

3A5 SOLUTIONS 2022 – Thermodynamics & Power Generation

Examiners' comments:

Q1. *Equations of state and Maxwell relations.* Nearly all candidates were able to derive the Maxwell relation and most correctly applied the Gibbs relation in part (a). Most spotted that the throttle was isenthalpic in part (b) but there were no completely correct attempts at the rest of this part of the question, with many students incorrectly manipulating the partial differential relations. Determining the critical temperature from the van der Waal's EOS was tackled well by many, though a significant number got lost in the algebra.

Q2. *Chemical exergy and ammonia as fuel.* Nearly all candidates were able to derive the maximum work expression, though in some cases the derivations lacked rigour and clarity. In part (b) most candidates could see which equations to combine to determine the Gibbs free energy change for oxidation of ammonia, though relatively few carried this through to the correct numerical result. Most then went off on a tangent in computing the exergy density, not realising they only needed to multiply by mass density. Very few made much headway with the minimum work required for air separation.

Q3. *Compressed Air Energy Storage (CAES).* This was a new topic this year, which (along with the length of the question's text) may have deterred many candidates. Part (a) on the exergy density of isobaric CAES was very similar to an examples paper question. There were numerous correct attempts at this part, but several candidates did not spot that the storage was isobaric. *T-s* diagrams were drawn well in most cases for part (b), but few candidates knew how to correctly apply exergy analysis.

Q4. *Steam plant and biofuel combustion.* This question began with a straightforward analysis of a superheated Rankine cycle. This part was generally well done, although indifferent accuracy in the use of the steam chart resulted in a considerable spread of numerical answers. There were some well-constructed answers to the subsequent analysis of biofuel composition, but many candidates found this difficult. Relatively few candidates produced a convincing discussion of the technical issues around Carbon Capture and Storage.

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Q1. (a) (i) The isotherms are horizontal near A $\Rightarrow h \neq f(p)$, which is evidence for IG behaviour. The pressure is low, hence molecules are well spaced, so intermolecular forces will be small. [2]

(ii) On isobar: $Tds = dh - vdp$
 $\therefore \frac{ds}{dh} = \frac{1}{T} = \frac{1}{T_s(p)}$

$\therefore \Delta s \approx \frac{500}{373} = \underline{1.34 \text{ kJ/kgK}}$ [3]

(b) $g = h - Ts$

$\therefore dg = dh - Tds - sdT$
 $= dh - (dh - vdp) - sdT$
 $= vdp - sdT \Rightarrow v = \left(\frac{\partial g}{\partial p}\right)_T ; s = -\left(\frac{\partial g}{\partial T}\right)_p$

$\therefore \underline{\left(\frac{\partial v}{\partial T}\right)_p} = -\left(\frac{\partial s}{\partial p}\right)_T$ [2]

(c) SFEE etc. $\Rightarrow h = \text{const.}$ for nozzle

$dh = \left(\frac{\partial h}{\partial T}\right)_p dT + \left(\frac{\partial h}{\partial p}\right)_T dp = 0$

$= c_p dT + \left(\frac{\partial h}{\partial p}\right)_T dp = 0$

$\therefore \left(\frac{\partial T}{\partial p}\right)_h = -\frac{1}{c_p} \left(\frac{\partial h}{\partial p}\right)_T$ (1)

$$\text{But } Tds = dh - vdp$$

$$\begin{aligned}\therefore \left(\frac{\partial h}{\partial p}\right)_T &= T \left(\frac{\partial s}{\partial p}\right)_T + v \\ &= -T \left(\frac{\partial v}{\partial T}\right)_p + v\end{aligned}$$

