Chapter 4 Material Balances

(Refs: Geankoplis CJ: Cht 1; Felder RM: Cht 4; Himmelblau Cht 3(6th Edition))

1. Introduction

The **conservation of mass and energy** is the **law of nature**. It states that mass and energy cannot be created or destroyed. The application of these conservation laws in the chemical and other processes leads to Material (mass) and Energy balances, the **balance of input material or energy with that of output**. Material and energy balances are important considerations in engineering practice and process plants, for design, operation and analysis of the plants and process units and for inventory and economical evaluation. Material and energy balances are often used as the major conditions (constraints) in developing or establishing many design equations. In a word, material and energy balances are the basic principles of chemical engineering and process technology.

Therefore, the general concepts of material and energy balances and their applications to physical, chemical and biochemical processes in process technology are major objectives of this subject. The skills developed in analysing and solving the balance problems are not only useful for process technology but also for many other situations in your life and career.

Terminology

Types and characteristics of processes: Chemical engineering processes as well as many other processes such as food, pharmaceutical and biochemical are generally classified into *batch, continuous and semi-batch* based on the **mode of operation**.

- **Batch process:** The feed is charged into the system (a process unit such as a chemical reactor or a separation unit) at the beginning (t = 0), and the products are harvested all at a later time (t = batch time); no mass flows into or out of the system boundaries during the batch cycle.
- **Continuous process:** The feed is added to, and the product is withdrawn from the system continuously and constantly.
- **Semi-batch:** A process between batch and continuous, in which the feed is added to and/or the product are harvested from the system intermittently during a batch cycle.

Steady-state and unsteady-state processes:

- A process or system is at **steady-state** if all conditions (temperature, pressure, concentration, flow rates, volume and mass) remain constant and unchanged with time.
- A process is at **unsteady or transient-state** if any of the process conditions vary with time.

By their nature, batch and semi-batch processes are unsteady-state, and continuous processes may be either steady or unsteady process.

In this subject, we mainly deal with material balance problems in steady-state processes or processes that can be treated as steady state.

Q: Find examples of continuous, batch and semi-batch processes, at steady or unsteady state in your studies and other situations.

System: A **system** is any *arbitrary* portion or whole of a process, around which we set up a **boundary**. The materials and processes outside the system boundary are called the **surroundings**. An **open system** is one that has material flowing across the boundary (entering/exiting the system); a **closed system** is one without material crossing its boundary.



(Ref: http://granular.che.pitt.edu/~mccarthy/che0035/MB/mb/fund.html)

2. Basic concepts and equations of material balances

2.1. General balance equation

To introduce the concept of material balance in a simple way, we may consider the process

(physical or chemical) shown in the diagram as a system. Compound A is fed to the system at $m_{A in}$ and withdrawn from the system at $m_{A out}$, and the amount of A in the system is originally $m_{A sys}$; the process unit



has no leakage. If $m_{A in} \neq m_{A out}$, the two possible causes are,

1. *A* is *consumed* in the process unit as a reactant (then $m_{A out} < m_{A in}$) or generated as a product (then $m_{A out} > m_{A in}$).

2. *A* is *accumulated* in the system, with $m_{A sys}$ increased (then $m_{A out} < m_{A in}$) or decreased (then $m_{A out} > m_{A in}$).

The general material balance equation for a system is represented by

Input + generation - consumption - output = accumulation (1)

- **Input** = materials added or fed to the system (feed);
- **Output** = materials withdrawn from the system (products);
- Generation and consumption terms = products formed or reactants consumed in the system by chemical reactions.
- Accumulation term is the *increase* (+) *or decrease* (-) in the quantity of material (Q) *inside* the system with time *t*, usually represented by a derivative dQ/dt.

Ex. 1 Population change in a city. Each year 50,000 people move into a city, 75,000 people move out, 22,000 are born and 19,000 die. Calculate the yearly population change of the city.

 Δ (People/year) = 50,000 - 75,000 + 22,000 - 19,000 = -22,000 people/yr (Input) (Output) (Generate) (Consume) (Accumulate)

Ex. 2 Ethane (C₂H₆) is burned in a combustion reactor. The gas fed to the reactor contains 5.4% C₂H₆, 20.1% O2 and 74.5% N2 (all mol%). If C₂H₆ is burned completely into CO₂ and the reactor is operating at steady-state, determine the composition (in mol%) of the product gas exiting the reactor. Reaction involved: C₂H₆ + $3.5O_2 = 2CO_2 + 3H_2O$.

