

1 (a)

$$\begin{aligned} df &= du - Tds - sdT \\ &= du - (du + pdv) - sdT \\ &= -pdv - sdT \end{aligned}$$

Thus,

$$\left(\frac{\partial f}{\partial v}\right)_T = -p \quad \text{and} \quad \left(\frac{\partial f}{\partial T}\right)_v = -s$$

and hence

$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T \quad (1)$$

Similarly, starting from  $g = h - Ts$ ,

$$\begin{aligned} dg &= dh - Tds - sdT \\ &= dh - (dh - vdp) - sdT \\ &= vdp - sdT \end{aligned}$$

Thus,

$$\left(\frac{\partial g}{\partial p}\right)_T = v \quad \text{and} \quad \left(\frac{\partial g}{\partial T}\right)_p = -s$$

and hence

$$\left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial s}{\partial p}\right)_T$$

[3]

(b) Start from  $Tds = du + pdv$ , rearrange and consider a change at constant  $T$ :

$$T \left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial u}{\partial v}\right)_T + p$$

hence

$$\left(\frac{\partial u}{\partial v}\right)_T = T \left(\frac{\partial s}{\partial v}\right)_T - p$$

Substituting eq. (1):

$$\left(\frac{\partial u}{\partial v}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_v - p$$

But

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{(v-b)} = \frac{p}{T}$$

Thus,

$$\left(\frac{\partial u}{\partial v}\right)_T = T \times \frac{p}{T} - p = 0$$

(ii) Saturated liquid and vapour are in equilibrium so that  $g_g = g_f$ . Thus,

$$g_g - g_f = f_g - f_f + p_s(v_g - v_f) = 0$$

$$= \int_f^g -p dv + p_s(v_g - v_f)$$

$$= \int_f^g (p_s - p) dv = 0$$

where the integration is carried out over path  $f-k-m-l-g$ . The last equality shows that the two shaded areas must be equal. [4]

The internal energy is thus independent of volume such that its most general form is  $u = u(T)$ . The equation of state is clearly similar to that of an ideal gas but taking into account the 'excluded volume' of the molecules. There are no intermolecular forces, so there is no associated potential energy, making the internal energy independent of specific volume. [7]

(c) (i) Rearranging the equation of state,

$$p = \frac{RT}{(v-b)} - \frac{a}{v^2}$$

Differentiating w.r.t.  $v$ ,

$$\left(\frac{\partial p}{\partial v}\right)_T = -\frac{RT}{(v-b)^2} + \frac{2a}{v^3}$$

and again,

$$\left(\frac{\partial^2 p}{\partial v^2}\right)_T = \frac{2RT}{(v-b)^3} - \frac{6a}{v^4}$$

At the critical point, both these derivatives are zero, giving

$$\frac{RT_c}{(v_c-b)^2} = \frac{2a}{v_c^3}$$

$$\frac{RT_c}{(v_c-b)^3} = \frac{3a}{v_c^4}$$

Rearranging gives,

$$\underline{b = v_c/3} \quad \text{and} \quad \underline{a = 9RT_c v_c/8}$$

Now,

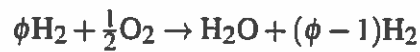
$$\begin{aligned} p_c &= \frac{RT_c}{(v_c-b)} - \frac{a}{v_c^2} \\ &= \frac{RT_c}{2v_c/3} - \frac{9RT_c v_c}{8v_c^2} = \frac{3RT_c}{8v_c} \end{aligned}$$

Thus,

$$\underline{Z_c = \frac{p_c v_c}{RT_c} = \frac{3}{8}}$$

[6]

2 (a) The reaction is :



The steady flow energy equation may be written

$$(H_P - H_{P0}) = (H_R - H_{R0}) + (H_{R0} - H_{P0}) = 0 - \Delta H_{T_0}^0$$

where the first term on the RHS is zero because reactants are supplied at  $T_0$ . Thus,

$$(\bar{h}_{\text{H}_2\text{O}}(T) - \bar{h}_{\text{H}_2\text{O}}(T_0)) + (\phi - 1)(\bar{h}_{\text{H}_2}(T) - \bar{h}_{\text{H}_2}(T_0)) = -\Delta H_{T_0}^0$$

Giving,

$$\phi = 1 - \frac{\Delta H_{T_0}^0 + (\bar{h}_{\text{H}_2\text{O}}(T) - \bar{h}_{\text{H}_2\text{O}}(T_0))}{(\bar{h}_{\text{H}_2}(T) - \bar{h}_{\text{H}_2}(T_0))} \quad (2)$$

