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New Approaches

DEVELOPMENT OF THE CONCEPT OF ENTROPY: A SIMPLER ALTERNATIVE TO CARNOT CYCLE

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Abstract. The relationship between entropy and reversible heat and temperature is developed using a simple cycle, in which an ideal gas is subjected to isothermal expansion and compression and heated and cooled between states. The procedure is easily understood by students if they have knowledge of calculations involving internal energy, reversible work, and heat capacity for an ideal gas. This approach avoids the more time-consuming Carnot cycle. The treatment described here illustrates how the total entropy change resulting from an irreversible process is always positive.

Keywords: Thermodynamics; Entropy; reversible work; reversible heat; irreversible process

Introduction

The concept of entropy is one of the more challenging ones encountered by the undergraduate students of thermodynamics. A complete development of the concept of entropy needs a study of the Carnot cycle, and a mention of steam engine and its efficiency (Atkins & de Paula 2001). An alternative approach is to just define entropy change as the amount of reversible heat transferred divided by the temperature. Sometimes this is necessitated by the fact that the time available for teaching all the essential topics in an undergraduate physical chemistry course is not sufficient for the purpose.

This article describes a method which leads logically to the definition of entropy. It obviates the need for just presenting entropy to students and having them accept it for granted. The method also avoids the more involved treatment of the Carnot cycle. In its place a much simpler cycle is described here, which is applicable to a more restricted process, but still leads logically to the concept of entropy. The background material needed to understand this treatment is usually covered in the First Law calculations on ideal gases.

Background material

Learners should be familiar with the mathematical statement of the First Law, namely, ΔU = heat + work, calculations involving work, heat, heat capacity, internal energy, and reversible and irreversible processes (Laidler et al. 2003; Ahmad 2013; Ahmad & Ddamba 2006). They should understand the concept of state functions and should appreciate the fact that during a cyclic process, where a system returns to its starting state, the net change in the value of any thermodynamic property is zero (Engel & Reid 2010). They should know that for an ideal gas, internal energy, U, depends only on its temperature and is independent of pressure and volume. This last fact can be taken as a part of the definition of an ideal gas at this stage.

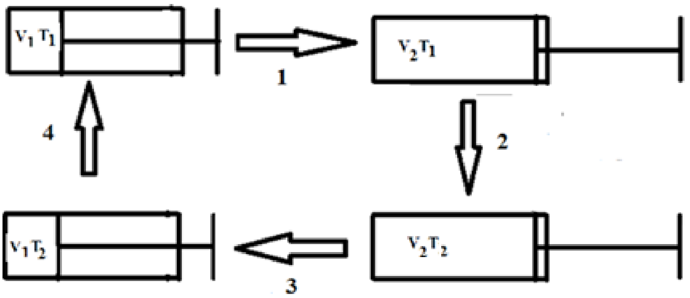

Figure 1. The cycle. Each step is carried out reversibly

Step 1: Isothermal expansion of 1 mole of an ideal gas at T_1 from volume V_1 to V_2.

Step 2: Heating the gas at constant volume V_2 from T_1 to T_2.

Step 3: Isothermal compression of the ideal gas at T_2 from volume V_2 to $V_{1.}$

Step 4: Cooling the gas at constant volume, V_1, from T_2 to T_1.

Fig. 1

The cycle devised is shown in the Fig. 1. An ideal gas is contained in a cylinder with a frictionless piston. The cylinder can be placed in a thermostatted bath when the process requires an isothermal change, or placed in contact with a heat source or a heat sink to supply or remove heat when desired. The system is defined as the cylinder containing the gas and the piston. The processes in the cycle shown take place clockwise starting from the upper left state.

This cycle is restricted to just two types of processes: isothermal volume change and heat transfer. The advantage of this cycle is that it is very simple to understand but still illustrates why entropy is defined the way it is.

