FINAL PROJECT (VERSION 2.0)

PHYSICAL CHEMISTRY 1 – PROF. DAVID M. ROGERS

1. Objective

Your objective for the final project will be to write a complete thermodynamic analysis of one non-PV energy conversion cycles from the following list:

- steam engine - vaporization of water produces steam, which creates an equilibrium high-pressure region. That region passes through a turbine to create a low-pressure region, which then condenses to back water, and must be pressurized. Balancing forces on the turbine requires the torque on the axle to equal the pressure drop per unit area on the wings.
- portable warming packs - use of heat to regenerate crystal form of acetic acid
- redox flow batteries - conversion of electrical potential energy to redox state of a metal-ligand complex
- mechanical / concentration - conversion of energy stored in a pressure gradient to a concentration difference in sodium chloride
- concentration / chemical - conversion of pH gradient to ATP production
- chemical / mechanical - conversion of diesel gas to work (rotation of an axle)
- informational / mechanical - use of a 'clean' memory containing mostly 0-s on a stored data tape to power an elevator lift
- hydroelectric - potential energy of water at altitude (or mechanical wind or wave energy) to electricity
- thermoelectric - use of ocean to high-atmosphere (or Earth core / mantle) temperature gradient to generate work
- solar - conversion of a high concentration of light at wavelength 400 nm to its equilibrium value at a blackbody spectrum of 300 K
- nuclear energy - conversion of energy stored in a high concentration of radioactive isotopes to a high-concentration of x-rays and heat
- rubber-band energy - conversion of mechanical energy in the stretching of a rubber band to create a refrigeration device
- refrigeration cycle - use the work of ammonia compression to cool room temperature air to 4 C

2. Prototypical cycles

Cycles working off of chemical energy usually have a chemical reaction, $A \to B + Q$, that produces energy in the form of heat or increasing concentration of Q. Two of the steps in the cycle then involve introducing new A molecules and removing molecules of B.

Some of the cycles, like the steam engine cycle, operate continuously and so have to be analyzed in terms of small changes: dn for the number of moles of water evaporated, dx for the distance traveled by every point in the fluid during a cycle, $d\theta$ for the amount of rotation of the axle, etc. There are still distinct states, since the pressure drop across the turbine should be approximated as an instantaneous change from boiling conditions back to atmospheric.

Other cycles discard large portions of usable work - like the use of portable warming packs, which could generate work but is not used for this purpose. Compute the work anyway. The portable warming pack example is also one which is less of a cycle, and more of a conversion between 2 states that takes 2 different paths (one giving off heat and another taking up heat during regeneration). Be very careful to define the 'system' as some region of space that contains definite (possibly variable) quantities of each molecular species.

3. Requirements

Each analysis must have 4 parts:

(1) Description of the system and its operation: What is a reasonable size and range of operation? What independent variables are moving during the engine cycle? Are there any special manufacturing challenges for obtaining them?
(2) Description of the working materials: What is the input energy source? What waste stream does the device generate? Is there useful energy left in the waste stream? Are there special environmental challenges associated with obtaining inputs or disposing of outputs?
(3) Cost analysis of the energy supply: Use a reasonable method to estimate the cost of supplying consumable materials and the potential revenues (or shortfall) from selling (or paying damages for) the waste stream.
(4) Equilibrium analysis of intermediate states: Provide a complete description of each intermediate state reached by the engine. What variables determine its thermodynamic state? What other state variables are relevant to the engine's operation (entropy, enthalpy, Gibbs free energy, economic value per ton)?

Reports will be graded on how thoroughly and convincingly it answers the questions posed for each of these parts. They must also contain diagrammatic sketches where appropriate and derivations that justify the thermodynamic calculations used. Diagrams, thermodynamic arguments, etc. can be copied from the textbook and any relevant literature source as long as appropriate citations are given.

4. Cautions

Although you may find a ready-made analysis online, if you base your work off of others you must cite them. Failing to do so will result in a zero for the assignment, and depending on the severity, probably also for the course. Using work from others without citation or submitting significant portions of others' work as your own is a violation of the academic integrity policy, and has serious academic consequences. Don't be afraid to use textbook and online sources – just be sure to keep a list of them as you gather information.

Group work and peer discussion is allowed, as long as each group creates and submits one single report. The grade will be divided equally among the participants at 50 points per complete analysis up to a maximum of 2 cycles per member. A group of 3 submitting analyses of 6 engine cycles and receiving 45$\times$6 points will each receive a 90 out of 100.

All work is expected to be presented following the format of the example analyses to be handed out soon.

