

Question 1

$$P_r = \frac{T_r \beta}{\alpha v_r - 1} - \frac{\alpha}{v_r^2}$$

(a) The Helmholtz energy is a state function, and hence $df = -sdT - Pdv$ is an exact differential. $\frac{\partial f}{\partial T}_v = -s$ and $\frac{\partial f}{\partial v}_T = -P$. The order of differential does not matter so $\frac{\partial^2 f}{\partial T \partial v} = -\frac{\partial s}{\partial v}_T = -\frac{\partial P}{\partial T}_v$.

(b) For a fluids above the critical temperature and pressure, there is no phase change if the fluid is either cooled isobarically or compressed isothermally. This means that at the critical point (i.e. the limiting case where phase change is only just possible), the isotherm has a maximum and point of inflection $\frac{\partial P}{\partial v}_T = 0$ and $\frac{\partial^2 P}{\partial v^2}_T = 0$. This means that

$$\left(\frac{\partial P_r}{\partial v_r}\right)_T = -\alpha \frac{T_r \beta}{(\alpha v_r - 1)^2} + \frac{2\alpha}{v_r^3} \quad (1)$$

$$\left(\frac{\partial^2 P_r}{\partial v_r^2}\right)_T = 2\alpha^2 \frac{T_r \beta}{(\alpha v_r - 1)^3} - \frac{6\alpha}{v_r^4} \quad (2)$$

Both of these must be zero at the critical point where $v_r = P_r = T_r = 1$.

$$\alpha \frac{\beta}{(\alpha - 1)^2} = 2\alpha \quad (3)$$

$$2\alpha^2 \frac{\beta}{(\alpha - 1)^3} = 6\alpha \quad (4)$$

Dividing

$$\frac{\alpha - 1}{2\alpha} = \frac{2}{6} \Rightarrow 6\alpha - 6 = 4\alpha \Rightarrow \alpha = \mathbf{3}$$

Then from (3)

$$\beta = 2(\alpha - 1)^2 \Rightarrow \beta = \mathbf{8} \quad (5)$$

(c) Starting from $du = Tds - Pdv$

$$du = Tds - Pdv$$

$$\left(\frac{\partial u}{\partial T}\right)_v = T \left(\frac{\partial s}{\partial T}\right)_v = c_v$$

differentiating with respect to v at constant T

$$\left(\frac{\partial c_v}{\partial v}\right)_T = \frac{\partial^2 u}{\partial v \partial T} = T \frac{\partial^2 s}{\partial v \partial T}$$

Changing the order of the second derivatives

$$\left(\frac{\partial c_v}{\partial v}\right)_T = T \frac{\partial^2 s}{\partial T \partial v}$$

Using the maxwell relation $\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$

$$\left(\frac{\partial c_v}{\partial v}\right)_T = T \frac{\partial}{\partial T} \left(\frac{\partial P}{\partial T}\right)_v$$

Using the equation of state, $P_r = \frac{T_r\beta}{\alpha v_r - 1} - \frac{\alpha}{v_r^2}$

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{P_c\beta}{T_c(\alpha v_r - 1)}$$

and

$$\left(\frac{\partial^2 P}{\partial T^2}\right)_v = 0$$

Therefore $\left(\frac{\partial c_v}{\partial v}\right)_T = 0$ and $C_v = f(T)$ only.

(d) Starting from $du = Tds - Pdv$,

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

using the maxwell relation $\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$

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

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{P_c\beta}{T_c(\alpha v_r - 1)}$$

and

$$P = \frac{P_c T_r \beta}{\alpha v_r - 1} - \frac{P_c \alpha}{v_r^2}$$

$$\Delta u = \int_{v_o}^v \frac{TP_c\beta}{T_c(\alpha v_r - 1)} - \frac{P_c T \beta}{T_c(\alpha v_r - 1)} + \frac{P_c \alpha}{v_r^2} dv \quad (6)$$

$$\Delta u = \int_{v_o}^v \frac{P_c v_c^2 \alpha}{v^2} dv \quad (7)$$

$$\Delta u = 3P_c v_c^2 \left[\frac{1}{v_o} - \frac{1}{v} \right] \quad (8)$$

(e) Therefore can write $u(T, v) = u_o + \Delta u_1 + \Delta u_2$. Δu_1 is the difference in u between v_o and v evaluated at T_o (calculated above, and noting that , there is no temperature dependance in (8)). Δu_2 is the difference in u between T_o and T evaluated at v . However, since c_v is not a function of v , $\Delta u_2 = \int_{T_o}^T c_v dT$, is not a fuction of v , and since we are told it c_v is a constant,

$$u(T, v) = u_o + 3P_c v_c^2 \left[\frac{1}{v_o} - \frac{1}{v} \right] + c_v(T - T_o)$$

