Module 3A5: Thermodynamics
Notes on Examples Paper 1

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Abstract

This document outlines the methods used to answer each question on the first Thermodynamics examples paper. Additionally, the interesting results are highlighted and commented on. This material is intended to complement to the more detailed worked solutions available in the official cribs. Statements of physical principles and definitions are highlighted in **bold**, while assumptions are *emphasised*.

Q1: Laws of Thermodynamics

Assume that flow is from Station (1) to Station (2) and check for a contradiction later. We are interested in the rate of entropy production due to irreversibility, $\dot{S}_{\text{irrev}}$, so start by applying the **Second Law** to the duct. Rearranging and taking air as a *perfect gas*, find an expression for $\dot{S}_{\text{irrev}}$ in terms of the given thermodynamic states and an unknown heat flow $\dot{Q}$ into the duct. Applying the **First Law** to the duct gives an expression for $\dot{Q}$ in terms of changes in specific enthalpy and kinetic energy. Since we are assuming a *perfect gas*, uniform static temperature implies uniform enthalpy and the enthalpy change is zero. The velocity at Station (1), together with **Conservation of Mass** and the *ideal gas* equation of state allows the kinetic energy term to be evaluated. In turn, the heat flow $\dot{Q}$ and rate of entropy production due to irreversibility $\dot{S}_{\text{irrev}}$ can then be calculated.

As $\dot{S}_{\text{irrev}} \geq 0$ as required by the Second Law, our earlier assumption was correct and the flow direction is from Station (1) to Station (2). If the flow was in the other direction, $\dot{S}_{\text{irrev}} \leq 0$ which is non-physical and indicates that the problem has been set up incorrectly (or a mistake has been made in the calculations).

Note the distinction between change in entropy through the control volume, $\dot{m}(s_2 - s_1)$, and production of entropy due to irreversibility, $\dot{S}_{\text{irrev}}$. The Second Law is sometimes stated as 'entropy can never decrease', which is true only for an isolated system. For a non-adiabatic system, if the heat flow is sufficiently negative, then $\dot{m}(s_2 - s_1)$ is negative. This is not a violation of the Second Law, because $\dot{S}_{\text{irrev}}$ will remain positive.

Q2: Availability

(a)

It is stated that the flow is steady, and exchanges heat with the environment at a single temperature T_0 only. Under these conditions the concept of **availability** can be used, i.e. the maximum shaft power is equal to the decrease in availability function. Taking air as a *perfect gas*, the change in availability can be evaluated directly.

(b)

Ideal isentropic processes correspond to vertical lines on T–s diagram. Ideal isothermal processes correspond to horizontal lines on T–s diagram. The entropy at state (2) is lower than state (1). To reduce the flow entropy, heat must be extracted, which must take place over an infinitesimal temperature difference from the environment to be reversible. The above information is sufficient to sketch a process delivering the maximum shaft power.

Any reversible process between the two states will deliver the maximum shaft power, because for a reversible process the net shaft power is independent of the path taken.

(c)

The task is to prove analytically that the net shaft power for the process in (b) is equal to the maximum shaft power given by availability in (a). First derive separate expressions for the net shaft power for each process in (b), using the **First Law** and **Second Law** applied to each component. If these expressions are summed, the result should be a restatement of **availability** theory.

Q3: Lost power

(a)

The decrease in available work due to heat loss is given by,

$$\dot{W}_{\text{L,Q}} = \int_{\text{A}} \left(1 - \frac{T_0}{T} \right) \mathrm{d}\dot{Q}_0. \tag{1}$$

This term appears in both the decomposition of maximum shaft power in Lecture 1, and the **exergy equation** in Lecture 3. What this means physically is that, for every element of heat loss, the maximum shaft power that we can extract from the flow decreases by an amount equal the shaft power which could otherwise have be extracted by a Carnot engine operating between the local temperature T and the environment at T_0.

The integral in Eqn. (1) can be evaluated by substituting the **First Law** for an infinitesimal control volume at some point along the pipe, and taking the air as an *ideal gas*,

$$\dot{m}\mathrm{d}h = \mathrm{d}\dot{Q} - \mathrm{d}\dot{W}_x \Rightarrow -\mathrm{d}\dot{Q}_0 = -\dot{m}\mathrm{d}h = -\dot{m}c_p\mathrm{d}T,$$

Now, the lost power due to creation of entropy due to irreversibility, is given by,

$$\dot{W}_{\mathrm{L,CR}} = T_0 \dot{S}_{\mathrm{irrev}},$$

which again appears in the **exergy equation**. An expression for $\dot{S}_{\mathrm{irrev}}$ is needed, which can be found by applying the **Second Law** between states (1) and (2) and assuming a *perfect gas*.