Solution: Assuming 100 mol gas fed to the reactor.



At steady state, the quantities of materials in reactor do not change with time, accumulation = 0.

When there are many components, the material balance can be written in a table, the balance sheet (as doing account balance).

Component	Input	Consumption	Generation	Outpout	Output mol%
С2Н6	5.4	5.4	0	0	0
02	20.1	18.9	0	1.2	1.17
N2	74.5	0	0	74.5	72.54
CO2	0	0	10.8	10.8	10.5
H2O	0	0	16.2	16.2	15.8
Total	100 mol			102.7 mol	100.0%

Ex. 3 The liquid volume in a container V_L is related to the feed rate F (vol/h) and discharge rate D (vol/h) by,

$$F - D = \frac{dV_L}{dt} \tag{2}$$

(1) If the input F equals the output D, $dV_L/dt = 0$ or vice versa.

(2) If F > D, $dV_L/dt > 0$: liquid volume in tank increases with time.

(3) If F < D, $dV_L/dt < 0$: liquid volume in tank decreases with time.

(Ref: http://www.cbu.edu/~rprice/lectures/matlbal.html)

2.2. Material balances for steady-state systems

Under steady-state conditions, all process variables in the system including the total quantity of material Q remain constant with time (dQ/dt = 0), i.e., there is no accumulation of material within the system, so that,

Input + generation - consumption - output =
$$0$$
 (3)

Steady-state systems without chemical reactions

Generation and consumption terms are all zero, then,

$$Input = Output \qquad (4)$$

A material balance on a system mostly refers to a mass balance (total mass), but it may also apply to the balance of moles of an atomic species (element), the moles of a chemical compound and the total moles of all chemicals.

2.3. Further notes on material balances

1) The terms in the balance equations may be a rate (amount per unit time, e.g., mass/time,



mole/time), a total amount (mass, mole), or a concentration (mass/vol). In any case, all terms should be on the same basis (to maintain dimensional consistency).

- 2) In the following study on material balances, we only need to consider steady-state processes. Therefore, accumulation term always goes to zero.
- 3) The generation and consumption occurs only when chemical reactions are involved, i.e., the consumption of reactants and the generation of products. However, when the balance is on the total mass of all components, we always have input = output.

3. Material balance calculations

3.1. Non-reactive systems

Case I Single unit systems; Case II Multiple-unit systems

Examples: Mixing, such as making up solutions; various separation processes, such as distillation, absorption, evaporation, crystallization and drying, and their combinations; oxygen balance in a bioreactor. Several exercise problems are given at the end of this chapter.

(Ref: <u>http://everything2.com/index.pl?node_id=1863343</u>)

Key steps for solving material balance problems: (Geankoplis p10, Felder sec.4.3e)

- 1) Draw a diagram of the process and indicate the input and output streams/materials and compositions;
- 2) If chemical reactions are involved, write down and balance the chemical equations;
- 3) List the known terms and the terms to be determined; organize these terms in a table if there are many;
- 4) Choose a basis of calculation;
- 5) Find the quantitative relationships among the terms, consider these relationships when setting up the balance equations;
- 6) In case that several unknown terms need to be solved, start from the balance that involves the fewest unknown variables; (solve the easiest one first!)
- 7) Use the right formula (if there is one) for the calculations; write the calculations in neat form;
- 8) Check the result.

Choose the basis of calculation:

- 1) If a stream amount or flow rate is given in a problem statement, it is usually most convenient to use this quantity as a basis of calculation.
- 2) If no stream amounts or flow rates are given, **assume one**. In this case, chose the amount of a stream with a known composition. If mass fractions or percents are known, choose 1 kg or 100 kg of the mixture as the basis; if mole fractions or percents are given, choose a 1 mole or 100 mole of the mixture as the basis.
- 3) For one system, you can only specify one stream as the basis, and then all the others will be fixed accordingly.

3.2 Reactive processes (Case III)

Important terms

Stoichiometric equations of chemical reactions. A chemical reaction equation provides a variety of quantitative and qualitative information about a chemical reaction. It tells the mole ratios (stoichiometric ratios) among reactants and products, which allows us to calculate the combining weights of materials involved in a chemical process.

E.g. $CH_4 + 2O_2 = CO_2 + 2 H_2O$ means that 1 mole CH_4 reacts with 2 mole O_2 , producing 1 mole CO₂ and 2 mole H₂O.