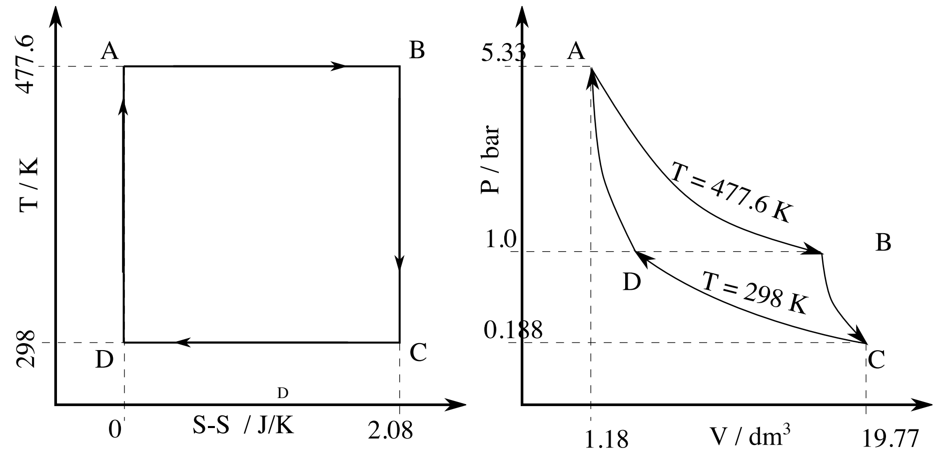

FIGURE 1. Carnot cycle plotted two different ways.

5. Example analysis: Carnot Cycle

5.1. **Description of the system.** The Carnot cycle is an idealized engine that uses a fixed amount of gas as the working material. The gas must be held inside a canister that can change volume and exchange heat with the surroundings.

Figure 1 shows the Carnot cycle plotted in temperature / entropy space (left side) and in pressure / volume space (right side). During each cycle, the canister undergoes an isothermal expansion and an adiabatic expansion (to generate work), followed by an isothermal compression and an adiabatic compression (to reset). During the isothermal steps, temperature remains constant, and volume, entropy, and pressure change. During the adiabatic steps, entropy remains constant and temperature, volume, and pressure change.

A reasonably sized Carnot cycle could be carried out between room temperature and the temperature of a hot oven (400 F = 477.6 K). For size, we assume it occupies a maximum volume after expansion of a gas at 1 bar 477.6 to 20 L and 298 K. The canister should be easy to manufacture, since this is the temperature and size range of common steel cookware.

5.2. **Working Materials.** The engine uses a fixed amount of air (we chose 0.5 mol ambient air). The data at engineeringtoolbox.com indicates its heat capacity is $\bar{C}_p(298\text{ K}, 1\text{ bar}) = 29.14$ J/(mol K) and $C_p(477.6\text{ K}, 1\text{ bar}) = 29.74$ J/(mol K). For simplicity, we assume ideal gas relationships and set $\bar{C}_p = 29.5$ J/(mol K) to be constant at all conditions.

During each cycle, the canister must be heated. If we choose to accomplish this with a natural gas stove, then there is efficiency data available on Engineering Toolbox.[1] Natural gas is plentiful in the US, and can usually be obtained from local utility companies.

The combustion reaction for methane (a major component of natural gas), is,

$$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$$

It is well-known that uncombusted hydrocarbons and CO_2 byproducts from combustion are environmental hazards. Natural gas also contains some amount of sulphur-containing hydrocarbons, which leads to SO_2 and H_2SO_4. The CO_2 is dealt with naturally as part of the carbon cycle. Other undesirable products are minimized by the use of catalytic converters and scrubbers.

The work output from the Carnot cycle is in the form of mechanical energy – from outward expansion of the canister. If it is not used immediately, it could be stored in a flywheel[2], or a pneumatic (compressed-air storage) system at 80-90% efficiency.

5.3. **Cost of Energy Supply.** The heat of combustion for methane at STP is $\Delta_c H^0 =$ -890.36 kJ/mol (McQuarrie's example 19-10). According to Ref. [1], heating an oven from 25 to 204.6 C at 15% excess air has an efficiency around 81.4%. Isothermal heating of an ideal gas requires an energy of $Q = nRT_B \ln(V_B/V_A) = 0.96$ kJ, and will thus require input heat, $Q_{\text{inp}} = Q/.814 = 1.19$ kJ. This equates to $1.33 \cdot 10^{-3}$ mol methane.

Rather than by mass, natural gas is usually charged per cubic foot. According to Ref. [3], the energy content per cubic foot averages 1036 Btu = 1093 kJ. Assuming a (commercial) gas cost of \$8.40 per thousand cubic feet,[4] the fuel cost to run one cycle of the engine is

$$Q_{\text{inp}} = 1.08 \cdot 10^{-3} \text{ ft}^3 = \$9.11 \cdot 10^{-6}. \tag{1}$$

The work output by the engine (per cycle) is

$$Q_h + Q_c = 0.344 \text{ kJ}. \tag{2}$$

5.4. **Intermediate States.** Both adiabatic lines follow:

$$T_B/T_C = (P_B/P_C)^{R/\bar{C}_p} = (V_B/V_C)^{-R/(\bar{C}_p - R)} \tag{3}$$

(from Problem 19-17).

