MODULE 3A5 – THERMODYNAMICS AND POWER GENERATION SOLUTIONS

1. (a) The reaction is: $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

Per kmol of H_2 the SFEE is (with heat flow in the direction shown):

$$-\tilde{Q} - \tilde{W}_E = \tilde{H}_P - \tilde{H}_R \qquad (1)$$

where subscripts P and R denote products and reactants and the ~ denotes quantities per kmol of H_2 .

Maximum work will be when all processes are reversible, so the SFSE is:

$$-\tilde{Q} = T(\tilde{S}_P - \tilde{S}_R) \qquad (2)$$

Substitution of (2) into (1) gives:

$$[\tilde{W}_E]_{MAX} = \tilde{H}_R - \tilde{H}_P - T(\tilde{S}_R - \tilde{S}_P) = -\Delta\tilde{G}_T^0$$

where the final equality comes from the definition of $\Delta\tilde{G}_T^0$ (reactants and products all being at p_0 and T).

The Gibbs potential E_G is obtained by equating the maximum work to the electrical work, which is given by the product of E_G and the charge passed in consuming one kmol of H_2. Thus,

$$[\tilde{W}_E]_{MAX} = -\Delta\tilde{G}_T^0 = E_G(2F)$$

$$\therefore \qquad E_G = \frac{-\Delta\tilde{G}_T^0}{2F} = \frac{\tilde{R}T \ln K_p}{2F}$$

where F is the Faraday constant. From the data book (reaction 5 at 1200 K):

$$E_G = \frac{8,314 \times 1200 \times 18.182}{2 \times 9.648 \times 10^7} = \underline{0.940 \text{ v}}$$

[7]

(b)
$$\Delta \tilde{G}_T^0 = \sum_i \nu_i \tilde{g}_i(T, p_0)$$

Assuming ideal gas relations (so molar enthalpies depend only on T and the molar entropy of species i depends only on T and its partial pressure p_i):

$$\Delta \tilde{G}_T = \sum_i \nu_i \tilde{g}_i(T, p_i)$$

Now,

$$\tilde{g}_i(T, p_i) = \tilde{h}_i(T) - T\tilde{s}_i(T, p_i) = \tilde{g}_i(T, p_0) - T\{\tilde{s}_i(T, p_i) - \tilde{s}_i(T, p_0)\}$$

$$= \tilde{g}_i(T, p_0) - T\{-\tilde{R}\ln\frac{p_i}{p_0}\} = \tilde{g}_i(T, p_0) + \tilde{R}T\ln\frac{p_i}{p_0}$$

$\therefore$
$$\Delta \tilde{G}_T = \Delta \tilde{G}_T^0 + \tilde{R}T\sum_i \nu_i \ln\frac{p_i}{p_0}$$
[5]

(c) (i)
$$E_N = -\frac{\Delta \tilde{G}_T}{2F} = E_G - \frac{\tilde{R}T}{2F}\sum_i \nu_i \ln\frac{p_i}{p_0}$$

$$= E_G - \frac{\tilde{R}T}{2F}\sum_i \nu_i \left\{\ln X_i + \ln\frac{p}{p_0}\right\}$$

$$= E_G + \frac{\tilde{R}T}{2F}\left\{\ln\frac{X_{H_2}X_{O_2}^{1/2}}{X_{H_2O}} + \tfrac{1}{2}\ln\left(\frac{p}{p_0}\right)\right\}$$
(3)

$$= 0.940 + \frac{8,314 \times 1200}{2 \times 9.648 \times 10^7}\left\{\ln\frac{0.5 \times 0.21^{1/2}}{0.375} + \tfrac{1}{2}\ln 6\right\}$$

$$= 0.9401 + 0.05170 \times \{-0.4926 + 0.8959\}$$

$$\underline{= 0.961 \text{v}}$$
[4]

(ii) When current is drawn, the voltage of individual cells falls below the open-circuit value due to losses (mainly Ohmic losses, but possibly also "activation" and concentration losses).

