 kJ/kg: carbon, 70.0%; hydrogen, 5.5%; nitrogen, 1.5%; sulphur, 3.0%; oxygen: 13.0%; ash, 7.0%. Calculate the net heating value given that the latent heat of vaporization of water is 2370 kJ/kg water.

Solution *Basis:* 1 kg of coal burned

The amount of hydrogen present in the coal is

$$\frac{5.5}{100 \times 2.016} = 27.28 \times 10^{-3} \text{ kmol}$$

The amount of water formed on combustion is

$$27.28 \times 10^{-3} \text{ kmol} = 0.492 \text{ kg}$$

The amount of heat required for vaporization of 0.492 kg of water is

$$0.492 \times 2370 = 1164.9 \text{ kJ}$$

The net heating value of the coal is the heat given out when all the water formed is in the vapour state. Therefore, the net heating value will be less than the gross heating value by the quantity of heat required for vaporization of the water formed on combustion. Thus, the net heating value is

$$29\,000 - 1164.9 = 27\,835.1 \text{ kJ/kg}$$

EXAMPLE 13.5 Calculate the heat of reaction for the esterification of ethyl alcohol with acetic acid if the standard heats of combustion are: ethyl alcohol (l), –1366.91 kJ/mol; acetic acid (l), – 871.69 kJ/mol; ethyl acetate (l), –2274.48 kJ/mol.

Solution The esterification reaction may be represented as

$$C_2H_5OH\ (l) + CH_3COOH\ (l) \rightarrow C_2H_5COOCH_3\ (l) + H_2O\ (l) \qquad \Delta H^0_{298} = ?$$

Using Eq. (13.2): To calculate heat of reaction from the heat of combustion data Eq. (13.2) may be directly used.

$$\Delta H^0 = \sum_{\text{Reactants}} \Delta H_c^0 - \sum_{\text{Products}} \Delta H_c^0$$

Here,

$$\sum_{\text{Reactants}} \Delta H_c^0 = -1366.91 - 871.69 = -2238.6 \text{ kJ}$$

$$\sum_{\text{Products}} \Delta H_c^0 = -2274.48 + 0 = -2274.48 \text{ kJ}$$

(Note that the heats of combustion of H_2O and CO_2 are zero.)

Substituting these into Eq. (13.2), we get

$$\Delta H^0 = -2238.6 - (-2274.48) = 35.88 \text{ kJ}$$

Using Hess's law: The given data on heat of combustion may be used to write the following chemical equations:

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l) \qquad \Delta H_c^0 = -\ 1366.91 \text{ kJ} \qquad \text{(A)}$$

$$CH_3COOH(l) + 2O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l) \qquad \Delta H_c^0 = -\ 871.691 \text{ kJ} \qquad \text{(B)}$$

$$C_2H_5COOCH_3(l) + 5O_2(g) \rightarrow 4CO_2(g) + 4H_2O(l) \qquad \Delta H_c^0 = -\ 2274.48 \text{ kJ} \qquad \text{(C)}$$

Add Eqs. (A) and (B) and subtract Eq. (C) from the result. We get

$$C_2H_5OH\ (l) + CH_3COOH\ (l) \rightarrow C_2H_5COOCH_3\ (l) + H_2O\ (l)$$

By Hess's law the same algebraic operations may be performed on the heat of combustion data as well, with the result that

$$\Delta H^0_{298} = \Delta H_c^0(\text{A}) + \Delta H_c^0(\text{B}) + \Delta H_c^0(\text{C}) = -1366.91 - 871.69 - (-2274.48) = 35.88 \text{ kJ}$$

EXAMPLE 13.6 The vapour-phase hydration of ethylene to ethanol is represented by:

$$C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(g)$$

Calculate the standard heat of reaction if the following data are available:

$$2CO_2(g) + 3H_2O(l) \rightarrow C_2H_5OH(l) + 3O_2(g) \quad \Delta H^0_{298} = 1366.91 \text{ kJ}$$

The standard heat of combustion of ethylene at 298 K is −1410.99 kJ/mol and heats of vaporization of water and ethanol are, respectively, 44.04 kJ/mol and 42.37 kJ/mol.

