TEACHING MODULE: MATERIAL BALANCES, ENERGY BALANCES AND HEAT TRANSFER

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CHAPTER 1

INTRODUCTION TO ENGINEERING CALCULATIONS

1.1 Introduction

What do chemical engineers do? Although their backgrounds and professional skills are similar, chemical engineers work in a wide variety of industries, in addition to chemicals and petroleum, such as:

- Biotechnology
- Consulting
- Drugs and pharmaceuticals
- Fats and oils
- Fertilizer and agricultural chemicals
- Environment
- Lime and cement
- Man-made fibers
- Metallurgical and metal products
- Paints, varnishes, and pigments
- Pesticides and herbicides
- Waste water treatment

All the industries as mentioned above are involving numerous of chemical process unit. Therefore, chemical engineers play an important role on design, operation, control, troubleshooting, research and management in the chemical process. Chemical process is a combination of process equipment designed to efficiently convert raw materials into finished or intermediate products. Figure 1 shows the example of chemical processes converting the raw material into desired product.

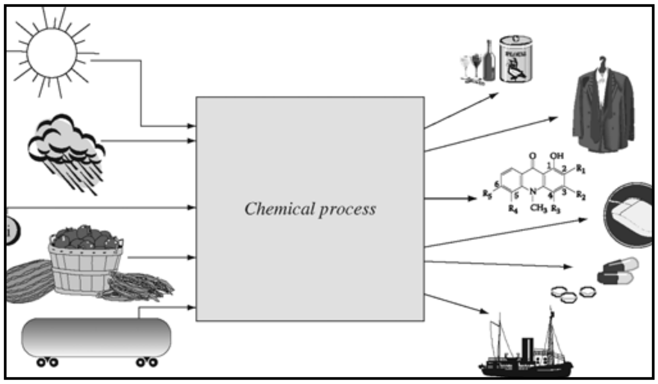


Figure 1.1: Chemical process

1.2 Units and Dimensions

"What are units and dimensions and how do they differ?"

Dimensions are basic concepts of measurement such as length (L), mass (M), time (t), temperature (T), amount of substance (n) and so on. Besides, **units** are the mean of expressing the dimensions as *feet or centimeters* for length, or *hours or seconds* for time. By attaching units to all numbers that are not fundamentally dimensionless, you are able to easy interrelating the physical meaning to the numbers use. Moreover, a logical approach to the problem rather than remembering a formula and plugging numbers could also help the chemical engineers in engineering calculation. **SI units** are universally accepted for engineering calculation. Thus, **American engineering system** (based on British standards) is still used extensively in the U.S.

Example 1.1

What are the dimensions of mass flux (mass flow rate per unit area perpendicular to the flow)?

$$G = \frac{1}{A}\frac{dm}{dt} \qquad \text{dimensions are} \qquad \frac{M}{L^2 t}$$

The rules for handling units are essentially quite simple by addition, subtraction or equality.

- Values could be added if **UNITS** are the **same**.
- Values **cannot** be added if **DIMENSIONS** are **different**.

Example 1.2

(i) $6\,ft + 10\,^0\text{C} = ???$

* Different dimensions: length, temperature -- **cannot be added**

$$6ft + 4in = ???$$

$$72in + 4in = 76in = 6.3ft$$

* Same dimension: length, different units -- **can add**

Table 1.1: SI Units

Physical Quantity	Name of Unit	Symbol for Unit*	Definition of Unit
	Basic SI Units		
Length	metre, meter	m	
Mass	kilogramme, kilogram	kg	
Time	second	s	
Temperature	kelvin	K	
Amount of substance	mole	mol	
	Derived Sl Units		
Energy	joule	J	$kg.m^2.s^{-2}$
Force	newton	N	$kg.m.s^{-2} = J.m^{-1}$
Power	watt	W	$kg.m^2.s^{-3} = J.s^{-1}$
Density	kilogram per cubic meter		$kg.m^{-3}$
Velocity	meter per second		$rn.s^{-1}$
Acceleration	meter per second squared		$rn.s^{-2}$
Pressure	newton per square meter, pascal		$N.m^{-2}$, Pa
Heat Capacity	joule per (kilogram - kelvin)		$J.kg^{-1}$,K^{-1}
	Alternative Units		
Time	minute, hour, day, year	min, h, d, y	
Temperature	degree Celsius	°C	
Mass	tonne, ton (Mg), gram	t, g	
Volume	litre, liter (dm^3)	L	

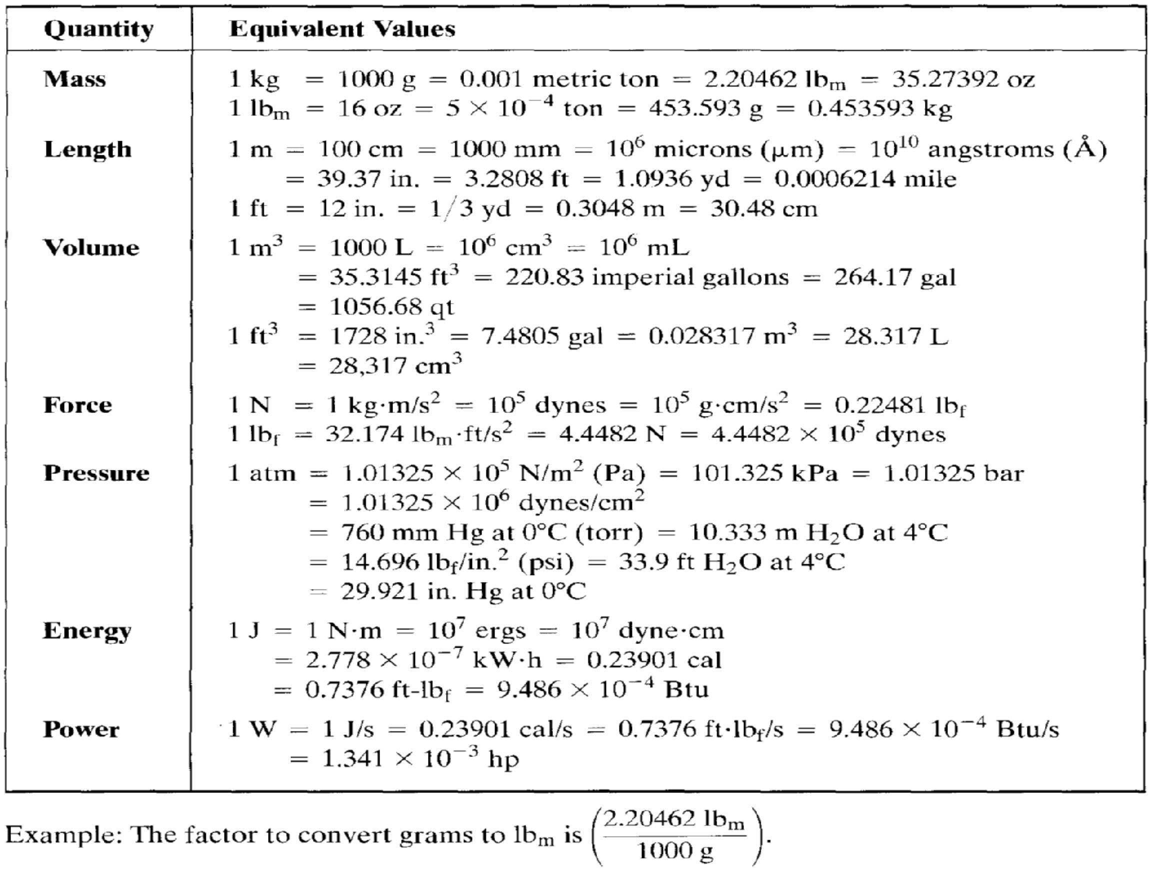
Table 1.2: American Engineering System Units

Physical Quantity	Name of Unit	Symbol
	Basic Units	
Length	feet	ft
Mass	pound (mass)	lb_m
Force	pound (force)	lb_f
Time	second, hour	s, hr
Temperature	degree Rankine	°R
	Derived Units	
Energy	British thermal unit, foot pound (force)	Btu, (ft)(lb_f)
Power	horsepower	hp
Density	pound (mass) per cubic foot	lb_m/ft^3
Velocity	feet per second	ft/s
Acceleration	feet per second squared	ft/s^2
Pressure	pound (force) per square inch	lb_f/in^2
Heat capacity	Btu per pound (mass) per degree F	$Btu/lb_m.^0F$

1.3 Conversion of Units

Conversion factors are statements of equivalent values of different units in the same system or between systems of units. The concept is to multiply any number and its associated units with dimensionless ratios termed conversion factors to arrive at desired answer and its associated units. The factors for conversion units are show in table 1.3.

Table 1.3: Factors for unit conversions



Quantity	Equivalent Values
Mass	$1\ \text{kg} = 1000\ \text{g} = 0.001\ \text{metric ton} = 2.20462\ \text{lb}_m = 35.27392\ \text{oz}$ $1\ \text{lb}_m = 16\ \text{oz} = 5 \times 10^{-4}\ \text{ton} = 453.593\ \text{g} = 0.453593\ \text{kg}$
Length	$1\ \text{m} = 100\ \text{cm} = 1000\ \text{mm} = 10^6\ \text{microns}\ (\mu\text{m}) = 10^{10}\ \text{angstroms}\ (\text{Å})$ $= 39.37\ \text{in.} = 3.2808\ \text{ft} = 1.0936\ \text{yd} = 0.0006214\ \text{mile}$ $1\ \text{ft} = 12\ \text{in.} = 1/3\ \text{yd} = 0.3048\ \text{m} = 30.48\ \text{cm}$
Volume	$1\ \text{m}^3 = 1000\ \text{L} = 10^6\ \text{cm}^3 = 10^6\ \text{mL}$ $= 35.3145\ \text{ft}^3 = 220.83\ \text{imperial gallons} = 264.17\ \text{gal}$ $= 1056.68\ \text{qt}$ $1\ \text{ft}^3 = 1728\ \text{in.}^3 = 7.4805\ \text{gal} = 0.028317\ \text{m}^3 = 28.317\ \text{L}$ $= 28{,}317\ \text{cm}^3$
Force	$1\ \text{N} = 1\ \text{kg}\cdot\text{m/s}^2 = 10^5\ \text{dynes} = 10^5\ \text{g}\cdot\text{cm/s}^2 = 0.22481\ \text{lb}_f$ $1\ \text{lb}_f = 32.174\ \text{lb}_m\cdot\text{ft/s}^2 = 4.4482\ \text{N} = 4.4482 \times 10^5\ \text{dynes}$
Pressure	$1\ \text{atm} = 1.01325 \times 10^5\ \text{N/m}^2\ (\text{Pa}) = 101.325\ \text{kPa} = 1.01325\ \text{bar}$ $= 1.01325 \times 10^6\ \text{dynes/cm}^2$ $= 760\ \text{mm Hg at } 0°\text{C (torr)} = 10.333\ \text{m}\ H_2O\ \text{at } 4°\text{C}$ $= 14.696\ \text{lb}_f/\text{in.}^2\ (\text{psi}) = 33.9\ \text{ft}\ H_2O\ \text{at } 4°\text{C}$ $= 29.921\ \text{in. Hg at } 0°\text{C}$
Energy	$1\ \text{J} = 1\ \text{N}\cdot\text{m} = 10^7\ \text{ergs} = 10^7\ \text{dyne}\cdot\text{cm}$ $= 2.778 \times 10^{-7}\ \text{kW}\cdot\text{h} = 0.23901\ \text{cal}$ $= 0.7376\ \text{ft-lb}_f = 9.486 \times 10^{-4}\ \text{Btu}$
Power	$1\ \text{W} = 1\ \text{J/s} = 0.23901\ \text{cal/s} = 0.7376\ \text{ft}\cdot\text{lb}_f/\text{s} = 9.486 \times 10^{-4}\ \text{Btu/s}$ $= 1.341 \times 10^{-3}\ \text{hp}$

Example: The factor to convert grams to lb_m is $\left(\frac{2.20462\ \text{lb}_m}{1000\ \text{g}}\right)$.

Example 1.3

Convert an acceleration of 1 cm/s^2 to its equivalent in km/yr^2.

$$\frac{1cm}{s^2}\times\frac{1m}{100cm}\times\frac{1km}{1000m}\times\frac{3600^2 s^2}{1hr^2}\times\frac{24^2 hr^2}{1day^2}\times\frac{365^2 day^2}{1^2 yr^2}$$

$$=9.95\times10^9\ km/yr^2$$

Do It Yourself:

Convert 400 in^3/day to cm^3/min.

(Answer: 4.56 cm^3/min)

1.4 Processes and Process Variables

A process is any operation or series of operations by which a particular objective is accomplished. Those mentioned operations are involving a physical or chemical change in a substance or mixture of substances. The material that enters a process is referred to as the input or feed, and that which leaves is the output or product. Therefore, several process variables are associated through input or output of a process stream.

1.3.1 Instructional Objectives

The objectives in studying this section are to be able to:

1. Draw a simple block flow diagram representing a process, showing input and output streams, and essential process variables.
2. Calculate the quantities of mass (or mass flow rate), volume (or volumetric flow rate), and moles (or molar flow rates) from a knowledge of the third quantity for any species of known density and molar mass.
3. Explain:
   (a) The meaning of gram-mole, lb-mole, mol and kmol;
   (b) At least two methods of measuring temperature and at least two for measuring fluid pressure;
   (c) The meaning of the terms absolute pressure and gauge pressure.
4. Convert a pressure expressed as a head of a fluid to the equivalent pressure expressed as a force per unit area, and vice versa
5. Convert a manometer reading into a pressure difference for an open end manometer, a sealed end manometer and a differential manometer.
6. Convert among temperatures expressed in K, °C, °F and °R.

1.3.2 Process

A process is any operation or series of operations that cause a physical or chemical change in a substance or mixture of substances. Figure 1.2 shows a process stream with several examples of process variables of input and output. Meanwhile, the details about process variables are stated in table 1.4.

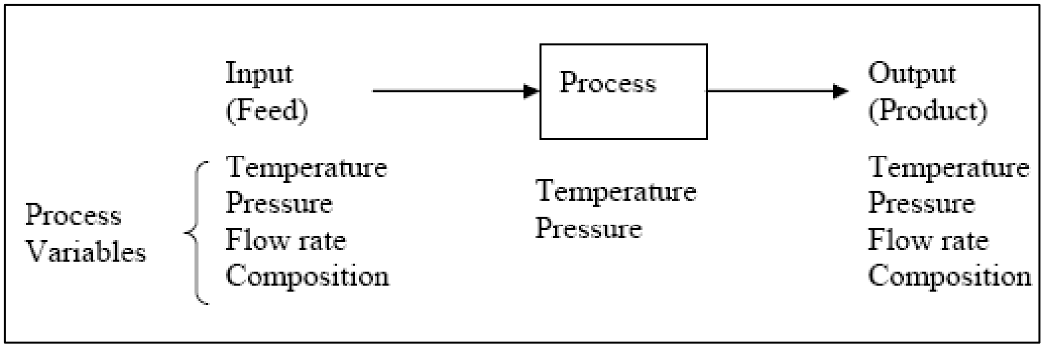


Figure 1.2: Process streams with various process variables.

Table 1.4: Process variables

Quantity	Symbol	Derivation	Dimension	Standard Unit	
				SI	AES
Mass	m		M	kg	lb$_m$
Volume	V	(Length)^3	L^3	m	ft
Density	ρ	m/V	$M L^{-3}$	kg/m^3	lb$_m$/ft^3
Specific gravity	sp gr	ρ / ρ_{ref}			
Specific volume	$\hat{V}$	V/m	$L^3 M^{-1}$	m^3/kg	ft^3/lb$_m$
(Specific) molar volume	$\hat{V}$	V/n	$L^3 M^{-1}$	m^3/mol	ft^3/lb-mole
Mass flow rate	$\dot{m}$	m/t	$M \theta^{-1}$	kg/s	lb$_m$/s
Molar flow rate	$\dot{n}$	n/t	$M \theta^{-1}$	mol/s	lb-mole/s
Volumetric flow rate	$\dot{V}$	V/t	$L^3 \theta^{-1}$	m^3/s	ft^3/s
Temperature	T		T	K	°F
Pressure	P	F/A	$M L^{-1} \theta^{-2}$	Pa = N/m^2	ft-lb$_f$

1.3.3: Mass and Volume

The density of a substance is the mass per unit volume of the substance (kg/m^3, g/m^3, lb/ft^3, etc). The specific volume of a substance is the volume occupied by a unit mass of the substance; it is the inverse of density. Densities of pure solids and liquids are essentially independent of pressure and vary relatively slightly with temperature. Densities of many pure compounds, solutions and mixtures can be found in standard references. The density of a substance can be used as a conversion factor to relate the mass and the volume of a quantity of the substance.

Example 1.4

The density of carbon tetrachloride is 1.595 g/cm^3, the mass of 35 cm^3 of CCl_4 is therefore,

$$\begin{array}{c|c} 35\ \text{cm}^3 & 1.595\ \text{g} \\ \hline & \text{cm}^3 \end{array} = 55.825\ \text{g}$$

and the volume of 9.3 lb_m of CCl_4 is

$$\begin{array}{c|c|c} 9.3\ \text{lb}_\text{m} & 454\ \text{g} & \text{cm}^3 \\ \hline & 1\ \text{lb}_\text{m} & 1.595\ \text{g} \end{array} = 2647.47\ \text{cm}^3$$

The specific gravity of a substance is the ratio of the density ρ of the substance to the density *ρref* of a reference substance at a specific condition:

$$SG = \frac{\rho}{\rho_{ref}} \qquad (1.1)$$

The reference most commonly used for solids and liquids is water at 4 oC, which has the following density:

$$\begin{aligned} \rho H_2O\ (4\ °C) &= 1\ \text{g/cm}^3 \\ &= 1000\ \text{kg/m}^3 \\ &= 62.43\ \text{lbm/ft}^3 \end{aligned}$$

If you are given the specific gravity of a substance, multiply it by the reference density in any units to get the density of a substance in the same units. Special density units called degrees Baumé (°Bé), degrees API (°API) and degrees Twaddell (°Tw).

Example 1.5

Calculate the density of mercury in lb/ft^3 from a tabulated specific gravity, and calculate the volume in ft^3 occupied by 215 kg of mercury.
(Given that the specific gravity of mercury at 20 ^{o}C as 13.546)

$$\begin{aligned}\rho_{Hg} &= S.G \times \rho_{ref} \\ &= 13.546 \times 62.43\, lb/ft^3 \\ &= 845.67\, lb/ft^3\end{aligned}$$

$$\text{Volume} = \begin{array}{c|c|c} 215\text{ kg} & \text{lb}_m & \text{ft}^3 \\ \hline & 0.454\text{ kg} & 845.67\text{ lb} \end{array} = 0.56\text{ ft}^3$$

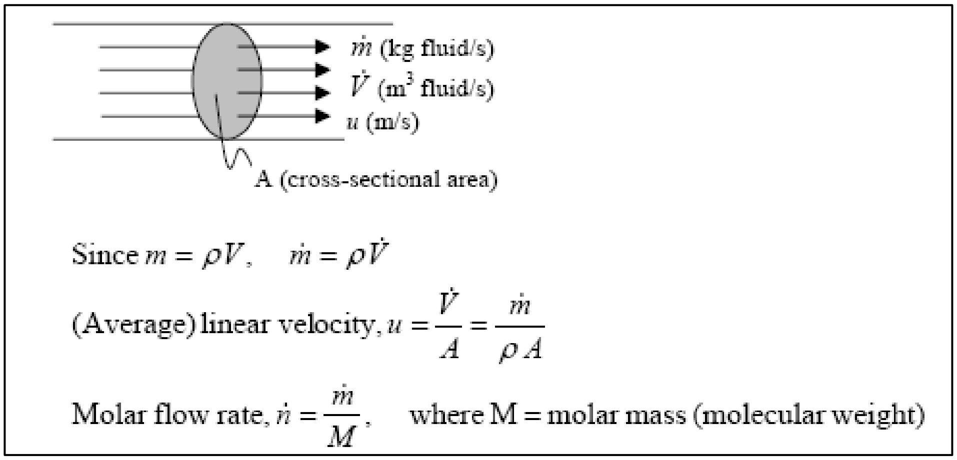
Do It Yourself:

A liquid has a specific gravity of 0.5.

i. What is its density in g/cm^3?	(Answer: 0.5 g/cm^3)
ii. What is its specific volume in cm^3/g?	(Answer: 2 cm^3/g)
iii. What is its density in lb/ft^3?	(Answer: 0.032 lb/ft^3)
iv. What is the mass of 3 cm^3 of this liquid?	(Answer: 1.5 g)
v. What volume is occupied by18g?	(Answer: 36 cm^3)

1.3.4: Flow rate

Most processes involve the movement of material from one point to another. The rate at which a material is transported through a process line is the ***flow rate*** of that material. The flow rate of a process stream can be expressed as a ***mass flow rate*** (mass/time) or as a ***volumetric flow rate*** (volume/time) as show in figure 1.3 as below.



Since $m = \rho V$, $\dot{m} = \rho \dot{V}$

(Average) linear velocity, $u = \dfrac{\dot{V}}{A} = \dfrac{\dot{m}}{\rho A}$

Molar flow rate, $\dot{n} = \dfrac{\dot{m}}{M}$, where M = molar mass (molecular weight)

Figure 1.3: Flow rate

Example 1.6

The volumetric flow rate of CCl_4 in a 1.0-cm-diameter pipe is 100 cm^3/min.
(Given that the molecular weight of CCl_4 = 153.838 and density of ρ CCl_4 = 1.595 g/cm^3.)

i. What is the mass flow rate?

$$\dot{m} = \dot{V}\rho = 100\ cm^3/min \times 1.595\ g/cm^3 = 159.5\ g/min$$

ii. What is the molar flow rate?

$$\dot{n} = \frac{\dot{m}}{M} = 159.5\ \text{g-}CCl_4/\text{min} \times \text{g mol-}CCl_4/153.838\ \text{g-}CCl_4$$

$$= 1.034\ \text{g mol-}CCl_4/\text{min}$$

iii. What is the linear velocity of CCl_4?

$$v = \frac{m}{A\rho} = \frac{159.5\,g/\min}{\frac{\pi(1cm)^2}{4}\times 1.595g/cm^3} = 127.32cm/\min$$

Do It Yourself:

The mass flow rate of n-hexane (ρ=0.659 g/cm^3) in a pipe is 6.59 g/s.

(a) What is the volumetric flow rate of the hexane?
(b) What is the linear velocity of hexane in the pipe with internal diameter of 5 cm?

(Answer: (a) 10 cm^3/s; (b) 0.509 cm/s)

1.3.5: Chemical Composition

Most materials encountered in nature and in chemical process systems are mixtures of various species. The physical properties of a mixture depend strongly on the mixture composition. In this section we will review different ways to express mixture compositions and also outline the methods of estimating physical properties of a mixture from the properties of the pure components.

1.3.5(a): Moles and Molecular Weight

The **atomic weight** of an element is the mass of an atom on a scale that assigns. The atomic weights of all the elements in their naturally isotopic proportions are listed in the table given. The molecular weight of a compound is the sum of the atomic weights of the atoms that constitute a molecule of the compound: For example atomic oxygen (O) has an atomic weight of approximately 16 and therefore molecular oxygen (O_2) has a molecular weight of approximately 32. A gram-mole (g-mole or mol in SI units) of a species is the amount of that species whose mass in grams is numerically equal to its molecular weight. Hence, one g-mole of any species contains approximately $6.02\text{x}10^{23}$ (*Avogadro's number*) molecules of that species.

Moles and molar mass: $$\text{moles, } n = \frac{\text{mass}}{\text{molar mass}} = \frac{m}{M}$$

Moreover, there are other types of moles such as **kg-moles**, **lb-moles**, and **ton-moles**. For example: Carbon monoxide (CO) has a molecular weight of 28; 1 mol of CO therefore contains 28g, 1 lb-mole contains 28 lbm, 1 ton-mole contains 28 tons and so on. Besides, the same factors used to convert masses from a unit to another can also be used to convert the equivalent molar units: there is 454 g/lb for example, and therefore there is 454 mol/lb-mole, regardless of the substance involved.

100 g CO_2	1 mol CO_2
	44.01 g CO_2

Example 1.7

How many of each of the following are contained in 100g of CO_2 (M=44.01)?

i. Mol CO_2

= 2.273 mol CO_2

ii. lb-moles CO_2

2.273 mol CO_2	1 lb-mol	= $5.011 \text{ x } 10^{-3}$ lb-mole CO_2
	453.6 mol	

Each molecules of CO_2 contains one atom of C, one molecule of O_2 or two atoms of O. Therefore, each $6.02\text{x}10^{23}$ molecules of CO_2 (1mol) contains 1 mol C, 1 mol O_2, or 2 mol O. Thus,

iii. mol C

2.273 mol CO_2	1 mol C	= 2.273 mol C
	1 mol CO_2	

iv. mol O

$$\begin{array}{c|c} 2.273\ \text{mol}\ CO_2 & 2\ \text{mol O} \\ \hline & 1\ \text{mol}\ CO_2 \end{array} = 4.546\ \text{mol O}$$

v. mol O_2

$$\begin{array}{c|c} 2.273\ \text{mol}\ CO_2 & 1\ \text{mol}\ O_2 \\ \hline & 1\ \text{mol}\ CO_2 \end{array} = 2.273\ \text{mol}\ O_2$$

vi. gram O

$$\begin{array}{c|c} 4.546\ \text{mol O} & 16\ \text{g O} \\ \hline & 1\ \text{mol O} \end{array} = 72.7\ \text{g O}$$

vii. gram O_2

$$\begin{array}{c|l} 2.273\ \text{mol}\ O_2 & 32\ \text{g}\ O_2 \\ \hline & 1\ \text{mol}\ O_2 \end{array} = 72.7\ \text{g}\ O_2$$

viii. molecules of CO_2

$$\begin{array}{c|c} 2.273\ \text{mol}\ CO_2 & 6.02 \times 10^{23}\ \text{molecules} \\ \hline & 1\ \text{mol} \end{array} = 1.37 \times 10^{24}\ \text{molecules}$$

Do It Yourself:

Calcium carbonate is a naturally occurring white solid used in the manufacture of lime and cement. Calculate the number of lb mol of calcium carbonate in:

(a) 50 g mol of $CaCO_3$.
(b) 150 kg of $CaCO_3$.
(c) 100 lb of $CaCO_3$.

(Answer: (a) 0.11 lb mol; (b) 3.3 lb mol; (c) 1 lb mol)

1.3.5 (b): Mass and Mole Fractions

Process streams occasionally contain one substance, but more often they consist of mixtures of liquids or gases, or solution s of one or more solutes in a liquid solvent. The following terms can be used to define the composition of a mixture of substances, including a species A.

