Chapter 7 Ideal and Real Gases

Problem 7.1

A steel tank having a capacity of 25 m^3 holds carbon dioxide at 30°C and 1.6 atm. Calculate the weight, in grams, of the carbon dioxide.

Solution

$$T = 30^\circ C = 30 + 273.15 = 303K$$

$$p = 1.6 \text{ atm}$$

$$V = 25 \text{ m}^3$$

Use pV = nRT

The gas constant has to be chosen to be consistent with the units of pressure, temperature, and volume. Use standard conditions to calculate R

$$R = \frac{1.00\text{atm}}{\left|\frac{22.415\text{m}^3}{\text{kgmol}}\right|\,\left|273.15\text{K}\right|} = 0.08206 \frac{(\text{atm})(\text{m}^3)}{(\text{kgmol})(\text{k})}$$

$$n = \frac{(p)(V)}{(R)(T)} = \frac{(1.6)(25)}{(0.08206)(303)} = 1.608 \text{ kg mol or } 1{,}608 \text{ g mol}$$

$$\text{Weight of carbon dioxide} = \frac{1{,}608\text{gmol}}{\left|\frac{44\text{gCO}_2}{\text{gmolCO}_2}\right.} = \mathbf{70.7 \times 10^3 \text{ g CO}_2}$$

Alternate Solution:

Use V = 22.415 m^3/kg mol at T = 273K and p = 1 atm abs.

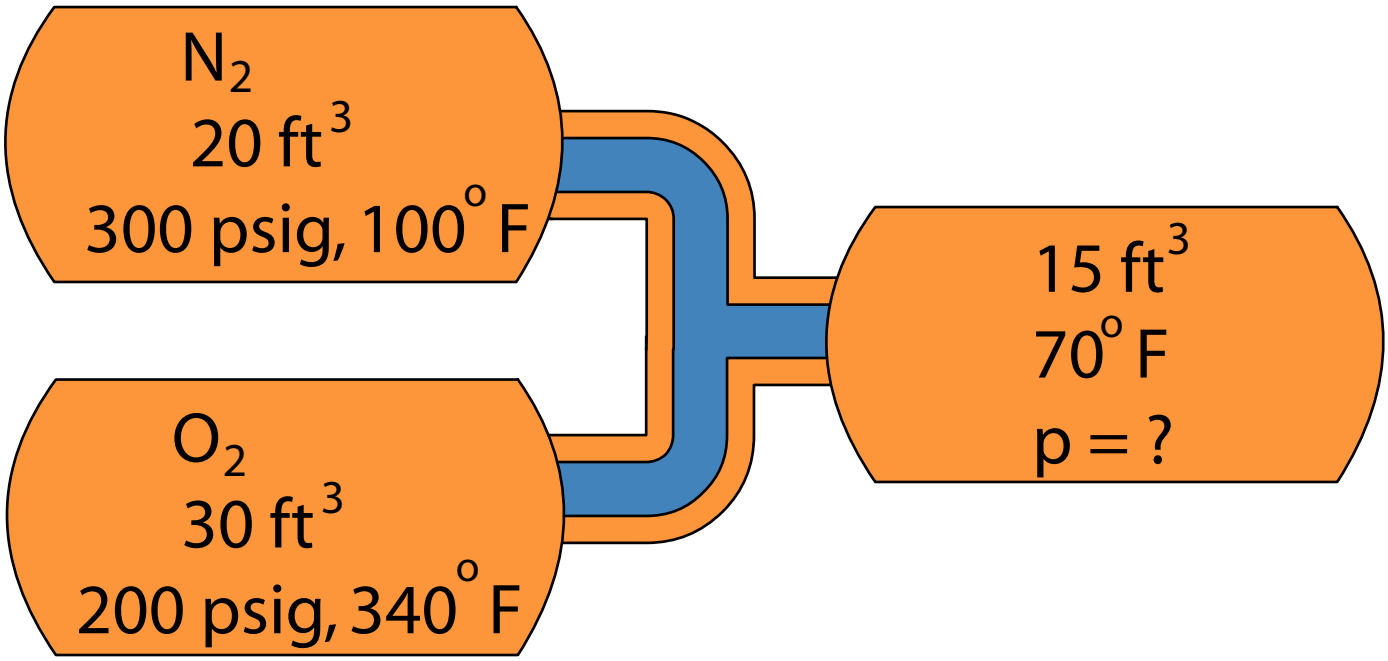
$$\text{and } \left(\frac{p_2}{p_1}\right)\left(\frac{V_2}{V_1}\right) = \left(\frac{n_2}{n_1}\right)\left(\frac{T_2}{T_1}\right)$$

$$\frac{25\text{m}^3}{\left|\frac{1.6\text{atmabs}}{1\text{atmabs}}\right.}\,\left|\frac{273\text{K}}{303\text{K}}\right.\,\left|\frac{1\text{kgmol}}{22.415\text{m}^3}\right.\,\left|\frac{44\text{kgCO}_2}{1\text{kgmolCO}_2}\right.\,\left|\frac{1000\text{g}}{1\text{kg}}\right. = 70.7 \times 10^3 \text{ g CO}_2$$

Problem 7.2

20 ft^3 of nitrogen at 300 psig and 100ûF and 30 ft^3 of oxygen at 200 psig and340ûF are injected into a 15 ft^3 vessel. The vessel is then cooled to 70ûF. Find the partial pressure of each component in the 15 ft^3 vessel. Assume that the ideal gas law applies.

Solution



The problem can be solved by determining the number of moles of oxygen and nitrogen and solving for the total pressure at the final conditions. Then the partial pressures are calculated using the mole fractions.

Nitrogen
V = 20 ft^3
p = 300 psig = 314.7 psia
T = 100ûF = 560ûR

$$n_{N_2} = \frac{pV}{RT} = \frac{(314.7)(20)}{(10.73)(560)} = 1.05 \text{ lb mol}$$

Oxygen
V = 30 ft^3
p = 200 psig = 214.7 psia
T = 340ûF = 800ûR

$$n_{O_2} = \frac{(214.7)(30)}{(10.73)(800)} = 0.75 \text{ lb mol}$$

$$n_T = n_{N_2} + n_{O_2} = 1.80 \text{ lb mol}$$

$$\text{Final pressure } p_T = \frac{n_T RT}{V} = \frac{(1.80)(10.73)(530)}{15} = 682 \text{ psia}$$

	moles	*mole fr*(y_i)	$p_i = p_T(y_i)$
O_2	0.75	0.42	**286**
N_2	1.05	0.58	**396**
	1.80	1.00	682 *psia*

Problem 7.3

A steel container has a volume of 200 m^3. It is filled with nitrogen at 22˚C and atmospheric pressure. If the container valve is opened and the container heated to 200˚C, calculate the fraction of the nitrogen which leaves the container.

Solution

The solution involves determining the number of moles of nitrogen in the tank at the final given temperature and pressure (T_2 and p_2), and at the initial conditions, and subtracting.

$T_1 = 22^\circ C = 295K$ $\quad$ $T_2 = 200^\circ C = 473K$

$p_1 = 1$ atm $\quad$ $p_2 = 1$ atm

$V_1 = 200\ m^3$ $\quad$ $V_2 = 200\ m^3$

$$n_1 = \frac{p_1 V_1}{RT_1} \qquad n_2 = \frac{p_2 V_2}{RT_2}$$

$$n_1 = \frac{(1)(200)}{(0.08206)(295)} \qquad n_2 = \frac{(1)(200)}{(0.08206)(473)}$$

$= 8.26$ kg mol $\quad$ $= 5.15$ kg mol

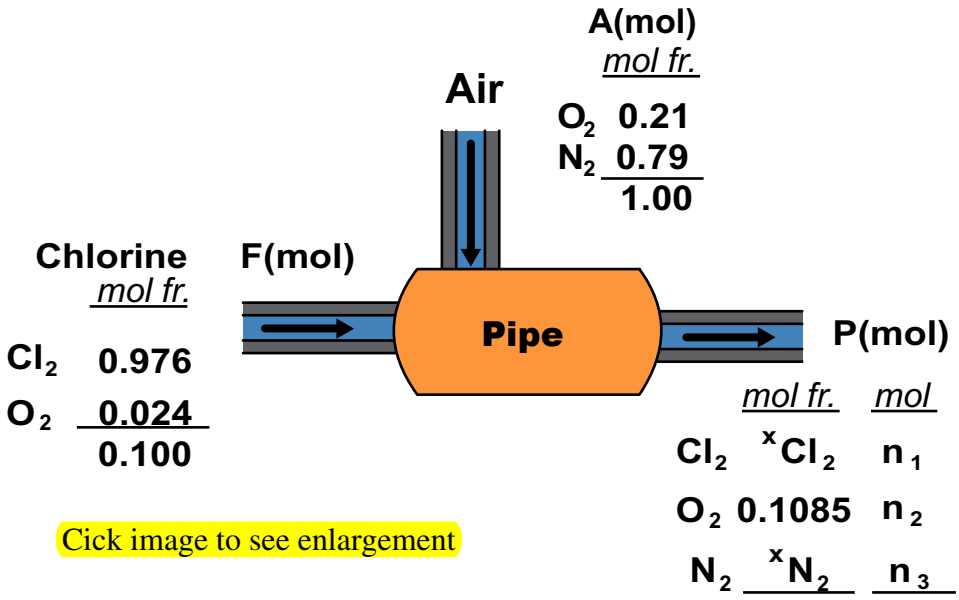
The fraction of N_2 leaving $= \dfrac{8.26 - 5.15}{5.15} =$ **0.60**