(i) Assuming PG relations with  $\bar{c}_p = 30 \text{ kJ kmol}^{-1} \text{ K}^{-1}$ :

$$\phi = -\frac{\Delta H_{T_0}^0}{\bar{c}_p(T - T_0)} = \frac{241.8}{0.03 \times (2200 - 298.15)} = \underline{4.2380}$$

[4]

(ii) Substituting in (2) from the 'Molar enthalpies of common gases' section of the data book:

$$\phi = 1 + \frac{241.8 - 93.01 + 9.90}{64.84 - 8.46} = \underline{3.8147}$$

[2]

The assumption in (i) is rather approximate because over the large temperature range there is likely to be considerable variation of specific heat capacities, particularly due to excitation of vibrational energy modes. Furthermore,  $\text{H}_2$  is diatomic whereas  $\text{H}_2\text{O}$  is triatomic and so they will have different numbers of 'degrees of freedom'. Assigning the same  $\bar{c}_p$  is therefore also very approximate. The semi-perfect gas assumption in (ii) is much more reasonable. ( $\text{H}_2\text{O}$  at 1 bar might be considered fairly non-ideal, but at such high temperature the intermolecular forces are unlikely to significantly alter heat capacities.)

[2]

(b) (i) The only relevant reactions in the data book are (1), (3), (5) and (6), from which the additional species are H, O,  $\text{O}_2$  and OH.

[1]

(ii) As stated in the question, the concentrations of H, O,  $\text{O}_2$  and OH will be small. The temperature may therefore be assumed unchanged and the number of moles of  $\text{H}_2\text{O}$  and  $\text{H}_2$  remain at approximately 1 and  $\phi - 1$  respectively. Since

the pressure is  $p_0$ , the equilibrium relations may be written in terms of the mole fractions. Noting the total number of moles is  $n \simeq \phi$ , gives:

$$X_{\text{H}_2\text{O}} \simeq \frac{1}{\phi} = 0.26214; \quad X_{\text{H}_2} \simeq 1 - X_{\text{H}_2\text{O}} = 0.73786$$

$$\frac{X_{\text{H}_2}}{X_{\text{H}}^2} = K_1$$

giving

$$X_{\text{H}} = \sqrt{\frac{X_{\text{H}_2}}{K_1}} = \sqrt{\frac{0.73786}{\exp(10.353)}} = \underline{0.485\%}$$

Similarly, for reaction (5):

$$\frac{X_{\text{H}_2\text{O}}}{X_{\text{H}_2} X_{\text{O}_2}^{1/2}} = K_1$$

giving

$$X_{\text{O}_2} = \left( \frac{X_{\text{H}_2\text{O}}}{K_5 X_{\text{H}_2}} \right)^2 \simeq \left( \frac{0.23214}{\exp(6.768) \times 0.73786} \right)^2 = \underline{1.669 \times 10^{-5}\%}$$

For reaction (3) :

$$X_{\text{O}} = \sqrt{\frac{X_{\text{O}_2}}{K_3}} = \sqrt{\frac{1.669 \times 10^{-7}}{\exp(11.827)}} = \underline{1.1 \times 10^{-4}\%}$$

And for reaction (6) :

$$X_{\text{OH}} = \frac{X_{\text{H}_2\text{O}}}{K_6 X_{\text{H}_2}^{1/2}} \simeq \frac{0.23214}{\exp(7.148) \times 0.73786^{1/2}} = \underline{0.024\%}$$

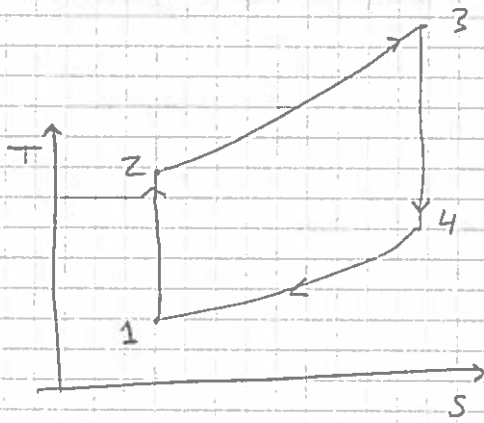
The only significant concentration is that of H, which is sufficiently small ( $< 0.5\%$ ) that the assumptions are reasonably accurate. [9]

(c) All dissociation reactions increase the numbers of moles, so increasing the pressure will decrease the degree of dissociation. All dissociation reactions are also endothermic. Increasing the pressure will therefore increase the temperature for a given  $\phi$ . [2]

**END OF PAPER**

SOLUTIONS TO Q3 & Q4

3 (a)



$$\eta = \frac{W_{net}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}} = 1 - \frac{C_p(T_4 - T_1)}{C_p(T_3 - T_2)}$$

