9.25　a.　$CH_4(g) + O_2(g) \rightarrow HCHO(g) + H_2O(g)$

10 L, 200 kPa
n_0 (mol feed gas) at 25°C

0.85₁ mol CH₄/mol
0.15 mol O₂/mol

n_3 (mol HCHO)
n_4 (mol H_2O)
n_5 (mol CH₄)
T (°C), P(kPa), 10L.

Q (kJ)

$\underline{\text{Basis}}: n_0 = \dfrac{200\ kPa}{} \bigg| \dfrac{1000\ Pa}{1\ kPa} \bigg| \dfrac{10\ L}{} \bigg| \dfrac{10^{-3}\ m^3}{1\ L} \bigg| \dfrac{1\ mol\ K}{8.314\ m^3\ Pa} \bigg| \dfrac{}{298\ K}$

= 0.8072 mol feed gas mixture

$\underline{0.8072\ mol\ feed\ gas\ mixture} \Rightarrow (0.85)(0.8072) = 0.6861\ mol\ CH_4,$
$\Rightarrow (0.15)(0.8072) = 0.1211\ mol\ O_2$

$\underline{CH_4\ consumed}: \dfrac{1\ mol\ CH_4}{1\ mol\ O_2\ fed} \bigg| \dfrac{0.1211\ mol\ O_2\ fed}{} = 0.1211\ mol\ CH_4$

$\Rightarrow n_5 = (0.6861 - 0.1211)\ mol\ CH_4 = 0.5650\ mol\ CH_4$

$\underline{HCHO\ produced}: n_3 = \dfrac{1\ mol\ HCHO}{1\ mol\ CH_4\ consumed} \bigg| \dfrac{0.1211\ mol\ CH_4\ consumed}{} = 0.1211\ mol\ HCHO$

$\underline{H_2O\ produced}: n_4 = \dfrac{1\ mol\ H_2O}{1\ mol\ CH_4\ consumed} \bigg| \dfrac{0.1211\ mol\ CH_4\ consumed}{} = 0.1211\ mol\ H_2O$

$\underline{\text{Extent of reaction}}: \xi = \dfrac{|(n_{O_2})_{out} - (n_{O_2})_{in}|}{|v_{O_2}|} = \dfrac{|0 - 0.1211|}{|1|} = 0.1211\ mol$

References: $CH_4(g)$, $O_2(g)$, $HCHO(g)$, $H_2O(g)$, at 25°C

Substance	n_{in} mol	$\hat{U}_{in}$ kJ/mol	n_{out} mol	$\hat{U}_{out}$ kJ/mol
CH₄	0.6861	0	0.5650	$\hat{U}_1$
O₂	0.1211	0	–	–
HCHO	–	–	0.1211	$\hat{U}_2$
H₂O	–	–	0.1211	$\hat{U}_3$

$\hat{U}_i = \int_{25}^{T} (C_v)_i\, dT = \int_{25}^{T} (C_p - R)_i\, dT \quad i = 1,2,3$

Using $(C_p)_i$ from Table B.2 and $R = 8.314 \times 10^{-3}$ kJ / mol·K.

$\hat{U}_1 = (0.02599\,T + 2.7345 \times 10^{-5}\,T^2 + 0.1220 \times 10^{-8}\,T^3 - 2.75 \times 10^{-12}\,T^4 - 0.6670)$ kJ / mol

$\hat{U}_2 = (0.02597\,T + 2.1340 \times 10^{-5}\,T^2 - 2.1735 \times 10^{-12}\,T^4 - 0.6623)$ kJ / mol

$\hat{U}_3 = (0.02515\,T + 0.3440 \times 10^{-5}\,T^2 + 0.2535 \times 10^{-8}\,T^3 - 0.8983 \times 10^{-12}\,T^4 - 0.6309)$ kJ / mol

$Q = \dfrac{100\ J}{s} \bigg| \dfrac{85\ s}{} \bigg| \dfrac{1\ kJ}{1000\ J} = 8.5\ kJ$

$\Delta\hat{H}_r^o = (\Delta\hat{H}_f^o)_{HCHO} + (\Delta\hat{H}_f^o)_{H_2O} - (\Delta\hat{H}_f^o)_{CH_4} \overset{\text{Table B.1}}{=} ((-115.90) + (-241.83) - (-74.85))$ kJ / mol

$= -282.88$ kJ / mol

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

$= -282.88\ kJ\ /\ mol - \dfrac{8.314\ J}{mol\ K} \bigg| \dfrac{298\ K}{} \bigg| \dfrac{(1+1-1-1)}{} \bigg| \dfrac{1\ kJ}{10^3\ J} = -282.88\ kJ\ /\ mol$

Energy Balance :

$$Q = \xi \Delta \hat{U}_r^o + \sum (n_i)_{out} (\hat{U}_i)_{out} - \sum (n_i)_{in} (\hat{U}_i)_{in}$$

$$= (0.1211)(-282.88 \text{ kJ / mol}) + 0.5650 \, \hat{U}_1 + 0.1211 \, \hat{U}_2 + 0.1211 \, \hat{U}_3$$

⇓ Substitute for $\hat{U}_1$ through $\hat{U}_3$ and Q

$$0 = 0.02088 \, T + 1.845 \times 10^{-5} \, T^2 + 0.09963 \times 10^{-8} \, T^3 - 1.926 \times 10^{-12} \, T^4 - 43.29 \text{ kJ / mol}$$
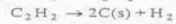
Solve for T using E - Z Solve $\Rightarrow T = 1091^\circ \text{C} = 1364 \text{ K}$

$$\Rightarrow P = nRT / V = \frac{0.8072 \text{ mol}}{} \left| \frac{8.314 \text{ m}^3 \cdot \text{Pa}}{\text{mol} \cdot \text{K}} \right| \frac{1364 \text{ K}}{10 \text{ L}} \left| \frac{1 \text{ L}}{10^{-3} \text{ m}^3} \right. = 915 \times 10^3 \text{ Pa} = \underline{915 \text{ kPa}}$$
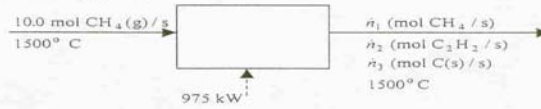
b. Add heat to raise the reactants to a temperature at which the reaction rate is significant.

c. Side reaction : $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$. T would have been higher (more negative heat of reaction for combustion of methane), volume and total moles would be the same, therefore $P = nRT / V$ would be greater.