Problem 7.4

Chlorine gas containing 2.4 percent O_2 is flowing through an earthenware pipe. The gas flow rate is measured by introducing air into it at the rate of 115 m^3/min. Further down the line, after mixing is complete, the gas is found to contain 10.85 percent O_2. How many m^3 of the initial gas were flowing per minute through the pipe?

Solution

The problem is similar to other nonreacting material balance problems. It is convenient to imagine the pipeline between the point of injection of air to the point of sampling as a mixer. The process may be considered to be a steady state process without reaction.



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Step 5 We could use F = 100 mol as the basis instead of the given flowrate. All flow rates can be then be converted to the basis of 1 minute at the end of the problem. However, it is easier to use the given flow rate in m^3 assuming that the temperature and pressure are the same for all streams so that moles are proportional to m^3 in each stream.

$$A = 115\ m^3$$

Step 6 Let x_{Cl_2} and x_{N_2} be the respective mole fractions in P.
The unknowns are: F, P, x_{Cl_2} , and x_{N_2} (or n_1 and n_3).

Step 7 The balances are: Cl_2, O_2, N_2, and $\Sigma x_i = 1$ (or $\Sigma n_i = P$) so the problem has a unique solution.

Step 8	Total	$F + 115 = P$	(1)
	Oxygen Balance	$0.024F + 0.21(115) = 0.1085\ P$	(2)
	Chlorine Balance	$0.976F = x_{Cl_2}\ (P)$	(3)
	Nitrogen Balance	$0.79(115) = x_{N_2}P$	(4)
	$\Sigma x_i = 1.000$	$0.1085 + x_{Cl_2} + x_{N_2} = 1.000$	(5)

Steps 8 and 9

Only 4 of the balances are independent. Substitute the total balance for one component balance and solve (1) and (2) together to get

$$P = 253\ m^3 \text{ at T and p}$$

$$V_{in} = \mathbf{138\ m^3} \text{ at T and p}$$

Step 10 Use Σx_i as a check

from (4) $x^P_{N_2} = 0.79(115)/253 = 0.359$

from (3)&(1) $x^P_{Cl_2} = (0.976)(138)/253 = 0.532$

from (5) $0.359 + 0.532 + 0.1085 = 1.00$

Problem 7.5

A synthetic gas generated from coal has the following composition: CO_2, 7.2%; CO, 24.3%; H_2, 14.1%; CH_4, 3.5%; N_2, 50.9%.

(a) Calculate the cubic feet of air necessary for complete combustion per cubic foot of synthetic gas at the same conditions.

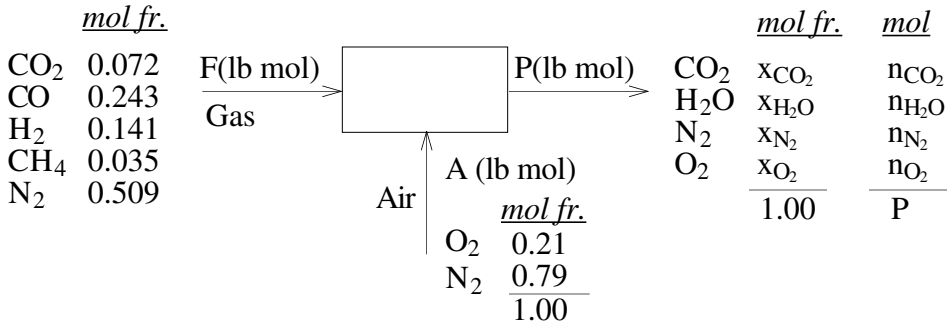
(b) If 38% excess air were used for combustion, what volume of flue gas at 750˚F and 738 mm Hg would be produced per cubic foot of synthetic gas at standard conditions?

(c) Calculate the flue gas analysis for (a) and (b).

Solution

The problem is just a material balance problem with volumes of inlet and outlet gases specified instead of moles. We could select ft^3 or moles as a basis.

Steps 1, 2, 3, and 4 This is a steady state problem with reaction.



Part (a)

Calculate the required air first.

Step 5 Basis 100 mol F

Step 4

Component	*mol*	*Reaction*	*mol reqd O_2*
CO_2	7.2		
CO	24.3	$CO + \frac{1}{2}O_2 \rightarrow CO_2$	12.15
H_2	14.1	$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$	7.15
CH_4	3.5	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	7.0
N_2	50.9		
	100.0		26.3
Accompanying N_2:26.3 (79/21)			98.9
		Total	125.2

a. $\frac{A}{F} = \frac{125.2 \text{mol air}}{100 \text{mol feed}} = 1.25 \frac{\text{mol air}}{\text{mol feed}} = \mathbf{\frac{1.25 ft^3 air}{1.00 ft^3 feed}}$

(both at same conditions)

Since the temperature and pressure are the same for both streams, the mole ratio and the volume ratio are the same.

Next, let us make a material balance for the case in which the air supplied is 38% in excess. Keep the same basis.

$$A = 125.2\ (1.38) = 172.7 \text{ mol}$$

Part (b)

Step 6 Unknowns: P, and x_{CO_2}, x_{H_2O}, x_{N_2}, x_{O_2} (or $n_{CO_2}, n_{H_2O}, n_{N_2}, n_{O_2}$)

Steps 7, and 8 The element balances are:

Carbon balance: $7.2 + 24.3 + 3.5 = Px_{CO_2} = n_{CO_2}$ (1)

Hydrogen balance: $14.1(2) + 3.5(4) = 2Px_{H_2O} = 2n_{H_2O}$ (2)

Oxygen balance: $7.2(2) + 24.3 + 0.21\ (172.7)(2) = 2Px_{CO_2} + Px_{H_2O} + 2Px_{O_2}$ (3)

Nitrogen balance(N2): $50.9 + 0.79\ (172.7) = Px_{N_2} = n_{N_2}$ (4)

Also: $x_{H_2O} + x_{CO_2} + x_{N_2} + x_{O_2} = 1$ (5)

or $n_{H_2O} + n_{CO_2} + n_{N_2} + n_{O_2} = P$

Step 9

From the above equstions we get

Component	*mol*
CO_2	35
H_2O	21.1
O_2	10.1
N_2	187.3
Total	253

Vol. of P @ 750˚F, 738 mm Hg

$$T = 750^\circ F = 1210^\circ R$$

$$p = 738 \text{ mm Hg}$$

$$V_P = \frac{253 \text{lbmol}}{1 \text{lbmol}} \left| \frac{359 ft^3}{492^\circ R} \right| \frac{1210^\circ R}{738 \text{mmHg}} \left| \frac{760 \text{mmHg}}{} \right. = 2.30 \times 10^5 \text{ ft}^3$$

$$V_F = \frac{100 \text{lbmol}}{1 \text{lbmol}} \left| \frac{359 ft^3}{} \right. = 3.59 \times 10^4 \text{ ft}^3$$

$$\frac{V_P}{V_F} = \frac{2.30 \times 10^5}{3.59 \times 10^4} = \mathbf{6.41}\ \frac{\mathbf{ft^3 fluegas}}{\mathbf{ft^3 air at SC}}\ \mathbf{at\ T\ and\ p}$$

Part (c) Flue gas analysis.

a. The water and carbon dioxide are the same as in part b, and there is no O_2 in the flue gas.

	mol	*mol fr*
CO_2	35	**0.23**
H_2O	21.1	**0.14**
N_2	98.9	**0.63**
	155	1.00

b.