The heat, q, and work, w, for each of the steps can be calculated as follows:

Step 1: In step1 one mole of the ideal gas undergoes isothermal expansion from (T_1, V_1) to (T_1, V_2). Since the temperature of the ideal gas is kept constant during the process, there is no change in the internal energy of the system; $\Delta U = 0$. Using the First Law,

$\Delta U = q_1 + w_1 = 0$, Hence $q_1 = -w_1 = \int_{V1}^{V2} PdV = RT_1 \ln \frac{V_2}{V_1}$

Step 2: $q_2 = C_v (T_2 - T_1)$; where C_v is the heat capacity of the gas at constant volume. For ideal gases, C_v is constant at all temperatures

Step 3: Here the gas at T_2 is compressed isothermally from V_2 to V_1.

$q_3 = -w = \int_{V2}^{V1} PdV = RT_2 \ln \frac{V_1}{V_2}$

Step 4: The gas is cooled from T_2 to T_1, keeping the volume constant. This step completes the cycle taking the system back to the starting point.

$q_4 = C_v (T_1 - T_2)$

For the entire cycle:

Total $q = q_1 + q_2 + q_3 + q_4 = RT_1 \ln \frac{V_2}{V_1} + C_v (T_2 - T_1) + RT_2 \ln \frac{V_1}{V_2} + C_v (T_1 - T_2)$.

Since the second the fourth terms on the right hand hand side are equal and opposite to each other, they cancel out and the total heat $q = q_{1\,+}\, q_3 = RT_1 \ln \frac{V_2}{V_1} + RT_2 \ln \frac{V_1}{V_2}$

This can be written as: $q = q_{1\,+}\, q_3 = RT_1 \ln \frac{V_2}{V_1} - RT_2 \ln \frac{V_2}{V_1}$

If the expression for each of q_1 and q_3 is divided by the respective temperatures at which the process takes place, we get $\frac{q_1}{T_1} = R \frac{T_1}{T_1} \ln \frac{V_2}{V_1}$ and $\frac{q_3}{T_2} = -R \frac{T_2}{T_2} \ln \frac{V_2}{V_1}$.

This gives $\frac{q_1}{T_1} + \frac{q_3}{T_2} = R \ln \frac{V_2}{V_1} - R \ln \frac{V_2}{V_1} = 0$. [Eq. 1]

The conclusion is that for the whole cycle, every step of which is reversible $\sum \frac{q}{T} = 0$, even though $q \neq 0$. This is a property of a state function; the change in its value for a cycle is zero. This state function is called entropy, with symbol S.

For the whole cycle, $\Delta S = \sum \frac{q_{REV}}{T} = 0$. For each of the steps, $\Delta S = \frac{q_{REV}}{T}$.

Eq [1], which gives the sum of all the steps in the cycle, does not have terms corresponding to steps 2 and 4. This is because the two terms cancel out, having equal magnitude but opposite signs. However we can still include them in the sum. Since the temperature during the steps are not constant, we need to use the differential form of the definition of entropy change, namely, $dS = \frac{dq_{REV}}{T}$, and its integrated form: $\Delta S = \int_{T_1}^{T_2} \frac{dq_{REV}}{T}$, where the integration is from the starting T to the final T.

Since $dq = C_v\, dT$, we have $\Delta S_2 = \int_{T_1}^{T_2} \frac{C_v}{T} dT = C_v \ln \frac{T_2}{T_1}$ and $\Delta S_4 = C_v \ln \frac{T_1}{T_2}$

It can be seen that $\Delta S_2 = - \Delta S_4$, and the terms cancel out, as noted before.

It should be emphasized that since S is a state function, the value of ΔS depends only on the entropies of the initial and the final states. $\Delta S = (S_2 – S_1)$, no matter how the system goes from state 1 to state 2. So ΔS has to be calculated using the value of q_{REV} (heat for a hypothetical reversible path) irrespective of what the actual path is.