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\gamma-1/\gamma}$$

$$r_p = \frac{P_2}{P_1} = \frac{P_3}{P_4}$$

$$\frac{T_3}{T_4} = \left(\frac{P_3}{P_4}\right)^{\gamma-1/\gamma}$$

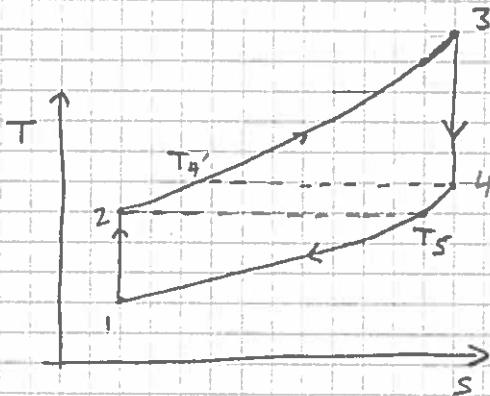
$$= P_3/P_4 = P_2/P_1 \Rightarrow \frac{T_4}{T_1} = \frac{T_3}{T_2}$$

$$\Rightarrow \eta = 1 - \frac{T_1(T_4/T_1 - 1)}{T_2(T_3/T_2 - 1)}$$

$$= 1 - \frac{T_1}{T_2}$$

$$= 1 - r_p^{1-\gamma/\gamma}$$

(b)



Ideal recuperated cycle

means no pressure losses in the heat exchanger,

h.e. effectiveness of unity

$$(\therefore 1 = \frac{T_4' - T_2}{T_4 - T_2})$$

$$\Rightarrow T_5 = T_2 \quad \& \quad T_4' = T_4$$

Net work =  $w_{turb} - w_{comp}$

$$= C_p T_3 \left(1 - \frac{1}{r_p}\right) - C_p T_1 (r_p - 1)$$

$$= C_p T_1 \left[\theta \left(1 - \frac{1}{r_p}\right) - (r_p - 1)\right]$$

unchanged from basic cycle

$$r_p = \frac{T_3}{T_4} = \frac{T_2}{T_1}$$

$$\& \quad r_p = r_p^{\gamma-1/\gamma}$$

$$\begin{aligned}
 \text{Heat input} &= q_{in} = C_p (T_3 - T_4') \\
 &= C_p (T_3 - T_4) \\
 &= C_p T_3 \left(1 - \frac{1}{r_t}\right) \\
 &= C_p T_1 \theta \left(1 - \frac{1}{r_t}\right)
 \end{aligned}$$

$$\begin{aligned}
 \therefore \eta_{\text{recup}} &= 1 - \frac{T_4'}{T_3} \\
 &= 1 - \frac{1}{r_t^{\gamma-1/\gamma}} \frac{1}{\theta}
 \end{aligned}$$

(c) Real cycle has polytropic efficiency in compressor

$\epsilon_{\text{turbine}} = 0.9$        $\epsilon_{\text{comp}} = 0.8$        $r_p = 6$  ,  $\gamma = 1.4$   
 $\theta = 6$

$$\epsilon = \frac{T_4' - T_2}{T_4 - T_2}$$

$$T_1 = 300 \text{ K} \Rightarrow \frac{T_2}{T_1} = r_p^{\gamma-1/\gamma} \Rightarrow T_2 = 529.85 \text{ K}$$

$$T_3 = 1800 \text{ K} \Rightarrow \frac{T_3}{T_4} = r_p^{\eta_c(\gamma-1)/\gamma} \Rightarrow T_4 = 1135.47 \text{ K}$$

Using effectiveness,  $T_4' = T_2 + \epsilon(T_4 - T_2) \Rightarrow T_4' = 1014.35 \text{ K}$

$$w_{\text{comp}} = C_p (T_2 - T_1) = 1.005 \cdot (529.85 - 300) \text{ kJ/kg} = 231 \text{ kJ/kg}$$

$$w_{\text{turb}} = C_p (T_3 - T_4) = 1.005 \cdot (1800 - 1135.47) \text{ kJ/kg} = 667.8 \text{ kJ/kg}$$

$$q_{in} = C_p (T_3 - T_4') = 1.005 \cdot (1800 - 1014.35) = 789.58 \text{ kJ/kg}$$

