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DISSIPATION OF HEAT: ESSENTIAL FEATURE OF CYCLIC IRREVERSIBLE PROCESSES

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Abstract. The article discusses one key characteristic of irreversible processes: in order to bring the system back to its original state following such a process, some energy is inevitably dissipated as heat into the surroundings. Greater dissipation indicates greater irreversibility. In the limit that the amount of energy dissipated approaches zero, the process is said to be reversible. This concept is illustrated by considering isothermal expansion of an ideal gas, free expansion of an ideal gas into vacuum, heat transfer from a hotter object to a colder one, phase change, and chemical reactions.

Keywords: reversible process; irreversibility; cyclic process, isothermal expansion; phase change; heat transfer

Introduction

Reversibility is a key concept in thermodynamics, an understanding of which is essential in order to grasp the concept of entropy (Atkins & de Paula, 2001; Klotz & Rosenberg, 2008; Ahmad, 2013; Ahmad & Ddamba, 2006). There are various ways to explain the concept of reversibility to students. A common approach is to state that during a reversible process the system remains at equilibrium. On a more operational level, it is explained in terms of the process being carried out infinitesimally slowly. These explanations are accurate, but they do not make the concept any clearer on their own. A system remaining at equilibrium but at the same time undergoing change, however slowly, is somewhat difficult to comprehend. Explaining a reversible process as one taking place slowly can give the erroneous impression that thermodynamic properties somehow depend on the speed of the process taking place.

In the following treatment it will be shown, using examples of a number of irreversible processes, that in order to restore a system to its exact original state after the process, some of the work (electrical or mechanical, for example) done on it will necessarily be dissipated as heat into the surroundings. In other words, after a system has undergone an irreversible process, it cannot be restored or reversed to its initial state unless some energy is dissipated as heat. Greater the heat dissipated, larger is the irreversibility. If the process is carried out in such a way that less energy gets dissipated as heat, the extent of irreversibility becomes lower. In the limit that this dissipated heat reaches zero, the process approaches reversibility. It is to be understood that this is a theoretical limit, not realizable in actual processes. Thus a reversible process can be defined as one in which the system can be restored exactly to its initial state without dissipating any energy as heat.

This way of looking at reversibility makes it easier to develop the concept of entropy for students. Change in entropy can then be thought of as being related to the energy that has been dissipated as heat into surroundings. Clearly this definition of reversibility implies that a cyclic reversible process does not result in any increase in the overall entropy for system plus surroundings, since in that case no heat is dissipated into the surroundings.

In the following treatment the processes commonly encountered in an undergraduate thermodynamics course will be used to illustrate this point (Laidler et al. 2003, Engel & Reid, 2010). These processes are: expansion of an ideal gas against an external pressure, free expansion of a gas into vacuum, heat transfer from a hotter object to a colder one, phase change, and chemical reactions. It will be shown that after a system has undergone an irreversible change, any process to restore it to its original state necessarily involves dissipation of heat to surroundings.

Isothermal expansion of an ideal gas

Let us consider a process whereby n moles of an ideal gas expand from a pressure P_1 to P_2 at a constant temperature T. The expansion is done against a constant external pressure. For the expansion to be possible, $P_2 < P_1$. Suppose the external pressure against which the expansion takes place equals the final pressure P_2. After the gas has expanded, we bring it back to the initial state, i.e., to P_1 at T. During the expansion, work equals $– P_2(V_2 –V_1)$, or $–P_2\Delta V$. Since the internal energy does not change during the process (ideal gas, constant T) the First Law of Thermodynamics requires that the system extract an amount of heat equal in magnitude to this work from the surroundings, such as a water bath at the constant temperature, T.

Now we restore the system to its initial state (P_1, V_1, T). One way is to impose a pressure P_1 on it, which will compress it till the final pressure equals P_1. The work done on the system is $–P_1(V_1 –V_2)$, which equals $P_1\Delta V$, given the above definition of $\Delta V = V_2 –V_1$. An equivalent amount of heat gets transferred to the surroundings. Now $|P_1\Delta V| > |P_2\Delta V|$, since $P_1 > P_2$. That means the work done on the system during the compression is greater than the work that was done by the system during the expansion. Since (heat + work) = 0 for a cyclic process, according to the First Law, the heat given out during the compression is greater than the heat that was originally extracted from the surroundings. The net result is that to restore the system to its initial, pre-expansion state, work has been changed to heat, which has been dissipated into the surroundings. Another way to look at it is that during the cyclic process an amount of energy ($|P_1\Delta V| - |P_2\Delta V|$) has had to be dissipated into the surroundings in the form of heat.