- **Limiting reactant** in a reaction is the reactant that is present in the smallest stoichiometric amount. In other words, if the reaction involves two or more reactants and if the reaction were to proceed to completion according to the chemical equation, whether or not it does, the reactant that would first disappear is the limiting reactant.
- **Conversion** of a reactant (e.g. A) is the percentage of A reacted in the reaction,

Conversion
$$x_A = \frac{Input - output}{inpt} \times 100\%$$

Combustion reaction: the reaction between a fuel and oxygen, such as C (s), CO, H_2 , CH₄, C_2H_6 , to produce CO_2 (and CO) and H_2O .

- **Complete combustion** means, (1) all fuel components are burnt (100% conversion);

(2) for a fuel containing the carbon element C, all the carbon burnt to CO_2 but not CO. Combustion that does not satisfy these two conditions is **incomplete combustion**.

- **Theoretical air** is the amount of air (or oxygen) required (stoicheometrically) for the _ complete combustion reactions.
- **Excess air** is the amount of air (or oxygen) in excess of that for complete combustion. It is the actual input air or oxygen less the theoretically required amount. These definitions also apply to other chemicals (theoretical or excess reactants).

Problem solving tips for material balances with chemical reactions

- 1) Write down the correct reaction equations and make full use of them in your calculation.
- 2) It is usually more convenient to perform mole balances (than mass balances). In case mass quantities are given, convert into moles and then set up the balances.

Ex 4 Himmelblau 2.29. When pure carbon is burned in air, some of it oxidizes into CO_2 and some to CO. The molar ratio of N_2 to O_2 is 7.18 and the ratio of CO to CO_2 is 2.0 in the product gas. What is the percent excess air used? The exit gases contain only N₂, O₂, CO and CO₂. (Ans: 40%)

Solution

Te process flow chart



As the product (output) gas composition is specified more clearly, we may use it as starting point.

N2 as an inert gas: input = output = 7.18 mol

O2 input with air = 7.18 (21/79) = 1.91 mol

Total O2 consumption = 1.91-1 = 0.91 mol

If R1 uses n₁ mol O2, generating n₁ mol CO2, R2 uses 0.91-n₁ mol O2, generating 2 (0.91-n₁) mol CO.

Since CO/CO2 in the product gas = 2, 2 $(0.91-n_1)/n_1 = 2$

 $n_1 = 0.91/2 = 0.455 \text{ mol}$

Therefore, total moles of C input = $3 n_1 = 1.365 mol$

O2 required for complete combustion of 1.365 mol C = 1.365 mol (for R1 only)

O2 excess $\% = (1.91 - 1365)/1.365 \times 100\% = 39.9\% = 40\%$

Ex 5 In a continuous, steady-state bioreactor (or fermentor), the flow rate of feed to the fermentor is F (L/h) and the cell concentration is X_0 in the feed and X (g/L) in the fermentor and the effluent. The culture liquid vol. of the fermentor is V_R (L). The specific growth rate is μ and specific death rate of cells in the fermentor is k_d (h⁻¹). Derive an equation for the specific growth rate of the cells relating to other given variables in the bioreactor. Specific growth rate is a kinetic constant of cell growth, and the growth rate of cells is μX ; the death rate = $k_d X$. (Hints: Set up a material balance on the cells).

Answer: Balance on biomass rate (g cell/h): $F(X_0 - X) + V_R(\mu - k_d)X = 0$

Therefore
$$\mu - k_d = \frac{F(X - X_o)}{V_R X}$$

If the feed contains no cells, $X_0 = 0$ and the death rate is neglected ($k_d = 0$), then $\mu = F/V_R = D$ (where $D = F/V_R$, known as the **dilution rate**). This is very useful equation for bioreactor design and analysis.

4. Processes involving recycle, bypass (Case IV)

- Recycle stream in a process is a flow of material that returns to an upstream point from a downstream point in the process.
- Bypass stream is a flow of material that skips one or more stages of the process and goes directly to another Fresh feed (F) stage.



Q: Find out the recycle and bypass streams from the process flow diagrams shown in previous chapters (cht 1-2) and tell why these flow arrangements are needed.