	mol	*mol fr*
CO_2	35	**0.14**
H_2O	21.1	**0.08**
N_2	187	**0.74**
O_2	10.1	**0.04**
	253	1.00

Problem 7.6

An old way of producing hydrogen gas in the laboratory was by the reaction of sulfuric acid with zinc metal

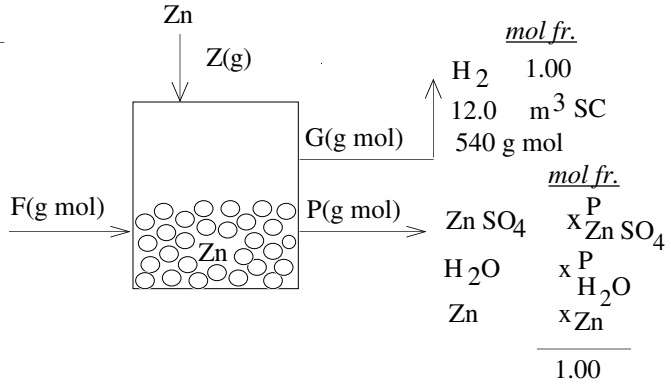
$$H_2\,SO_4(l) + Zn(s) \rightarrow ZnSO_4(s) + H_2(g)$$

How many grams of sulfuric acid solution (98%) must act on an excess of zinc to produce 12.0 m^3/hr of hydrogen at standard conditions. Assume all the acid used completely reacts.

Solution

Steps 1, 2, 3, and 4 You first must determine the number of moles of hydrogen produced, and then calculate the acid required via stoichiometry. This is a steady state process with reaction except for the Zn (which can be assumed to exit the vessel).

	mass fr.	*MW*	10^3 *g mol*	*mol fr.*
H_2SO_4	0.98	98	10.0	0.90
	0.02			
H_2O		18	1.111	0.100
	1.00		11.11	1.00



Step 5 Basis 1 hr (12.0 m^3 at SC in G)

$$\text{moles of hydrogen} = n = \frac{pV}{RT}$$

$$\text{vol of hydrogen} = V = \frac{12.0 m^3 \left| \frac{1000 L}{1 m^3} \right.}{} = 1.20 \times 10^4 L$$

$$n = \frac{(1 atm)(1.20 \times 10^4)}{(0.08206)(273)} = 5.36 \times 10^2 \text{g mol}$$

Step 6 Unknowns are: F, P, $x^P_{ZnSO_4}$, $x^P_{H_2O}$, and x^P_{Zn}. The only unknown we want to solve for is F.

Steps 7 and 8 Balances: We can make H, S, O, and Zn element balances (they may not all be independent) plus $\Sigma x_i = 1$. The easiest balance to make to get F is an H_2SO_4 compound balance, but other reasonable balances can be used.

In		*Out*		*Generation*		*Consumption*		*Accum.*
0.90F	–	0	+	536	–	0	=	0

$$F = 596 \text{ g mol } H_2SO_4$$

$$\frac{596 \text{gmol } H_2SO_4 \text{soln} \left| \frac{10.0 \text{gsoln}}{11.11 \times 10^{-3} \text{gmol} 98\% \text{soln}} \right.}{} = \mathbf{5.37 \times 10^4 \text{ g } 98\% \text{ soln}}$$

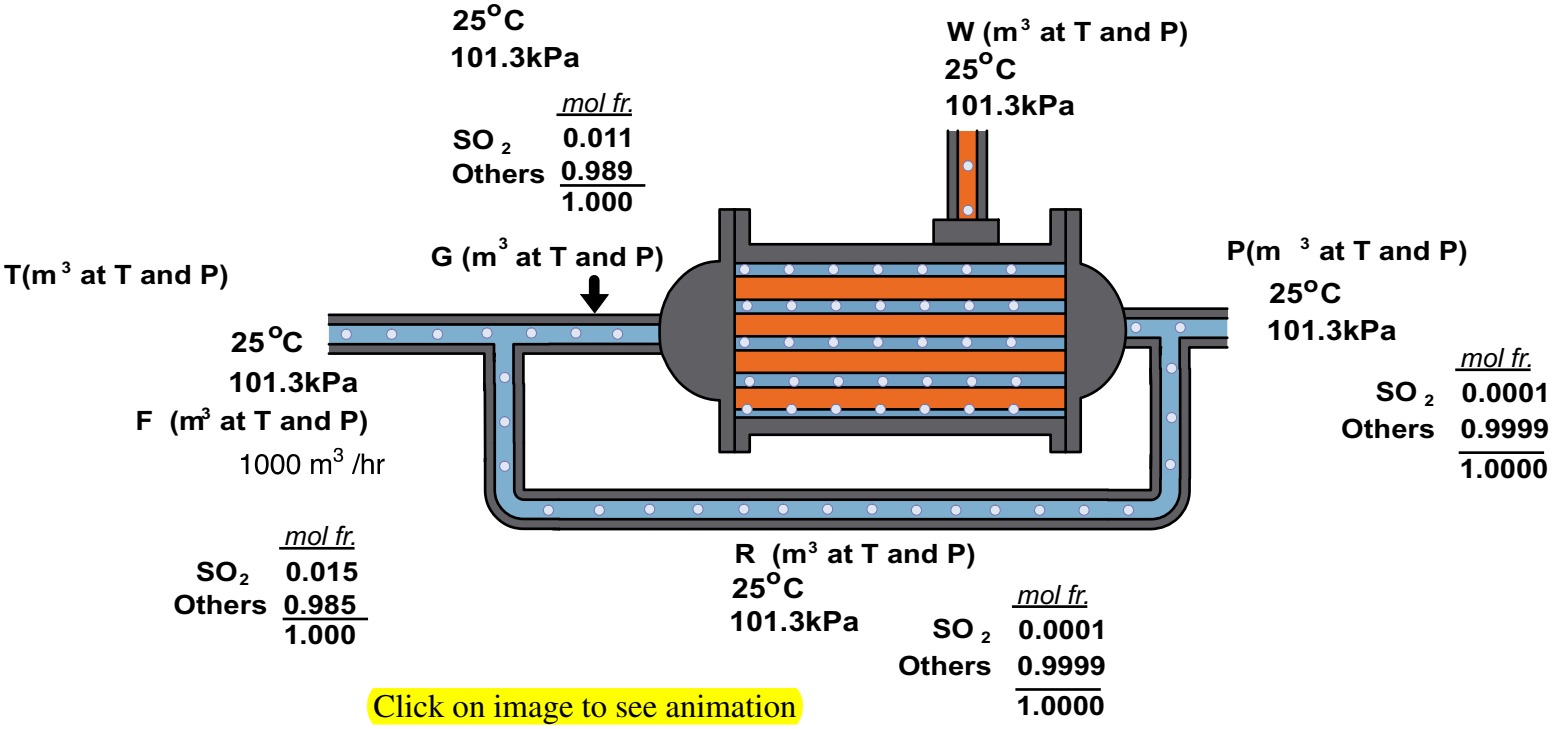
Problem 7.7

Polymeric membranes are proposed to be used to reduce the SO_2 concentration in the waste gas of a sulfuric acid plant from 1.5% to 0.01%. Hollows fibers (made of polymeric membrane) fill the separations unit. The waste gas containing 1.5% SO_2 is the fresh feed in the amount of 1000 m^3 hr at 25˚C and 1 atm (101.3 kPa). To meet the product gas specifications, part of the product stream has to be recycled to reduce the concentration of SO_2 entering the separator itself to 1.10% SO_2 in G, the process feed. The process is isothermal at 25˚C and isobaric at 1 atm.

(a) Determine the recycle stream flow rate R in m^3/hr.
(b) Determine the waste stream flowrate W in m^3/hr.

Solution

Steps 1, 2, 3, and 4 This is a steady state process with reaction and recycle. All the known data have been placed in the figure. No reaction occurs.



Click on image to see animation

Step 5 Basis: F = 1000 m^3 at 25ûC and 101.3kPa (same basis as 1 hr)

Step 6 Ignore the exit stream from the reactor. Then G, P, W, and R are unknowns and their compositions are known.

Since the temperature and pressure are constant throughout, volume balances can be used (mole fraction is the same as volume fraction). The balances could be made in moles and then converted to the basis of 1000 m^3.

