Principles Of Chemical Engineering Calculations

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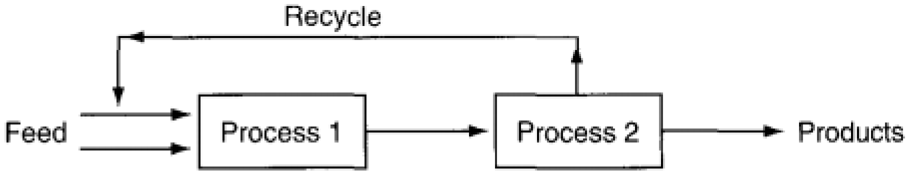
Lecture 13

Product separation and Recycle

Recycle is fed back from a downstream unit to an upstream unit, as shown in Figure . The stream containing the recycled material is known as a recycle stream.

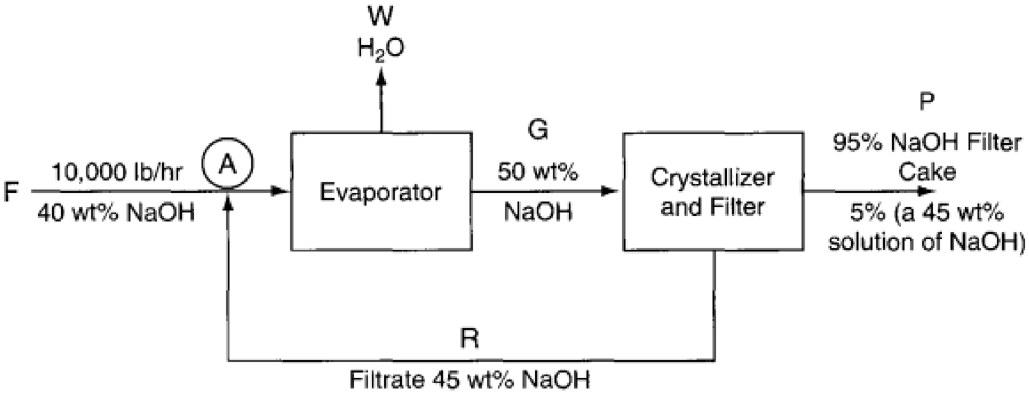
Recycle system is a system that includes one or more recycle streams.



Recycle without Chemical Reaction

Example 13

Figure below is a schematic of a process for the production of flake NaOH. The fresh feed to the process is 10,000 lb/hr of a 40% aqueous NaOH solution.



a. Determine the flow rate of water removed by the evaporator(W), and the recycle rate for this process (R).

b. Assume that the same production rate of NaOH flakes occurs, but the filtrate is not recycled. What would be the total feed rate of 40% NaOH have to be then? Assume that the product solution from the evaporator still contains 50% NaOH.

Solution

Open, steady-state process.

a. Basis: 10,000 lb fresh feed (equivalent to 1 hour)

The unknowns are W, G, P, and R.

<u>Overall NaOH mass balance</u>

input = output

(0.4)(10,000) = 0.95 P + (0.45) (0.05) P

P = 4113 lb

<u>Overall H_2O mass balance</u>

input = output

(0.6) (10,000) = W+ [(0.55)(0.05)](4113)

W= 5887 lb

The total amount of NaOH exiting with P is [(0.95) + (0.45)(0.05)](4113) = 4000 lb

<u>NaOH mass balance on the crystallizer</u>

0.5 G = 4000 + 0.45 R (1)

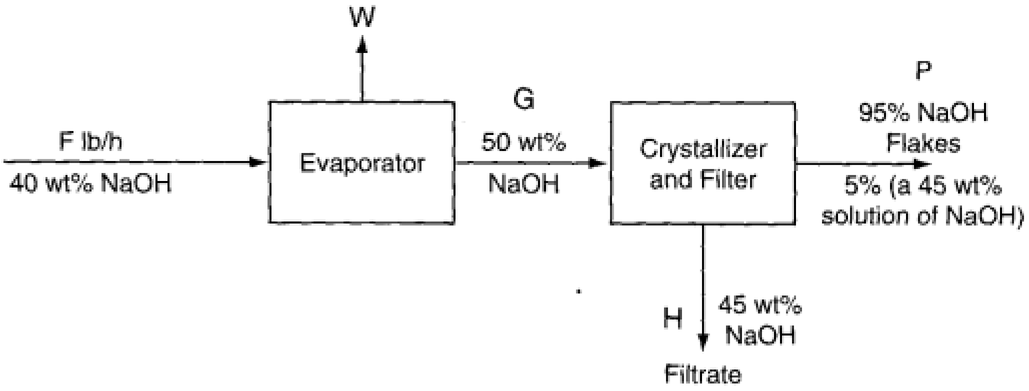
<u>H_2O mass balance on the crystallizer</u>

0.5 G = 113 + 0.55 R (2)

Solving equations 1 and 2 gives:

R = 38,870 lb

b. The basis is now P = 4113 lb (the same as 1 hour)



The unknowns are now F, W, G, and H.

NaOH mass balance on the crystallizer

0.5 G = [(0.95) + (0.05) (0.45)] (4113) + 0.45 H (1)

H_2O mass balance on the crystallizer

0.5G = [(0.05) (0.55) (4113)] + 0.55 H (2)

By solving equations 1 and 2 gives:

H = 38,870 lb

Overall NaOH mass balance

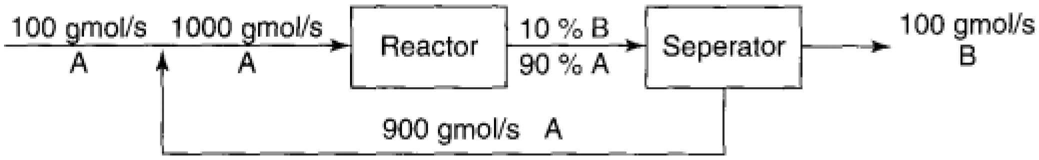
0.40 F = 0.45(38,870) + 4000

F = 53,730 lb

Note that without recycle, the feed rate must be 5.37 times larger than with recycle to produce the same amount of product.

Recycle with Chemical Reaction

The most common application of recycle for systems involving chemical reaction is the recycle of reactants, an application that is used to increase the overall conversion in a reactor. Figure below shows a simple example for the reaction $A \rightarrow B$



If you calculate the extent of reaction for the overall process based on B

$$\xi_{\text{overall}} = \frac{100-0}{1} = 100 \text{ moles reacting}$$

If you use material balances to calculate the output P of the reactor(on the basis of 1 second) you get A = 900 g mol and B = 100 g mol

And the extent of reaction based on B for the reactor by itself as the system is:

$$\xi_{\text{reactor}} = \frac{100-0}{1} = 100 \text{ moles reacting}$$

Two types of conversion when reactions occur:

1. Overall fraction conversion:

$$\frac{\text{reactant input to process} - \text{reactant output from process}}{\text{reactant input to process}}$$

2. Single - pass fraction conversion:

$$\frac{\text{reactant input to reactor} - \text{reactant output from reactor}}{\text{reactant input to reactor}}$$

For the simple recycle reactor in Figure , the overall conversion is:

$\frac{100-0}{100} * 100 = 100\ \%$

And the single-pass conversion is:

$\frac{1000-900}{1000} * 100 = 10\ \%$

The overall conversion and the single-pass conversion can be expressed in terms of the extent of reaction, ξ.

Overall conversion of species A= $f_{OA} = \frac{-\nu_A \xi}{n_A^{process\ \ feed}}$

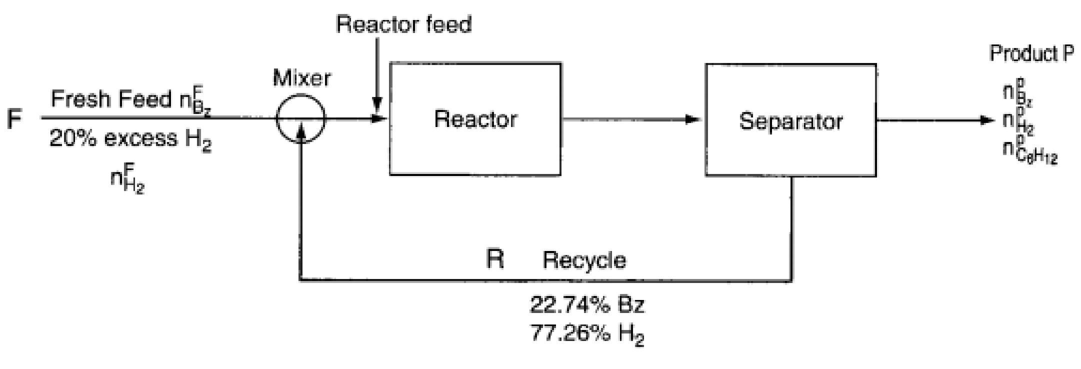
Single pass conversion of species A= $f_{SP} = \frac{-\nu_A \xi}{n_A^{reactor\ \ feed}}$

Example 14

Cyclohexane (C_6H_{12}) can be made by the reaction of benzene (Bz) (C_6H_6) with hydrogen according to the following reaction:

$C_6H_6 + 3H_2 \rightarrow C_6H_{12}$

For the process shown in Figure below, determine the ratio of the recycle stream to the fresh feed stream if the overall conversion of benzene is 95%, and the single-pass conversion is 20%. Assume that 20% excess hydrogen is used in the fresh feed, and that the composition of the recycle stream is 22.74 mol % benzene and 77.26 mol % hydrogen.



Solution

The process is open and steady state.

Basis = 100 mol of fresh benzene feed

$$\text{excess } H_2 = \frac{\text{in} - \text{required}}{\text{required}}$$

In H_2(Feed):

$$0.2 = \frac{\text{in} - 3(100)}{3(100)}$$

In H_2 = 360 mol

The total process feed = 100 +360 = 460 mol

From Equation of overall conversion for benzene (ν_{Bz}= - 1):

$$0.95 = \frac{-(-1)\xi}{100}$$

ξ= 95 reacting moles.