Ex 6 (Ex.2.20 Himmelblau 5th ed, p167), An absorption-distillation two-unit process as shown in the diagram below is used to recover acetone from an acetone-air mixture (gas). In the absorber column, acetone in the gas mixture is absorbed by water which flows downward. The water-acetone mixture (liquid) from the absorber is then fed to the distillation column to separate acetone and water. The reflux ratio of the distillation column R/D = 1.51 (D, R, and V have the same composition). All the

concentrations shown in the diagram are wt%. Determine the flow rates (kg/hr) of W, A, F, B, D, R and V. (Ans: A = 1336.7 kg/h, F =221.05 kg/h, W =157.75 kg/h, D = 34.90 kg/h, B = 186.15 kg/h, R = 52.70 kg/h, V = 87.60 kg/h)



Solution:

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Balance on air in absorber column (system 1): G(0.95) + W(0) = E(0.995) + F(0)

E = 1400(0.95/0.995) = 1336.7 kg/h

Balance of acetone on absorber column (system 1):

G(0.03) + W(0) = E(0) + F(0.19)

Acetone water solution leaving the absorber = Feed to distillation

F = G (0.03)/0.19 = 1400 kg/h (0.03)/0.19 = 221.05 kg/h

Water input: W = E + F - G = 1336.7 + 221.05 - 1400 kg/h = 157.75 kg/h

Balance on distillation column +condenser (system 2):

$$F = B + D \qquad \text{so that } B = F - D$$

$$F (0.19) = D (0.99) + B (0.04) = D (0.99) + (F - D) (0.04)$$

$$D (0.99 - 0.04) = F (0.19 - 0.04)$$

$$D = F (0.19 - 0.04)/(0.99 - 0.04) = 221.05 \text{ kg/h} (0.15)/0.95 = 34.90 \text{ kg/h}$$

$$B = F - D = 186.15 \text{ kg/h}$$

$$= 1.51 \text{ D} = 52.70 \text{ kg/h}; \qquad V = R + D = 34.90 + 52.70 = 87.60 \text{ kg/h}$$

Summary on material balances

- 1. Processes and systems: batch and continuous, steady and unsteady state, system boundary and know how to set up system boundaries for material balance calculations.
- 2. Understand the following equations and know in what situations they apply

Input + Generation - Consumption = Output (Steady state, with reactions)

Input = Output (Steady state, without chemical reactions)

3. Capable of solving material balance problems for reactive and non-reactive processes with and without recycle/by-pass streams.

4. Familiar with the terms used in specifying compositions of gas, liquid and solid mixtures (i.e., mole or mass fraction or percentage), and the terms related to chemical reactions, conversion, complete and incomplete combustion, theoretical (required) and excess air or oxygen. (Theoretical and excess input for other reactions as well).

Review questions

1. Find examples for the application of material balances as a major condition (constraint) for developing design/process equations in chemical and biological processes.

2. Find examples and applications of material balance concepts for natural, industrial and social processes in your knowledge and experience.

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Assignment #3 (Material balances, due date:

Felder: 4.1 (process terms), 4.2 (CSTR kinetics); Geankoplis: 1.5-2, 1.5-8 (Recycle in dryer), 1.5-10 (Evap bypass orange juice), 1.5-13 (combustion)

Hints: 1.5-2, "Dry" fish (dried solid) still contains water, though less than wet solid; Bone-dry = free of water.

1.5-13, Calculate on the basis of 100 kg coke input.

More exercises of material balances

Ex 7 (P1.38, Murphy): Microorganisms contain a complex mix of proteins, carbohydrates, and fats that are sometimes lumped together as a *pseu*do-chemical compound, such as bacterial biomass with an empirical formula of $CH_{1.666}N_{0.20}O_{0.27}$. Under aerobic conditions, bacteria take up glucose $(CH_{12}O_6)$, oxygen (O₂) and ammonia (NH₃) and make more bacteria plus lactic acid $(CH_3)CH(COOH)$, CO2, and water.

- (a) Write three balanced chemical reaction equations for glucose reacting to form (1) CO_2 , (2) lactic acid, and (3) bacteria. In each reaction, O_2 and/or NH_3 can be additional reactants, and CO_2 and/or H_2O can be additional products.
- (b) We mixed 1.0 g bacteria, 18.0 g glucose and some ammonia in a large vessel of water and bubbled air through the solution. After some time we found that all the glucose had been consumed and vessel contained 2.1 g bacteria, 3.6 g lactic acid (along with water). (1) How many grams of CO2 were generated? (2) What fraction of glucose was consumed to make bacteria, and to lactic acid? Assume that there are no other reactions for glucose consumption other than the three you wrote.

