## MODULE 3A5 - THERMODYNAMICS AND POWER GENERATION SOLUTIONS

1. (a)

$$
\begin{align*}
& f=u-T s \\
& d f=d u-T d s-s d T \\
& =d u-(d u+p d v)-s d T \\
& =-p d v-s d T \\
& \therefore \quad p=-\left(\frac{\partial f}{\partial v}\right)_{T} \quad \text { and } \quad s=-\left(\frac{\partial f}{\partial T}\right)_{v} \\
& \text { but } \quad \frac{\partial^{2} f}{\partial T \partial v}=\frac{\partial^{2} f}{\partial v \partial T} \\
& \therefore \quad \underline{\underline{\left(\frac{\partial p}{\partial T}\right)_{v}=\left(\frac{\partial s}{\partial v}\right)_{T}}} \tag{2}
\end{align*}
$$

(b) $\quad p=-\left(\frac{\partial f}{\partial v}\right)_{T}=\frac{R T}{v-b}$
$\therefore \quad \underline{\underline{p(v-b)=R T}}$
Note that $u=f+T s$ so need to find $s$ before $u$ can be obtained.

$$
\begin{array}{ll} 
& \left.\begin{array}{rl}
s & =-\left(\frac{\partial f}{\partial T}\right)_{v}=-\alpha\left(1-\ln \frac{T}{T_{r}}-T \frac{1}{T}\right)+\beta\left(T-T_{r}\right)+R \ln \left(\frac{v-b}{v_{r}-b}\right) \\
& =\alpha \ln \frac{T}{T_{r}}+\beta\left(T-T_{r}\right)+R \ln \left(\frac{v-b}{v_{r}-b}\right) \\
\therefore & \\
& u
\end{array}\right)=\alpha\left(T-T_{r}-T \ln \frac{T}{T_{r}}\right)-\frac{\beta}{2}\left(T-T_{r}\right)^{2}-R T \ln \left(\frac{v-b}{v_{r}-b}\right) \\
& +\alpha T \ln \frac{T}{T_{r}}+\beta T\left(T-T_{r}\right)+R T \ln \left(\frac{v-b}{v_{r}-b}\right) \\
\text { Hence } \quad & \\
\text { and } \quad & \\
& \\
& \\
&  \tag{6}\\
c_{v} & =\left(\frac{\partial u}{\partial T}\right)_{v}=\alpha+\beta T
\end{array}
$$

The molecular model is similar to that of an ideal gas, but with account taken of the 'excluded volume' associated with the finite size of molecules. The internal energy is independent of $v$ which implies no intermolecular forces. $c_{v}$ depends on $T$, which implies 'internal energy' modes of the molecules (e.g., vibration), similar to the semi-perfect gas model. $b$ is the excluded volume (per unit mass of gas) and $v_{r}$ and $T_{r}$ are the reference specific volume and temperature at which $f, u($ and $s)$ are zero.
(c) Assume the flow is adiabatic and neglect changes in KE and PE (the usual assumptions). Thus, flow through valve is isenthalpic.

$$
h=u+p v=u+R T+p b=\alpha\left(T-T_{r}\right)+\frac{\beta}{2}\left(T^{2}-T_{r}^{2}\right)+R T+p b
$$

Note that $h$ depends on $p$ even though $u$ is independent of $v$.

Thus, $\quad \frac{\beta}{2} T_{2}^{2}+(\alpha+R) T_{2}=\frac{\beta}{2} T_{1}^{2}+(\alpha+R) T_{1}+b\left(p_{1}-p_{2}\right)$
$\therefore \quad 0.0025 T_{2}^{2}+1.4 T_{2}=0.0025 \times 450^{2}+1.4 \times 450+0.05 \times \underline{1000}$.
$\therefore \quad \underline{T_{2}=463.57 \mathrm{~K}}$

Now

$$
\begin{aligned}
s_{2}-s_{1} & =\alpha \ln \frac{T_{2}}{T_{1}}+\beta\left(T_{2}-T_{1}\right)+R \ln \left(\frac{v_{2}-b}{v_{1}-b}\right) \\
& =\alpha \ln \frac{T_{2}}{T_{1}}+\beta\left(T_{2}-T_{1}\right)+R \ln \left(\frac{T_{2} p_{1}}{T_{1} p_{2}}\right) \\
& =1.0 \ln \frac{463.57}{450}+0.005 \times(13.57)+0.4 \ln \left(\frac{463.57 \times 50}{450 \times 40}\right) \\
& =0.19872 \mathrm{~kJ} \mathrm{~K}^{-1} \mathrm{~kg}^{-1}
\end{aligned}
$$

