10.213 Chemical Engineering Thermodynamics
Spring 2000

Test 1 Solution (Test Date = February 25, 2000)

Problem 1 (40 points)

A frictionless piston-and-cylinder system shown in Figure A is subjected to 1.013 bar of external pressure. The piston mass is 200 kg, it has an area of 0.1 m^2, and the initial volume of the entrapped gas (40 mol % CO_2 and 60 mol % O_2) is 0.15 m^3. The piston and cylinder do not conduct heat, but heat can be added to the gas by a heating coil. The blocks in Figure A are removed so the piston can move freely.

a) If heat is added so to raise the temperature from 35 to 400 °C, determine the amount of added heat, the amount of work done by the piston, and the change in internal energy of the gas. You may assume that CO_2 and O_2 behave ideally under these conditions. (25 points)

SOLUTION TO A):

The process is constant pressure and we want Q, W and ΔU^t. For a constant pressure process,

$$Q = n_{total}\Delta H = n_{total}\int_{T_1}^{T_2} C_{p,eff}^{ig}\, dT$$

Thus, we need to determine the moles of CO_2 and O_2 in the chamber. As the gas can be assumed to behave ideally, $PV^t = n_{total}RT$, where we need to determine P, the pressure in the chamber.

$$P = P_{external} + \frac{mg}{A} = 1.013\, bar + \frac{(200\, kg)(9.8\, m/s^2)}{0.1\, m^2}\frac{1\, bar}{10^5\ \text{kg/m - s}^2} = (1.013 + 0.196)\, bar = 1.21\, bar$$

By ideal gas law, $n_{total} = \dfrac{PV^t}{RT} = \dfrac{(1.21\,\text{bar})(0.15\,\text{m}^3)}{(83.14\times10^{-6}\ \text{m}^3\text{ - bar / mol - K})(308\,\text{K})} = 7.08\ \text{moles}$

Thus, $n_{CO2} = 0.4\, n_{total} = 2.83$ moles and $n_{O2} = 0.6\, n_{total} = 4.25$ moles.

Returning to Q:

$$Q = n_{total}\Delta H = n_{CO2}\Delta H_{CO2} + n_{O2}\Delta H_{O2} = n_{CO2}\int_{T_1}^{T_2} C_{p,CO2}^{ig} dT + n_{O2}\int_{T_1}^{T_2} C_{p,O2}^{ig} dT$$

As T_1 = 308 K and T_2 = 673 K for both integrals, $Q = \int_{308K}^{673K}\left[n_{CO2}C_{p,CO2}^{ig} + n_{O2}C_{p,O2}^{ig}\right]dT$

$$Q = \int_{308K}^{673K}\left[A_{eff} + B_{eff}T + \frac{D_{eff}}{T^2}\right]RdT = R\left[A_{eff}(673-308) + \frac{B_{eff}}{2}\left(673^2 - 308^2\right) - D_{eff}\left(\frac{1}{673} - \frac{1}{308}\right)\right]$$

Where
$A_{eff} = n_{CO2}A_{CO2} + n_{O2}A_{O2} = (2.83)(3.639) + (4.25)(5.457) = 30.91$
$B_{eff} = n_{CO2}B_{CO2} + n_{O2}B_{O2} = (2.83)(0.506\text{x}10^{-3}) + (4.25)(1.045\text{x}10^{-3}) = 5.11\text{x}10^{-3}$
$D_{eff} = n_{CO2}D_{CO2} + n_{O2}D_{O2} = (2.83)(-0.227\text{x}10^{5}) + (4.25)(-1.157\text{x}10^{5}) = -4.24\text{x}10^{5}$

$$Q = R\left[(30.91)(673-308) + \frac{(5.11\text{x}10^{-3})}{2}\left(673^2 - 308^2\right) - (-4.24\text{x}10^5)\left(\frac{1}{673} - \frac{1}{308}\right)\right]$$

Q = (R)[(11282 + 915 - 747)mol-K] = (8.314 J/mol-K)(11450 mol-K) = **95.2 kJ (Q)**

For constant pressure case, $W = -n_{total}\int PdV$, where for ideal gas $W = -n_{total}\int RdT$

W = - (7.08 moles)(8.314 J/mol-K)(673 K – 308 K) = **-21.5 kJ (work done by piston = -W)**