The isothermal lines obey Boyle's law:

$$P_A V_A = P_B V_B \tag{4}$$

The entropy of an ideal gas is (integrating Eq. 20.2):

$$S(T, V) = \text{const.} \ + C_V \ln T + nR \ln V \tag{5}$$

The following table summarizes state variables at each point (n =0.15 mol):

State	P/bar	V/L	T/K	(S - S_D)/(J/K)
A	5.33	1.18	477.6	0.00
B	1.00	5.96	477.6	2.08
C	0.188	19.77	298	2.08
D	1.00	3.72	298	0.00

6. Example analysis: Diamond Manufacture

6.1. **Description of the system.** An engine converting mechanical to chemical energy could use work to compress graphite to diamond for resale. Diamonds are useful technologically for their strength and extremely high thermal conductivity.[5] Diamond is naturally formed under high temperature and pressure conditions in the earth's crust. At depths around 150-200 km, temperatures average 900 to 1300 Celsius and pressures reach 45 to 60 kilobars (6 GPa).[6] Commercial production is done in a 2-stage process involving formation of small seed crystals followed by crystal growth at an interface with vapor or liquid.

For the purpose of this analysis, we simplify the process to that of compressing a sample of graphite to about 5.5 GPa[7] at 1350 Celsius or above.[8] We use the adiabatic compression/expansion cycle shown in Fig. **??** to achieve these conditions. The independent variables shown are composition, pressure, and temperature. This type of triangular graph is popular for showing phase diagrams.

Since diamond and graphite have different heat capacities, we also need cooling at constant pressure to return the materials fully to ambient conditions. The cycle includes a materials exchange step where produced diamond is replaced with input graphite.

The construction of a high-pressure cell is prohibitively costly for very large diamonds, but diamonds grown for semiconductor applications could be as small as a tens of millimeters thick. For dimensions, let's assume the final diamond to be produced is 1000 $\text{mm}^3 =$ 1 1mL.

6.2. **Working Materials.** Mechanical energy is expended and created in the adiabatic compression/expansion steps. Typical setups use an electric-operated hydraulic press. We will calculate its energy requirements using standard P-V work. For cooling we can move the setup into a conventional kitchen refrigerator.

Assuming the pressure cell is filled with graphite and 100% conversion to diamond occurs, the working materials have the following properties (estimates from Engineering Toolbox):

Material	$\bar{C}_p$ / J/(g K)	ρ / (g/mL)
graphite	0.71	2.4
diamond	0.52	3.2

6.3. **Cost of Energy Supply.** The compression/expansion steps require work equal to

$$-\int PdV = \tag{6}$$

The cooling step requires ...

6.4. **Intermediate States.** Five states would be involved:

- A: chamber containing graphite at STP,
- B: heated and compressed chamber containing graphite,
- C: heated and compressed chamber containing diamond,
- D: decompressed, hot chamber containing diamond,
- E: cooled chamber containing diamond at STP.

State
A
B
C
D
E

References

[1] Engineering ToolBox. Combustion efficiency and excess air. https://www.engineeringtoolbox.com/boiler-combustion-efficiency-d_271.html, 2003. accessed October 29, 2019.

[2] Wikipedia contributors. Flywheel energy storage. https://en.wikipedia.org/w/index.php?title=Flywheel_energy_storage&oldid= accessed October 29, 2019.

[3] US Energy Information Administration. Frequently asked questions: What are ccf? https://www.eia.gov/tools/faqs/faq.php?id=45&t=7. accessed October 29, 2019.

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[5] Alexander A. Balandin. Better computing through CPU cooling. https://spectrum.ieee.org/semiconductors/materials/better-computing-through-cpu-cooling, 2009. accessed October 29, 2019.

[6] How are diamonds formed? https://www.capetowndiamondmuseum.org/about-diamonds/formation-of-diamonds/. accessed October 29, 2019.

[7] Qi-Gang Han, Ming-Zhe Li, Xiao-Peng Jia, Hong-An Ma, and Yuefen Li. Modeling of effective design of high pressure anvils used for large scale commercial production of gem quality large single crystal diamond. *Diamond and Related Materials*, 20(7):969–973, 2011.

[8] Qi-Gang Han, Qing-Chu Ban, and Pin-Wen Zhu. Design of a novel large volume cubic high pressure apparatus for raising the yield and quality of synthetic diamond. *Journal of Crystal Growth*, 422:29–35, 2015.