Mass fraction – mass of a component per unit mass of total (mixture)

$$x_A = \frac{\text{mass of A}}{\text{total mass}}\left(\frac{\text{kg A}}{\text{kg total}} \text{ or } \frac{\text{g A}}{\text{g total}} \text{ or } \frac{\text{lb}_m\text{A}}{\text{lb}_m\text{total}}\right)$$

Mole fraction - mole of a component per mole of total (mixture)

$$y_A = \frac{\text{moles of A}}{\text{total moles}}\left(\frac{\text{kmol A}}{\text{kmol total}} \text{ or } \frac{\text{mol A}}{\text{mol total}} \text{ or } \frac{\text{lb - moles A}}{\text{lb - moles total}}\right)$$

Mass percent of A is $100x_A$
Mole percent of A is $100y_A$

Example 1.8

A solution contains 15% A by mass ($x_A = 0.15$) and 20 mole % B ($y_B = 0.20$)

a) Calculate the mass of A in 175 kg of the solution.

$$\begin{array}{c|c} \text{175 kg solution} & \text{0.15 kg A} \\ \hline & \text{kg solution} \end{array} \quad = 26.25 \text{ kg A}$$

b) Calculate the mass flow rate of A in a stream of solution flowing at a rate of 53 lb/h.

$$\begin{array}{c|c} \text{53 lb} & \text{0.15 lb A} \\ \hline \text{h} & \text{lb} \end{array} \quad = 7.95 \text{ lb A/ h}$$

c) Calculate the molar flow rate of B in a stream flowing at a rate of 1000 mol/min.

$$\begin{array}{c|c} \text{1000 mol} & \text{0.2 mol B} \\ \hline \text{min} & \text{mol} \end{array} \quad = 200 \text{ mol B/min}$$

d) Calculate the total solution flow rate that corresponds to a molar flow rate of 28 kmol B/s.

$$\begin{array}{c|c} \text{28 k mol B} & \text{1 k mol solution} \\ \hline \text{s} & \text{0.2 k mol B} \end{array} \quad = 140 \text{ kmol solution/s}$$

e) Calculate the mass of the solution that contains 300 lb of A.

$$\begin{array}{c|c} \text{300 lb A} & \text{1 lb solution} \\ \hline & \text{0.15 lb A} \end{array} \quad = 2000 \text{ lb solution}$$

1.3.5 (c): Concentration

The mass concentration of a component of a mixture or solution is the mass of this component per unit volume of the mixture.

$$\text{Mass concentration} = \frac{\text{mass of component or solute}}{\text{volume of mixture or solution}}\left(\frac{\text{g}}{\text{cm}^3}, \frac{\text{lb}_\text{m}}{\text{ft}^3}, \frac{\text{kg}}{\text{l}}, \text{etc.}\right)$$

The molar concentration of a component is the number of moles of the component per unit volume of the mixture.

$$\text{Molar concentration} = \frac{\text{moles of component or solute}}{\text{volume of mixture or solution}}\left(\frac{\text{mol}}{\text{cm}^3}, \frac{\text{lb - mole}}{\text{ft}^3}, \text{etc.}\right)$$

The molarity of a solution is the value of the molar concentration of the solute expressed in g-moles solute / liter solution.

$$\text{Molarity} = \frac{\text{moles of solute}}{\text{volume in liter of solution}}\left(\frac{\text{mol}}{\text{l}}\right)$$

Example 1.9

A 0.5 molar aqueous solution of sulfuric acid flows into a process unit at a rate of 1.25 m^3/min. The specific gravity of the solution is 1.03 and molecular weight of sulfuric acid is 98.08. Calculate:

a) The mass concentration of H_2SO_4 in kg/m^3

$$= \frac{0.5\, mol\ H_2SO_4}{L} \times \frac{98g}{mol} \times \frac{1kg}{1000g} \times \frac{1000L}{1m^3} = 49\, kg\, H_2SO_4 / m^3$$

b) The mass flow rate of H_2SO_4 in kg/s

$$= \frac{49\ kg\ H_2SO_4}{m^3} \times \frac{1.25\,m^3}{\min} \times \frac{1\min}{60\,s} = 1.02\, kg\, H_2SO_4 / s$$

c) The mass fraction of H_2SO_4

The mass fraction of H_2SO_4 equals the ratio of the mass flow rate of H_2SO_4 to the total mass flow rate, which can be calculated from the total volumetric flow rate and the solution density.

$$\rho_{Solution} = 1.03 \times (\frac{1000kg}{m^3}) = 1030 kg / m^3$$

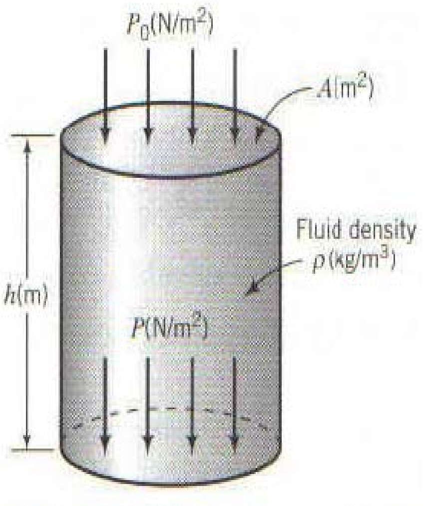
$$m_{solution}\left(\frac{kg}{s}\right) = \frac{1.25 m^3\ solution}{\min} \times \frac{1030 kg}{m^3 solution} \times \frac{1 \min}{60 s} = 21.46 kg/s$$

$$x_{H_2SO_4} = \frac{m_{H_2SO_4}}{m_{solution}} = \frac{1 kg\ H_2SO_4 / s}{21.46\ kg\ solution / s} = 0.048\ kg\ H_2SO_4 / kg\ solution$$

1.3.6: Pressure

A pressure is the ratio of a force to the area on which the force acts. Pressure units are force units divided by area units such as N/m^2 or Pascal (Pa), dynes/cm^2, and lbf/in^2 or psi.

Hydrostatic pressure = pressure at the base of a fluid column



$$P = P_0 + \rho g h$$

$$P - P_0 = \rho g h$$

If P_0 is **atmospheric pressure**, then $P - P_0 = \rho g h$ is called the **gauge pressure**, and P is the **absolute pressure**.

$$P_{abs} = P_{gauge} + P_{atm}$$

Fluid Pressure Measurement

Most common pressure measuring devices are stated in Figure 1.4. Bourdon gauge manometers can show measurement nearly perfect vacuums to about 700 atm. Meanwhile, manometers only can measure pressures below about 3 atm.

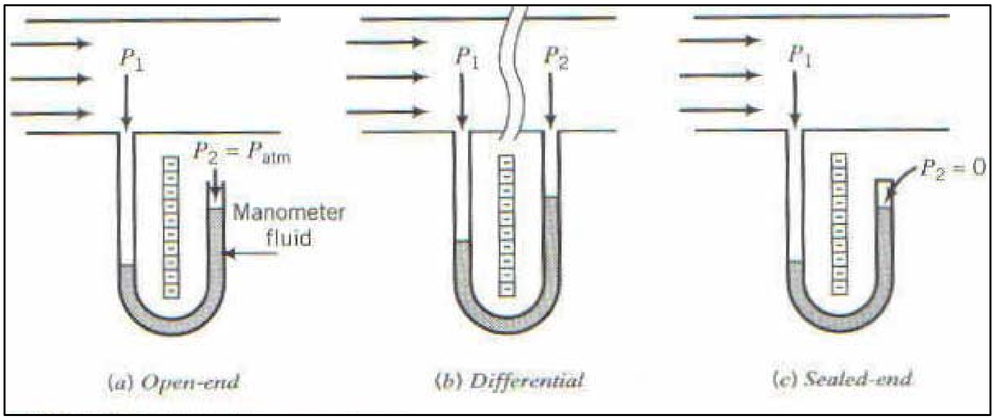


Figure 1.4: Pressure measurement device.

Manometer principle is showing in figure 1.5. The fluid pressure must be the same at any two points at the same height in a continuous fluid.

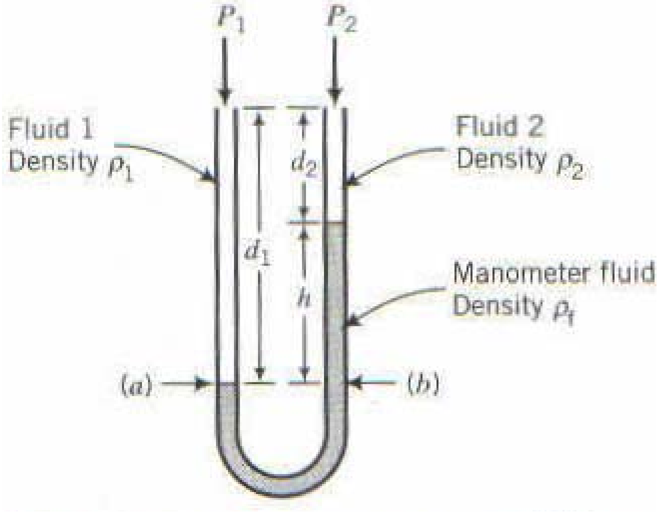


Figure 1.5: Manometer principle

General manometer equation:

$$P_1 + \rho_1 g d_1 = P_2 + \rho_2 g d_2 + \rho_f g h$$

Differential manometer equation:

$$P_1 - P_2 = (\rho_f - \rho)\, gh, \text{ since } \rho_1 = \rho_2$$

1.3.7: Temperature

Temperature is a measurement of the average kinetic energy possessed by the substance molecules. It must be determined indirectly by measuring some temperature-dependent physical properties of another substance. The temperature measuring devices are:

a) Resistance thermometer (by means of electrical resistance of a conductor)
b) Thermocouple (by voltage at the junction of two dissimilar metals)
c) Pyrometer (by spectra of emitted radiation)
d) Thermometer (by volume of a fixed mass of fluid)

The temperature conversions are:

$T(K) = T(^0C) + 273.15;$ $T(^0R) = T(^0F) + 459.67;$

$T(^0R) = 1.8\ T\ (K);$ $T(^0F) = 1.8\ T(^0C) + 32$

Problems:

1. Convert the following to the desired units:
   (a) 60 mi/hr to m/s (b) 30 N/m^2 to lb_f/ft^2
   (c) 16.3 J to Btu (d) 4.21 kW to J/s

2. Change the following to the desired units:
   (a) 235 g to pounds. (b) 610 L to cubic feet.
   (c) 30 g/L to pounds/cubic feet. (d) 14.7 lb/in^2 to kg/cm^2

3. Convert the following quantities to the ones designated:
   (a) 42 ft^2/hr to cm^2/s.
   (b) 25 psig to psia.
   (c) 100 Btu to hp-hr.

4. The specific gravity of a fuel oil is 0.82.
   (a) What is the density of oil in lb/ft^3?

5. The density of a liquid is 1500 kg/m^3 at 20 °C.
   (a) What is the specific gravity 20°C/4°C of this material?
   (b) What volume (ft^3) does 140 lb_m of this material occupy at 20°C?

6. Silver nitrate (lunar caustic) is a white crystalline salt, used in marking inks, medicine and chemical analysis. How many kilograms of silver nitrate ($AgNO_3$) are there in:
   (a) 13.0 lb mol $AgNO_3$.
   (b) 55.0 g mol $AgNO_3$

7. Complete the table below with the proper equivalent temperatures.

° C	° F	K	° R
- 40.0			
	77.0		
		698	
			69.8

CHAPTER 2
FUNDAMENTALS OF MATERIAL BALANCES

2.1 Introduction

Material balances are important first step when designing a new process or analyzing an existing one. They are almost always prerequisite to all other calculations in the solution of process engineering problems. Material balances are nothing more than the application of the law of conservation of mass, which states that mass can neither be created nor destroyed. Thus, as an example, you cannot specify an input to a reactor of one ton of naphtha and an output of two tons of gasoline or gases or anything else. One ton of total material input will only give one ton of total output, i.e. total mass of input = total mass of output.

A material balance is an accounting for material. Thus, material balances are often compared to the balancing of current accounts. They are used in industry to calculate mass flow rates of different process streams entering or leaving chemical or physical processes.

2.2 Process Classification

A. Based on manner of delivering process streams

Batch process

The feed is charged into a vessel at the beginning of the process and the vessel contents are removed some time later. No mass transfer across the boundary between the time the feed is charged and the time the product is removed.

Example: Rapidly add reactants to a tank and remove the products and unconsumed reactants sometime later when the system has come to equilibrium.

Continuous process

Inputs and outputs flow continuously through the duration of the process.

Example: Pump a mixture of liquids into a distillation column at constant rate and steadily withdraw product streams from the top and bottom of the column.

Semi batch process

Any process that is neither batch nor continuous.

Example: Allow the contents of pressurized gas container to escape to the atmosphere; slowly blend several liquids in a tank from which nothing is being withdrawn.

B. According to variation of the process variables with time

Steady state

The values of all process variables (i.e. all temperatures, pressures, compositions, flow rates) do not change with time. For example, batch or semi batch processes.

Unsteady state or **transient**

Any of the process variables change with time. Continuous processes may be either steady-state or transient.

2.3 The General Balance Equation

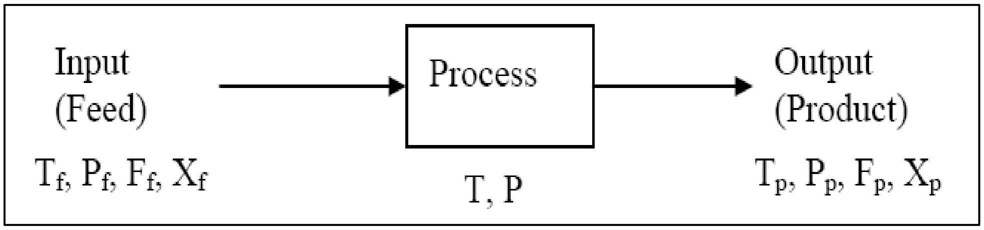


Figure 2.1: Process balance

A balance on a conserved quantity (total mass, mass of a particular species, energy, and momentum) in a system as show in figure 2.1 can be written in the following general way:

Input + generation - output - consumption = accumulation [2.1]

where,

Input - enters through system boundary
Generation - produced within system
Output - leaves through system boundary
Consumption - consumed within system
Accumulation - builds up within system

Example 2.1

Each year 50000 people move into a city, 75000 people move out, 22000 are born, and 19000 die. Write a balance on the population of the city.

Input + generation - output - consumption = accumulation

50000 + 22000 – 75000 – 19000 = - 22000

Therefore, the city's population decreases by 22,000 people each year.

Two types of balances:

A. Differential balance

- Balance that indicates what is happening in a system at an instant in time.
- Each term of the balance equation is a rate (rate of input, rate of generation, etc) and has units of the balanced quantity unit divided by the time unit (people/yr, barrels/day).
- This is the type of balance usually applied to a continuous process.

B. Integral balance

- Balance that describes what happens between two instants of time.
- Each term of the equation is an amount of the balanced quantity and has the corresponding unit (people, barrels).
- This type of balance is usually applied to a batch process, with the two instants of time being the moment after the input takes place and the moment before the product is withdraw.

The following rules can be used to simplify the material balance equation:

- If the balanced quantity is total mass, *generation* = 0 *consumption* = 0:

  Input - output = accumulation

- If the balanced substance is non-reactive species, *generation* = *consumption* = 0:

  Input - output = accumulation

- If a system is at steady state, *accumulation* = 0:

  Input + generation = output + consumption

2.4 Balance on Continuous Steady-State Process

For continuous processes at steady state, the accumulation term in the general balance equation, (Eq 2.1), equals zero and the equation simplifies as below:

$$\text{Input} + \text{generation} = \text{output} + \text{consumption} \qquad [2.2]$$

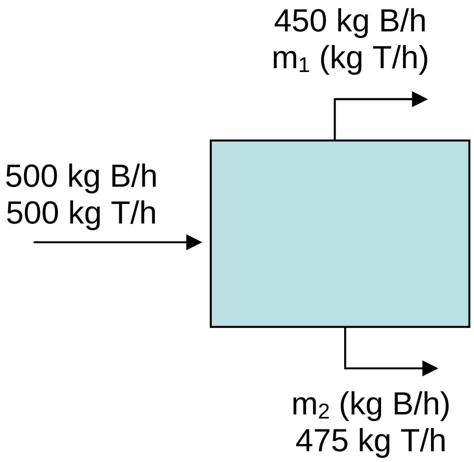
If the equation is on a non-reactive species or on total mass, the generation and consumption terms equal zero and the equation reduces to the equation as below:

$$\text{Input} = \text{Output} \qquad [2.3]$$

Example 2.2

One thousand kilograms per hour of mixture of benzene (B) and toluene (T) containing 50% benzene by mass is separated by distillation into two fractions. The mass flow rate of benzene in the top stream is 450 kg B/h and that of toluene in the bottom stream is 475 kg T/h. The operation is at steady state. Write balance on benzene and toluene to calculate the unknown component flow rates in the output streams.

The process can be depicted schematically as follows:



Since the process is at steady state there can be no buildup of anything in the system, so the accumulation term equals zero in all material balances. In addition, since no chemical reactions occur, there can be no nonzero generation or consumption terms. For all balances, Eq 2.3 are apply here:

$$\text{Input} = \text{Output}$$

For Benzene balance:

$500 \text{ kg B/h} = 450 \text{ kg B/h} + m_2$

$m_2 = 50 \text{ kg B/h}$

For Toluene balance:

$500 \text{ kg T/h} = m_2 + 475 \text{ kg T/h}$

$m_1 = 25 \text{ kg T/h}$

Hence,

Total Mass Balance:

$1000 \text{ kg/h} = 450 \text{ kg/h} + m_1 \text{kg/h} + m_2 \text{ kg/h} + 475 \text{ kg/h}$

$1000 \text{ kg/h} = 1000 \text{ kg/h}$

2.5 Integral Balance on Batch Process

Ammonia is produced from nitrogen and hydrogen in a batch reactor. At time t=0 there are n_0 mol of NH_3 in the reactor, and at later time t_f the reaction terminates and the contents of the reactor, which include n_f mol of ammonia are withdraw. Between t_0 and t_f no ammonia enters or leaves through the reactor boundaries, so general balance equation (1) is simply ***generation = accumulation***. Moreover, the quantity of ammonia that builds up (accumulates) in the reactor between t_0 and t_f is simply $n_f – n_0$, the final amount minus the initial amount. The same reasoning may be applied to any substance participating in a batch process to obtain the following equation:

Accumulation = final output – initial input (by definition)
= generation – consumption

Therefore, equating these two expressions for the accumulation yields:

$$\text{Initial input} + \text{generation} = \text{final output} + \text{consumption} \qquad [2.4]$$

Example 2.3: Balance on a Batch Mixing Process

Two methanol water mixtures are contained in separate flasks. The first mixture contains 40 wt% methanol, and the second contains 70 wt% methanol. If 200g of the first mixture is combined with 150g of the second, what are the mass and composition of the product?

The process can be depicted schematically as follows:

Observe that the input and output 'streams' shown on the chart denote the initial and final states for this batch process. Since no reactions are involved, the generation and consumption terms of Eq (4) can be omitted so that all balance have the simple form '*input = output*'.

Total Mass Balance
200g + 150g = m
m = 350g

Methanol Balance:

$$(\frac{200g \times 0.4gCH_3OH}{g}) + (\frac{150g \times 0.7gCH_3OH}{g}) = (\frac{m\,(g)\ \times\ x\,(gCH_3OH)}{(g)})$$

x = 0.529 g CH_3OH/g

2.6 Integral Balance on Semi-batch Process

Integral balances can also be written for semi-batch and continuous processes. The procedure is to write a differential balance on the system and then to integrate it between two instants of time. In most cases the required calculations are more complex than those we have seen so far. However, some problems of this type are relatively straight forward solutions.

Example 2.4

Air is bubbles through a drum of liquid hexane at a rate of 0.1 kmol/min. The gas stream leaving the drum contains 10 mole% hexane vapors. Air may be considered insoluble in liquid hexane. Use an integral balance to estimate the time required to vaporize 10m^3 of the liquid.

The process can be depicted schematically as follows:

We begin with a differential balance on air. Since we assume that air neither dissolves in the liquid nor reacts with hexane in the process unit, the balance reduces to *input* = *output*:

$$\frac{0.1\,kmol\ air}{\min} = \frac{0.9\,kmol\ air}{kmol} \times \frac{n\ kmol}{\min}$$
$$n = 0.111\,kmol/\min$$

We next write an integral hexane balance, proceeding from time t=0 to t_f (min), the time we seek to calculate. The balance has the form *accumulation* = - *output.* The accumulation term, which is the total change in the moles of liquid hexane in the system during time t_f, must be negative since hexane is being lost from the system. Since the total number of moles of hexane evaporated occupied a liquid volume of 10 cubic meters and the specific gravity of liquid hexane is 0.659, the accumulation term equals:

$$\Delta n = -10\ m^3 \times \frac{0.659\ kg}{m^3} \times \frac{1\ kmol}{86.2\ kg} = -76.45\ kmol\ C_6H_{14}$$

The output term in the balance is the rate at which hexane is leaving the system [0.1n (kmol C_6H_{14}/min)] times the total process time, tf (min). The balance (*accumulation* = -*output*) is therefore;

$$- 76.45 \text{ kmol } C_6H_{14} = -0.1n\ t_f$$
$$n = 0.111 \text{ kmol /min}$$
$$t_f = 6887 \text{ min}$$

2.7 General procedure for material balance calculations

1) Choose a basis of calculation an amount or flow rate of one of the process streams.
   - If no stream amount or flow rate is specified in the problem statement, take as a basis an arbitrary amount or flow rate of a stream with a known composition.

2) Draw the flowchart of the process, using boxes or other symbols to represent the process units, and lines with arrows to represent input and output streams.

3) Fully label the chart when it is first drawn with values of known process variables and symbols for unknown variables being written for each input and output stream.

4) Do the degree-of-freedom analysis.

5) If the problem is solvable, the starting balance should be an equation with minimum number of unknowns, preferably with only one unknown.

6) After the one unknown in step 4 has been calculated, use that value to give an equation with one variable for another unknown.

7) As each unknown variable is determined, its value is filled so that the chart provides a continuous record of where the solution stands and what must still be done.

Notes:

- **The maximum numbers of independent equations that can be derived by writing balances on a non-reactive system equal the number of chemical species in the input and output streams.**
- The additional equations can be written from the fact that the component mass or mole fractions of a stream adds up to 1.0 (Σ xi = 1.0).

  (You can use these constrains to reduce the number of unknowns in the flow chart (step 2 above) to a minimum.)

- If you are given that the mass of stream 1 is half that of stream 2, label the masses of these streams m and 2m rather than m1 and m2; if you know that there is three times as much nitrogen (by mass) in a stream as oxygen, label the mass fractions of O_2 and N_2 y and 3y rather than y1 and y2.
  (This can also reduce the number of unknowns in step 2 above, or can provide additional equation needed for solution.)
- Balances are not normally written on volumetric quantities. If a volumetric flow rate is given, it is generally useful to calculate the mass or molar flow rate for the balance.

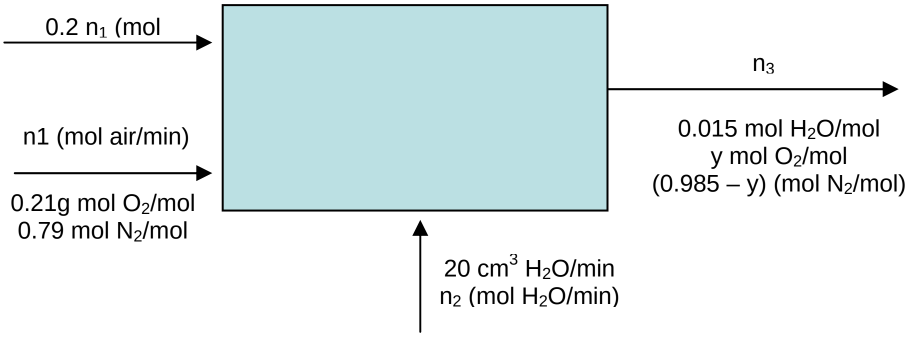
Example 2.5

An experiment on the growth rate of certain organisms requires an environment of 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 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 analyzed and is found to contain 1.5 mole% of water. Draw and label a flowchart of the process, and calculate all unknown stream variables

The process can be depicted schematically as follows:



Notes on the labeling:

1. Since the one known flow rate (20 cm^3 H_2O/min) is given on a per minute basis, it is most convenient to label all stream flow rates on this basis.
2. Once the variable name (n_1) is chosen for the air flow rate, the given information about the ratio of the air and O_2 flow rates may be used to label the O_2 flow rate $0.2n_1$.
3. The mole fractions of the components of any stream must add up to 1. Since the mole fraction of H_2O in the outlet stream is known to be 0.015, once the mole

fraction of O_2 is labeled y, that of N_2 must be 1 – (y + 0.015) = (0.985 – y) (mol N_2/mol).

The quantity n_2 can be calculated from the given volumetric flow rate and the density of liquid water:

$$n_2 = \frac{20\,cm^3\,H_2O}{\min} \times \frac{1g}{cm^3} \times \frac{1mol}{18.02g} = 1.11 mol\,H_2O/\min$$

The three remaining unknowns (n_1; n_2 and y) can be determined from balance, all of which have the simple form *input = output* for this non-reactive steady state process. The balances are easily written by referring to the flow chart.

Water balance:
n_2 (mol H_2O/min) = n_3 (0.015 mol H_2O/min)
n_3 = 74 mol/min

Total Mole Balance:

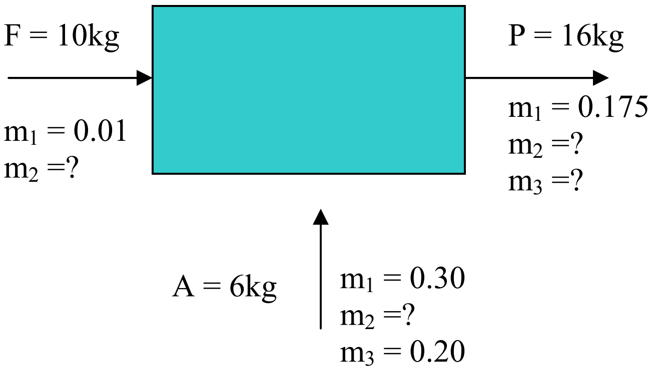
$0.2n_1 + n_1 + n_2 = n_3$
n_1 = 60.74 mol/min

Nitrogen Balance:

$$\frac{n_1\ mol}{\min} \times \frac{0.79 mol\,N_2}{mol} = \frac{n_3\,mol}{\min} \times \frac{(0.985 - y) mol\,N_2}{mol}$$
$$\therefore 0.79 n_1 = n_3\,(0.985 - y)$$
$$y = 0.337\ mol\,O_2\,/\,mol$$

Do It Yourself:

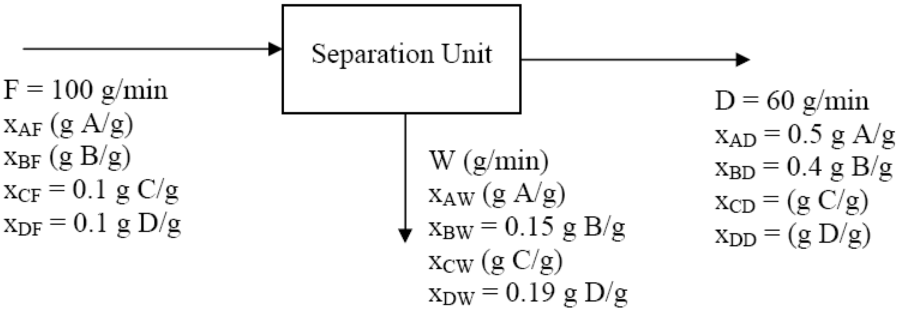
In the steady state flow process shown in the figure below, a number of values of m (mass fraction) are not given. Mary says that nevertheless the problem has a unique solution for the unknown values of m. Kelly says that 4 values of m are missing, that you can write 3 component material balances, and that you can use 3 relations for $\sum m_i = 1$, one for each stream, a total of 6 equations, so that a unique solution is not possible. Who is right?



(Answer: Stream F, $m_2 = 0.90$; stream A, $m_2 = 0.5$; stream P, $m_2 = 0.75$, $m_3 = 0.075$)

2.7 Balancing a process

Consider the following process flowchart for a separation unit at steady state:



Number of unknowns = 7
Number of mass balance equations:

4 component balances: $F x_{iF} = D x_{iD} + W x_{iW}$ for i = A, B, C, and D
1 overall balance: $F = D + W$
3 mass fraction constraints of streams: $\Sigma x_{iF} = 1.0$, $\Sigma x_{iD} = 1.0$, $\Sigma x_{iW} = 1.0$

Total number of equations = 8. They are not all independent, because the summing of the four component balances and then using the mass fraction constraint of each stream results in the overall balance. Thus the number of independent equations = 7.
Since number of unknowns = number of independent equations, the problem is solvable. Then how will you solve the problem in the easiest way?