The exergy equation is not in the Data Book, so it, or its derivation, should be committed to memory for Tripos.

(b)

There is no actual shaft power, so the two lost power terms already calculated should account for all the change in availability between the two states.

(c)

Irreversibility can be caused by:

- Heat transfer across a finite temperature difference
- Momentum transfer across a finite velocity gradient, i.e. viscous shear
- Mass transfer across a finite concentration gradient

These processes all fall under the same general description: the mixing out of a non-uniformity in a conserved quantity.

- Non-equilibrium processes such as shock waves
- Spontaneous chemical reactions

Draw a picture of the flow field at the valve, and consider which of the above processes are the most likely candidate.

Q4: Exergy analysis of a gas turbine cycle

(a)

Calculation of the properties around the circuit is straightforward using Part I knowledge, but great care must be taken to avoid arithmetic slips. Check your answers in the table below. You will have to do this quickly and accurately in the examination, so it is worth practising.

Station	p/bar	T/K	h/kJ kg^{-1}	s/J kg^{-1} K^{-1}	e/kJ kg^{-1}
1: Inlet	1.00	298.0	0.0	0.0	0.0
2: Compressor exit	15.00	661.5	399.6	88.0	373.4
3: Heater exit	15.00	1400.0	1212.0	912.7	939.9
4: Turbine exit	1.05	784.5	535.0	1050.0	221.9
5: Stack exit	1.00	784.5	535.0	1064.2	217.4

(b)

The following two equations will be used to answer this question: the **First Law** and the **exergy equation** stated below,

$$\dot{m}\Delta h = \dot{Q} - \dot{W}_X,$$

$$\dot{m}\Delta e = \dot{E}_Q - \dot{W}_X - \dot{W}_{L,CR} - \dot{W}_{L,Q}.$$

Properties at every state have been calculated, so the left-hand sides are known. The turbomachinery is adiabatic, leaving $\dot{W}_X$ and $\dot{W}_{L,CR}$ as unknowns. The stack is adiabatic and exchanges no work, leaving $\dot{W}_{L,CR}$ as the only unknown. The heater exchanges no work, and has no pressure loss implying no irreversible entropy generation, so the unknowns are $\dot{E}_Q$ and $\dot{W}_{L,Q}$. In each case there are two equations and one or two unknowns.

Component	$\dot{Q}$/MW	$\dot{W}_X$/MW	$\dot{E}_Q$/MW	$\dot{W}_{L,Q}$/MW	$\dot{W}_{L,CR}$/MW
Compressor	0.00	-9.99	0.00	0.00	0.65
Heater	20.31	0.00	14.16	0.00	0.00
Turbine	0.00	16.93	0.00	0.00	1.02
Stack	0.00	0.00	0.00	0.00	0.11

4

(c) The energy equation is the **First Law**. The question is asking for the values of the exit enthalpy flow rate, and the contributions to each.

$$\text{Compressor: } \dot{m}h_2 = \dot{m}h_1 + \dot{Q}_{12} - \dot{W}_{X,12} \quad \Rightarrow \quad 9.99 = 0 + 0 - (-9.99).$$
$$\text{Heater: } \dot{m}h_3 = \dot{m}h_2 + \dot{Q}_{23} - \dot{W}_{X,23} \quad \Rightarrow \quad 30.30 = 9.99 + 20.31 - 0.$$
$$\text{Turbine: } \dot{m}h_4 = \dot{m}h_3 + \dot{Q}_{34} - \dot{W}_{X,34} \quad \Rightarrow \quad 13.38 = 30.30 + 0 - 16.93.$$
$$\text{Stack: } \dot{m}h_5 = \dot{m}h_4 + \dot{Q}_{45} - \dot{W}_{X,45} \quad \Rightarrow \quad 13.38 = 13.38 + 0 - 0.$$

The energy analysis suggests that nothing is happening in the stack, which is not true.