Solution The following equations may be formulated using the given data:

$$2CO_2(g) + 3H_2O(l) \rightarrow C_2H_5OH(l) + 3O_2(g) \qquad \Delta H^0_{298} = 1366.91 \text{ kJ} \qquad \text{(A)}$$

$$C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2 + 2H_2O(l) \qquad \Delta H^0_{298} = -1410.99 \text{ kJ} \qquad \text{(B)}$$

$$H_2O(l) \rightarrow H_2O(g) \qquad \Delta H_{v,298} = 44.04 \text{ kJ} \qquad \text{(C)}$$

$$C_2H_5OH(l) \rightarrow C_2H_5OH(g) \qquad \Delta H_{v,298} = 42.37 \text{ kJ} \qquad \text{(D)}$$

Perform the following arithmetic operations on the above equations:

$$\text{Eq. (A)} + \text{Eq. (B)} + \text{Eq. (D)} - \text{Eq. (C)}$$

The result is

$$C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(g)$$

$$\Delta H^0_{298} = \Delta H^0_{298}(\text{A}) + \Delta H^0_{298}(\text{B}) + \Delta H^0_{298}(\text{D}) - \Delta H^0_{298}(\text{C}) = -45.75 \text{ kJ}$$

EXAMPLE 13.7 Calculate the standard heat of formation of acetylene (C_2H_2) given that the standard heat of combustion of acetylene is − 1299.61 kJ, the standard heat of combustion of carbon is − 393.51 kJ and the standard heat of formation of liquid water is − 285.84 kJ.

Solution We have the following data:

$$C_2H_2(g) + \frac{5}{2}O_2(g) \rightarrow 2CO_2(g) + H_2O(l) \qquad \Delta H^0_{298} = -1299.61 \text{ kJ} \qquad (A)$$

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H^0_{298} = -393.51 \text{ kJ} \qquad (B)$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \Delta H^0_{298} = -285.84 \text{ kJ} \qquad (C)$$

We can apply Hess's law to calculate the heat of the desired formation reaction.

$$2C(s) + H_2(g) \rightarrow C_2H_2(g) \qquad \Delta H^0_{298} = ?$$

Multiply Eq. (B) by 2, add Eq. (C) to it and subtract Eq. (A) from the result. We get

$$2C(s) + H_2(g) \rightarrow C_2H_5(g)$$

$$\Delta H^0_{298} = 2 \times (-393.51) - 285.84 - (-1299.61) = 226.75 \text{ kJ}$$

EXAMPLE 13.8 In a sulphuric acid plant, sulphur dioxide is obtained by the roasting of iron pyrites containing 80.0% FeS_2 and 20% gangue. Iron sulphide reacts with oxygen according to the reaction

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$

The cinder formed on the combustion analyzes 5.0% FeS_2. Determine the standard heat of reaction per kilogram of ore, given the following standard heat of formation values at 298 K: $FeS_2(s) = -178.02$ kJ/mol, $Fe_2O_3(s) = -822.71$ kJ/mol and $SO_2(g) = -296.9$ kJ/mol.

Solution *Basis:* 100 kg of pyrites charged.

Let x kg of FeS_2 be leaving with the cinder unburned. Then the cinder has the following composition:

Material	*Weight* (kg)
FeS_2	x
Fe_2O_3	$\frac{(80-x)}{119.98}\times\frac{1}{2}\times 159.69 = 0.6655(80-x)$
Gangue	20
Total	$73.24 + 0.3345x$

Since the cinder contains 5.0% FeS_2, we have $\frac{x}{73.24 + 0.3345x} = 0.05$, which gives x = 3.724 kg.

Therefore, the amount of FeS_2 reacted is

$$80 - 3.724 = 76.276 \text{ kg} = \frac{76.276}{119.98} = 0.6357 \text{ kmol} = 635.7 \text{ mol}$$

The heat of reaction for the following reaction can be calculated from the heat of formation data.

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$

Using Eq. (13.3)

$$\Delta H^0 = \sum_{\text{Products}} \Delta H_f^0 - \sum_{\text{Reactants}} \Delta H_f^0$$

$$= 2 \times (-822.71) + 8 \times (-296.9) - 4 \times (-178.02) - 0 = -3308.54 \text{ kJ}$$

This is the heat of reaction when 4 mol FeS_2 is completely consumed. Here 635.7 mol FeS_2 is consumed. Therefore, the heat of reaction is

$$\frac{-3308.54}{4} \times 635.7 = -5.258 \times 10^5 \text{ kJ}$$

The heat of reaction per 1 kg of pyrites burned is

$$\frac{-5.258 \times 10^5}{100} = -5.258 \times 10^3 \text{ kJ}$$

EXAMPLE 13.9 Calculate the standard heat of formation of liquid methanol, given the standard heat of combustion of liquid methanol is -726.55 kJ/mol and the standard heat of formation of gaseous CO_2 and liquid water are, respectively, -393.51 and -285.84 kJ/mol.