The unknowns are R, $n_{Bz}^{P}, n_{H_2}^{P}$ *and* $n_{C_6H_{12}}^{P}$

The species overall balances are:

$$n_i^{out} = n_i^{in} + \nu_i \xi_{overall}$$

Bz overall balance

$$n_{Bz}^{P} = 100 + (-1)(95) = 5\,mol$$

H_2 overall balance

$$n_{H_2}^{P} = 360 + (-3)(95) = 75\,mol$$

C_6H_{12} overall balance

$$n_{C_6H_{12}}^{P} = 0 + (1)(95) = 95\,mol$$

P = 5 + 75 + 95 =175 mol

The amount of the Bz feed to the reactor is 100 + 0.2274 R, and ξ= 95. Thus, for benzene:

$$0.2 = \frac{-(-1)95}{100+0.227\mathrm{R}}$$

R = 1649 mol

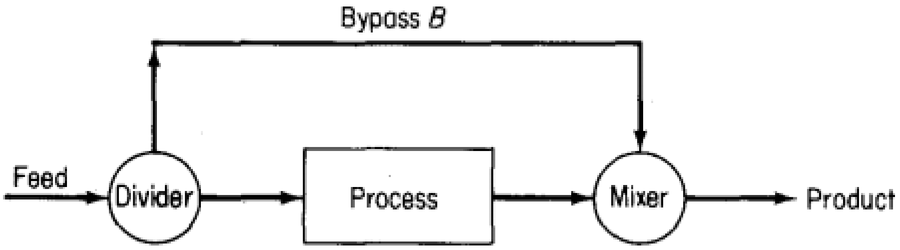
Finally, the ratio of recycle to fresh feed is:

$$\frac{\mathrm{R}}{\mathrm{F}} = \frac{1649\ \mathrm{mol}}{460\ \mathrm{mol}} = 3.58$$

Lecture 14

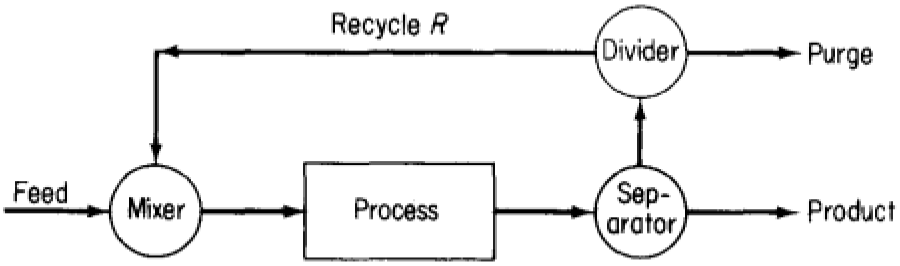
Bypass and Purge

1. A **bypass stream**—a stream that skips one or more stages of the process an goes directly to another downstream stage .



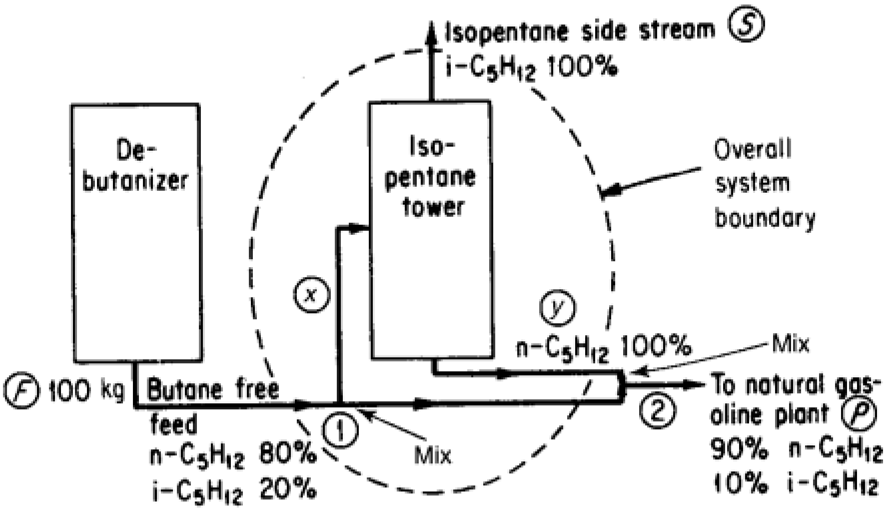
A bypass stream can be used to control the composition of a final exit stream from a unit by mixing the bypass stream and the unit exit stream in suitable proportions to obtain the desired final composition.

2. **A purge stream**—a stream bled off from the process to remove an accumulation of inert or unwanted material that might otherwise build up in the recycle stream.



Example 15

In the feedstock preparation section of a plant manufacturing natural gasoline, isopentane is removed from butane-free gasoline. What fraction of the butane-free gasoline is passed through the isopentane tower? The process is in the steady state and no reaction occurs.



Solution

Basis: 100 kg feed

Overall balances

1. Total material balance:

   In = out

   100 = S + P

2. Component balance for n-C_5 (tie component)

   In = out

   100 (0.8) = S(0) + P(0.9)

Consequently,

$$P = 100\left(\frac{0.8}{0.9}\right) = 88.9\ kg$$

S = 100 – 88.9 = 11.1 kg

Balance around isopentane tower:

Let x be the kg of butane-free gas going to the isopentane tower, and y be the kg of the n-C_5H_{12} stream leaving the isopentane tower.

3. Total material balance:

   In = Out

   x = 11.1 + y

4. Component balance for n-C_5,

   x (0.80) = y

Consequently, combining (3) and (4) yields :

x = 55.5 kg, or the desired fraction is 0.55.

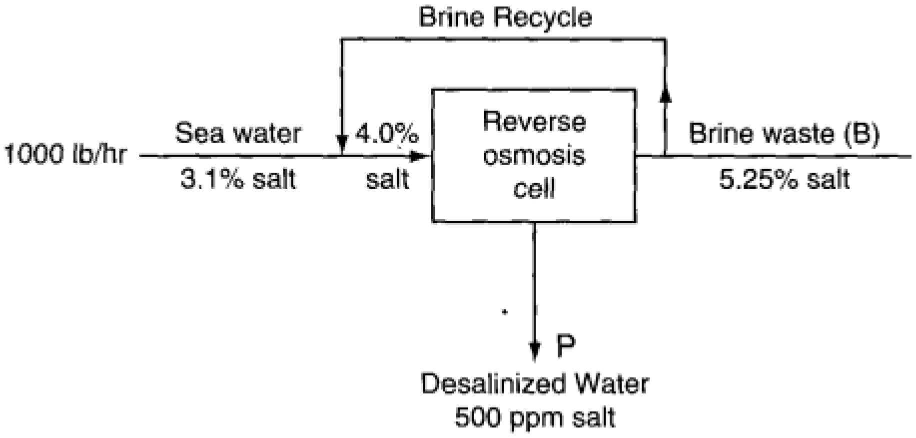
Problems

1. Sea water is to be desalinized by reverse osmosis using the scheme indicated in Figure. Use the data given in the figure to determine:

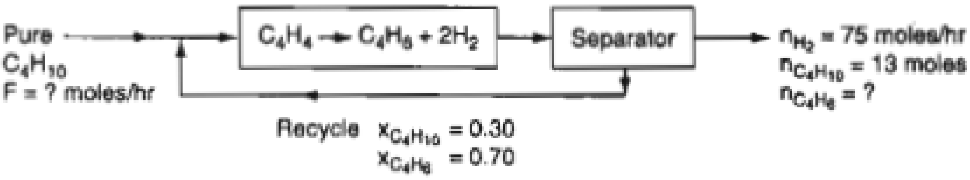
   (a) the rate of waste brine removal (B)

   (b) the rate of desalinized water (called potable water) production(P)

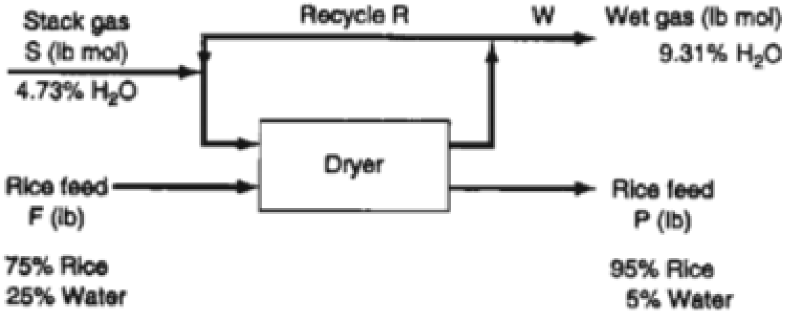
   (c) the fraction of the brine leaving the reverse osmosis cell (which acts in essence as a separator) that is recycled.



2. A catalytic dehydrogenation process, produces 1,3 butadiene (C_4H_6) from pure normal butane (C_4H_{10}). The product stream contains 75 mol/h of H_2 and 13 mol/h of C_4H_{10} as well as C_4H_6. The recycle stream is 30% (mol) C_4H_{10} and 70% (mol) C_4H_6 and the flow is 24 mol/h.
   a. What is the feed rate, F, and the product flow rate of C_4H_6 leaving the process?
   b. What is the single-pass conversion of butane in the process?



3. To save energy, stack gas from a furnace is used to dry rice. What is the amount of recycle gas (in lb mol) per 100 lb of P if the concentration of water in the gas stream entering the dryer is 5.2%?



Lecture 15

Gases, Vapors, Liquids

- **Property** is meaning any measurable characteristic of a substance, such as pressure, volume, or temperature, or a characteristic that can be calculated or deduced, such as internal energy.
- **State :** A system will possess a unique set of properties, such as temperature, pressure, density, and so on, at a given time, and thus is said to be in a particular state. A change in the state of the system results in a change in at least one of its properties.
- **By equilibrium** : we mean a state in which there is no tendency toward spontaneous change. When a system is in equilibrium with another system, or the surroundings, it will not change its state unless the other system, or the surroundings, also changes.
- **A phase** is defined as a completely homogeneous and uniform state of matter. Liquid water would be a phase; ice would be another phase. Two immiscible liquids in the same container, such as mercury and water, would represent two different phases because the liquids have different properties.

3.1 Ideal Gas Law Calculations

The Ideal Gas Law

Under conditions such that the average distance between the molecules in a substance is great enough to neglect the effect of the intermolecular forces and the volume of the molecules themselves, a gas can be termed an ideal gas.

More properly, an ideal gas is an imaginary gas that obeys exactly the following relationship:

$$pV = nRT \qquad (1)$$

Where p = absolute pressure of the gas

V= total volume occupied by the gas

n= number of moles of the gas

R= ideal gas constant in appropriate units

T= absolute temperature of the gas

Sometimes the ideal gas law is written as

$$p\hat{V} = RT$$

Where $\hat{V}$ is the specific volume (volume per mole or mass) of the gas.

