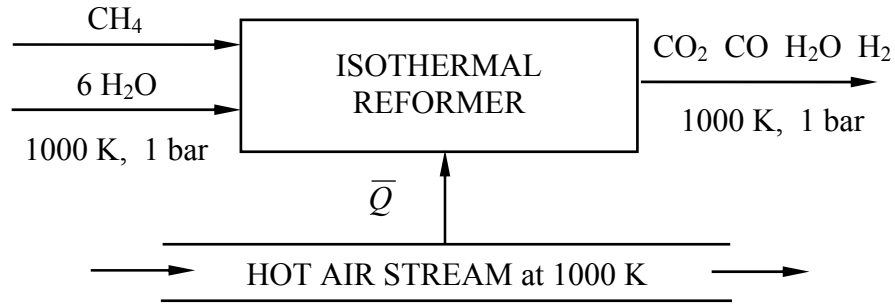**ENGINEERING TRIPOS   PART IIA   2013**

MODULE 3A5 – THERMODYNAMICS AND POWER GENERATION
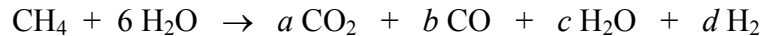

SOLUTIONS TO TRIPOS QUESTIONS

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1.

(a) The chemical reaction is :

$$CH_4 + 6\,H_2O \rightarrow a\,CO_2 + b\,CO + c\,H_2O + d\,H_2$$

Conservation of atomic C : $a + b = 1$

Conservation of atomic O : $2a + b + c = 6$ $\rightarrow$ $a + c = 5$

Conservation of atomic H : $2c + 2d = 16$ $\rightarrow$ $c + d = 8$

If $b = 0.366$ (given), then $a = 0.634$, $c = 4.366$, $d = 3.634$ [10%]

The equilibrium equation for the water-gas shift reaction (Reaction 8 in the Data Book) is,

$$\left(\frac{p_{CO}}{p_0}\right)^{-1}\left(\frac{p_{H_2O}}{p_0}\right)^{-1}\left(\frac{p_{CO_2}}{p_0}\right)^{+1}\left(\frac{p_{H_2}}{p_0}\right)^{+1} = K_{p8}(T)$$

where p_0 is standard pressure (1 bar). The partial pressures are,

$$p_{CO_2} = \frac{a}{n}p,\quad p_{CO} = \frac{b}{n}p,\quad p_{H_2O} = \frac{c}{n}p,\quad p_{H_2} = \frac{d}{n}p,$$

where p is the actual mixture pressure and $n = a + b + c + d$. Hence,

$$K_{p8}(T) = \frac{a\,d}{b\,c} = \frac{0.634 \times 3.634}{0.366 \times 4.366} = 1.4418$$

From the Data Book, $\ln(K_{p8}) = 0.366$, so $K_{p8} = 1.4419$. Hence the gas mixture in the outlet stream is at chemical equilibrium subject to the water-gas shift reaction.   [15%]

(b) The SFEE applied to the reformer gives (per kmol CH_4 supplied),

$$\overline{Q} = (a\,\overline{h}_{CO_2} + b\,\overline{h}_{CO} + c\,\overline{h}_{H_2O} + d\,\overline{h}_{H_2}) - (\overline{h}_{CH_4} + 6\,\overline{h}_{H_2O})$$

$$= (0.634\,\overline{h}_{CO_2} + 0.366\,\overline{h}_{CO} + 4.366\,\overline{h}_{H_2O} + 3.634\,\overline{h}_{H_2}) - (\overline{h}_{CH_4} + 6\,\overline{h}_{H_2O})$$

$$= 0.634\,\overline{h}_{CO_2} + 0.366\,\overline{h}_{CO} - 1.634\,\overline{h}_{H_2O} + 3.634\,\overline{h}_{H_2} - \overline{h}_{CH_4}$$

where all the molar enthalpies are evaluated at 1000 K.