Steps 7, 8, and 9 The system is the overall process. The balances are

Total: $1000 = P + W$

SO_2: $(0.015)(1000) = 0.0001\ P + W\ (1.000)$

Other: $(0.985)(1000) = 0.9999\ P$ (a tie component)

SEPARATION BY MEMBRANES

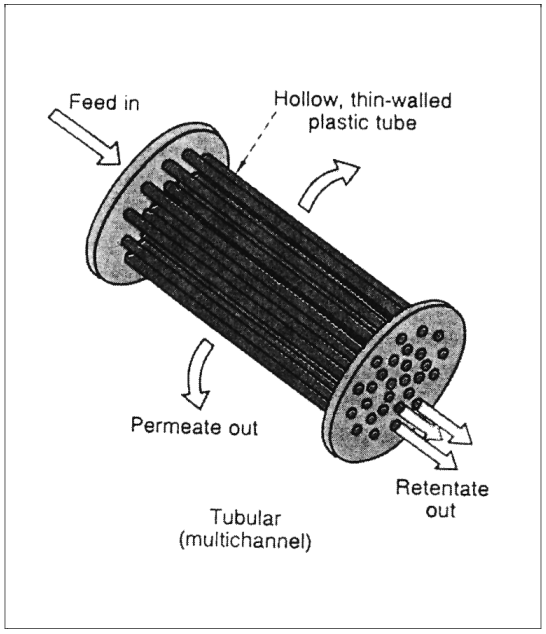


Fig. 17a Tubular membrane separator

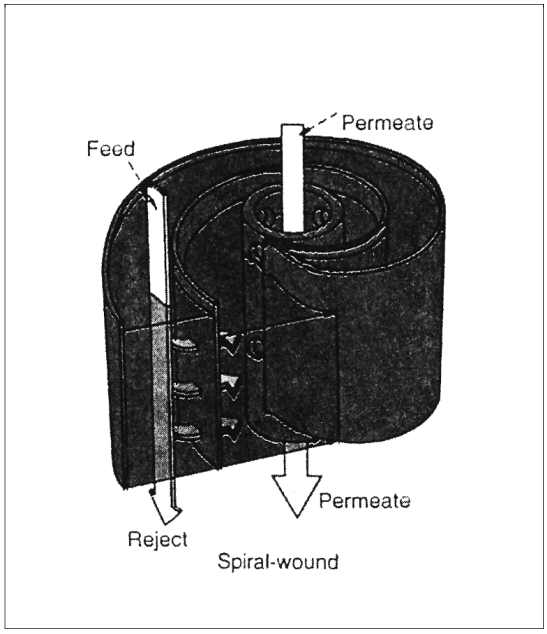


Fig. 17b Spiral wound membrane separator

Membranes are used to separate gaseous mixtures or liquid mixtures. Membrane modules can be tubular, spiral-wound, or plate and frame configurations. Membrane materials are usually proprietary plastic films, ceramic or metal tubes, or gels with hole size, thickness, chemical properties, ion potential, and so on appropriate for the separation. Examples of the kinds of separation that can be accomplished are separation of one gas from a gas mixture, separation of proteins from a solution, dialysis of blood of patients with kidney disease, and separation of electrolytes from non electrolytes.

Two of the balances are independent. Solve any two to get

P = 985.1 m^3/hr at 25˚C and 1 atm
W = 14.9 m^3/hr at 25˚C and 1 atm

To get R we make a balance on the mixing point where F and R combine to make G

Total: 1000 + R = G

SO_2: 0.015(1.000) + 0.0001R = 0.011G

Other: (0.985)(1000) + 0.9999R = 0.989G

(Two of the balances are independent). Solve the first two to get

R = 364 m^3/hr at 25˚C and 1 atm
G = 1364 m^3/hr at 25˚C and 1 atm

Step 10 Check

$$0.15(1000) \stackrel{?}{=} 0.001\,(985.1) + 14.9$$
$$15 = 15 \text{ OK.}$$

Problem 7.8

In a sulfuric acid plant, sulfur is burned in the presence of excess oxygen to produce sulfur dioxide which in turn is further reacted in the next step with oxygen in a converter to produce sulfur trioxide.

In the plant SO_2 along with 10% excess air is fed into the converter which operates at 1500˚C and 1 atm. The per pass conversion of SO_2 is 75% and overall conversion is 100%. If 10^6 m^3/hr of SO_3 at 1100˚C and 1 atm is fed to the converter, calculate the:

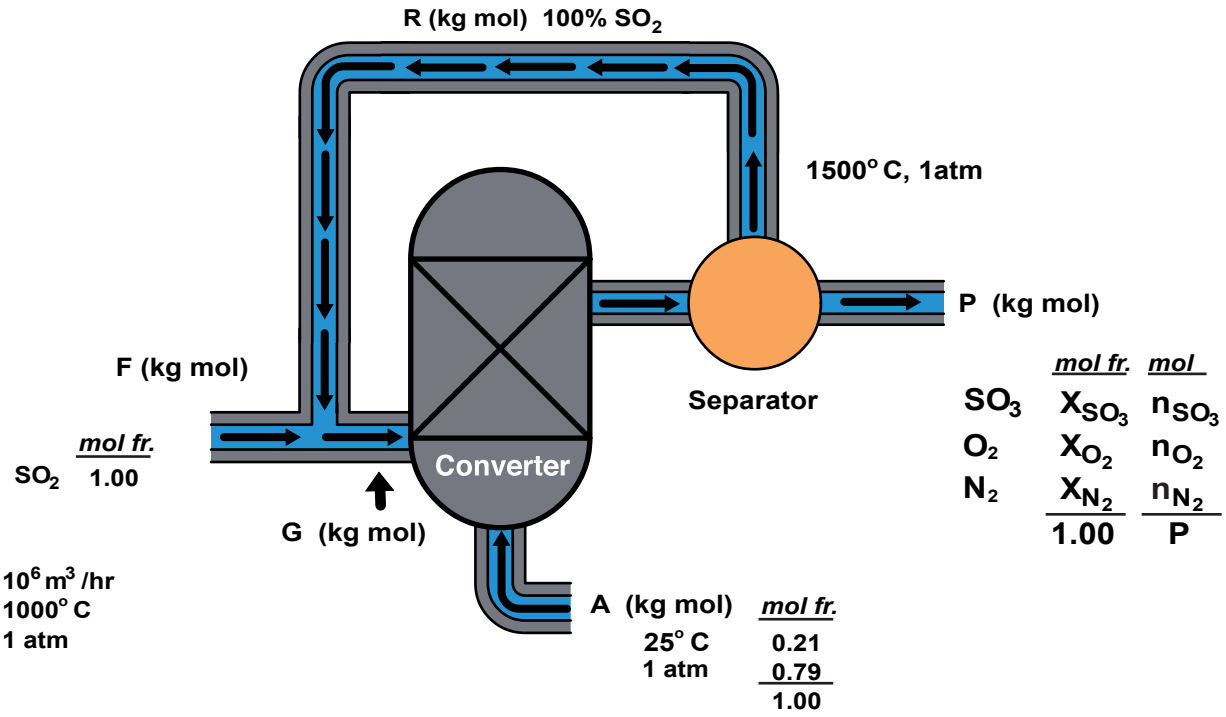
(a) flow rate of the product stream P in m^3/hr at 1500˚C and 1 atm and its composition in mole percent;
(b) flow rate of the recycle stream R in m^3/hr at 1500˚C and 1 atm.

Solution

This is a steady state problem with reaction and recycle.

Steps 1, 2, and 3

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



Step 5 Basis: F = 10^6 m^3 at 1100ûC and 101.3kPa (equivalent to 1 hr)

Step 4 We will make the balance in moles (m^3 could also be used if A and F are adjusted to 1 atm and 1500°C).

$$n = \frac{pV}{RT} = \frac{101.3(10^6)}{\hat{E}8.314\hat{E}(1100\hat{E}+\hat{E}273)} = 8874 \text{ kg mol } SO_2$$

Next, calculate the value of A, the entering air.

		kg mol
Required	O_2:	$8874\left(\frac{1}{2}\right) = 4{,}437$
Excess	O_2:	$0.1(4{,}437) = \hat{E}\hat{E}\hat{E}\hat{E}444$
	Total	4,881
N_2:	$4881\left(\frac{0.79}{0.21}\right) =$	18,360

Step 6 The system is the overall process. The unknowns are P, n_{SO_3}, n_{O_2}, and n_{N_2} (or P, x_{SO_3}, x_{O_2}, x_{N_2})

Step 7 The balances are: S, O, N, and $\Sigma n_i = P \left(\text{or } \Sigma x_i = 1\right)$

Steps 8 and 9 For the overall process the element balances are (units are kg mol):

S: $8{,}874 = P\,(x_{SO_3}) = n_{SO_3}$
N2: $18{,}360 = P\,(x_{N_2}) = n_{N_2}$
O: $8{,}874\,(2) + 4{,}881(2) = 8{,}874(3) + n_{O_2}(2)$

$$n_{SO_3} = 8{,}874 \qquad n_{N_2} = 18{,}360 \qquad n_{O_2} = 444$$

Thus P = 8,874 + 18,360 + 444 = 27,618 kg mol or 27,620 kg mol

a. Apply pV = nRT

$$V = \frac{(27{,}620)(8.314)(1500+273)}{101.3} = \mathbf{4.02 \times 10^6 m^3/hr \text{ at } 1500°C \text{ and } 1 \text{ atm}}$$

At the mixing point of F and R we get G: F + R = G

b. Make the system the reactor plus the separator to avoid having to calculate information about the converter outlet stream. Use an SO_2 balance in kg mol.

