Q1 - Combustion of methane with 100% excess air

Calculate adiabatic flame temperature using mean $\bar{C_p}$

$$CH_4 + 4O_2 + 3.76 \times 4 N_2 \rightarrow CO_2 + 2H_2O + 2O_2 + 3.76 \times 4 N_2$$

Adiabatic flame temperature (T_{af}) is given by:

$$T_{af} = T_0 - \frac{m_f \Delta h_0}{\sum_{\text{Products}} m_i \bar{C_{p_i}}}$$

assuming reactants start at T_0 (25°C)

$\tilde{m}$	Products	n_i per kmol fuel	m_i per kmol of fuel	m_i per kg of fuel ($\tilde{m}_{CH_4} = 16$ kg/kmol)
44	CO_2	1	44	2.75
18	H_2O	2	36	2.25
32	O_2	2	64	4.0
28	N_2	15.04	421.12	26.32

[**Note** The Δh_0 used in this calculation must be that when water in products is as a vapour. This is because the enthalpy change evaluated by the expression $\sum m_i C_{p_i}$ does not include a term for any phase change in any of the products. If a Δh_0 corresponding to gross calorific value had been used, then a term must be added to $\sum m_i C_{p_i}$ equal to $m_{H_2O} h_{fg}$ (@25°C)]

Guess a flame temperature of 1500°C. Mean product temp is 763°C (1036K) - assume 1050K. Look up $\bar{C_p}$ from Table P17.

Q1 contd $\bar{C}_p \; CO_2 = 1{\cdot}247$ kJ/kgK
$\bar{C}_p \; H_2O = 2{\cdot}323$ "
$\bar{C}_p \; O_2 = 1{\cdot}097$ "
$\bar{C}_p \; N_2 = 1{\cdot}177$ "

$$\sum m_i \bar{C}_{pi} = (2{\cdot}75 \times 1{\cdot}247 + 2{\cdot}25 \times 2{\cdot}323 + 4 \times 1{\cdot}097 + 26{\cdot}32 \times 1{\cdot}177)$$
$$= 44{\cdot}02 \text{ kJ/K}$$

$\Delta h_0 = -50010$ kJ/kgK $(m_f = 1 \text{ kg})$

$$T_{af} = 25 - \frac{(-50010)}{44{\cdot}02} = 1161°C$$

This flame temp is lower than initial guess, so re-evaluate $\bar{C}_p$ at a lower temperature. If $T_{af} = 1161°C$, mean product temp $= 593°C$ $= 866$ K, assume 900K.

Look up new values for $\bar{C}_p$ from P17 of Tables

This then gives $\sum m_i C_{pi} = 42{\cdot}76$ kJ/K

$$T_{af} = 25 - \frac{(-50010)}{42{\cdot}76} = 1195°C \; (1468 \text{ K})$$

This is close to previous value of 1161°C so no need to iterate again

(i) Adiabatic flame temperature is 1470 K

ii) Calculate adiabatic flame temperature using molar enthalpies.

$$CH_4 + 4O_2 + 3{\cdot}76 \times 4 N_2 \longrightarrow CO_2 + 2H_2O + 2O_2 + 3{\cdot}76 \times 4 N_2$$

For adiabatic combustion $\sum\limits_{\text{reactants}} n_i \tilde{h}_i = \sum\limits_{\text{products}} n_i \tilde{h}_i$

$$\tilde{h} = \underbrace{\tilde{h}_{f_0}}_{\hookrightarrow \text{ enthalpy of formation.}} + \Delta \tilde{h}$$

All reactants are at 25°C $\therefore \Delta\tilde{h} = 0$ for reactants

For N_2 & O_2, $\tilde{h}_{fo} = 0$ as they are elements.

$$\therefore \sum_{\text{reactants}} n_i \tilde{h}_i = \tilde{h}_{fo\,CH_4} = -74906 \text{ kJ}$$

For products $\sum n_i \tilde{h}_i$ is:

$$\underbrace{(\underset{\substack{\downarrow\\-393520}}{\tilde{h}_{fo}} + \Delta h)_{CO_2} + 2(\underset{\substack{\downarrow\\-241830}}{\tilde{h}_{fo}} + \Delta\tilde{h})_{H_2O}}_{\text{Tables P.22}} + 2(\underset{\substack{\downarrow\\=0}}{\cancel{\tilde{h}_{fo}}} + \Delta\tilde{h})_{O_2} + 3{\cdot}76\times4(\underset{\substack{\downarrow\\=0}}{\cancel{\tilde{h}_{fo}}} + \Delta\tilde{h})_{N_2}$$