Solution

Using Eq. (13.3): The combustion of liquid methanol is

$$CH_3OH(l) + \frac{3}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H_{298}^0 = -726.55 \text{ kJ} \qquad \text{(A)}$$

By Eq. (13.3), the heat of reaction is given as

$$\Delta H^0 = \sum_{\text{Products}} \Delta H_f^0 - \sum_{\text{Reactants}} \Delta H_f^0$$

Applying this equation to reaction (A), we can write

$$-726.55 = \Delta H_{f,CO_2}^0 + 2\Delta H_{f,H_2O}^0 - \Delta H_{f,CH_3OH}^0$$

$$= -393.51 + 2 \times (-285.84) - \Delta H_{f,CH_3OH}^0$$

$$= -965.19 - \Delta H_{f,CH_3OH}^0$$

or

$$\Delta H_{f,CH_3OH}^0 = -965.19 + 726.55 = -238.64 \text{ kJ}$$

Using Hess's law: The desired reaction is the formation of liquid methanol from the constituent elements.

$$C(s) + 2H_2(g) + \frac{1}{2}O_2(g) \rightarrow CH_3OH(l)$$

The available data may be put into the following forms:

$$CH_3OH(l) + \frac{3}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H^0_{298} = -726.55 \text{ kJ} \qquad (A)$$

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H^0_{298} = -393.51 \text{ kJ} \qquad (B)$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \Delta H^0_{298} = -285.84 \text{ kJ} \qquad (C)$$

The stoichiometric equation representing the formation of liquid methanol is obtained by performing the following algebraic operations on these equations.

$$\text{Eq. (B)} + 2 \times \text{Eq. (C)} - \text{Eq. (A)}$$

Therefore, the heat of formation of methanol is

$$-393.51 + 2 \times (-285.84) - (-726.55) = -238.64 \text{ kJ}$$

EXAMPLE 13.10 Calculate the gross heating value and net heating value expressed in kJ/m^3 at STP of a fuel gas having the following analysis:

CO: 21.0%, H_2 = 15.6%, CO_2: 9.0%, CH_4: 2.0%, C_2H_4: 0.4% and N_2: 52.0%

Given that the standard heats of combustion are –282.99 kJ/mol for CO, –285.84 kJ/mol for hydrogen, – 890.4 kJ/mol for methane and – 1410.99 kJ/mol for ethylene, and the heat of vaporization of water at 298 K is 44.04 kJ/mol.

Solution *Basis:* 100 mol fuel gas

The total heat evolved on combustion of the fuel is

$$21 \times (282.99) + 15.6 \times (285.84) + 2.0 \times (890.4) + 0.4 \times (1410.99) = 12\,747 \text{ kJ}$$

Since 100 mol gas at STP occupies a volume of $100 \times 22.4 \times 10^{-3} = 2.24$ m^3, the gross heating value of the fuel is

$$\frac{12\,747}{2.240} = 5691 \frac{\text{kJ}}{\text{m}^3}$$

On combustion one mol hydrogen gives one mol water, one mol methane gives two mol water and one mol ethylene gives two mol water. The number of moles of water formed on combustion of 100 mol fuel gas = 15.6 + 4.0 + 0.8 = 20.4. The amount of heat required to vaporize the water formed on combustion = 20.4 × 44.04 = 898.42 kJ.

Therefore, the net heating value is

$$5691 - 898.42 = 4792.58 \text{ kJ}$$

EXAMPLE 13.11 Calculate the standard heat of the following reaction at 298 K:

$$C_5H_{12}(g) + 8O_2(g) \rightarrow 5CO_2(g) + 6H_2O(l)$$

The standard heats of formation are as follows:

$$CO_2(g) = -393.51 \text{ kJ}, \; H_2O(g) = -241.826 \text{ kJ}, \; C_5H_{12}(g) = -146.4 \text{ kJ}$$

The latent heat of vaporization of water at 298 K is 43.967 kJ/mol.