In		*Out*		*Gen.*		*Consum.*		*Accum.*
(1.00)(8874+R)	–	R(1.00)	+	0	–	0.75(8874+R)	=	0

R = 2958 kg mol which corresponds **0.43×10^6 m^3/hr at 1500˚C and 1 atm**

Problem 7.9

Seven pounds of N_2 at 120˚F are stored in a cylinder having a volume of 0.75 ft^3. Calculate the pressure in atmospheres in the cylinder

(a) assuming N_2 to be an ideal gas
(b) assuming the pressure of N_2 can be predicted by van der Waal's equation
(c) using the compressibility factor method
(d) using the Redlich-Kwong equation of state.

Solution

$V = 0.75\ ft^3$
$T = 120^\circ F = 580^\circ R$
$n = \dfrac{7 lb N_2}{} \left| \dfrac{1 lb mol}{28 lb N_2} \right. = 0.25$ lb mol N_2

} Basis

$R = 10.73$ (psia)(ft^3)/(lb mol)(˚R)

a. Using the ideal gas relation pV = nRT

$$p = \frac{(0.25)(10.73)(580)}{0.75}\left(\frac{1\ atm}{14.7\ psia}\right) = \mathbf{141\ atm\ (2074\ psia)}$$

b. Using van der Waals, equation

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

From the text for nitrogen $a = 1.347 \times 10^6 \left(\dfrac{cm^3}{g\ mol}\right)^2$ and $b = 38.6\left(\dfrac{cm^3}{g\ mol}\right)$

$$a = 1.347 \times \frac{\left(\dfrac{cm^3}{g\ mol}\right)^2}{1\left(\dfrac{cm^3}{g\ mol}\right)^2} \left| \frac{3.776 \times 10^{-3}\left(\dfrac{ft^3}{lb\ mol}\right)^2}{} \right. = 5086\left(\frac{ft^3}{lb\ mol}\right)^2$$

$$b = \frac{38.6\left(\dfrac{cm^3}{g\ mol}\right)^2}{1\left(\dfrac{ft^3}{g\ mol}\right)^2} \left| \frac{1.60 \times 10^{-2}\left(\dfrac{ft^3}{lb\ mol}\right)^2}{} \right. = 0.6176\left(\frac{ft^3}{lb\ mol}\right)^2$$

Then $$\left(p + \frac{(0.25)^2\ 5086}{(0.75)^2}\right)[0.75 - 0.25\ (0.6176)] = 0.25\ (10.73)\ (580)$$

$$(p + 565.1)\ [0.596] = 1556$$

$$\mathbf{p = 20.46\ psi\ (139\ atm)}$$

c. Using the compressibility factor

$$pV = znRT$$

From Appendix D in the text the critical properties for nitorgen are

$$p_c = 33.5\ \text{atm and } T_c = 126.2\text{K } (227^\circ\text{R})$$

$$V_c' = \frac{RT_c}{p_c}\ \frac{(0.7302)(227)}{(33.5)} = 4.95\ \text{ft}^3\text{/lb mol}$$

$$T_r = \frac{T}{T_c} = \frac{580^\circ\text{R}}{227^\circ\text{R}} = 2.56$$

$$V_r' = \frac{V}{V_c'} = \frac{0.75\text{ft}^3/0.25\text{lbmol}}{4.95\text{ft}^3/\text{lbmol}} = 0.61$$

On one of the compressibility charts having the right domain determine the intersection of the $V_r' = 0.61$ and the $T_r = 2.56$ lines. Some approximation may be required. From this point you can read z on the vertical and p_r on the horizontal axis:

$z = 1.05 \qquad p_r = 4.5$

$$p = \frac{znRT}{V} = \frac{(1.05)(0.25)(10.73)(580)}{(0.75)} = 2178\ \text{psia (148 atm)}$$

or use p_r: $\qquad p_r = p/p_c$

$$p = (p_r)(p_c) = 4.5\ (33.5) = 151\ \text{atm}$$

These answers are close enough in view of the accuracy of the original data.

d. Using the Redlich Kwong Equation of State

$$\left[p + \frac{a}{T^{1/2}\ \hat{V}\left(\hat{V} + b\right)}\right]\left(\hat{V} - b\right) = RT$$

where $a = 0.4278\ \dfrac{R^2T_c^{2.5}}{p_c}$ and $b = 0.0867\ \dfrac{RT_c}{p_c}$

$$a = 0.4278 \frac{(0.7302)^2 (227)^{2.5}}{(33.5)} = 5286\ (°R)^{0.5}\ (atm)\ (ft^3/lb\ mol)^2$$

$$b = 0.0867 \frac{(0.7302)(227)}{(33.5)} = 0.429\ ft^3/lb\ mol$$

Substitute these values into the equation

$$\left[p + \frac{5286}{(580)^{1/2}\ 3\ (3 + 0.429)}\right] (3 - 0.429) = (0.7302)\ (580)$$

$$(p + 20.96)\ (2.571) = 4235$$

$$p = 144\ atm$$

The pressures determined by three methods are comparable although not exactly same.

Problem 7.10

Suppose 1.00 g mol of CO_2 at a temperature of 220K is placed in a Dewar vessel of unknown volume, and the pressure reading made is 690 kPa. What is the volume of the vessel?

Solution

Basis: 1.00 g mol CO_2

Let us use the Soave-Redlich-Kwong equation which is cubic in V. Calculate the coefficients (the equations are listed in Chapter 15) for the equation, and use Polymath, or another nonlinear equation solving program, to find $\hat{V}$.

$$p = \frac{RT}{\hat{V} - b} - \frac{a'\lambda}{\hat{V}(\hat{V} + b)}$$

$p = 690$ kPa $\quad R = 8.314 (kPa)(m^3)/(kg\ mol)(K) \quad T = 220K$

$b = 2.97 \times 10^{-5}\ m^3/(g\ mol)$

$a' = 0.370\ (m^6)\ (Pa)/(g\ mol)^2 \quad \kappa = 0.826 \quad \lambda = 1.34$

Arrange the equation so that p is subtracted from the right hand side (the equation then equals zero), and solve for $\hat{V} = 2.38 \times 10^{-3}\ m^3/g\ mol$.

Problem 7.11

A gas analyzes 60% methane and 40% ethylene by volume. It is desired to store 12.3 kg of this gas mixture in a cylinder having a capacity of $5{\cdot}14 \times 10^{-2}$ m^3 at a maximum temperature of 45˚C. Calculate the pressure inside the cylinder by

(a) assuming that the mixture obeys the ideal gas laws;
(b) using the compressibility factor determined by the pseudo critical point method.

