Thermal Physics Homework Seven

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Chapter Four, Problem 21 – Part A

Question: the ingenious **sterling engine** is a true heat engine that absorbs hear from an external source. The working substance can be air or any other gas. The engine consists of *two* cylinders with pistons, one in thermal contact with each reservoir (see Figure 4.7, Schroeder p. 133). The pistons are connected to a crankshaft in a complicated way that we'll ignore and let the engineers worry about. Between the two cylinders is a passageway where the gas flows past a **refrigerator**: a temporary hear reservoir, typically made of wire mesh, whose temperature varies gradually from the hot side to the cold side. The heat capacity of the refrigerator is very large, so its temperature is affected very little by the gas flowing past. The four steps of the engine's (idealized) cycle are as follows:

1. Power Stroke. While in the hot cylinder at temperature T_h, the has absorbs heat and expands isothermally, pushing the hot piston outward. The piston in the cold cylinder remains at rest, all the way inward as shown in the figure.

2. Transfer to the cold cylinder. The hot piston moves in while the cold piston moves out, transferring the gas to the cold cylinder at constant volume. While on its way, the gas flows past the regenerator, giving up heat and cooling to T_c

3. Compression Stroke. The Cold piston moves in, isothermally compressing the gas back to its original volume as the gas gives up heat to the cold reservoir. The hot piston remains at rest, all the way in.

4. Transfer to the hot cylinder. The cold piston moves the rest of the way in the while the hot piston moves out, transferring the gas back to the hot cylinder at constant volume. While on its way, the gas flows past the regenerator, absorbing hear until it is again at T_h.

Draw a PV diagram for this idealized Stirling cycle.
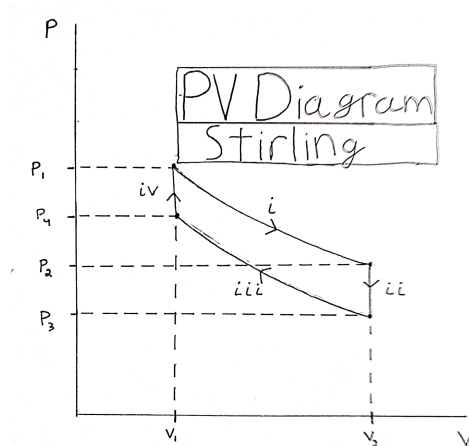**Answer:** See Figure 1

Figure 1: PV Diagram for an idealized Stirling Engine.

Chapter Five, Problem 1

Question: Let the system be one mole of argon gas at room temperature and atmospheric pressure. Compute the total kinetic energy (kinetic only, neglecting atomic rest energies), entropy, enthalpy, Helmholtz free energy, and Gibbs free energy.

Express all answers in SI units.

Answer: I start by using the equipartition theorem to calculate the kinetic energy of this system

$$U = \frac{f}{2} NkT$$

because Argon gas is monotonic it has three degrees of freedom ($f = 3$), so then

$$U = \frac{3}{2}(6.02 \times 10^{23})(1.38 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})$$
$$U = 3713 \text{ J}$$

Now entropy can be calculated from the Sackur–Tetrad equation

$$S = Nk \left[\ln \left(\frac{V}{N} \left(\frac{4\pi mU}{3Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right]$$

However we do know know that the volume is. We can use the Ideal Gas Law to refactor this in terms of the pressure (which we do know)

$$S = Nk \left[\ln \left(\frac{kT}{P} \left(\frac{4\pi mU}{3Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right]$$

Now we simply plug numbers in to get an entropy (using the mass of Argon in kg which I calculate to be 66.9×10^{-27} kg). I do this in maple and report the value here.

$$S = 154.79 \text{ J K}^{-1}$$

Next to calculate the enthalpy we use the definition

$$H \equiv U + PV$$

which I can refactor into

$$H \equiv U + NKT$$

so then

$$H = 3713 \text{ J} + (6.02 \times 10^{23})(1.38 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})$$
$$H = 6189 \text{ J}$$