Solution The desired reaction can be obtained as the sum of the following two reactions:

$$C_5H_{12}(g) + 8O_2(g) \rightarrow 5CO_2(g) + 6H_2O(g) \quad \Delta H_1$$

$$6H_2O(g) \rightarrow 6H_2O(l) \quad \Delta H_2$$

The heat of reaction $\Delta H^0 = \Delta H_1 + \Delta H_2$

$$\Delta H_1 = \sum_{\text{Products}} \Delta H_f^0 - \sum_{\text{Reactants}} \Delta H_f^0$$

$$= 5 \times \Delta H^0_{f,CO_2} + 6 \times \Delta H^0_{f,H_2O(g)} - \Delta H_{f,C_5H_{12}(g)}$$

$$= 5 \times (-393.51) + 6 \times (-241.826) - (-146.4) = -3272.106 \text{ kJ}$$

$$\Delta H_2 = -6 \times 43.967 = -263.802 \text{ kJ}$$

$$\Delta H^0 = \Delta H_1 + \Delta H_2 = -3272.106 - 263.802 = -3535.908 \text{ kJ}$$

13.2 EFFECT OF TEMPERATURE ON STANDARD HEAT OF REACTION

Chemical reaction can be represented as

$$\sum_i v_i A_i = 0 \tag{13.9}$$

where v_i represents the stoichiometric number of the substance taking part in the reaction. The stoichiometric number v_i is positive for products and negative for the reactants. For example, consider the reaction

$$aA + bB \rightarrow lL + mM$$

Here, a, b, l and m are called stoichiometric coefficients. This reaction may be written as

$$lL + mM - aA - bB = 0$$

in which $-a$, $-b$, l and m are called the stoichiometric numbers. If the standard heat of the reaction at temperature T_1 is known, the standard heat at any other temperature T can be determined. Generally, the standard heat of reaction at temperature 298 K (T_1) will be available, and it would be necessary to determine the standard heat at some other temperature (T). The specific heat of the components constituting the reaction system should be known as function of temperature. The calculation makes use of the fact that enthalpy is a state property. The change in enthalpy for a process occuring from a given initial state to a given final state is the same whatever be the path along which the process is carried out. The actual reaction occurring at temperature T, for which the standard heat of reaction is ΔH_T^0, may be treated as occurring along the three paths as shown in Figure 13.1.

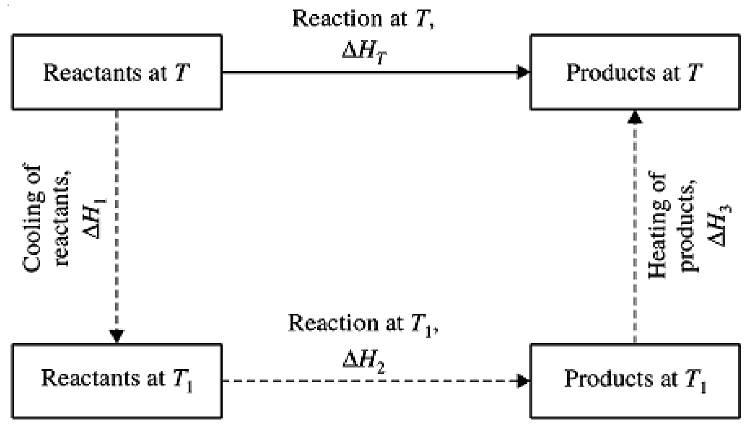


Figure 13.1 Effect of temperature on heat of reaction.

Step 1: From the initial state of temperature T the reactants are cooled to temperature T_1. The enthalpy change for this step is

$$\Delta H_1 = \sum_{\text{Reactants}} \int_{T}^{T_1} n_i C_{P,i}\, dT = \sum_{\text{Reactants}} \int_{T_1}^{T} v_i C_{P,i}\, dT \tag{13.10}$$

Step 2: The reaction is allowed to occur at temperature T_1. The enthalpy change is

$$\Delta H_2 = \Delta H_{T_1}^0 \tag{13.11}$$

Step 3: The temperature of the products is raised from T_1 to T in this step. The enthalpy change is

$$\Delta H_3 = \sum_{\text{Products}} \int_{T_1}^{T} n_i C_{P,i}\, dT = \sum_{\text{Products}} \int_{T_1}^{T} v_i C_{P,i}\, dT \tag{13.12}$$

Since the enthalpy change depends on the terminal conditions, the standard heat of reaction at temperature T is obtained by adding the preceding three equations.