Solution Basis: 12.3 kg

a. *Ideal Gas Law* $pV = nRT$

$$\text{av mol wt} = \sum y_i MW_i = 0.60\,(16) + 0.40\,(28) = 20.8\ \frac{\text{kg}}{\text{kgmol}}$$

$$n = \frac{12.3\text{kg}}{\left|\frac{1\text{kgmolmixture}}{20.8\text{kgmixture}}\right.} = 0.591\ \text{kg mol}$$

$T = 45^\circ\text{C} = 318\text{K}$ $V = 5.14 \times 10^{-2}$ m^3 $R = 8.314$ (kPa) (m^3)/(kg mol)(K)

$$p = \frac{nRT}{V} = \frac{0.591(8.314)(318)}{5.14 \times 1\ 0^{-2}} = \mathbf{30{,}400\ kPa}$$

b. *Pseudocritical method*

$$p_c' = \sum_i p_{ci}\, y_i \qquad T_c' = \sum_i T_{ci}\, y_i \qquad V_c' = \sum_i V_{ci}'\, y_i$$

Methane

$T_c = 190.7\text{K}$

$p_c = 45.8$ atm (4640 kPa)

$$V_c' = \frac{RT_c}{p_c} = 0.342\ \frac{\text{m}^3}{\text{kgmol}}$$

Ethylene

$T_c = 283.1$ K

$p_c = 50.5$ atm (5116 kPa)

$$V_c' = \frac{RT_c}{p_c} = 0.460\ \frac{\text{m}^3}{\text{kgmol}}$$

$T_c' = 0.60\,(190.7) + 0.40\,(283.1) = 227.7\text{K}$ $p_c' = 0.60\,(4640) + 0.40\,(5116) = 4830$ kPa

$$V_c' = 0.60\,(0.342) + 0.40\,(0.460) = 0.389\ \frac{\text{m}^3}{\text{kgmol}}$$

$$T_r' = \frac{T}{T_c'} = \frac{318\text{K}}{227.7\text{K}} = 1.40$$

$$V_r' = \frac{\hat{V}}{\hat{V}_c'} = \frac{5.14 \times 10^{-2}\text{m}^3/0.591\text{kgmol}}{0.389\text{m}^3/\text{kgmol}} = 0.22$$

Using T_r' and V_r', we get $p_r = 5.3$ (approximately) so that $p = p_r p_c' = (5.3)(4830) = \mathbf{26{,}000\ kPa}$

Chapter 8 Multiphase Equilibrium

Problem 8.1

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), and compare it with the experimental value (taken from a handbook).

Solution

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

From Appendix G in the text the coefficients are

Benzene: A = 15.9008 T = K
B = 2788.51 p^* = mmHg
C = –52.36

a. Vapor Pressure of benzene at 50˚C

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

$$p^* = \textbf{270 mmHg abs}$$

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

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

Solving, T = **353.3K**

From Appendix D in the text the normal boiling point of benzene is **353.26K**. The two values agree well.

Problem 8.2

Prepare a Cox chart for ethyl acetate. The vapor pressure of ethyl acetate is 200 mmHg abs. at 42˚C and 5.0 atm at 126.0˚C. By using the chart estimate the

a. boiling point of ethyl acetate at 760 mmHg and compare with the experimental value (77.1˚C).
b. vapor pressure of ethyl acetate at its critical temperature of 523.1K. Compare with the experimental value of 37.8 atm.

Solution

To construct the temperature scale the following data for the vapor pressure of water are used:

T(˚C):	30.0	50.0	100.0	150.0	200.0	250.0
p(atm):	0.042	0.122	1.00	4.70	15.36	39.22

The procedure is as follows:

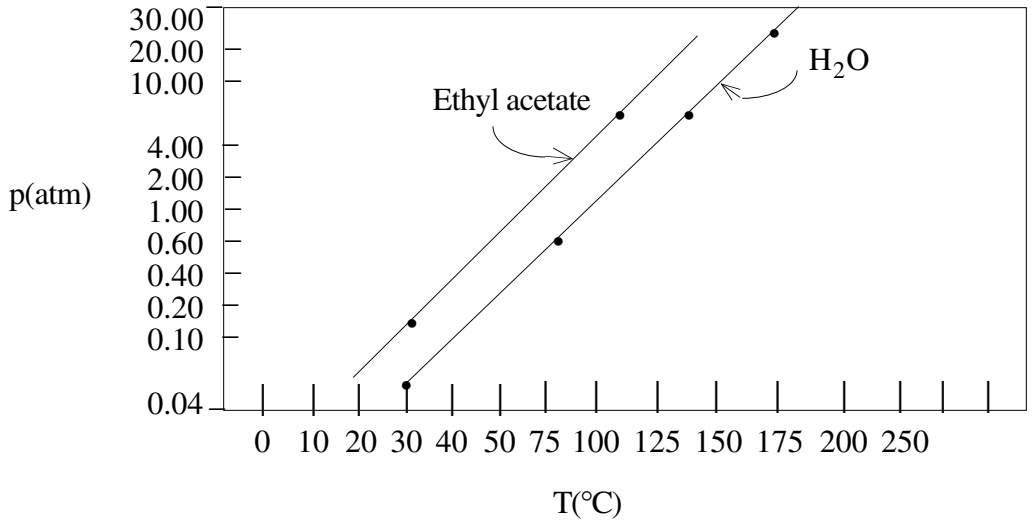
1. First, select a logarithmic vertical scale and place even values of the vapor pressure on the vertical scale to cover the desired pressure range.

2. Then draw a straight line representing the vapor pressure of water at any suitable angle so that you cover the range of temperatures and pressures needed for the problem.

3. To locate each integer value of the water temperature (such as 30, 50, 100, etc.) on the horizontal scale, note the corresponding vapor pressure on the vertical axis, and move horizontally to the line. Then drop vertically down to the temperature axis and mark the axis with the selected temperature (the spacing will not be at even intervals). Repeat to get a series of temperatures.

4. Finally, put the two points given for ethyl acetate on the chart and draw a line between them for ethyl acetate.

Cox Chart

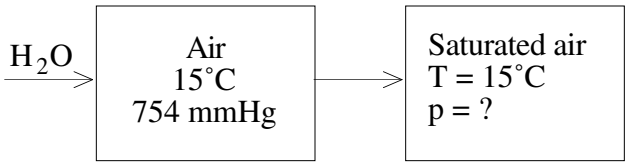


The normal boiling point is estimated to be between 75˚C and 80˚C (a bigger chart would produce a more accurate result), and at the critical point (250˚C), the estimated vapor pressure is about 50 atm.

Problem 8.3

If sufficient water is placed in a vessel containing a dry gas at 15˚C and 100.5 kPa to thoroughly saturate it, what will be the absolute pressure in the vessel after saturation? The temperature and volume of the vessel remain constant.

Solution



Once the air is saturated with water vapor, the water (if the water vapor is in equilibrium with liquid water) exerts a pressure equal to its vapor pressure at 15˚C.

Basis: Dry gas at 15˚C and 100.5 kPa

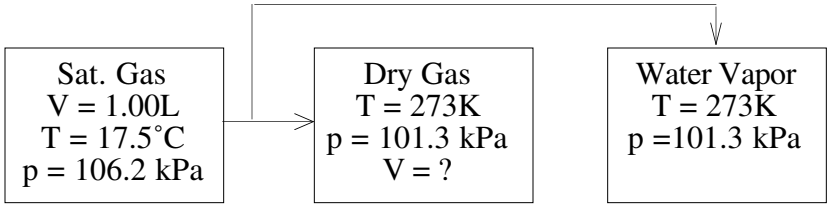
The vapor pressure of H_2O at 15˚C = 1.7 kPa. Since the temperature and volume remain constant

$$p_T = p_{air} + p_{H_2O} = 100.5 + 1.7 = \mathbf{102.2\ kPa}$$

Problem 8.4

A gas saturated with water vapor in a tank has a volume of 1.00L at 17.5˚C and a pressure of 106.2 kPa. What is the volume of dry gas under standard conditions? How many grams of water vapor are present in the gas?

Solution



At the initial conditions the total pressure is the sum of gas pressure and vapor pressure of the water. The first step in the solution involves determining the pressure of the dry gas assuming constant temperature and volume. Look up: $p_{H_2O} = p^*_{H_2O}$ (at 17.5˚C) = 2.00 kPa

$p_T = 106.2\ \text{kPa} = p^*_{H_2O} + p_{gas} = 2.00 + p_{gas}$ $\qquad p_{gas} = 104.2\ \text{kPa}$

a. $$\frac{1.00\text{L}}{} \left| \frac{273\text{K}}{290.5\text{K}} \right| \frac{104.2\text{kPa}}{101.3\text{kPa}} = \mathbf{0.97L\ at\ SC}$$

b. One solution technique is to apply pV = nRT to the water vapor.

$$\frac{1.00\text{L}}{} \left| \frac{2.00\text{kPa}}{290.5\text{K}} \right| \frac{1\text{atm}}{101.3\text{kPa}} \left| \frac{1(\text{gmol})(\text{K})}{0.08206(\text{L})(\text{atm})} \right| \frac{18\text{gH}_2\text{O}}{1\text{gmolH}_2\text{O}} = \mathbf{0.015\ g\ H_2O}$$

Another approach is to use pV = nRT to calculate the total moles present and multiply the result (0.039 g mol) by the mole fraction water (2.00/106.2).