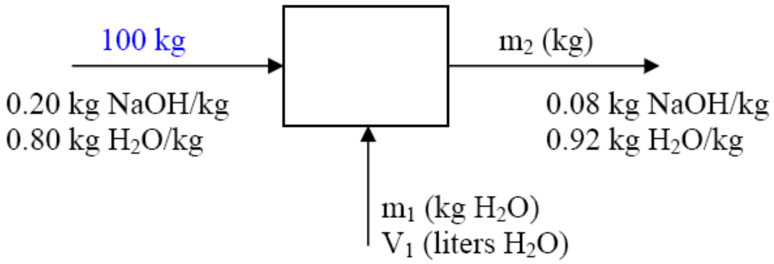
Example 2.6

An aqueous solution of sodium hydroxide contains 20% NaOH by mass. It is desired to produce an 8.0% NaOH solution by diluting a stream of the 20% solution with a stream of pure water. Calculate the ratios (liters H_2O needed / kg feed solution) and (kg product solution / kg feed solution).

Solution:

Basis: 100 kg of 20% feed solution

Step 2:



Step 3 (in conjunction with Steps 1 and 2):

Degree of freedom analysis:
Number of unknowns needed to be solved = 2 (V_1 in terms of m_1, and m_2)
Since it is a nonreactive process and involves two species,
Number of independent equations = 2
So, degree of freedom = 2-2 = 0. Thus the problem is solvable.

Step 4 (solution procedure):

Number of mass balance equations involved: 2

The balance equation that contains only one unknown is NaOH balance since it is not present in pure water stream. So choose it.

NaOH mass balance: $100 \times 0.2 = 0.08\ m_2$

$m_2 = 250$ kg

The remaining two balances (H_2O and overall) contain 2 unknowns, and simplest of these is overall balance, so choose it.

Overall mass balance: $100 + m_1 = m_2$

So, $m_1 = m_2 - 100$

$= 250 - 100 = 150$ kg

Volume of diluents water, $V_1 = m_1/\rho_w$ = 150 kg x 1.0 liter/kg = 150 liter

Thus,

V1/100 kg = 150 liter/100 kg = 1.5 liters H_2O/kg feed solution

m_2/100 kg = 250 kg/100 kg = 2.5 kg product solution/kg feed solution

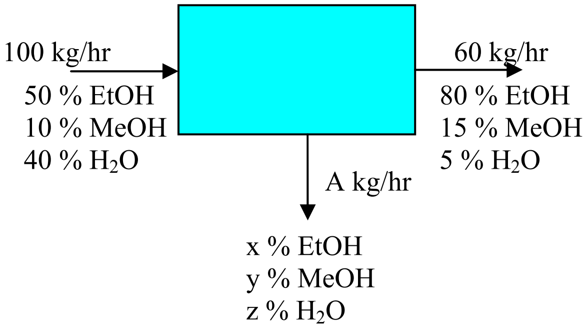
Do It Yourself:

A solution composed of 50% ethanol (EtOH), 10% methanol (MeOH), and 40% water (H_2O) is fed at the rate of 100 kg/hr into a separator that produces one stream at the rate of 60 kg/hr with the composition of 80% EtOH, 15% MeOH, and 5% H_2O, and a second stream of unknown composition.

(a) Sketch and completely label a flow chart of the process.

(b) Calculate the composition (in %) of the three compounds in the unknown stream and its flow rate in kg/hr.

Answer: (a)



Answer: (b) A = 40 kg/hr; x = 5%; y = 2.5%; z = 92.5%

2.8 Balances on Multiple Unit Processes

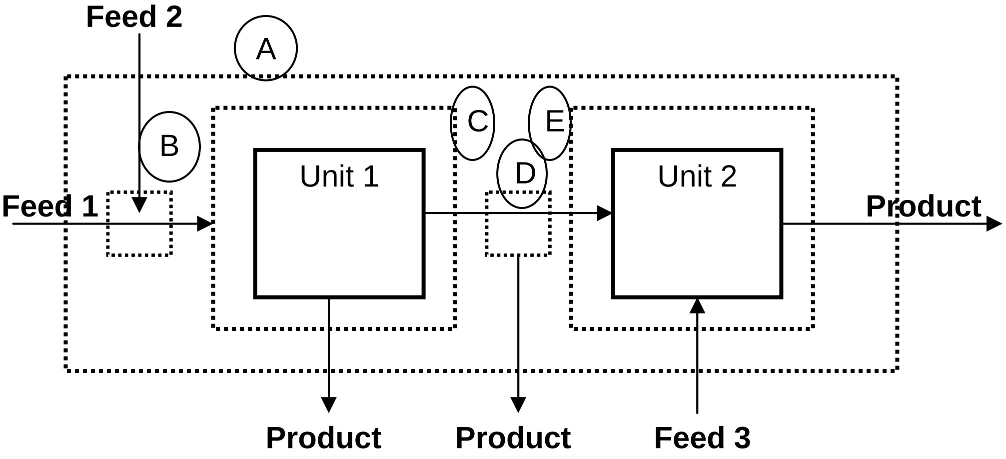
Plants in the process industries are comprised of many interconnected units. However, you can easily apply the same techniques discussed in the previous sections to solve material balance problems in such plants.

List and count up the number of variables whose values are unknown, making sure you do not count the same variable more than once, and then list and count up the number of independent balances that you can make, making sure that balances for one unit do not render formerly independent balances for another unit into dependent balances.

If the number of independent equations equals the number of variables whose values are unknown, at least for a set of linear equations, you can generally solve the equations for a unique answer.

If you ignore all the internal streams and variables within a set of connected subsystem, you can treat the overall system exactly as you treated a single system by drawing a boundary about the entire set of subsystem.

A flow chart for a two unit process is show as below.

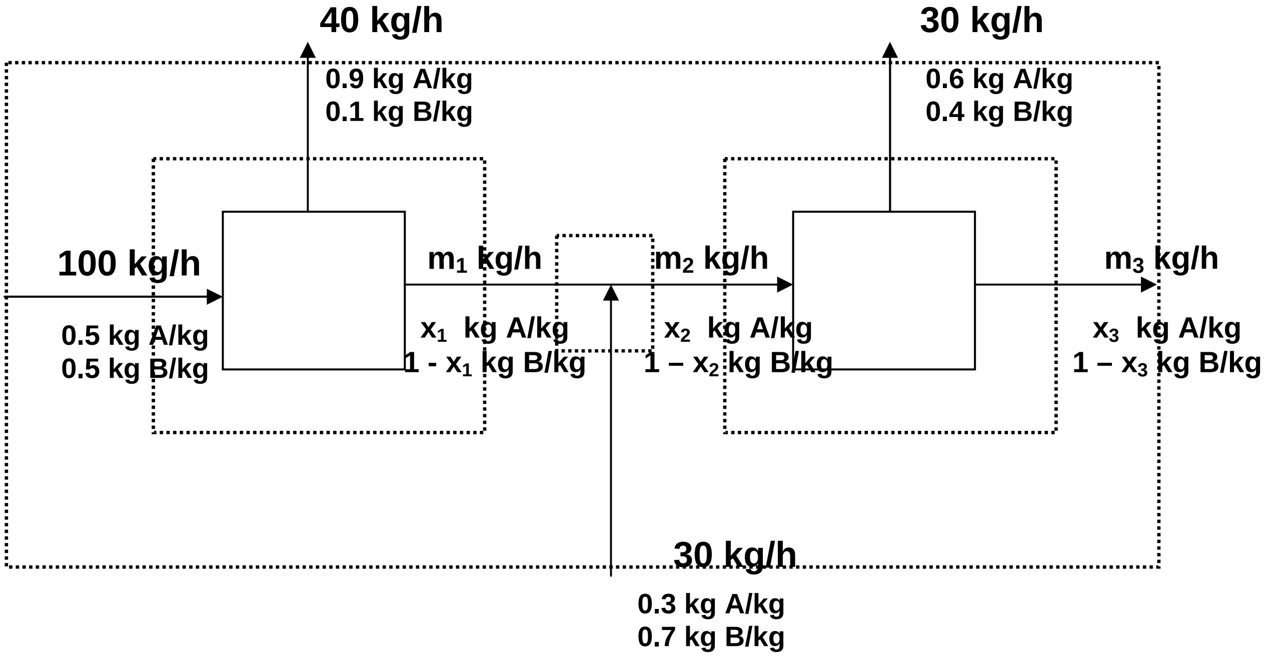


Five boundaries drawn above portions of the process define systems on which balances can be written. Boundary A encloses the entire process; the system defined by this boundary has as inputs Feed Streams 1, 2 and 3 and Product Stream 1, 2 and 3.Balances on this system are referred to as overall balances. The stream that connects Unit 1 and 2 is internal system are referred to this system and so would not either into overall system balances.

Boundary B encloses a feed stream mixing point. Feed Streams 1 and 2 are inputs to this system and the stream flowing to Unit 1 is an output. Boundary C encloses Unit 1 (one input stream and two output streams). Boundary D encloses a stream splitting point (one input stream and two output streams). Boundary E encloses Unit 2 (two input streams and one output stream).

Example 2.7

A labeled flow chart of a continuous steady state process is shown below. Each stream contains of two components; A and B, in different proportions. Three streams whose flow rates and compositions are not known are labeled 1, 2 and 3.



Solution:

Overall Mass Balance:

$(100 + 30)$ kg/h = $(40 + 30)$ kg/h + m_3
$m_3 = 60$ kg/h

Overall Mass Balance on A: (kg A/h)

$(0.5)(100) + (0.3)(30) = (0.9)(40) + (0.6)(30) + x_3\,(60)$
$x_3 = 0.0833$ kg A/kg

Mass Balance on Unit 1:

$100 = 40 + m_1$
$m_1 = 60$ kg /h

Balance on A in Unit 1: (kg A/h)

$(0.5)(100) = (0.9)(40) + x_1\,(60)$
$x_3 = 0.233$ kg A/kg

Mass Balance on Stream Mixing Point:

$m_1 + 30 = m_2$; $m_1 = 60$ kg/h
$m_2 = 90$ kg/h

Balance on A in Stream Mixing point: (kg A/h)

$x_1\, m_1 + (0.3)(30) = x_2\, m_2;$ $x_1 = 0.233$ kg A/kg
$m_1 = 60$ kg /h
$m_2 = 90$ kg /h

$x_2 = 0.255$ kg A/kg

Do It Yourself:

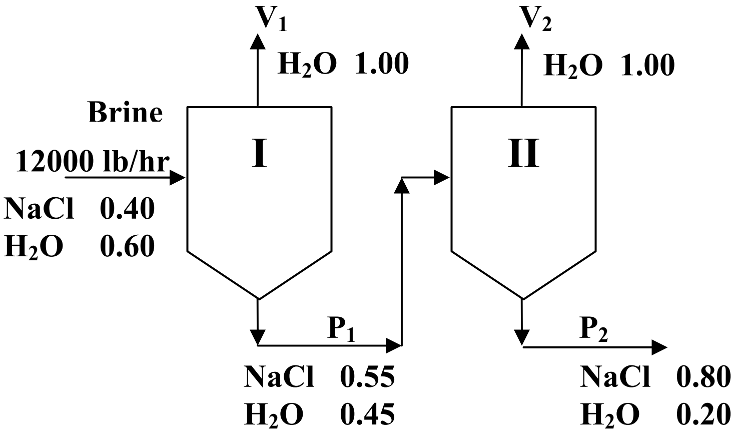
A labeled flow chart of a continuous steady state double effect evaporator is shown below. The system of evaporator is designed to reduce water from an incoming brine (NaCl + H_2O) stream from 60 wt % to 20 wt %. If the evaporator unit is receiving 12000 lb/hr of NaCl (along with 60 wt % H_2O), determine:

(a) The product rate (P_2) of brine in lb/hr.

(Answer: $P_2 = 6000$ kg/hr)

(b) The water removed from the brine in each evaporator (V_1 V_2) in lb/hr.

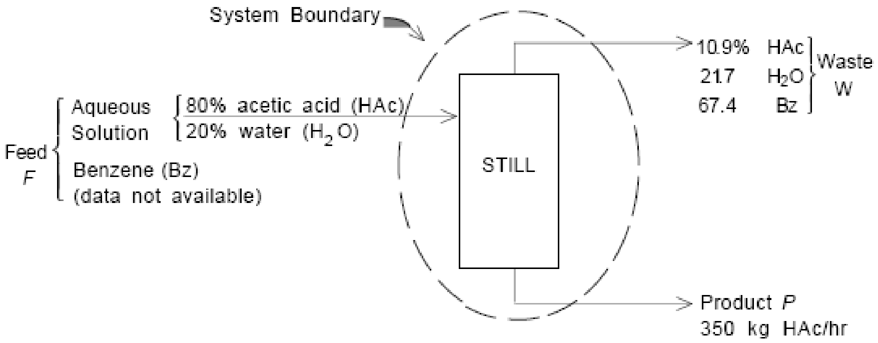
(Answer: $V_1 = 3272.73$ kg/hr; $V_2 = 2727.27$ kg/hr)



Problems:

1. Classify the following processes as (1) batch, (2) flow, (3) neither, or (4) both on a time scale of one day:
    - (a) Oil storage tank at a refinery
    - (b) Flush tank on a toilet
    - (c) Catalytic converter on an automobile
    - (d) Gas furnace in a home

2. A continuous still is to be used to separate acetic acid, water, and benzene from each other. On a trial run, the calculated data were as shown in the figure. Data recording the benzene composition of the feed were not taken because of an instrument defect. The problem is to calculate the benzene flow in the feed per hour. How many independent material balance equations can be formulated for this problem? How many variables whose values are unknown exist in the problem?

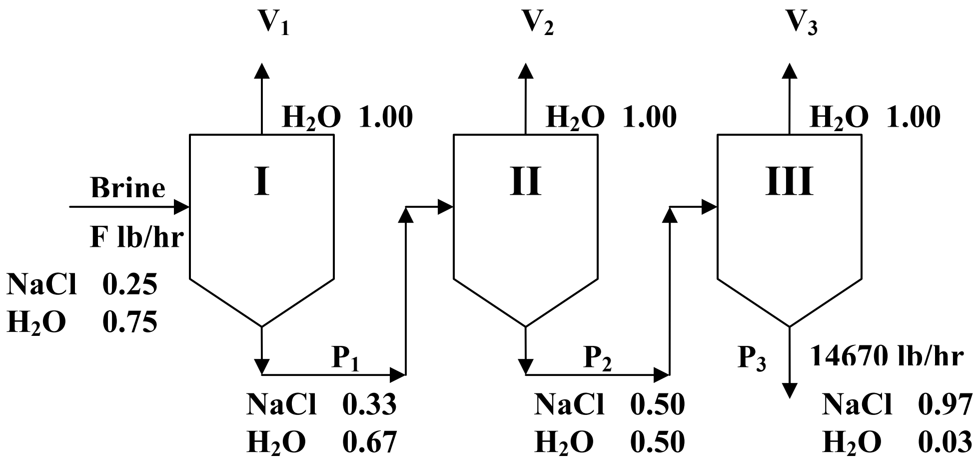


3. A liquid adhesive, which is used to make laminated boards, consists of a polymer dissolved in a solvent. The amount of polymer in the solution has to be carefully controlled for this application. When the supplier of the adhesive receives an order for 3000 kg of an adhesive solution containing 13 wt % polymer, all it has on hand is (A) 500 kg of a 90 wt % solvent, (B) a very large quantity of a 20 wt % solvent, and (C) pure solvent. Sketch the flow charts for the scaled processes and calculate the weight of each of the three stocks that must be blended together to fill the order.

4. An evaporator is fed continuously with 25,000 kg/h of a solution containing 10% NaOH, 10% NaCl, and 80% H_2O. During evaporation, water is boiled off, and salt precipitates as crystals, which are settled and removed from the remaining liquor. The concentrated liquor leaving the evaporator contains 50% NaOH, 2% NaCl, and 48% H_2O. Calculate:
    - a) The kilograms of water evaporated per hour
    - b) The kilograms of salt precipitated per hour
    - c) The kilograms of concentrated liquor produced per hour.

5. A waste solution of acid from titration process contains 33% of sulfuric acid (H_2SO_4), 36% of nitric acid (HNO_3) and 31% of water (H_2O) by mass. 98% of pure sulfuric acid and 78% of pure nitric acid have to be added through the waste solution of acid to produce final mixed solution of acid which contains 40% H_2SO_4 and 43% HNO_3.
   - (a) Draw and completely label a flow chart of the process.
   - (b) Calculate the quantity of waste solution of acid and pure acid that's needed to be added together to produce 1500 kg of mixed solution of acid.

6. A labeled flow chart of a continuous steady state triple effect evaporator is shown below. The system of evaporator is designed to reduce water from an incoming brine (NaCl + H2O) stream from 75 wt % to 3 wt %. If the evaporator unit is to produce 14,670 lb/hr of NaCl (along with 3 wt % H2O), determine:
   - (a) The feed rate (F) of brine in lb/hr.
   - (b) The water removed from the brine in each evaporator (V_1 V_2 V_3) in lb/hr.



CHAPTER 3
ENERGY AND ENERGY BALANCES

3.1 Forms of Energy

Three component of total energy of a system:

- **Kinetic energy (E_k)**
  - energy due to the translational motion of the system as a whole relative to some frame of reference (usually the earth's surface) or to rotation of the system about some axis.
- **Potential energy (E_p)**
  - energy due to the position of the system in a potential field (such as a gravitational or electromagnetic field).
- **Internal energy (U)**
  - all energy possessed by a system other than kinetic and potential energy; or
  - Energy due to translation, rotation, vibration & electromagnetic interactions of the molecules, atom and subatomic particle within the system.

3.2 Transfer of Energy

- In closed system (i.e. no mass is transferred across the system boundaries while the process is taking place), energy may be transferred between such a system and its surroundings in two ways as heat or work.

Heat

- Energy that flows as a result of temperature difference between a system and its surroundings.
- The direction of flow is always from a higher temperature to a low one.
- Heat is defined as positive when its transferred to the system from the surroundings.

Work

- Energy that flows in response to any driving force other a temperature difference, such as a force, a torque or a voltage.
- Work is defined as positive when it is done by the system on the surroundings.

3.3 First Law of Thermodynamics

- Law of conservation of energy, which state that energy can neither be created nor destroyed.
- General form of first law of thermodynamics

Inlet Energy + Heat - Outlet Energy – Work = Accumulation

where;

Inlet energy and outlet energy is summation/total of all energy such as potential, kinetic and internal energy.

3.4 Kinetic Energy Equation (E_k)

- Kinetic energy, E_k (J) of an object of mass ***m*** (kg) moving with velocity ***u*** (m/s) relative to the surface of the earth is

$$E_k = \frac{1}{2}mu^2 \qquad [3.1]$$

- If the fluid enters a system with a mass flow rate $\dot{m}$ (kg/s) and uniform velocity u (m/s), the rate at which kinetic energy $\dot{E}_K$ (J/s) is transported into the system is

$$\dot{E}_k = \frac{1}{2}\dot{m}u^2 \qquad [3.2]$$

Example 3.1

Water flows into a 2 cm internal diameter (ID) pipe at a rate of 2.00 m³/h. Calculate $\dot{E}_k$ for this stream in J/s.

Solution:

$$\dot{E}_K = \frac{1}{2}\dot{m}u^2$$

First, we calculate the velocity (u).

$$\text{Velocity (u)} = \frac{\text{Volumetric flowrate}}{\text{Pipe cross sectional area}} = u = \frac{\dot{V}}{A(\pi r^2)}$$

$$= \frac{2.00m^3}{h} \times \frac{1}{\pi(1)^2 cm^2} \times \frac{100^2 cm^2}{1^2 m^2} \times \frac{1h}{3600s} = 1.77m/s$$

Then, we calculate the mass flow rate of the water $(\dot{m})$.

$$\dot{m} = \dot{V}\rho = \frac{2.00m^3}{h} \times \frac{1000kg}{m^3} \times \frac{1h}{3600s} = 0.556kg/s$$

Finally, calculate $\dot{E}_K$

$$\dot{E}_K = \frac{1}{2}\dot{m}u^2 = \frac{0.556 kg/s}{2} \times \frac{(1.77)^2 m^2}{s^2} \times \frac{1N}{1kg.m/s} = 0.870 N.m/s = 0.870 J/s$$

3.5 Potential Energy Equation (E_p)

- Gravitational potential energy, E_p of an object is given below

$$E_p = mgz \qquad [3.3]$$

- If the fluid enters a system with a mass flow rate $\dot{m}$ (kg/s) and an elevation z relative to the potential energy reference plane.

$$\dot{E}_p = \dot{m}gz \qquad [3.4]$$

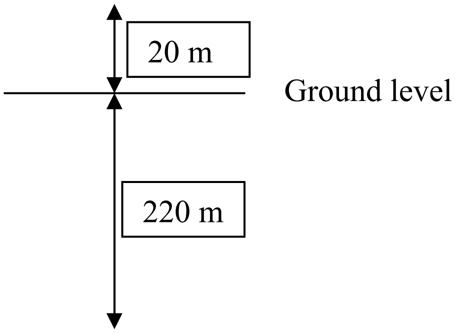
- Normally we are interested in the change of potential energy during energy balance calculation;

$$\Delta\dot{E}_p = \dot{E}_{p_2} - \dot{E}_{p_1} = \dot{m}g(z_2 - z_1) \qquad [3.5]$$

Example 3.2

Crude pump oil is pumped at a rate of 15.0 kg/s from a point 220 meters below the earth's surface to a point 20 meters above the ground level. Calculate the attendant rate of increase of potential energy.

Solution:



$$\Delta\dot{E}_p = \dot{E}_{p2} - \dot{E}_{p1} = \dot{m}g(z_2 - z_1)$$
$$= \frac{15kg}{s} \times \frac{9.81m}{s^2} \times \frac{[20 - (-220)]m}{} \times \frac{1N}{1kg.m/s^2}$$
$$= 35300 N.m/s = 35300 J/s = 35300 W$$

3.6 Energy Balances on Closed System

- Closed system is defined as no mass is transferred across the system boundaries while the process is taking place.
- Energy balance for closed system;

Final System Energy – Initial System Energy = Net Energy Transferred to the System

where;

Initial energy system $= U_{(initial)} + E_{K(initial)} + E_{P(initial)}$
Final energy system $= U_{(final)} + E_{K(final)} + E_{P(final)}$
Net energy transfer $= Q - W$

$$\boxed{(U_{(final)} - U_{(initial)}) + (E_{K(final)} - E_{K(initial)}) + (E_{P(final)} - E_{P(initial)}) = Q - W}$$

or

$$\boxed{\Delta U + \Delta E_k + \Delta E_p = Q - W} \qquad [3.6]$$

- When applying energy balance equation to a given process, the following point must be aware;
  1. The internal energy of a system depends almost entirely on the chemical composition, state of aggregation (solid, liquid, or gas), and temperature of the system materials. If no temperature changes, phase changes, or chemical reactions occur in a closed system and if pressure changes are less than a few atmospheres, then $\Delta U \approx 0$.
  2. If a system is not accelerating, then $\Delta E_K = 0$. If a system is not rising or falling, then $\Delta E_P = 0$.
  3. If a system and its surroundings are at the same temperature or the system is perfectly insulated, then $Q = 0$. The process is then termed adiabatic.
  4. Work done on or by a closed system is accomplished by movement of the system boundary against a resisting force or the passage of an electrical current or radiation across the system boundary. If there no moving parts or electrical current at the system boundary, then $W = 0$.

3.7 Energy Balances on Open System

- In open system, mass is transferred across the system boundaries while the process is taking place.
- Therefore work must be done on open system to push mass in and work is done on the surrounding by mass that emerges from the systems.
- Both work terms must be include in the energy balance for open system.

- The net work done by an open system;

$$\dot{W} = \dot{W}_s + \dot{W}_{fl}$$
$$\dot{W}_{fl} = \dot{W}_{out} - \dot{W}_{in} = P_{out}\dot{V}_{out} - P_{in}\dot{V}_{in}$$

where;
$\dot{W}_S$ - shaft work (rate of work done by the process fluid on a moving part within the system such as a pump rotor.)

$\dot{W}_{fl}$ - flow work (rate of work done by the fluid at the system outlet minus rate of work done by the fluid at the system inlet.)

- ^ symbol is used to denote the specific property (property divided by mass or by mole) such as specific internal energy ($\hat{U}$ kJ/kg), specific volume ($\hat{V}$ m^3/kg) and so on.
- One important property for energy balance on open system is specific enthalpy ($\hat{H}$ kJ/kg).

$$\hat{H} = \hat{U} + P\hat{V} \tag{3.7}$$

- Sometimes, universal gas law constant can be used as a conversion factor to evaluate specific enthalpy.

Example 3.3

The specific internal energy of helium at 300 K and 1 atm is 3800 J/mol, and the specific molar volume at the same temperature and pressure is 24.63 L/mol. Calculate the specific enthalpy of helium at this temperature and pressure, and the rate at which enthalpy is transported by a stream of helium at 300 K and 1 atm with a molar flowrate of 250 kmol/h.

Solution:

$$\hat{H} = \hat{U} + P\hat{V} = 3800J/mol + (1atm)(24.63L/mol) = 3800J/mol + 24.63L.atm/mol$$

To convert *L.atm/mol* into *J/mol*, we need the factor *J/(L.atm).* From the gas constant table,

$$0.08206 \text{ L.atm/(mol.K)} = 8.314 \text{ J/(mol.K)}$$

By dividing these two, the desired factor will be obtained;

$$\frac{8.314J/(mol.K)}{0.08206L.atm/(mol.K)} = 101.3J/(L.atm)$$

So;

$$\hat{H} = 3800 J/mol + \left[\frac{24.63 L.atm}{mol} \times \frac{101.3 J}{L.atm}\right] = 6295 J/mol$$

If n = 250 kmol;

$$\dot{H} = n\hat{H} = \frac{250 kmol}{h} \times \frac{6295 J}{mol} \times \frac{1000 mol}{1 kmol} \times \frac{1 h}{3600 s} = 437150 J/s = 437 kW$$

Answer:

- Energy balances equation for open system;

$$\Delta\dot{H} + \Delta\dot{E}_k + \Delta\dot{E}_p = \dot{Q} - \dot{W}_s \qquad [3.8]$$

where;

$$\Delta\dot{H} = \sum_{\substack{output\\stream}} m_j\hat{H}_j - \sum_{\substack{input\\stream}} m_j\hat{H}_j$$

$$\Delta\dot{E}_K = \sum_{\substack{output\\stream}} \frac{m_j u_j^2}{2} - \sum_{\substack{input\\stream}} \frac{m_j u_j^2}{2}$$

$$\Delta\dot{E}_P = \sum_{\substack{output\\stream}} m_j g z_j - \sum_{\substack{input\\stream}} m_j g z_j$$

3.8 Reference States and State Properties

- It is not possible to know the absolute value of $\hat{U}$ and $\hat{H}$ for a process material, but we can determine the change in $\Delta\hat{U}$ and change in $\Delta\hat{H}$ corresponding to a specific change of state (temperature, pressure, phase).
- A convenient way to tabulate $\Delta\hat{U}$ and $\Delta\hat{H}$ is to choose a temperature, pressure and state of aggregation (i.e. phase) as a reference state.
- Since $\hat{H}$ cannot be known absolute, for convenience we may assign a value $\hat{H}_O = 0$ to be a reference state. Then $\Delta\hat{H}_1 = \hat{H}_1 - 0$; $\Delta\hat{H}_2 = \hat{H}_2 - 0$; and so on.
- Some enthalpy tables give the reference states on which the listed values of $\hat{H}$ are based and others do not.
- However, we do not have to know the reference state to calculate $\Delta\hat{H}$ for the transition from one state to another state since the values are based on the same reference in the table.