Next I can calculate the Helmholtz free energy

$$F \equiv U - TS$$
$$F = 3713 \text{ J} - (298 \text{ K})(154.79 \text{ J K}^{-1})$$
$$F = -42414.42 \text{ J}$$

Finally I calculate the Gibbs free energy
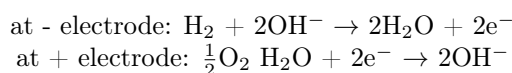
$$G \equiv F + PV$$

which I refactor as

$$G \equiv F + NKT$$

then, plugging in numbers

$$G = -42414.42 \text{ J} + (6.02 \times 10^{23})(1.38 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})$$
$$G = -39938.75 \text{ J}$$

Chapter Five, Problem 4

Question: In a hydrogen fuel cell, the steps of the chemical reaction are

$$\text{at - electrode: } H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$$
$$\text{at + electrode: } \tfrac{1}{2}O_2 \ H_2O + 2e^- \rightarrow 2OH^-$$

Calculate the voltage of the cell. What is the minimum voltage required for electrolysis of the water? Explain briefly.
Answer: We start by comparing the two reactions, we see that at the (–) electrode 2 waters are produced, where one water is consumed at the positive electrode, we also see that for ever electron liberated at the negative eletrode, an electron is consumed at the positive electrode. Finally we see that for every OH^- produced at the positve electrode, one is consumed at the negative electrode. So then we can write the overall form of this reaction as

$$\tfrac{1}{2}O_2 + H_2 \rightarrow H_2O$$
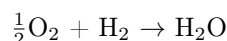
then by looking up the values for the change in Gibbs free energy from the back of the book we find that the total change in the Gibbs Free energy is (as the reaction does not specify liquid of gas water, I will assume gas)

$$\Delta G_{total} = \Delta G_{reactants} - \Delta G_{products}$$
$$\Delta G_{total} = \frac{1}{2}0 \text{ kJ} + 0 \text{ kJ} - (-228.57 \text{ kJ})$$
$$\Delta G_{total} = 228.57 \text{ kJ}$$

since we see from the reaction presented in the problem that at each step in the reaction there is a flow of two moles of electrons, then we can say that

$$W_{e^-} = \frac{1}{2}\frac{228.57 \text{ kJ}}{6.02 \times 10^{23}}$$
$$W_{e^-} = 1.898 \times 10^{-19} \text{ J}$$
$$W_{e^-} = 1.19 \text{ eV}$$

So since one volt is required to impart an energy of 1 electron volt to an electron, the potential of this fuel cell is 1.19 volts. This also means that the minimum voltage needed to make electrolysis take place would be 1.19 volts (because electrolysis would just be the opposite of this fuel cell, so all the calculations would be the same just with a reversed sign).

Chapter Five, Problem 11

Setup: Suppose that a hydrogen fuel cell, as described in the text, is to be operated at 75°C and atmospheric pressure. We wish to estimate the maximum electrical work done by the cell, using only the room–temperature data at the back of this book. It is convenient to first establish a zero–point for each of the three substances, H_2, O_2, and H_2O. Let us take G for both H_2 and O_2 to be zero at 25°C, so that G for H_2O is -237 kJ at 25°C.

(a) Using these conversions, estimate the Gibbs free energy of a mole of H_2 at 75°C. Repeat for O_2 and H_2O.

(b) Using the results of part (a), calculate the maximum electrical work done by the cell at 75°C, for one mole of hydrogen fuel. Compare to the ideal performance of the cell at 25°C.

Part A

Question: Using these conversions, estimate the Gibbs free energy of a mole of H_2 at 75°C. Repeat for O_2 and H_2O.
Answer: Starting from my work on the previous problem I know that the reaction looks like

$$\tfrac{1}{2}O_2 + H_2 \rightarrow H_2O$$
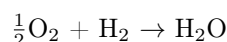
I can then find the differences in the Gibbs free energy for each of these at 75°C by using the thermodynamic identities