Examiner's Comments: Although relatively straight forward, this question was not the most popular, with around half the candidates attempting it. Parts (a) and (b) were answered correctly. Part (c) proved to very difficult, and only one candidate took the expected route to the solution. In a few cases (c) was answered by doing parts (d) and (e) first, which, whilst longer, was also acceptable. Some students were able to give a convincing answer to parts (d) and (e), but many either didn't know where to start, or integrated the wrong derivatives. It is clear that students find basic manipulation of thermodynamic quantities very difficult, despite the fact that the example sheet contains a related question using the same equation of state.

Question 2

(a) i) Starting from $Td\bar{s} = d\bar{h} - \bar{v}dP$ substitute in $\bar{g} = \bar{h} - T\bar{s}$, to give $Td\bar{s} = d\bar{g} + Td\bar{s} + \bar{s}dT - \bar{v}dP$ i.e.

$$0 = d\bar{g} + \bar{s}dT - \bar{v}dP$$

$$d\bar{g} = -\bar{s}dT + \bar{v}dP$$

Therefore,

$$\left(\frac{\partial\bar{g}}{\partial T}\right)_P = -\bar{s}$$

ii)

$$\ln(K_p) = -\frac{\Delta G^\circ}{RT}$$

Differentiating

$$\frac{\partial}{\partial T}\ln(K_p) = -\frac{\partial}{\partial T}\frac{\Delta G^\circ}{RT}$$

$$\frac{\partial}{\partial T}\ln(K_p) = -\frac{1}{R}\frac{\partial}{\partial T}\left(\frac{\sum \nu_i \bar{g}_i^\circ}{T}\right)$$

$$\frac{\partial}{\partial T}\ln(K_p) = -\frac{1}{R}\sum \nu_i \frac{\partial}{\partial T}\left(\frac{\bar{g}_i^\circ}{T}\right)$$

$$\frac{\partial}{\partial T}\ln(K_p) = -\frac{1}{R}\sum \nu_i \left(\frac{1}{T}\frac{\partial \bar{g}_i^\circ}{\partial T} - \frac{\bar{g}_i^\circ}{T^2}\right)$$

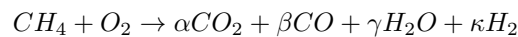
we also have $\left(\frac{\partial\bar{g}}{\partial T}\right)_P = -\bar{s}$ and $\bar{g}_i^\circ = \bar{h}_i^\circ - T\bar{s}_i^\circ$

$$\frac{\partial}{\partial T}\ln(K_p) = -\frac{1}{R}\sum \nu_i \left(-\frac{1}{T}\bar{s}_i^\circ - \frac{\bar{h}_i^\circ - T\bar{s}_i^\circ}{T^2}\right)$$

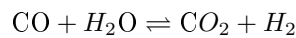
$$\frac{\partial}{\partial T}\ln(K_p) = -\frac{1}{R}\sum \nu_i \left(-\frac{\bar{h}_i^\circ}{T^2}\right)$$

$$\frac{\partial}{\partial T}\ln(K_p) = \left(\frac{\Delta H_T^\circ}{RT^2}\right)$$

(b)i)



At the outlet of the burner the water gas shift reaction is at equilibrium



The reaction has the same number of moles on either side of reaction, so by Le Chatelier's principle won't be affected by pressure. Alternatively note that

$$K_p = \frac{P_{CO_2}P_{H_2}}{P_{CO}P_{H_2O}} = \frac{y_{CO_2}y_{H_2}}{y_{CO}y_{H_2O}},$$

hence there is no pressure dependence in the equilibrium equation or the atom balances which govern the composition.