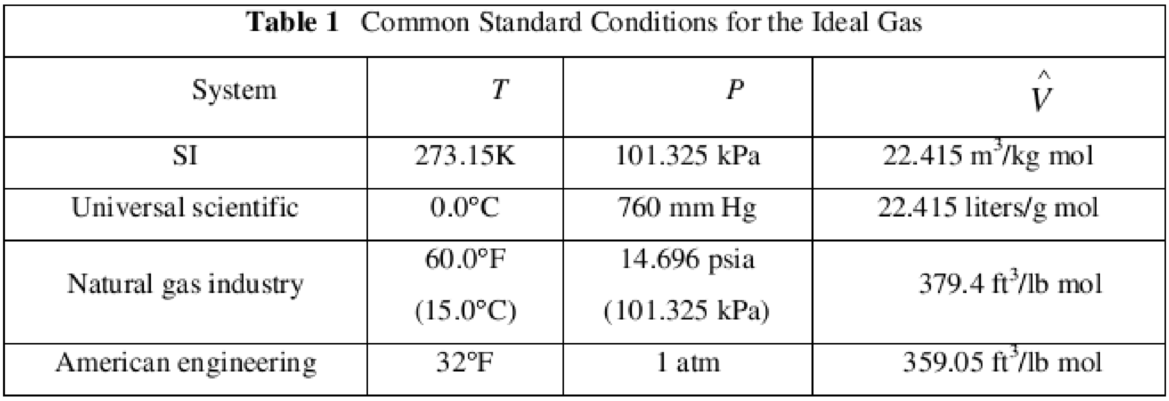


Table 1 Common Standard Conditions for the Ideal Gas

System	T	P	$\hat{V}$
SI	273.15K	101.325 kPa	22.415 m^3/kg mol
Universal scientific	0.0°C	760 mm Hg	22.415 liters/g mol
Natural gas industry	60.0°F (15.0°C)	14.696 psia (101.325 kPa)	379.4 ft^3/lb mol
American engineering	32°F	1 atm	359.05 ft^3/lb mol

Example 1

Calculate the volume, in cubic meters, occupied by 40 kg of CO_2 at standard conditions.

Solution

Basis: 40 kg of CO_2

$$40\ kg\ CO_2 \left| \frac{1\ kmol\ \ CO_2}{44\ kg\ CO_2} \right| \frac{22.42\ m^3 CO_2}{1\ kmol\ \ CO_2} = 20.4\ m^3 CO_2\ at\ S.C.$$

Example 2

Find the value for the universal gas constant R for the following combinations of units: For 1 mol of ideal gas when the pressure is in atm, the volume in cm^3, and the temperature in K.

Solution

at standard conditions we will use the approximate values:

p = 1 atm

$$\hat{V} = 22415\ \ cm^3/mol$$

T = 273.15 K

$$R = \frac{p\hat{V}}{T} = \frac{1\ atm}{273.15\ K} \left| \frac{22415\ cm^3}{1\ mol} \right. = 82.06 \frac{(cm^3)(atm)}{(K)(mol)}$$

In many processes going from an initial state to a final state, you can use the ratio of ideal gas law in the respective states and eliminate R as follows (the subscript 1 designates the initial state, and the subscript 2 designates the final state);

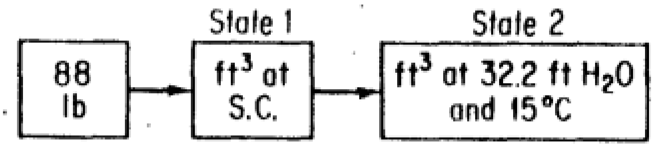
$$\frac{p_1V_1}{p_2V_2} = \frac{n_1RT_1}{n_2RT_2}$$

$$\left(\frac{p_1}{p_2}\right)\left(\frac{V_1}{V_2}\right) = \left(\frac{n_1}{n_2}\right)\left(\frac{T_1}{T_2}\right) \tag{2}$$

Example 3

Calculate the volume occupied by 88 lb of CO_2 at a pressure of 32.2 ft of water and at 15°C.

Solution



$$\left(\frac{p_1}{p_2}\right)\left(\frac{V_1}{V_2}\right) = \left(\frac{n_1}{n_2}\right)\left(\frac{T_1}{T_2}\right)$$

$$V_2 = V_1\left(\frac{p_1}{p_2}\right)\left(\frac{T_2}{T_1}\right)$$

Assume that the pressure is absolute pressure.

	At state 1 (S.C)	At state 2
Pressure (ft H_2O)	33.91	32.2
Temperature (K)	273	15+273 = 288

Basis: 88 lb of CO_2

$$V_2 = \underbrace{88\ lb\ CO_2 \left| \frac{1\ lb\ mol\ CO_2}{44\ lb\ CO_2} \right| \frac{359\ ft^3}{1\ lb\ mol}}_{V_1} \left| \frac{288}{273} \right| \frac{33.91}{32.2} = 798\ ft^3 CO_2$$

The Gas Density

The density of a gas is defined as the mass per unit volume and can be expressed in kilograms per cubic meter, pounds per cubic foot, grams per liter, or other units

Example 4

What is the density of N_2 at 27°C and 100 kPa in SI units?

Solution

Basis: 1 m^3 of N_2 at 27ºC and 100 kPa

$$1\,m^3 \,\Big|\, \frac{273\,K}{300\,K} \,\Big|\, \frac{100\,kPa}{101.3\,kPa} \,\Big|\, \frac{1\,kmol}{22.4\,m^3} \,\Big|\, \frac{28\,kg}{1\ kmol} = 1.123\,kg$$

Density = 1.123 kg/m^3 of N_2 at 27 ºC and 100 kPa

The Gas Specific Gravity

The specific gravity of a gas is usually defined as the ratio of the density of the gas at a desired temperature and pressure to that of air (or any specified reference gas) at a certain temperature and pressure.

Example 5

What is the specific gravity of N_2 at 80°F and 745 mm Hg compared to air at 80°F and 745 mm Hg?

Solution

Basis: I ft^3 of air at 80 ºF and 745 mm Hg

$$1 \,\Big|\, \frac{492}{540} \,\Big|\, \frac{745}{760} \,\Big|\, \frac{1}{359} \,\Big|\, \frac{29}{1} = 0.0721\frac{lb}{ft^3} at\ 80ºF\ and\ 745\ mm\ Hg$$

Basis: 1 ft^3 of N_2 at 80 ºF and 745 mm Hg

$$1 \,\Big|\, \frac{492}{540} \,\Big|\, \frac{745}{760} \,\Big|\, \frac{1}{359} \,\Big|\, \frac{28}{1} = 0.0697\frac{lb}{ft^3} at\ 80ºF\ and\ 745\ mm\ Hg$$

$$(sp.gr.)_{N_2} = \frac{0.0697}{0.0721} = 0.0967\frac{lb\ N_2/ft^3}{lb\ air\ /ft^3}$$

Ideal Gas Mixtures and Partial Pressure

The partial pressure of gas; i defined by Dalton, p_i, namely the pressure that would be exerted by a single component in a gaseous mixture if it existed by itself in the same volume as occupied by the mixture and at the same temperature of the mixture is:

$$p_i V_{total} = n_i R T_{total} \qquad (3)$$

Where p_i is the partial pressure of component i . If you divide Eq. (3) by Eq. (1), you find that:

$$\frac{p_i V_{total}}{p_{total}\ V_{total}} = \frac{n_i R T_{total}}{n_{total}\ R T_{total}}$$

Or, $p_i = p_{total} \frac{n_i}{n_{totl}} = p_{total}\, y_i$ (4)

Where y_i is the mole fraction of component i.

Can you show that Dalton's law of the summation of partial pressures is

true using Eq.4?

$$p_1 + p_2 + \cdots + p_n = p_t \qquad (5)$$

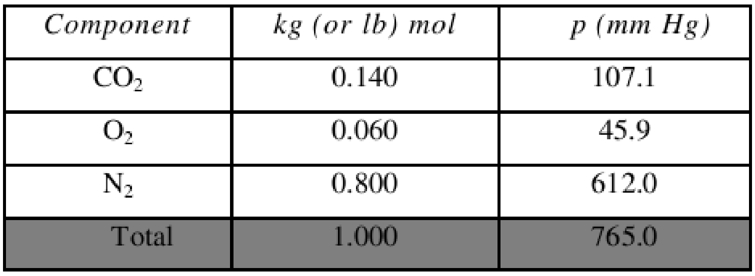
Example 6

A flue gas analyzes 14.0% CO_2, 6.0% O_2, and 80.0% N_2. It is at 400°F and 765.0 mm Hg pressure. Calculate the partial pressure of each component.

Solution

Use Eq, (4) $p_i = p_t\, y_i$

Basis: 1.00 kg (or lb) mol flue gas



Component	*kg (or lb) mol*	*p (mm Hg)*
CO_2	0.140	107.1
O_2	0.060	45.9
N_2	0.800	612.0
Total	1.000	765.0

Lecture 16

Real Gas Relationships

We have said that at room temperature and pressure many gases can be assumed to act as ideal gases.

However, for some gases under normal conditions, and for most gases under conditions of high pressure, values of the gas properties that you might obtain using the ideal gas law would be at wide variance with the experimental evidence

Thus it is clear that we need some way of computing the p-V-T properties of a gas that is not ideal, i.e. the real gas.

Three methods of getting or predicting real gas properties in lieu of having experimental data:

1. Compressibility charts
2. Equations of state
3. Estimated properties

Critical State, Reduced Parameters, and Compressibility

The critical state for the gas-liquid transition is the set of physical conditions at which the density and other properties of the liquid and vapor become identical.

A supercritical fluid, that is, a compound in a state above the critical point, combines some of the properties of both gases and liquids.

Another set of terms with which you should immediately become familiar are the reduced parameters. These are corrected, or normalized, conditions of temperature, pressure, and volume and are expressed mathematically as:

$$T_r = \frac{T}{T_c}, \qquad P_r = \frac{P}{P_c}, \qquad V_r = \frac{V}{V_c}$$

Compressibility Factor (z)

One common way is to modify the ideal gas law by inserting an adjustable coefficient z, the compressibility factor, a factor that compensates for the non ideality of the gas. Thus, the ideal gas law becomes a real gas law, a generalized equation of state:

$$pV = znRT \qquad (6)$$

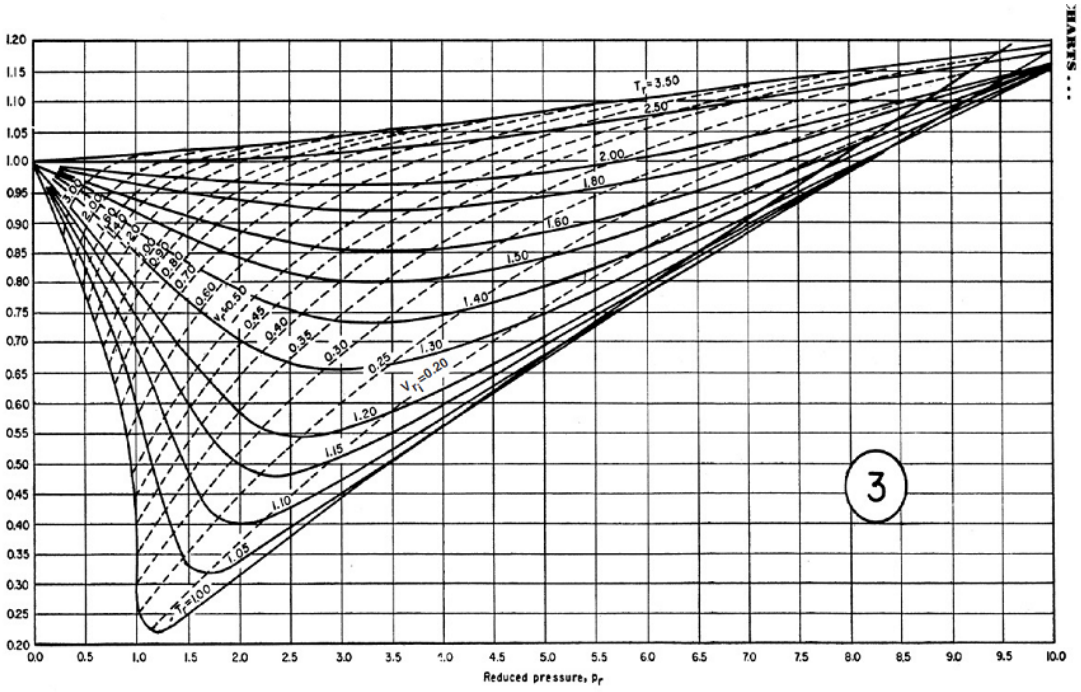
Figure below show the generalized compressibility charts or z– factor chart prepared by Nelson and Obert.

