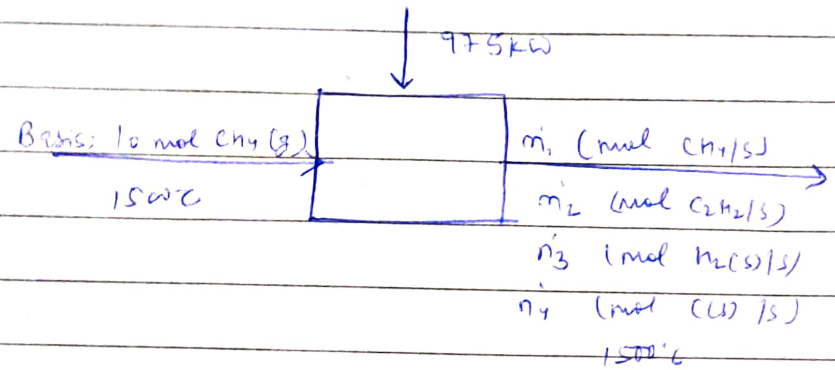
# ASSIGNMENT-8

9.36




$2CH_4 \longrightarrow C_2H_2 + 3H_2$

$C_2H_2 \longrightarrow 2C_{(s)} + H_2$

a) 60% conversion $\rightarrow \dot{n}_1 = 10(1-0.6) = 4$ mol $CH_4$/s

C balance: $10(1) = 4(1) + 2\dot{n}_2 + \dot{n}_4$

$2\dot{n}_2 + \dot{n}_4 = 6$ — (1)

H balance: $10(4) = 4(4) + 2\dot{n}_2 + 2\dot{n}_3$

$\dot{n}_2 + \dot{n}_3 = 12$ — (2)

References for enthalpy calculation

$C_{(s)}, H_{2(g)}$ @ 25°C

$H_i = (\Delta\hat{H}_f^{\circ})_i + C_{pi}(1500-25)$

$i = CH_4, C_2H_2, C, H_2$

| Substance | $\dot{n}_{in}$ (mol/s) | $\hat{H}_{in}$ (kJ/mol) | $\dot{n}_{out}$ (mol/s) | $\hat{H}_{out}$ (kJ/mol) |
|---|---|---|---|---|
| $CH_4$ (g) | 10 | 41.68 | 4 | 41.68 |
| $C_2H_2$ (g) | – | – | $\dot{n}_2$ | 303.45 |
| $H_2$ (g) | – | – | $\dot{n}_3$ | 45.32 |
| C(s) | – | – | $\dot{n}_4$ | 32.45 |

Energy balance:- $Q = \Delta H \Rightarrow 975 = \sum_{out} \dot{n}_i\hat{H}_i - \sum_{in} \dot{n}_i\hat{H}_i$ — (3)

Solving eqs. ①, ② & ③

$\dot{n}_2 = 2.5$ mol $C_2H_2/s$

$\dot{n}_3 = 9.5$ mol $H_2/s$

$\dot{n}_4 = 1$ mol C/s

Yield of Acetylene $= \dfrac{2.5 \text{ mol } C_2H_2/s}{6 \text{ mol } CH_4 \text{ consumed}/s} = 0.417$ mol $C_2H_2$/mol $CH_4$ consumed.

b) If there is no side reaction

$\dot{n}_1 = 10(1-0.6) = 4$ mol $CH_4/s$

$\dot{n}_3 = 0 \Rightarrow \dot{n}_2 = 3$ mol $C_2H_2/s$

$\dot{n}_1 = 9$ mol $H_2/s$

Yield of Acetylene $= \dfrac{3 \text{ mol } C_2H_2/s}{6 \text{ mol } CH_4 \text{ consumed}/s} = 0.5$ mol $C_2H_2$/mol $CH_4$ consumed.

Reactor Efficiency $= \dfrac{0.417}{0.5} = \underline{\underline{0.834}}$ or 83.4 %

9.43

a) $CaCl_2(s) + 10H_2O(l) \longrightarrow CaCl_2(aq, r=10)$ ① $\Delta\hat{H}_{r_1}^{\circ} = -64.85$ kJ/mol

$CaCl_2 \cdot 6H_2O(s) + 4H_2O(l) \longrightarrow CaCl_2(aq, r=10)$ ② $\Delta\hat{H}_{r_2}^{\circ} = 32.41$ kJ/mol

① − ② $\longrightarrow$ $CaCl_2(s) + 6H_2O(l) \longrightarrow CaCl_2 \cdot 6H_2O(s)$