ii)

$$K_p = \frac{y_{CO_2} y_{H_2}}{y_{CO} y_{H_2O}} = 1$$

From the carbon balance: $\alpha + \beta = 1 \Rightarrow \beta = 1 - \alpha$

From the oxygen balance: $2\alpha + \beta + \gamma = 2 \Rightarrow \gamma = 2 - 2\alpha - (1 - \alpha) = 1 - \alpha = \beta$

From the hydrogen balance: $\gamma + \kappa = 2 \Rightarrow \kappa = 2 - (1 - \alpha) = 1 + \alpha = 2 - \beta$

Since the total number of moles cancels out in the equilibrium expression

$$K_p = \frac{\alpha\kappa}{\beta\gamma} = 1$$

$$\alpha\kappa = \beta\gamma$$

$$\alpha(\alpha + 1) = (1 - \alpha)(1 - \alpha)$$

$$\alpha^2 + \alpha = 1 - 2\alpha + \alpha^2$$

$$3\alpha = 1$$

Therefore, $\alpha = \frac{1}{3}, \beta = \frac{2}{3}, \gamma = \frac{2}{3}, \kappa = \frac{4}{3}$.

iii) The material balance equations are unchanged by the change in temperature, with the only temperature dependence on K_p .

$$K_p = \frac{y_{CO_2} y_{H_2}}{y_{CO} y_{H_2O}}$$

$$K_p = \frac{\alpha\kappa}{\beta\gamma}$$

$$K_p = \frac{(1 - \beta)(2 - \beta)}{\beta^2}$$

$$\ln(K_p) = \ln(1 - \beta) + \ln(2 - \beta) - 2\ln(\beta)$$

$$\frac{\partial}{\partial T} \ln(K_p) = \left(\frac{\Delta H_T^o}{RT^2} \right) = \left(-\frac{1}{1 - \beta} - \frac{1}{2 - \beta} - \frac{2}{\beta} \right) \frac{\partial \beta}{\partial T}$$

The sign of $\frac{\partial \beta}{\partial T}$ can now be determined. Noting that $\beta < 1$ otherwise $\alpha < 0$ implies that

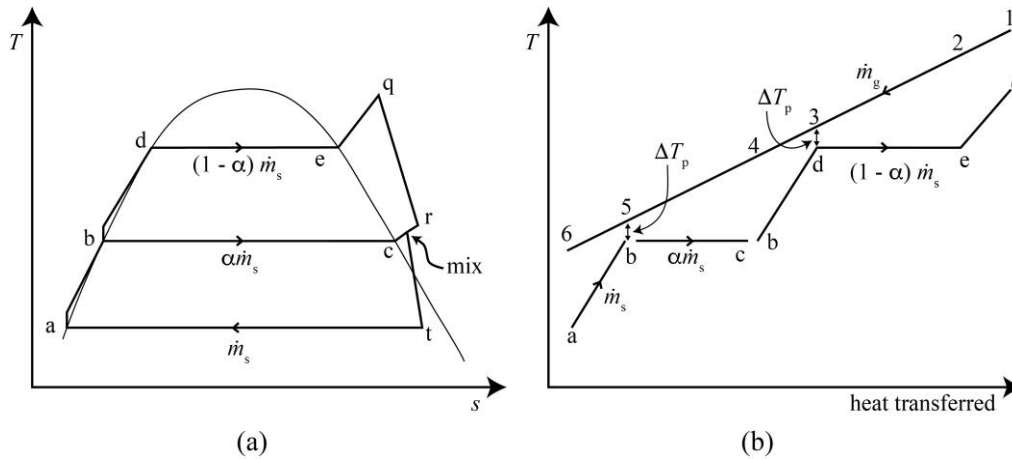
$$-\frac{1}{1 - \beta} - \frac{1}{2 - \beta} - \frac{2}{\beta} < 0$$

ΔH_T^o can be found from the data book and is roughly constant at about -30 MJ per kmole (i.e. negative). Therefore $\frac{\partial \beta}{\partial T} > 0$ and to decrease the amount of CO, whilst increasing the amount of H₂, the temperature must be reduced. Introducing steam could also shift the equilibrium to consuming more of the CO. This is the basis for the industrial process used to make hydrogen gas.

Examiner's Comments: Part (a) answered correctly by almost all candidates. Only about half of the candidate could give a convincing proof in (a)(ii), with many resorting to incorrect assertions (e.g. entropy of reaction is either zero or not a function of temperature). Most were able to make a reasonable attempt at part (b). When looking at the sign of the derivative, the highest marks were awarded to those who has looked up the enthalpy of reaction in the data book.