$$\Delta H_T^0 = \Delta H_1 + \Delta H_2 + \Delta H_3$$

$$\Delta H_T^0 = \sum_{\text{Reactants}} \int_{T_1}^{T} v_i C_{P,i}\, dT + \Delta H_{T_1}^0 + \sum_{\text{Products}} \int_{T_1}^{T} v_i C_{P,i}\, dT$$

The above result can be written as

$$\Delta H_T^0 = \Delta H_{T_1}^0 + \int_{T_1}^{T} \left(\sum_i v_i C_{P,i} \right) dT \tag{13.13}$$

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

$$C_P = \alpha + \beta T + \gamma T^2 \tag{13.14}$$

Utilizing Eq. (13.14), Eq. (13.13) can be written as

$$\Delta H_T^0 = \Delta H_{T_1}^0 + \int_{T_1}^{T} \Delta C_P \, dT \tag{13.15}$$

where

$$\Delta C_P = \Delta\alpha + \Delta\beta T + \Delta\gamma T^2 \tag{13.16}$$

and

$$\Delta\alpha = \Sigma v_i \alpha, \quad \Delta\beta = \Sigma v_i \beta, \quad \text{and} \quad \Delta\gamma = \Sigma v_i \gamma \tag{13.17}$$

Equation (13.15) may be expanded as

$$\Delta H_T^0 = \Delta H_{T_1}^0 + \Delta\alpha (T - T_1) + \frac{1}{2}\Delta\beta (T^2 - T_1^2) + \frac{1}{3}\Delta\gamma (T^3 - T_1^3)$$

The constants appearing in the above equation can be grouped together to a single constant $\Delta H'$, so that we have

$$\Delta H_T^0 = \Delta H' + \Delta\alpha T + \frac{\Delta\beta}{2}T^2 + \frac{\Delta\gamma}{3}T^3 \tag{13.18}$$

The constant $\Delta H'$ in Eq. (13.18) can be evaluated if the heat of reaction at a single temperature is known. Equation (13.18) can now be used for the evaluation of the standard heat of reaction at any temperature T.

EXAMPLE 13.13 Ammonia is synthesized according to the following reaction:

$$\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightarrow NH_3 \qquad \Delta H_{298}^0 = -46.191 \text{ kJ}$$

The specific heats of the components are represented by

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

where C_P is in J/mol K and the constants α, β and γ are:

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

Determine the heat of reaction at 700 K.

Solution Equation (13.18) can be used to calculate the heat of reaction at any temperature.

$$\Delta H_T^0 = \Delta H' + \Delta\alpha T + \frac{\Delta\beta}{2}T^2 + \frac{\Delta\gamma}{3}T^3$$

$$\Delta\alpha = \alpha_{NH_3} - \frac{1}{2}\alpha_{N_2} - \frac{3}{2}\alpha_{H_2}$$

$$= 25.48 - \frac{1}{2}\times 27.31 - \frac{3}{2}\times 29.09 = -31.81$$

$$\Delta\beta = \beta_{NH_3} - \frac{1}{2}\beta_{N_2} - \frac{3}{2}\beta_{H_2}$$

$$= 36.89\times 10^{-3} - \frac{1}{2}\times 5.2335\times 10^{-3} - \frac{3}{2}\times(-8.374\times 10^{-4})$$

$$= 35.5294 \times 10^{-3}$$

$$\Delta\gamma = \gamma_{NH_3} - \frac{1}{2}\gamma_{N_2} - \frac{3}{2}\gamma_{H_2}$$

$$= -6.305\times 10^{-6} - \frac{1}{2}\times(-4.1868\times 10^{-9}) - \frac{3}{2}\times(2.0139\times 10^{-6})$$

$$= -9.3238 \times 10^{-6}$$

Substituting these values in Eq. (13.18), we get

$$\Delta H_T^0 = \Delta H' - 31.81T + \frac{35.5294\times 10^{-3}}{2}T^2 - \frac{9.3238\times 10^{-6}}{3}T^3$$

At 298 K, $\Delta H_T^0 = -46\,191$ J. Substituting this in the above equation, we get $\Delta H' = -38\,207$ J.

