

Homework 5 solutions

1. Short questions

The following questions test the basic concepts of classical thermodynamics. When giving your answer, please provide a brief explanation on how you were led to this answer.

- a. In the comic song by Flanders and Swann about the laws of thermodynamics, they summarize the first law by the statement: “Heat is work and work is heat.” Is this statement correct based on your understanding of the first and second law of thermodynamics? Explain your reasoning with regards to the two laws.

According to the first law, $\Delta U = \Delta Q + \Delta W$, where only U is a state function. Therefore, having $\Delta Q = 5$ and $\Delta W = 2$ or $\Delta Q = 2$ and $\Delta W = 5$ could both lead to the same final state. In that sense, we can “convert” heat to work and vice versa, so we could say that the quote is accurate.

On the other hand, Kelvin’s formulation of the second law states that it is not possible to have a process whose sole effects are to completely convert heat into work. Therefore, according to the second law, the quote would be inaccurate.

- b. What is the difference between an adiabatic process and an isentropic one (i.e. a process at constant entropy)?

During an adiabatic process, no heat is exchanged and thus $\Delta Q = 0$.

In a process at constant entropy, $\Delta S = 0$.

If the process is reversible, $\delta Q = TdS$ according to the second law and thus a change in heat means a change in entropy. Thus, for the special case of reversible processes, the two concepts are the same. For irreversible processes, this is not true anymore.

- c. The change of Gibbs free energy for 1 mole of water at 2 and 10 degrees Celsius is about 50 J. Can you approximate the change in the Helmholtz free energy of the same system? Would your method work if it were a gas in question?

The Gibbs and the Helmholtz free energy are related by $A = G - pV$.

Since there is no mention of the pressure in the text, we assume that the heating process is taking place at constant pressure (most likely: ambient pressure). For such processes, the change in the Gibbs and Helmholtz free energy between the initial and final state are related by:

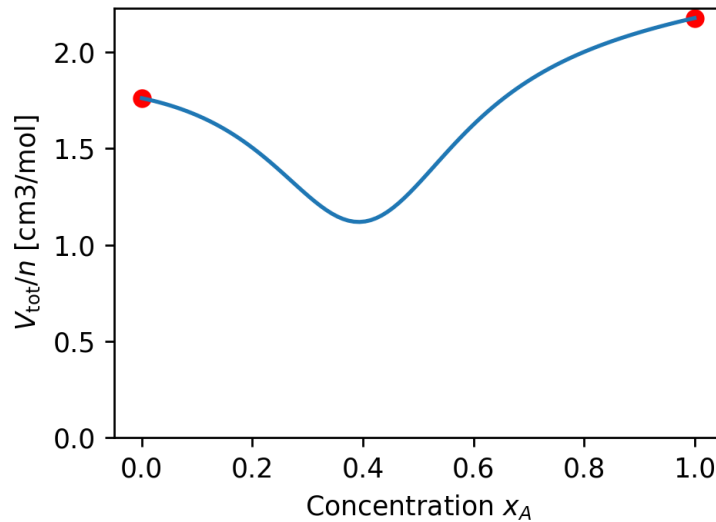
$$\Delta A = \Delta G - p\Delta V$$

For most condensed materials like solids and liquids, the change in the volume due to a change in temperature by 8 degrees Celsius is not going to be significant, and we can thus drop the second term (this is especially true for water which first contracts up to 4 degrees Celsius, which compensates some of the expansion afterwards). We can thus approximately say that

$$\Delta A \approx \Delta G = 50 \text{ J}$$

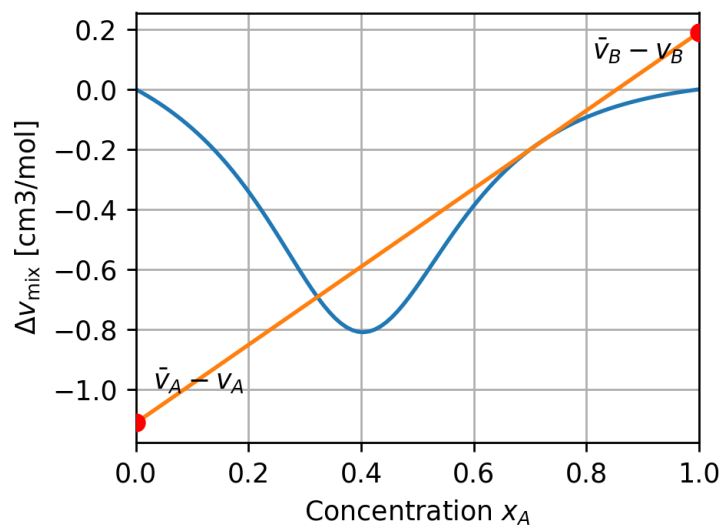
For a gases, the change in volume would typically be larger by many orders of magnitude. Thus, neglecting the change in volume would not be acceptable.