Entropy change for the surrounding

For the above reversible cycle, it is obvious that the entropy change for the surrounding for each step is equal to the negative of the entropy change for the system. This is because the $q_{SYSTEM} = - q_{SURROUNDING}$. Hence, $\Delta S_{SYSTEM} = - \Delta S_{SURROUNDING,}$ or $(\Delta S_{SYSTEM} + \Delta S_{SURROUNDING}) = 0$, which is consisting with the fact that the total entropy change of the Universe resulting from a reversible process is zero.

This assumes that the steps 2 and 4 involve reversible transfer of heat. The process of transfer of heat is reversible when the objects between which the transfer takes place are at temperatures that are only infinitesimally different from each other. How heat is transferred reversibly is not discussed in this article for the sake of simplicity and in order to remain focused on the main theme, namely, the definition of entropy. Instead it is just assumed that the heat transfer in the two steps is reversible.

Irreversibility in the cycle

It is instructive to see what happens when at least a part of the cyclic process above is irreversible. Again let us consider the simplest case. Suppose step 1, instead of being a reversible expansion, were a free expansion into vacuum. In that case $w_1 = 0$, which implies that $q_1 = 0$, since $\Delta U = 0$ (ideal gas, constant T).

Now, ΔS for the system in step 1 is the same as for the reversible process calculated above, S being a state function. $\Delta S_1 = R \ln \frac{V_2}{V_1}$. The entropy change for *surrounding*, however, is different now, when step 1 is a free expansion. Now the surrounding is not affected in the process and does not undergo any change during the free expansion when no heat is exchanged between the system and the surrounding. So, $\Delta S_{SURROUNDING} = 0$ for this step. While now for the system for the entire cycle, ΔS_{SYSTEM} is still zero, for the surrounding, this is not the case. The total entropy change for the system plus surrounding as a result of the cyclic process is now positive, since the entropy increase in the system in step 1 is not compensated by a corresponding decrease of the entropy of the surroundings (a change of $– R \ln \frac{V_2}{V_1}$) as happened in the reversible process. This causes the total entropy of the system plus the surroundings to increase by $R \ln \frac{V_2}{V_1}$. Looking at it in another way, we notice that although for each of the reversible steps, entropy change of the surrounding is equal and opposite in sign to the entropy change of the system, for any irreversible process the entropy change in the surrounding does not compensate for the change in the system. Such is the case for the irreversible step 1. Thus ($\Delta S_{SYSTEM} + \Delta S_{SURROUNDING}$) > 0 if there is any irreversibility in the cycle.

Let us consider a slightly more complicated case; the one where the process in step 1 is still irreversible, but is not a free expansion and some heat is in fact transferred to the system. In that case the heat being transferred from the surrounding to the system, though not zero, is still less in magnitude than q_{REV}. This is because the magnitude of the work done by the system during a reversible process is greater than what can be obtained from an irreversible process. Consequently the heat given up by the surroundings is less in magnitude compared to the reversible process, leading to a smaller decrease in the entropy for the surroundings causing the total entropy change to be positive. This result illustrates the fact that for any process where there is any irreversibility, the total entropy change for the system plus surrounding is positive.

It needs to be mentioned that $\Delta S_{SURROUNDING} = \frac{q_{SURROUNDINGS}}{T}$, since surroundings see all heat as reversible, irrespective of what the source of this heat may be, whether arising from a reversible or an irreversible process taking place in the system. That is because the effect of heat transferred on the state of the surrounding is the same irrespective of how it is generated or used up within the system.

The question naturally arises whether we can get a similar function for the work done, since for this simple cycle the sum of $\frac{w}{T}$ values for all the steps is zero, just like it is for the sum of $\frac{q}{T}$ values. However it can be shown that if there is an adiabatic step in the cycle, the sum of $\frac{w}{T}$ values for all the steps in the cycle may not be equal to zero, as indeed is the case for the Carnot cycle.

Conclusion

With the help of the simple cycle described above one can arrive at the definition of entropy and also show that for an irreversible process, the total entropy change of the system and surrounding is positive, while it is equal to zero for a reversible process.

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