In addition, finite current implies a finite rate of consumption of H_2 (and finite rate of production of H_2O) so that the concentration of H_2 decreases at the anodes between the inlet and exit of the fuel channels and the concentration of H_2O increases. This makes the first term in brackets in eq. (3) more negative, so the voltage drops between cells at the inlet and those at the exit.
[2]

(iii) Higher pressure makes the second term in brackets in eq. (3) more positive so increases the cell voltage (and hence the power density). Higher pressure operation would also be used to integrate the fuel cell into a gas turbine cycle, thereby extracting further work from the high-temperature exit flow and increasing the exergetic efficiency.

The high temperature is necessary because the ion conductivity of the electrolyte is too low at ambient temperatures. (Note that higher temperature actually reduces the cell voltages because the reaction is exothermic, so $\ln K_p$ decreases with T).
[2]

2. (a)
$$f = u - Ts$$
$$df = du - Tds - sdT$$
$$= du - (du + pdv) - sdT$$
$$= -pdv - sdT$$

$\therefore$ $p = -\left(\dfrac{\partial f}{\partial v}\right)_T$ and $s = -\left(\dfrac{\partial f}{\partial T}\right)_v$

but $\dfrac{\partial^2 f}{\partial T \partial v} = \dfrac{\partial^2 f}{\partial v \partial T}$

$\therefore$ $\left(\dfrac{\partial p}{\partial T}\right)_v = \left(\dfrac{\partial s}{\partial v}\right)_T$ [2]

(b) $du = Tds - pdv$

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

but $pv = RT$

$\therefore$ $\left(\dfrac{\partial p}{\partial T}\right)_v = \dfrac{R}{v} = \dfrac{p}{T}$

Thus, $\left(\dfrac{\partial u}{\partial v}\right)_T = T \times \dfrac{p}{T} - p = 0$ i.e., u is independent of v at fixed T, as required   [4]

(c)   (i) The ideal gas model assumes no intermolecular forces. There is therefore no potential energy associated with interaction between the molecules, so the total internal energy is independent of molecular separation (and hence v).   [1]

(ii) The dependence of c_v (and c_p) on T stems from the internal structure of the molecule: at higher temperatures more "internal" modes are excited. (It is usually the excitation of vibrational energy modes that leads to semi-perfect gas behaviour.)   [1]

(d)   (i)   Entropy from Gibbs' relation: $Tds = dh - vdp$ (1)

For an adiabatic process: $dw_c = dh$ (2)

For an isentropic process: $dh = vdp$ (3)

$\therefore$ For a *polytropic* compression: $dh = \dfrac{vdp}{\eta_p}$ (4)

Combining (4) and (1): $Tds = (\dfrac{1}{\eta_p} - 1)vdp = (\dfrac{1}{\eta_p} - 1)\dfrac{RT}{p}dp$

Integrating: $\Delta s = (1/\eta_p - 1)R\ln\left(\dfrac{p_2}{p_1}\right)$

$\therefore$ $k = (1/\eta_p - 1)R = (1/0.85 - 1) \times 189 = 33.35 \ \mathrm{J\,kg^{-1}K^{-1}}$

$\therefore$ Specific entropy change: $\Delta s = 33.5 \times \ln 5 = 53.6 \ \mathrm{J\,kg^{-1}K^{-1}}$

Exergetic loss, $$w_{L,CR} = T_0 \Delta s_{irr}$$

The compression is adiabatic so all entropy increase is due to irreversibility.

$\therefore$ $$w_{L,CR} = kT_0 \ln\left(\frac{p_2}{p_1}\right) = 33.35 \times 298 \times \ln 5 = 16 \, \text{kJ kg}^{-1}$$ [6]

(ii)   General process for CO_2: $$ds = c_p \frac{dT}{T} - \frac{v}{T} dp = \left(\frac{a}{T} + b + cT\right) dT - R\frac{dp}{p}$$

Integrating: $$\Delta s = a \ln\left(\frac{T_2}{T_1}\right) + b(T_2 - T_1) + \frac{c}{2}\left(T_2^2 - T_1^2\right) - R\ln\left(\frac{p_2}{p_1}\right)$$