- d. i. Consider a binary mixture of the components A and B. The figure below shows the total volume per mole, i.e. V_{tot}/n , as a function of the concentration x_A . Which quantity do the endpoints (red points on the plot) correspond to?



The height of the endpoints simply are the molar volumes of the pure substances B (at $x_A = 0$) and A (at $x_A = 1$), respectively.

- ii. Based on the mixture above, plot qualitatively the change of volume of mixing per mole $\frac{\Delta_{mix}V}{\sum n}$ as a function of the mole fraction x_A and label both axes. Draw the tangent of the curve at $x_B = 0.3$ and annotate the intercepts with the y axis.



2. Entropy of the universe

While walking along Lac Lemman one summer day, Pierre spots a crumpled-up aluminium can whose mass is 100 grams. It has been sitting in the sun all day and it is at a temperature of 80 °C. Pierre is not thinking about the environment and throws the hot aluminium can into the lake, which has a temperature of 20 °C. Calculate the change of entropy of the universe after the can has finished transferring its energy into the lake.

Data: The specific heat capacity of aluminium is $890 \frac{J}{kg \cdot K}$.

The change of the entropy of the universe is determined by the change in the entropy of the can and the change in the entropy of the lake.

$$\Delta S_{universe} = \Delta S_{can} + \Delta S_{lake}$$

The change in the entropy of the can is calculated as following:

$$\begin{aligned} \Delta S_{can} &= \frac{q_{can}}{T} \\ \rightarrow \Delta S_{can} &= \int_{T_I}^{T_F} \frac{\partial q_{can}}{T} = \int_{T_I}^{T_F} \frac{m \cdot c \cdot dT}{T} = m \cdot c \cdot \ln\left(\frac{T_F}{T_I}\right) \\ \Delta S_{can} &= 0.1 [kg] \cdot 890 \left[\frac{J}{kg \cdot K}\right] \cdot \ln\left(\frac{293.15 [K]}{353.15 [K]}\right) = -16.6 \left[\frac{J}{K}\right] \end{aligned}$$

The change in the entropy of the lake is calculated as following:

$$\begin{aligned} \Delta S_{lake} &= \frac{q_{lake}}{T_{lake}} = -\frac{q_{can}}{T_{lake}} \\ \rightarrow \Delta S_{lake} &= \int_{T_I}^{T_f} -\frac{\partial q_{can}}{T_{lake}} = \int_{T_I}^{T_F} -\frac{m \cdot c \cdot dT}{T_{lake}} \end{aligned}$$

We assume the temperature of the lake to be constant as the lake is playing the role of a heat reservoir in this problem. Thus

$$\begin{aligned} \Delta S_{lake} &= -\frac{1}{T_{lake}} \cdot \int_{T_I}^{T_f} m \cdot c \cdot dT = -m \cdot c \cdot \frac{(T_F - T_I)}{T_{lake}} \\ \Delta S_{lake} &= -0.1 [kg] \cdot 890 \left[\frac{J}{kg \cdot K}\right] \cdot \frac{293.15 [K] - 353.15 [K]}{293.15 [K]} = 18.2 \left[\frac{J}{K}\right] \end{aligned}$$

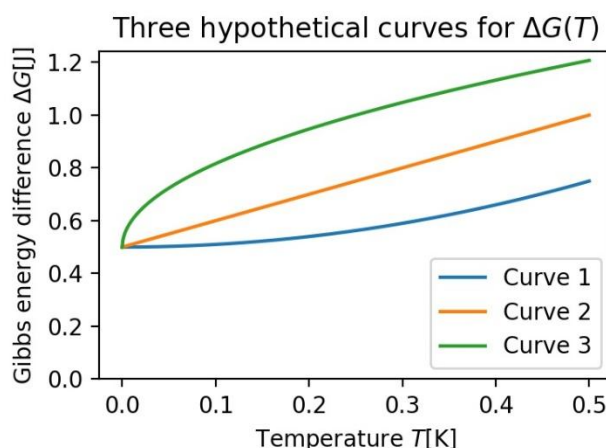
Thus, the change of entropy of the universe after the can has finished transferring its energy into the lake is

$$\Delta S_{universe} = \Delta S_{can} + \Delta S_{lake} = -16.6 \left[\frac{J}{K}\right] + 18.2 \left[\frac{J}{K}\right] = 1.6 \left[\frac{J}{K}\right]$$

This result agrees with the second law of thermodynamics. It also means that on top of polluting the lake, Pierre is also increasing the entropy of the universe by throwing the aluminum can in the lake!

