## Problem 13



The reaction occurring in the furnace is

 $CH_4 + 2O_2 CO_2 + 2H_2O_3$ 

On the basis of 1 mole per unit time of methane in the feed stream, we calculate the molar flow rate of the components in the feed stream (stream 1)  $n_{11} = 1$  mole

The stoichiometric amount of  $O_2$  is 2 mole. We use 20% excess. Therefore,  $n_{21} = 2 * 1.2 = 2.4$  mole

The ratio of N<sub>2</sub> to O<sub>2</sub> in air is 79:21. Therefore,  $n_{31} = 2.4 * 79 / 21 = 9.03$  mol

The feed stream is saturated with water vapor. Therefore the partial pressure of water in the feed stream equals the vapor (saturated) pressure of water.  $a = a^{-sat}$ 

 $p_4 = p_4{}^{sat}$ 

We can get the saturation pressure of water from the steam tables at 30 °C (S+VN p. 669).  $p_4^{sat} = 4.241 \text{ kPa} = p_4$ 

We know that the partial pressure equals the mole fraction multiplied by the total pressure.  $p_4 = x_{41} P$ 

Assuming that the furnace operates at 1 bar, we get  $x_{41} = 4.241 / 100 = 0.04241$ 

Now, can calculate the amount of water in stream 1.

 $x_{41} = \frac{n_{41}}{N_1} = \frac{n_{41}}{n_{11} + n_{21} + n_{31} + n_{41}}$  Subtracting the numerator from the denominator on both sides (math trick), we get

$$\frac{\mathbf{x}_{41}}{1 - \mathbf{x}_{41}} = \frac{\mathbf{n}_{41}}{\mathbf{n}_{11} + \mathbf{n}_{21} + \mathbf{n}_{31}}$$

Therefore,  $n_{41} = 0.04241 * (1 + 2.4 + 9.03) / (1 - 0.04241) = 0.551$  mole

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Now, we calculate the molar flow rates of the product stream. Since the reaction goes to completion  $\varepsilon = 1$  mole  $n_{12} = n_{11} + v_1 \varepsilon = 1 + (-1) 1 = 0$  mole  $n_{22} = 2.4 + (-2) 1 = 0.4$  mole  $n_{32} = 9.03$  mole  $n_{42} = 0.551 + (2) 1 = 2.551$  mole  $n_{52} = 0 + (1) 1 = 1$  mole  $N_2 = 0.4 + 9.03 + 2.551 + 1 = 12.981$  mole

With the usual assumptions that the kinetic and potential energy changes are negligible and the fact that there is no shaft work, the overall energy balance for the process reduces to  $\Delta H = Q$  (Q is heat transferred **to** the system). Since H is a state function, we use a path that simplifies the calculations as shown.



 $\Delta H = \Delta H_R^{o} + \Delta H_{298}^{o} + \Delta H_P^{o}$ 

The heat of reaction can be calculated from the heats of formation. Heats of formations at standard conditions and 298 K  $CH_4: -74,520 \text{ J}$   $CO_2: -393,509 \text{ J}$  $H_2O$  (g): -241,818

Since,

$$\Delta H^{\rm o} \equiv \sum_i \nu_i \, \Delta H^{\rm o}_{\rm fi}$$

Therefore,  $\Delta H^{0}_{298} = -393,509 + (2) (-241,818) - (-74,520) = -802,625 \text{ J}$ 

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The enthalpy change of the reactants as they are cooled from 303 K (30 °C) to 298 K is given by

$$\Delta H_{R}^{o} = \left(\sum_{i} n_{i} \left\langle C_{Pi}^{o} \right\rangle_{H}\right) (298 - 303) = \left\langle C_{P}^{o} \right\rangle_{H} (298 - 303)$$