$$\left(\frac{\partial G}{\partial T}\right)_{N,P} = -S$$

Then rearranging to solve for ∂G

$$\partial G = -(\partial T)(S)$$

Now I look up the values for S in the back of the text

$$\partial G_{\text{H}_2\text{O}} = -(50 \text{ K})(69.91 \text{ J K}^{-1})$$
$$\partial G_{\text{H}_2\text{O}} = -3.5 \text{ kJ}$$
$$\partial G_{\text{H}_2} = -(50 \text{ K})(130.68 \text{ J K}^{-1})$$
$$\partial G_{\text{H}_2} = -6.5 \text{ kJ}$$
$$\partial G_{\text{O}_2} = -(50 \text{ K})(205.14 \text{ J K}^{-1})$$
$$\partial G_{\text{O}_2} = -10.3 \text{ kJ}$$

Now if we take the sum of these with our original Gibbs free energies

$$G_{\text{H}_2\text{O}} = -3.5 \text{ kJ} - 237 \text{ kJ}$$
$$G_{\text{H}_2\text{O}} = -240.5 \text{ kJ}$$
$$G_{\text{H}_2} = -6.5 \text{ kJ} + 0 \text{ kJ}$$
$$G_{\text{H}_2} = -6.5 \text{ kJ}$$
$$G_{\text{O}_2} = -10.2 \text{ kJ} + 0 \text{ kJ}$$
$$G_{\text{O}_2} = -10.2 \text{ kJ}$$

Part B

Question: Using the results of part (a), calculate the maximum electrical work done by the cell at 75°C, for one mole of hydrogen fuel. Compare to the ideal performance of the cell at 25°C.
Answer: We simply take the values from part (a) and combine these in the proportions based on the net reaction presented in part (a)

$$\Delta G_t = -240.5 \text{ kJ} + 6.5 \text{ kJ} + \frac{1}{2}10.2 \text{ kJ}$$
$$\Delta G_t = -228.9 \text{ kJ}$$

so we see that the maximum electrical work which can be done here (228.9 kJ) is lower than the maximum work which could have been done at 25°C (which was simply 273 kJ).

Chapter Five, Problem 21

Question: Is heat capacity (C) extensive or intensive? What about specific heat (c)? Explain briefly.
Answer: We should consider the definitions of heat, and specific heat capacities. First looking at the definition of heat capacity (C)

$$C = \frac{Q}{\Delta T}$$

we see that this is an extensive quantity divided by an intensive quantity. Remembering that the definition of an extensive quantity is that it has a direct relation to N, then as we double N the numerator will double. An intensive quantity on the other hand is independent of N, so as N doubles the denominator will not change. Therefore on the whole C will double, showing a direct relationship to N, therefore *C is an extensive quantity*. We can apply the same argument to specific heat capacity, the numerator will still double, but since mass (which is in the denominator) will also double those factors will divide out, therefore *specific heat capacity is an intensive quantity*.

Chapter Five, Problem 28

Setup: Calcium carbonate, $CaCO_3$, has two common crystalline forms, calcite and aragonite. Thermodynamic data for these phases can be found at the back of this book.

(a) Which is stable at earth's surface, calcite or aragonite?

(b) Calculate the pressure (still at room temperature) at which the other phase should become stable.

Part A

Question: Which is stable at earth's surface, calcite or aragonite?
Answer: From the back of the book I find that calcite has an Gibbs free energy of formation of 1128.8 kJ, and aragonite has a Gibbs free energy of formation of 1127.8 kJ. So from this we can see that calcite is more stable, because it has a lower Gibbs free energy.

Part B

Question: Calculate the pressure (still at room temperature) at which the other phase should become stable.
Answer: To do this I make two simple equations for lines representing the Gibbs free energy vs the volume. I do this using the relation:

$$\left(\frac{\partial G}{\partial P}\right)_{N,T} = V$$

so then I end up with one line for calcite, and one for aragonite

$$G(P)_c = 36.93 \times 10^{-6} \text{ m}^3 P$$
$$G(P)_a = 34.15 \times 10^{-6} \text{ m}^3 P + 1000\text{J}$$