The heat of reaction can now be expressed as a function of temperature as

$$\Delta H_T^0 = -38\,207 - 31.81T + \frac{35.5294\times 10^{-3}}{2}T^2 - \frac{9.3238\times 10^{-6}}{3}T^3$$

At $T = 700$ K,

$$\Delta H_T^0 = -38\,207 - 31.81\times 700 + \frac{35.5294\times 10^{-3}}{2}(700)^2 - \frac{9.3238\times 10^{-6}}{3}(700)^3$$

$$= -52\,835 \text{ J}$$

Therefore, the heat of reaction at 700 K is − 52.835 kJ.

EXAMPLE 13.14 Methanol is synthesized according to the following reaction:

$$CO(g) + 2H_2(g) \rightarrow CH_3OH(g)$$

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

$$C_P(CH_3OH) = 18.382 + 101.564 \times 10^{-3}T - 28.683 \times 10^{-6}T^2$$

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

$$C_P(H_2) = 27.012 + 3.509 \times 10^{-3}T + 6.9006 \times 10^{4}T^{-2}$$

Calculate the standard heat of reaction at 1073 K.

Solution Enthalpy of cooling the reactants consisting of 1 mol CO and 2 mol hydrogen from 1073 K to 298 K:

$$\Delta H_1 = 1\int_{1073}^{298} (28.068 + 4.631\times10^{-3}T - 2.5773\times10^{4}T^{-2})\,dT$$

$$+ 2\int_{1073}^{298} (27.012 + 3.509\times10^{-3}T + 6.9006\times10^{4}T^{-2})\,dT$$

$$= \int_{1073}^{298}(82.092 + 11.649\times10^{-3}T + 11.2239\times10^{4}T^{-2})\,dT = -70\,082.01\ \text{J}$$

Enthalpy for heating the products from 298 to 1073 K:

$$\Delta H_2 = \int_{298}^{1073} (18.382 + 101.564\times10^{-3}T - 28.683\times10^{-6}T^{2})\,dT = 56\,644.78\ \text{J}$$

The standard heat of reaction at 298 K is

$$\Delta H_{298}^0 = \sum_{\text{Products}} \Delta H_f^0 - \sum_{\text{Reactants}} \Delta H_f^0 = \Delta H_{f,\text{methanol(g)}}^0 - (\Delta H_{f,\text{CO(g)}}^0 + 2\Delta H_{f,\text{H}_2\text{O(g)}}^0) \qquad \text{(A)}$$

The standard heat of formation of methanol (g) can be obtained from the standard heat of formation of methanol (l) and the heat of vaporization.

$$\text{CO(g)} + 2\text{H}_2\text{(g)} \rightarrow \text{CH}_3\text{OH(l)} \quad \Delta H_f^0 = -238.64\ \text{kJ}$$

$$\text{CH}_3\text{OH(l)} \rightarrow \text{CH}_3\text{OH(g)} \quad \Delta H_v^0 = +37.98\ \text{kJ}$$

Adding these two equations we get the desired reaction for the formation of methanol (g).

$$\text{CO(g)} + 2\text{H}_2\text{(g)} \rightarrow \text{CH}_3\text{OH(g)} \quad \Delta H_f^0 = -200.66\ \text{kJ}$$

Substituting the heat of formation values in Eq. (A) we get

$$\Delta H_{298}^0 = \Delta H_{f,\text{methanol(g)}}^0 - (\Delta H_{f,\text{CO(g)}}^0 + 2\Delta H_{f,\text{H}_2\text{(g)}}^0)$$

$$= -200.66 - (-110.6 + 0) = -90.06\ \text{kJ}$$

The heat of reaction at 1073 K is now calculated:

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

$$= -70.082 - 90.06 + 56.645 = -103.497\ \text{kJ/mol}$$

EXAMPLE 13.15 Pure CO is mixed with 100 percent excess air and completely burned at constant pressure. The reactants are originally at 400 K. Determine the heat added or removed if the products leave at 600 K. The standard heat of reaction at 298 K is –282.99 kJ per mol CO burned. The mean specific heats applicable in the temperature range of this problem are 29.10, 29.70, 29.10, and 41.45 J/mol K respectively for CO, O_2, N_2 and CO_2.