3. (a) Multiple steam pressures, usually three are employed, allow the temperature difference between the gas turbine exhaust side and the steam side of the HRSG to be reduced (as compared to a single steam pressure). This reduces the irreversibilities (exergy losses) in the HRSG and also increases the amount of heat transferred.

(b)



$$h_a = 121.4 \text{ kJ kg}^{-1} \text{ (from table, wet saturated at 0.04 bar)}$$

$$h_b = 1087.5 \text{ kJ kg}^{-1} \text{ (from table, wet saturated at 40 bar)}$$

$$h_c = 2800.8 \text{ kJ kg}^{-1} \text{ (from table, dry saturated at 40 bar)}$$

$$h_d = 1610.3 \text{ kJ kg}^{-1} \text{ (from table, wet saturated at 150 bar)}$$

$$h_e = 2610.8 \text{ kJ kg}^{-1} \text{ (from table, dry saturated at 150 bar)}$$

$$h_q = 3450.4 \text{ kJ kg}^{-1} \text{ (from table, 150 bar, 550 }^\circ\text{C)}$$

$$h_r = 3095.0 \text{ kJ kg}^{-1} \text{ (given)}$$

$$h_t = 2140 \text{ kJ kg}^{-1} \text{ (given)}$$

$$T_1 = 650 \text{ }^\circ\text{C} \text{ (given)}$$

$$T_3 = T_d + 25 = 342.16 + 25 = 367.16 \text{ }^\circ\text{C}$$

$$T_5 = T_b + 25 = 250.35 + 25 = 275.35 \text{ }^\circ\text{C}$$

(b)(i) Assuming that the HRSG is, overall, adiabatic, we can write two SFEE's:

From exhaust station 1 to 3:

$$c_p(T_1 - T_3) = (1 - \alpha) \frac{\dot{m}_s}{\dot{m}_g} (h_q - h_d) \quad .$$

From exhaust station 1 to 5:

$$c_p(T_1 - T_5) = (1 - \alpha) \frac{\dot{m}_s}{\dot{m}_g} (h_q - h_b) + \alpha \frac{\dot{m}_s}{\dot{m}_g} (h_c - h_b) .$$

Rearranging the first equation gives,

$$\frac{\dot{m}_s}{\dot{m}_g} = \frac{c_p(T_1 - T_3)}{(1 - \alpha)(h_q - h_d)} ,$$

which can be substituted in the second equation to yield,

$$c_p(T_1 - T_5) = \frac{c_p(T_1 - T_3)}{(1 - \alpha)(h_q - h_d)} \left[(1 - \alpha)(h_q - h_b) + \alpha(h_c - h_b) \right] .$$

Rearranging,

$$\frac{(T_1 - T_5)}{(T_1 - T_3)} = \frac{(h_q - h_b)}{(h_q - h_d)} + \frac{\alpha}{(1 - \alpha)} \frac{(h_c - h_b)}{(h_q - h_d)} ,$$

$$\frac{(650 - 275.35)}{(650 - 367.16)} = \frac{(3450.4 - 1087.5)}{(3450.4 - 1610.3)} + \frac{\alpha}{(1 - \alpha)} \frac{(2800.8 - 1087.5)}{(3450.4 - 1610.3)} ,$$

and, hence,

$$\alpha = 0.0421 ,$$

$$\frac{\dot{m}_s}{\dot{m}_g} = \frac{c_p(T_1 - T_3)}{(1 - \alpha)(h_q - h_d)} = \frac{1.10 \times (650 - 367.16)}{(1 - 0.0421) \times (3450.4 - 1610.3)} = 0.177 .$$

(b)(ii) Assuming the mixing process is adiabatic, the SFEE gives,

$$(1 - \alpha)\dot{m}_s h_r + \alpha\dot{m}_s h_c = \dot{m}_s h_{mix} ,$$

$$h_{mix} = (1 - 0.0421) \times 3095.0 + 0.0421 \times 2800.8 = 3083 \text{ kJ kg}^{-1}$$

(b)(iii) To evaluate the cycle efficiency we require the turbine work output and the heat input.