Now I simply equate these two functions to find their intersection

$$G(P)_c = G(P)_a$$
$$36.93 \times 10^{-6} \text{ m}^3 P = 34.15 \times 10^{-6} \text{ m}^3 P + 1000 \text{ J}$$
$$36.93 \times 10^{-6} \text{ m}^3 P - 34.15 \times 10^{-6} \text{ m}^3 P = 1000 \text{ J}$$
$$P(36.93 \times 10^{-6} \text{ m}^3 - 34.15 \times 10^{-6} \text{ m}^3) = 1000 \text{ J}$$

$$P = \frac{1000 \text{ J}}{36.93 \times 10^{-6} \text{ m}^3 - 34.15 \times 10^{-6} \text{ m}^3}$$
$$P = 3.60 \times 10^8 \text{ Pa}$$

So we see that aragonite becomes more stable that calcite at a pressure of 3.60 kBar.

Chapter Five, Problem 32

Setup: The density of ice is 917 kg/m^3.

(a) Use the Clausius–Clapeyron relation to explain why the slope of the phase boundary between water and ice is negative.

(b) How much pressure would you have to put on an ice cube to make it melt at $-1°$C.

(c) Approximately how deep under a glacier would you have to be before the weight of the ice above gives the pressure you found in part (b)? (Note that the pressure can be greater at some locations, as where the glacier flows over a protruding rock.)

(d) Make a rough estimate of the pressure under the blade of an ice skate, and calculate the melting temperature of ice at this pressure. Some authors have claimed that skaters glide with very little friction because of the increased pressure under the blade melts the ice to create a thin layer of water. What do you think of this explanation?

Part A

Question: Use the Clausius–Clapeyron relation to explain why the slope of the phase boundary between water and ice is negative.
Answer: The Clausius–Clapeyron says that the slope of the boundaries on the phase diagram is a function of the change in entropy, and the change in volume. When water freezes is volume decreases, therefore the change in volume is negative, so the slope in the phase diagram is negative.

Part B

Question: How much pressure would you have to put on an ice cube to make it melt at $-1°$C.
Answer: I will use the relation

$$\frac{dP}{dT} = \frac{L}{T\Delta V}$$

So I need to calculate ΔV, which since the transition is from ice to water will be the difference between the volume of water and the volume of the same mass of ice. So

$$\Delta V = \frac{1 \text{ kg}}{1000 \text{ kg m}^{-3}} - \frac{1 \text{ kg}}{917 \text{ kg m}^{-3}}$$

$$\Delta V = -9.05 \times 10^{-5} \text{ m}^3$$

we know we want $dT = 1°$C, and from tabulated data we know that for 1 kg of water $L = 3.33 \times 10^5$J kg^{-1} so then

$$\frac{dP}{-1 \text{ K}} = \frac{3.33 \times 10^5 \text{ J kg}^{-1}}{(273 \text{ K})(-9.05 \times 10^{-5} \text{ m}^3)}$$

$$dP = \frac{(-1 \text{ K})3.33 \times 10^5 \text{ J kg}^{-1}}{(273 \text{ K})(-9.05 \times 10^{-5} \text{ m}^3)}$$

$$dP = 1.35 \times 10^7 \text{ Pa}$$

$$dP = 135 \text{ Bar}$$

so the pressure would need to increase by 135 Bars to melt the ice by one degree.

Part C

Question: Approximately how deep under a glacier would you have to be before the weight of the ice above gives the pressure you found in part (b)? (Note that the pressure can be greater at some locations, as where the glacier flows over a protruding rock.)
Answer: Making the assumption that the entire glacier is made of pure water, and that it it is thermally isotropic throughout, at $-1°$C. Then we need to find the depth at which the pressure form the material above is 135 Bars above atmospheric pressure

$$P = \rho g h$$

$$h = \frac{P}{\rho g}$$

$$h = \frac{1.35 \times 10^7 \text{ Pa}}{(917 \text{ kg m}^{-3})(9.8 \text{ m s}^{-2})}$$

$$h = 1502.2 \text{ m}$$

SO you would need to be about 1.5 km deep in the glacier for the pressure to increase the temperature enough to melt the ice into water.