Hess' Law $\Rightarrow \Delta\hat{H}_{r_3}^{\circ} = \Delta\hat{H}_{r_1}^{\circ} - \Delta\hat{H}_{r_2}^{\circ} = -97.26$ kJ/mol

b) From ①, $\Delta\hat{H}_{r_1}^{\circ} = (\Delta\hat{H}_f^{\circ})_{CaCl_2(aq, r=10)} - (\Delta\hat{H}_f^{\circ})_{CaCl_2(s)}$

$(\Delta\hat{H}_f^{\circ})_{CaCl_2(aq, r=10)} = (-64.85 - 794.96)$

$= -859.81$ kJ/mol

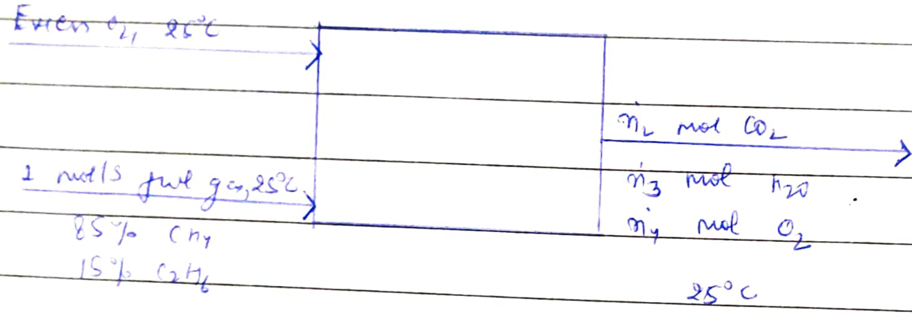
9.51 a) Basis:- 1 mol/s fuel gas

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(v)$

$\Delta \hat{H}_c^\circ = -890.36$ KJ/mol

$C_2H_6(g) + \frac{7}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(v)$

$\Delta \hat{H}_c^\circ = -1559.9$ KJ/mol




1 mol/s fuel gas → 0.85 mol $CH_4$/s, 0.15 mol $C_2H_6$/s

Theoretical Oxygen: $\frac{2 \text{ mol } O_2}{1 \text{ mol } CH_4} \Big| \frac{0.85 \text{ mol } CH_4}{s} + \frac{3.5 \text{ mol } O_2}{1 \text{ mol } C_2H_6} \Big| \frac{0.15 \text{ mol } C_2H_6}{s}$

$= 2.225$ mol $O_2$/s

Assume 10% excess $O_2$ ⇒ $O_2$ fed $= 1.1 \times 2.225 = 2.448$ mol $O_2$/s

C balance: $\dot{n}_2 = 0.85(1) + 0.15(2) \Rightarrow \dot{n}_2 = 1.15$ mol $CO_2$/s

H balance: $2\dot{n}_3 = 0.85(4) + 0.15(6) \Rightarrow \dot{n}_3 = 2.15$ mol $H_2O$/s

10% excess $O_2$: $\dot{n}_4 = 0.1(2.225) \Rightarrow \dot{n}_4 = 0.223$ mol $O_2$/s

Extents of reaction: $\xi_1 = \dot{n}_{CH_4} = 0.85$ mol/s

$\xi_2 = \dot{n}_{C_2H_6} = 0.15$ mol/s

Reference states: $CH_4(g)$, $C_2H_6(g)$, $N_2(g)$, $O_2(g)$, $H_2O(l)$, $CO_2(g)$

@ 25°C

Date
Page 4

| Substance | $\dot{n}_{in}$ mol | $\hat{H}_{in}$ kJ/mol | $\dot{n}_{out}$ mol | $\hat{H}_{out}$ kJ/mol |
|---|---|---|---|---|
| $CH_4$ | 0.85 | 0 | - | - |
| $C_2H_6$ | 0.15 | 0 | - | - |
| $O_2$ | 2.225 | 0 | 0.223 | 0 |
| $CO_2$ | - | - | 1.15 | 0 |
| $H_2O(v)$ | - | - | 2.15 | $H_1$ |

$\hat{H}_1 = \Delta\hat{H}_v \ (25°C) = 44.01$ kJ/mol

Energy Balance

$$\dot{Q} = \dot{n}_{CH_4} (\Delta \hat{H}^o_c)_{CH_4} + \dot{n}_{C_2H_6} (\Delta \hat{H}^o_c)_{C_2H_6} + \sum_{out} \dot{n}_i \hat{h}_i - \sum_{in} \dot{n}_i \hat{h}_i$$

$$= (0.85)(-890.36) + (0.15)(-1559.9) + 2.15\,(44.01)$$

$$= -896 \text{ kW}$$

$-\dot{Q} = 896$ kW (transfered from heater).