Lost power $=\dot{m} T_{0}\left(s_{2}-s_{1}\right)=0.75 \times 298.15 \times 0.19872=44.43 \mathrm{~kW}$

For ideal gas, $T_{2}=T_{1}$ so $s_{2}-s_{1}=R \ln \left(p_{1} / p_{2}\right)=0.4 \times \ln (50 / 40)=0.08926 \mathrm{~kJ} \mathrm{~K}^{-1} \mathrm{~kg}^{-1}$

Lost power $=\dot{m} T_{0}\left(s_{2}-s_{1}\right)=0.75 \times 298.15 \times 0.08926=\underline{\underline{19.96} \mathrm{~kW}}$

Assessor's comment: This was the least popular question. Most candidates succeeded in Part (a), though often with more algebra than anticipated. In Part (b), many candidates derived the $\mathrm{p}-\mathrm{v}$ - T relation but fewer were able to obtain the expression for $c_{\mathrm{v}}$ (differentiation of a logarithmic function was a common error). Only a few candidates identified that the flow through the valve in Part (c) is isenthalpic.

Q2. (a) The reaction is exothermic $\left(\Delta \tilde{H}_{0}^{T}<0\right)$ hence $\ln K_{p}$ increases with $(1 / T)$ and therefore $K_{p}$ decreases with $T$ (this is also obvious from the tabulated values of $\ln K_{p}$ in the databook). Assuming ideal gas relations,

$$
\begin{equation*}
\left(\frac{P_{N H_{3}}}{P_{0}}\right)^{+1}\left(\frac{P_{N_{2}}}{P_{0}}\right)^{-1 / 2}\left(\frac{P_{H_{2}}}{P_{0}}\right)^{-3 / 2}=K_{p}(T) \tag{1}
\end{equation*}
$$

Thus an increase in $T$ (reduction in $K_{p}$ ) causes a reduction in the partial pressure of $\mathrm{NH}_{3}$ an increase in the partial pressures of $\mathrm{N}_{2}$ and $\mathrm{H}_{2}$ - i.e., the reaction shifts to the left hand side as $T$ increases. Explanation by "Le Chatelier" principle also OK.
(b) The reaction may be written:

$$
\frac{1}{2} \mathrm{~N}_{2}+\frac{3}{2} \mathrm{H}_{2} \rightarrow x \mathrm{NH}_{3}+y \mathrm{~N}_{2}+z \mathrm{H}_{2}
$$

Conservation of N :

$$
1=x+2 y \quad \Rightarrow \quad y=\frac{1}{2}(1-x)
$$

Conservation of H: $\quad 3=3 x+2 z \quad \Rightarrow \quad z=\frac{3}{2}(1-x)$
Total no. of kmols: $\quad n=x+y+z=2-x$

$$
\begin{array}{ll}
\text { Using (1): } & \left(\frac{x}{n}\right)^{+1}\left(\frac{y}{n}\right)^{-1 / 2}\left(\frac{z}{n}\right)^{-3 / 2}\left(\frac{P}{P_{0}}\right)^{-1}=K_{p}(T) \\
\therefore & \frac{x}{\left\{\frac{1}{2}(1-x)\right\}^{1 / 2}\left\{\frac{3}{2}(1-x)\right\}^{3 / 2}}=\frac{1}{n} \frac{P}{P_{0}} K_{p}(T)
\end{array}
$$

Ideal gas relations: $\quad P V=n \tilde{R} T ; \quad P_{0} V=2 \tilde{R} T_{0} \Rightarrow \frac{P}{P_{0}}=\frac{n}{2} \frac{T}{T_{0}}$

$$
\begin{equation*}
\therefore \quad \frac{x}{(1-x)^{2}}=\frac{\sqrt{27}}{8} K_{p}(T) \frac{T}{T_{0}} \quad \text { i.e., } C=\frac{\sqrt{27}}{8} \tag{2}
\end{equation*}
$$