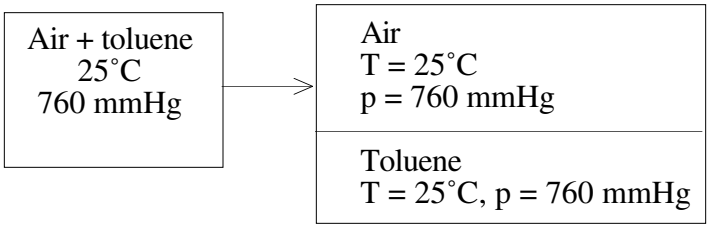
Problem 8.5

Dry air at 25˚C is saturated with toluene under a total pressure of 760 mmHg abs. Is there adequate air for complete combustion of all the toluene? If so, determine the percent excess air present for combustion.

Solution

The solution involves first determining the number of moles of toluene and the moles of oxygen in a specified volume

Steps 1, 2, 3 $C_7H_8 + 9O_2 \rightarrow 7CO_2 + 4H_2O$



Step 5 Basis: 1 g mol C_7H_8

Step 4 From the chemical equation we see 9 mol of O_2 are need per mol of toluene hence (9/0.21) = 42.86 mol of air is needed per mol of toluene. The mole fraction C_7H_8 would be (1/43.86) = 0.0228.

Steps 6, 7, 8 and 9 At 25˚C, C_7H_8 exerts a vapor pressure of

$$\ln(p^*) = 16.0137 - \frac{3096.52}{-53.67+(25+273.1)}$$

$$p^* = 28.22 \text{ mm Hg abs.}$$

At saturation

$$760 - 28.22 = 731.78 \text{ mm Hg abs.} = p_{air}$$

$$\frac{p_{air}}{p_{toluene}} = \frac{n_{air}}{n_{toluene}} = \frac{731.78}{28.22} = 25.93$$

Since the molar ratio of air/toluene required for complete combustion is 42.9, and under the given conditions the air/toluene ratio is only 25.93, the amount of air available is not adequate.

Problem 8.6

Assume that Raoult's Law holds for the following mixture

	mole%
n-Hexane	20
Benzene	50
Toluene	30

a. What is the dew point pressure of the mixture if it is at 150˚F?
b. What is the dew point temperature of the mixture if it is at 85 psia?
c. What is the bubble point temperature of the mixture if it is at 70 psig? The barometer reads 780 mmHg.
d. What is the bubble point pressure if the mixture is 150˚F?

Solution

a. The dew point pressure is the pressure of which the vapor first starts to condense at 150˚F. The mixture is assumed to be all vapor and the condensate composition is determined by

$$1 = p_T \sum_{i=1}^{n} \frac{y_i}{p_i^*} \qquad \text{or} \qquad \frac{1}{p_T} = \sum_{i=1}^{n} \frac{y_i}{p_i^*}$$

Assume an ideal solution exists and use the Antonine Equation to determine p_i^* for the pure components

$$\ln (p^*) = A - \frac{B}{C+T} \qquad T = 150^\circ F = 338.6K$$

	A	B	C	p_i^*	y_i	y_i/p_i^*
n-Hexane	15.8366	2697.55	–48.78	684.67	0.20	2.921×10^{-4}
Benzene	15.9008	2788.51	–52.36	472.93	0.50	1.057×10^{-3}
Toluene	16.0137	3096.52	–53.67	171.75	0.30	1.747×10^{-3}
						3.096×10^{-3}

$$\frac{1}{p_T} = \sum \frac{y_i}{p_i^*} = 3.096 \times 10^{-3}$$

$$\mathbf{p_T = 333 \text{ mmHg}}$$

b. The dew point temperature is the temperature at which the vapor first condenses when the vapor and liquid are in equilibrium. For an ideal solution at 85 psia (4395 mmHg) the relation to use is

$$\frac{1}{p_T} = \sum \frac{y_i}{p_i^*}$$

$$p^* = \exp\left[A - \frac{B}{C+T}\right]$$

$$\frac{1}{4394.6} = \left[\frac{0.2}{e^{\left(15.8366 - \frac{2697.55}{-48.78+T}\right)}} + \frac{0.5}{e^{\left(15.9008 - \frac{2788.51}{-52.36+T}\right)}} + \frac{0.3}{e^{\left(16.0137 - \frac{3096.52}{-53.67+T}\right)}}\right]$$

Solve for T by trial and error (or on a computer) to get

T = 500K	p_T = 13105 mmHg	
T = 425K	p_T = 3842 mmHg	**T ~ 435K**
T = 435K	p_T = 4321 mmHg	

c. The bubble point temperature at a given pressure is the temperature at which the liquid mixture vapor pressure equals the total pressure. The mixture is assumed to be all liquid and the vapor composition is assumed to be in equilibrium with the liquid. The relation used under these assumptions for an ideal liquid is

$$p_T = \sum p_i^* x_i$$

$$\frac{70\text{psi}\,|\,760.0\text{mmHg}}{|\,14.696\text{psia}} = 3619 \text{ mmHg}$$

$$p_T = 3619 + 780 = 4399 \text{ mmHg abs.}$$

$$4399 = \left[0.20\, e^{\left(15.8366 - \frac{2697.55}{-48.78 + T}\right)} + 0.5\, e^{\left(15.9008 - \frac{2788.51}{-52.36 + T}\right)} + 0.3\, e^{\left(16.0137 - \frac{3096.52}{-53.67 + T}\right)}\right]$$

Solve for T by trial and error (or on a computer) to get

T = 400K	p = 2372 mmHg	
T = 425K	p = 4070 mmHg	**T = 429K**
T = 430K	p = 4496 mmHg	

d. The bubble point pressure at 150˚F (338.6K) is the pressure at which the liquid first starts to vaporize when the vapor and liquid are in equilibrium

For an ideal liquid

$$p_T = \sum p_i^* x_i$$

	A	B	C	p_i^*	x_i	$p_i^* x_i$
n-Hexane	15.8366	2697.55	–48.78	684.67	0.20	136.93
Benzene	15.9008	2788.51	–52.36	472.93	0.50	236.47
Toluene	16.0137	3096.52	–53.67	171.75	0.30	51.53
						424.9

p_T = 425 mmHg

Problem 8.7

A natural gas has the following analysis at 400 kPa

	Mole%
Propane	78.0
Butane	12.0
Pentane	10.0

Its temperature must be kept above what value to prevent condensation? If it were cooled, what would be the composition of the liquid that first condenses out of the gas?

Solution

Basis: 1.00 mol gas at 400 kPa.

Assume ideal vapor and liquid at the dew point. $x_i = y_i/K_i$ $\sum x_i = 1$ $K_i = p_i^* / p_T$

$\sum (y_i / K_i) = 1$ or $p_T \sum (y_i / p_i^*) = 1$ for an ideal solution.

Procedure

Assume a temperature and obtain values for p_i^* from the Antonine equation or, a handbook. Calculate $\left(\sum y_i / p_i^*\right) p_T$ to see if the sum equals 1.0. If not, repeat to bracket the value 1.

1st iteration, let T = 310K

	p_i^* (kPa)	y_i / p_i^*	$p_T \sum (y_i / p_i^*)$
C_3	1269	6.147×10^{-4}	
C_4	343.4	3.494×10^{-4}	$400(1.999 \times 10^{-3}) = 0.768$
C_5	104.7	9.551×10^{-4}	
		$\sum = 1.919 \times 10^{-3} (\text{kPa})^{-1}$	

2nd iteration, let T = 290K

	p_i^*	y_i / p_i^*	$p_T \sum (y_i / p_i^*)$
C_3	765	1.020×10^{-3}	
C_4	186.5	6.434×10^{-3}	$400\ (3.644 \times 10^{-3}) = 1.457$
C_5	50.5	1.980×10^{-3}	
		$\sum = 3.644 \times 10^{-3} (\text{kPa})^{-1}$	

3rd iteraction T = 300K

	p_i^*	y_i / p_i^*	$p_T \sum (y_i / p_i^*)$
C_3	993.5	7.851×10^{-4}	$400\ (2.610 \times 10^{-3}) = 1.04$
C_4	255.9	4.689×10^{-4}	close enough
C_5	73.76	1.356×10^{-3}	
		$\sum = 2.610 \times 10^{-3} (\text{kPa})^{-1}$	$T \cong 300\text{K}$

At the dew point temperature, the liquid which first condenses has the composition

$$x_i = y_i p_T / p_i^*$$

$$\frac{y_i p_T}{p_i^*}$$

$$x_{C_3} = \frac{(0.78)(400\ \text{kPa})}{993.5\ \text{kPa}} = 0.314$$

$$x_{C_4} = \frac{(0.12)(400\ \text{kPa})}{255.9\ \text{kPa}} = 0.188$$

$$x_{C_5} = \frac{(0.10)(400\ \text{kPa})}{73.76\ \text{kPa}} = 0.542$$

$$\sum x_i = 1.04$$

PART 3 – ADDITIONAL PROBLEMS
(Answers will be found in Appendix A)

Chapter 7

7.1 In a test on an oil-fired boiler, it is not possible to measure the amount of oil burned, but the air used is determined by inserting a venturi meter in the air line. It is found that 5000 ft^3/min of air at 80°F and 10 psig is used. The dry gas analyzes CO_2, 10.7 percent; CO, 0.55 percent; O_2, 4.75 percent; and N_2, 84.0 percent. If the oil is assumed to be all hydrocarbon, calculate the gallons per hour of oil burned. The sp gr of the oil is 0.94.