- $\hat{H}$ and $\hat{U}$ can be said as state properties (property whose change of value in any process depend only on it initial and final states and do not depend on the path take to reach the state.

Example 3.4

The following data are for methyl chloride:

State	***T(°F)***	***P(psia)***	$\hat{V}(ft^3/lb_m)$	$\hat{H}(Btu/lb_m)$
Liquid	-40	6.878	0.01553	0.0
Vapor	0	18.9	4.969	196.23
Vapor	50	51.99	1.920	202.28

(a) What reference state was used to generate the given enthalpies?
(b) Calculate $\Delta\hat{H}$ and $\hat{\Delta}U$ for the transition of saturated methyl chloride vapor from 50°F to 0°F.

Solution:

(a) Liquid at -40 °F and 6.878 psia (the state at which $\hat{H}=0$).

(b) $\Delta\hat{H}=\hat{H}_{final}-\hat{H}_{initial}=(196.23-202.28)Btu/lb_m=-6.05Btu/lb_m$

From equation 3.7,

$$\Delta\hat{H}=\Delta\hat{U}+\Delta P\hat{V}$$

$$\therefore \Delta U=\Delta H-\Delta(PV)=-6.05Btu/lb_m-\left[\frac{(93.914-99.821)psia.ft^3/}{lb_m}\times\frac{1.987Btu}{10.73ft^3.psia}\right]$$

$$\Delta U=-4.96Btu/lb_m$$

3.9 Steam Table

The simplest phase diagrams are pressure-temperature diagrams of a single simple substance, such as water. Figure 3.1 shows the water phase diagram. The axes correspond to the pressure and temperature. The phase diagram shows, in pressure-temperature space, the lines of equilibrium or phase boundaries between the three phases of solid, liquid, and gas.

The phase boundary between liquid and gas does not continue indefinitely. Instead, it terminates at a point on the phase diagram called the critical point. This reflects the fact that, at extremely high temperatures and pressures, the liquid and gaseous phases become indistinguishable, in what is known as a supercritical fluid. In water, the critical point occurs at around T_c=647.096 K (1,164.773 °R), p_c=22.064 MPa (3,200.1 psi) and ρ_c=356 kg/m³.

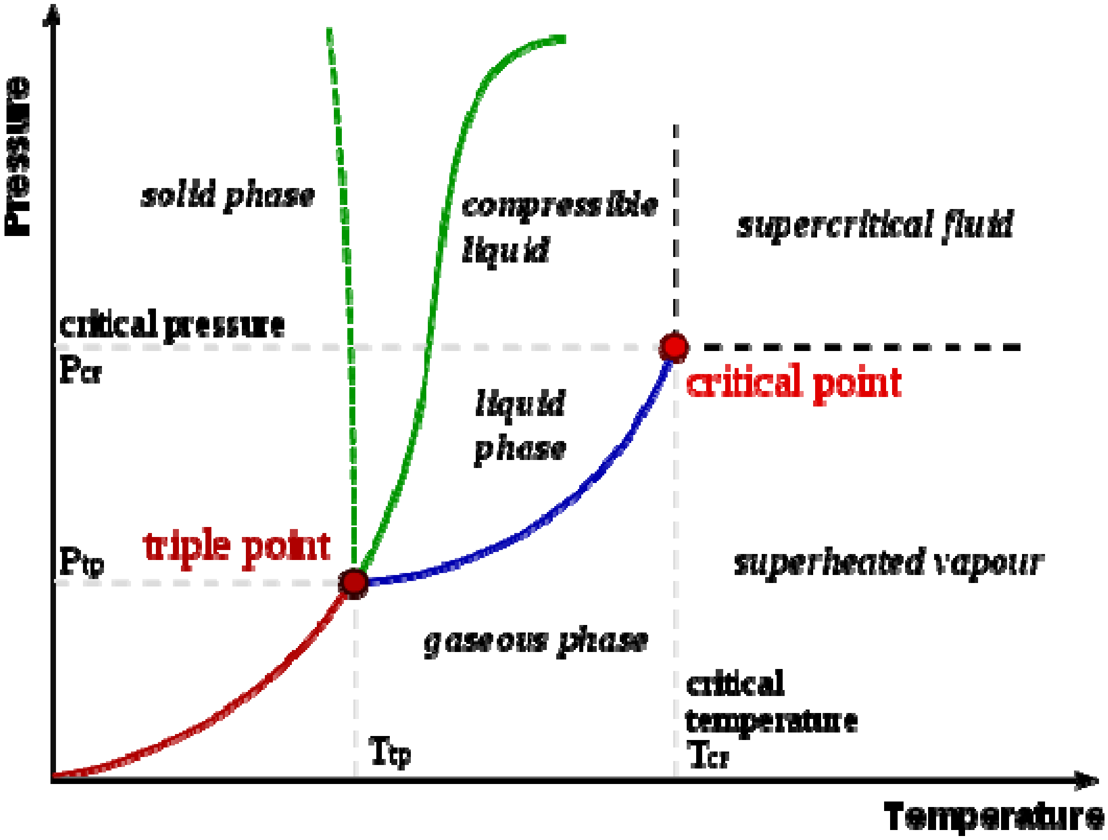


Figure 3.1: Water Phase Diagram

Appendix 1 lists properties of saturated liquid water and saturated steam at temperature from 0.01 °C to 100 °C. The following properties can be determined for each tabulated temperature:

Column 2. The pressure

Column 3. The specific volumes, $\hat{v}_g / v_g$ (m³/kg), of gas or saturated steam.

Column 4 – 5. The specific internal energies; u_f for liquid/fluid, u_g for gas.

Column 6-8. The specific enthalpies; h_f for liquid/fluid, h_{fg} for intermediate (liquid and gas), h_g for gas.

Column 9 – 11. The entropies. s_f for liquid/fluid, s_{fg} for intermediate (liquid and gas), s_g for gas.

Page 2 (Appendix 1) list the same properties as page 1(Appendix 1), except the pressure is the first column and temperature the second and the table covers a much broader range of temperatures and pressures. Appendix 2 is known as superheated steam table. It is used for superheated properties of steam.

Example 3.5

(a) Determine the pressure, specific internal energy and specific enthalpy of saturated steam at 330.8 °C.

(b) Show that water at 400 °C and 10 bar is superheated steam and determine its specific volume, specific internal energy and specific enthalpy.

Solution:

(a) Data in page 1 (Appendix 1) does not go to 330.8 °C, so we take a look at Page 2.

$$p = 130\text{bar}; u_g = 2496\text{kJ/kg};\ h_g = 2662\text{kJ/kg}$$

(b) The data in Appendix 1 does not cover temperature more than 374.15, therefore it is superheated steam.

$$v = 0.3065;\ u_g = 2957\text{kJ/kg};\ h_g = 3262\text{kJ/kg}$$

3.9 Energy Balance Tips

- When labeling flowchart, write down together the temperature, pressure and state of aggregation of the process material.
- Normally (depend on the process description) for chemical process unit; shaft work, kinetic and potential energy change tend to be negligible compared to heat flows, internal energy and enthalpy changes.
- Then simplified energy balance become;
  For closed system

$$Q = \Delta U \qquad [3.9]$$

For open system

$$\dot{Q} = \Delta\dot{H} \qquad [3.10]$$

Problems

1. Liquid methanol is pumped from a large storage tank through a 1 inch internal pipe (ID) at the rate of 3.00 gal/min. At what rate in **ft.lbf/s** and **hp** is kinetic energy being transported by the in the pipe methanol? (Given: Density of methanol = 49.5 lbm/ft^3).

2. Air at 300 °C and 130 kPa flows through a horizontal 7 cm ID pipe at velocity of 42.0 m/s. Calculate $\dot{E}_K(W)$, assuming ideal gas behavior.

3. If you pour 1 gallon of water on a yowling cat 10 ft below your bedroom window, how much potential energy (ft.lbf) does the water lose?

4. Carbon monoxide (CO) at 120 K and 45 atm has a tabulated specific volume of 5.23 cm^3/g and specific internal energy of 1813 J/mol. Calculate the specific enthalpy of CO in this state.

5. Oxygen at 150 K and 41.64 atm has a tabulated specific volume of 4.684 cm^3/g and a specific internal energy of 1706 J/mol. Calculate the specific enthalpy of O_2 in this state.

6. Values of the specific internal energy of a fuel gas at two conditions are listed below.

State *[Fasa]*	**T(K)**	**P(bar)**	$\hat{V}$ **(L/mol)**	$\hat{U}$ **(kJ/mol)**
Liquid *[Cecair]*	320	0.505	0.0978	0.000
Vapor *[Wap]*	320	0.550	97.78	35.4

i) What reference state was used to generate the listed specific internal energies?

ii) Calculate $\Delta\hat{U}$ (kJ/mol) for a process in which a fuel gas vapor at 320 K is condensed at constant pressure. Then, calculate $\Delta\hat{H}$ (kJ/mol) for the same process. Finally, calculate $\Delta\hat{H}$ (kJ) for 25 mol of the fuel gas that undergo the process.

7. Complete the following table.

T(^{O}C)	**P(Bar)**	$\hat{V}$ **(m^3/kg)**	$\hat{U}$ **(kJ/kg)**	**Phase** ***[Fasa]***
88	....	....	....	Saturated steam
....	....	....	1511	Water
....	32	....	....	Water
475	15	....	....	....
....	197	....	....	Saturated steam

CHAPTER 4
ENERGY BALANCE ON NONREACTIVE SPECIES

4.1 Introduction

- Normally in chemical process unit, W_S =0; ΔE_P=0; ΔE_K=0; Then energy balance equation become:

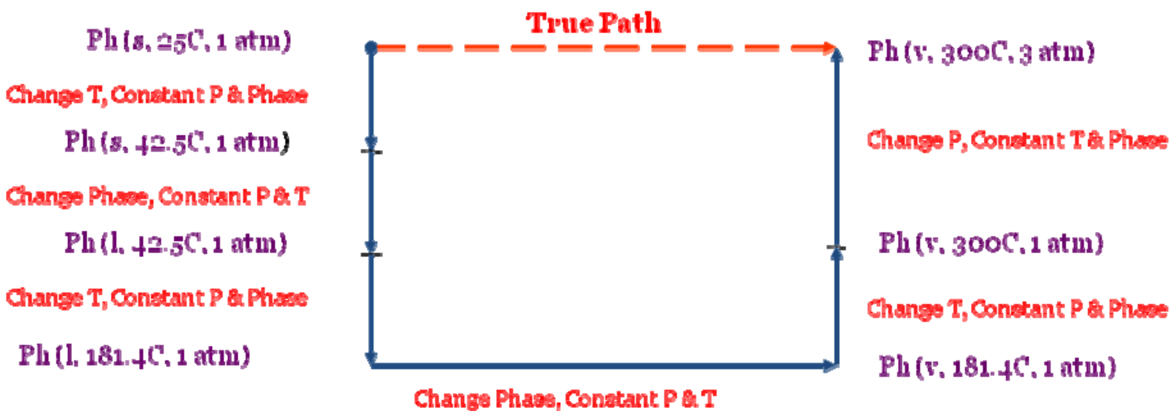
Close System $Q = \Delta U$	Open System $Q = \Delta H$

- For this chapter, we will learn the procedure for evaluating ΔU and ΔH when table $\hat{H}$ and $\hat{U}$ are not available for all process species.
- Method to calculate $\Delta \hat{H}$ and $\Delta \hat{U}$ associated with certain process such as:
  1. Change in P, at constant T & constant state of aggregation.
  2. Change in T, at constant T & constant state of aggregation.
  3. Phase changes at constant T & constant P.
  4. Mixing at constant T & constant P.
  5. Chemical reaction at constant T & constant P.

4.2 Hypothetical Process Path

- **State properties**
  - Properties that depend on the state of the species (primarily on its temperature and state of aggregation, and to lesser extent on its pressure).
  - Specific enthalpy ($\hat{H}$) and specific internal energy ($\hat{U}$) are state properties species.
  - When a species passes from one state to another state, both $\Delta \hat{H}$ and $\Delta \hat{U}$ for the process are independent of the path taken from the first state to the second state.
- We can construct a hypothetical process path which can consist of several step based on our convenience, as long as we reach to the final state starting from their initial state.
- For example, the enthalpy change ($\Delta \hat{H}$) of solid phenol at 25 ^oC and 1 atm to phenol vapor at 300 ^oC and 3 atm.

  $\Delta \hat{H}_{phenol}$ = (vapor, 300˚C, 3 atm) – (solid, 25˚C, 1 atm)
  - Cannot determine directly from enthalpy table – must use hypothetical process path consist of several step.
  - Check Table of Physical Properties Data Appendix 5: P= 1 atm; T_m= 42.5°C and T_b= 181.4°C



$$\boxed{\Delta\hat{H} = \Delta\hat{H}_1 + \Delta\hat{H}_2 + \Delta\hat{H}_3 + \Delta\hat{H}_4 + \Delta\hat{H}_5 + \Delta\hat{H}_6}$$

4.3 Procedure Energy Balance Calculations

1. Perform all required material balance calculations.
2. Write the appropriate form of the energy balance (closed or open system) and delete any of the terms that are either zero or negligible for the given process system.
3. Choose a reference state – phase, temperature, and pressure – for each species involved in the process.
4. Construct inlet-outlet table for specific internal energy (close system) or specific enthalpy (close system)
    - For closed system, construct a Table with columns for initial and final amounts of each species (m_i or n_i) and specific internal energies ($\hat{U}$) relative to the chosen reference states.
    - For an open system, construct a table with columns for inlet and outlet stream component flow rates (m_i or n_i) and specific enthalpies ($\hat{H}$) relative to the chosen references states.
5. Calculate all required values of $\hat{H}$ or $\hat{U}$ and insert the values in the appropriate places in the table. Then calculate $\Delta\hat{H}$ or $\Delta\hat{U}$ for the system.
6. Calculate any work, kinetic energy, or potential energy terms that you have not dropped from the energy balance.
7. Solve the energy balance for whichever variable is unknown (often Q).

Example of Inlet-Outlet Enthalpy Table:

References: Ac (liquid, 20˚C, 5atm); N_2 (gas, 25˚C, 1atm)

Substance	**Inlet**		**Outlet**	
	$\dot{n}_{in}$	$\hat{H}_{in}$	$\dot{n}_{out}$	$\hat{H}_{out}$
Ac (vapor)	66.9		3.35	
Ac (l)	-	-	63.55	0
N_2	33.1		33.1	

4.4 Change in Pressure (P) at Constant Temperature (T) & Constant Phase

- **Solid & Liquid**
  - Nearly independent of pressure.

$$\boxed{\begin{aligned}\Delta\hat{U} &= 0\\ \Delta\hat{H} &= \hat{V}\Delta P\end{aligned}}$$

- **Ideal Gases**
  - Independent of pressure (unless undergo very large pressure changes).

$$\boxed{\begin{aligned}\Delta\hat{U} &= 0\\ \Delta\hat{H} &= 0\end{aligned}}$$

4.5 Change in Temperature (T) at Constant Pressure (P) & Constant Phase

- <u>Sensible heat</u> is the heat that must be transferred to RAISE or LOWER the temperature of substance or mixture of substance.
  - C_P - Heat capacity at constant pressure (given in Appendix 3 the form of polynomial and the equation is the function of temperature).
  - C_V - Heat capacity at constant volume.

$$\boxed{\begin{array}{ll} C_p = C_v & \textit{Liquid \& Solid} \\ C_p = C_v + R & \textit{Ideal Gas} \end{array}}$$

- Specific internal energy change:

$$\boxed{\Delta\hat{U} = \int_{T1}^{T2} C_v(T)dT}$$

Ideal gas	: exact
Solid or liquid	: good approximation
Nonideal gas	: valid only if volume (V) is constant

- Specific enthalpy change:

$$\boxed{\Delta\hat{H} = \int_{T1}^{T2} C_p(T)dT}$$

Ideal gas : exact
Nonideal gas : exact only if pressure (P) is constant

$$\boxed{\Delta\hat{H} = \hat{V}\Delta P + \int_{T1}^{T2} C_p(T)dT}$$

Solid & liquid

4.6 Heat Capacities, Cp

- Estimation of heat capacities, Cp
    - Kopp's rule is the simple empirical method for estimating Cp of solid or liquid at 20 °C based on the summation of atomic heat capacities of the molecular compound.

$$(C_P)_{Ca(OH)_2} = (C_{P_a})_{Ca} + 2(C_{P_a})_O + 2(C_{P_a})_H$$
$$= 26 + (2\times 17) + (2\times 9.6) = 79 J/mol.^O C$$

- Estimation for heat capacities of mixtures

$$\boxed{(C_p)_{mix}(T) = \sum y_i C_{pi}(T)}$$

C_{P_i} = C_p for ith component
y_i = mass or moles fraction

Example 4.1

Calculate the heat required to raise 200 kg nitrous oxide (N_2O) from 20 °C to 150 °C in a constant volume vessel. The constant volume heat capacity of N_2O in this temperature range is given by this equation;

$$C_v(kJ/kg.^\circ C) = 0.855 + 9.42\times 10^{-4} T$$

where T is °C.

Solution:

$$\Delta U(kJ/kg) = \int_{20^\circ C}^{150^\circ C} \left(0.855 + 9.42\times 10^{-4} T\right) dT$$
$$= \left[0.855T\right]_{20^\circ C}^{150^\circ C} + \left[\frac{9.42\times 10^{-4} T^2}{2}\right]_{20^\circ C}^{150^\circ C}$$
$$= [0.855(150-20)] + \left[\frac{9.42\times 10^{-4}(150^2 - 30^2)}{2}\right]$$
$$= 111.15 + 10.491$$
$$= 121.56 kJ/kg$$

Example 4.2

15 kmol/min of air is cooled from 430 °C to 100 °C. Calculate the required heat removal rate using 1) heat capacities formulas from Heat Capacities Table (Appendix 3) and 2) Specific Enthalpies Table (Appendix 4).

Solution:

1. Write the energy balance for open system:

$$\Delta\dot{H} + \cancelto{0}{\Delta\dot{E}_K} + \cancelto{0}{\Delta\dot{E}_p} = \dot{Q} + \cancelto{0}{\dot{W}_s}$$

$$\dot{Q} = \Delta\dot{H} = \dot{n}_{air}\hat{H}_{air,out} - \dot{n}_{air}\hat{H}_{air,in} = \dot{n}\hat{H}$$

2. Using the heat capacities table (Appendix 3):

$$\Delta\hat{H}(kJ/mol) = \int_{430^\circ C}^{100^\circ C} C_p(T)dT$$

$$\Delta\hat{H}(kJ/mol) = \int_{430^\circ C}^{100^\circ C} \left[28.94\times10^{-3} + 0.4147\times10^{-5}T + 0.3191\times10^{-8}T^2 - 1.965\times10^{-12}T^3\right]dT$$

$$\Delta\hat{H}(kJ/mol) = \left[28.94\times10^{-3}T\right]_{430\circ C}^{100^\circ C} + \left[\frac{0.4147\times10^{-5}T^2}{2}\right]_{430\circ C}^{100^\circ C} + \left[\frac{0.3191\times10^{-8}T^3}{3}\right]_{430\circ C}^{100^\circ C} - \left[\frac{1.965\times10^{-12}T^4}{4}\right]_{430\circ C}^{100^\circ C}$$

$$\Delta\hat{H}(kJ/mol) = \left[28.94\times10^{-3}T(100-430)\right] + \left[\frac{0.4147\times10^{-5}(100^2-430^2)}{2}\right] + \left[\frac{0.3191\times10^{-8}(100^3-430^3)}{3}\right]$$

$$-\left[\frac{1.965\times10^{-12}(100^4-430^4)}{4}\right]$$

$$\Delta\hat{H}(kJ/mol) = -9.98kJ/mol$$

3. Using Tabulated Enthalpies (Appendix 4):

Read the value directly from the table according to the temperature desired:

$$\hat{H}(100^\circ C) = 2.19kJ/mol$$

$$\hat{H}(430^\circ C) = 12.179kJ/mol$$

$$\Delta\hat{H} = (2.19 - 12.179)kJ/mol = -9.98kJ/mol$$

4. Calculate the heat removal rate.

$$Q = \Delta\dot{H} = \dot{n}\Delta\hat{H} = \frac{15kmol}{\min}\times\frac{1000mol}{1kmol}\times\frac{1\min}{60s}\times\frac{-9.98kJ}{mol}\times\frac{1kW}{1kJ/s} = 2495kW$$

Note: We can use Table in Appendix 4 if the gases are covered in the table. If not, you have to calculate using the harder way that is heat capacities (Appendix 3).

Example 4.3

Calculate the heat required to bring 150 mol/h of a stream containing 50% C_2H_6 and 50% C_3H_8 by volume from 0 ^{O}C to 400 ^{O}C. Determine a heat capacity for the mixture.

Solution:

From heat capacities table;

$$C_{P(C_2H_6)} = 49.37\times10^{-3} + 13.92\times10^{-5}T - 5.816\times10^{-8}T^2 + 7.28\times10^{-12}T^3$$

$$C_{P(C_3H_8)} = 68.032\times10^{-3} + 22.59\times10^{-5}T - 13.11\times10^{-8}T^2 + 31.71\times10^{-12}T^3$$

$$(Cp)_{mix}[kJ/(mol.^{\circ}C)] = 0.5\int_{0^{\circ}C}^{400^{\circ}C} 49.37\times10^{-3} + 13.92\times10^{-5}T - 5.816\times10^{-8}T^2 + 7.28\times10^{-12}T^3$$

$$+0.5\int_{0^{\circ}C}^{400^{\circ}C} 68.032\times10^{-3} + 22.59\times10^{-5}T - 13.11\times10^{-8}T^2 + 31.71\times10^{-12}T^3$$

Try to integrate and calculate by yourself.

$$\Delta\hat{H} = 36.19kJ/mol$$

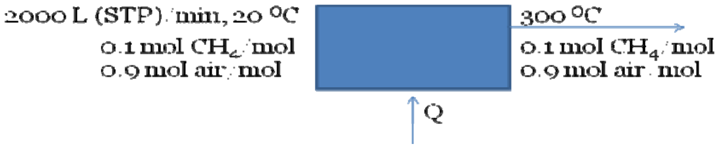
$$\dot{Q} = \Delta\dot{H} = \dot{n}\Delta\hat{H} = \frac{150mol}{h}\times\frac{36.19kJ}{mol}\times\frac{1h}{3600s} = 1.51kW$$

Example 4.4

A stream of gas containing 10 % CH_4 and 90 % air by volume is to be heated from 20 $^{\circ}$C to 300 $^{\circ}$C. Calculate the required rate of heat input in kW if the flow rate of the gas is 2.00 x 10^3 liters (STP)/min.

Solution:

1. Draw the flow chart.



2. Change the flow rate in STP to mol:

$$\dot{n} = \frac{2000L(STP)}{\min}\times\frac{1mol}{22.4L(STP)} = 89.3mol$$

CH_4= 0.1(89.3 mol) =8.93 mol; Air = (89.3-8.93)mol =80.4mol

3. Write the energy balance;

$$\Delta\dot{H} + \cancelto{0}{\Delta\dot{E}_k} + \cancelto{0}{\Delta\dot{E}_p} = \cancelto{0}{\dot{Q}} + W_s$$

$$\dot{Q} = \Delta\dot{H}$$

4. Construct inlet-outlet table.

References: CH_4 (gas, 20˚C, 1atm); air (gas, 25˚C, 1atm)

Substance	**Inlet**		**Outlet**	
	$\dot{n}_{in}$	$\hat{H}_{in}$	$\dot{n}_{out}$	$\hat{H}_{out}$
CH_4	8.93	0	8.93	$\hat{H}_1$
air	80.4	$\hat{H}_2$	80.4	$\hat{H}_3$

Why we choose air at 25°C and 1 atm as our reference? This is because it is the reference state for gases in Table B.8, so we can still calculate the enthalpy at 20°C.

5. Calculate the enthalpies.

$$\hat{H}_1 = \int_{20^\circ C}^{300^\circ C} (C_p)_{CH_4}\, dT$$

$$= \int_{20^\circ C}^{300^\circ C} (34.31\times10^{-3} + 5.469\times10^{-5}T + 0.3661\times10^{-8}T^2 - 11.0\times10^{-12}T^3)dT$$

$$= 12.1 kJ/mol$$

To calculate H_2 and H_3, use Table in Appendix 4:

$$\hat{H}_{(air,25^\circ C)} = 0.0 kJ/mol \qquad \hat{H}_{(air,25^\circ C)} = 0.0 kJ/mol$$

$$\hat{H}_{(air,20^\circ C)} = -0.144 kJ/mol \qquad \hat{H}_{(air,300^\circ C)} = 8.17 kJ/mol$$

$$\Delta\hat{H}_2 = (-0.144 - 0) kJ/mol \qquad \Delta\hat{H}_2 = (8.17 - 0) kJ/mol$$

Why we calculate $\Delta\hat{H}$ of air using Table B.8 instead of Table B.2? It is because the air is included in Table B.8. We can still integrate and calculate using the long way. You will get the same answer.

Insert the value of enthalpies inside the inlet-outlet table.

References: CH_4 (gas, 20˚C, 1atm); air (gas, 25˚C, 1atm)

Substance	**Inlet**		**Outlet**	
	$\dot{n}_{in}$	$\hat{H}_{in}$	$\dot{n}_{out}$	$\hat{H}_{out}$
CH_4	8.93	0	8.93	12.1
air	80.4	-0.144	80.4	8.17

6. Calculate the heat.

$$\dot{Q} = \Delta\dot{H} = \sum_{out} \dot{n}_i \hat{H}_i - \sum_{in} \dot{n}_i \hat{H}_i$$
$$= \left[(8.93 mol/\min)(12.1 kJ/mol) + (80.4 mol/\min)(8.17 k)/mol\right]$$
$$- \left[(80.4 mol/\min)(-0.144 kJ/mol) + (8.93 mol/\min)(0 kJ/mol)\right]$$
$$= 776.5 \frac{kJ}{\min} \times \frac{1\min}{60 s} = 12.94 kW$$

4.7 Phase Change Operations

Phase change such as melting and evaporation are usually accompanied by large changes in internal energy and enthalpy.

- **Latent heat**
  - Specific enthalpy change associated with the phase at constant temperature and pressure.
- **Heat of fusion or heat of melting, $\Delta\hat{H}_m$ (T,P)**
  - Specific enthalpy different between solid and liquid forms of species at T & P.
  - Heat of solidification (liquid to solid) is negative value of heat of fusion.
- **Heat of vaporization, $\Delta\hat{H}_v$ (T,P)**
  - Specific enthalpy different between liquid and vapor forms of species at T & P
  - Heat of condensation (vapor to liquid) is negative value of heat of vaporization.

The latent heat of phase change may vary considerably with the temperature at which the changes occurs but hardly varies with the pressure at the transition point.