(c) $1^{\text {st }}$ Law: $\quad Q-W=\Delta U=0 \quad$ [Note: $U$ is constant, not $H$ )

$$
\therefore \quad H_{p}-P V=H_{R}-P_{0} V
$$

$$
\therefore \quad\left(H_{p}-H_{p}^{0}\right)=\left(H_{R}-H_{R}^{0}\right)-\left(H_{p}^{0}-H_{R}^{0}\right)+\left(P V-P_{0} V\right)
$$

$$
\therefore \quad n \tilde{C}_{p}\left(T-T_{0}\right)=0-x \Delta \tilde{H}_{0}^{T_{0}}+n \tilde{R} T-2 \tilde{R} T_{0}
$$

$$
\therefore \quad(2-x)\left(\tilde{C}_{p}-\tilde{R}\right)\left(T-T_{0}\right)=-x\left(\Delta \tilde{H}_{0}^{T_{0}}+\tilde{R} T_{0}\right)
$$

$$
\begin{equation*}
\therefore \quad T=T_{0}-\frac{x\left(\Delta \tilde{H}_{0}^{T_{0}}+\tilde{R} T_{0}\right)}{(2-x)\left(\tilde{C}_{p}-\tilde{R}\right)} \tag{3}
\end{equation*}
$$

To find $K_{p}$ at 500 K we need to interpolate in $(1 / T)$. From the data book,

$$
\begin{aligned}
\ln K_{p}(500) & =\ln K_{p}(400)+\frac{\frac{1}{500}-\frac{1}{400}}{\frac{1}{600}-\frac{1}{400}}\left\{\ln K_{p}(600)-\ln K_{p}(400)\right\} \\
& =1.778+0.6 \times(-3.191-1.778) \\
& =-1.2034
\end{aligned} \quad \begin{aligned}
& \therefore \quad K_{p}=0.30017
\end{aligned}
$$

Rearranging (2) gives:

$$
F x^{2}-(2 F+1) x+1=0 \quad \Rightarrow \quad x=\frac{2 F+1 \pm \sqrt{4 F+1}}{2 F} \text { where } F=\frac{\sqrt{27}}{8} K_{p} \frac{T}{T_{0}}
$$

Substitution for $K_{p}$ and $T$ gives $\underline{x=0.20608}$ (the other root is $>1$ )

Substitution in (3) then gives:

$$
T=298.15-\frac{0.20608 \times(-45900 .+8.3145 \times 298.15)}{(2.0-0.20608) \times(33.0-8.3145)}=500.22 \mathrm{~K}
$$

Thus $T \approx 500 \mathrm{~K}$ is consistent with solution to both (2) and (3).
(d) Doubling the pressure by the addition of an inert gas will not affect the partial pressures of $\mathrm{NH}_{3}, \mathrm{~N}_{2}$ and $\mathrm{H}_{2}$, hence $x$ remains at 0.206 kmol . (Note that this is in contrast to doubling the pressure by reducing the volume, for which the equilibrium would shift to the right).

Assessor's comment: Part (a) and (b) was well answered. The process in Part (c) is at constant volume and so is at constant internal energy (not constant enthalpy). Part (d) was answered incorrectly by almost all candidates.

Q3. (a) Cooling the turbine allows an increased turbine entry temperature (TET). For an ideal Joule cycle, the cycle efficiency is only a function of pressure ratio so that increasing the TET does not affect the cycle efficiency but does increase the specific work output. For a real cycle, with irreversible turbomachinery, raising TET increases cycle efficiency as well as specific work output. An increased specific work output will either result in more power output for a fixed gas turbine size (fixed massflow) or a smaller (cheaper) gas turbine for a given power output.
(b)(i)

Let the temperature of the air extracted from the compressor be $T_{\mathrm{c}}$, and the temperature of the main turbine flow when the coolant is added be $T_{\mathrm{t}}$

$$
\begin{aligned}
\frac{T_{c}}{T_{1}} & =\left(\frac{\alpha r_{p} p_{1}}{p_{1}}\right)^{\frac{\gamma-1}{\frac{p}{\eta}}}=\left(\alpha r_{p}\right)^{\frac{\gamma-1}{\gamma \eta}} \\
& =2.411 \\
T_{c} & =718.9 \mathrm{~K}
\end{aligned}
$$

and

$$
\begin{aligned}
& \frac{T_{3}}{T_{t}}=\left(\frac{r_{p} p_{1}}{\alpha r_{p} p_{1}}\right)^{\frac{(\gamma-1) \eta}{\gamma}}=\left(\frac{1}{\alpha}\right)^{\frac{(\gamma-1) \eta}{\gamma}} \\
& T_{t}=T_{3} \alpha^{\frac{(\gamma-1) \eta}{\gamma}} \\
& T_{t}=T_{1} \theta \alpha^{\frac{(\gamma-1) \eta}{\gamma}} \\
& \frac{T_{t}}{T_{1}}=4.721 \\
& T_{t}=1407.6 \mathrm{~K}
\end{aligned}
$$