One of these helpful parameters is the ideal reduced volume defined as:

$$V_{ri} = \frac{\hat{V}}{\hat{V}_{ci}}$$

V_{ci} the ideal critical volume. Or,

$$\hat{V}_{ci} = \frac{RT_c}{p_c}$$



***Generalized Compressibility Chart, Medium Pressure*.**

Note

The value z = 1 represents ideality, and the value z = 0.27 is the compressibility factor at the critical point.

Example 7

for the system below, a tank of volume 120 ft^3 contains 125 lb of NH_3 gas at 292 psig and 125ºF. the specific volume calculated was 1.20 ft^3/lb and hence there are only 100 lb of NH_3 in the tank. Is this correct?

Solution

Based on ideal gas law for I lb:

$$R = 10.73 \frac{(\mathrm{psia})(\mathrm{ft}^3)}{(\mathrm{lb\ mol})(\mathrm{ºR})}$$

p = 292 + 14.7 = 306.7 psia

T = 125 ºF + 460 = 585 ºR

$$n = \frac{1\ lb}{17 lb/lb\ mol} = \frac{1}{17}\, lb\, mol$$

$$\hat{V} = \frac{RT}{p} = \frac{\frac{1}{17}(10.73)(585)}{306.7} = 1.20\ \mathrm{ft}^3/\mathrm{lb}$$

However, he should have used the compressibility factor, because NH_3 does not behave as an ideal gas under the observed conditions of temperature and pressure. Let us again compute the mass of gas in the tank this time using:

$$pV = znRT$$

From Appendix D: $T_c = 729.9\ R,\ \ p_c = 1636\ psia$

$$T_r = \frac{585\ R}{729.9\ R} = 0.801 \qquad , \ P_r = \frac{306.7 psia}{1636\ psia} = 0.187$$

From figure 3, you can read z = 0.855. Now $\hat{V}$ can be calculated as:

$$\hat{V} = \frac{1.20\ ft^3\ ideal}{lb} \left| \frac{0.855}{1} \right. = 1.03\ \mathrm{ft}^3/\mathrm{lb}\ \ NH_3$$

$$\frac{1\ lb\ NH_3}{1.03\ ft^3}\Big|\,120\ \text{ft}^3 = 117\ \text{lb}\ \ NH_3$$

2. Equations of State

Equations of state relate the p-V-T properties of a pure substance (or mixtures) by theoretical or empirical relations.

The simplest example of an equation of state is the ideal gas law itself.

Van der Waals equation

$$p = \frac{nRT}{V-nb} - \frac{n^2a}{V^2}$$

$$a = \left(\frac{27}{64}\right)\frac{R^2T_c^2}{P_c}$$

$$b = \left(\frac{1}{8}\right)\frac{RT_c}{P_c}$$

Example 8

A cylinder 0.150 m^3 in volume containing 22.7 kg of propane C_3H_8 stands in the hot sun. A pressure gauge shows that the pressure is 4790 kPa gauge. What is the temperature of the propane in the cylinder? Use van der Waals equation.

Solution

Basis: 22.7 kg of propane

From handbook, $a = 9.24 * 10^6 atm\left(\frac{cm^3}{mol}\right)^2$, $b = 90.7\frac{cm^3}{mol}$

$$\left(p + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$

$$\text{p} = (4790 + 101)\text{kPa}\,\Big|\,\frac{1\ \text{atm}}{101.3\ \text{kPa}} = 48.3\ \text{atm abs.}$$

$$R = 82.06\ \frac{(cm^3)(atm)}{(mol)(K)}$$

$$\text{n} = \frac{22.7\ \text{kg}}{44\ \text{kg/kmol}} = 0.516\ \ \text{kmol propane}$$

$$\left[48.3+\frac{(0.516*10^3)^2(9.24*10^6)}{(0.150*10^6)^2}\right]\left(0.150*10^6-(0.516*10^3)*(90.7)\right)=(0.516*10^3)(82.06)(T_K)$$

T = 384 K

Gaseous mixture

$$p_c^{'}=p_{c_A}y_A+p_{c_B}y_B+\cdots$$

$$T_c^{'}=T_{c_A}y_A+T_{c_B}y_B+\cdots$$

$$p_r^{'}=\frac{p}{p_c^{'}}$$

$$T_r^{'}=\frac{T}{T_c^{'}}$$

Example 9

A gaseous mixture has the following composition (in mole percent):

Methane, CH_4	20
Ethylene, C_2H_4	
Nitrogen, N_2	50

at 90 atm pressure and 100°C. Compare the volume per mole as computed by the methods of:

(a) the perfect gas law

(b) the pseudoreduced technique (Kay's method)

Solution

Basis: 1 mol of gas mixture

Component	**T_c (K)**	**p_c (atm)**
CH_4	191	45.8
C_2H_4	283	50.5
N_2	126	33.5

$R = 82.06\ \frac{(cm^3)(atm)}{(mol)(K)}$

(a) Perfect gas law:

$$\hat{V} = \frac{RT}{p} = \frac{1(82.06)(373)}{90} = 340\ cm^3$$

(b)

$$p_c' = p_{c_A}y_A + p_{c_B}y_B + p_{c_C}y_C = (45.8)(0.2) + (50.5)(0.3) + (33.5)(0.5) = 41.2\ atm$$

$$T_c' = T_{c_A}y_A + Ty_B + T_{c_C}y_C = (191)(0.2) + (283)(0.3) + (126)(0.5) = 186\ K$$

$$T_r' = \frac{T}{T_c'} = \frac{373}{186} = 2.01$$

$$p_r' = \frac{p}{p_c'} = \frac{90}{41.2} = 2.18$$

From figure 3, z = 0.965

$$\hat{V} = \frac{zRT}{p} = \frac{0.965(1)(82.06)(373)}{90} = 328\ cm^3$$

Lecture 17

Vapor Pressure and Liquids

- The word vapor will be reserved to describe a gas below its critical point in a process
- The word gas or non-condensable gas will be used to describe a gas above the critical point or a gas in a process in which it cannot condense.
- If the vapor and liquid of a pure component are in equilibrium, then the equilibrium pressure is called the vapor pressure .
- Any substance has an infinite number of boiling points, but by custom we say the "normal" boiling point is the temperature at which boiling takes place under a pressure of 1 atm (101.3 kPa, 760 mm Hg).
- When the solid passes directly into the vapor phase without first melting to become a liquid it is said to sublime.

Change of Vapor Pressure with Temperature

We will use the Antoine equation— it has sufficient accuracy for our needs:

$$\ln p^* = A - \frac{B}{C+T}$$

Where A, B , C are constants different for each substance and T is a temperature, K

Example 10

Calculate the vapor pressure of benzene at 50°C using the Antoine Equation. Also estimate the normal boiling point of benzene (the vapor pressure at 1 atm).

Solution

$$\ln p^* = A - \frac{B}{C+T}$$

From Appendix G, the coefficients are:

A = 15.9008,

B = 2788.51,

C = -52. 36

p^* in mm Hg and T in K.

a. Vapor pressure of benzene at 50 ºC is:

$$\ln p^* = 15.9008 - \frac{2788.51}{-52.36+(50+273)}$$

p^*= 270 mmHg abs.

b. At the boiling point, the vapor pressure is 1 atm (760 mmHg abs.)

$$\ln(760) = 15.9008 - \frac{2788.51}{-52.36+T}$$

T = 353.3 K

Saturation

The volume of the air plus the water vapor increases until the air is saturated with water vapor, after which stage the volume remains constant.

Assuming that the ideal gas law applies to both air and water vapor with excellent precision, we can say that the following relations hold at saturation:

$$\frac{p_{air}\,V}{p_{H_2O}V} = \frac{n_{air}\,RT}{n_{H_2O}RT}$$

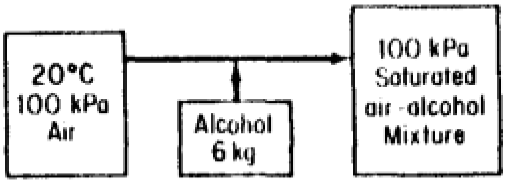
$$\frac{p_{air}}{p_{H_2O}} = \frac{n_{air}}{n_{H_2O}} = \frac{p_{air}}{p_{total}-p_{air}}$$

Example 11

What is the minimum number of cubic meters of dry air at 20ºC and 100 kpa necessary to evaporate 6.0 kg of ethyl alcohol if the total pressure remains constant at 100 kpa and the temperature remains 20ºC? Assume that the air is blown through the alcohol to evaporate it in such away that the exit pressure of the air alcohol mixture is at 100 kPa. (Given: p^*_{alcohol} at 20ºC = 5.93 kPa, mol. wt. ethyl alcohol = 46.07).

Solution

Assume that the process is isothermal.