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

$$\therefore \left(\frac{\partial h}{\partial p}\right)_T = -T \left(\frac{v-b}{T}\right) + v = b$$

$$\& \text{ from (1) above: } \underline{\left(\frac{\partial T}{\partial p}\right)_h = -\frac{b}{c_p}}$$

b is the "excluded volume" and must be positive; so is c_p

$$\therefore \left(\frac{\partial T}{\partial p}\right)_h < 0 \Rightarrow \Delta T > 0 \quad (\text{pressure drops through nozzle}) \quad [8]$$

(d) At critical point, $\left(\frac{\partial p}{\partial v}\right)_T = \left(\frac{\partial^2 p}{\partial v^2}\right)_T = 0$ (i.e., point of inflexion on the T_c isotherm)

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

$$\therefore \left(\frac{\partial p}{\partial v}\right)_T = \frac{-RT}{(v-b)^2} + \frac{2a}{v^3} = 0 \Rightarrow \frac{RT_c}{(v_c-b)^2} = \frac{2a}{v_c^3} \quad (2)$$

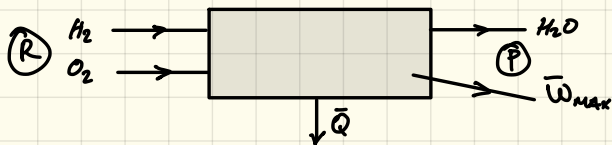
$$\left(\frac{\partial^2 p}{\partial v^2}\right)_T = \frac{2RT}{(v-b)^3} - \frac{6a}{v^4} = 0 \Rightarrow \frac{RT}{(v-b)^3} = \frac{3a}{v_c^4} \quad (3)$$

$$(2)/(3): (v_c-b) = \frac{2}{3}v_c \Rightarrow v_c = 3b$$

$$\text{Sub in (2)} \Rightarrow T_c = \frac{2a(2b)^2}{R(3b)^3} = \frac{8a}{27Rb} = \frac{8 \times 1680}{27 \times 461.5 \times 0.0077} = \underline{634.5\text{K}}$$

This is a reasonably good estimate - the correct value (database) is 647.1 K, and the van der Waals equation is renowned for its modest accuracy! [5]

Q2. (a)



N_2 and any excess O_2 come and leave at P_0 & T_0 so have no effect. Per kmol,

$$\text{SFEE: } -\bar{Q} - \bar{W}_{\max} = \bar{H}_P - \bar{H}_R \quad (1)$$

where R & P denote reactants & products respectively.

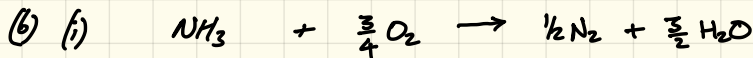
$$\text{SFSE: } -\bar{Q} = T_0 (\bar{S}_P - \bar{S}_R) \quad (2)$$

$$\begin{aligned} (1) - (2): \quad \bar{W}_{\max} &= \bar{H}_R - \bar{H}_P - T_0 (\bar{S}_R - \bar{S}_P) \\ &= -\Delta \bar{H}_{T_0}^\circ + T_0 \Delta \bar{S}_{T_0}^\circ \\ &= \underline{-\Delta \bar{G}_{T_0}^\circ} \quad (\text{all products and reactants being at } p_0 \text{ \& } T_0) \end{aligned}$$

$$\begin{aligned} \text{For } H_2, -\Delta \bar{G}_{T_0}^\circ &= +RT_0 \ln K_p = 8314 \times 298.15 \times 92.107 \\ &= 228.6 \text{ MJ/kmol} \end{aligned}$$

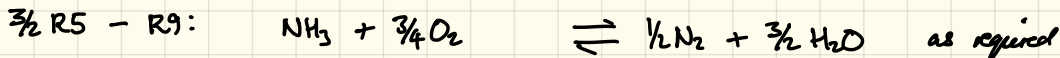
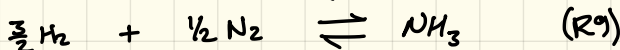
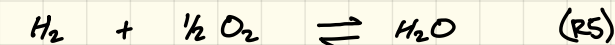
$$\therefore \underline{\bar{W}_{\max} = 114.3 \text{ MJ/kg}}$$