The steady flow energy equation then gives the mixed out temperature,

$$
\begin{align*}
T_{m} & =m T_{c}+(1-m) T_{t}  \tag{4}\\
& =\underline{\underline{1338.8 \mathrm{~K}}}
\end{align*}
$$

(b) (ii)


The temperature of the mixed out flow must always be $T_{m}$. If the mixing takes place at constant pressure, the entropy of the mixed out flow is,

$$
s_{m}-s_{1}=c_{p} \ln \frac{T_{m}}{T_{1}}-R \ln \frac{p_{m}}{p_{1}}
$$

If the coolant and mainstream flows are combined by a process that is fully reversible, "FR", the mixed out entropy would be,

$$
\begin{aligned}
& s_{F R}-s_{1}=m\left(s_{c}-s_{1}\right)+(1-m)\left(s_{t}-s_{1}\right) \\
& =m\left(c_{p} \ln \frac{T_{c}}{T_{1}}-R \ln \frac{p_{m}}{p_{1}}\right)+(1-m)\left(c_{p} \ln \frac{T_{t}}{T_{1}}-R \ln \frac{p_{m}}{p_{1}}\right) \\
& =m c_{p} \ln \frac{T_{c}}{T_{1}}+(1-m) c_{p} \ln \frac{T_{t}}{T_{1}}-R \ln \frac{p_{m}}{p_{1}}
\end{aligned}
$$

and

$$
s_{m}-s_{F R}=c_{p}\left(\ln \frac{T_{m}}{T_{1}}-m \ln \frac{T_{c}}{T_{1}}-(1-m) \ln \frac{T_{t}}{T_{1}}\right) .
$$

The lost work, as a fraction of the turbine work without cooling is given by

$$
\begin{equation*}
\frac{w_{\text {lost }}}{w_{t, \text { no cool }}}=\frac{T_{1}\left(s_{m}-s_{F R}\right)}{c_{p} \theta T_{1}\left(1-\left(\frac{1}{r_{p}}\right)^{\frac{(\gamma-1) \eta}{\gamma}}\right)}=\frac{\ln (4.490)-0.1 \times \ln (2.411)-0.9 \times \ln (4.721)}{5 \times 0.537}=\underline{\underline{0.63 \%}} \tag{8}
\end{equation*}
$$

(b)(iii)

$$
\begin{align*}
\frac{w_{t}}{w_{t, \text { no cool }}} & =\frac{c_{p}\left((1-m)\left(T_{3}-T_{t}\right)+\left(T_{m}-T_{4}\right)\right)}{c_{p} \theta T_{1}\left(1-\left(\frac{1}{r_{p}}\right)^{\frac{(\gamma-1) \eta}{\gamma}}\right)}=\frac{(1-m)\left(\theta-\frac{T_{t}}{T_{1}}\right)+\frac{T_{m}}{T_{1}}\left(1-{\frac{1}{\alpha r_{p}}}_{\frac{(\gamma-1) \eta}{\gamma}}^{\alpha\left(1-\left(\frac{1}{r_{p}}\right)^{\frac{(\gamma-1) \eta}{\gamma}}\right)}\right.}{\theta \times 0.537} \\
& =\frac{0.9 \times(5-4.721)+4.490 \times(1-0.490)}{\theta}=\underline{\underline{0.946}} \tag{3}
\end{align*}
$$

(c) It is not normally possible to extract the flow from the compressor at the same pressure as the flow in the turbine where the coolant will be added. Hence, the flow is extracted from the compressor at a higher pressure and throttled (entropy creation due to irreversibilities) to the desired pressure. When the coolant is ejected into the turbine, the kinetic energy (neglected in the above analysis) of the coolant will be dissipated (entropy creation due to irreversibilities).

Assessor's comment: Part (a) was well answered. Most candidates had little difficulty in identifying the mixed out temperature in Part (b). Many candidates interpreted the "lost work in the mixing process" as the change in turbine work output with cooling rather than the expected $T_{0} \Delta s_{\text {mix }}$.