Basis: 6 kg of alcohol

$$\frac{p_{\text{alcohol}}}{p_{\text{air}}} = \frac{n_{\text{alcohol}}}{n_{\text{air}}}$$

$$p_{air} = p_{total} - p^{*}_{alco\,hol} = (100 - 5.93)kPa = 94.07\ kPs$$

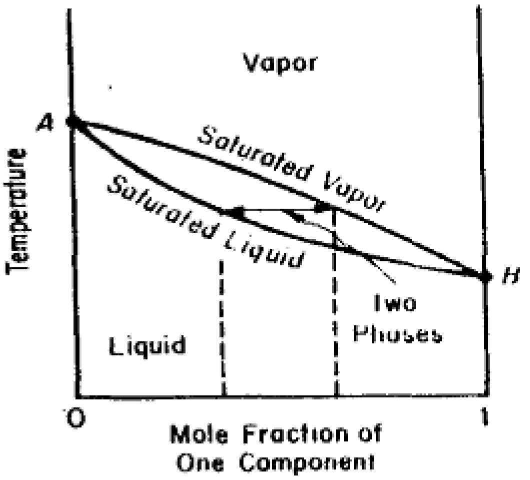
$$6\ kg\ alcohol \left| \frac{1\ kmol\ \ alco\,hol}{46.07\ kg\ \ alco\,hol} \right| \frac{94.07\ kmol\ \ air}{5.93\ kmol\ \ alco\,hol} = 2.07\ kmol\ air$$

$$V_{air} = 2.07\ kmol\ air \left| \frac{8.314\ (kPa)(m^3)}{(kmol)(K)} \right| \frac{293\ K}{100\ kPa} = 50.3\ m^3$$

$$at\ 20ºC\ and\ 100\ kPa$$

Vapor-Liquid Equilibria for Multicomponent Systems

In two-phase vapor-liquid mixture at equilibrium, a component in one phase is in equilibrium with the same component in the other phase. The equilibrium relationship depends on the temperature, pressure, and composition of the mixture.



(a) Constant Pressure

Henry's law: Used primarily for a component whose mole fraction approaches zero, such as a dilute gas dissolved in a liquid:

$p_i = H_i x_i$

Where p_i is the pressure in the gas phase of the dilute component at equilibrium at some temperature, x_i is mol fraction of component i in the liquid phase and H_i is the Henry's law constant.

$$y_i = \frac{p_i}{p_{tot}} = \frac{H_i x_i}{p_{tot}}$$

Raoult's law. Used primarily for a component whose mole fraction approaches unity or for solutions of components quite similar in chemical nature, such as straight chain hydrocarbons.

$$p_i = p_i^* x_i$$

p_i be the partial pressure of component i in the gas phase, y_i be the gas-phase mole fraction, and x_i be the liquid-phase mole fraction.

Note that in the limit where $x_i = 1$, $p_i = p_i^*$

Equilibrium constant K_i

$$K_i = \frac{y_i}{x_i} = \frac{p_i^*}{p_{tot}}$$

This Equation gives reasonable estimates of K_i values at low pressures for components well below their critical temperatures.

Example 12

A gas containing nitrogen, benzene, and toluene is in equilibrium with 40 mole% benzene and 60 mole% toluene liquid mixtures at 100 ºC and 10 atm. Estimate the gas phase composition (mole fractions) using Raoult's law.

Solution

$$\ln p^* = A - \frac{B}{C+T}$$

$$p_B^* = \text{Exp}\left[15.9008 - \frac{2788.51}{-52.36+373}\right] = 1344.9 \text{ mmHg}$$

$$p_T^* = \mathrm{Exp}\left[16.0137 - \frac{3096.52}{-53.67 + 373}\right] = 553.8 \text{ mmHg}$$

Raoult's law, $p_i = p_i^* x_i$ and $p_i = y_i p_{tot}$

$$y_B p_t = p_B^* x_B$$

$$y_B = \frac{0.4 * 1344.9}{(10)(760)} = 0.071$$

$$y_T = \frac{0.6 * 553.8}{(10)(760)} = 0.044$$

y_{N2} = 1- 0.071- 0.044 = 0.885

Example 13

Air and liquid water are contained at equilibrium in a closed chamber at 75° C and 760 mm Hg. Calculate the molar composition of the gas phase. $p*_{H2O}$ (75° C) = 289 mm Hg.

Solution

Since the gas and liquid are in equilibrium, the air must be saturated with water vapor (if it was not, more water would evaporate), so that Raoult's law may be applied:

$$y_{H2O} = \frac{p_{H2O}^*}{P} = \frac{289 \text{ mmHg}}{760 \text{ mmHg}} = 0.38$$

$y_{dry\ air}$ = 1 – y_{H2O} = 1 – 0.38 = 0.62

Problems

1. An oxygen cylinder contains 1.0 ft^3 of O_2 at 70 ºF and 200 psig. Calculate the volume of this O_2 in a dry-gas holder at 90 ºF and 4.0 in. H_2O above atmospheric. The barometer reads 29.92 in. Hg.
2. A cylinder has a volume of 1.0 ft^3 and contains dry methane at 80 ºF and 200 psig. What weight of methane is in the cylinder? The barometer pressure is 29.0 in. Hg.
3. What weight of ethane is contained in a gas cylinder that is 1.0 ft^3 in volume if the gas is at 100 ºF and 2000 psig? Solve this problem by Van der Waals' equation.
4. A large chamber contains dry N_2 at 27 ºC and 101.3 kPa. Water is injected into the chamber. After saturation of the N_2 with water vapor, the temperature in the chamber is 27 ºC.
   a-What is the pressure inside the chamber after saturation?
   b-How many moles of H_2O per moles of N_2 are present in the saturated mixture?
5. Water in an enclosed vessel at 17 ºC contains a concentration of dissolved oxygen of 6 mg/L. At equilibrium, determine the concentration of oxygen in the air space above the water in mg/L. Henry's law constant is 4.02 $*10^6$ kPa/mol fraction and the pressure in the vessel is 1 atm.

Lecture 18

1. Energy Balances: Terminology And Thermodynamic Law

- A system is an object or a collection of objects that an analysis is carried out on. The system has a definite boundary, called the system boundary.
- Once a system is defined, through the choice of a system boundary, everything external to it is called the surroundings.
- All energy and material that are transferred out of the system enter the surroundings, and vice versa.
- An isolated system is a system that does not exchange heat, work, or material with the surroundings.
- A closed system is a system in which heat and work are exchanged across its boundary, but material is not.
- An open system can exchange heat, work, and material with the surroundings.

1.1.1 Forms of Energy: The First Law of Thermodynamics

- Energy is often categorized as kinetic energy, potential energy, and internal energy.
- Although energy cannot be created or destroyed, it can be converted from one form to another.
- Energy can also be transferred from one point to another or from one body to another one.
- Energy transfer can occur by flow of heat, by transport of mass, or by performance of work .
- The general energy balance for a thermodynamic process :

$$\text{accumulation} = \text{input} - \text{output}$$

- Energy can cross the boundaries of a closed system in the form of heat and work (Figure1.1).

The energy balance for a closed system takes the form:

$$Q - W = \Delta U + \Delta KE + \Delta PE$$

where heat (Q), work (W), internal energy (U), kinetic energy (KE), and potential energy (PE) are defined as follows.

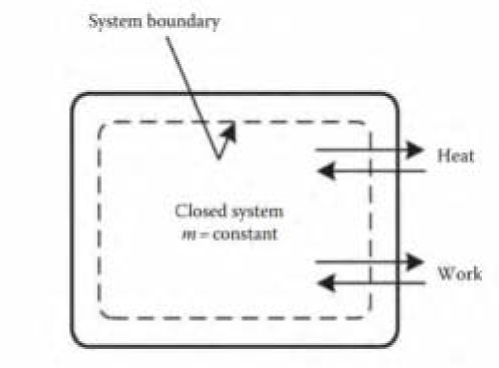


FIGURE1.1 Energy balance for a closed system.

Work is the energy that flows in response to any driving force (e.g., applied force, torque) other than temperature, and is positive when the surroundings perform work on the system. Work is negative when the system performs work on the surroundings . In chemical processes, work may, for instance, come from pumps, compressors, moving pistons, and moving turbines.

Heat is the energy that flows due to a temperature difference between the system and its surroundings and always flows from regions at high temperatures to regions at low temperatures. By convention, heat is defined to be positive if it flows to a system (i.e., gained). For systems with no significant heat exchange with the surroundings, Q = 0. Such a system is said to be adiabatic.

An Isothermal system is one where the temperature does not change with time and in space.

Kinetic Energy

Kinetic energy is the energy carried by a moving system because of its velocity.

- The kinetic energy KE of a moving object of mass m, traveling

with speed υ, is given by:

$$\mathrm{KE} = \frac{1}{2}\mathrm{m}\mathrm{v}^2$$

Where KE in J.

- If a fluid enters a system with a mass flow rate (kg/s) and uniform velocity (m/s), then;

$$\dot{\mathrm{K}}\mathrm{E} = \frac{1}{2}\dot{\mathrm{m}}\mathrm{v}^2$$

Where $\dot{\mathrm{K}}\mathrm{E}$ in J/s.

Example 1

Water flows into a process unit through a 2 cm ID pipe at a rate of 2 m^3/h. calculate the kinetic energy for this stream in joules/second.

Solution

$$\mathrm{v} = \frac{2\ \mathrm{m}^3}{\mathrm{h}} \left| \frac{100^2\mathrm{cm}^2}{1^2\mathrm{m}^2} \right| \frac{1}{\pi(1)^2\mathrm{cm}^2} \left| \frac{1\ \mathrm{h}}{3600\ \mathrm{s}} = 1.77\ \mathrm{m/s} \right.$$

$$\dot{\mathrm{m}} = \frac{2\ \mathrm{m}^3}{\mathrm{h}} \left| \frac{1000\ \mathrm{kg}}{\mathrm{m}^3} \right| \frac{1\ \mathrm{h}}{3600\ \mathrm{s}} = 0.556\ \mathrm{kg/s}$$

$$\dot{\mathrm{KE}} = \frac{0.556\ \mathrm{kg/s}}{2} \left| \frac{(1.77)^2\mathrm{m}^2}{\mathrm{s}^2} \right| \frac{1\ \mathrm{N}}{1\ \mathrm{kg}.\frac{\mathrm{m}}{\mathrm{s}^2}} = 0.87\ \mathrm{N}.\frac{\mathrm{m}}{\mathrm{s}} = 0.87\ \mathrm{J/s}$$

Potential Energy

Potential energy is the energy due to the position of the system in a potential field (e.g., earth's gravitational field, $g=9.81\ m/s^2$).

- For mass (m) at an elevation (h) in a gravitational field, relative to its gravitational potential energy at a reference elevation:

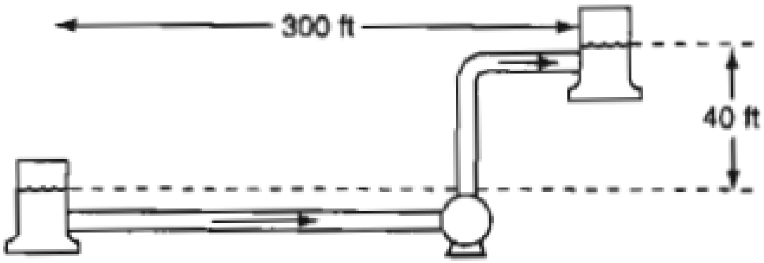
$$\mathrm{PE} = \mathrm{mgh}$$

Where PE in J.