First, the turbine work (per kg of steam),

$$w_t = (1 - \alpha)(h_q - h_r) + (h_{mix} - h_t) .$$

The heat input is given by (per kg of steam),

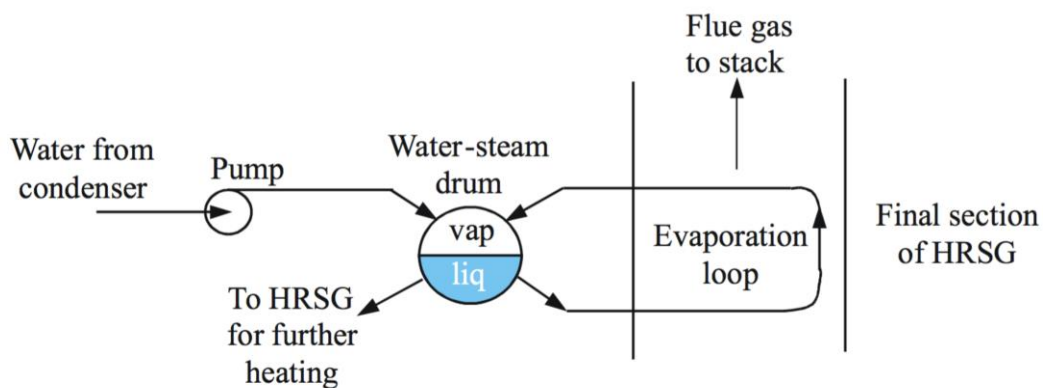
$$q_{in} = (h_b - h_a) + \alpha(h_c - h_b) + (1 - \alpha)(h_q - h_b) .$$

The cycle efficiency is (neglecting feed pump work),

$$\begin{aligned} \eta_c &= \frac{w_t}{q_{in}} = \frac{(1 - 0.0421) \times (3450.4 - 3095.0) + (3083 - 2140)}{(1087.5 - 121.4) + 0.0421 \times (2800.8 - 1087.5) + (1 - 0.0421) \times (3450.4 - 1087.5)} \\ &= \frac{1283}{3302} = 0.39 . \end{aligned}$$

(c) Feed heating is not used in combined cycle plants because feed heating raises the temperature of the feed water entering the HRSG. This means that the gas turbine exhaust temperature at HRSG exit is raised and the exergy loss in the exhaust increases. This results in a reduced overall efficiency for the combined cycle plant.

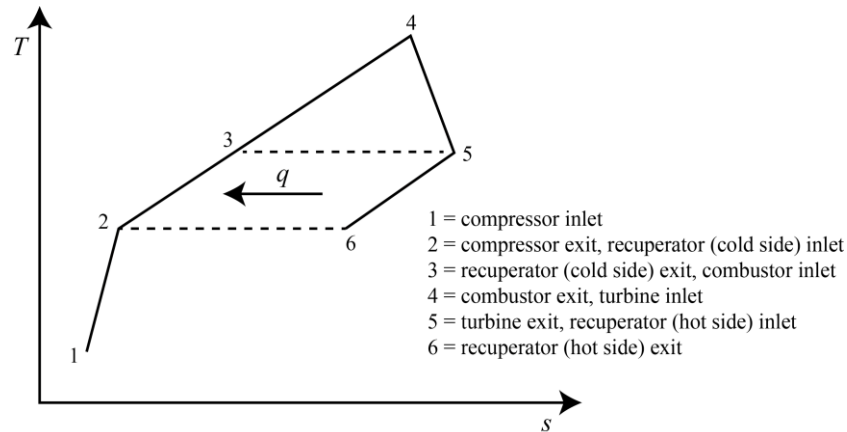
The exhaust gases in the HRSG must remain above their dew point in order to avoid corrosion of the HRSG. A preheating loop ensures that this happens by passing saturated liquid (with a saturation temperature that is *higher* than the dew point of the exhaust gases) into the final (coldest) section of the HRSG. This water then evaporates (at constant temperature) and so there is no opportunity for condensation of the exhaust gases.



Examiner's comments: Most were able to produce reasonable answers to this question, and were able to set up the pinch point equations correctly. Marks were lost in manipulating the equations to a solution. The descriptive parts in (a) and (c) were well answered.