For internal energy (ΔU^t), $\mathbf{DU^t}$ = Q + W = 95.2 kJ - 21.5 kJ = **73.7 kJ ($\mathbf{DU^t}$)**

b) If the operation were to be repeated and fresh gases were to be added to an empty chamber, determine what volumes of CO_2 and O_2 would need to be removed from compressed gas cylinders at 3650 psia that each contain a pure gas and are stored at 35 °C. Note that CO_2 and O_2 are not ideal gases as 3650 psia. (15 points)

SOLUTION TO PART B):

Want to know the volumes of CO_2 and O_2 that would need to be removed from tanks at 3650 psia and 35 °C in order to fill an empty chamber to contain 2.83 moles of CO_2 (n_{CO2}) and 4.25 moles of O_2 (n_{O2}). The gases do not behave ideally under the cylinder conditions.

In this problem, we are given P and T and need to find $V^t = nV$. Thus, the most direct way to solve the problem is to use generalized correlations.

For CO_2:

$T_c = 304.2$ K $\quad$ $P_c = 73.83$ bar $\quad$ and $\omega = 0.224$

$$\text{Thus } T_r = \frac{T}{T_c} = \frac{308\text{ K}}{304.2\text{ K}} = 1.01 \approx 1.0 \text{ and } P_r = \frac{P}{P_c} = \frac{3650\text{ psia}}{73.83\text{ bar}}\frac{1\text{ bar}}{14.504\text{ psia}} = 3.41 \approx 3.4$$

For $T_r = 1.0$ and $P_r = 3.4$, $Z^0 = 0.49$ and $Z^1 = -0.12$

As $Z = Z^0 + wZ^1 = 0.49 + (0.224)(-0.12) = 0.463$

$$V^t_{CO2} = \frac{n_{CO2}Z_{CO2}RT}{P} = \frac{(2.83\text{ mol})(0.463)(83.14\text{ cm}^3\text{-bar/mol-K})(308\text{ K})}{(3650\text{ psia})}\frac{14.5038\text{ psia}}{1\text{ bar}} = \mathbf{133\ cm^3}$$

For O_2:

$T_c = 154.6$ K $\quad$ $P_c = 50.43$ bar $\quad$ and $\omega = 0.022$

$$\text{Thus } T_r = \frac{T}{T_c} = \frac{308\text{ K}}{154.6\text{ K}} = 1.99 \approx 2.0 \text{ and } P_r = \frac{P}{P_c} = \frac{3650\text{ psia}}{50.43\text{ bar}}\frac{1\text{ bar}}{14.504\text{ psia}} = 4.99 \approx 5.0$$

For $T_r = 2.0$ and $P_r = 5.0$, $Z^0 = 0.975$ and $Z^1 = 0.275$

As $Z = Z^0 + wZ^1 = 0.975 + (0.022)(0.275) = 0.98$

$$V^t_{O2} = \frac{n_{CO2}Z_{CO2}RT}{P} = \frac{(4.25\text{ mol})(0.98)(83.14\text{ cm}^3\text{-bar/mol-K})(308\text{ K})}{(3650\text{ psia})}\frac{14.5038\text{ psia}}{1\text{ bar}} = \mathbf{424\ cm^3}$$

Problem 2 (30 points)

The process for making nitrobenzene is shown in Figure 1. Benzene and a mixture of nitric and sulfuric acids in water are fed to a reactor where the following reaction goes to completion:

$$C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$$

Benzene and nitric acid in the feed streams are in a stoichiometric ratio. Effluent from the reaction is phase separated and the acid solution, containing 70 wt % H_2SO_4, 30 wt % H_2O and no HNO_3, is re-concentrated in an evaporator. The resulting 93 wt % H_2SO_4 solution is recycled, mixed with fresh 64 wt % HNO_3 (36 wt % H_2O) and fed to the reactor. Calculate the values of B, S, W, C, and N, each expressed in tons per ton of nitrobenzene produced. Note: the molecular weights are C_6H_6 (78), HNO_3 (63), $C_6H_5NO_2$ (123), and H_2O (18).

