

Solution to Assignment 1

1. Read the descriptions below of some thermodynamic systems undergoing various changes and classify the type of system. Explain in one sentence for each case why your choice is appropriate.

- (a) The system is a litre of hot coffee placed inside a high-quality, sealed thermos that has an evacuated space between an inner rigid cylinder where the liquid is placed and the outside walls of the container.

Based on the given information, which is that the system (the coffee) is stored in a rigid, sealed volume that restricts heat transfer, we could state that this is approximately an isolated system. Of course, as with any real system, the isolation is not perfect... the coffee eventually gets cold as heat slowly escapes the container.

- (b) If the thermos described above had flexible rather than perfectly rigid walls, what kind of system would we have?

If the walls of the container are flexible, then the volume of the system is not forced to be constant and a system that restricts heat transfer but can change volume (allowing work to be done on/by the system) is an adiabatic system.

- (c) The system is a puddle of water on the sidewalk.

Because water molecules can evaporate or condense on the puddle, and the puddle could be heated or cooled depending on its surroundings, this is an open system.

- (d) You have a glass jar of strawberry jam and the metal screw-top lid is stuck (the jam is your system). You really want a peanut butter and jelly sandwich, so you place the jar under a stream of hot water to loosen the lid.

You have a closed system (jam can't get out of the jar, but heat is clearly going to pass through the glass walls of the jar).

- (e) You are the system. You're on a ski trip and you are wearing a high-tech insulated parka, hood, and snow pants to keep you warm. It's -10°C on the ski slope, but as you trudge up to the ski lift, you are getting warm.

Assuming your parka is a perfect (or at least very good) insulator, we could state that you are an isolated system. (If you assume the parka isn't a good insulator, then you are a closed system.) The fact that you feel warmer after exerting yourself is due to the transformation of internal chemical energy stored in your body into some waste heat during the process of walking to the ski lift. This fact might further suggest that the parka is a good insulator and no heat is transferring out of you into the surroundings (in practice of course, some heat is always leaking into the surroundings).

2. The temperature and pressure dependence of volume of an ideal gas, $V = V(T, P)$, can be expressed by the ideal gas law, $PV = nRT$. Determine the coefficient relations for the function $V = V(T, P)$ and, using Maxwell relation, prove that all of these functions are state variables.

Differentiating $PV = nRT$ completely,

$$PdV + VdP = nRdT$$

$$dV = (nR/P)dT - (V/P)dP$$

Hence, the coefficient relations are:

$$nR/P = (\partial V/\partial T)_P \quad \text{and} \quad -V/P = (\partial V/\partial P)_T$$

Now, the Maxwell relation is

$$(\partial/\partial P) [nR/P]_T = -(\partial/\partial T) [V/P]_P$$

$$\text{Here, the right hand side term, } (\partial/\partial P) [nR/P]_T = -nR/P^2$$

$$\text{And the left hand side term, } -(\partial/\partial T) [V/P]_P = -(\partial/\partial T) [nRT/P^2]_P = -nR/P^2$$

Thus, the Maxwell relation is valid and P, V, and T are state variables.

3. The two key thermodynamic characteristics of an ideal gas are an equation of state $PV = nRT$ and that the change in internal energy is only a function of temperature ($\Delta U = 1.5nRT$) (We shall discuss this relation in chapter 4). Suppose we have 1 mole of an ideal gas confined in a cylinder with a movable piston top, which allows the volume of the gas to be controlled. The gas starts at an initial volume $V_0 = 10 \text{ L}$ at a pressure of 1 atm. We want to consider the effect of two different two-step processes, each of which starts with the gas in the same initial state and ends with the gas in the same final state:

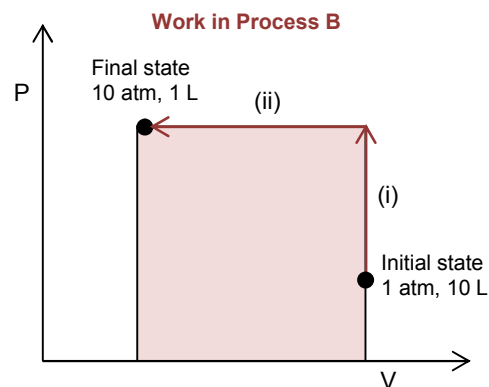
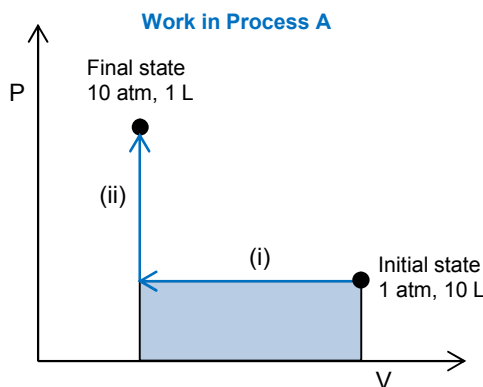
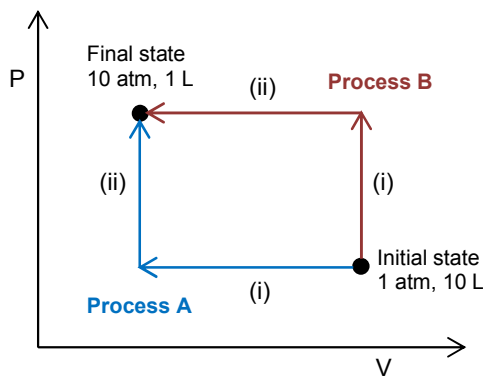
Process A: (i) The gas is compressed to a volume of 1 L at constant pressure ($P = 1 \text{ atm}$). (ii) The pressure is then slowly increased from 1 atm to 10 atm at constant volume.