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By definition,

$$[\Delta \overline{H}_{1000}^0]_{ref} = \overline{h}_{CO} + 3\overline{h}_{H_2} - \overline{h}_{CH_4} - \overline{h}_{H_2O}$$

$$[\Delta \overline{H}_{1000}^0]_{shift} = \overline{h}_{CO_2} + \overline{h}_{H_2} - \overline{h}_{CO} - \overline{h}_{H_2O}$$

Hence,

$$[\Delta \overline{H}_{1000}^0]_{ref} + 0.634[\Delta \overline{H}_{1000}^0]_{shift} =$$

$$0.634\overline{h}_{CO_2} + 0.366\overline{h}_{CO} + 3.634\overline{h}_{H_2} - 1.634\overline{h}_{H_2O} - \overline{h}_{CH_4} = \overline{Q} \qquad [25\%]$$

(c) The SFSE applied to the reformer gives (per kmol CH_4 supplied),

$$\Delta \overline{S}_{irrev} + \frac{\overline{Q}}{T} = (a\overline{s}_{CO_2} + b\overline{s}_{CO} + c\overline{s}_{H_2O} + d\overline{s}_{H_2}) - (\overline{s}_{CH_4} + 6\overline{s}_{H_2O})$$

where all molar entropies are evaluated at 1000 K and 1 bar (as instructed in the question). Proceeding as for (b) but replacing h with s gives,

$$\Delta \overline{S}_{irrev} = [\Delta \overline{S}_{1000}^0]_{ref} + 0.634[\Delta \overline{S}_{1000}^0]_{shift} - \frac{\overline{Q}}{T} \qquad [30\%]$$

(d) Evaluating $\overline{Q}$ and $\Delta \overline{S}_{irrev}$ gives,

$$\overline{Q} = 225.70 + 0.634 \times (-34.74) = 203.67 \text{ MJ/(kmol } CH_4)$$

$$\Delta \overline{S}_{irrev} = 0.253 + 0.634 \times (-0.032) - \frac{203.67}{1000} = 0.0290 \text{ MJ/(kmol } CH_4)/K$$

If the environment is at $T_0 = 298.15$ K, then the lost work due to irreversible entropy creation in the reformer is $T_0 \Delta \overline{S}_{irrev}$. Hence the maximum possible rational efficiency of a power plant supplied by methane at 25 °C and 1 bar is,

$$[\eta_{rational}]_{max} = 1 - \frac{T_0 \Delta \overline{S}_{irrev}}{[-\Delta G_{298}^0]} = 1 - \frac{298.15 \times 0.0290}{800.70} = 0.989 \equiv 98.9 \% \qquad [20\%]$$

2. (a) (i) Making the approximations h_{fg} = constant, $v_f \ll v_g$ and $v_g = RT/p_{sat}$ we obtain,

$$\frac{dp_{sat}}{p_{sat}} = \frac{h_{fg}}{R}\frac{dT}{T^2} \quad \rightarrow \quad \ln(p_{sat}) = -\frac{h_{fg}}{RT} + \text{const.}$$

Hence, given that $p_{sat} = p_{sat,0}$ at $T = T_0$,

$$p_{sat} = p_{sat,0} \exp\left[\frac{h_{fg}}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]$$

[15%]

(ii) Applying $Tds = dh - vdp$ to small changes in saturated vapour states,

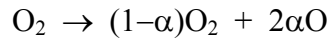$$T\frac{ds_g}{dT} = \frac{dh_g}{dT} - v_g\frac{dp_{sat}}{dT}$$

As the saturated vapour behaves as a perfect gas, $dh_g/dT = c_{pg}$. Thus,

$$\frac{ds_g}{dT} = \frac{c_{pg}}{T} - \frac{h_{fg}}{T^2} \quad \rightarrow \quad s_g = c_{pg}\ln(T) + \frac{h_{fg}}{T} + \text{const.}$$

Hence, as $s_g = s_{g,0}$ at $T = T_0$,

$$s_g = s_{g,0} + c_{pg}\ln\left(\frac{T}{T_0}\right) + h_{fg}\left(\frac{1}{T} - \frac{1}{T_0}\right)$$

[25%]

(b) If the degree of dissociation is α then,

$$O_2 \rightarrow (1-\alpha)O_2 + 2\alpha O$$

Total number of moles, $n = 1+\alpha$. The mole fractions are,

$$X_{O_2} = \frac{1-\alpha}{1+\alpha} \qquad X_O = \frac{2\alpha}{1+\alpha}$$

[10%]

Denote the half dissociated state by subscript 1 and the reduced pressure state by subscript 2. As a mixture of ideal gases behaves itself as a ideal gas, we have,

$$\frac{V_2}{V_1} = \frac{p_1}{p_2}\frac{n_2}{n_1} = \frac{p_1}{p_2}\frac{(1+\alpha_2)}{(1+\alpha_1)}$$

[10%]

For the reaction $-2O + O_2 = 0$, the equation of chemical equilibrium is,

$$K_p(T) = \left(\frac{p_O}{p_0}\right)^{-2}\left(\frac{p_{O_2}}{p_0}\right)^{+1} = \left(\frac{X_O p}{p_0}\right)^{-2}\left(\frac{X_{O_2} p}{p_0}\right)^{+1} = \frac{X_{O_2}}{(X_O)^2}\frac{p_0}{p} = \frac{(1-\alpha)(1+\alpha)}{4\alpha^2}\frac{p_0}{p}$$