- If a fluid enters a system with a mass flow rate and an elevation relative to the potential energy reference plane, then:
  $\dot{\mathrm{PE}} = \dot{\mathrm{m}}\mathrm{gh}$
  Where $\dot{\mathrm{PE}}$ in J/s.
- Since we are normally interested in the change in potential energy when a body or fluid moves from one elevation to another:
  $\dot{\mathrm{PE}}_2 - \dot{\mathrm{PE}}_1 = \dot{\mathrm{m}}\mathrm{g}(\mathrm{h}_2 - h_1)$

Example 2

Water is pumped from one reservoir to another 300 ft away. The water level in the second reservoir is 40 ft above the water level of the first reservoir. What is the increase in specific potential energy of the water in Btu/lb$_\mathrm{m}$?



Solution

$$\Delta\widehat{\mathrm{PE}} = \frac{32\ \mathrm{ft}}{\mathrm{s}^2}\left|(40-0)\mathrm{ft}\right|\frac{1(\mathrm{lb_f})(\mathrm{s}^2)}{32.2\ (\mathrm{lb_m})(\mathrm{ft})}\left|\frac{1\ \mathrm{Btu}}{778.2\ (\mathrm{ft})(\mathrm{lb_f})}\right. = 0.0514\ \mathrm{Btu/lb_m}$$

Internal Energy

Internal energy (U) is a macroscopic concept that take into account all of the molecular, atomic, and subatomic energies.

$$\Delta\hat{U} = \widehat{U_2} - \widehat{U_1} = \int_{\widehat{U_1}}^{\widehat{U_2}} d\hat{U} = \int_{T_1}^{T_2} C_v dT$$

Example 3

What is the change in internal energy when 10 kmol of air is cooled from 60 ºC to 30 ºC in a constant volume process? Given that C_v is 2.1 $*10^4$ J/(kmol)ºC.

Solution

$$\Delta \mathrm{U} = 10\ \mathrm{kmol}\int_{60^{\circ}\mathrm{C}}^{30^{\circ}\mathrm{C}}\left(2.1*10^4\frac{\mathrm{J}}{(\mathrm{kmol})(^{\circ}\mathrm{C})}\right)\mathrm{dT} = 2.1*10^5(30-60) = -6.3*10^6\mathrm{J}$$

Enthalpy

From energy balance, we will find:

$$H = U + pV$$

The combined variables are called enthalpy. Where P is the pressure and V is the volume.

$$\Delta\hat{H} = \widehat{H_2} - \widehat{H_1} = \int_{\widehat{H_1}}^{\widehat{H_2}} d\hat{H} = \int_{T_1}^{T_2} C_p dT$$

As with internal energy, enthalpy has no absolute value, only changes in enthalpy can be calculated.

Example 4

Calculate the enthalpy change when 10 kmol of air is cooled from 60 ºC to 30 ºC in a constant pressure process? Given that C_p is 2.9 *10^4 J/(kmol)ºC.

Solution

$$\Delta\mathrm{H} = 10\ \mathrm{kmol} \int_{60^\circ\mathrm{C}}^{30^\circ\mathrm{C}} \left(2.9 * 10^4 \frac{\mathrm{J}}{(\mathrm{kmol}\ )(^\circ\mathrm{C})}\right) \mathrm{dT} = 2.9 * 10^5 (30 - 60) = -8.7 * 10^6 \mathrm{J}$$

Lecture 19

Energy balance for processes without chemical reaction

The principle of the conservation of energy (or energy balance) states that the total energy of the system plus the surroundings can neither be created nor destroyed.

1. **Energy balance for closed, unsteady state system**

   A batch process system is, by definition, closed, and semibatch and continuous systems are open. An integral energy balance may be derived for a closed system between two instants of time.

   $\text{accumulation} = \text{input} - \text{output}$

   $\text{final system energy} - \text{initial system energy} =$

   $\text{net energy transfered to the system}$

   $\text{initial system energy} = U_i + KE_i + PE_i$

   $\text{final system energy} = U_f + KE_f + PE_f$

   $\text{energy transfered} = Q + W$

   $$(U_f - U_i) + (KE_f - KE_i) + (PE_f - PE_i) = Q + W$$

   $$\Delta(U + KE + PE) = Q + W$$

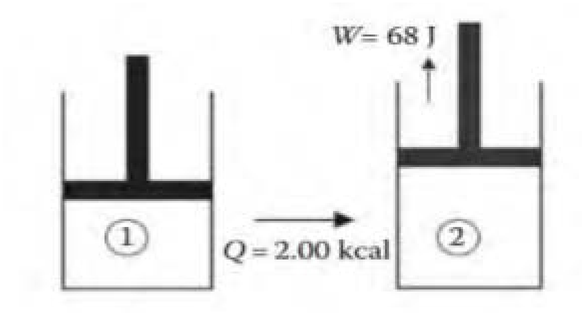
   remember that Q and W are both positive when transferred into the system.

   In general for closed system, ΔKE and ΔPE are zero, so the energy balance becomes:

   $\Delta U = Q + W$

   Example 5

   A cylinder fitted with a movable piston is filled with gas. An amount of 2.00 kcal of heat is transferred to the gas to raise the gas temperature 100°C higher. The gas does 68 J of work in moving the piston to its new equilibrium position. Calculate the change in internal energy of the system.



Solution

Because No change in kinetic and potential energy; accordingly, both are set to zero. The equation is reduced to

$\Delta U = Q - W$

$$\Delta U = (2\ \text{kcal}) \left[\frac{1000\ \text{cal}}{\text{kcal}} \;\middle|\; \frac{1\ \text{J}}{0.239\ \text{cal}}\right] - 68\ \text{J} = 8300\ \text{J}$$

2. **Energy balance for closed, steady state system**

$\Delta KE = 0, \Delta U = 0$
$\Delta PE = 0, \Delta E = 0$

Then:

$$Q + W = 0$$
$$W = -Q$$

Meaning that all of the work done on a closed, steady-state system must be transferred out as heat (-Q). However, the reverse is false.

3. **Energy balance for open, unsteady state systems**

$$\Delta E = \left(\hat{U}_1 + \widehat{KE}_1 + \widehat{PE}_1\right)m_1 - \left(\hat{U}_2 + \widehat{KE}_2 + \widehat{PE}_2\right)m_2 + Q + W + p_1\hat{V}_1 m_1 - p_2\hat{V}_2 m_2$$

Or,

$$\Delta E = \left(\hat{H}_1 + \widehat{KE}_1 + \widehat{PE}_1\right)m_1 - \left(\hat{H}_2 + \widehat{KE}_2 + \widehat{PE}_2\right)m_2 + Q + W$$

Example 6:

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.

Solution

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

Since 0.082 L.atm/mol K = 8.314 J/mol K

$$\frac{8.314\frac{J}{mol\ .K}}{0.082\ \frac{L.atm}{mol\ .K}} = 101.3\frac{J}{L.atm}$$

$$\hat{H} = 3800\frac{J}{mol} + \left(24.63\frac{L.\ atm}{mol}\right) \mid \frac{101.3J}{1\ L.\ atm} = 6295\ J/mol$$

4. Energy balance for open, steady state systems

$$Q + W = \Delta(H + KE + PE)$$

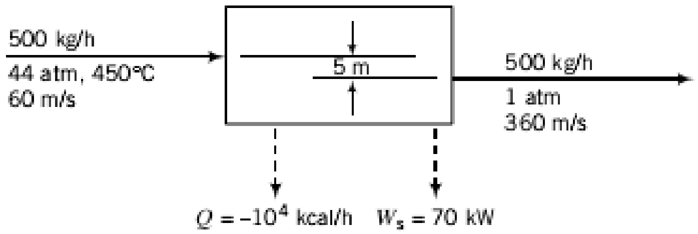
And because ΔKE and ΔPE are always equal zero,

$$Q + W = \Delta H$$

Example 6

Five hundred kilograms per hour of steam drives a turbine. The steam enters the turbine at 44 atm and 450 C at a linear velocity of 60 m/s and leaves at a point 5 m below the turbine inlet at atmospheric pressure and a velocity of 360 m/s. The turbine delivers shaft work at a rate of 70 kW, and the heat loss from the turbine is estimated to be 10 kcal/h. Calculate the specific enthalpy change associated with the process.

Solution



$$\Delta\dot{H} = \dot{Q} - \dot{W}_S - \Delta\dot{KE} - \Delta\dot{PE}$$

$$\Delta\dot{KE} = \frac{1}{2}\dot{m}({v_2}^2 - {v_1}^2) = \frac{1}{2}0.139\ kg/s \mid \frac{1\ N}{1\ kg.m/s^2} \mid (360^2 - 60^2)\frac{m^2}{s^2} \mid \frac{1\ W}{1\ N.\frac{m}{s}} \mid \frac{1\ kW}{10^3 W} = 8.75\ kW$$

$$\Delta\dot{PE} = \dot{m}g(h_2 - h_1) = \frac{0.139\ kg}{s} \Big| \frac{9.81\ N}{kg} \Big| (-5)m \Big| \frac{1\ kW}{10^3 N.\frac{m}{s}} = -6.81 * 10^{-3} kW$$

$$\dot{Q} = \frac{-10^4\ \text{kcal}}{\text{h}} \Big| \frac{1\ \text{J}}{0.239*10^{-3}\text{kcal}} \Big| \frac{1\ \text{h}}{3600\ \text{s}} \Big| \frac{1\ \text{kW}}{\frac{10^3\text{J}}{\text{s}}} = -11.6\ \text{kW}$$

$$\Delta\dot{H} = -11.6 - 70 - 8.75 - (-6.81 * 10^{-3}) = -90.3\ \text{kW}$$

$$\Delta\hat{H} = \frac{\Delta\dot{H}}{\dot{m}} = \frac{-90.3\ \text{kJ/s}}{0.139\ \text{kg/s}} = -650\ \text{kJ/kg}$$

Example 7

Water is pumped from a well in which the water level is a constant 20 feet below the ground level. The water is discharged into a level pipe that is 5 feet above the ground at a rate of 0.5 ft^3/s. Calculate the electric power required by the pump if it is 100% efficient.

Solution

Q = 0 (given assumption)

ΔKE = 0 (negligible change in KE)

ΔH =0 because the temperature of water is the same in well and in discharge water.