9.36

$$2CH_4 \rightarrow C_2H_2 + 3H_2$$
$$C_2H_2 \rightarrow 2C(s) + H_2$$

Basis: 10 mol $CH_4(g)$ fed/s

10.0 mol $CH_4(g)/s$ $\dot{n}_1$ (mol CH_4/s)

1500° C $\dot{n}_2$ (mol C_2H_2/s)

                   $\dot{n}_3$ (mol $C(s)/s$)

                   1500° C

975 kW

a.

$\underline{60\% \text{ conversion}} \Rightarrow \dot{n}_1 = 10(1-0.600) = 4.00$ mol CH_4/s

$\underline{C \text{ balance:}}$ $10(1) = 4(1) + 2\dot{n}_2 + \dot{n}_4 \Rightarrow 2\dot{n}_2 + \dot{n}_4 = 6$ (1)

$\underline{H \text{ balance:}}$ $10(4) = 4(4) + 2\dot{n}_2 + 2\dot{n}_3 \Rightarrow 2\dot{n}_2 + 2\dot{n}_3 = 24$ (2)

$\underline{\text{References for enthalpy calculations}}$: $C(s)$, $H_2(g)$ at 25°C

$$H_i = \left(\Delta \hat{H}_f^o\right)_i + C_{pi}(1500-25), \; i = CH_4, C_2H_2, C, H_2$$

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
$H_2(g)$	–	–	$\dot{n}_3$	45.72
$C(s)$	–	–	$\dot{n}_4$	32.45

$\underline{\text{Energy Balance:}}$ $Q = \Delta H \Rightarrow 975$ kJ/s $= \displaystyle\sum_{out} \dot{n}_i \hat{H}_i - \sum_{in} \dot{n}_i \hat{H}_i$ (3)

Solve (1) - (3) simultaneously $\Rightarrow \begin{cases} \dot{n}_2 = 2.50 \text{ mol } C_2H_2/s \\ \dot{n}_3 = 9.50 \text{ mol } H_2/s \\ \dot{n}_4 = 1.00 \text{ mol } C/s \end{cases}$

$\underline{\text{Yield of acetylene}} = \dfrac{2.50 \text{ mol } C_2H_2/s}{6.00 \text{ mol } CH_4 \text{ consumed}/s} = 0.417$ mol C_2H_2/mol CH_4 consumed

b.

If no side reaction,

$\dot{n}_1 = 10.0(1-0.600) = 4.00$ mol CH_4/s

$\dot{n}_3 = 0 \Rightarrow \dot{n}_2 = 3.00$ mol C_2H_2/s, $\dot{n}_4 = 9.00$ mol H_2/s

$\underline{\text{Yield of acetylene}} = \dfrac{3.00 \text{ mol } C_2H_2/s}{6.00 \text{ mol } CH_4 \text{ consumed}/s} = 0.500$ mol C_2H_2/mol CH_4 consumed

$\underline{\text{Reactor Efficiency}} = \dfrac{0.417}{0.500} = 0.834$

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O(l)$, $HHV = -\Delta \hat{H}_c^o = 890.36$ kJ/mol (Table B.1)

$C_2H_6 + \frac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O(l)$, $HHV = 1559.9$ kJ/mol

$CO + \frac{1}{2}O_2 \rightarrow CO_2$, $HHV = 282.99$ kJ/mol
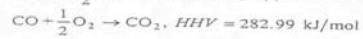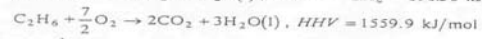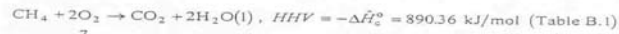
Initial moles charged: $\dfrac{2.000 \text{ L}}{\text{(Assume ideal gas)}} \left| \dfrac{273.2\text{K}}{(25+273.2)\text{K}} \right| \dfrac{2323 \text{ mm Hg}}{760 \text{ mm Hg}} \left| \dfrac{1 \text{ mol}}{22.4 \text{ L(STP)}} \right. = 0.25$ mol

Average mol. wt.: $(4.929 \text{ g})/(0.25 \text{ mol}) = 19.72$ g / mol

Let $x_1 = $ mol CH_4/mol gas, $x_2 = $ mol C_2H_6/mol gas $(\Rightarrow (1 - x_1 - x_2)$mol CO(mol gas))

$\overline{MW} = 19.72 \Rightarrow x_1(16.04 \text{ g/mol } CH_4) + x_2(30.07) + (1 - x_1 - x_2)(28.01) = 19.72$ (1)

$\overline{HHV} = 963.7$ kJ/mol $\Rightarrow x_1(890.36) + x_2(1559.9) + (1 - x_1 - x_2)(282.99) = 963.7$ (2)

Solving (1) & (2) simultaneously yields

$x_1 = \underline{0.725 \text{ mol } CH_4/\text{mol}}$, $x_2 = \underline{0.188 \text{ mol } C_2H_6/\text{mol}}$, $1 - x_1 - x_2 = \underline{0.087 \text{ mol } CO/\text{mol}}$