Process B: (i) The pressure is slowly increased from 1 atm to 10 atm at constant volume ($V = V_0$). (ii) The gas is then compressed from 10 L to 1 L at constant pressure ($P = 10 \text{ atm}$).

Assume the changes occur slowly enough for the gas to remain in equilibrium at all times (reversible processes).

- (a) By which composite process, A or B, is more work done by the gas? Show why using a P vs. V diagram and also quantitatively by calculation.

A P-V diagram for this problem looks like this:



From the P-V diagram, it is clear that the more work is done by the system is in Process B.

Mathematically, work done in Process A:

Step (i): Work done in this isobaric process, $W_P = -P(V_2 - V_1) = -(1 \text{ atm})(10 \text{ L} - 1 \text{ L}) = -9 \text{ L-atm}$

Step (ii): Work done in this isochoric process, $W_V = -PdV = 0$ (as $dV = 0$)

So, the total work done on the system during this composite process A = -9 L-atm

Now, work done in Process B:

Step (i): Work done in this isochoric process, $W_V = -PdV = 0$ (as $dV = 0$)

Step (ii): Work done in this isobaric process, $W_P = -P(V_2 - V_1) = -(10 \text{ atm})(10 \text{ L} - 1 \text{ L}) = -90 \text{ L-atm}$

So, the total work done on the system during this composite process A = -90 L-atm

Thus, more work is performed in Process B.

- (b) Is the change in internal energy of the gas the same for each composite process? Why?

Yes. Internal energy is a state function, and thus changes in internal energy do not depend on the path taken, only the identity of the initial and final states. Since the initial and final states of the system undergoing each process are the same, the change in internal energy must be the same.

- (c) With the given information, can you calculate the heat transferred into/out of the gas during process A? Why or why not? If yes, show your calculation.

Amount of heat transferred into the gas during process A can be calculated from the first law:

$$Q_{\text{rev}} = \Delta U - W_{\text{rev}}$$

Now for the ideal gas, the change in internal energy is: $dU = ncP dT$. Thus

$$\Delta U = (1 \text{ mol}) (5R/2) (T_2 - T_1)$$

Using $PV = nRT$,

$$T_1 = (1 \text{ atm}) (10 \text{ L}) / (1 \text{ mol}) (0.082 \text{ L-atm/mol-K}) = 121.9 \text{ K}$$

$$T_2 = (10 \text{ atm}) (1 \text{ L}) / (1 \text{ mol}) (0.082 \text{ L-atm/mol-K}) = 121.9 \text{ K}$$

$$\text{Then, } \Delta U = (1 \text{ mol}) (5R/2) (121.9 \text{ K} - 121.9 \text{ K}) = 0$$

Thus, $Q_{\text{rev}} = -W_{\text{rev}} = 90 \text{ L-atm}$ i.e., 90 L-atm amount of heat leave the system

Suppose now we carry out a four-step process: Starting in the initial state ($V = V_0$, $P = 1 \text{ atm}$), we perform composite process A, followed by composite process B in reverse.

- (d) What is the total internal energy change for the gas after all 4 steps?

The composite process described is a cycle-the initial and final states are the same; therefore, the change in internal energy is zero.

- (e) Can you determine the total heat transferred into/out of the gas for this 4-step composite process? If yes, show your calculation.

Yes. Applying the first law:

$$Q_{\text{rev}} = W_A + Q_A + (-W_B) + Q_B = 0$$

$$-9 \text{ L-atm} + Q_A + 90 \text{ L-atm} + Q_B = 0$$

$$Q_{\text{total}} = Q_A + Q_B = 81 \text{ L-atm}$$

4. One mole of an ideal gas is compressed adiabatically in a piston-cylinder device from 2 bar and 25 °C to 7 bar. The process is irreversible and requires 35% more work than a reversible, adiabatic compression from the same initial state to the same final state. What is the entropy change of the gas during this irreversible process?

An adiabatic process is also an isentropic process. So the change in entropy for this irreversible adiabatic process is zero.