[6]



[1]

(ii) We need $\Delta \bar{G}_{T_0}^\circ$ for this reaction, but it is not available in the data book directly. Instead we combine:



$$\begin{aligned} \therefore \Delta \bar{G}_{T_0}^{\circ} &= \frac{5}{2} \Delta \bar{G}_{T,RS}^{\circ} - \Delta \bar{G}_{T,R_2}^{\circ} \\ &= -\bar{R}T_0 \left(\frac{3}{2} \ln K_{P,5} - \ln K_{P,9} \right) \end{aligned}$$

$$\therefore \bar{W}_{\max} = 8314 \times 298.15 \times (1.5 \times 92.207 - 6.593) = 326.5 \text{ MJ/kmol}$$

$$\therefore w_{\max} = \frac{\bar{W}_{\max}}{M_{\text{NH}_3}} = \frac{326.5}{17} = \underline{19.2 \text{ MJ/kg}} \quad [5]$$

$$(ii) \rho_E^{\text{NH}_3} = \rho w_{\max} = 600 \times 19.2 = \underline{11.5 \text{ GJ/m}^3}$$

$$\rho_E^{\text{H}_2} = \frac{p}{RT} w_{\max} = \frac{10^6 \times 2}{8314 \times 298.15} \times 114.3 = \underline{92.2 \text{ MJ/m}^3} \quad [3]$$

More than 100 times greater for ammonia!

(c) Per kmol of air:

$$\begin{aligned} \bar{W}_{\min} &= +\Delta \bar{G}_{T_0}^{\circ} = \cancel{\Delta \bar{G}_{T_0}^{\circ}} - T_0 \Delta \bar{S}_{T_0}^{\circ} = +T_0 \Delta \bar{S}_{\text{mix}} \\ &= -\bar{R}T_0 \left(X_{\text{N}_2} \ln X_{\text{N}_2} + X_{\text{O}_2} \ln X_{\text{O}_2} \right) \\ &= -8314 \times 298.15 \times \left(0.79 \ln 0.79 + 0.21 \ln 0.21 \right) \\ &= 1.274 \text{ MJ/kmol air.} \end{aligned}$$

↙ 1% @ const. T

1 kmol of air produces 0.79 kmol N_2

1 kg NH_3 requires $\frac{1}{2 \times 17} = \frac{1}{34}$ kmol N_2

$$\therefore w_{\text{sep, min}} = \frac{1}{34} \times \frac{1.274}{0.79} = \underline{0.047 \text{ MJ per kg of NH}_3}$$

Air separation likely to be by liquefaction in practice, involving numerous irreversible processes. The estimate is thus unrealistically low (but nonetheless small cf. $\Delta \bar{G}^{\circ}$ for oxidizer of NH_3). [5]

Q:

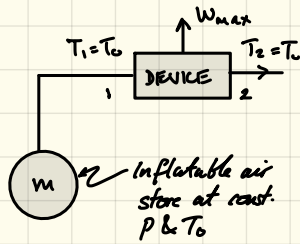
(a) Air is supplied at const. p & T

$$\begin{aligned} \therefore W_{\max} &= m(b_1 - b_2) \\ &= \frac{pV}{R T_0} + R T_0 \ln\left(\frac{p}{p_0}\right) \\ &= pV \ln\left(\frac{p}{p_0}\right) \end{aligned}$$