SOLUTION:

The provided equation:

$$C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$$

gives useful stoichiometric information about the different chemical species. Overall, every mole of $C_6H_5NO_2$ produced requires that one mole of C_6H_6 and one mole of HNO_3 enter the process. We use 1 ton $C_6H_5NO_2$ of product as our basis. Thus, we can write:

for C_6H_6: $$B = 1\,\text{ton } C_6H_5NO_2 \frac{78 \text{ mass units } C_6H_6}{123 \text{ mass units } C_6H_5NO_2} \Rightarrow \mathbf{B = 0.634\ ton}\ C_6H_6$$

for HNO_3: $$(64\,\text{wt\%}\,HNO_3)\,N = 1\,\text{ton } C_6H_5NO_2 \frac{63 \text{ mass units } HNO_3}{123 \text{ mass units } C_6H_5NO_2} = 0.512 \text{ ton } HNO_3$$

N = 0.800 ton solution

Now, with values for B, N, and output nitrobenzene, we can do an overall mass balance to get W:

$$B + N = 1 \text{ ton } C_6H_5NO_2 + W$$
$$0.632 \text{ ton} + 0.800 \text{ ton} = 1 \text{ ton} + W; \quad \text{thus } \mathbf{W = 0.432\ ton}$$

H_2SO_4 balance around evaporator:

$$(70 \text{ wt \% } H_2SO_4)\, S = (93 \text{ wt \% } H_2SO_4)\, C$$
or $S = 1.33\, C$

H_2O balance around evaporator:

$$(30 \text{ wt \% } H_2O)\, S = (7 \text{ wt \% } H_2O)\, C + W$$

Subbing in S = 1.33 C and W = 0.432 ton water:

$$(0.3)(1.33\, C) = 0.07\, C + 0.432 \text{ ton} \quad \text{gives} \quad \mathbf{C = 1.31\ ton}$$

As S = 1.33 C, then **S = 1.75 ton**

Problem 3 (30 points)

A two-stage separator is shown in Figure 2. The stream to be extracted flows at a constant flow rate F moles/hr through the system. The solute concentration in the feed is x_0 moles solute per mole of solvent. The total flow of extractant is 2S moles/hr, and the feed concentration is y_3 moles per mole of extractant. Half of the extractant is fed to stage 2. The other half is mixed with the extractant effluent from stage 2 and fed to stage 1. The equilibrium relationship at each stage is

$$y_i = Kx_i$$

Determine an expression for x_2 that is a function of x_0, x_3, and B, where $x_3 = y_3/K$ and $B = SK/F$.

SOLUTION:

Material balance around unit 1 and the mixing point (Input = Output as no reaction/accumulation):

$$F x_0 + S y_2 + S y_3 = F x_1 + 2 S y_1$$

As $y_i = K x_i$, rewrite above equation in terms of x's:

$$F x_0 + S K x_2 + S K x_3 = F x_1 + 2 S K x_1$$

Divide through by F and substitute B for SK/F:

$$x_0 + B x_2 + B x_3 = x_1 + 2 B x_1$$

Can rewrite a:

$$B x_2 = (2 B + 1) x_1 - x_0 - B x_3 \quad (***)$$

Thus, need an expression for x_1 in terms of B, x_0, x_2, and x_3.

Material balance around unit 2:

$$F x_1 + S y_3 = F x_2 + S y_2$$

As $y_i = K x_i$, rewrite above equation in terms of x's:

$$F x_1 + S K x_3 = F x_2 + S K x_2$$

Divide through by F and substitute B for SK/F:

$$x_1 + B x_3 = x_2 + B x_2$$

Express as x_1 in terms of B, x_0, x_2, and x_3.

$$x_1 = x_2 + B x_2 - B x_3 \quad (\clubsuit\clubsuit)$$

Substitute the ♣♣'ed expression for x_1 into earlier ***'ed expression and solve for x_2:

$$B x_2 = (2 B + 1)(x_2 + B x_2 - B x_3) - x_0 - B x_3$$

$$B x_2 = x_2 (2 B^2 + 3 B + 1) + (2 B + 2)(- B x_3) - x_0$$

$$(2 B x_3)(B + 1) + x_0 = x_2 (2 B^2 + 2 B + 1)$$

$$\mathbf{x_2 = \frac{2B(B+1)x_3 + x_0}{2B^2 + 2B + 1}}$$

A strategic note for analyzing this problem: In the figure, there are eight variables: F, S, x_0, x_1, x_2, y_1, y_2, and y_3. As each "y_i" is proportional to an "x_i", the problem reduces to having seven variables: F, S, x_0, x_1, x_2, x_3, and K. We are asked to generate an equation for x_2 that includes only the variables x_0, x_3, and B where B = SK/F. Thus, we need to generate two independent equations that contain x_1 and would thus allow x_1 to be defined in terms of the other variables.