Now this energy, which is dissipated as heat, can be reduced if the original expansion was not in one step against P_2, but in a series of steps, with each expansion being against a pressure which is progressively lowered, till the final pressure P_2 is reached. The work done by the gas in reaching P_2 will then be greater. Suppose the steps were P_1 to P', and P' to P_2, with $P_2 < P' < P_1$. The total work would then be given by

$$w_2 = -P'(V' - V_1) - P_2 (V_2 - V') \qquad (1)$$

To see how the magnitude compares with the original one-step expansion, we can write the latter as

$$w_1 = -P_2 (V_2 - V_1) = -P_2 (V' - V_1) - P_2 (V_2 - V'). \qquad (2)$$

From Eqs. (1) and (2), we see that the magnitude of the work done in the two-step expansion, $|w_2|$, is greater than that of the work, $|w_1|$, in the one- step process, since $P' > P_2$ Since more work is done by the system in the one-step process compared to the two-step one, more heat is absorbed in the former than in the latter according to the First Law, as internal energy, being a state function, changes by the same amount in the two processes. In the reverse processes equal amounts of heat leaves the system in each of the two cyclic processes. Hence in the cyclic process with the one-step expansion, the net heat given out is greater in magnitude than for the other cyclic process. This heat dissipated will keep decreasing as the number of steps is increased in expansion, finally reaching a limit, when the number of steps becomes infinite. At that stage the expansion is said to be reversible.

Free expansion of an ideal gas into vacuum

Suppose an ideal gas, initially at a pressure P_1, is allowed to expand into vacuum such that its volume increases from V_1 to V_2 at a constant temperature, T. To bring the system back to its original state, work will have to be done on it. If the temperature remains the same, and the internal energy remains constant, the First Law requires that an equivalent amount of heat is discarded to the surroundings. Thus, consistent with our stipulation of irreversibility, this is another example of a cyclic process containing irreversibility where energy has to be dissipated as heat.

Chemical reactions

Unlike the expansion of an ideal gas just considered, a chemical reaction system cannot be restored to its original state simply by mechanical means. In certain case, however, the system can be restored if the reaction takes place in an electrochemical cell and a suitable external electrical potential is applied to it. We will consider the example of the reaction: $Zn(s) + Cu^{++}(aq) \leftrightarrows Zn^{++}(aq) + Cu(s)$. The reaction can be carried out in an electrochemical cell comprising two compartments, one containing an aqueous solution of $ZnSO_4$ along with a solid Zn electrode, and the other compartment containing $CuSO_4$ solution and solid Cu. The two compartments are connected through a salt bridge containing a KCl solution. An external potential can be applied between the two electrodes.

When the electrodes are connected to each other using a metal wire, the following overall reaction takes place irreversibly:

$$Zn(s) + Cu^{++}(aq) \rightarrow Zn^{++}(aq) + Cu(s)$$

Negative charge flows through the wire from Zn to Cu electrode. This causes the wire to be heated and the heat energy gets dissipated to the surroundings. To reverse the reaction and restore the system to its original condition, an opposing potential has to be applied across the electrode. When the cyclic process is complete and the system has been restored to its initial state, the net result is that during the cycle heat has been dissipated to the surroundings.

If, instead of the electrodes being connected directly, an external potential is applied which just opposes the cell potential, no reaction will take place. Now if the opposing potential is decreased minimally, the reaction will take place under near reversible conditions, with a minimal current, and hence with minimal heat being dissipated. In such a cycle, in the limit that no heat is dissipated, the process will be said to be reversible.

Irreversible heat transfers from a hotter object to a colder one

Suppose a hot object, A, is brought in contact with a colder one, B, and heat flows between them till they reach thermal equilibrium. After their temperatures become equal, the process can be reversed to bring back A and B to their original temperatures by the help of a gas contained in a cylinder with a piston. To do so, the two objects are separated from each other, and the cylinder is brought in contact with B and allowed to expand isothermally, whereby it extracts heat from B, and can cools it to its original temperature. The cylinder is now brought into thermal contact with A and compressed isothermally, thus raising the temperature of A to its original, pre-process, value. The following analysis will show that in order to restore A and B to their original temperatures some heat has to be dissipated into the surroundings.