Thus

$$\Delta s = 497 \times \ln\left(\frac{442}{298}\right) + 1.37 \times (442 - 298)$$

$$- \frac{0.67 \times 10^{-3}}{2}\left(442^2 - 298^2\right) - 189 \times \ln 5$$

$$= \quad 53.5 \, \text{J kg}^{-1}\text{K}^{-1} \approx \text{result above}$$

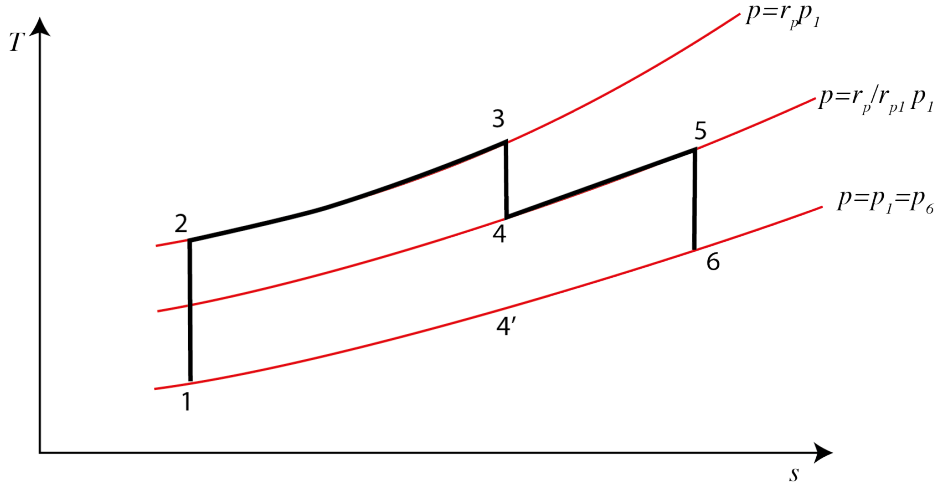$\therefore$ Exit temperature of 442 K is consistent with entropy change.

Specific work input:

$$w_c = \Delta h = \int c_p \, dT = a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) + \frac{c}{3}(T_2^3 - T_1^3)$$

$$= 497 \times (442 - 298) + \frac{1.37}{2}(442^2 - 298^2) - \frac{0.67 \times 10^{-3}}{3}(442^3 - 298^3)$$

$$= 131.2 \, \text{kJ kg}^{-1}$$

[6]

(Note that the lost work is 12.2 % of the actual work)

3. (a)

Reheat (heat addition in reheater is from 4 to 5 in cycle diagram) increases the specific net work output from the cycle (the area enclosed on the T-s diagram is increased) but reduces the cycle efficiency (the pressure ratio of the additional cycle 4'-4-5-6 formed by the reheat is less than the original cycle pressure ratio 1-2-3-4'; for an ideal Joule cycle the cycle efficiency is only a function of pressure ratio).

[4]

(b) let

$$r_t = r_p^{\frac{\gamma-1}{\gamma}} \quad \text{and} \quad r_{t1} = r_{p1}^{\frac{\gamma-1}{\gamma}}$$

The turbine work output is then given by (ideal Joule cycle has isentropic turbomachinery)

$$
\begin{aligned}
w_t &= w_{t1} + w_{t2} \\
&= c_p(T_3 - T_4) + c_p(T_5 - T_6) \\
&= c_p T_3 \left(1 - \frac{T_4}{T_3} + 1 - \frac{T_6}{T_3}\right) \\
&= c_p T_3 \left(2 - \frac{1}{r_{t1}} - \frac{r_{t1}}{r_t}\right)
\end{aligned}
$$

and

$$\frac{w_t}{c_p \theta T_1} = 2 - \frac{1}{r_{t1}} - \frac{r_{t1}}{r_t}$$

The maximum specific net work output is when the turbine work is at a maximum, so

$$\frac{d\left(\dfrac{w_t}{c_p \theta T_1}\right)}{dr_{t1}} = \frac{1}{r_{t1}^2} - \frac{1}{r_t} = 0$$

$$r_{t1} = \sqrt{r_t} \quad \text{and} \quad \underline{\underline{r_{p1} = \sqrt{r_p}}}$$

<div align="right">[4]</div>

(c)(i) For recuperation, the turbine outlet temperature must be higher than the compressor outlet temperature.