4.8 Estimation of Heat of Vaporization

1. Trouton's rule – accuracy between 30%.

$\Delta\hat{H}_v (kJ/mol) = 0.088 T_b$ nonpolar liquid

$\Delta\hat{H}_v (kJ/mol) = 0.109 T_b$ water or low MW alcohol

where;
T_b = Boiling point temperature

2. Chen's equation – accuracy between 2%.

$$\Delta\hat{H}_v (kJ/mol) = \frac{T_b[0.0331(T_b/T_c) - 0.0327 + 0.0297 \log_{10} P_c]}{1.07 - (T_b/T_c)}$$

where;

T_b = Normal boiling point temperature

T_c = Critical temperature

P_c = Critical Pressure

3. Clausius-Clapeyron equation - plot ln p* versus 1/T.

$$In\ p^* = -\frac{\Delta\hat{H}_v}{RT} + B$$

4. Chaperon equation

$$\frac{d(In\ p^*)}{d(1/T)} = -\frac{\Delta\hat{H}_v}{R}$$

5. Watson correlation – estimate $\Delta\hat{H}_v$ at T_2 from known $\Delta\hat{H}_v$ at T_1.

$$\Delta\hat{H}_v(T_2) = \Delta\hat{H}_v(T_1)\left(\frac{T_c - T_2}{T_c - T_1}\right)^{0.38}$$

where;

T_c = Critical temperature

4.8 Estimation of Heat of Fusion

$\Delta\hat{H}_m$ (kJ/mol) = 0.0092 T_m (K)	metallic elements
= 0.0025 T_m (K)	inorganic compound
= 0.050 T_m (K)	organic compound

Example 4.5

The normal boiling point of methanol is 337.9 K, and the critical temperature of this substance is 513.2 K. Estimate the heat of vaporization of methanol at 300 °C .

Solution:

First, we calculate the standard heat of vaporization using Trouton's rule:

$\Delta\hat{H}_V(kJ/mol) \approx 0.109 T_b(K)$

$\approx (0.109(337.9))$

$\approx 36.83 kJ/mol$

Then, we calculate the latent heat using Watson's correlation:

$$\Delta\hat{H}_V(T_2) = \Delta\hat{H}_V(T_1)\left(\frac{T_c - T_2}{T_c - T_1}\right)^{0.38} = 36.83\left(\frac{513.2 - 473}{513.2 - 337.9}\right)^{0.38} = 21.0 kJ/mol$$

Problems:

1. Estimate the specific enthalpy of steam (kJ/kg) at 350 °C and 100 bar relative to steam at 100 °C and 1 atm using:
   (a) The steam tables
   (b) Heat capacities table

2. Chlorine gas is to be heated from 100 °C and 1 atm to 200 °C.
   (a) Calculate the heat input (kW) required to heat a stream of the gas flowing at 5.0 kmol/s at constant pressure.
   (b) Calculate the hat input (kJ) required to raise the temperature of 5.0 kmol of chlorine in a closed rigid vessel from 100 °C and 1 atm to 200 °C.

3. A stream of water vapor flowing at a rate of 250 mol/h is brought from 600 °C and 10 bar to 100 °C and 1 atm.
   (a) Estimate the required cooling rate (kW) three ways: (i) from the steam tables, (ii) using heat capacity data and (iii) using specific enthalpy data.
   (b) Which of the answers in part (a) is most accurate and why?

4. A fuel gas containing 95 mole% methane and the balance ethane is burned completely with 25% excess air. The stack gas leaves the furnace at 900 °C and is cooled to 450 °C in a waste heat boiler, a heat exchanger in which heat lost by cooling gases is used to produce steam from liquid water for heating , power generation, or process applications.
   (a) Taking as abasis of calculation 100 mol of the fuel gas fed to the furnace, calculate the amount of heat (kJ) that must be transferred from the gas in the waste heat boilerto accomplish the indicated cooling.
   (b) How much saturated steam at 50 bar can be produced from boiler feedwater at 40 °C for the same basis of calculation?

CHAPTER 5
ENERGY BALANCE OF REACTIVE SYSTEMS

5.1 Types of reaction

- ***Exothermic reaction*:** the product molecules have lower internal energies than the reactants at the same T and P. ΔH = NEGATIVE, reaction produces heat.

- ***Endothermic reaction*:** the product molecules have higher internal energies than the reactants. ΔH = POSITIVE, reaction consumes heat.

5.2 Heat of reaction

- ΔH depends on how the stoichiometric equation is written.

$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2(g) + 2H_2O(l)\ \Delta H_{r1}\ (25^{O}C) = -890.3$ kJ/mol ➔ for 1 CH_4

$2CH_4\,(g) + 4O_2\,(g) \rightarrow 2CO_2\,(g) + 4H_2O\,(l)\ \Delta H_{r2}\ (25^{O}C) = -1780.6$ kJ/mol ➔ for 2 CH_4

- ΔH depends on the states of aggregation (gas, liquid, or solid)

$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(l)$ $\quad\Delta H_{r1}$ (25°C)= -890.3 kJ/mol

$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(g)$ $\quad\Delta H_{r2}$ (25°C)= -802.3 kJ/mol

5.3 Standard heat of reaction (ΔH_r^o)

- heat of reaction when both reactants and products are at reference conditions (usually 25 °C and 1 atm).

$C_4H_{10}\,(g) + 13/2O_2\,(g) \rightarrow 4CO_2\,(g) + 5H_2O(l)$ $\quad\Delta H_{r1}$ (25 °C)= -2878 kJ/mol

Example: For 2400 mol/s CO_2 produced;

$$\Delta H_{r2} = \frac{2400}{4mol/s} \times \left(-2878 \frac{kJ}{mol} \right) = -1.73 \times 10^{6} kJ/s$$

5.4 Reaction in a REACTOR (constant V)

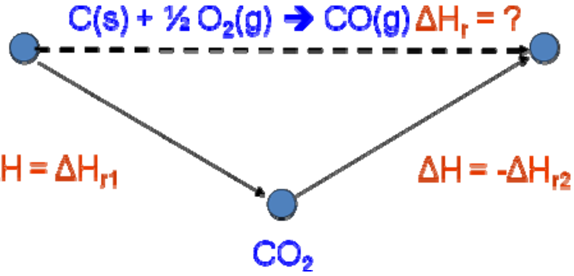
$\Delta U_r(T) = U_{products} - U_{reactants}$

$$\Delta U_r(T) = \Delta H_r(T) - RT \left(\sum_{\substack{\text{gaseous}\\\text{products}}} |v_i| - \sum_{\substack{\text{gaseous}\\\text{reactants}}} |v_i| \right)$$

5.5 Hess's Law

- Look at this reaction.

C (s) + ½ O_2 (g) ➔ CO (g): $\Delta H_r = ?$
(1) C (s) + O_2 (g) ➔ CO_2 (g): $\Delta H_{r1} = -393.51$ kJ/mol
(2) CO (g) + ½ O_2 (g) ➔ CO_2 (g): $\Delta H_{r2} = -282.99$ kJ/mol



$$\mathbf{\Delta H_r = \Delta H_{r1} + (-\Delta H_{r2})} = (-393.51 + (-282.99)) = -110.52 \text{ kJ/mol}$$

Example 5.1

The standard heats of the following combustion reactions have been determined experimentally:

1. $C_2H_6 + 7/2\ O_2 \rightarrow 2\ CO + 3\ H_2O$: $\Delta\hat{H}^0_{r1} = -1559.8 kJ/mol$
2. $C + O_2 \rightarrow CO_2$: $\Delta\hat{H}^0_{r2} = -393.5 kJ/mol$
3. $H_2 + ½\ O_2 \rightarrow H_2O$: $\Delta\hat{H}^0_{r3} = -285.8 kJ/mol$

Use Hess's law and the given heats of reaction to determine the standard heat of reaction

4. $2\ C + 3\ H_2 \rightarrow C_2H_6$ $\Delta\hat{H}^0_{r4} = ?$

Solution:

1) Rearrange the given equations:

(Eq. 2 x 2) $2C + 2O_2 \rightarrow 2CO_2$ $\Delta\hat{H}^0_{r2} = (-393.5 \times 2) kJ/mol = -787 kJ/mol$
(Eq. 3 x 3) $3H_2 + 3/2\ O_2 \rightarrow 3H_2O$ $\Delta\hat{H}^0_{r3} = (-285.8 \times 3) kJ/mol = -857.4 kJ/mol$
(Eq. 1) $C_2H_6 + 7/2\ O_2 \rightarrow 2\ CO + 3\ H_2O$ $\Delta\hat{H}^0_{r3} = -1559.8 kJ/mol$

2) Substrate or add these equations to form the desired equation:

$3H_2 + 3/2\ O_2 \rightarrow 3H_2O$ $\Delta\hat{H}^0_{r3} = -857.4 kJ/mol$
\+ $2C + 2O_2 \rightarrow 2CO_2$ $\Delta\hat{H}^0_{r2} = -787 kJ/mol$

$3H_2 + 7/2\ O_2 + 2C \rightarrow 3H_2O + 2CO_2$ $\Delta\hat{H}^0_{r(3-2)} = -1644.4 kJ/mol$
\- $C_2H_6 + 7/2\ O_2 \rightarrow 2\ CO_2 + 3\ H_2O$ $\Delta\hat{H}^0_{r1} = -1559.8 kJ/mol$

$3H_2 + 2C \rightarrow C_2H_6$ $\Delta\hat{H}^0_{r4} = -84.6 kJ/mol$

5.6 Heat of combustion (ΔH_c)

- The heat of the combustion of a substance with oxygen to yield specific products.

C_2H_5OH (l) + 3 O_2 (g) ➔ 2 CO_2 (g) + 3 H_2O (l): ΔH_c (25 °C, 1 atm) = -1366.9 kJ/mol

- The value of H_c for the substance is indicated in Table B.1.

$$\Delta H_r^o = -\sum_i v_i (\Delta H_c^o)_i = \left(\sum_{\text{reactants}} |v_i| (\Delta H_c^o)_i - \sum_{\text{products}} |v_i| (\Delta H_c^o)_i \right)$$

Example 5.2:

Calculate the heat of reaction for the dehydrogenation of ethane:

C_2H_6 ➔ $C_2H_4 + H_2$

Then, use Hess's law to find the standard heat of reaction for the above equation, using these reactions:

1. $C_2H_6 + 7/2O_2$ ➔ $2CO_2 + 3H_2O$
2. $C_2H_4 + 3\ O_2$ ➔ $2CO_2 + 2H_2O$
3. $H_2 + ½\ O_2$ ➔ H_2O

Compare the answer.

Solution:

1) Find standard heat of combustion for every substance. From Appendix 5;

$$(\Delta H_c^0)_{C_2H_6} = -1559.9 kJ/mol$$
$$(\Delta H_c^0)_{C_2H_4} = -1410.99 kJ/mol$$
$$(\Delta H_c^0)_{H_2} = -285.84 kJ/mol$$

2) Use the formula to calculate the standard heat of reaction:

$$\Delta H_r^o = -\sum_i v_i (\Delta H_c^o)_i = \left(\sum_{\text{reactants}} |v_i| (\Delta H_c^o)_i - \sum_{\text{products}} |v_i| (\Delta H_c^o)_i \right) = [(-1559.9) - (-1410.99 - 285.84) kJ/mol)$$

$$\Delta H_r^o = -136.9 kJ/mol$$

3) Find the standard heat of reaction for each equation using standard heat of combustion:

$$\Delta H^0_{r\,(Eq.1)} = -1559.9 kJ/mol$$

$$\Delta H^0_{r\,(Eq.2)} = -1410.99 kJ/mol$$

$$\Delta H^0_{r\,(Eq.3)} = -285.84 kJ/mol$$

4) Substrate or add these equations to form the desired equation:

	(1) – (2) – (3)	
	$C_2H_6 + 7/2O_2 \rightarrow 2CO_2 + 3H_2O$	$\Delta H^0_{r\,(Eq.1)} = -1559.9 kJ/mol$
-	$C_2H_4 + 3O_2 \rightarrow 2\ CO_2 + 2\ H_2O$	$\Delta H^0_{r\,(Eq.2)} = -1410.99 kJ/mol$
	$C_2H_6 + ½\ O_2 \rightarrow C_2H_4 + H_2O$	$\Delta H^0_{r\,(Eq.1-2)} = -148.91 kJ/mol$
-	$H_2 + ½\ O_2 \rightarrow H_2O$	$\Delta H^0_{r\,(Eq.3)} = -285.84 kJ/mol$
	$C_2H_6 \rightarrow C_2H_4 + H_2$	$\Delta H^0_{r} = -136.93 kJ/mol$

5.7 Heat of formation (ΔH_f)

- Enthalpy change associated with the formation of 1 mole of a compound from its elemental constituents (in nature) at a reference T and P.

N_2 (g) + 2 H_2 (g) + 3/2 O_2 (g) ➔ NH_4NO_3 (c) ΔH_r^o = -365.14 kJ/mol
6 C(s) + 3 H2 (g) ➔ C_6H_6 (l) ΔH_r^o = 48.66 kJ/mol
Note: standard heat of formation of an elemental species is **ZERO.**

$$\Delta H_r^{\,o} = \sum_i v_i \Delta H^o_{fi} = \left(\sum_{\text{products}} |v_i| \Delta H^o_{fi} - \sum_{\text{reactants}} |v_i| \Delta H^o_{fi} \right)$$

Example 5.3

Determine the standard heat of reaction for the combustion of liquid n-pentane, assuming H_2O(l) is a combustion product.
C_5H_{12} (l) + 8O_2 (g) ➔5CO_2 (g) + 6H_2O (l)

Then, use Hess's law to find the standard heat of reaction for the above equation, using these reactions:

1. 5C (s) + 6H_2 ➔C_5H_{12}
2. C (s) + O_2 (g) ➔CO_2
3. H_2 (g) + ½O_2 (g) ➔H_2O (l)

Compare the answer.

Solution:

1) Find standard heat of formation for every substance. From table B.1;

$$(\Delta H_f^0)_{C_5H_{12}} = -173.0 kJ/mol$$
$$(\Delta H_f^0)_{CO_2} = -393.5 kJ/mol$$
$$(\Delta H_f^0)_{H_2O} = -285.84 kJ/mol$$

2) Use the formula to calculate the standard heat of reaction:

$$\Delta H_r^{\,o} = -\sum_i v_i (\Delta H_f^o)_i = \left(\sum_{\text{products}} |v_i| (\Delta H_f^o)_i - \sum_{\text{reactants}} |v_i| (\Delta H_f^o)_i \right) = [(5 \times -393.5) + (6 \times -285.84) - (-173.0) kJ/mol)$$

$$\Delta H_r^{\,o} = -3509 kJ/mol$$

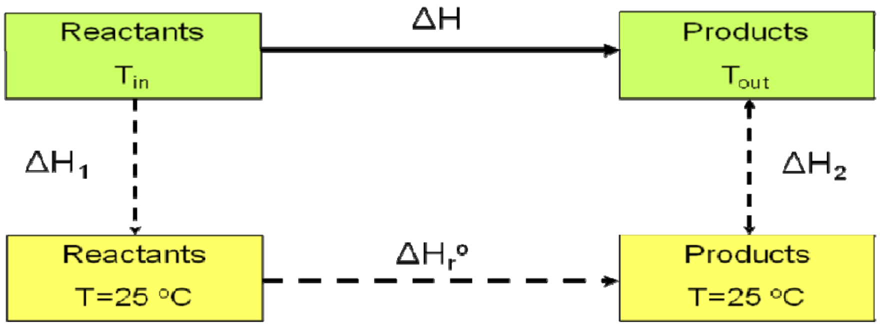
3) Find the standard heat of reaction for each equation using standard heat of formation and use Hess Law to calculate the desired equation:

1. 5C (s) + $6H_2$ ➔C_5H_{12}
2. C (s) + O_2 (g) ➔CO_2
3. H_2 (g) + ½O_2 (g) ➔H_2O (l)

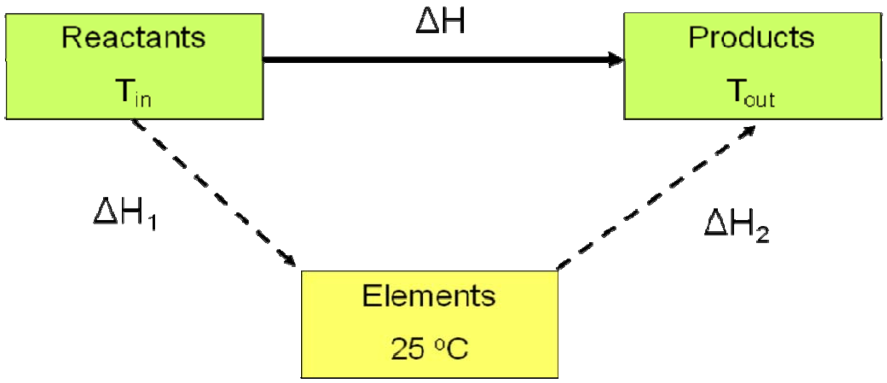
The desired reaction can be obtained by; $5 \times (2) + 6 \times (3) - (1)$, and the $\Delta H_r^{\,o}$ can be obtained from Hess Law.

5.8 Energy Balances (General Procedures)

- Heat of reaction method:



- Heat of formation method:



Some notes (extent of reaction)

- For a single reaction, extent of reaction (ξ) can be calculated:

$$\xi = \frac{|n_{A-out} - n_{A-in}|}{|v_A|}$$

where A is any reactant or product known

Some notes (inlet-outlet enthalpy table)

Components	n_{in}	H_{in}	n_{out}	H_{out}
A				
B				
C				

Some notes

- Latent heat ➔ heat transferred without change of T. It could be as heat of vaporization (or condensation). There is a phase change.

$$\Delta\hat{H} = \Delta\hat{H}_v$$

- Sensible heat ➔ heat transferred due to the T difference. There is a change of T, but no phase change.

$$\Delta\hat{H} = \int_{T_1}^{T_2} C_p dT$$

Since Cp = *f* (T), then don't forget to integrate it. See Appendix 3.

STEP-by-STEP procedure of calculation:

- Material balance calculation of reactor.
- Choose reference states (usually 25 °C, 1 atm).
- Calculate extent of reaction.
- Prepare inlet-outlet enthalpy table.
- Calculate unknown component enthalpy.
- Calculate ΔH for the reactor.

$$\Delta H = \xi \Delta \hat{H}_r^o + \sum n_{out} \hat{H}_{out} - \sum n_{in} \hat{H}_{in} \text{ (single reaction)}$$

$$\Delta H = \sum_{reaction} \xi_j \Delta \hat{H}_{rj}^o + \sum n_{out} \hat{H}_{out} - \sum n_{in} \hat{H}_{in} \text{ (multiple reactions)}$$

then

$Q - W = \Delta H + \Delta E_k + \Delta E_p$ can be evaluated

Example 5.4

Normal heptane is dehydrocyclized to toluene in a continuous vapor-phase reaction:

$$C_7H_{16} \rightarrow C_6H_5CH_3 + 4H_2$$

Pure heptane at 400 °C is fed to the reactor. The reactor operates isothermally at 400 °C and the reaction goes to completion.

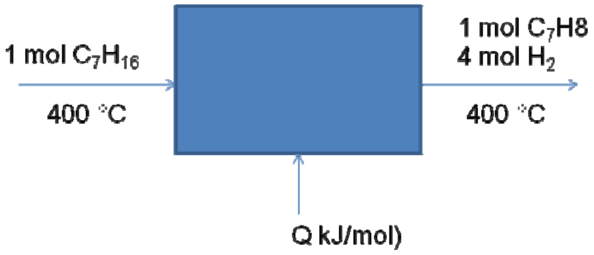
(a) Taking basis of 1 mol of heptane fed, draw and label a flowchart.
(b) Taking elemental species [C(s), H_2(g)] at 25 °C as references, prepare and fill in an inlet-outlet enthalpy table.
(c) Calculate the required heat transfer.

Given: $C_7H_{16(g)} = 137.44\text{x}10^{-3} + 40.85\text{x}10^{-5}\,T - 23.92\text{x}10^{-8}\,T^2 + 57.66\text{x}10^{-12}\,T^3$.

Solution:

1) Draw the flowchart.

Basis: 1 mol heptane fed



2) Prepare inlet-outlet Table

References: C(s), H (g) at 25 °C

Substance	**Inlet**		**Outlet**	
	$\dot{n}_{in}$	$\hat{H}_{in}$	$\dot{n}_{out}$	$\hat{H}_{out}$
C_7H_{16}	1	$\hat{H}_1$	-	-
C_7H_8	-	-	1	$\hat{H}_2$
H_2	-	-	4	$\hat{H}_3$

3) Find all the enthalpies

$$\hat{H}_1 = \hat{H}^0_{f(C_7H_{16})} + \int_{25^\circ C}^{400^\circ C} C_p dT$$

$$= -187.8 kJ/mol + \int_{25^\circ C}^{400^\circ C} 137.44\times10^{-3} + 40.85\times10^{-5}T - 23.92\times10^{-8}T^2 + 57.66\times10^{-12}T^3 dT$$

$$= (-187.8 + 79.34) kJ/mol = -108.46 kJ/mol$$

$$\hat{H}_2 = \hat{H}^0_{f(C_7H_8)} + \int_{25^\circ C}^{400^\circ C} C_p dT$$

$$= +50.00 kJ/mol + \int_{25^\circ C}^{400^\circ C} 94.18\times10^{-3} + 38.00\times10^{-5}T - 27.86\times10^{-8}T^2 + 80.33\times10^{-12}T^3 dT$$

$$= (+50.00 + 60.17) kJ/mol = 110.17 kJ/mol$$

H_3 can be obtained directly from Appendix 4:

$$\hat{H}_3 = \hat{H}_{(H_2, 400^\circ C)} - \hat{H}_{(H_2, 25^\circ C)} = (10.89 - 0) kJ/mol = 10.89 kJ/mol$$

3) Insert the H values calculated inside the inlet-outlet table.

References: C(s), H (g) at 25 °C

Substance	**Inlet**		**Outlet**	
	$\dot{n}_{in}$	$\hat{H}_{in}$	$\dot{n}_{out}$	$\hat{H}_{out}$
C_7H_{16}	1	$\hat{H}_1$= -108.46	-	-
C_7H_8	-	-	1	$\hat{H}_2$= 110.17
H_2	-	-	4	$\hat{H}_3$= 10.89

5) Calculate the standard heat of reaction.

$$\Delta H_r^{o} = \sum_i v_i \Delta H_{fi}^{o} = \left(\sum_{\text{products}} |v_i| \Delta H_{fi}^{o} - \sum_{\text{reactants}} |v_i| \Delta H_{fi}^{o} \right)$$

$$\hat{H}_r^0 = [(4(0) + 50.00 - (-187.8)]kJ/mol$$
$$= 237.8 kJ/mol$$

6) Calculate the overall enthalpy:

$$\Delta H = \xi \Delta \hat{H}_r^o + \sum n_{out} \hat{H}_{out} - \sum n_{in} \hat{H}_{in}$$

$$\dot{\xi} = \frac{n_{C_7H_{16},r}}{\left| v_{C_7H_{16}} \right|} = \frac{1}{1} = 1$$

$$\Delta H = \xi \Delta \hat{H}_r^o + \sum n_{out} \hat{H}_{out} - \sum n_{in} \hat{H}_{in}$$
$$= (1)(237.8\text{kJ/mol}) + [(1)(60.17) + (4)(10.89) - (1)(79.34)]\text{kJ/mol}$$
$$= 262.2 kJ/mol$$

Problems:

1. Use Hess's law to calculate the standard heat of the water-gas shift reaction;

$$CO(g) + H_2O(v) \rightarrow CO_2(g) + H_2(g)$$

from each of the two sets of data given here.

(a) $CO(g) + H_2O(l) \rightarrow CO_2(g) + H_2(g)$: $\Delta\hat{H}_r^0 = +1226 Btu/lbmole$

$H_2O(l) \rightarrow H_2O(v)$: $\Delta\hat{H}_r^0 = +18{,}935 Btu/lbmole$

(b) $CO(g) + \frac{1}{2} O_2(g) \rightarrow CO_2(g)$: $\Delta\hat{H}_r^0 = -121{,}740 Btu/lbmole$

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(v)$: $\Delta\hat{H}_r^0 = -104{,}040 Btu/lbmole$

2. Formaldehyde maybe produced in the reaction between methanol and oxygen:

$$2CH_3OH(l) + O_2(g) \rightarrow 2HCHO(g) + 2H_2O(l):$$

The standard heat of combustion of hydrogen is

$$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l):$$

Use these heats of reaction and Hess's Law to determine the standard heat of the direct decomposition of methanol to form formaldehyde:

$$CH_3OH(l) \rightarrow HCHO(g) + H_2(g)$$

3. Trichloroethylene, a widely used degreasing solvent for machine parts, is produced in a 2 steps reaction sequence. Ethylene is first chlorinated to yield tetrachloroethane, which is dehydrochlorinated to form trichloroethylene.

$C_2H_4(g) + 2Cl_2(g) \rightarrow C_2H_2Cl_4(l) + H_2(g)$ $\Delta\hat{H}_r^0 = -385.76 kJ/mol$

$C_2H_2Cl_4(l) \rightarrow C_2HCl_3(l) + HCl(g)$

The standard heat of formation of liquid trichloethylene is -276.2 kJ/mol.

(a) Use the given data and tabulated standard heats of formation of ethylene and hydrogen chloride to calculate the standard heat of formation of tetrachloroethane and the standard heat of the second reaction.

(b) Use Hess's Law to calculate the standard heat of the rection

$C_2H_4(g) + 2Cl_2(g) \rightarrow C_2HCl_3(l) + H_2(g) + HCl(g)$

4. The standard heat of reaction for the oxidation of ammonia isgiven below:

$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(v)$

500 mol NH_3/s and 800 mol O_2 at 25 °C are fed into a reactor in which the ammonia is completely consumed. The product gas emerges at 300 °C. Calculate the rate at which heat must be transferred to or from the reactor, assuming operation at approximately 1 atm.

CHAPTER 6
BASIC CONCEPT OF HEAT TRANSFER

6.1 Introduction

- What is heat transfer?
  Heat transfer is thermal energy in transit due to a temperature difference. In other words, heat transfer is to predict the energy transfer between material bodies.
  [*In the simplest of terms, the discipline of heat transfer is concerned with only two things:* ***temperature****, and the* ***flow of heat****. Temperature represents the amount of thermal energy available, whereas heat flow represents the movement of thermal energy from place to place.]*

- How Science of heat transfer explain:
  - How heat energy may be transfer?
  - Predict the rate at which the exchange will take place?
  - Different between thermodynamics and heat transfer ?

- Thermodynamics deal with system in equilibrium, it may used to predict of energy required to change a system from one equilibrium state to another. But it does not predict how fast a change will take place.

Example 6.1

Consider the cooling of a hot steel bar which is placed in a pail of water. Thermodynamics may used to predict the final equilibrium temperature of steel bar-water combination. However, thermodynamics will not tell:

- how long to reach the equilibrium or,
- what the temperature of steel bar after certain length of time?

Table 6.1: Comparison between heat transfer and thermodynamics

HEAT TRANSFER	**THERMODYNAMICS**
• Heat transfer is a study which predicts the energy transfer which takes place between material bodies. • It is due to the temperature difference • Heat transfer explains how heat energy may be transferred. • It also predicts the rate at which the exchange will take place under certain condition.	• Thermodynamics deals with systems in equilibrium. • Thermodynamics may used to predict the amount of energy required to change a system from one equilibrium state to another. • Thermodynamics may not used to predict how fast a change will take place since the system is not in equilibrium during the process.

Three modes of heat transfer are:
(1) Conduction
(2) Convection
(3) Radiation

6.2 Conduction Heat Transfer

- Energy transfer from high temperature region to low temperature region. We said that the energy is transferred by conduction. And, the heat transfer rate per unit area is proportional to the normal temperature gradient.

$$q/A \sim dT/dx$$

where,
q/A = heat transfer rate (W/m^2)
dT/dx = temperature gradient in the direction of the heat flow

When proportionality constant is inserted,

$$q = -kA\, dT/dx \qquad [6.1]$$

- The positive constant k = thermal conductivity of the material. The minus (-) sign is inserted so that the second principle of thermodynamics will be satisfied i.e. heat must flow downhill on the temperature scale as indicated in Figure 6.1.