$\Delta\tilde{h}$ = enthalpy as given on P18-20 of Table as these assume $h=0$ at 25°C

Guess an adiabatic flame temp of 1600K

$$\sum_{\text{Products}} n_i\tilde{h}_i = -393520 + 67580 + 2(-241830 + 52844) + 2(44279) + 15{\cdot}04(41903)$$

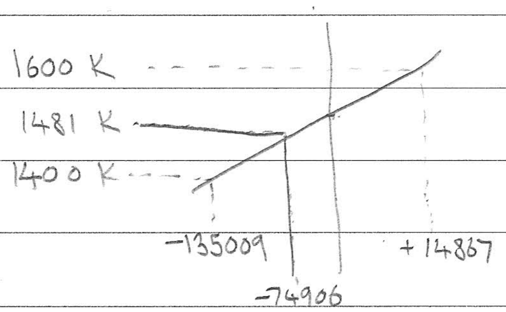
$= 14867$ kJ ← too high, should be -74906 kJ

Try Temp = 1400K

$$\sum n_i\tilde{h}_i = -393520 + 55907 + 2(-241830 + 43447) + 2(36966) + 15{\cdot}04(34936)$$

$= -135009$ kJ ← too low

by linear interpolation



ii) Adiabatic flame temperature = 1481 K

Q2. $\log_e K^\ominus = \dfrac{-\Delta G^\ominus_{(T)}}{\tilde{R}T}$ $\tilde{R} = 8.314$ kJ/kmol

$$\Delta G^\ominus_{(T)} = \underset{\text{Products}}{\sum} n_i \tilde{g}^\ominus_{i(T)} - \underset{\text{Reactants}}{\sum} n_i \tilde{g}^\ominus_{i(T)}$$

$$\tilde{g} = \tilde{h} - T\tilde{s}$$

Reaction is $CO + H_2O \rightleftharpoons CO_2 + H_2$

At 1200K

Products	CO_2	H_2	
$\tilde{h}_{f0}$	−393520	0	kJ/kmol
$\Delta\tilde{h}_i$	44484	26794	"
$\tilde{s}_i$	279.31	171.68	kJ/kmolK
$\tilde{g}_i$	−863430		kJ/kmol

Reactants	CO	H_2O	
$\tilde{h}_{f0}$	−110530	−241827	kJ/kmol
$\Delta\tilde{h}_i$	28426	34476	"
$\tilde{s}_i$	240.56	240.33	kJ/kmolK
$\tilde{g}_i$	−866523		kJ/kmol

$\Delta G^\ominus_{(T)} = +3093$ kJ/kmol at 1200K

$\therefore -\Delta G/\tilde{R}T \; (\log_e K^\ominus) = -0.310$ (This is −1× value in Tables as reaction is written other way round)

$\underline{K^\ominus = 0.7334}$

Q3.

$$0.4\,CO + 0.2\,H_2O \longrightarrow w\,CO + x\,H_2O + y\,CO_2 + z\,H_2$$

At equilibrium

$$w\,CO + x\,H_2O \rightleftharpoons y\,CO_2 + z\,H_2$$

$w + y = 0.4$ — carbon balance $y = (0.4 - w)$

$x + z = 0.2$ — H_2 balance

$w + x + 2y = 0.6$ — O balance.

$\underline{y = 0.4 - w}$

$w + x + 0.8 - 2w = 0.6$

$\underline{x = w - 0.2}$

$z + w - 0.2 = 0.2.$

$\underline{z = 0.4 - w}$

As there is no change in the number of moles as the reaction takes place $n = 0.6.$

Pressure can be calculated from $pV = n\tilde{R}T$

$$p = \frac{0.6 \times 8314 \times 1110}{10} = 5.537 \text{ bar}$$

Calc $K^{\ominus}$ from $\dfrac{(x_{CO_2})(x_{H_2})}{(x_{CO})(x_{H_2O})} \underset{=1}{\cancel{(R)}^{n}}$

$\leftarrow\rightarrow$ n=0 in this case as all stoichiometric coeffs are = 1.

x_i = mole fractions

$$K = \frac{\left(\frac{0.4-w}{0.6}\right)\cdot\left(\frac{0.4-w}{0.6}\right)}{\left(\frac{w}{0.6}\right)\left(\frac{w-0.2}{0.6}\right)} = 0.909.$$

$$\therefore \quad (0.4 - w)^2 = w(w - 0.2)\,0.909$$

$$0.16 - 0.8w + w^2 = w^2\,0.909 - 0.1818w$$

$$0.091w^2 - 0.6182w + 0.16 = 0$$

$$w = \frac{0.6182 \pm 0.5691}{0.182} = 0.2698$$ (other value is impossible)