(d) Similar to part (c) but with the exergy equation.

$$\text{Compressor: } \dot{m}e_2 = \dot{m}e_1 + \dot{E}_{Q,12} - \dot{W}_{X,12} - \dot{W}_{L,CR,12} - \dot{W}_{L,Q,12},$$
$$\Rightarrow \quad 9.34 = 0 + 0 - (-9.99) - 0.65 - 0.$$
$$\text{Heater: } \dot{m}e_3 = \dot{m}e_2 + \dot{E}_{Q,23} - \dot{W}_{X,23} - \dot{W}_{L,CR,23} - \dot{W}_{L,Q,23},$$
$$\Rightarrow \quad 23.50 = 9.34 + 14.16 - 0 - 0 - 0.$$
$$\text{Turbine: } \dot{m}e_4 = \dot{m}e_3 + \dot{E}_{Q,34} - \dot{W}_{X,34} - \dot{W}_{L,CR,34} - \dot{W}_{L,Q,34},$$
$$\Rightarrow \quad 5.55 = 23.50 + 0 - 16.93 - 1.02 - 0.$$
$$\text{Stack: } \dot{m}e_5 = \dot{m}e_4 + \dot{E}_{Q,45} - \dot{W}_{X,45} - \dot{W}_{L,CR,45} - \dot{W}_{L,Q,45},$$
$$\Rightarrow \quad 5.44 = 5.55 + 0 - 0 - 0.11 - 0.$$

No new information is gained in Parts (c) and (d) of this question, because the equations used in parts (a) and (b) are simply restated in a different arrangement.

(e) The overall energy balance demonstrates what happens to the heat input. It only includes 'real' heat and work values.

Energy supply	Inlet enthalpy flow rate	0.00 MW	0%
	Heater supply rate	20.31 MW	100%
Energy usage	Compressor power output	−9.99 MW	-49%
	Turbine power output	16.93 MW	83%
	Exit enthalpy flow rate	13.38 MW	66%

The compressor consumes energy equal to half of the supply, and the heat lost in the exhaust is equal to two-thirds of the supply. It is easy to see why the early pioneers of gas turbine technology had a hard time just getting a machine to run under its own power.

The thermal efficiency is what you get over what you pay for, i.e. net work output over heat input. Thermal efficiency can also be thought of as a 'First Law efficiency', or a conversion factor between the energy out and the energy in. 100% efficiency implies that all the heat input is converted to work; this is not realistic as the Second Law prohibits this and we are limited to the Carnot efficiency.

(f) An exergy balance shows how much of the maximum available power which is supplied to the machine is converted to useful power. It includes 'real' and 'lost' work values.

Exergy supply	Inlet exergy flow rate	0.00 MW	0
	Heater power potential addition	14.16 MW	100%
Exergy usage	Compressor power output	−9.99 MW	-70%
	Compressor lost power	0.65 MW	5%
	Turbine power output	16.93 MW	120%
	Turbine lost power	1.02 MW	7%
	Stack lost power	0.11 MW	1%
	Exit exergy flow rate	5.44 MW	38%

Only a total of 13% of the available power is lost to irreversibility within the gas turbine. Twice as much available power is lost up the chimney. Recovering this is standard practice in modern power plants (see second half of the 3A5 course).

The maximum possible thermal efficiency is the maximum available power over the heat input rate. This is analogous to the Carnot efficiency but for a more complicated heat addition process (non-uniform temperature).

The rational efficiency is the net power over the maximum available power, the exergy supply rate. This can be thought of a as a 'Second Law efficiency', or the performance of the machine relative to a Carnot engine.

Q5: Air-fuel ratio

(a)

The general equation is the stoichiometric equation plus some amount of air on each side.

(b)

This is a straightforward calculation but care must be taken with the units. Use the values of specific heat capacity c_p and molar mass M from the Thermofluids Data Book, "Properties of Perfect Gases". The water can be assumed to be in the gaseous phase during combustion so look up c_{pg} in the "Transport Properties of Saturated Water and Steam" for ambient temperature.

The molar heat capacities are similar because the gases are similar on a molecular level. Hydrogen, oxygen and nitrogen are all diatomic gases, which on a molecular level store energy in three translational, one vibrational and one rotational degrees of freedom. Water has a different structure, with extra rotational and vibrational degrees of freedom, allowing it to store more energy resulting in a higher molar heat capacity. This behaviour is explored in Module 4A9: Molecular Thermodynamics.