<div align="right">[1]</div>

(ii) Without reheat, we require, from (c)(i):

$$\theta T_1 \frac{1}{r_t^{\eta}} > T_1 r_t^{\frac{1}{\eta}}$$

$$\theta > r_t^{\frac{1}{\eta}+\eta}$$

$$r_t < \theta^{\frac{\eta}{\eta^2+1}}$$

With reheat, we require:

$$\theta T_1 \frac{r_{t1}^{\eta}}{r_t^{\eta}} > T_1 r_t^{\frac{1}{\eta}}$$

$$\theta r_{t1}^{\eta} > r_t^{\frac{1}{\eta}+\eta}$$

$$r_t < \left(\theta r_{t1}^{\eta}\right)^{\frac{\eta}{\eta^2+1}}$$

Hence, the maximum isentropic temperature ratio (and hence pressure ratio) has been increased by reheat. This is because, for the same overall pressure ratio, reheat will increase the temperature at turbine outlet.

<div align="right">[6]</div>

(d) Reheat – requires 2 combustor stages and 2 high temperature turbine stages. These high temperature components are expensive and require cooling air. This significantly adds to the cost and complexity of the gas turbine.

Recuperator – this heat exchanger is large item (to transfer the heat at minimum pressure loss). It is most effective at low gas turbine pressure ratios (hence high turbine outlet temperatures) but this implies a low GT cycle efficiency. Combined cycle gas turbine plants are a more common way of reducing exergy loss of a power generation GT exhaust.

<div align="right">[5]</div>

4. (a)

$$\eta_{ov} = \frac{\dot{W}_{GT}}{\dot{m}_f \Delta H^0_{298}} \qquad \eta_b = \frac{\dot{Q}_{inST}}{\dot{Q}_{outGT\,max}} \qquad \eta_{ST} = \frac{\dot{W}_{ST}}{\dot{Q}_{inST}}$$
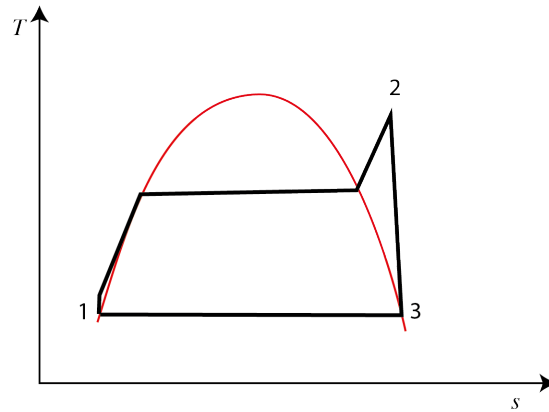
and

$$\dot{Q}_{outGT\,max} = (1 - \eta_{ov})\dot{m}_f \Delta H^0_{298}$$

so

$$\eta_{cc} = \frac{\dot{W}_{GT} + \dot{W}_{ST}}{\dot{m}_f \Delta H^0_{298}} = \frac{\dot{W}_{GT}}{\dot{m}_f \Delta H^0_{298}} + \frac{\eta_{ST}\eta_b(1-\eta_{ov})\dot{m}_f \Delta H^0_{298}}{\dot{m}_f \Delta H^0_{298}} = \underline{\underline{\eta_{ov} + \eta_{ST}\eta_b(1-\eta_{ov})}}$$ [3]

(b)

Maximum work output when the turbine is reversible. If we assume the condenser is at the dead state temperature, then,

$$w_{max} = b_2 - b_1$$
$$= (h_2 - T_1 s_2) - (h_1 - T_1 s_1)$$

From the databook,

$$T_1 = 29.96\ °\text{C} = 302.11\ \text{K}$$

$$h_1 = 121.4\ \text{kJ/kg}$$

$$s_1 = 0.422\ \text{kJ/kgK}$$

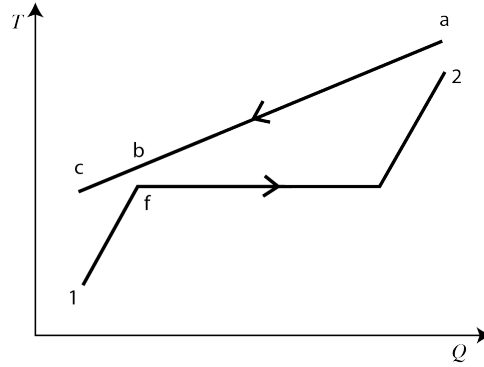$$h_2 = 3450.4\ \text{kJ/kg}$$

$$s_2 = 6.5230\ \text{kJ/kgK}$$

$$w_{max} = (3450.4 - 121.4) - 302.11 \times (6.5230 - 0.422)$$
$$= \underline{\underline{1485.8\ \text{kJ/kg}}}$$