Solution:

(a) Three stoichiometric reaction equations:

$$\begin{aligned} & \text{R1} \ [1]C_6H_{12}O_6 + [6]O_2 \rightarrow [6]CO_2 + [6]H_2O \\ & \text{R2} \ [1]C_6H_{12}O_6 + [3]O_2 \rightarrow [1]C_3H_6O_3 + [3]H_2O + [3]CO_2 \\ & \text{R3} \ [1]C_6H_{12}O_6 + [0.3425]O_2 + [1]NH_3 \rightarrow [5]CH_{1.666}N_{0.20}O_{0.27} + [3.335]H_2O + [1]CO_2 \\ & \text{N: Left side} = 1 \times 1 = \text{Right side } 5 \times 0.20 = 1 \\ & \text{C: L} = 1 \times 6 = \text{R} = 5 \times 1 + 1 \times 1 = 6 \end{aligned}$$

(b) This is a reactive process, for which the moles of reactants and products can be derived from the stoichiometric equations.

Molecular weights of bacteria and lactic acid,

M_{bacteria}=12×1+1×1.666+14×0.20+16×0.27=20.786 (g/mol)

 $M_{\text{lactic acid}} = 12 \times 3 + 1 \times 6 + 16 \times 3 = 90 \text{ (g/mol)}$

Bacteria generated = $2.10-1.0 = [1.10] \text{ g} = \frac{[1.10g]}{[20.786g / mol]} = 0.053 \text{ mol.}$

Lactic acid generated = $3.6 \text{ g} = \frac{[3.60]}{[90]} = 0.04 \text{ mol.}$

From R3: Glucose consumed for bacteria generation = 0.053/5 = 0.0106 mol.

 CO_2 produced = 0.0503/5=0.0106 mol.

From R2: Glucose consumed for lactic acid generation: 0.04 mol.

 CO_2 produced = 0.04×3=0.12 mol.

Glucose input (or initial glucose) = $\frac{[18.0]}{[180]} = 0.1$ mol

Since there is no glucose generation during the process and all input glucose was consumed,

Glucose input = Consumption (by all three reactions)

Therefore, Glucose used in R1 = 0.1-0.04 (in R2) -0.0106 (in R3) = 0.0494 mol.

 CO_2 produced in R1 = 0.0496×6 = 0.2964 mol.

The total amount of CO2 from all 3 reactions,

 $0.2964+0.12+0.0106 = 0.427 \text{ mol} \times 44 = 18.79 \text{ g}.$

Fraction of glucose used for bacteria production: $\frac{[0.0106]}{[0.1]} = [0.106] = 10.6\%$

For lactic acid: $\frac{[0.04]}{[0.1]} = [0.40] = 40\%$.

Ex 8 (P4.24, Felder): The indicator dilution method is a technique used to determine flow rate of fluids in channels for which devices like rotameters and orifice meters cannot be used (e.g., rivers, blood vessels, and large diameter pipelines). A stream of an easily measured substance (the tracer) is injected into the channel at a known rate and the tracer concentration is measured at a point far enough downstream of the injection point for the tracer to be completely mixed with the flowing fluid. The larger the flow rate of fluid, the lower the tracer concentration at the measurement point.

A gas stream that contains 1.50 mole% CO_2 flows through a pipeline. 20.0 kg of CO_2 /min is injected into the line. A sample of the gas is drawn from a point in the line 150 m downstream of the injection point and found to contain 2.3 mol% CO_2 .

- (a) Estimate the gas flow rate (kmol/min) upstream of the injection point (after steady state has been reached).
- (a) If the CO_2 concentration at the measurement points (150 m downstream) begins to rise at 18 s after the additional CO_2 was first injected. Assuming that the tracer travels at the average velocity of the gas in the pipeline (i.e. neglecting diffusion of CO_2), estimate the average velocity (m/s). If the

molar gas density is 0.123 kmol/m³, what is the pipe diameter?

Solution

a) Since there is no reaction or accumulation in the pine line, input of CO₂ equals the output:

Upstream + Injection=Downstream



Assuming x is the flow rate of gas (kmol/min), there is the following balance:

0.015×x+20/44=0.023× (x+20/44), and y=55.51 kmol/min

The molar flow rate of gas N = 55.51 kmol/min.

b) The length of the pipe line between the injection point and the sampling point is 150 m.

The velocity of tracer u = 150 m/18 s = 8.333 m/s.

Volumetric flow rate of gas Q = (55.51 kmol/min)/(0.123 kmol/m³) = 451.3 m³/60 s =7.522 m³/s Let pipe diameter = D, then the cross-section area A = $\pi D^2/4$ Since average velocity u = Q/A, 8.333 m/s = (7.522 m³/s)/($\pi D^2/4$) D = $[4 \times 7.522/8.333\pi]^{0.5}$ m = 1.149^{0.5} = 1.072 m.