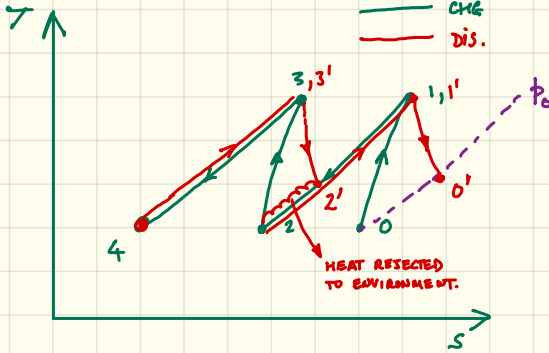
$$\begin{aligned} p &= p_0 + (\rho_w g) = 10^5 + 1038 \times 9.81 \times 700 \text{ N/m}^2 \\ &= 72.28 \text{ bar} \end{aligned}$$

$$\therefore W_{\max} = 72.28 \times 10^5 \times 10^5 \times \ln 72.28 = \underline{3.09 \times 10^{12} \text{ J}} \quad (= 859.4 \text{ MWh}) \quad [5]$$

(Note, the (-ve) GPE of the air has been neglected. This amounts to about $0.06 \times 10^{12} \text{ J}$)



(b) (i)



$$W_{\text{in}} = m C_p \left((T_1 - T_0) + (T_3 - T_2) \right) = 2 m C_p T_0 \left(\beta^{\frac{\gamma-1}{\gamma}} - 1 \right)$$

$$\begin{aligned} m &= \rho_0 V \\ &= \frac{\rho_0 V}{R T_0} \end{aligned}$$

$$\beta = \sqrt{72.28} = 8.502 \quad \therefore W_{\text{in}} = 2 \times \frac{72.28 \times 10^{10} \times 1005 \times 700}{287 \times 700} \left(8.5^{\frac{0.4}{1.4}} - 1 \right)$$

$$= \underline{4.92 \times 10^{12} \text{ J}} \quad (\approx 1.37 \text{ GWh}) \quad [5]$$

(i) If there is no loss in HX1 or HX2 then the energy transferred to the thermal oil equals the energy drop in air.

$$\begin{aligned} \therefore \text{Energy stored in each tank} &= m(b_1 - b_2) = m c_p (T_1 - T_0 - T_0 \ln \left(\frac{T_1}{T_0} \right)) \\ &= m c_p T_0 \left(\frac{T_1}{T_0} - 1 - \ln \left(\frac{T_1}{T_0} \right) \right) \end{aligned}$$

$$\begin{aligned} \left(\frac{T_1}{T_0} \right) = \beta^{\frac{\gamma-1}{\gamma}} = 1.973 \quad \Rightarrow \quad \Delta F_{\text{tank}} &= \frac{72.24 \times 10^3}{287 \times 1.4} \times 1005 \times T_0 \times \left(0.973 - \ln 1.973 \right) \\ &= \underline{0.742 \times 10^{12} \text{ J}} \quad (\approx 206 \text{ MWh}) \end{aligned}$$

$$\begin{aligned} \text{RANKINE EFFICIENCY OF CHARGE PROCESS} &= \frac{\text{ENERGY STORED}}{\text{WORK INPUT}} \\ &= \frac{859.4 + 2 \times 206}{1370} = \underline{92.8\%} \end{aligned} \quad [5]$$

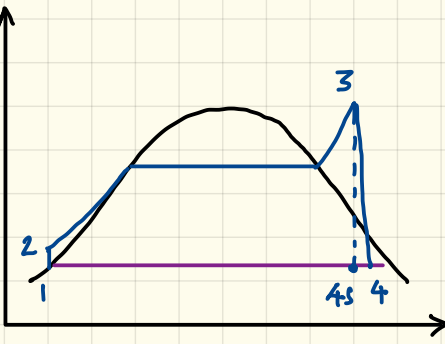
(c) (i) See T-s diagram above
An air cooler is required after the first turbine to cool the air back to T_0 , otherwise the first store cannot be cooled back to its initial state (T_0).

$$\begin{aligned} \text{(ii)} \quad \eta_{\text{net}} &= \frac{w_{T1} + w_{T2}}{w_{C1} + w_{C2}} = \frac{T_1 - T_0'}{T_1 - T_0} = \frac{T_1 \left(1 - \beta^{\frac{\gamma-1}{\gamma}} \right)}{T_1 - T_0} \\ &= \frac{1.973 \left(1 - 8.5^{\frac{-(\gamma-1)}{\gamma}} \right)}{1.973 - 1} \end{aligned}$$

$$\eta_{\text{net}} = \underline{85.8\%} \quad [3]$$

Q4.