4. (a) Recuperation means adding a heat exchanger to transfer heat from the gas turbine exhaust to the compressor delivery air. This means that a reduced heat input (less fuel) is required in the combustor to obtain the same turbine inlet temperature. The objective is to make use of some of the exergy that would, without recuperation, be lost in the gas turbine exhaust. For large gas turbines, this objective is achieved using combined cycle power plants, where a higher overall efficiency can be obtained.

(b)



For recuperation to be possible, we require,

$$T_5 > T_2 .$$

Assuming that the air (and combustion products) in the gas turbine can be modelled as a perfect gas, with constant c_p and g throughout, we obtain

$$\frac{T_2}{T_1} = r_t^{\left(\frac{1}{\gamma}\right)} \quad \text{and} \quad \frac{T_4}{T_5} = r_t^{\gamma} ,$$

since r_t is the same for the compressor and the turbine. As $T_4 / T_1 = q$, the requirement for recuperation to be possible becomes,

$$\frac{q}{r_t^{\gamma}} > r_t^{\left(\frac{1}{\gamma}\right)} ,$$

$$q > r_t^{\left(\frac{\gamma^2 + 1}{\gamma}\right)} .$$

(c) The pressure drop in the recuperator means that,

$$\frac{p_3}{p_2} = \frac{p_6}{p_5} = a \quad (\text{as before, } p_4 = p_3 \text{ and } p_6 = p_1) .$$

The pressure ratio across the turbine is obtained from,

$$p_4 = ap_2 \quad \text{and} \quad p_5 = \frac{p_1}{a} ,$$

so

$$\frac{p_4}{p_5} = a^2 \frac{p_2}{p_1} = a^2 r_p$$

where r_p is the compressor pressure ratio. The temperature ratio across the turbine is,

$$\frac{T_4}{T_5} = \left(a^2 r_p \right)^{\frac{(g-1)h}{g}} = a^{\frac{2(g-1)h}{g}} r_t^h .$$

The specific turbine work output is then given by,

$$w_t = c_p q T_1 \left(1 - \frac{1}{a^{\frac{2(g-1)h}{g}} r_t^h} \right) .$$

The reduction in turbine work, compared to the zero pressure drop recuperator case, is,

$$Dw_t = c_p q T_1 \left[\left(1 - \frac{1}{r_t^h} \right) - \left(1 - \frac{1}{a^{\frac{2(g-1)h}{g}} r_t^h} \right) \right] = \frac{c_p q T_1}{r_t^h} \left(\frac{1}{a^{\frac{2(g-1)h}{g}}} - 1 \right) .$$

Expressing Dw_t as a fraction of the zero pressure drop recuperator case, we obtain,

$$\frac{Dw_t}{w_{t,a=1}} = \frac{\frac{1}{r_t^h} \left(\frac{1}{a^{\frac{2(g-1)h}{g}}} - 1 \right)}{1 - \frac{1}{r_t^h}} = \frac{\left(\frac{1}{a^{\frac{2(g-1)h}{g}}} - 1 \right)}{r_t^h - 1} .$$

For $r_t = 2$, $h = 0.9$, $a = 0.9$ and $g = 1.4$,

$$\frac{Dw_t}{w_{t,a=1}} = \frac{\left(\frac{1}{0.9^{\frac{2 \times (1.4-1) \times 0.9}{1.4}}} - 1 \right)}{2^{0.9} - 1} = \frac{0.0557}{0.866} = 0.064 .$$

(d) Intercooling without recuperation. This increases the net specific work output but lowers the cycle efficiency. This can be seen on a T - s diagram of an intercooled Joule cycle: intercooling has the effect of increasing the enclosed area of the cycle (increasing the net work output) by adding a cycle with a lower pressure ratio than the original Joule cycle (hence lowering the cycle efficiency).

Intercooling with recuperation. This lowers the compressor delivery temperature and hence allows more heat to be transferred from the exhaust of the gas turbine. This increases the cycle efficiency.

Intercooling can be done by dividing the compression between low pressure and high pressure compressors and employing a heat exchanger in between. Alternatively, fine water droplets can be sprayed at compressor inlet; as the droplets evaporate, heat is removed from the air.

Examiner's comments:

Almost all answered parts (a) and (b) correctly. Part (c) was more difficult, but there were many complete and correct answers. Most were able to make some attempt at this, even if they did not quite set the problem up correctly. The descriptive parts in (a) and (d) were generally well answered; most marks were lost here by only partially answering the question posed.