$$\Rightarrow \eta = \frac{w_{\text{net}}}{q_{in}} = 0.55$$

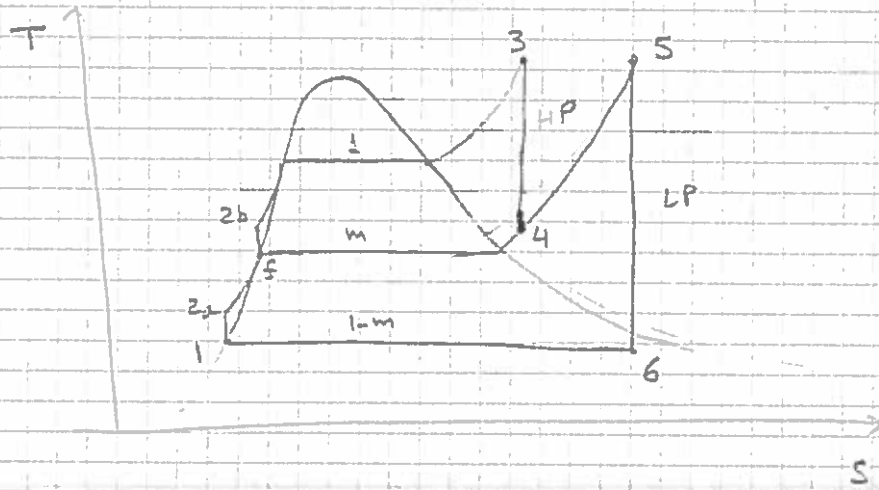
$$\eta_{\text{ideal}} = 1 - \frac{1}{r_p^{\gamma-1/\gamma}} = 0.72$$

(A) Recuperation is used in low  $\eta_p$  g.t.'s (so that turbine exit  $T >$  compressor delivery  $T$ ). Such g.t.'s are seldom used in modern aero-engines or land-based power generation, but are often used in small-scale machines (e.g. micro-turbines) & for road transport applications. The advantage is that  $\eta$  increases. The disadvantage is the cost, volume & weight of the heat exchanger. In real devices, there is also a pressure loss in the heat exchanger, which implies lower power output & reduced efficiency.



2

(a)



(b) For unit mass flow rate through the boiler, and with  $m$  the mass flow rate extracted from the HP turbine for the feed heater, the SFEE in the feed heater becomes:

$$1 \cdot h_5 = (1-m)h_{2a} + m \cdot h_4 \Rightarrow m \approx \frac{h_5 - h_1}{h_4 - h_1}$$

The heat input is  $q_{in} = h_3 - h_{2b} \approx h_3 - h_5$  (neglecting pump)

The reheat input is  $q_{reheat} = (h_5 - h_4)(1-m)$

Net work output is  $(h_3 - h_4) + (h_5 - h_6)(1-m)$  (neglecting pump)

$$\Rightarrow \eta \approx \frac{(h_3 - h_4) + (1-m)(h_5 - h_6)}{(h_3 - h_5) + (h_5 - h_4)(1-m)}$$

- Work output has been reduced by  $m(h_5 - h_6)$  compared to the cycle without reheat. But the heat input has been reduced by a larger amount, so  $\eta \uparrow$ .

(c) Condenser at 0.06 bar  $\rightarrow h_1 = 151.5 \text{ kJ/kg}$  (tables)

Saturated liquid at 40 bar  $\rightarrow h_2 = 1087.5 \text{ kJ/kg}$  (tables)

Boiler at 150 bar  $\Rightarrow h_3 = 3450 \text{ kJ/kg}$  (chart)

Exhaust of HP (40 bar)  $\rightarrow h_4 = 3060 \text{ kJ/kg}$  (chart)  $s = \text{const}$

Exit of reheater (40 bar,  $550^\circ\text{C}$ )  $\rightarrow h_5 = 3560 \text{ kJ/kg}$  (chart)

Exhaust of LP turbine  $\rightarrow h_6 = 2240 \text{ kJ/kg}$  (chart)

Assume isentropic expansion

Neglecting feed pump work:

$$m = \frac{h_2 - h_1}{h_4 - h_1} \Rightarrow m = \frac{936}{2908.5} = 0.322$$

$$\text{Heat in at boiler } Q_b \rightarrow S = h_3 - h_{2b} \approx h_3 - h_2 = 2362.5 \text{ kJ/kg}$$

Heat in at reheat

stage (4  $\rightarrow$  5)

$$= (h_5 - h_4)(1 - m)$$

$$= (3560 - 3060)(1 - 0.322)$$

$$= 339 \text{ kJ/kg (a steam through boiler)}$$

HP turbine work

$$= h_3 - h_4$$

$$= 390 \text{ kJ/kg}$$

LP turbine work

$$= (h_5 - h_6)(1 - m)$$

$$= (3560 - 2240)(1 - 0.322)$$

$$= 895 \text{ kJ/kg}$$

$$\Rightarrow \eta = \frac{390 + 895}{2362.5 + 339} = 0.475$$

$$Q_{\text{condenser}} = (1 - m)(h_6 - h_1) = (1 - 0.322)(2240 - 151.5) = 1416 \text{ kJ/kg}$$