Equation (8.0) is called Fourier's Law of heat conduction. Above is defining equation for the thermal conductivity and *k* has the unit of Watts per meter per Celsius degree (W/m.^{0}C), which the heat flow is expressed in watts.

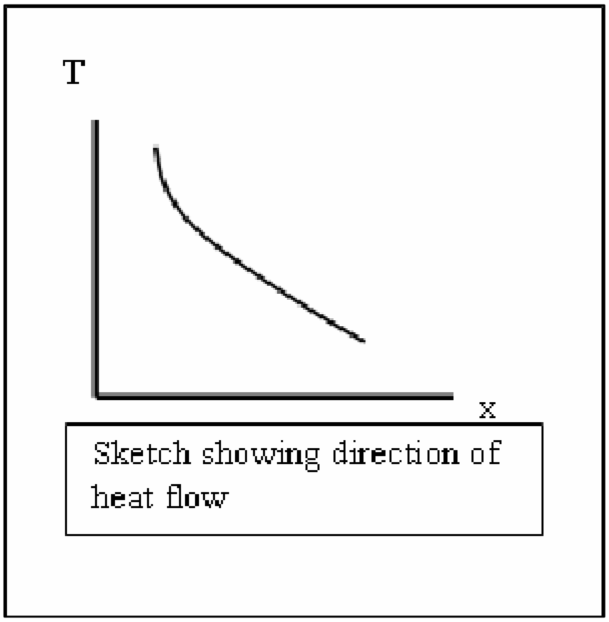


Figure 6.1: Sketch showing direction of heat flow

Table 6.2: Lists typical values of the thermal conductivities of some metal (thermal conductivity at 300 K(W/m K)).

Metal	***k***
Copper, pure	396
Aluminium	238
Carbon steel, 1% C	42
Plastics	0.2 - 0.3
Air	0.026

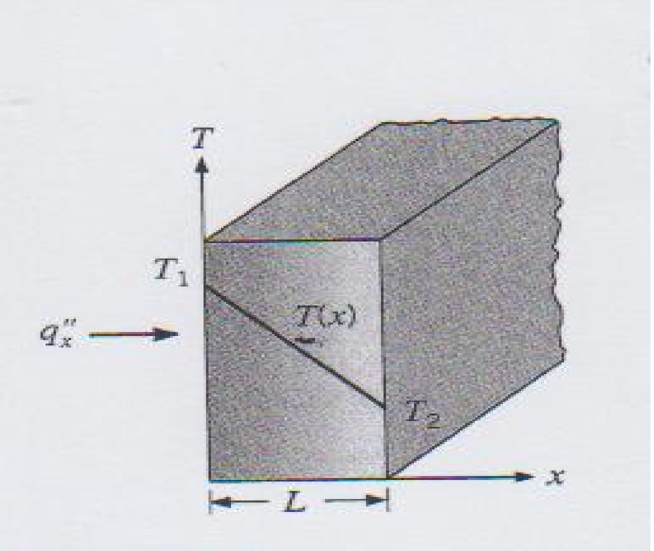


Figure 6.2: One –dimensional plane wall

- Consider the one-dimensional plane wall shown in Figure above, if the system in a steady state, i.e., if the temperature does not change with time, then only integrate Equation (8.0) and substitute the appropriate values.

$$\frac{q}{A}\int_{0}^{x} dx = \int_{T2}^{T1} kdT$$

- Where temperature at the left face (x=0) is uniform at T_1 and the temperature at right face is uniform at T_2. If *k* is independent of T, we obtain after integration :

$$\frac{q}{A} = -k\frac{T_1 - T_2}{L}$$

- Under the steady state conditions, where the distribution is linear, the temperature gradient may be expressed as:

$$\frac{dT}{dx} = \frac{T_2 - T_1}{L}$$

- And the heat transfer rate:

$$\frac{q}{A} = -k\frac{T_2 - T_1}{L}$$

or;

$$\frac{q}{A} = k\frac{T_1 - T_2}{L} = k\frac{\Delta T}{L}$$

- Since dT/dx = - q/k for the same q, if *k* is low (i.e: for an insulator), dT/dx will be large .i.e. there will be a large temperature difference across the wall, and if *k* is high (i.e. for a conductor), dT/dx will be small, or there will be a small temperature difference across the wall.

Example 6.2

One face of a copper plate 3 cm thick is maintained at 400 °C, and the other face maintained at 100 °C. How much heat is transferred through the plate? Given: k = 370 W/m.K.

From Fourier's Law,

$$\frac{q}{A} = -k\frac{dT}{dx}$$

Integrating gives

$$\frac{q}{A} = -k\frac{\Delta T}{\Delta x} = \frac{-(370)W/m.K(100-400)K}{3\times10^{-2}m}$$

$$q/A = 3.7\ MW/m^2$$

6.3 Convection Heat Transfer

- It is well known that hot plate of metal will cool faster when placed in front of a fan than when exposed to still air. We say that, heat is convected away, and we call the process, convection heat transfer. The velocity at which the air blows over the hot plate obviously influence the heat transfer rate.

6.3.1 Mechanism of convection

- Consider the heated plate shown on Figure 8.3. Temperature of plate is T_W and temperature of the fluid is T_∞. The velocity of the flow will appear as shown in the figure.

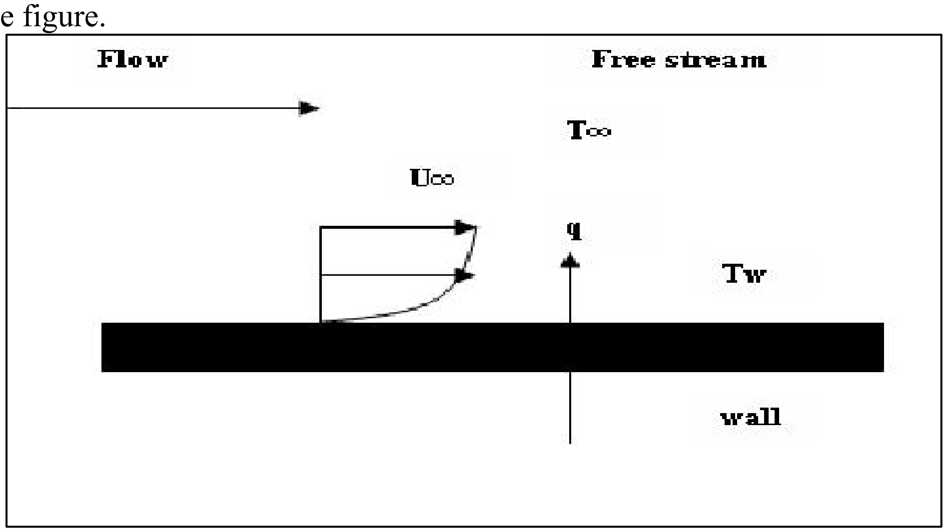


Figure 6.3: Convection heat transfer from a plate

- The velocity is being reduced to zero at the plate as a result of viscous action. Since the velocity of fluid layer at the wall will be zero, the heat must be transferred only by conduction. Thus we might compute the heat transfer, using:

  $$q = -kA\,(dT/dx)$$

  but with little changes. We use thermal conductivity of fluid and the fluid temperature gradient at the wall.The temperature gradient is dependent on the rate at which the fluid carries the heat away. High velocity produces a large temperature gradient. Thus, the temperature gradient at the wall depends on the flow field. To express the overall effect of convection, we use Newton's law of cooling:

  $$q = hA\,(T_w - T_\infty) \qquad [6.2]$$

  where,

  h = convection heat-transfer coefficient (heat-transfer coefficient = film conductance)
  h = watt per square meter per Celsius degree ($W/m^2 \cdot °C$) when the heat flow is in Watt.

- Heat-transfer rate is related to overall temperature difference between the wall and fluid and the surface area.

6.3.2 Free and Forced Convection

- If heated plate were exposed to ambient room air without an external source of motion, a movement of the air would be experienced as a result of the density gradients near the plate.
- We call this as free convection. When the mass motion of the fluid is caused by an external device like a pump, compressor, blower or fan, the process is called forced convection.

Example 6.3

Air at 20 °C blows over a hot plate 50 by 75 cm maintained at 250 °C. The convection heat transfer coefficient is 25 W/m².°C. Calculate the heat transfer?

Solution:

From Newton's Law of cooling;

$$q = hA(T_w - T_\infty)$$

$$q = (25) W/m^2.K\ (0.5x0.75)\ m^2 (250-20) K$$

$$q = 2.156\ kW$$

Example 6.4

An electric current is passed through a wire 1 mm in diameter and 10 cm long. The wire is submerged in liquid water at atmospheric pressure, and the current is increased until the water boils. For this situation *h = 5000 W/m².°C*, and the water temperature will be 100 °C. How much electric power must be supplied to the wire to maintain the wire surface at 114 °C.

Solution:

Total convection loss is

$$q = hA(T_w - T_\infty)$$

The surface area of the wire

$$A = \pi dL = \pi\ (1x10^{-3})(10x10^{-2})$$

$$= 3.142\ x\ 10^{-4}\ m^2$$

Therefore, the heat transfer is

$$q = (5000 w/m^2.°C)(3.142\ x\ 10^{-4}\ m^2)(114-100)$$

= 21.99 W and this is equal to the electric power which must be applied.

6.4 Radiation Heat Transfer

- Heat may also transfer through regions where perfect vacuum exist. The mechanism in this case is electromagnetic radiation which is propagated as a result of a temperature difference. This is called *thermal radiation.*
- This is confirmed by our experienced everyday experience of being warmed by the sun, which separated from the earth by approximately 1.5 x 10^{11} m of empty space.
- Thermal radiation can of course transport through any 'transparent' medium such as air. Ideal *thermal radiator, or black body*, will emit energy at a rate

$$q_{\text{emitted}} = \sigma A T^4 \qquad [6.3]$$

where;
σ is the proportionality constant and is called the Stefan-Boltzmann constant with value of $5.669 \times 10^{-8}\ \text{W/m}^2.\text{K}^4$.

- This equation is called Stefan-Boltzmann law of thermal radiation and it apply to only blackbodies. This equation is valid only for thermal radiation; other type of electromagnetic radiation may not be treated so simply.

$q_{\text{emitted}} = \sigma A T^4$ govern only radiation emitted by a blackbody.

The net radian exchange between two surface will be proportional to the difference in absolute temperature to the fourth power. i.e: q net exchange/ A $\alpha\ (T_1^4 - T_2^4)$

$$q\ \text{net exchange}/\ A = \sigma\ (T_1^4 - T_2^4)$$

6.4.1 Blackbody

- It is a perfect emitter of radiation. At a particular temperature the blackbody would emit the maximum amount of energy possible for that temperature.
- This value is known as the blackbody radiation. It would emit at every wavelength of light as it must be able to absorb every wavelength to be sure of absorbing all incoming radiation.
- The maximum wavelength emitted by a blackbody radiator is infinite. It also emits a definite amount of energy at each wavelength for a particular temperature, so standard black body radiation curves can be drawn for each temperature, showing the energy radiated at each wavelength (Fig. 6.4).

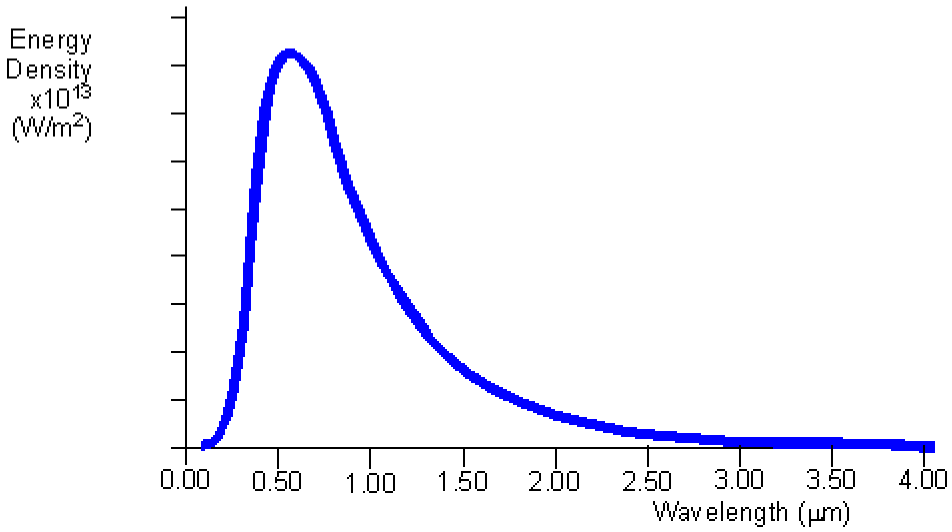


Figure 6.4: Theoretical black body curve for 5000K

- Again, blackbody is a body which radiates energy according to the T^4 law. Other type of surface, such as glossy painted surface or a polished metal plate, do not radiate as much energy as the blackbody.
- However, the total radiation emitted by this body still generally follows the T_1^4 proportionality. To take account of the "gray" nature of such surfaces we introduce another factor, called the emissivity, ϵ which relates the radiation of the "gray" surface to that of an ideal black surface. In addition, we must take into account the fact that not all the radiation leaving one surface will reach the other surface since electromagnetic radiation travels in straight line and some will lost to the surrounding.

- Therefore two new factors in (Eq 8.2)take into account both situation, so that

$$q= F_\epsilon F_G \sigma A (T_1^4 - T_2^4) \qquad [6.4]$$

F_ϵ = emissivity function

F_G = geometric "view factor" function

A simple radiation problem is encounter when we have a heat-transfer surface at temperature T_1 completely enclosed by much larger surface maintained at T_2. The net radiant exchange in this case can be calculated with,

$$q = \epsilon_1 A\sigma_1 (T_1^4 - T_2^4)$$

where,

ϵ_1 = emissivity of material

Example 6.5

Two infinite black plates at 800 ^{0}C and 300 ^{0}C exchange heat by radiation. Calculate the heat transfer per unit area. Given: $\sigma = 5.669 \times 10^{-8}$ W/m^2.K^4

Solution:

$$q/A = \sigma (T_1^4 - T_2^4)$$

$$= 5.669 X 10^{-8})W/m^2.K^4 (10734 - 5734)K^4$$

$$= \underline{69.03 \ kW/m^2}$$

Problems

1. If 3 kW is conducted through a section of insulating material 0.6 m^2 in cross-section and 2.5 cm thick and the thermal conductivity may be taken as 0.2 W/m^0C, compute the temperature difference across the material.
2. A temperature difference of 85^0C is impressed across a fiberglass layer of 13 cm thickness. The thermal conductivity of the fiberglass is 0.035 W/m.^{0}C. Compute the heat transferred through the material per hour per unit area.
3. Two perfectly black surfaces are constructed so that all the radiant energy leaving a surface at 800^0C reaches the other surface. The temperature of the other surface is maintained at 250^0C. Calculate the heat transfer between the surfaces per hour and per unit area of the surface maintained at 800^0C.
4. One side of a plane wall is maintained at 100^0C, while the other side is exposed to a convection having T = 10^0C and h=10 W/m2.^{0}C. The wall has k = 1.6 W/m.^{0}C and is 40 cm thick. Calculate the heat transfer rate through the wall.
5. A vertical square plate, 30cm on a side, is maintained at 50^0C and exposed to room air at 20^0C. The surface emissivity is 0.8. Calculate the total heat lost by both sides of the plate.

CHAPTER 7
HEAT EXCHANGERS

7.1 Introduction

A heat exchanger is a device that facilitates exchange of heat between two fluids that are at different temperatures and separated by a solid wall. In other words, heat exchangers are devices built for efficient heat transfer from one fluid to another and are widely used in engineering processes. The specific applications of heat exchanger are space heating and air conditioning, power production, waste heat recovery, food and chemical processing, oil refining, and in vehicles.

7.2 Heat exchanger types

Heat exchangers are classified according to *flow arrangement* and *type of construction*. Six (6) types of heat exchanger are:

(a) Concentric Tube Heat Exchangers
(b) Cross-Flow Heat Exchangers
(c) Cross-counter Flow (Coil) Heat Exchangers
(d) Shell-and-Tube Heat Exchangers
(e) Compact Heat Exchangers
(f) Plate-Type Heat Exchangers

(a) Concentric Tube Heat Exchanger

- It also called double-pipe heat exchangers or co-axial flow heat exchangers [*Figure 7.1*].
- One fluid flows inside the tube and the other fluid flows inside the annulus.
- In parallel-flow heat exchangers, the two fluids enter the exchanger at the same end, and travel in parallel to exit at the other side. [*Figure7.2a*]
- In counter-flow heat exchangers the fluids enter the exchanger from opposite ends. Counter current design is more efficient, in that it can transfer more heat [*Figure 7.2b*].

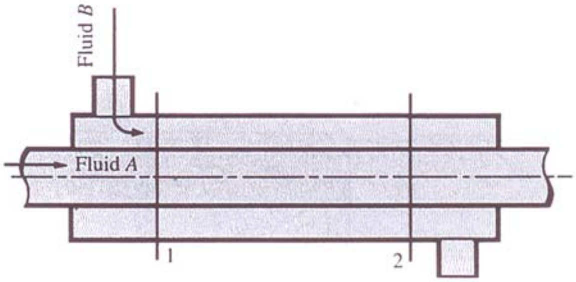
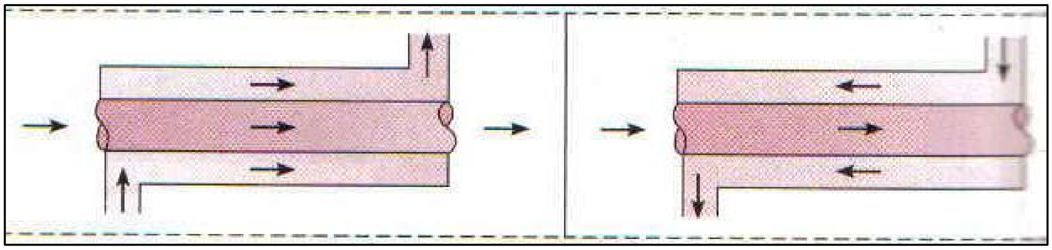


Figure 7.1: Concentric tube heat exchangers



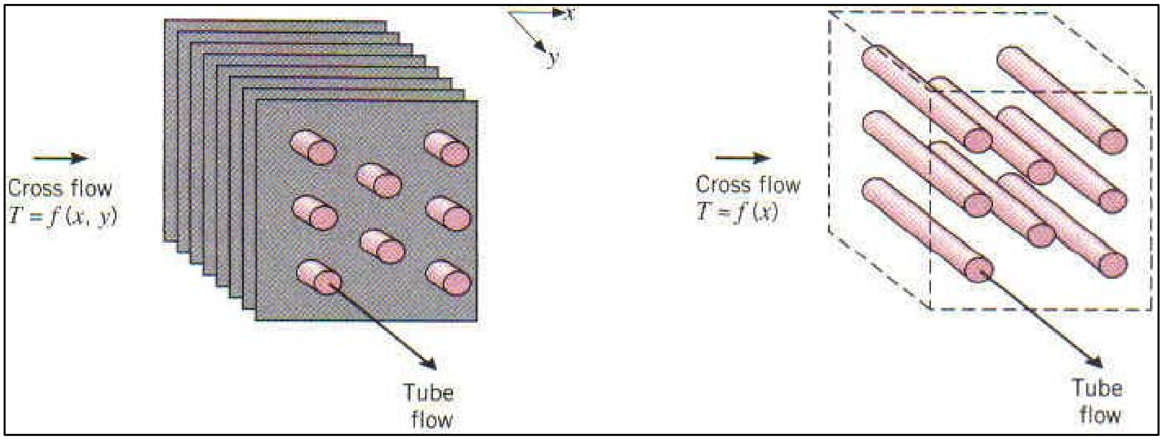
(a) Parallel flow

(b) Counterflow

Figure 7.2: Concentric tube heat exchangers

(b) Cross Flow Heat Exchanger

- In a cross-flow heat exchanger, the fluids travel roughly perpendicular to one another through the exchanger.
- In finned tubular heat exchangers, the fin-side fluid is unmixed because the fins confine the flow to one direction. Example: automobile radiator.
- In unfinned tubular heat exchangers, the fin-side fluid is mixed because the flow in transverse direction is possible. [*Figure 7.3*]
- The use of fins to improve the convection coefficient of fin-side fluid by increasing the outside surface area.

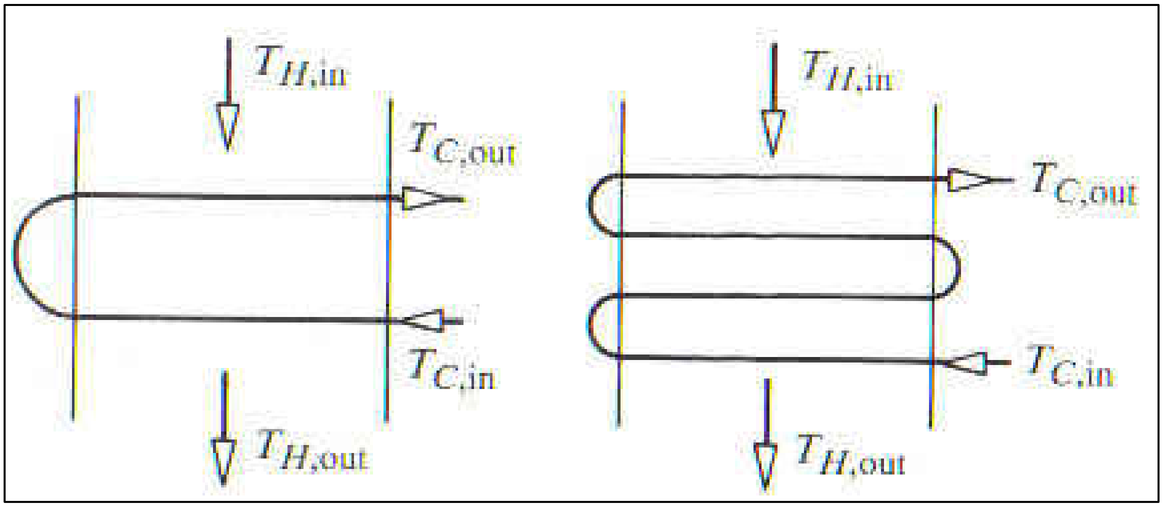


(a) Finned with both fluids unmixed

(b) Unfinned with one fluid mixed and the other unmixed

Figure 7.3: Cross-flow heat exchangers

(c) Cross-counter Flow (Coil) Heat Exchangers



(a) Two-pass **(b) Four-pass**

Figure 7.4: Cross-counter Flow (Coil) Heat Exchangers

(d) Shell-and-Tube Heat Exchangers

- Tubular heat exchangers consist of a tube bank enclosed by a shell. One fluid flows inside the tubes and the other flows inside the shell.
- Figure 8.5, show the simplest form of shell and tube heat exchanger which involves single tube and shell passes.
-

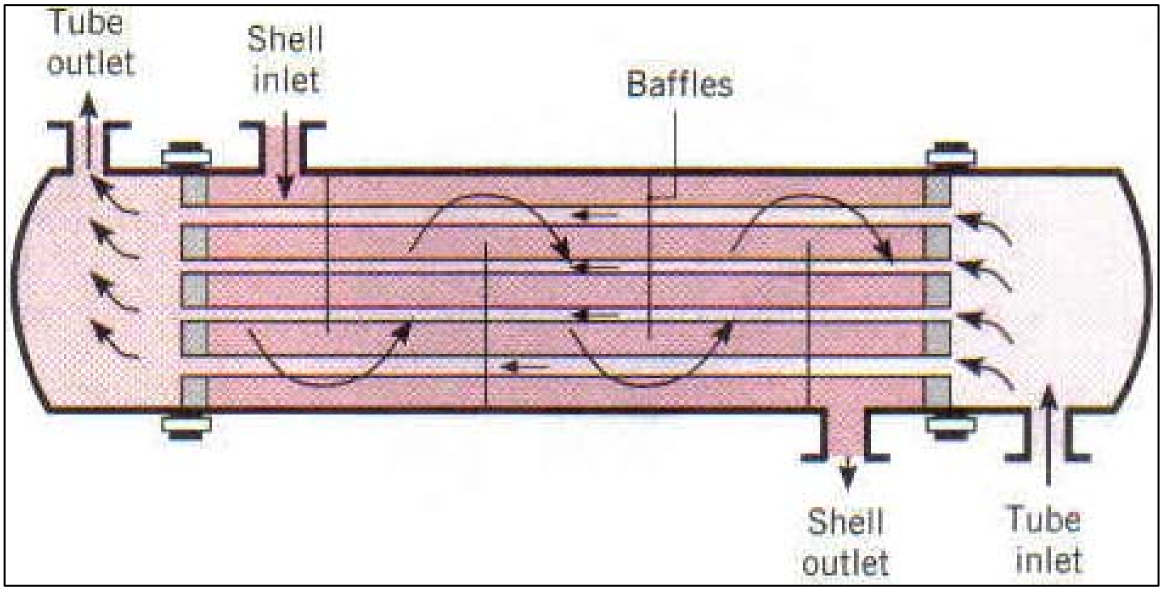


Figure 7.5: Shell and tube heat exchanger with one-shell pass one-tube pass (1-1) (cross-counterflow mode of operation)

- Baffles are usually installed to increase the convection coefficient of the shell-side fluid by inducing turbulence and a cross-flow velocity component.

- Baffled heat exchanger with one shell pass and two tube passes and with two shell passes and four tube passes are shown in Figures 7.6a and 7.6b, respectively.

