Homework 2 Solution

Short questions

1. Apply the first law of the thermodynamics to (a) a closed system (b) an isolated system. Write an expression for the change of the internal energy of each system.

   a) A closed system does not exchange matter but energy with the surroundings. Therefore, the change of internal energy of a closed system can be expressed as:
   $$\Delta U_{closed} = w + q$$

   b) An isolated system exchanges neither matter, heat, nor work with the surroundings. Therefore,
   $$\Delta U_{isolated} = w + q = 0$$

2. Which of the following are state functions? (1) Volume (2) Work (3) Density

   A state function is a property of a system whose value depends upon the current state of the system, independent of how the system arrived at that state. Thus, volume and density are state functions.

   In a process, work appears when the force moves along some path in space. As a result, the amount of work involved depends on its path. Thus, work is NOT a state function.

3. The higher the internal energy a system has, in general, the more capacity it has to do work. True or false? Please briefly explain.

   True. According to the first law of thermodynamics, $\Delta U = w + q$. Without considering the heat term q, in general when a system does useful work ($w < 0$), its internal energy U decreases. Thus, the more the internal energy a system has, the more energy available to extract for useful work.

4. If you heat a copper bar and its temperature goes from T_1 to T_2 (assuming $T_2>T_1$), the change of entropy of the copper bar is positive. True or false? Please use the second law of thermodynamics to briefly explain your answer.

   True. First, let us consider the case in which the process is reversible. Then, by the second law $dS_{rev} = \delta q/T$, the change in entropy can be computed using the integral $\Delta S_{rev} = \int \frac{\delta q}{T}$. If we heat up the system, heat flows into the system, so $\delta q > 0$ and thus $\Delta S > 0$ since the temperature is always positive.

If the process is irreversible, again by the second law, $S_{irrev} > \delta q/T$ and thus $\Delta S_{irrev} = \int \frac{\delta q}{T} > 0$. Thus, in both cases, the change in entropy is positive.

5. How is it possible that one can boil water without changing the entropy of the universe?

   Heating must be done reversibly, for example, by allowing water to exchange heat with consecutive heat reservoirs at incrementally (infinitesimally) higher temperature.

6. The work that is performed by the expansion of a system composed of 1 mole of ideal gas is always numerically equal to the heat that is absorbed by the system. True or false?

   False. There are different types of expansion: the gas could expand adiabatically (not absorbing any heat), in which case the heat is zero. On the other hand, the gas could expand isothermally. Since the energy of an ideal gas only depends on the temperature, in this case, the energy doesn't change and we obtain $\Delta U = 0 = q + w$ from the first law, leading to $q = -w$ or $|q| = |w|$. There are also other types of expansion, and the heat would be different again.

7. The internal energy of a system and its surrounding is conserved during an irreversible process. True or false?

   True. Energy must be conserved. Energy only flows between systems, but the total amount remains the same.

8. According to the second law of thermodynamics, one cannot realize a process adiabatically that results in a decrease in entropy. True or false?

   True. According to the second law of thermodynamics, the entropy $dS \geq \frac{\delta q}{T}$. In an adiabatic process δq=0, therefore entropy never decreases.

9. For any closed system in a reversible isothermal process, it is always true that $q = T\Delta S$. True or False?

   True. Divide the heat into incremental change, $dS = \frac{\delta q_{rev}}{T}$ according to the second law. Therefore,

$$\Delta S = \int \frac{\delta q_{rev}}{T} = \frac{1}{T}\int \delta q_{rev} = \frac{q}{T}$$

$$q = T\Delta S$$

Exercise 1

One mole of an ideal gas is expanded from a volume of 1 L to a volume 2 L at a constant temperature of 20°C.

a. The gas is expanded **reversibly**.
b. The gas is expanded **irreversibly** against a constant external pressure equal to the final pressure of the gas.
c. The gas is expanded against zero external pressure (free expansion).

In all cases, calculate the work performed by the gas. For which case the work is the largest/smallest? Does your result obey the second law of thermodynamics? Please explain.

a) Reversible expansion:

$$\delta w = -pdV$$

$$p = \frac{nRT}{V}$$

$$w_{rev} = -\int_{V1}^{V2} \frac{nRT}{V} dV = -nRT \ln \ln \left(\frac{V_2}{V_1}\right) = -nRT \ln \ln \left(\frac{2}{1}\right) = -nRT \ln (2)$$

b) Irreversible expansion:

$$p = const = p_2$$

In this case, the path of the irreversible process is known:

$$w_{irr} = -\int_{V1}^{V2} p_2 dV = -p_2(V_2 - V_1)$$

From the ideal gas law:

$$p_2 = \frac{nRT}{V_2}$$

If we put it in the previously found work:

$$w_{irr} = -p_2(V_2 - V_1) = -\frac{nRT}{V_2}(V_2 - V_1) = -\frac{nRT}{2}$$

c) This is an irreversible process doing zero work.

All three expansion processes (at constant temperature) start at the same initial state and end at the same final state. The maximum useful work is produced in the reversible process in **a**. It is larger than that from the two irreversible processes in **b** and **c**, respectively (i.e. more energy is transferred to work in a reversible process). The minimum useful work limit is zero in case **c**. The result indeed obeys the second law that dictates the limit for extraction of useful work from any process. The maximum amount of work can only be obtained if that process is carried out reversibly.

Since entropy is a state function, it depends only on the initial and final states and is the same in all cases.

$$\Delta S_{gas} = nRln\left(\frac{V_2}{V_1}\right) = nRln(2)$$

For the bath, the entropy change is always computed from the bath's own temperature and the actual heat it exchanges, independent of whether the process is reversible for the gas.

- Reversible (a): $q_{rev} = -w_{rev} = nRTln(2)$

$$\Delta S_{bath} = -\frac{q_{rev}}{T} = -nRln(2)$$

$$\Delta S_{univ} = \Delta S_{gas} + \Delta S_{bath} = 0$$

- Irreversible (b): $q_{irr} = -w_{irr} = \frac{nRT}{2}$

$$\Delta S_{bath} = -\frac{q_{irr}}{T} = -\frac{nR}{2}$$

$$\Delta S_{univ} = \Delta S_{gas} + \Delta S_{bath} = nR\left(ln(2) - \frac{1}{2}\right) > 0$$

- Irreversible, Free (c): $q_{irr} = -w_{irr} = 0$

$$\Delta S_{bath} = -\frac{q_{rev}}{T} = 0$$

$$\Delta S_{univ} = \Delta S_{gas} + \Delta S_{bath} = nRln(2) > 0$$

These results obey the second law as the reversible bath produces zero entropy (ΔS_{univ}=0) and the irreversible paths produce entropy (ΔS_{univ}>0).

Exercise 2

An elastomer is a polymer that can stretch and contract.

In a perfect elastomer the force opposing extension is proportional to the displacement x from the resting state of the elastomer, so $|F| = k_f\, x$, where k_f is a constant. But suppose that the restoring force weakens as the elastomer is stretched, and $k_f\,(x) = a - bx^{1/2}$. Evaluate the work done on extending the polymer from x=0 to a final displacement l.

The work done on extending the polymer from x=0 to a final displacement l:

$$w = \int_0^l |F|dx = \int_0^l k_f x\,dx = \int_0^l \left(a - bx^{\frac{1}{2}}\right) xdx = \int_0^l ax - bx^{\frac{3}{2}}dx$$
$$= \frac{1}{2}ax^2 - \frac{2}{5}bx^{\frac{5}{2}}|_0^l = \frac{1}{2}al^2 - \frac{2}{5}bl^{\frac{5}{2}}$$