b) Constant volume Process :- Same as in part (a)

1 mol fuel gas $\Rightarrow$ 0.85 mol $CH_4$, 0.15 mol $C_2H_6$

Theoretical oxygen $\Rightarrow$ 2.225 mol $O_2$

Assume 10 % excess $O_2$ $\Rightarrow$ $O_2$ fed = 1.1 + 2.225 = 2.448 mol $O_2$

C balance : $n_2 = 0.85(1) + 0.15(2) \Rightarrow \dot{n}_2 = 1.15$ mol $CO_2$

H balance ; $2n_3 = 0.85(4) + 0.15(6) \Rightarrow \dot{n}_3 = 2.15$ mol $H_2O$

10 % excess $O_2$ $\Rightarrow$ $n_4 = 0.1(2.225)$ mol $O_2$ $\Rightarrow \dot{n}_4 = 0.223$ mol $O_2$

Reference states : $CH_4(g)$, $C_2H_6(g)$, $N_2(g)$, $O_2(g)$, $H_2O(l)$, $CO_2(g)$ @ 25 °C

| Substance | $n_{in}$ mol | $\hat{U}_{in}$ kJ/mol | $n_{out}$ mol | $\hat{U}_{out}$ kJ/mol |
|---|---|---|---|---|
| $CH_4$ | 0.85 | 0 | - | - |
| $C_2H_6$ | 0.15 | 0 | - | - |
| $O_2$ | 2.225 | 0 | 0.223 | 0 |
| $CO_2$ | - | - | 1.15 | 0 |
| $H_2O$ (v) | - | - | 2.15 | $\hat{U}_1$ |

$\hat{U}_v = \Delta\hat{U}_v(25°C) = \Delta\hat{H}_v(25°C) - RT = 44.01 \text{ kJ/mol} - \frac{8.314 \text{ J}}{\text{mol K}} \Big| \frac{1 \text{ kJ}}{10^3 \text{ J}} \Big| 298$

$= 41.53 \text{ kJ/mol}$

$$\Delta\hat{U}_c^{o} = \Delta\hat{H}_c^{o} - RT\left(\sum_{\substack{\text{gaseous}\\\text{products}}} \nu_i - \sum_{\substack{\text{gaseous}\\\text{reactants}}} \nu_i\right)$$

$$(\Delta\hat{U}_c^{o})_{CH_4} = (-890.36) - \frac{8.314 \text{ J}}{\text{mol K}} \Big| 298 \text{ K} \Big| (1+2-1-2) \Big| \frac{1 \text{ kJ}}{10^3 \text{ J}}$$

$= -890.36 \text{ kJ/mol}$

$$(\Delta\hat{U}_c^{o})_{C_2H_6} = (-1559.9) - \frac{8.314 \text{ J}}{\text{mol K}} \Big| 298 \text{ K} \Big| (3+2-3.5-1) \Big| \frac{1 \text{ kJ}}{10^3 \text{ J}}$$

$= -1561.14 \text{ kJ/mol}$

Energy balance

$$Q = \Delta U = n_{CH_4}(\Delta\hat{U}_c^{o})_{CH_4} + n_{C_2H_6}(\Delta\hat{U}_c^{o})_{C_2H_6} + \sum_{out} n_i\hat{U}_i - \sum_{in} n_i\hat{U}_i$$

$= 0.85(-890.36) + (0.15)(-1561.14) + 2.15(41.53)$

$= -902 \text{ kJ}$

$-Q = 902 \text{ kJ}$ (transferred from reactor).

c) Since the $O_2$ used is @ 25°C at both the inlet and outlet, their specific enthalpies or internal energies are 0 and their amounts therefore have no effect on the calculated values of $\Delta H$ & $\Delta U$.