To get  $\langle Cp^0 \rangle_H$  of the reactant stream, we use equation (4.8) (S+VN p. 122)

$$\frac{\langle C_{\rm p} \rangle_{\rm H}}{\rm R} = {\rm A} + \frac{{\rm B}}{2} {\rm T_o} (\tau + 1) + \frac{{\rm C}}{3} {\rm T_o}^2 (\tau^2 + \tau + 1) + \frac{{\rm D}}{\tau {\rm T_o}^2}$$

to get

$$\left\langle C_{P}^{o}\right\rangle_{H} = R\left(\sum_{i} n_{i}A_{i} + \frac{\sum_{i} n_{i}B_{i}}{2}T_{o}(\tau+1) + \frac{\sum_{i} n_{i}C_{i}}{3}T_{o}^{2}(\tau^{2}+\tau+1) + \frac{\sum_{i} n_{i}D_{i}}{\tau T_{o}^{2}}\right)$$

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From table C.1, we get

Component	А	10 <sup>3</sup> B	106 <sup>6</sup> C	10 <sup>-5</sup> D
1	1.702	9.081	-2.164	
2	3.639	0.506		-0.227
3	3.280	0.593		.040
4	3.470	1.450		0.121
5	5.457	1.045		-1.157

We have  $T_0 = 303$ , and  $\tau = 298/303 = 0.9835$ . Using the molar flow rate of the feed stream and the above equation, we get

 $\langle Cp^{o} \rangle_{H} = 387.300 \text{ J/K}$  (for reactant stream)

Therefore,  $\Delta H_R^o = 387.3 * (298 - 303) = -1,936.5 \text{ J}$ 

Repeating the same procedure for the product stream, we get  $\langle Cp^{o} \rangle_{H} = 456.409 \text{ J/mole K}$  (for product stream)

Therefore,  $\Delta H_P^{o} = 456.409 * (1573 - 298) = 581,921.5 \text{ J}$ 

 $\Delta H = -1,936.5 - 802,625 + 581,921.5 = -222,640 J$ 

Therefore  $Q = \Delta H = -222,640 \text{ J}$  (negative because heat is transferred **from** the system)

Since there is no reaction occurring in the heat exchanger, we know that the molar flow rates in stream 2 equals those in stream 3. However, it is important to realize that at 50 °C some of the water might condense. To check for that, we refer to the vapor pressure of water at 50 °C from the stream tables (S+VN p. 669).  $p_4^{sat} = 12.34 \text{ kPa}$ 

If there is no condensation, the partial pressure of water vapor in stream 3 will be  $p_4$  =  $n_{43}$  /  $N_3$  \*  $P_t$  = 2.551 / 12.981 \* 100 kPa = 19.65 kPa

Since the partial pressure of water vapor, can not exceed that of saturation, condensation occurs. Stream 3 becomes saturated with water. The mole fraction of water vapor is 0.1234. The total dry molar flow rate is (12.981 - 2.551 = 10.43 mole). To get the amount of water vapor, we use the following ratio  $n_{43}^{v} / N_{3}^{dry} = x_{43}^{v} / (1 - x_{43}^{v})$ 

Therefore,  $n_{43}^v = 0.1234 * 10.43 / (1 - 0.1234) = 1.468$  mole

The amount of water condensed  $n_{43}^{l} = 2.551 - 1.468 = 1.083$  mole

To get the enthalpy change, we follow the following path.



 $\Delta H_1 = \langle Cp^0 \rangle_H (323 - 1573)$ 

We get  ${<}Cp^o{>}_H$  as before taking into consideration the different temperature range.  ${<}Cp^o{>}_H$  = 457.559 J

Therefore,  $\Delta H_1 = 457.559 * (323 - 1573) = -571,949 \text{ J}$ 

 $\Delta H_2 = n^l_{43} \; \{ H^l(323 \; K, \; 1 \; bar) - H^v(323 \; K, \; 1 \; bar) \}$ 

If we make the assumptions that the enthalpy of liquid is not a function of pressure (a good assumption) and that water vapor at 1 bar behaves as an ideal gas (i.e. its enthalpy is not a function of pressure either), we can use the heat of vaporization at 323 K and any pressure. Therefore, we use the saturated steam tables (S+VN p. 699) to get the heat of vaporization at 323 K = 2592.2 kJ/kg. Therefore,  $\Delta H_2 = 1.083$  mole \* 18 g /1 mole \* (-2592.2 J/g) = -50,532 J

Therefore,  $Q_2 = -571,949 - 50,532 = -622,481 \text{ J}$