3. The Third Law of thermodynamics

In this exercise, we will try to deepen our understanding of the third law and its experimental consequences. Consider two crystal structures of the same element carbon such as diamond and graphite, which we shall label A and B, respectively. We shall keep the pressure p fixed.



- a. The figure above shows the change in the Gibbs free energy $\Delta G(T)$ between the two structures as a function of temperature at constant pressure. Three hypothetical curves of $\Delta G(T)$ are included in the figure. All curves begin at the same point at absolute zero $\Delta G(0)$. Which change in a thermodynamic function (other than the Gibbs free energy) does the numerical value of that point represent?

The change in enthalpy $\Delta H(0)$, since $\Delta G(T) = \Delta H(T) - T\Delta S(T)$ and the second term is zero for $T=0$.

- b. What happens to $\Delta S(T) = S_B(T) - S_A(T)$ as $T \rightarrow 0\text{K}$? [based on your knowledge of thermodynamics]

It approaches zero by the third law, since the (molar) entropy of both structures approaches the same value at absolute zero temperature.

- c. Using the previous result, what can you say about the slope of $\Delta G(T) = G_B(T) - G_A(T)$ as $T \rightarrow 0\text{K}$? [Hint: $\Delta G(T) = \Delta H(T) - T\Delta S(T)$. For the enthalpy difference, you can assume that the slope as a function of T goes to zero as $T \rightarrow 0\text{K}$.]

The slope of $\Delta G(T)$ is given by $\Delta S(T)$, which approaches zero as $T \rightarrow 0\text{K}$. Therefore, by the third law, the slope must approach zero.

- d. The figure above shows three possible curves for the measured change in Gibbs free energies as a function of the temperature. Which of the three curves is thus most likely to be obtained experimentally? Explain.

The curve whose slope approaches zero as $T \rightarrow 0\text{K}$ is most likely, which is curve 1.

Next, we will study how we can experimentally determine the change of entropy between two structures at absolute zero.

- e. Let us assume that the experimental heat capacities of structures A and B follows Debye's law:

$$C_{p,A}(T) = aT^3, \quad C_{p,B}(T) = bT^3$$

Using this, express the entropy of A and B as a function of temperature and the constants a, b . Consider that the entropies at absolute zero are $S_{A,0} := S_A(T = 0)$ and $S_{B,0} = S_B(T = 0)$. (Hint: Express the heat capacity using the entropy first)

The heat capacities are related to the entropy by:

$$C_p(T) = \left(\frac{\partial H}{\partial T} \right)_p = T \left(\frac{\partial S}{\partial T} \right)_p$$

Dividing by the temperature and integrating both sides, we obtain

$$S_A(T) = S_A(0) + \int_0^T \frac{C_{p,A}}{T} dT = S_{A,0} + \frac{aT^3}{3}$$

$$S_B(T) = S_B(0) + \int_0^T \frac{C_{p,B}}{T} dT = S_{B,0} + \frac{bT^3}{3}$$

- f. At the temperature T_{equil} of equilibrium between A and B, we can determine the change of entropy between the two structures from heat capacities:

$$S_B(T_{equil}) - S_A(T_{equil}) = \Delta S_{equil}$$

Use this relation to express $\Delta S_0 = S_{B,0} - S_{A,0}$ at absolute zero as a function of $\Delta S_{equil}, T_{equil}, a, b$.

$$\begin{aligned} \Delta S_{equil} &= S_B(T_{equil}) - S_A(T_{equil}) \\ &= S_{B,0} + \frac{bT_{equil}^3}{3} - S_{A,0} - \frac{aT_{equil}^3}{3} = \Delta S_0 + \frac{(b-a)T_{equil}^3}{3} \end{aligned}$$

$$\text{Thus: } \Delta S_0 = \Delta S_{equil} - \frac{(b-a)T_{equil}^3}{3} = \Delta S_{equil} + \frac{(a-b)T_{equil}^3}{3}$$

- g. For two structures of Phosphine, the experimental parameters for 1 mole of substance are $\Delta S_{equil} = 3.75 \text{ J/K}$, $T_{equil} = 49.43 \text{ K}$, $a = 1.09 \cdot 10^{-4} \text{ J/K}^4$ and $b = 2.02 \cdot 10^{-4} \text{ J/K}^4$. Calculate the change of entropy at absolute zero. Discuss the result.