9.5

$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

$C_2H_6 + \frac{7}{2} O_2 \longrightarrow 2CO_2 + 3H_2O$

Basis: 100 mol stack gas

$n_1$ (mol $CH_4$)

~~$n_2$ (mol $C_2H_6$)~~

$V_f$ ($m^3$ @ 25°C, 1 atm)

$n_3$ (mol $O_2$)

3.76 $n_3$ (mol $N_2$)

200°C, 1 atm

100 mol @ 200°C, 1 atm

0.0532 mol $CO_2$ / mol

0.0160 mol CO / mol

0.732 mol $O_2$ / mol

0.1224 mol $H_2O$ / mol

0.7352 mol $N_2$ / mol

a) $N_2$ balance: $3.76 n_3 = 100(0.7352) \Rightarrow n_3 = 19.55$ mol $O_2$ fed

C balance: $n_1(1) + n_2(2) = 100(0.0532)(1) + 100(0.0160)(1)$ — (1)

H balance: $n_1(4) + n_2(6) = 100(0.1224)(2)$ — (2)

Solving (1) & (2)

$n_1 = 3.72$ mol $CH_4$, $n_2 = 1.60$ mol $C_2H_6$

$$V_f = \frac{(3.72 + 1.60)\text{ mol fuel gas}}{} \left|\frac{22.4\text{ L (STP)}}{1\text{ mol}}\right|\frac{298.2\text{ K}}{273.2\text{ K}}\left|\frac{1\text{ m}^3}{10^3\text{ L}}\right| = 0.13\text{ m}^3$$

Theoretical $O_2$: $\dfrac{3.72 \text{ mol } CH_4 \mid 2 \text{ mol } O_2}{\mid 1 \text{ mol } CH_4} + \dfrac{1.6 \text{ mol } C_2H_6 \mid 3.5 \text{ mol } O_2}{\mid 1 \text{ mol } C_2H_6}$

$= 13.04$ mol $O_2$

Fuel composition: 3.72 mol $CH_4$ } 69.9 mole % $CH_4$

1.6 mol $C_2H_6$ } 30.1 mole % $C_2H_6$

% Excess air: $\dfrac{(19.55 - 13.04)\text{ mole } O_2 \text{ in excess}}{13.04 \text{ mol } O_2 \text{ required}} \times 100\% = 50\%$ excess air.

b) References: $C(s), H_2(g), O_2(g), N_2(g)$ @ $25°C$

| Substance | $n_{in}$ mol | $\hat{H}_{in}$ kJ/mol | $n_{out}$ mol | $\hat{H}_{out}$ kJ/mol |
|---|---|---|---|---|
| $CH_4$ | 3.72 | -74.85 | – | – |
| $C_2H_6$ | 1.60 | -84.67 | – | – |
| $O_2$ | 17.55 | 5.31 | 7.32 | 25.35 |
| $N_2$ | 73.52 | 5.13 | 73.52 | 23.86 |
| $CO$ | – | – | 1.6 | -86.39 |
| $CO_2$ | – | – | 5.32 | -356.1 |
| $H_2O$ | – | – | 12.24 | -212.78 |

$$\hat{H} = \Delta\hat{H}_f^\circ + \int_{25}^{T} C_p\,dT$$

$$= \Delta\hat{H}_f^\circ + \hat{H}_i(T) \text{ for } O_2, N_2, CO, CO_2, H_2O(v)$$

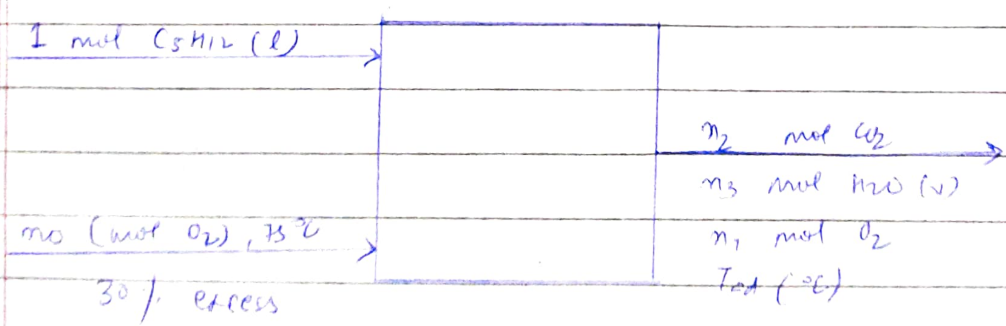
Energy Balance

$$Q = \Delta H = \sum_{out} n_i\hat{H}_i - \sum_{in} n_i\hat{H}_i = \frac{-2764\text{ kJ}}{0.130\text{ m}^3\text{ fuel}}$$

$$= -2.13\times10^4 \text{ kJ/m}^3 \text{ fuel}$$

9.65 Basis: 1 mol $C_5H_{12}(l)$

$C_5H_{12}(l) + 8O_2(g) \longrightarrow 5CO_2(g) + 6H_2O(v)$, $\Delta\hat{H}_c^\circ = -3509.5$ kJ/mol