(c)

Begin with the **First Law** for the combustor control volume as the question suggests. There is no shaft work $\dot{W}_x = 0$, and the combustor is adiabatic $\dot{Q} = 0$, so the enthalpy flow rate out must equal the enthalpy flow rate in. Mathematically,

$$\bar{h}_{H_2}(T_0) + (0.21A)\bar{h}_{O_2}(T_1) + (0.79A)\bar{h}_{N_2}(T_1) =$$
$$\bar{h}_{H_2O}(T_2) + (0.21A - 0.5)\bar{h}_{O_2}(T_2) + (0.79A)\bar{h}_{N_2}(T_2), \quad (2)$$

and rearranging,

$$\Rightarrow \bar{h}_{H_2}(T_0) + 0.5\bar{h}_{O_2}(T_2) - \bar{h}_{H_2O}(T_2) =$$
$$0.21A\left(\bar{h}_{O_2}(T_2) - \bar{h}_{O_2}(T_1)\right) + 0.79A\left(\bar{h}_{N_2}(T_2) - \bar{h}_{N_2}(T_1)\right). \quad (3)$$

Equation (3) is the first piece of information that is needed. The right-hand side of Eqn. (3), involving differences in enthalpies, can be evaluated assuming all species can be treated as *perfect gases* and using the molar specific heat capacities from part (b). The left-hand side cannot be directly evaluated, as it involves absolute enthalpies, so extra information must be introduced. This is the **standard enthalpy of reaction**, measured in an experiment, defined (products minus reactants),

$$h_{H_2O}(T_0) - h_{H_2}(T_0) - 0.5h_{O_2}(T_0) = \Delta\overline{H}_{T_0}^0. \quad (4)$$

Equation (4) is the second piece of information that is needed. Equations (3) and (4) are two exact relations which require no assumptions beyond the First Law to derive. They are just two independent statements which must always be true. The solution is as simple as adding Eqn. (4) to Eqn. (3), simplifying and rearranging to get an expression for A. No clever tricks are needed, e.g. imagining cooling the reactants down to T_0 etc.

(d)

The same expression for *A* derived in part (c) can be used here, but the assumption of perfect gas behaviour is relaxed and enthalpy changes are calculated directly from the Data Book.

The answer is different because of real gas effects.

Q6: Combustion irreversibility

(a)

The definition of the Gibbs function is $G = H - TS$. You will have to remember this in the exam. We have been given $\Delta \overline{H}^0_{T_0}$ in Q5(c) and $\Delta \overline{G}^0_{T_0}$ in this question, so a simple rearrangement gives $\Delta \overline{S}^0_{T_0}$.

(b)

This question is solved in a similar way to Q5(c). Apply the **Second Law** to the combustor to get an expression for the rate of entropy creation due to irreversibility,

$$\dot{S}_{\text{irrev}} = \left[s_{\text{H}_2\text{O}}(p, T_2) - 0.5 s_{\text{O}_2}(p, T_2) - s_{\text{H}_2}(p, T_0) \right]$$
$$+ 0.21 A \left[s_{\text{O}_2}(p, T_2) - s_{\text{O}_2}(p, T_1) \right] + 0.79 A \left[s_{\text{N}_2}(p, T_2) - s_{\text{N}_2}(p, T_1) \right] \quad (5)$$

To cope with the first term in square brackets, which is not a difference in entropy, the **definition of** $\Delta \overline{S}^0_{T_0}$ must be introduced (products minus reactants)

$$\Delta \overline{S}^0_{T_0} = s_{\text{H}_2\text{O}}(p_0, T_0) - 0.5 s_{\text{O}_2}(p_0, T_0) - s_{\text{H}_2}(p_0, T_0) \quad (6)$$

Subtracting Equation (6) and Equation (5) and collecting terms gives a suitable expression for $\dot{S}_{\text{irrev}}$.

(c)

Taking each species as a *perfect gas* allows the use of the Thermofluids Data Book expression for entropy change, so the entropy difference terms in the answer to part (b) can be evaluated.

(d)

In Lecture 3, it is proved that for a steady-flow process operating between two states at the same temperature, the maximum shaft power is equal to the decrease in Gibbs function. With the maximum shaft power known, and if the combustion loss is the only loss in the plant, the **exergy equation** can be applied to calculate the actual shaft power. The rational efficiency is this over the maximum shaft power.