Plugging in to the previous formula results in $\Delta S_0 = -0.012 \text{ J/K}$. This is indeed significantly smaller than ΔS_{equil} , and its discrepancy with the true value zero (as $\Delta S = 0$ at $T = 0 \text{ K}$) likely comes from measurement errors.

Finally, we look at an interesting application of these ideas.

- h. The material SiO_2 comes in crystalline α -quartz and β -quartz structures as well as an amorphous state (a glass). If we repeat the same experiment as above, the change of entropy at absolute zero between the two crystalline structures $S_\alpha - S_\beta$ goes to zero, but the change of entropy between the amorphous and the crystalline states $S_\alpha - S_{glass}$ and $S_\beta - S_{glass}$ remains finite. What do these experimental results tell us? In the initial figure showing the curves for $\Delta G(T)$, which of

the curves could correspond to the change of the Gibbs free energy between the amorphous and the crystalline structures?

[This sub-question h gives 2 extra-bonus points]

Since the third law states that the entropy difference should go to zero as $T \rightarrow 0$, the experimental results suggest that the third law does not apply to the glassy state of SiO_2 , although it does to the two crystalline phases.

In the initial figure, curve 2 shows a behavior that could correspond to the Gibbs free energy difference between the amorphous and the crystalline phases. Curve 3 strictly speaking has an infinite slope at $T=0$, but since this is not completely clear from the figure, if someone says that both curves 2 and 3 would work they should get the full points as well.

4. Thermodynamics of electrochemical cells

In general, an electrochemical cell is a simple device in which an electric current (a flow of electrons through a circuit) can be produced by two different types of chemical reaction. In the case of voltaic cells (also known as galvanic cells), the electric current is produced by a spontaneous chemical reaction, whereas in the case of electrolytic cells a non-spontaneous reaction occurs.

The objective of this exercise is to determine which cell is described by the following thermodynamic properties and understand its thermodynamic properties.

We consider the cell to provide a positive electromotive force ε that enables a transfer of a quantity of positive charge dZ to an external circuit. Under this convention, the electrical work is defined by:

$$\delta w_{el} = -\varepsilon dZ$$

Consider the system to be closed.

- a. Write the differential form of the enthalpy.

$$dH = TdS + Vdp - \varepsilon dZ$$

- b. Write the differential form of the Gibbs free energy.

$$dG = -SdT + Vdp - \varepsilon dZ$$

- c. Find a Maxwell's relationship for $\left(\frac{\partial S}{\partial Z}\right)_{p,T}$.

$$\begin{aligned} \left[\frac{\partial}{\partial Z} \left(\frac{\partial G}{\partial T} \right)_{p,Z} \right]_{p,T} &= \left[\frac{\partial}{\partial T} \left(\frac{\partial G}{\partial Z} \right)_{p,T} \right]_{p,Z} \\ - \left(\frac{\partial S}{\partial Z} \right)_{p,T} &= - \left(\frac{\partial \varepsilon}{\partial T} \right)_{p,Z} \\ \left(\frac{\partial S}{\partial Z} \right)_{p,T} &= \left(\frac{\partial \varepsilon}{\partial T} \right)_{p,Z} \end{aligned}$$

From now on, assume that the process is taking place under isothermal and isobaric conditions.

- d. Determine the change in the enthalpy ΔH with respect to the change of charge ΔZ . Note that the electromotive force is only temperature-dependent ($\varepsilon = \varepsilon(T)$).

$$\begin{aligned} dH &= TdS + Vdp - \varepsilon dZ = \overset{p \text{ is constant} \rightarrow dp=0}{\sim} TdS - \varepsilon dZ \\ \left(\frac{\partial H}{\partial Z} \right)_T &= T \left(\frac{\partial S}{\partial Z} \right)_T - \varepsilon \\ \left(\frac{\partial H}{\partial Z} \right)_T &= - \left[\varepsilon - T \left(\frac{\partial \varepsilon}{\partial T} \right)_Z \right] \end{aligned}$$