The energy balance is reduced to :

$$W = \Delta PE = \dot{m}g(h_{out} - h_{in})$$

Basis: 1 second

$$\dot{m} = \frac{0.5\ ft^3}{s} \Big| \frac{62.4\ lb_m}{ft^3} = 31.3\ lb_m/s$$

$$W = \Delta PE =$$

$$31.3\ \frac{\text{lb}_\text{m}}{\text{s}} \Big| \frac{32.2\ \text{ft}}{\text{s}^2}(5 - (-20)\text{ft}) \Big| \frac{\text{s}^2\text{lb}_\text{f}}{32.2\ \text{ft}\ \text{lb}_\text{m}} \Big| \frac{1.055\ \text{kW s}}{778.2\ \text{lb}_\text{f}\text{ft}} = 1.06\ \text{kW}$$

Problems

1. Write and simplify the closed-system energy balance for each of the following processes:
   a. A tray filled with water at 20 ºC is put into a freezer. The water turns into ice at -5 ºC.
   b. A chemical reaction takes place in a closed adiabatic rigid container.
2. 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.
3. Prove that for an ideal gas, $\hat{U} and\ \hat{H}$ are related as $\hat{H} = \hat{U} + RT$ where R is the gas constant. Then calculate ΔH(cal) for a process in which the temperature of 2.5 mol of an ideal gas is raised by 50 ºC, resulting in a specific internal energy of 3500 cal/mol.
4. Air is heated from 25ºC to 150ºC prior to entering a combustion furnace. The change in specific enthalpy associated with this transition is 3640 J/mol. The flow rate of air at the heater outlet is 1.25 m^3/min and the air pressure at this point is 122 kPa absolute. Calculate the heat requirement in kW.(make your assumptions)
5. Steam at 260ºC and 7 bar absolute is expanded through a nozzle to 200ºC and 4 bar. Negligible heat is transferred from the nozzle to its surroundings. The approach velocity of the steam is negligible. The specific enthalpy of steam is 2974 kJ/kg at 260ºC and 7 bar and 2860 kJ/kg at 200ºC and 4 bar. Calculate the exit steam velocity.
6. Air is being compressed from 100 kPa and 255 K (where it has an enthalpy of 489 kJ/kg) to 1000 kPa and 278 K (where it has an enthalpy of 509 kJ/kg). the exit velocity of the air from compressor is 60 m/s. What is the power required (in kW) for the compressor if the load is 100 kg/h of air?

Lecture 20

Energy balance for processes with chemical reaction

For continuous, steady state processes, the general energy balance reduces to two choices:

- With the effects of chemical reactions merged with the sensible heats:
  $Q = \Delta H = [H(T) - H(25^oC)]_{outputs} - [H(T) - H(25^oC)]_{inputs}$
  $= \Delta H_{output} - \Delta H_{input}$ ------------------------(1)
- With the effects of chemical reaction lumped in the heat of reaction
  $Q = [H(T) - H(25^oC)]^{sensible\ +phase\ change}{}_{outputs} -$
  $[H(T) - H(25^oC)]^{sensible\ +phase\ change}{}_{inputs} + \Delta H_{rxn}$ ---------(2)

  Here are some application of the above equation:
  - What is the temperature of one stream given data for other streams?
  - How much heat has to be added to or removed from the process?
  - What is the temperature of the reaction?
  - How much material must be added or removed from the process to give a specified value of heat transfer.
    We focus how to determine the heat added or removed due to chemical reaction.

For the following reaction :

$$aA + bB \rightarrow cC + dD$$

The heat of reaction, $\Delta H_{Rx}(T,P)$, is the **enthalpy change** for a process in which stoichiometric quantities of reactants at temperature T and pressure P react completely to form products at the same temperature and pressure.

The standard heat of reaction (ΔH_{Rx}^o) is calculated as the difference between the product and reactant enthalpies when both reactants and products are at standard conditions, that is, at 25°C and 1 atm. The symbol "o" denotes standard conditions. Therefore,

$$\Delta H^{o}_{Rx}\left[\frac{kJ}{mol}\right] = H_{products} - H_{reactants}$$

$$= c\Delta H^{o}_{f,C} + d\Delta H^{o}_{f,D} - a\Delta H^{o}_{f,A} - b\Delta H^{o}_{f,B}$$

$$= \sum v_i \Delta H^{o}_{f,i}$$

where ΔH_f^o is the standard heat of formation.

Also ,

$$\Delta H^{o}_{Rx} = -\sum v_i (\Delta H^{o}_{c})_i$$

Where $(\Delta H_c^o)_i$ is the standard heat of combustion of species i. If any reactants or products are combustion products (i.e., CO_2, H_2O, SO_2), their heats of combustion are equal to zero.

The standard enthalpy of combustion is the **enthalpy change** when 1 mol of a reactant completely burns in excess oxygen under standard thermodynamic conditions.

Example 8

Consider the following reaction:

$$\mathrm{A} + 2\mathrm{B} \rightarrow 3\mathrm{C}, \quad \mathrm{HR_x}(100\ {}^{o}\mathrm{C}, 1\ \mathrm{atm}) = -50\ \mathrm{kJ/mol}$$

The enthalpy change for the given reaction is;

$$\frac{-50\ kJ}{1\ mol\ \ A\ consumed} = \frac{-50\ kJ}{2\ mol\ \ B\ consumed} = \frac{-50\ kJ}{3\ mol\ \ C\ generated}$$

If 150 mol/s of C was generated at 100 ºC and 1 atm, then:

$$\Delta\dot{H} = \left(\frac{-50\ kJ}{3\ mol\ \ C\ generated}\right)\left(\frac{150\ mol\ \ C\ generated}{s}\right) = 2500\ kJ/s$$

Or :

$$\Delta\dot{H} = \dot{\xi}\Delta H_{Rx}(T,P)$$

If $\Delta H_{Rx}(T)$ is negative, the reaction is exothermic; that is, energy must be removed from the reactor to prevent the temperature from increasing. If

ΔH_{Rx} (T) is positive, the reaction is endothermic; that is, energy must be added to the reactor to prevent the temperature from decreasing.

Example 9

Consider the combustion of liquid ethanol as shown in the following reaction scheme:

$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O\ (l)$

Use heat of formation and heat of combustion to determine the standard heat of reaction.

Solution

Values for standard heat of combustion and standard heat of formation are available in the Tables.

$$\Delta H^{o}_{Rx} = 3\Delta H^{o}_{f,H2O(l)} + 2\Delta H^{o}_{f,CO2} - 0 - \Delta H^{o}_{f,C2H5OH_{(l)}}$$

$$\Delta H^{o}_{Rx} = 3(-285.84) + 2(-393.51) - 0 - (-277.63) = -1366.9\ kJ/mol$$

The standard heat of reaction is also calculated from the standard heat of combustion as:

$$\Delta H^{o}_{Rx} = \Delta H^{o}_{c,C2H5OH(l)} + 3\Delta H^{o}_{c,O2} - 3\Delta H^{o}_{c,H2O(l)} - 2\Delta H^{o}_{c,CO2_{(g)}}$$

The standard heat of combustion of oxygen, water, and carbon dioxide are zero:

$$\Delta H^{o}_{Rx} = -1366.91 + 0 - 0 - 0 = -1366.9\ kJ/mol$$

Results reveal that both values of standard heat of reactions are identical.

- For a single reaction at a reference state of 25^{o}C and 1 atm while reactant and product are at different inlet and exit temperatures:

$$\Delta\dot{H} = \dot{\xi}\Delta H^{o}_{Rx} + \sum_{out} \dot{n}_i\bar{h}_i - \sum_{in} \dot{n}_i\bar{h}_i$$

where h_i(J/mol) is the specific molar enthalpy of a definite component.

Example 10

Consider the following gas phase reaction :

$CO_2(g) + 4H_2(g) \rightarrow 2H_2O(g) + CH_4(g)$

Which proceed with 100% conversion of CO_2. Assume stoichiometric amounts of the reactants enter the reactor. Determine the heat of reaction if the gases enter and leave at 1 atm and 500 ºC. given that:

Compound	$\boldsymbol{\Delta\hat{H}_f^o(\frac{kJ}{mol})}$	$\boldsymbol{\Delta\hat{H}_{25^oC}^{500^oC}(\frac{kJ}{mol})}$
CO_2 (g)	-393.25	21.425
H_2 (g)	0	13.834
H_2O (g)	-241.835	17.010
CH_4 (g)	-74.848	23.126

Solution

Basis: 1 gmol CO_2 (g) at 1 atm and 500 ºC

$$\Delta H = \xi \Delta H_{Rx}^{o} + \sum_{out} n_i \bar{h}_i - \sum_{in} n_i \bar{h}_i$$

$$\Delta H_{Rx}^{o}\left[\frac{kJ}{mol}\right] = H_{products} - H_{reactant} = \sum v_i \Delta H_{f,i}^{o}$$

$$\Delta H_{Rx}^{o} = [(1)(-74.848) + 2(-241.835)] - [(1)(-393.25) + 4(0)]$$

$$= -165.27 \text{ kJ}$$

$$\sum_i^{input} [H(500^oC) - H(25^oC)] = [(1)(21.425) + 4(13.834)]$$

$$= 76.761 \text{ kJ}$$

$$\sum_i^{output} [H(500^oC) - H(25^oC)] = [(2)(17.010) + 1(23.126)]$$

$$= 57.146 \text{ kJ}$$

$$\Delta H(500^oC) = (-165.27) + 57.146 - 76.761 = -184.9 \text{ kJ}$$

Example 11

Consider the same reaction of example 3, but CO_2 entering from another process at 800 K, and reacting with 4 gmol H_2 entering at 298 K, that only 70% conversion of CO_2 occurred. The products exited from the reactor at 1000 K. Calculate the heat transfer to or from the reactor. Given that;

Compound	**Temperatute K**		$\boldsymbol{\Delta\hat{H}^{T}_{25^{\circ}C}(\frac{kJ}{mol})}$	
CO_2 (g)	800	1000	22.798	33.396
H_2 (g)	298	1000	0	20.62
H_2O (g)	1000		25.986	
CH_4 (g)	1000		38.325	

Solution

The system is steady state and open with reaction. Assume 1 atm.