[10%]

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where p_0 is standard pressure (1 bar). Because the sample pressure is reduced isothermally the equilibrium constant does not change so that,

$$\frac{(1-\alpha_1^2)}{4\alpha_1^2}\left(\frac{p_0}{p_1}\right) = \frac{(1-\alpha_2^2)}{4\alpha_2^2}\left(\frac{p_0}{p_2}\right) \qquad\qquad [10\%]$$

We have $\alpha_1 = 1/2$ and $p_2/p_1 = 1/3$. Hence,

$$\frac{(1-\alpha_2^2)}{4\alpha_2^2} = \frac{1}{4} \quad \rightarrow \quad \alpha_2 = \frac{1}{\sqrt{2}} \qquad\qquad [10\%]$$

Finally,

$$\frac{V_2}{V_1} = \frac{p_1}{p_2}\frac{(1+\alpha_2)}{(1+\alpha_1)} = 3\times\frac{(1+1/\sqrt{2})}{(1+1/2)} = (2+\sqrt{2}) \qquad\qquad [10\%]$$

3. The following designations for points around the cycle will be used:

1 – compressor inlet

2 – compressor exit

3 – turbine inlet

4 – turbine exit

4' – combustor inlet (with recuperation)

(a) A recuperated gas turbine cycle employs a heat exchanger to transfer heat from the turbine exhaust gas to the air at compressor exit. The aim is to increase the temperature of the air entering the combustor and therefore reduce the amount of fuel needed to achieve the same temperature at turbine inlet.

[5%]
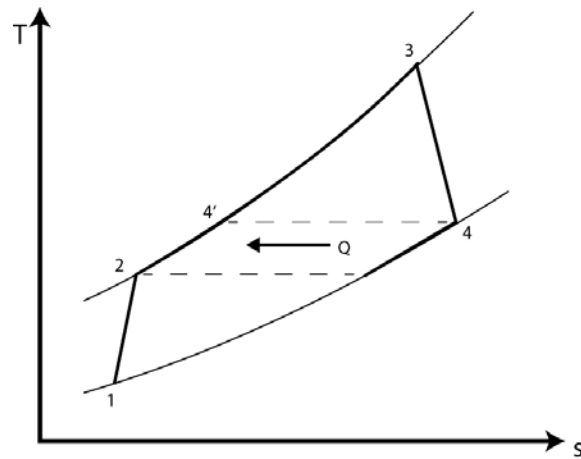
[5%]

(b) Recuperation can only work if the turbine exit temperature T_4 is higher than the compressor exit temperature T_2.

[5%]

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{\frac{\gamma-1}{\gamma\eta}} = r_t^{1/\eta}$$

$$\frac{T_3}{T_4} = \left(\frac{p_3}{p_1}\right)^{\frac{(\gamma-1)\eta}{\gamma}} = r_t^{\eta}$$

$$T_4 = \frac{T_3}{r_t^{\eta}} = \frac{\theta T_1}{r_t^{\eta}}$$

and we require $T_4 > T_2$, so that $\dfrac{\theta T_1}{r_t^{\eta}} > T_1 r_t^{1/\eta}$ and hence $\theta > r_t^{\frac{\eta^2+1}{\eta}}$.

[15%]

5

(c) c_p is the same for the gas on both sides of the heat exchanger, as is the mass flow. So the effectiveness is given by,

$$\varepsilon = 0.8 = \frac{T_{4'} - T_2}{T_4 - T_2}$$

$$T_{4'} = \varepsilon T_1 \left(\frac{\theta}{r_t^\eta} - r_t^{1/\eta} \right) + T_1 r_t^{1/\eta}$$

$$\eta_c = \frac{w_t - w_c}{q_{in}} = \frac{(T_3 - T_4) - (T_2 - T_1)}{(T_3 - T_{4'})}$$

$$\eta_c = \frac{\theta T_1 (1 - 1/r_t^\eta) - T_1 (r_t^{1/\eta} - 1)}{\theta T_1 - \left[\varepsilon T_1 \left(\dfrac{\theta}{r_t^\eta} - r_t^{1/\eta} \right) + T_1 r_t^{1/\eta} \right]}$$

with $\theta = 5.5$, $r_t = 2$, $\eta = 0.9$ and $\varepsilon = 0.8$ we obtain $\eta_c = 0.514$

(d)   A pressure drop in the recuperator will reduce cycle efficiency because it will both reduce the turbine inlet pressure and increase the turbine exit pressure. Hence less work obtained from the turbine.