Assuming negligible feed pump work:

$$q_{in} = h_2 - h_1 = 3329\ \text{kJ/kg}$$

$$\eta_{ST} = \frac{1485.8}{3329} = \underline{\underline{0.446}}$$ [3]

(c)(i)

From the databook,
$$T_f = 342.16 \text{ °C}$$
$$h_f = 1610.3 \text{ kJ/kg}$$

From the pinch point temperature difference,
$$T_b = 352.16 \text{ °C}$$

SFEE for the hot portion of the HRSG (steam above pinch point temperature):
$$\dot{m}_g c_p (T_a - T_b) = \dot{m}_s (h_2 - h_f)$$
$$\frac{\dot{m}_s}{\dot{m}_g c_p} = \frac{T_a - T_b}{h_2 - h_f} = \frac{600 - 352.16}{3450.4 - 1610.3} = 0.135 \text{ kgK/J}$$

SFEE for the cold portion of the HRSG:
$$\dot{m}_g c_p (T_b - T_a) = \dot{m}_s (h_f - h_1)$$
$$T_c = T_b - \frac{\dot{m}_s}{\dot{m}_g c_p}(h_f - h_1) = 352.16 - 0.135 \times (1610.3 - 121.4) = 151.6 \text{ °C}$$
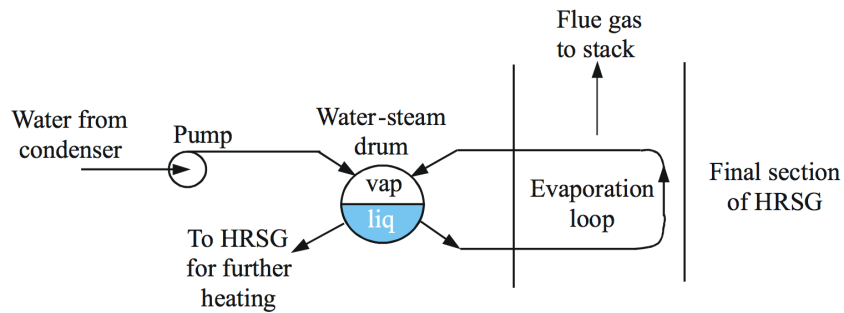$$\eta_b = \frac{600 - 151.6}{600 - 28.96} = \underline{\underline{0.785}}$$

[5]

(c)(ii)
$$\Delta S_{irrev} = \dot{m}_s (s_2 - s_1) + \dot{m}_g (s_c - s_a)$$
$$= \dot{m}_s (s_2 - s_1) + \dot{m}_g c_p \ln\left(\frac{T_c}{T_a}\right)$$
$$\Delta s_{irrev} = (s_2 - s_1) + \frac{\dot{m}_g c_p}{\dot{m}_s} \ln\left(\frac{T_c}{T_a}\right)$$

8

Lost work per kg of steam $= T_1 \Delta s_{irrev}$

$$= 302.11 \times \left[6.5230 - 0.422 + \frac{1}{0.135} \times \ln\left(\frac{424.75}{873.15}\right) \right]$$

$$= 230.6 \text{ kJ/kg}$$

$$= 0.155 w_{max}$$

[4]

(d)

Preheating loop for the HRSG of a combined cycle power plant

The preheater loop avoids condensation of the flue gases on the water pipes in the HRSG (which would cause corrosion). The water from the condenser is pumped to pressure such that the saturation temperature at this pressure is higher than the dew point temperation of the flue gases in the HRSG. A two-phase mixture exists as shown, with water being drawn through the HRSG where it evaporates and returns to the drum as vapour. Thus, heat is transferred from the flue gases but the temperature of the water/steam in the pipe is always above the HRSG dew point temperature, so no flue gases condense on the pipe.

[5]

AJW / GP