The boiler pressure of 60 bar means the maximum steam temperature is 275 deg C . This is low compared to fossil-fired steam plane (boiler pressures of $>160 \mathrm{bar}$ ). The nuclear reactor is cooled by high pressure water. To prevent boiling, the water in this "primary circuit" is limited to a maximum temperature of approximately 300 deg C and this places the limit on the steam cycle ("secondary circuit") temperature. Without reheat, the expansion to the condenser would lead to intolerably wet steam (low LP turbine efficiency and erosion of the turbine blades).
parts (b), (c) and (d) use the following location numbers:
1 - condenser exit, $\quad 2$ - feed pump exit, $3-$ HP turbine inlet,
4 - HP turbine exit, $\quad 5$ - LP turbine inlet, 6 - LP turbine exit.
(b) At HP turbine inlet, from the saturation tables: $h_{3}=2784.6 \mathrm{~kJ} / \mathrm{kg}$ and $s_{3}=5.890 \mathrm{~kJ} / \mathrm{kg} \mathrm{K}$.

At HP exit (10 bar):

$$
\begin{array}{ll}
s_{4 \mathrm{f}}=2.138 \mathrm{~kJ} / \mathrm{kg} \mathrm{~K} ; & s_{4 \mathrm{~g}}=6.585 \mathrm{~kJ} / \mathrm{kg} \mathrm{~K} ; \\
h_{4 \mathrm{f}}=762.5 \mathrm{~kJ} / \mathrm{kg} ; & \\
h_{4 \mathrm{~g}}=2777.1 \mathrm{~kJ} / \mathrm{kg} .
\end{array}
$$

Dryness fraction, $x$, if the HP turbine were isentropic

$$
\begin{aligned}
& s=5.890=x(6.585-2.138)+2.138 \\
& x=0.844
\end{aligned}
$$

and

$$
\begin{aligned}
h_{4 s} & =762.5+x(2777.1-762.5) \\
& =2462.2 \mathrm{~kJ} / \mathrm{kg}
\end{aligned}
$$

The isentropic efficiency is 0.85 ,

$$
\begin{align*}
& 0.85=\frac{w_{H P}}{2784.6-2462.2} \\
& \Rightarrow w_{H P}=274.0 \mathrm{~kJ} / \mathrm{kg} \text { and } h_{4}=2510.6 \mathrm{~kJ} / \mathrm{kg} \tag{5}
\end{align*}
$$

(c) SFEE for the reheater:

$$
\begin{aligned}
(1-m)\left(h_{5}-h_{4}\right) & =m h_{3 / g} \\
(1-m)(2943.1-2510.6) & =1570.7 m \\
(1-m) & =3.632 m \\
m & =\underline{\underline{0.216}}
\end{aligned}
$$

(d) The maximum work is given by the difference in the availability functions at LP turbine inlet (station 5) and feed heater exit (station 2'), assuming that the condenser is at the dead state temperature.

$$
\begin{aligned}
w_{L P \max } & =b_{5}-b_{2^{\prime}} \\
& =\left(h_{5}-T_{1} s_{5}\right)-\left(h_{2^{\prime}}-T_{1^{\prime}} s_{2^{\prime}}\right) \\
& =\left(h_{5}-h_{2^{\prime}}\right)-T_{1}\left(s_{5}-s_{2^{\prime}}\right) \\
& =(2943.1-852.3)-302.11 \times(6.9265-2.331) \\
& =702.5 \mathrm{~kJ} / \mathrm{kg}
\end{aligned}
$$

The cycle efficiency is then given by

$$
\begin{align*}
\eta_{c} & =\frac{(1-m)\left(w_{H P}+w_{L P \max }\right)}{\left(h_{3}-h_{3 f}\right)+(1-m)\left(h_{3 f}-h_{2^{\prime}}\right)} \\
& =\frac{(1-0.216) \times(274.0+702.5)}{(2784.6-1213.9)+(1-0.216) \times(1213.9-852.3)} \\
& =\frac{765.6}{1570.7+283.5}=\underline{\underline{0.413}} \tag{5}
\end{align*}
$$

(Note that the total flow is heated from 3f to 3, but that the flow in the turbines and between $2^{\prime}$ and 3 f is reduced by the fraction $m$ ).
(e) AGR reactors are cooled by carbon dioxide gas. This removes the temperature restriction placed on the primary circuit of a PWR reactor. The steam cycle is then similar to a conventional fossil-fired station - 160bar boiler pressure with 40 bar reheat. This gives improved steam cycle efficiency.

Assessor's comment: Candidates found Part (a) and (b) straightforward, although a minority attempted, incorrectly, to use the perfect gas relations. Candidates who were able to keep track of the $m$ and (1-m) terms in Part (c) obtained the correct answer but relatively few correctly negotiated the availability question in Part (d).