Solution *Basis:* 1 mol CO reacted

$$CO + \frac{1}{2}O_2 \rightarrow CO_2$$

Oxygen theoretically required = 0.5 mol

Oxygen supplied = 1 mol (100 percent excess)

Nitrogen in the air supplied = 1 × 79/21 = 3.76 mol

Let ΔH_1 be the enthalpy of cooling the reactants from 400 K to 298 K. The reactants stream contains 1 mol oxygen, 3.76 mol nitrogen, and 1 mol CO.

$$\Delta H_1 = (1 \times 29.70 + 3.76 \times 29.10 + 1 \times 29.10)(298 - 400)$$
$$= -17.158 \text{ kJ}$$

Let ΔH_2 be the enthalpy of heating the products from 298 K to 600 K. The product stream contains 1 mol CO_2, 0.5 mol oxygen, and 3.76 mol nitrogen.

$$\Delta H_2 = (1 \times 41.45 + 3.76 \times 29.10 + 0.5 \times 29.70)(600 - 298)$$
$$= 50.046 \text{ kJ}$$

$$\Delta H = \Delta H_1 + \Delta H^0_{298} + \Delta H_2 = -17.158 - 282.99 + 50.046$$
$$= -250.102 \text{ kJ}$$

EXAMPLE 13.16 Carbon monoxide reacts with water vapour to form carbon dioxide and hydrogen.

$$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g) \qquad \Delta H^0_{298} = -41.190 \text{ kJ}$$

The reactants are at 298 K. 75 percent of CO is converted in the reaction. The products leave the reaction chamber at 800 K. The mean heat capacities in J/mol K are 30.35 for CO, 45.64 for CO_2, 36.00 for water vapour and 29.30 for hydrogen. Determine the quantity of heat to be added or removed in the reaction chamber per 1000 kg of hydrogen produced.

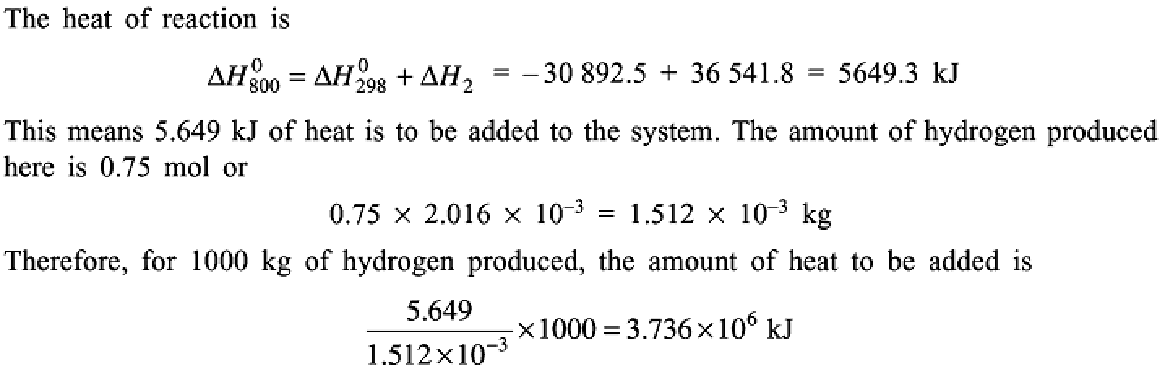
Solution Assume a reactant mixture consisting of 1 mol CO (g) and 1 mol water vapour. Since the reactants are at 298 K, $\Delta H_1 = 0$.

The products consists of 0.75 mol CO_2, 0.75 mol H_2, 0.25 mol CO and 0.25 mol water vapour. The enthalpy of heating the products from 298 K to 800 K is

$$\Delta H_2 = [0.75(45.64 + 29.30) + 0.25(30.35 + 36.00)](800 - 298)$$
$$= 36\,541.8 \text{ J}$$

The heat of reaction is

$$\Delta H^0_{298} = 0.75 \times (-41.190) = -30.8925 \text{ kJ} = -30\,892.5 \text{ J}$$



The heat of reaction is

$$\Delta H^0_{800} = \Delta H^0_{298} + \Delta H_2 = -30\,892.5 + 36\,541.8 = 5649.3 \text{ kJ}$$

This means 5.649 kJ of heat is to be added to the system. The amount of hydrogen produced here is 0.75 mol or

$$0.75 \times 2.016 \times 10^{-3} = 1.512 \times 10^{-3} \text{ kg}$$

Therefore, for 1000 kg of hydrogen produced, the amount of heat to be added is

$$\frac{5.649}{1.512\times10^{-3}}\times1000 = 3.736\times10^{6} \text{ kJ}$$

Reference:

BOOK: KV Narayanan and B Lakshmikutty, “Stoichiometry and Process Calculations” 2nd edition, 2016.