$x_{CO_2} = 0.217$, $x_{H_2} = 0.217$

$x_{CO} = 0.450$, $x_{H_2O} = 0.116$

Q3 CONT.

$$\therefore \quad x_i = \frac{p_i}{p} \qquad \therefore \quad p_i = p x_i$$

$\therefore$ Partial pressures are :

x_i

$CO \rightarrow 2.49$ bar

$H_2O \rightarrow 0.644$

$CO_2 \rightarrow 1.202$ bar

$H_2 \rightarrow 1.202$ bar

Q4.

Mole fractions

$x_{CO_2} = 0.0974$

$x_{CO} = 0.0074$

$x_{H_2O} = 0.1165$

$x_{H_2} = 0.0015$

$x_{O_2} = 0.0371$

$x_{N_2} = 0.740$

$P = 5$ bar

$K^\ominus$ for reaction $CO + \frac{1}{2}O_2 \rightleftharpoons CO_2$ is

$$K^\ominus = \frac{(x_{CO_2})}{(x)_{CO}\,(x)_{O_2}^{\frac{1}{2}}} \left(p\right)^{(1-1.5)}$$

$\underline{K^\ominus = 30.6}$ at 2500 K

For reaction $H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O$

$$\frac{(x_{H_2O})}{(x_{H_2})(x_{O_2})^{\frac{1}{2}}} (p)^{(1-1.5)}$$

$\underline{K^\ominus = 180.3}$ at 2500 K

Q5(a) $$NH_3 \rightleftharpoons \tfrac{1}{2}N_2 + \tfrac{3}{2}H_2$$

$$(1-\alpha)\,NH_3 \rightleftharpoons \frac{\alpha}{2}N_2 + \frac{3\alpha}{2}H_2$$

Total No. of moles $= (1-\alpha) + \frac{\alpha}{2} + \frac{3\alpha}{2} = (1+\alpha)$

$$K^{\ominus} = \frac{(x_{N_2})^{\frac{1}{2}}(x_{H_2})^{1.5}}{(x_{NH_3})}\left(\frac{p}{p_0}\right)$$

$$= \frac{(\alpha)^{\frac{1}{2}}}{\sqrt{2}\,(1+\alpha)^{\frac{1}{2}}}\left(\frac{3\alpha}{2(1+\alpha)}\right)^{\frac{3}{2}}\frac{(1+\alpha)}{(1-\alpha)}\left(\frac{p}{p_0}\right)$$

$$= \frac{\alpha^{\frac{1}{2}}(3)^{\frac{3}{2}}\alpha^{\frac{3}{2}}\cancel{(1+\alpha)}}{\sqrt{2}\,(2)^{\frac{3}{2}}\cancel{(1+\alpha)}(1-\alpha)(1+\alpha)}$$

$$K^{\ominus} = \frac{3\sqrt{3}}{4}\left(\frac{\alpha^2}{(1-\alpha^2)}\right)\left(\frac{p}{p_0}\right)$$

Q5(b) When $T = 400°C$ & $p = 1$ bar $\Delta G = -23730$ kJ/kmol

$$-\frac{\Delta G}{RT} = \log_e K = \frac{23730}{8.314 \times 673} = 4.241$$

$$K = 69.5 \text{ at } 400°C$$

At $p = 300$ bar $$69.5 = \frac{3\sqrt{3}}{4}\frac{\alpha^2}{(1-\alpha^2)}\left(\frac{300}{1}\right)$$

$$\frac{\alpha^2}{(1-\alpha^2)} = 0.17833$$

$$\alpha^2 = \frac{0.17833}{1.17833} \qquad \alpha = 0.389$$

$$\therefore \quad x_{NH_3} = \frac{(1-\alpha)}{} = 0.44$$

Q5(b) At $P = 600$ bar

$$69.5 = \frac{3\sqrt{3}}{4}\frac{\alpha^2}{(1-\alpha^2)}\left(\frac{600}{1}\right)$$

$$\therefore \quad \frac{\alpha^2}{(1-\alpha^2)} = 0.08917$$

$$\alpha^2 = \frac{0.08917}{1.08917}, \quad \alpha = 0.286$$

$$\therefore \quad x_{NH_3} = \frac{(1-\alpha)}{(1+\alpha)} = 0.5551$$

Thus as pressure increases more ammonia is formed as the mole fraction of ammonia increases.