(e)   If an inter-cooler is used in the compressor, the compressor delivery temperature would be reduced. This would allow the GT to operate at a higher pressure ratio while still having the turbine exit temperature greater than the compressor exit temperature (the condition required for a recuperator).

A cycle with an inter-cooler in the compressor, a reheat stage in the turbine and a recuperator would mean raise the average temperature of heat addition and drop the average temperature of heat rejection. This would raise the cycle efficiency.

4. The following designations for points around the cycle will be used:

    1 – condenser exit: $h_1 = 121.4$ kJ/kg; $s_1 = 0.422$ kJ/kgK

    2 – feed pump exit: $h_2 = h_1$

    3 – boiler exit: $h_3 = 3450.4$ kJ/kg; $s_3 = 6.5230$ kJ/kgK

    4 – turbine exit

    4s – turbine exit for an isentropic turbine

    g – saturated vapour at condenser pressure: $h_g = 2553.7$ kJ/kg; $s_g = 8.473$ kJ/kgK

    b – condition at which steam is bled from the turbine

    f – feedheater exit

(a) $s_{4s} = s_3$ (isentropic expansion)

    dryness fraction at turbine exit for isentropic turbine, x4s:

    $x_{4s} = (s_{4s} - s_1) / (s_g - s_1) = (6.5230 - 0.422) / (8.473 - 0.422) = 0.76$

    $h_{4s} = h_1 + x_{4s} (h_g - h_1) = 121.4 + 0.76 (2553.7 - 121.4) = 1964.6$ kJ/kg

    using the definition of isentropic efficiency,

    $0.85 = (h_3 - h_4) / (h_3 - h_{4s})$

    $h_4 = h_3 - 0.85(h_3 - h_{4s}) = 3450.4 - 0.85(3450.4 - 1964.6) = 2187.5$ kJ/kg

    $x_4 = (h_4 - h_1) / (h_g - h_1) = (2187.5 - 121.4) / (2553.7 - 121.4) = 0.85$

    $w_t = h_3 - h_4 = 3450.4 - 2187.5 = 1263$ kJ/kg

    $\eta_c = w_t / (h_3 - h_1) = 1263 / (3450.4 - 121.4) = 0.38$ [25%]

(b) from steam chart (straight expansion line, $p_b = 10$ bar):

    $h_b = 2890$ kJ/kg; $s_b = 6.83$ kJ/kg K

    at feedheater exit (saturated water at 10 bar):

    $h_f = 762.5$ kJ/kg

    $s_f = 2.138$ kJ/kgK   [5%]

    (i) SFEE for feedheater:

        $hf = (1 - m) h_1 + m h_b$

        $m = (h_f - h_1)/(h_b - h_1) = (762.5 - 121.4) / (2890 - 121.4) = 0.23$ [10%]

    (ii) $w_t = (h_3 - h_b) + (1 - m)(h_b - h_4)$

        $= (3450.4 - 2890) + (1 - 0.23)(2890 - 2187.5)$

        $= 1100$ kJ/kg

        $\eta_c = w_t / (h_3 - h_f) = 1100 / (3450.4 - 762.5) = 0.41$ [15%]

(c)   Assume a reversible all devices between inlet and exit states are reversible (e.g. turbine and feedheater(s)). Assume that all heat is exchanged with the environment at the condenser temperature, T_1.

$T_1 = 302.11$ K

$$w_{max} = e_3 - e_f$$
$$= (h_3 - T_1 s_3) - (h_f - T_1 s_f)$$
$$= (3450.4 - 762.5) - 302.11(6.5230 - 2.138)$$
$$= 1363.1 \text{ kJ/kg}$$

$\eta_{cmax} = w_{max} / (h_3 - h_f) = 1363.1 / (3450.4 - 762.5) = 0.51$

[25%]

(d)   (i)   cycle efficiency: $\eta_c = w_{net}/Q_{in}$
boiler efficiency: $\eta_b = Q_{in}/\dot{m}_f LCV$

overall efficiency: $\eta_{ov} = w_{net}/\dot{m}_f LCV$, hence $\eta_{ov} = \eta_c \eta_b$

[5%]

(ii)   To raise the boiler efficiency, we need to reduce the temperature of the combustion gases at boiler exit (ideally to the environmental temperature). However, if this temperature drops below the dew point, corrosion can occur in the stack.

[15%]