Part D

Question: Make a rough estimate of the pressure under the blade of an ice skate, and calculate the melting temperature of ice at this pressure. Some authors have claimed that skaters glide with very little friction because of the increased pressure under the blade melts the ice to create a thin layer of water. What do you think of this explanation?
Answer: A person has a mass of approximately 100 kg. the blade of an ice skate is approximately 10 cm long by 1 cm wide (probably an underestimate on the length and an overestimate on the width, those should counteract well). So the area of the blade on the ice will be approximately 10 cm square cm or in meters 1×10^{-3} m^2. The weight of the skater will be approximately 1000 N so using basic physics (assuming that the skater only ever has one foot on the ground at a time, i.e. a best case scenario for the ice to melt as this is the maximum pressure the skater can impart).

$$P = \frac{1000N}{1 \times 10^{-3} \text{ m}}$$

$$P = 10^6 \text{ Pa}$$

This is about 10 times too small to increase the temperature of the ice enough to melt it if the ice starts at $-1°$C. Given that the explanation that skaters slide so easily because of a thin film of water produced by melting ice due to the pressure of the skate seams far fetched.
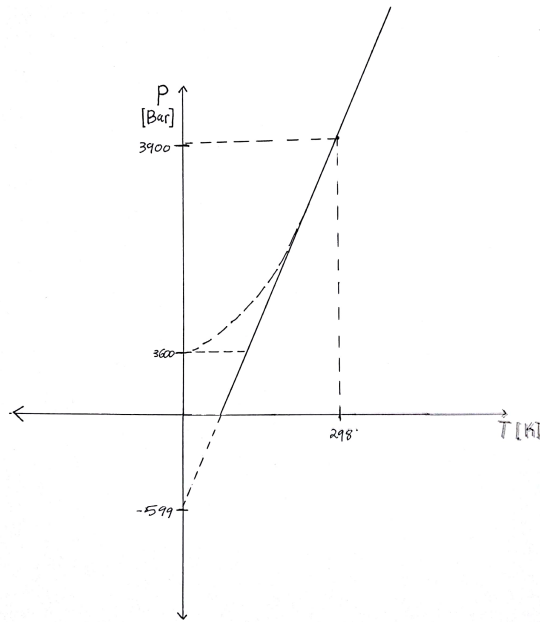
Figure 2: Phase diagram for calcite–aragonite. There is some curve connecting the boundary line with slope 0 at temperature 0 and the line with slope 15.1 at (T, P) = (298, 3900). I represent this curve with the curved dashed line, however I don't know the actual form of the curve.

Chapter Five, Problem 37

Question: Use the data in the back of this book to calculate the slope of the calcite–aragonite phase boundary (at 298 K). You located one point on this phase boundary in Problem 5.28; use this information to sketch the phase diagram of calcium carbonate.

Answer: We can use the Clausius–Clapeyron relation to find the slope of the phase boundary

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$$

$$\frac{dP}{dT} = \frac{88.7 \text{ J K}^{-1} - 92.9 \text{ J K}^{-1}}{34.15 \times 10^{-6} \text{ m}^3 - 36.93 \times 10^{-6} \text{ m}^3}$$

$$\frac{dP}{dT} = 1.51 \times 10^6 \text{ Pa K}^{-1}$$

$$\frac{dP}{dT} = 15.1 \text{ Bar K}^{-1}$$

So we know that the boundary between calcite and aragonite has a slope of 15.1 Bar K^{-1}. Then we can construct a basic function of a line for the boundary

$$P - P_1 = m(T - T_1)$$

$$P - P_1 = 15.1 \text{ Bar K}^{-1}(T - T_1)$$

$$P - 3.90 \times 10^3 \text{ Bar} = 15.1 \text{ Bar K}^{-1}(T - 298 \text{ K})$$

$$P = 15.1 \text{ Bar K}^{-1}T - 599.8 \text{ Bar}$$

Now we can get a better constraint on the shape of the line by looking at what the Clausius–Clapeyron relation says when T = 0, at this point entropy denominationally also equals zero so the slope of the line is zero. Then we use the fact that the y offset is given as 3600 bar and we arrive at something like Figure 2.