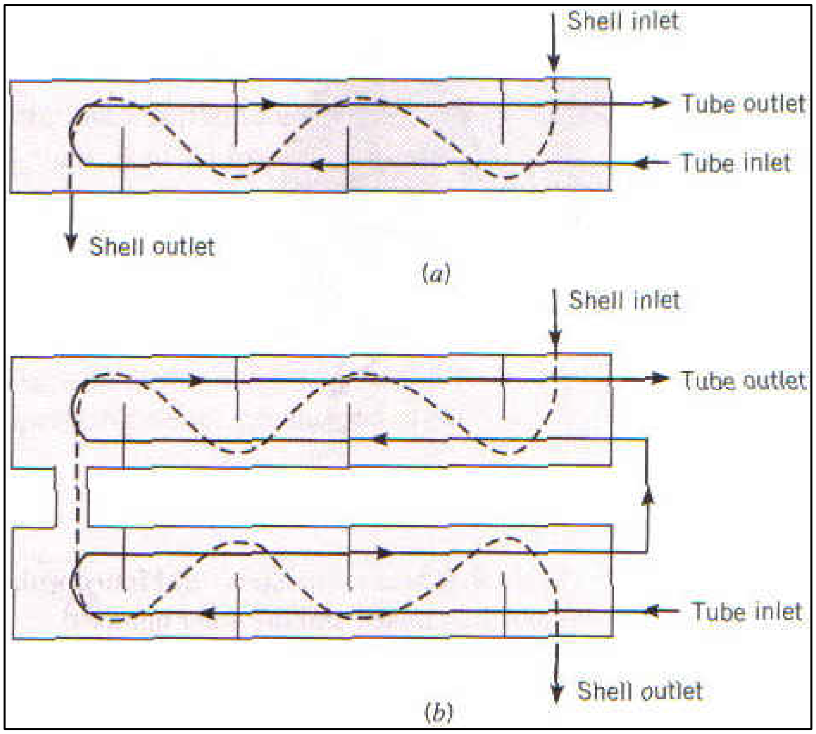
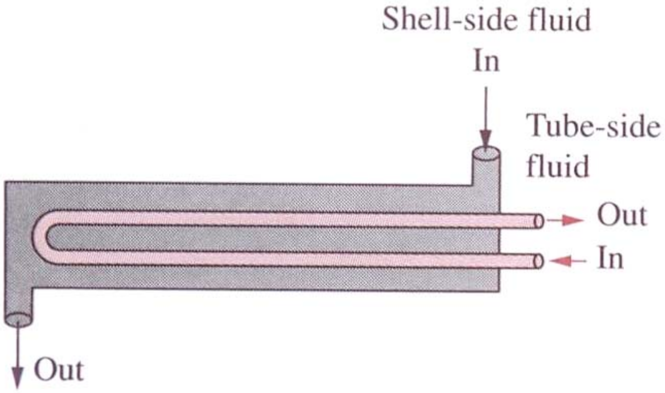
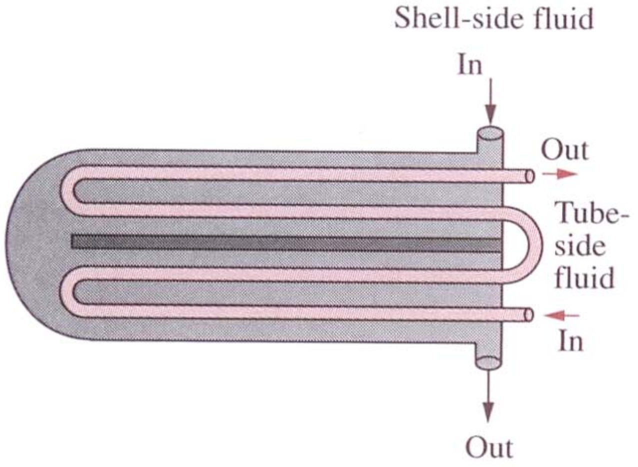


Figure 7.6: Shell-and-tube heat exchanger. (a) One shell pass and two tube passes. (b) Two shell passes and four tube passes

- Shell-and-tube heat exchangers are classified according to the number of shell and tube passes involved.
- Heat exchangers in which all the tubes make one U-turn in the shell, for example, are *called one-shell-pass and two-tube-passes* heat exchangers.
- Heat exchanger that involves two passes in the shell and four passes in the tubes is called a *two-shell-passes and four-tube-passes* heat exchanger [*Figure 7.7*]



(a) One-shell pass and two-tube passes



(b) Two-shell passes and four-tube passes

Figure 7.7: Multipass flow arrangement in shell-and-tube heat exchangers

(e) Compact Heat Exchanger

- Used to achieve very large heat transfer area per unit volume.
- Have dense arrays of finned tubes or plates.
- Typically used when at least one of the fluids is a gas, characterized by small convection coefficient.
- The tubes may be flat or circular, and the fins may be plate or circular (Figure 7.8a, 7.8b and 7.8c).
- Parallel plates may be finned or corrugated and may be used in single-pass or multi-pass mode (Figure 7.8d and 7.8e).

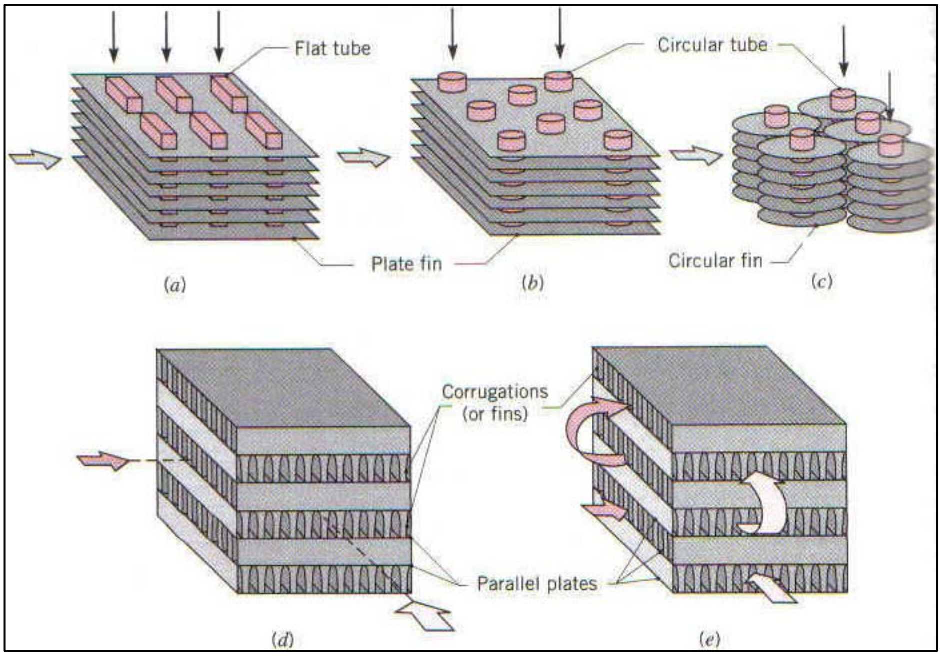
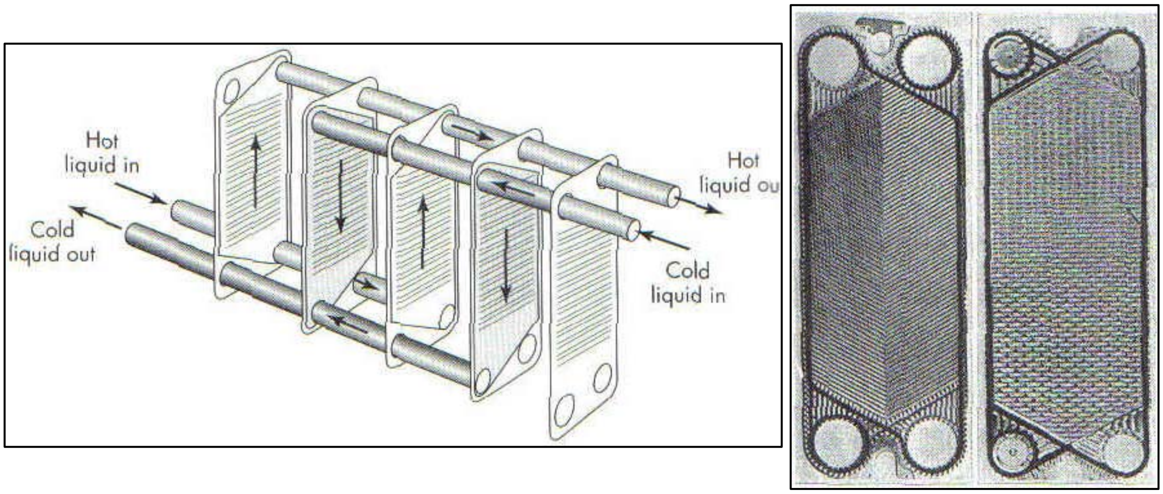


Figure 7.8: Compact heat exchanger cores. (a) Fin-tube (flat tubes, plate fins; (b) Fin-tube (circular tubes, plate fins); (c) Fin-tube (circular tubes, circular fins); (d) Plate-fin (single pass); (e) Plate-fin (multi-pass)

(f) Plate-Type Heat Exchangers

- Gasketed plate exchanger, alternative to shell-and-tube exchangers for applications at moderate temperature and pressure.
- Consists of many corrugated stainless steel sheets separated by polymer gaskets and clamped in a steel frame.
- Inlet portals in the gaskets direct the hot and cold fluid to alternate spaces between plates.
- Adjoining plates have different pattern or angle of corrugation. Corrugations induce turbulence for improved heat transfer.
- Widely used in dairy and food processing



(a) General layout (b) Detail of plate design

Figure 7.9: Plate-Type Heat Exchangers

The Overall Heat Transfer Coefficient

- The heat transfer between the two fluids across the solid wall involves convection of fluid films adjacent to the wall and conduction across the wall.
- The rate of heat transfer can be expressed by a single equation like Newton's law of cooling, with the overall heat transfer coefficient *U* incorporating convection and conduction terms:

$$q = UA\Delta T_m \qquad [7.1]$$

where,

ΔT_m = mean temperature difference between the two fluids along the exchanger length

- For the *unfinned* tubular heat exchanger, *U* can be calculated as follows:

$$\frac{1}{UA} = \frac{1}{U_i A_i} = \frac{1}{U_o A_o} \qquad [7.2]$$

$$\frac{1}{UA} = \frac{1}{h_i A_i} + \frac{R_{fi}}{A_i} + \frac{\ln(D_o / D_i)}{2\pi k L} + \frac{R_{fo}}{A_o} + \frac{1}{h_o A_o} \qquad [7.3]$$

where A_i, A_o = inside and outside heat transfer areas

U_i, U_o = overall heat transfer coefficients based on inside and outside surface areas

h_i, h_o = inside (tube-side) convection coefficient and outside (shell-side) convection coefficient

R_{fi}, R_{fo} = fouling resistances at inside and outside surfaces

D_i, D_o = inside and outside diameters of the tube

k = thermal conductivity of the tube wall

L = tube length of heat exchanger

7.3 Heat Exchanger Analysis: Use of the Log Mean Temperature Difference (LMTD)

To design or to predict the performance of a heat exchanger, it is essential to relate the total heat transfer rate to quantities such as *the inlet and outlet fluid temperatures*, *the overall heat transfer coefficient*, and *the total surface area* for heat transfer. A few steps to design or predict the performance of a heat exchanger:

- **Step 1**
  - Write down the overall energy balances between heat gain of cold fluid, heat loss of hot fluid, and heat transfer across the wall separating the two fluids.

$$q = \dot{m}_c \Delta \widehat{H}_c = \dot{m}_h \Delta \widehat{H}_h = UA\Delta T_{lm} \qquad [7.4]$$

  - If the fluids are not undergoing a phase change and constant specific heats are assumed, the equation becomes:

$$q = \dot{m}_h C_{p,h}(T_{h,i} - T_{h,o}) = \dot{m}_c C_{p,c}(T_{c,o} - T_{c,i}) = UA\Delta T_{lm} \qquad [7.5]$$

  - Determine any unknown that can be directly calculated from the above relations.

q = rate of heat transfer

$\dot{m}_c, \dot{m}_h$ = mass flow rate of cold fluid and hot fluid

T_{ci}, T_{co}, T_c = inlet, outlet, and mean temperature of cold fluid

T_{hi}, T_{ho}, T_h = inlet, outlet, and mean temperature of hot fluid

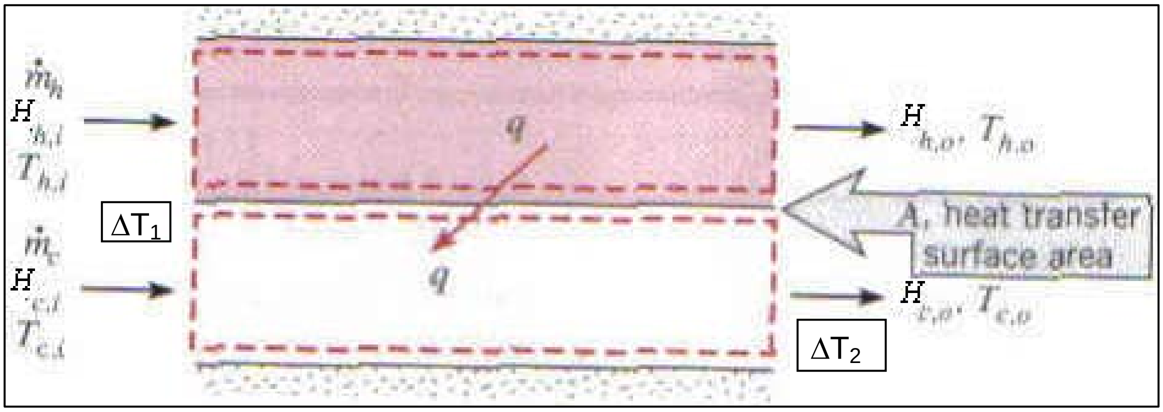
$\widehat{H}_c, \widehat{H}_h$ = specific enthalpies of cold fluid and hot fluid

U = overall heat ransfer coefficient

A = heat transfer surface area

ΔT_{lm} = log mean temperature difference (LMTD)

$= \dfrac{\Delta T_1 - \Delta T_2}{\ln\left(\Delta T_1 / \Delta T_2\right)}$, where ΔT_1 and ΔT_2 are temperature differences at the two ends of HE.



$$q = \dot{m}_c \Delta \widehat{H}_c = \dot{m}_h \Delta \widehat{H}_h = UA\Delta T_{lm}$$

Enthalpy change of cold fluid

Enthalpy change of hot fluid

Figure 7.10: Overall Energy Balances of the Hot and Cold Fluids of a Two-fluid Heat Exchanger

- **<u>Step 2</u>**
  - Enthalpies and LMTD depends on fluid temperature behavior:
  (a) Parallel flow
  For parallel flow with no phase change,

  $\Delta H_h = C_{ph}(T_{hi}\text{-}T_{ho})$, $\Delta H_c = C_{pc}(T_{co}\text{-}T_{ci})$

$$\Delta T_{lm} = \frac{(T_{hi} - T_{ci}) - (T_{ho} - T_{co})}{\ln[(T_{hi} - T_{ci})/(T_{ho} - T_{co})]}$$

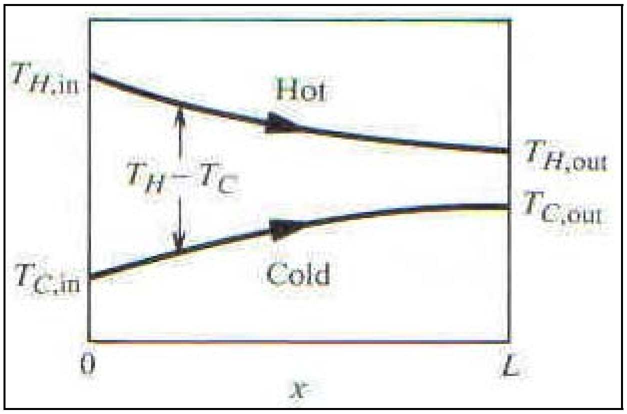


Figure 8.11: Temperature scheme for parallel flow

(b) Counterflow

For counterflow with no phase change,

$$\Delta H_h = C_{ph}(T_{hi}\text{-}T_{ho}),\ \Delta H_c = C_{pc}(T_{co}\text{-}T_{ci})$$

$$\Delta T_{lm} = \frac{(T_{ho} - T_{ci}) - (T_{hi} - T_{co})}{\ln[(T_{ho} - T_{ci})/(T_{hi} - T_{co})]}$$

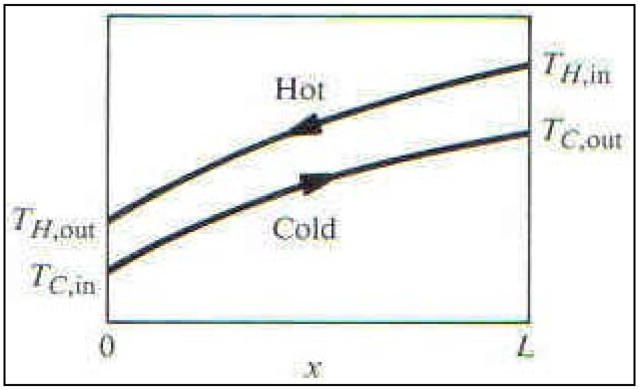


Figure 8.12: Temperature scheme for counterflow

(c) Condensers

$$\Delta H_h = \lambda_h,\ \Delta H_c = C_{pc}(T_{co}\text{-}T_{ci})$$

$$\Delta T_{lm} = \frac{T_{co} - T_{ci}}{\ln[(T_h - T_{ci})/(T_h - T_{co})]}$$

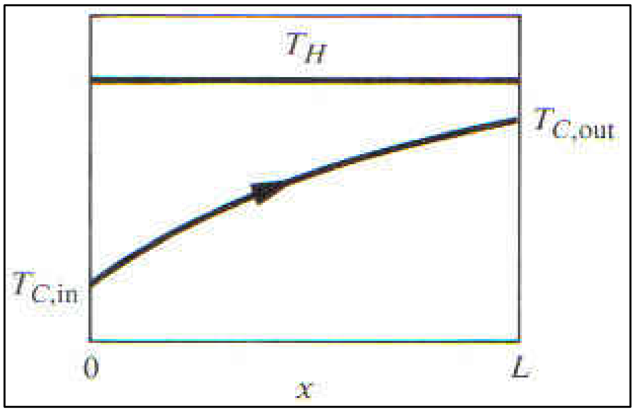


Figure 8.13: Temperature scheme for condenser

(d) Evaporators

$$\Delta H_c = \lambda_c,\ \Delta H_h = C_{ph}(T_{hi}\text{-}T_{ho})$$

$$\Delta T_{lm} = \frac{T_{hi} - T_{ho}}{\ln[(T_{hi} - T_c)/(T_{ho} - T_c)]}$$

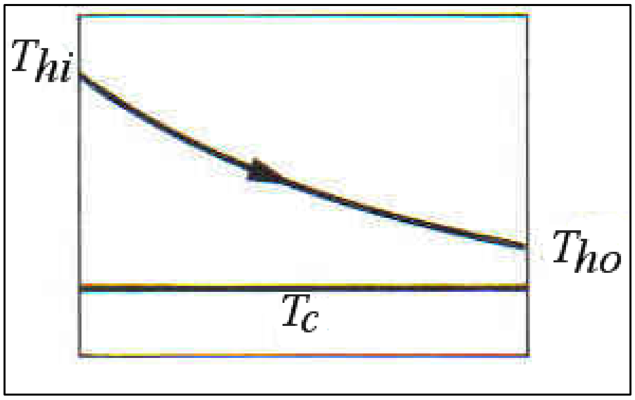


Figure 8.14: Temperature scheme for evaporator

where λ= latent heat of vaporization

- Miscellaneous
  - Overall heat transfer coefficient (U), if not known, can be determined Equation (10.3).
  - Heat transfer area (A) is related to tube length as $A = 2\pi rL$.

- **Step 3**
  - Determine any other unknowns from the overall energy balances (Eq. 8.4)
  - Determine the HE effectiveness and number of transfer units.

- If the heat exchanger other than the double pipe is used, the heat transfer is calculated by using a correction factor applied to the LMTD for a counter flow double-pipe arrangement with the same hot and cold fluids temperatures.
- The heat-transfer equation becomes :

$$q = UAF\,\Delta T_m \qquad [7.6]$$

- Values of the correction factor F are plotted in Figures 7.14 to 7.17 for several different types of heat exchangers.
- When phase changed is involved, as in condensation or boiling (evaporation), the fluid normally remains at essentially constant temperature.
- For this condition, P and R becomes zero and F = 1.0 (for boiling and condensation)

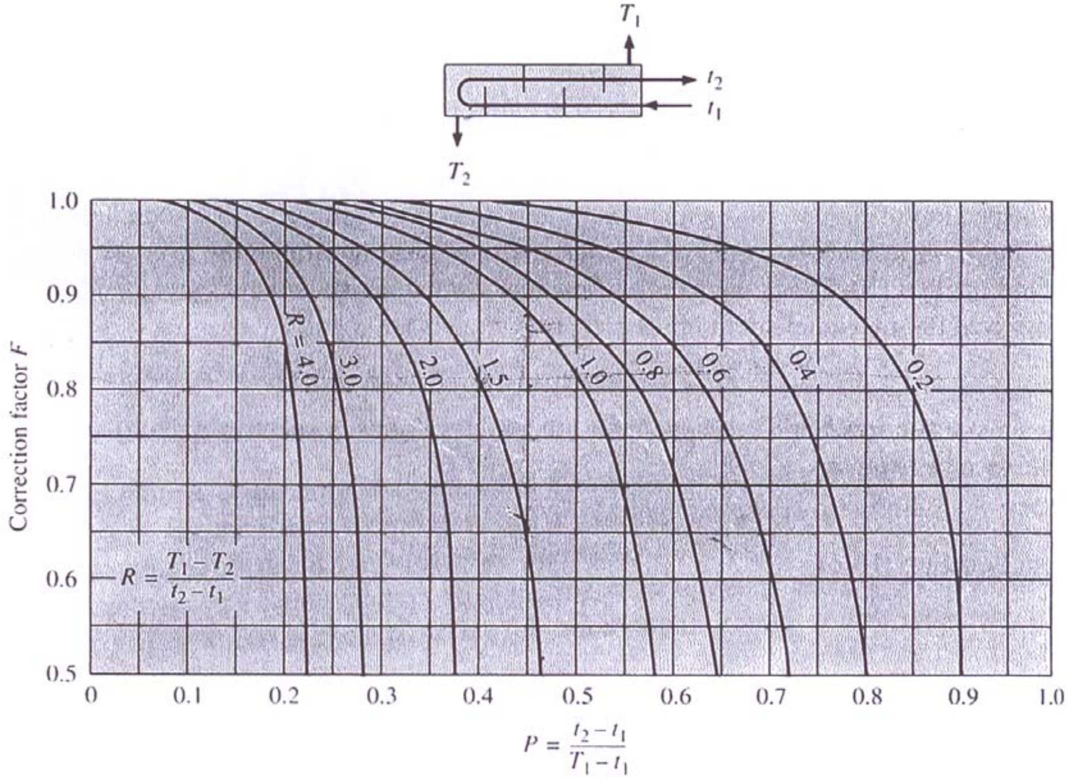


Figure 7.15: Correction factor plot for exchanger with one shell pass and two, four, or any multiple of tube passes.

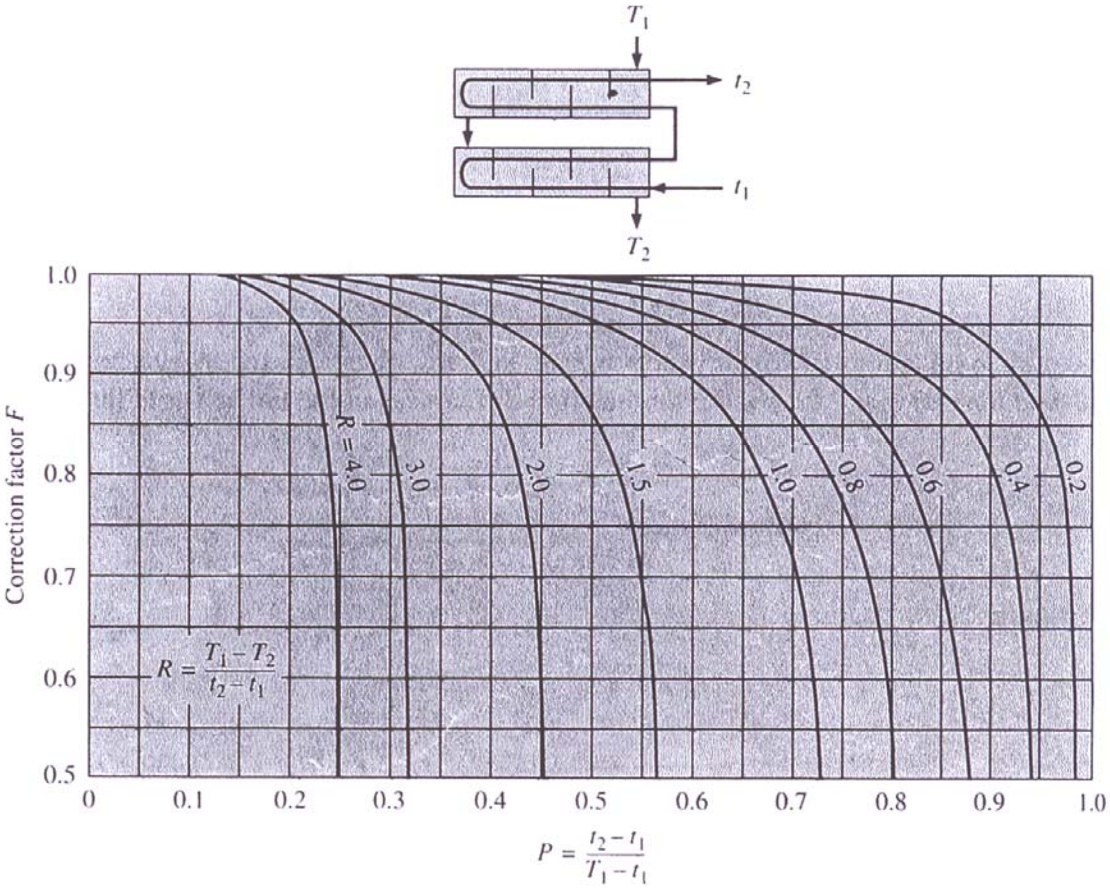


Figure 7.16: Correction factor plot for exchanger with two shell pass and four, eight, or any multiple of tube passes.

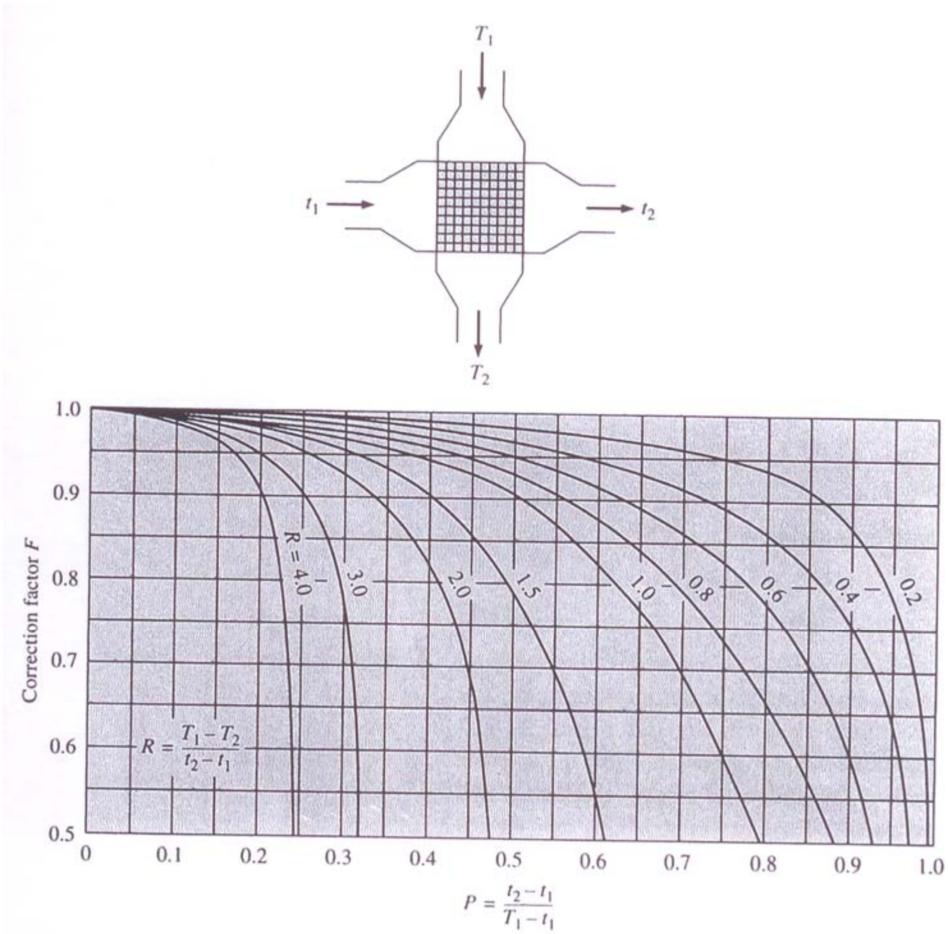


Figure 7.17: Correction-factor plot for single-pass cross-flow exchanger, both fluids unmixed.