Basis: 1 gmol of CO_2 (g)

The reference temperature is 25 ºC.

$$CO_2(g) + 4H_2(g) \rightarrow 2H_2O(g) + CH_4(g)$$

$$\Delta H = \xi \Delta H^{\circ}_{Rx} + \sum_{out} n_i \bar{h}_i - \sum_{in} n_i \bar{h}_i$$

The first step is to calculate the heat of reaction at the reference temperature.

$$\Delta H^{\circ}_{Rx} = [(1)(-74.848) + 2(-241.835)] - [(1)(-393.25) + 4(0)]$$

$$= -165.27 \text{ kJ}$$

For 70% conversion of the CO_2:

$$\Delta H^{\circ}_{Rx} = (0.7)(-165.27) = -115.69 \text{ kJ}$$

The next step is to calculate the enthalpy changes from 298 K to the respective temperatures of the compounds entering and leaving the reactor.

$$n_{CO2} = 1 + (0.7)(-1) \ = 0.3\, mol$$

$$n_{H_2} = 4 + (0.7)(-4) = 1.2\ mol$$

$$n_{H_2O} = 0 + (0.7)(2) = 1.4\ mol$$

$$n_{CH_4} = 0 + (0.7)(1) = 0.7\ mol$$

$$\sum_{\mathrm{i}}^{\mathrm{input}} [\mathrm{H(T) - H(25^{o}C)}] = [(1)(22.798) + 4(0)] = 22.798\ \mathrm{kJ}$$

$$\sum_{\mathrm{i}}^{\mathrm{output}} [\mathrm{H(T) - H(25^{o}C)}] = [(1.4)(25.986) + (0.7)(38.325) + (0.3)(33.396) + (1.2)(20.62)] = 97.971\ \mathrm{kJ}$$

The energy balance reduces to Q = ΔH

Q = ΔH = (-115.69) + (97.971) – (22.798) = - 40.517 kJ

Lecture 21

Ideal Processes, Efficiency, And The Mechanical Energy Balance

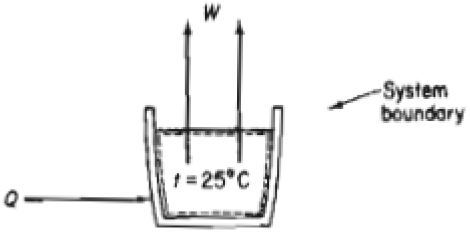
The ideal processes is a hypothetical process that rarely occurs in practice. Why bother with it then? The reason is that the calculations for energy changes can be made for an ideal process, and then an empirical efficiency used to convert the ideal work or energy change into the actual work or energy change.

1. **Ideal reversible processes**
   Reversible process is an idealized process (hypothetical) in which changes occur because of an infinitesimal (differential) imbalance((تفاضلي) اختلال متناهي الصغر) of temperature, pressure, and so on.
2. **Irreversible process**
   A process that is not reversible because it occurs with finite differences(اختلافات محدودة) of temperature, pressure, etc.- most real processes.

Example 1

How much work is done by 1 liter of saturated liquid water when it evaporates from an open vessel into the atmosphere where the pressure is 100 kPa?

Solution



Basis : 1 liter of water (liquid)

Open system and reversible process.

The unknown quantity is the work done by the liquid water pushing against the atmosphere. The general energy balance:

$$\Delta E = Q + W - \Delta[(\widehat{H} + \widehat{KE} + \widehat{PE})m]$$

Will not be useful because Q is unknown. We can imagine that an expandable bag is placed over the open face of the vessel so that the system comprised of the water becomes a closed system.

Because reversible process, the work for a closed system is:

$$W = -\int_{V_1}^{V_2} pdV = -p\Delta V$$

The specific volume of the liquid water from the SI steam tables is 0.001043 m^3/kg. The final volume of the water vapor is:

$$1\ \text{L liquid} \left| \frac{1\ m^3}{1000\ L} \right| \frac{1\ kg}{0.001043\ m^3 \text{liquid}} \left| \frac{1.694\ m^3\ \text{vapor}}{kg} = 1.624\ m^3\ \text{vapor} \right.$$

$$W = -100 * 10^3 Pa \left| \frac{1\ N/m^2}{1\ Pa} \right| \frac{1\ J}{1\ N.m} \left| 1.624\ m^3 = -1.624 * 10^5 J \right.$$

Efficiency

Efficiency, in general, is the ratio of the work done by machine to the amount of fuel consumed and to the energy expended.

General efficiency:

$$\eta_1 = \frac{\text{useful energy out}}{\text{energy in}}$$

Mechanical efficiency:

$$\eta_2 = \frac{\text{actual work output from the process}}{\text{work output for a reversible process}}$$

Heat engine efficiency:

$$\eta_4 = \frac{\text{actual work output from the process}}{\text{heat input from a source}}$$

Example 2

A small hydroelectric plant puts out 20 MW when the level of water above the generators is 25 m and the water flow rate through the generators is 100 m^3/s. What is the overall efficiency of the plant?

Solution

the mass flow rate of the water is:

$$\frac{100\ \mathrm{m}^3}{\mathrm{s}} \Big| \frac{1000\ \mathrm{kg}}{\mathrm{m}^3} = 10^5\ \mathrm{kg/s}$$

The potential energy change of the water per second is:

$$\Delta\dot{PE} = \dot{m}gh = \frac{10^5 kg}{s} \Big| 9.807\frac{m}{s^2} \Big| 25\ m \Big| \frac{Ns^2}{1\ kg.m} \Big| \frac{s.W}{1\ J} = 2.45 * 10^7 W$$

$$\eta_1 = \frac{\text{useful energy out}}{\text{energy in}}$$

$$\eta_1 = \frac{20*10^6\ \mathrm{W}}{2.45*10^7\ \mathrm{W}} = 0.82$$

The mechanical energy balance

In some processes, such as the compression of gases and pumping of liquids, work and the mechanical forms of energy(kinetic and potential energies) are the important factors. For these processes, an energy balance, including solely the mechanical forms of energy, becomes a useful tool.

The steady state mechanical energy balance is:

$$\Delta\left(\widehat{\mathrm{KE}} + \widehat{\mathrm{PE}}\right) + \int_{\mathrm{p}_1}^{\mathrm{p}_2} \hat{\mathrm{V}}\mathrm{dp} - \hat{\mathrm{W}} + \hat{\mathrm{E}}_{\mathrm{v}} = 0 \qquad (1)$$

Where E_v is the loss of mechanical energy into nonmechanical forms of energy.

For a reversible process in which $E_v = 0$, $W = 0$, and incompressible fluid, equation 1 becomes:

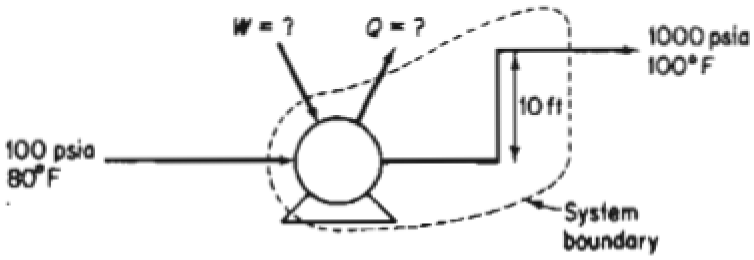
$$\frac{\Delta p}{\rho} + \frac{\Delta v^2}{2} + g\Delta h = 0 \qquad (2)$$

Equation 2 is called **Bernoulli equation.**

If each terms is divided by g, the units of the equation are those of Δh, and are known as heads of fluid.

Example 3

Calculate the work per minute required to pump 1 lb of water per minute from 100 psia and 80 ºF to 1000 psia and 100 ºF. the exit stream is 10 ft above entrance stream.



Solution

The system is a steady state process and the general mechanical energy balance is :

$$\Delta\left(\widehat{\mathrm{KE}} + \widehat{\mathrm{PE}}\right) + \int_{p_1}^{p_2} \hat{V} dp - \hat{W} + \hat{E}_v = 0$$

We assume:

1. ΔKE = 0
2. The process is reversible, so $E_v = 0$
3. Pump efficiency is 100%

So the general mechanical energy balance reduces to :

$$\hat{W} = \int_{p_1}^{p_2} \hat{V} dp + \Delta \widehat{\mathrm{PE}}$$

Basis: 1 minute of operation

From steam table, the specific volume of liquid water can be taken to be 0.0161 ft^3/lb.

$$\Delta\widehat{\mathrm{PE}} = 10 \text{ ft} \,\Big|\, 32.2 \frac{\text{ft}}{\text{s}^2} \,\Big|\, \frac{\text{lb}_f.\text{s}^2}{32.2 \text{ lb}_m.\text{ft}} \,\Big|\, \frac{1 \text{ Btu}}{778 \text{ ft.lb}_f} = 0.0129 \text{ Btu/lb}_m$$

$$\int_{100}^{1000} 0.0161 \, dp =$$

$$0.0161 \frac{\text{ft}^3}{\text{lb}_m} \,\Big|\, \frac{(1000-100) lb_f}{in.^2} \,\Big|\, \left(\frac{12 \, in.}{1 \, ft}\right)^2 \,\Big|\, \frac{1 \, Btu}{778 \, ft.lb_f} = 2.68 \, \frac{Btu}{lb_m}$$

$$\hat{W} = 2.68 + 0.0129 = 2.69 \frac{Btu}{lb_m}$$

Problems

1. Calculate the heat of reaction at SC for 1 g mol of $H_2(g)$ using the heat combustion data, and then calculate ΔH_{rxn} for $H_2(g)$ at 0ºC.

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

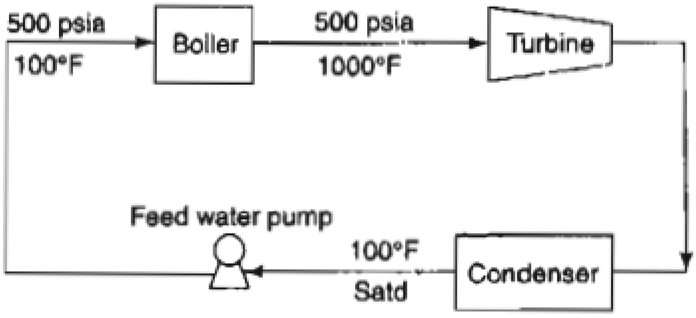
ΔH^o_c (kJ/g mol)	-285.84	0	0
C_p (J/g ºC)	14.36	0.908	4.184

2. Formaldehyde can be made by the oxidation of methanol:

   $$CH_3OH(g) + \frac{1}{2}O_2(g) \longrightarrow H_2CO(g) + H_2O(g)$$

$\Delta\hat{H}^\circ_f$(kJ / gmol):	-201.25	0	-115.89	-241.826

   If stochiometric amounts of methanol and oxygen enter the reactor at 100 ºC, the reaction is complete, and the products leave the reactor at 200 ºC, calculate the heat that is added or removed from the reactor per mole of methanol fed to the reactor.
3. Calculate the work done when 1 lb mol of water in an open vessel evaporates completely at 212 ºF. Express your result in Btu.
4. A motor is rated as 30 hp. However, the output horsepower of the motor is only 24.6 hp. What is the efficiency of the motor?
5. A power plant is as shown in figure. If the pump moves 100 gal/min into the boiler with an overall efficiency of 40%. Find the horsepower required for the pump. List all additional assumption required.



6. Water at 20 ºC is being pumped from a constant-head tank open to the atmosphere to an elevated tank kept at a constant pressure of 1150 kPa as shown in figure. If water is following in the 5 cm line at rate of 0.4 m^3/min, find:

   (a) The rating of the pump in joules per kilogram being pumped

(b) The rating of the pump in joules per minute
The pump and motor have an overall efficiency of 70% and the energy loss in the line can be determined to be 60 J/kg flowing.