(a)



$$P_1 = 0.01 \text{ bar}$$

$$P_3 = 160 \text{ bar} \quad T_3 = 560^\circ\text{C}$$

$$\eta_T = 0.85 \quad h_2 \approx h_1$$

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

TABLES/CHART: $h_3 = 3460 \text{ kJ/kg}$; $h_{4s} = 1962 \text{ kJ/kg}$

$$\eta_T = \frac{h_3 - h_4}{h_3 - h_{4s}} \quad \therefore h_4 = 3460 - 0.85(3460 - 1962) = 2187 \text{ kJ/kg}$$

(i)

$$\text{DRYNESS: } x_4 = \frac{(h_4 - h_{f4})}{h_{fg4}} = \frac{(2187 - 121.4)}{(2553.7 - 121.4)} = \underline{\underline{0.85}} \quad [\text{OR USE CHART}]$$

(ii) work output $\approx h_3 - h_4 = 1273 \text{ kJ/kg}$

heat input $= h_3 - h_2 = 3338.6 \text{ kJ/kg}$

$$\therefore \underline{\underline{\eta_{TH} \approx 0.38}}$$

[8]

(b) $P = 500 \text{ MW}$; $\Rightarrow \dot{Q}_{in} = \frac{500}{0.382} = 1309 \text{ MW}$

(i) Biomass composition:-

$$0.42 \text{ C needs } 0.42 \times \frac{32}{12} = 1.12 \text{ kg O}_2 / \text{kg fuel}$$

$$0.08 \text{ H needs } 0.08 \times \frac{16}{2} = 0.64 \text{ kg O}_2 / \text{kg fuel}$$

BUT 0.48 kg O₂ in fuel

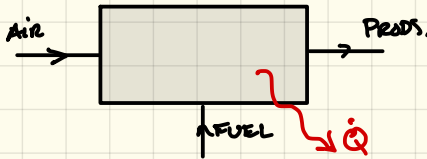
$$\text{Mass fraction of O}_2 \text{ in air} = \frac{0.21 \times 32}{0.21 \times 32 + 0.79 \times 28} = 0.233$$

∴ Stoichiometric combustion
1 kg of fuel needs

$$\frac{1.12 + 0.64 - 0.48}{0.233} = 5.49 \text{ kg air}$$

∴ FOR 15% EXCESS AIR; $\text{A.F.R.} = \underline{6.31 \text{ kg/kg}} \quad [4]$

(ii) SFEE



$$-\dot{Q} = \dot{H}_p - \dot{H}_R \Rightarrow \dot{Q} = \dot{H}_R - \dot{H}_p = (\dot{H}_p - \dot{H}_{p0}) + (\dot{H}_{R0} - \dot{H}_R) - (\dot{H}_p - \dot{H}_R) \\ = \dot{m}_f \left\{ \text{LCV} - (1 + \text{A.F.R.}) \bar{c}_{pp} (T_p - T_0) \right\}$$

$$\therefore \dot{m}_f = \frac{\dot{Q}}{\text{LCV} - (1 + \text{A.F.R.}) \bar{c}_{pp} (T_p - T_0)} = \frac{1309 \times 10^3}{18 \times 10^3 \times 7.31 \times 1.15 \times (80 - 25)} = \underline{74.7 \text{ kg/s}} \quad [4]$$

(c) Discuss the carbon-neutrality of biomass, set against the difficulties of CCS such as CO₂ separation from flue gas, transfer of CO₂ to storage; selection/maintenance of storage sites. [4]