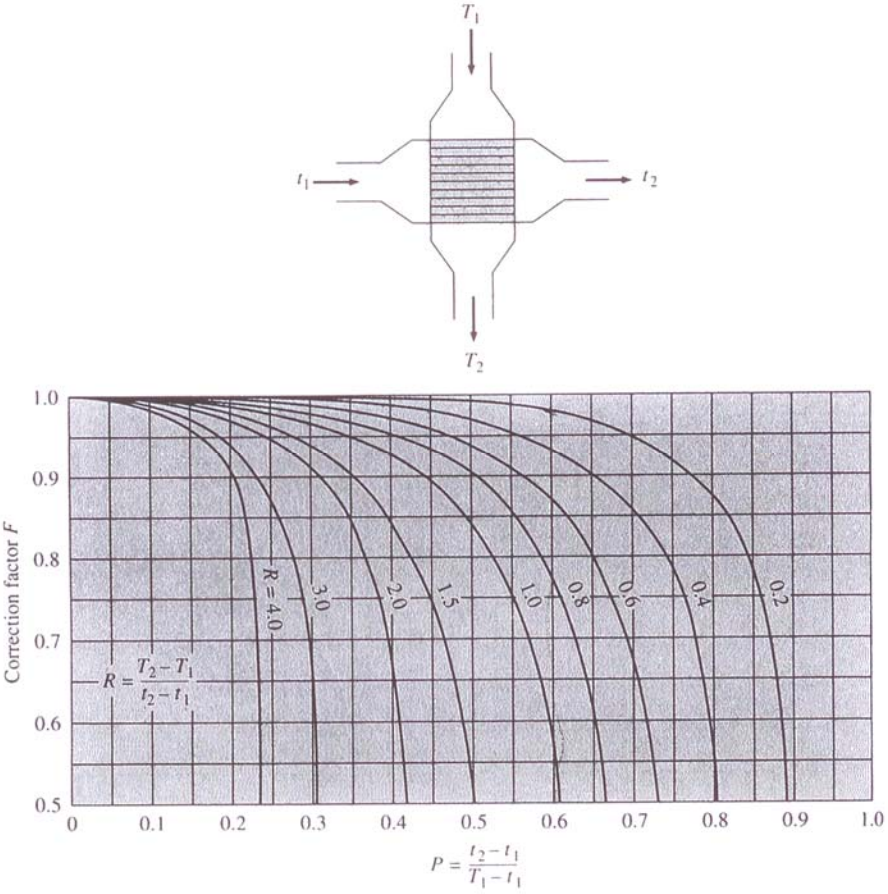


Figure 7.18: Correction-factor plot for single-pass cross-flow exchanger, one fluid mixed, the other unmixed.

Example 7.1

Water at the rate 68 kg/min is heated from 35 to 75^0C by an oil having specific heat of 1.9 kJ/kg.^{0}C. The fluids are used in a *counterflow double pipe heat exchanger* and the oil enter the exchanger at 110^0C and leaves at 75^0C. The overall heat-transfer coefficient is 320 W/m^2.^{0}C. Calculate the heat exchanger area.

Solution:

The total heat transfer is determined from the energy adsorbed by the water:

$$
\begin{aligned}
q &= \dot{m}_w C_w \Delta T_w \\
&= (68)(4180)(75-35) \\
&= 11.37 MJ/\min \\
&= 189.5 kW
\end{aligned}
$$

Since all the fluid temperature are known, the LMTD can be calculated by using the temperature scheme in Figure 10.12,

$$\Delta Tm = \frac{(110-75)-(75-35)}{\ln(110-75)/(75-35)} = 37.44^0 C$$

Then, since $q = UA\Delta Tm$

$$A = \frac{1.895x10^5}{(320)(37.44)} = 15.82m^2$$

Example 7.2

Instead of the double-pipe heat exchanger of Example 1 above, it is desired to use a shell-and-tube exchanger with the making one shell pass and the oil making two tube passes. Calculate the area required for this exchanger, assuming that the overall heat-transfer coefficient remains at 320 W/m^2.^{0}C.

Solution:

To solve this problem we determine a correction factor from Figure x to be used with the LMTF calculated on the basis of a counterflow exchanger. The parameters according to the nomenclature of Figure 8.15 are:

T_1=35 ^{0}C T_2=75 ^{0}C t_1=110 ^{0}C t_2=75 ^{0}C

$$P = \frac{t_2 - t_1}{T_1 - t_1} = \frac{75-110}{35-110} = 0.467$$

$$R = \frac{T_1 - T_2}{t_2 - t_1} = \frac{35-75}{75-110} = 1.143$$

$$A = \frac{1.895x10^5}{(320)(0.81)(37.44)} = 19.53m^2$$

$$P = \frac{t_2 - t_1}{T_1 - t_1} = \frac{75-110}{35-110} = 0.467$$

$$R = \frac{T_1 - T_2}{t_2 - t_1} = \frac{35-75}{75-110} = 1.143$$

So the correction factor is

$$F = 0.81$$

And the heat transfer is

$$q = UAF\Delta T_m$$

so that

$$A = \frac{1.895x10^5}{(320)(0.81)(37.44)} = 19.53m^2$$

Example 7.3

A cross flow heat exchanger is used to heat an oil in the tubes, c = 1.9 kJ/kg.^{0}C from 15^{0}C to 85^{0}C. Blowing across the outside of the tubes is steam which enters at 130^{0}C and leaves at 110^{0}C with mass flow of 5.2kg/sec. The overall heat transfer coefficient is 275 W/m^2.^{0}C and c for steam is 1.86 kJ/kg.^{0}C. Calculate the surface area of the heat exchanger.

Solution:

The total heat transfer may be obtained from an energy balance on the steam:

$$q = \dot{m}_s c_s \Delta T_s = (5.2)(1.86)(130-110) = 193kW$$

We can solve for the area from Eq.(8.6). The value of ΔTm calculated is as if the exchanger were counterflow double pipe.

Thus,

$$\Delta T_m = \frac{(130-85)-(110-15)}{\ln\left(\frac{130-85}{110-15}\right)} = 66.9^0 C$$

From Figure 8.18, t_1 and t_2 will represent the unmixed fluid (oil) and T_1 and T_2 will represent the mixed fluid (the steam) so that

$T_1 = 130^0$C $T_2 = 110^0$C $t_1 = 15\ ^0$C $t_2 = 85^0$C and we calculate

$$R = \frac{130-110}{85-15} = 0.286$$

$$P = \frac{85-15}{130-15} = 0.609$$

so the area is calculated from

$$A = \frac{q}{UF\Delta T_m}$$

7.4 Heat Exchanger Analysis: Use of the Effectiveness-NTU method

7.4.1 Introduction

The driving temperature across the heat transfer surface varies with position, but an appropriate mean temperature can be defined. In most simple systems this is the log mean temperature difference (LMTD). Sometimes direct knowledge of the LMTD is not available and the NTU method is used.

- The LMTD approach to heat-exchanger analysis is useful when inlet and outlet temperature are known or are easily determined.
- However, when the inlet or exit temperatures are to be evaluated for a given heat exchanger, the analysis involves an interactive procedure because of the logarithmic function in the LMTD.
- In these cases the analysis is performed more easily by utilizing a method based on the effectiveness of the heat exchanger in transferring a given amount of heat.
- The heat exchanger effectiveness can be define as:

$$Effectiveness, \varepsilon = \frac{\text{Actual rate of heat transfer}}{\text{Maximum possible rate of heat transfer}}$$

- The *actual rate heat transfer, q* may be computed by calculating either the energy lost by the hot fluid or the energy gained by the cold fluid.
- For the parallel-flow exchanger:

$$q = \dot{m}_h c_h (T_{h1} - T_{h2}) = \dot{m}_c c_c (T_{c2} - T_{c1})$$

- For the counter-flow exchanger :

$$q = \dot{m}_h c_h (T_{h1} - T_{h2}) = \dot{m}_c c_c (T_{c1} - T_{c2})$$

- The maximum possible heat transfer, q_{max} is the rate of heat transfer that a heat exchanger of infinite area would transfer with given inlet temperatures, flow rates, and specific heat.

- q_{max} occurs when the fluid with minimum product of flow rate and specific heat changes temperature to the entering temperature of the other fluid.

- Maximum possible heat transfer is expressed as

$$q_{\max} = (\dot{m} c)_{\min} (T_{hi} - T_{ci})$$

- The minimun fluid may be either hot or cold fluid depending on *mass-flowrates, m* and *specific heats, c*.

- For the parallel exchanger :

$$\varepsilon = \frac{\dot{m}_h c_h (T_{h1} - T_{h2})}{\dot{m}_h c_h (T_{h1} - T_{c1})} = \frac{T_{h1} - T_{h2}}{T_{h1} - T_{c1}}$$

$$\varepsilon = \frac{\dot{m}_c c_c (T_{c2} - T_{c1})}{\dot{m}_c c_c (T_{h1} - T_{c1})} = \frac{T_{c2} - T_{c1}}{T_{h1} - T_{c1}}$$

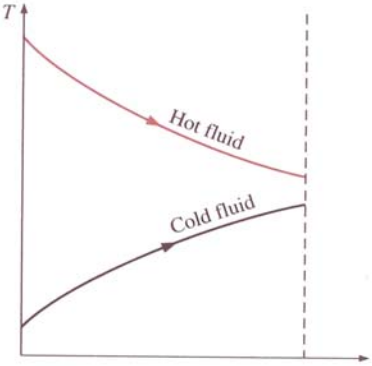


Figure 7.19 : Temperature profile for parallel exchanger

- For the counterflow exchanger :

$$\varepsilon = \frac{\dot{m}_h c_h (T_{h1} - T_{h2})}{\dot{m}_h c_h (T_{h1} - T_{c2})} = \frac{T_{h1} - T_{h2}}{T_{h1} - T_{c2}}$$

$$\varepsilon = \frac{\dot{m}_c c_c (T_{c1} - T_{c2})}{\dot{m}_c c_c (T_{h1} - T_{c2})} = \frac{T_{c1} - T_{c2}}{T_{h1} - T_{c2}}$$

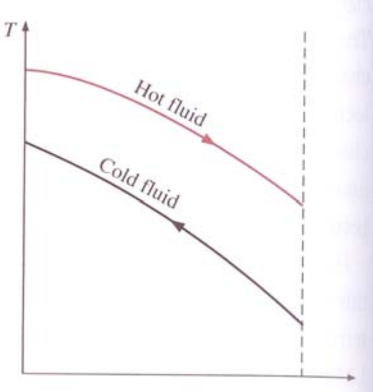


Figure 7.20: Temperature profile for parallel exchanger

- In the general way the effectiveness is expressed as :

$$\varepsilon = \frac{\Delta \text{T (minimum fluid)}}{\text{Maximum temperature difference in heat exchanger}}$$

- The effectiveness is usually written for parallel flow double pipe HE :

$$\varepsilon = \frac{1 - \exp[(-UA / \dot{m}_c c_c)(1 + \dot{m}_c c_c / \dot{m}_h c_h)}{1 + \dot{m}_c c_c / \dot{m}_h c_h}$$

$$\varepsilon = \frac{1 - \exp[(-UA / C_{\min})(1 + C_{\min} / C_{\max})}{1 + C_{\min} / C_{\max}}$$

where $C = \dot{m} c$ = capacity rate

- The number of transfer units (NTU) is indicative of the size of the heat exchanger. $NTU = UA / C_{\min}$

- Figure 7.21 to 7-26 presented effectiveness ratios for various heat exchanger arrangements.
- Table 7.1 and Table 7.2 summarizes the effectiveness relations

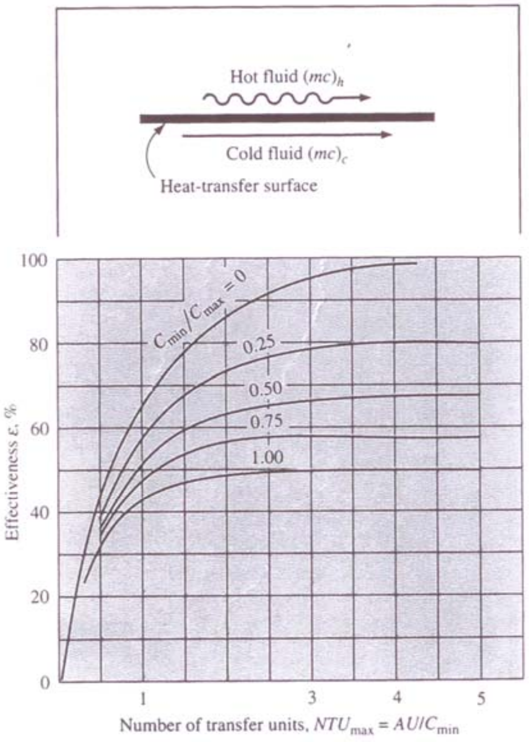


Figure 7.21: Effectiveness for parallelflow exchanger performance

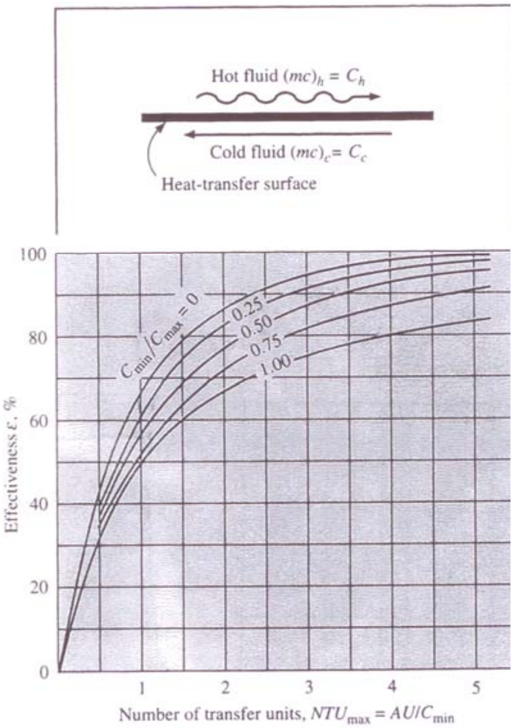


Figure 7.22: Effectiveness for counterflow exchanger performance

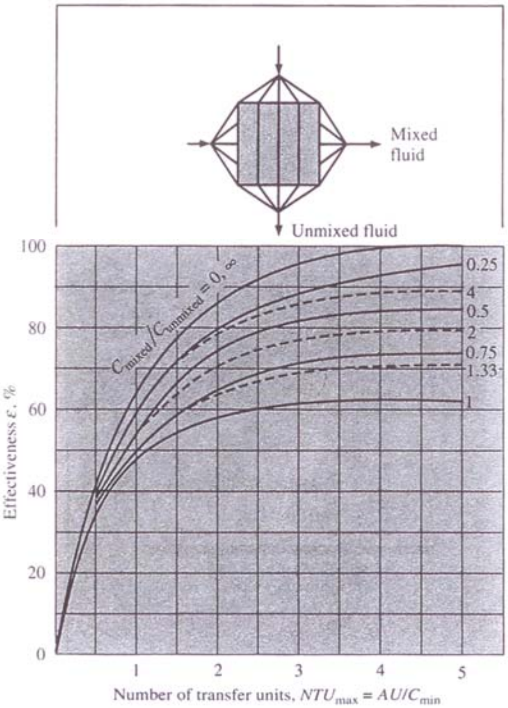


Figure 7.23 : Effectiveness for crossflow exchanger with one fluid mixed

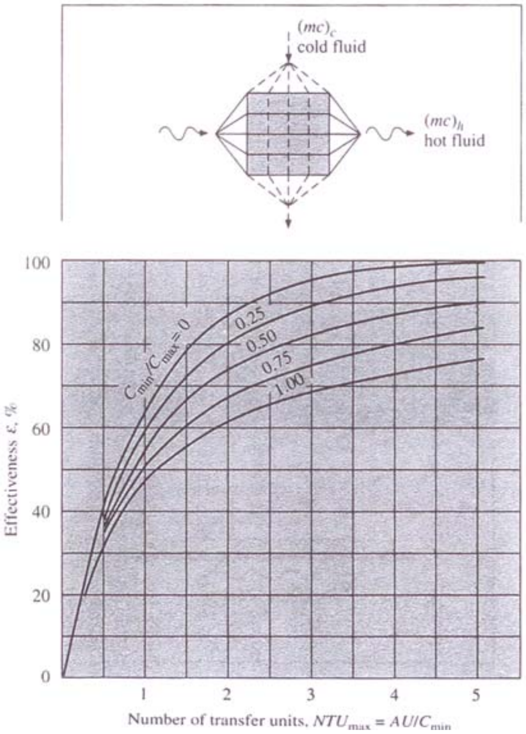


Figure 7.24: Effectiveness for crossflow exchanger with one fluid unmixed

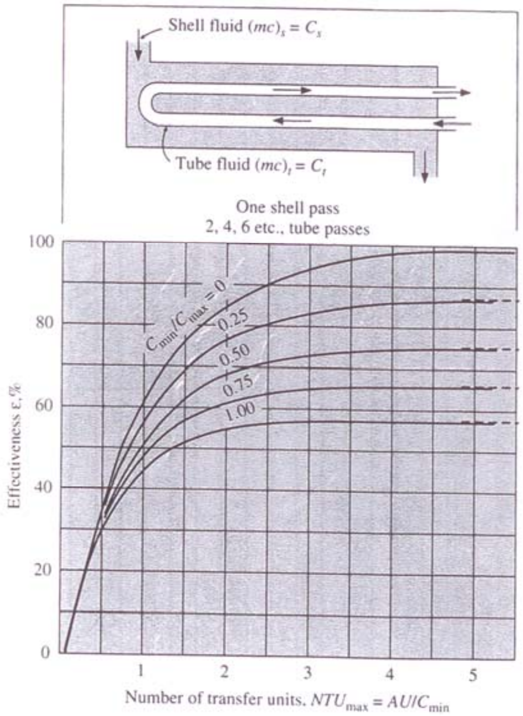


Figure 7.25 : Effectiveness for 1-2 parallel counterflow exchanger performance

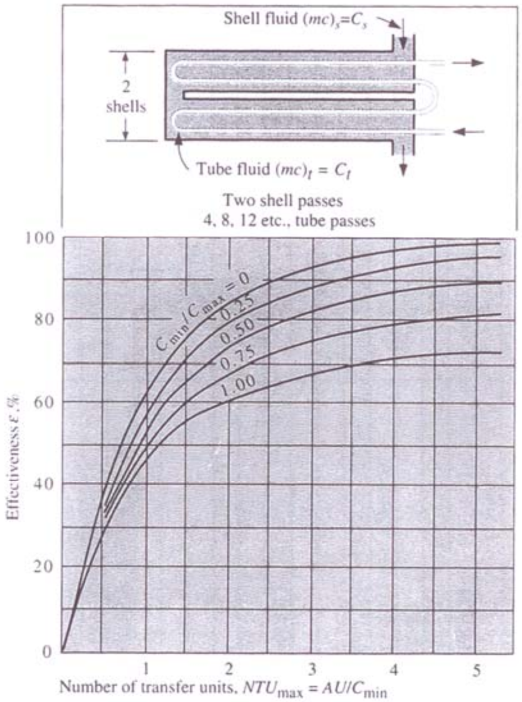
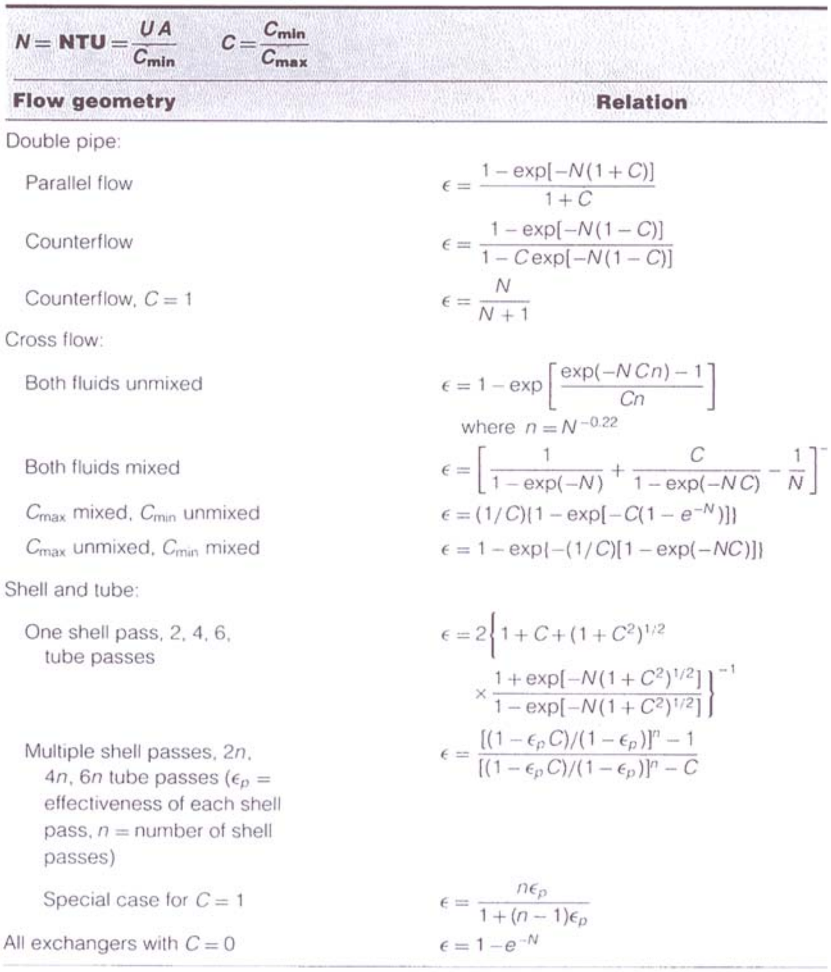


Figure 7.26 : Effectiveness for 2-4 multipass counterflow exchanger performance

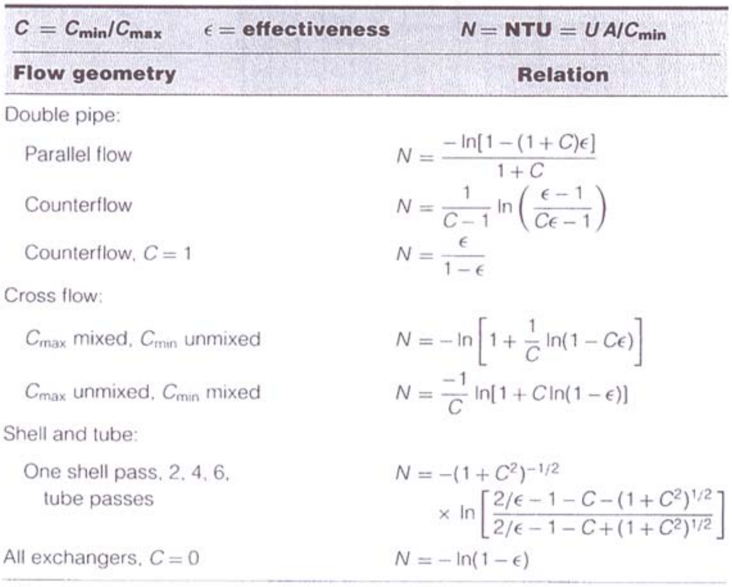
Table 7.1: Heat exchanger effectiveness relations



$N = \mathbf{NTU} = \dfrac{UA}{C_{\min}} \qquad C = \dfrac{C_{\min}}{C_{\max}}$

Flow geometry	**Relation**
Double pipe:	
Parallel flow	$\epsilon = \dfrac{1 - \exp[-N(1+C)]}{1+C}$
Counterflow	$\epsilon = \dfrac{1 - \exp[-N(1-C)]}{1 - C\exp[-N(1-C)]}$
Counterflow, $C = 1$	$\epsilon = \dfrac{N}{N+1}$
Cross flow:	
Both fluids unmixed	$\epsilon = 1 - \exp\left[\dfrac{\exp(-NCn) - 1}{Cn}\right]$ where $n = N^{-0.22}$
Both fluids mixed	$\epsilon = \left[\dfrac{1}{1-\exp(-N)} + \dfrac{C}{1-\exp(-NC)} - \dfrac{1}{N}\right]^{-}$
$C_{\max}$ mixed, $C_{\min}$ unmixed	$\epsilon = (1/C)\{1 - \exp[-C(1 - e^{-N})]\}$
$C_{\max}$ unmixed, $C_{\min}$ mixed	$\epsilon = 1 - \exp\{-(1/C)[1 - \exp(-NC)]\}$
Shell and tube:	
One shell pass, 2, 4, 6, tube passes	$\epsilon = 2\left\{1 + C + (1+C^2)^{1/2} \times \dfrac{1 + \exp[-N(1+C^2)^{1/2}]}{1 - \exp[-N(1+C^2)^{1/2}]}\right\}^{-1}$
Multiple shell passes, $2n$, $4n$, $6n$ tube passes (ϵ_p = effectiveness of each shell pass, n = number of shell passes)	$\epsilon = \dfrac{[(1-\epsilon_p C)/(1-\epsilon_p)]^n - 1}{[(1-\epsilon_p C)/(1-\epsilon_p)]^n - C}$
Special case for $C = 1$	$\epsilon = \dfrac{n\epsilon_p}{1 + (n-1)\epsilon_p}$
All exchangers with $C = 0$	$\epsilon = 1 - e^{-N}$

Table 7.2: NTU relations for heat exchangers



$C = C_{\min}/C_{\max}$ $\quad \epsilon$ = effectiveness	N = NTU = $UA/C_{\min}$
Flow geometry	**Relation**
Double pipe:	
Parallel flow	$N = \dfrac{-\ln[1-(1+C)\epsilon]}{1+C}$
Counterflow	$N = \dfrac{1}{C-1}\ln\left(\dfrac{\epsilon-1}{C\epsilon-1}\right)$
Counterflow, $C = 1$	$N = \dfrac{\epsilon}{1-\epsilon}$
Cross flow:	
$C_{\max}$ mixed, $C_{\min}$ unmixed	$N = -\ln\left[1+\dfrac{1}{C}\ln(1-C\epsilon)\right]$
$C_{\max}$ unmixed, $C_{\min}$ mixed	$N = \dfrac{-1}{C}\ln[1+C\ln(1-\epsilon)]$
Shell and tube:	
One shell pass, 2, 4, 6, tube passes	$N = -(1+C^2)^{-1/2} \times \ln\left[\dfrac{2/\epsilon-1-C-(1+C^2)^{1/2}}{2/\epsilon-1-C+(1+C^2)^{1/2}}\right]$
All exchangers, $C = 0$	$N = -\ln(1-\epsilon)$

Problems

1. Water flowing at a rate of 0.723 kg/s enters the inside of a countercurrent, double-pipe heat exchanger at 300 K and is heated by an oil stream that enters at 385 K at a rate of 3.2 kg/s. The heat capacity of the oil is 1.89 kJ/kg K, and the average heat capacity of water over the temperature range of interest is 4.192 kJ/kg K. The overall heat-transfer coefficient of the exchanger is 300 W/m^2.K, and the area for heat transfer is 15.4 m^2. What is the total amount of heat transferred?

2. A shell and tube exchanger operates with two passes and four tube passes. The shell fluid is ethylene glycol (c= 2.742 kJ/kg.^{0}C), which enters at 140^{0}C and leaves at 80 ^{0}C with flowrate of 45000 kg/h. Water flows in tubes (4.174 kJ/kg.^{0}C), entering at 35 ^{0}C and leaving at 85 ^{0}C. The overall heat transfer coefficient for this arrangement is 850 W/m^2.^{0}C. Calculate the flow rate of water required and the area of the heat exchanger.

3. A double pipe heat exchanger is used to heat an oil with c = 2.2 kJ/kg.^{0}C from 50 ^{0}C to 100^{0}C. The other fluid having c = 4.2 kJ/kg.^{0}C enters the exchanger at 160 ^{0}C and leaves at 90^{0}C. The overall heat transfer coefficient is 300 W/m^2.^{0}C. Calculate the area and effectiveness of the heat exchanger for a total heat transfer rate of 600 kW.

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