Since $\varepsilon = \varepsilon(T)$

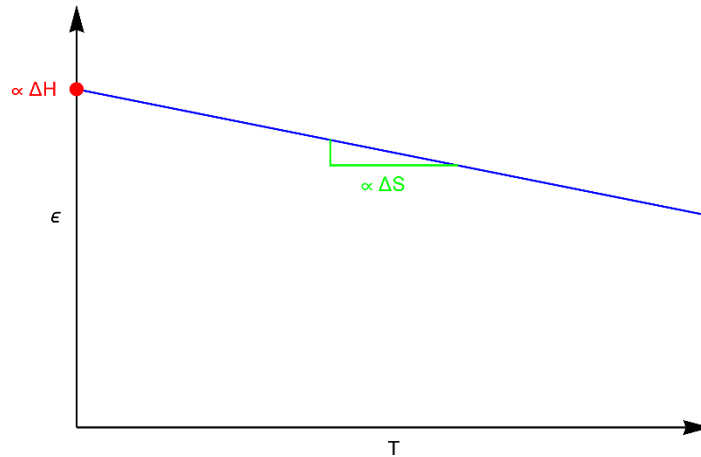
$$\left(\frac{\partial H}{\partial Z} \right)_{T,V} = - \left[\varepsilon - T \frac{d\varepsilon}{dT} \right]$$

Thus, we have

$$\int_{H_0}^H dH = - \int_{Z_0}^Z \left(\varepsilon - T \frac{d\varepsilon}{dT} \right) dZ$$

$$\Delta H = - \left(\varepsilon - T \frac{d\varepsilon}{dT} \right) \Delta Z$$

- e. It has been experimentally verified that the electromotive force varies linearly with temperature in this case. Draw, qualitatively, a plot of epsilon as a function of temperature and indicate which thermodynamic quantities i) the slope and ii) the intercept with the y axis of this curve relate to.



- f. Starting from the definition of the Gibbs free energy, calculate ΔG . Which of the two cells has a thermodynamic behavior that is consistent with your results? Explain.

$$dG = -SdT + Vdp - \varepsilon dZ$$

As we assume that the process is occurring under isobaric and isothermal conditions, we have $dT = 0$ and $dp = 0$. Thus, we get

$$dG = -\varepsilon dZ$$

$$\Delta G = -\varepsilon \Delta Z$$

As both the electromotive force ε and the change in charge ΔZ are positive, we have $\Delta G < 0$, which means the process is spontaneous and thus that the thermodynamic behavior consistent with this result is the behavior of a voltaic/galvanic cell.

Finally, let's calculate how efficient this electrochemical cell can be. It is reminded that the efficiency is related to the cell's conversion ability of its energy (which in the form of chemical energy) to electric energy.

- g. Consider that the cell generates an electromotive force of $\varepsilon = 1.015 \text{ V}$ at the temperature of 0°C and at atmospheric pressure. From the measurement of ε as a function of temperature the derivative at 0°C can be determined: $\left(\frac{\partial \varepsilon}{\partial T} \right)_{p,Z} = -4.02 \cdot 10^{-4} \frac{\text{V}}{\text{K}}$. Using these data, calculate the change of enthalpy of the cell, assuming that the change of charge is equal to 2 C . What part of heat produced in the cell cannot be used to perform work? In other words, do you think the cell is efficient? [Hint: Remember what are the physical meanings of ΔG and ΔH .]
Data: $1 \text{ V} = 1 \text{ J/C}$ where C is Coulomb (the unit of charge).

From d), we have

$$\Delta H = -\left(\varepsilon - T \frac{d\varepsilon}{dT}\right) \Delta Z$$

$$\Delta H = -\left(1.015[V] - 273.15[K] \cdot \left(-4.02 \cdot 10^{-4} \left[\frac{V}{K}\right]\right)\right) \cdot 2[C] = -2.25 [J]$$

The maximum work that can be obtained from a reversible cell at constant pressure and temperature is equal to ΔG .

The part of the enthalpy of reaction which can not be changed into work is equal to

$$\Delta H - \Delta G = T\Delta S = -\left(\varepsilon - T \frac{d\varepsilon}{dT}\right) \Delta Z + \varepsilon \Delta Z = T \frac{d\varepsilon}{dT} \Delta Z$$

$$= 273.15[K] \cdot \left(-4.02 \cdot 10^{-4} \left[\frac{V}{K}\right]\right) \cdot 2[C] = -0.22 [J]$$

This corresponds to 10% of the enthalpy of reaction. This means that 90% can be used to perform electrical work, meaning the cell has a 90% efficiency.