Q7: Fuel cell potentials

(a) The definition of Gibbs potential must be remembered,

$$E_G = \frac{-\Delta \overline{G}_T^{p0}}{zF},$$

where $\Delta \overline{G}_T^{p0}$ is the change in Gibbs function for the reaction at standard pressure, z is the number of electron charges transferred per molecule of fuel, and $F = 9.648 \times 10^7 \, \text{C}\,\text{kmol}^{-1}$ is Faraday's constant (in the Thermofluids Data Book). In a SOFC the charge carrier is the O^{2-} ion, one of which is needed per molecule of H_2 fuel oxidised, so $z = 2$. The standard change in Gibbs function can be calculated using the equation in the Thermofluids Data Book, which tabulates values of $\ln K_p$ at different temperatures.

(b) The Nernst potential is derived from the change in Gibbs function at the operating pressure and temperature,

$$E_N = \frac{-\Delta \overline{G}_T^{p}}{zF},$$

We know z and F. The definition of the change in Gibbs function is products minus reactants as usual,

$$\Delta \overline{G}_T^{p} = g_{H_2O}(T, p_{H_2O}) - g_{H_2}(T, p_{H_2}) - \frac{1}{2} g_{O_2}(T, p_{O_2}). \tag{7}$$

The derivation of the following general expression is given in Lecture 4,

$$g_i(T, p_i) = g_i(T, p_0) + RT \left(\ln \frac{p}{p_0} + \ln X_i \right). \tag{8}$$

To proceed we apply Equation (8) for each species in Equation (7) to yield,

$$\Delta \overline{G}_T^{p} = \Delta \overline{G}_T^{p0} + RT \left(\ln \frac{X_{H_2O}}{X_{H_2} X_{O_2}^{1/2}} - \frac{1}{2} \ln \frac{p}{p_0} \right) \tag{9}$$

Some thought must be given to what the mole fractions of each species are. The anode side and the cathode side must be treated separately as they are separated by an electrolyte. The question gives the anode side mixture as H_2, H_2O, and CO_2 with mole fractions 0.5, 0.375 and 0.125 respectively. The CO_2 does not take part in the reaction, so its mole fraction is irrelevant. This leaves

$$X_{H_2} = 0.5, \ X_{H_2O} = 0.375$$

It is also given that the mole fraction of O_2 is 0.21 throughout the plant so

$$X_{O_2} = 0.21$$

Note that the fractions do not have to add up to one! They appear in the equation only to account for the partial pressures of the different components, not for some kind of molar balance.

(c)

Consider the change in the fuel mixture (anode side) as it passes through the cell. The mole fractions at inlet are given. It is stated that 80% of the H_2 has been consumed at the exit, each molecule of H_2 which is oxidised produces one H_2O, the CO_2 does not take part in the reaction so remains unchanged, and it is given that the fraction of O_2 is uniform throughout the plant. Some simple calculations will reveal the correct mole fractions.

Q8: Fuel cell power

(a) Consider first an individual cell. The voltage across the cell is known at 85% of the average Nernst potential. The cell current can be found from the area of a cell and the fixed current density. The power of one cell is then current times voltage. Now consider a module. There are 20 cells on each side of a module, so a module comprises 40 cells, and 10 modules make a bundle, so the cell power is multiplied by 400 to get the bundle power. The number of bundles needed is then the required power output over the bundle power. Given the dimensions of a cell the volume required can also be calculated.

It turns out about $1\,m^3$ is required to produce $250\,kW$. Compared to a large industrial gas turbine, the power density is about 25 times lower.

(b)

Using the cell current (dimensions $C\,s^{-1}$) and the charge transferred per mole of H_2 (two H^+ ions $\Rightarrow 2F\ C\,kmol^{-1}$), the cell consumption can be found. Multiplying up up by the total number of cells gives the plant consumption.

(c)

From part (c) we know the H_2 flow rate needed for the reaction. If only 80% of the supply is utilised then extra must be provided. The stoichiometry of the steam reforming reaction allows this H_2 supply rate to be converted to CH_4 supply rate.

(d)

In the ideal plant, the maximum available power is given by the standard change in Gibbs function for the oxidation of methane. So the rational efficiency is just the power over the change in Gibbs function due to the methane oxidation.