Theoretical oxygen = $\frac{1 \text{ mol } C_5H_{12}}{} \Big| \frac{8 \text{ mol } O_2}{1 \text{ mol } C_5H_{12}} = 8 \text{ mol } O_2$

30 % excess $\rightarrow n = 1.3(8) = 10.4$ mol $O_2$

C balance: $n_2 = 1(5) \Rightarrow n_2 = 5$ mol $CO_2$

H balance: $2n_3 = 1(12) \Rightarrow n_3 = 6$ mol $H_2O$

30 % excess $O_2$, complete combustion

$\Rightarrow n_1 = 0.3(8)$ mol $O_2$

$n_1 = 2.4$ mol $O_2$

Reference states: $C_5H_{12}(l)$, $O_2(g)$, $H_2O(l)$, $CO_2(g)$ @ 25°C

| Substance | $n_{in}$ mol | $\hat{H}_{in}$ kJ/mol | $n_{out}$ mol | $\hat{H}_{out}$ kJ/mol |
|---|---|---|---|---|
| $C_5H_{12}$ | 1 | 0 | — | — |
| | 10.40 | $\hat{H}_2$ | 2.4 | $\hat{H}_2$ |
| | — | — | 5 | $\hat{H}_3$ |
| | — | — | 6 | $\hat{H}_4$ |

$$\hat{H}_i = \int_{25}^{T} (C_p)_i \, dT \quad i = 2, 3$$

$$= \Delta\hat{H}_v (25°C) + \int_{25}^{T} (C_p)_{H_2O(v)} \, dT \text{ for } H_2O(v)$$

$\hat{H}_1 = \hat{H}_{O_2}(75°C) = 1.48$ kJ/mol (from table B.8)

Substituting value of $(C_p)_i$ from table B.2

$$\hat{H}_2 = (0.0291 T_{ad} + 0.579 \times 10^{-5} T_{ad}^2 - 0.2025 \times 10^{-8} T_{ad}^3 + 0.3278 \times 10^{-12} T_{ad}^4 - 0.7311) \text{ kJ/mol}$$

$$\hat{H}_3 = (0.03611 T_{ad} + 2.1165 \times 10^{-5} T_{ad}^2 - 0.9623 \times 10^{-8} T_{ad}^3 + 1.866 \times 10^{-12} T_{ad}^4 - 0.9158) \text{ kJ/mol}$$

$\hat{H}_4 = 44.01 + (0.03376\, T_{ad} + 0.3470 \times 10^{-5}\, T_{ad}^2 + 0.2535 \times 10^{-8} \times T_{ad}^3 - 0.8183 \times 10^{-12}\, T_{ad}^4) - 0.8381$ kJ/mol

Doing Energy Balance : $\Delta H = 0$

$$n_{C_5H_{12}} (\Delta \hat{H}_c^{\circ})_{C_5H_{12}(l)} + \sum_{out} n_i \hat{H}_i - \sum_{in} n_i \hat{H}_i = 0$$

$(1 \text{ mol } C_5H_{12})(-3509.5) + (2.4)(\hat{H}_2) + (5)(\hat{H}_3) + (6)(\hat{H}_4) - (10.4)(\hat{H}_1) = 0$

Substitute for $\hat{H}_i$ through $\hat{H}_4$

$$\Delta i = [(0.4502)\, T_{ad} + (14.036 \times 10^{-5}\, T_{ad}^2) - (3.777 \times 10^{-8}\, T_{ad}^3) + (4.727 \times 10^{-12}\, T_{ad}^4) - 3272.20] = 0$$

$$\boxed{T_{ad} = 4414\,^{\circ}C}$$

b)

| Term | Tad | % Error |
|---|---|---|
| 1 | 7252 | 64.31 |
| 2 | 3481 | -21.1% |
| 3 | 3938 | -10.8% |

c)

| T | f(T) | f'(T) | Tnew |
|---|---|---|---|
| 7252 | 6.05E+3 | 3.74 | 5634 |
| 5634 | 1.73E+3 | 1.82 | 4680 |
| 4690 | 3.1E+2 | 1.22 | 4426 |
| 4426 | 1.41E+2 | 1.11 | 4414 |
| 4414 | 3.0 E-2 | 1.11 | 4414 |

d) The polynomial formulas are applicable only for $T \le 1500\,^{\circ}C$