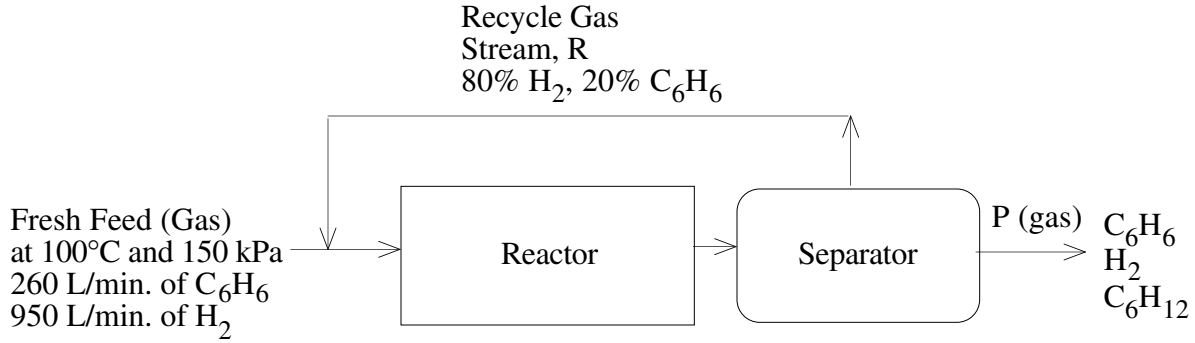
7.2 In the manufacture of dry ice, a fuel is burned to a flue gas which contains 16.2 percent CO_2, 4.8 percent O_2, and the remainder N_2. This flue gas passes through a heat exchanger and then goes to an absorber. The data show that the analysis of the flue gas entering the absorber is 13.1 percent CO_2 with the remainder O_2 and N_2. Apparently something has happened. To check your initial assumption that an air leak has developed in the heat exchanger, you collect the following data with a wet-test meter on the heat exchanger:

Entering flue gas in a 2-min period	47,800 ft^3 at 600°F and 740 mm of Hg
Exit flue gas in a 2-min period	30,000 ft^3 at 60°F and 720 mm of Hg

Was your assumption about an air leak a good one, or was perhaps the analysis of the gas in error? Or both?

7.3 Benzene (C_6H_6) is converted to cyclohexane (C_6H_{12}) by direct reaction with H_2. The fresh feed to the process is 260 L/min of C_6H_6 plus 950 L/min of H_2 at 100°C and 150 kPa. The single pass conversion of H_2 in the reactor is 48% while the overall conversion of H_2 in the process is 75%. The recycle stream contains 80% H_2 and the remainder benzene (no cyclohexane).

(a) Determine the molar flow rates of H_2, C_6H_6, and C_6H_{12} in the exiting product.
(b) Determine the volumetric flow rates of the product stream if it exits at 100 kPa and 200°C.
(c) Determine the molar flow rate of the recycle stream, and the volumetric flow rate if the recycle stream is at 100°C and 100 kPa.



7.4 A natural gas at 30°C has the composition of

CH_4	80%
C_2H_4	10
N_2	10

If the pressure in the line is 100 kN/m^2, what are the partial pressures of the three components? If the temperature is raised to 40°C, will the partial pressures change? If so, what will they be?

7.5 Find the molar volume (in cm^3/g mol) of propane at 375 K and 21 atm. Use the Redlich-Kwong and Peng-Robinson equations, and solve for the molar volume using (1) a nonlinear equation solver, and (2) the compressibility factor method. The acentric factor for propane to use in the Peng-Robinson equation is 0.1487. Also, check your results with the value found in a data base or a handbook.

7.6 What weight of ethane is contained in a gas cylinder of 1.0 ft^3 in volume if the gas is at 100°F and 2000 psig? Use (1) an equation of state and (2) the compressibility factor method.

7.7 Calculate the volume occupied by 2.0 lb air at 735 psia and 392°F.

Chapter 8

8.1 Estimate the vapor pressure of aniline at 350°C from the following vapor pressure data (the experimental vapor pressure is 40 atm):

t(°C)	184.4	212.8	254.8	292.7
p*(atm)	1.00	2.00	5.00	10.00

(a) Prepare a Cox chart to solve this problem.
(b) Fit the coefficients in Antoine equation using a nonlinear optimization code or a nonlinear regression code, and predict the value from the Antoine equation.

8.2 Estimate the vapor pressure of benzene at 125°C from the vapor pressure data

T(°F):	102.6	212
p* (psia):	3.36	25.5

by preparing a Cox chart.

8.3 Carbon disulfide (CS_2) at 20°C has a vapor pressure of 352 mm Hg. Dry air is bubbled through the CS_2 at 20°C until 4.45 kg of CS_2 are evaporated. What was the volume of the dry air required to evaporate this CS_2 (assuming that the air is saturated) if the air was initially at 20°C and 10 atm and the final pressure on the air-CS vapor mixture is 750 mm Hg?

8.4 A mixture of acetylene (C_2H_2) with an excess of oxygen measured 350 ft^3 at 25°C and 745 mm pressure. After explosion the volume of the dry gaseous product was 300 ft^3 at 60°C and its partial pressure of 745 mm. Calculate the volume of acetylene and of oxygen in the original mixture. Assume that the final gas was saturated and that only enough water was formed to saturate the gas.

8.5 An 8.00–liter cylinder contains a gas saturated with water vapor at 25.0°C and a pressure of 102.6 kPa. What is the volume of the gas when dry at standard conditions?

8.6 Oxalic acid ($H_2C_2O_4$) is burned with 248 percent excess air, 65 percent of the carbon burning to CO. Calculate the dew point of the flue gas.

8.7 Equilibrium flash vaporization of a liquid mixture of ethane (15 mol), propane (15 mol), n-butane (15 mol), and pentane (15 mol) at 140°F and 200 psia takes place in a vessel. What ratio of liquid to vapor exists when vaporization is complete. K-values are respectively 3.70, 1.38, 0.57, and 0.21.

8.8 A vapor composed of 30 percent n-hexane, 30% n-heptane, and 40% n-octane is partially condensed at 100 kPa. Assume that the vapor and liquid are ideal solutions. Calculate the mole fractions of the three components in the vapor at equilibrium if 80 percent of the original vapor condenses.

8.9 A solution containing 12 wt percent of dissolved nonvolatile solid is fed to a flash distillation unit. The molecular weight of the solid is 123.0. The effective vapor pressure of the solution is equal to

$$p = p^* x$$

where p = effective vapor pressure of the solution
x = mole fraction of water
p^* = vapor pressure of pure water

The pressure in the flash distillation unit is 1.121 psia and the temperature is 100°F. Calculate the pounds of pure water obtained in the vapor stream per 100 lb of feed solution and the weight percent of the dissolved nonvolatile solid leaving in the liquid stream.

8.10 Consider a tank of water at 0°C under a pressure of 101.3 kPa at the surface of the water. Would it be possible to maintain ice at the bottom of the water tank at 0°C in equilibrium with the water?

8.11 Determine the equilibrium vapor pressure in kPa of the following liquid at 21°C:

Component	Mole percent
C_2H_6	3.0
C_3H_8	68.0
C_4H_{10}	24.0
C_5H_{12}	5.0

Assume Raoult's law applies.

8.12 If all of the C_2H_6 were removed from the liquid cited in Problem 8.7, what would the equilibrium vapor pressure be?

8.13 What would the vapor composition be for Problem 8.7?

8.14 Calculate the total of lb of O_2 in a gas phase of 3 ft^3 in volume that exists in equilibrium with 180 lb of water at 30°C. Assume Henry's law applies.

8.15 Calculate (a) the boiling point at atmospheric pressure, and (b) the composition of the vapor in equilibrium with the liquid, of the following mixture (in mole %) n-butane: 5.0, n-pentane: 17.0, n-hexane: 65.0, n-haptene: 10.0, n-octane: 3.0.