This analysis can be carried out by assuming that the objects A and B are themselves containers of equal quantities of ideal gases. Further A is fitted with a frictionless piston. This explanation will be clearer, if we work with some assumed numbers. Supposed the initial temperature of A is 40 °C and that of B is 20 °C. After they are brought in contact and the irreversible process of the transfer of heat has taken place, A and B reach thermal equilibrium, with their temperature at 30°C. To restore them to their original states, both A and B are thermally insulated from the surroundings, but kept in contact with each other. The gas A is then expanded reversibly, with external pressure almost equal to the pressure of the gas throughout the expansion. This process takes place adiabatically, with the only transfer of heat being between A and B.

The expansion is continued till the temperature of both A and B reaches 20 °C. Then A and B are isolated from each other. A is then adiabatically compressed to reach its original state of 40 °C. The following treatment shows that the whole cyclic process requires some heat to be dissipated to the surroundings.

A is the cylinder with the piston, and B is the other container. Thermal properties of the two are identical, and each contains one mole of an ideal gas. When they are brought together and thermal equilibrium allowed to reach, both attain 30 °C. A is allowed to expand till the temperature of both decreases to 20 °C. A is then separated from B and compressed adiabatically such that its final temperature is 40 °C. Thus the entire system comprising A and B returns to the initial state.

The series of steps is illustrated in Fig. 1 (not to scale):

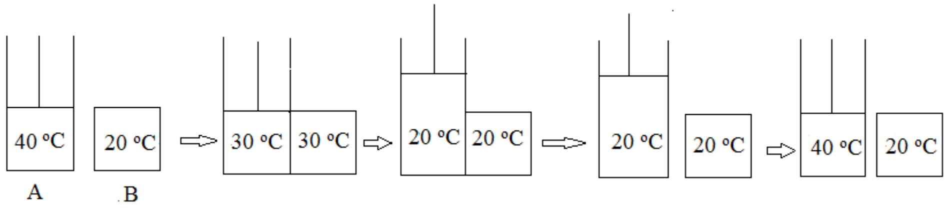

Figure 1. Steps of heat transfer from A to B, and restoration of the initial states of the two

When A is expanded adiabatically (except for its thermal contact with B) and the temperature of the two parts decreases to 20 °C, the final volume of A can be calculated by the usual treatment of adiabatic processes, as follows. If C_v is the heat capacity of each of A and B, we have

$$dU = 0 - PdV$$

$$2C_v dT = -(RT/V)dV$$

For heat capacity, we need the factor 2, since the thermal energy of both A and B is involved, while the work of expansion is done by only A. The integration can be carried out by separating the variables

$$2C_v dT/T = -(R/V)dV$$

On integration this yields:

$$2C_v \ln T_2/T_1 = -R\ln(V_2/V_1)$$

Using the appropriate values of temperature in Kelvin, and taking C_v to be 1.5 R, we find that the gas in A has to be expanded to 1.11 times its initial volume for it to go from 30 °C to 20 °C.

At this stage, A is at 20 °C, as is B. To bring the entire system to its pre-process state, A has to be brought to 40 °C, which can be done by compressing it adiabatically. For the calculation relating to this process we use the same mathematical treatment as above, except that the heat capacity of A alone is used now, which is $C_{v.}$ and not 2 C_v.

$$V_3/V_1 = 1.002.$$

Here V_3 is the volume that the gas attains when its temperature is brought to 40° C using the adiabatic compression.

Finally, the gas in A has then to be brought back to its original volume at 40°C. This can be done by compressing it isothermally, which will necessitate doing work on it and losing this energy as heat to the surroundings.

Irreversible phase change

Let us consider an equilibrium system of water and water vapor at 100°C and 1.0 atm contained in a cylinder with piston. We assume that that the volume of the vapour in the system is V. Now the pressure imposed on the system is suddenly increased to 1.1 atm keeping the temperature at 100°C. The vapor, now being at a higher pressure than the equilibrium vapour pressure, will condense irreversibly to form liquid, with the volume of the remaining vapor being negligible. The following irreversible process has taken place:

$$H_2O\ (g) \rightarrow H_2O\ (l);$$

$$w_1 = -(1.1)(0 - V) = (1.1\ V)\ \text{L.atm.}$$

Now to restore the system to its original state after this irreversible process, the vapor should be expanded to a final pressure of 1 atm. During this expansion, work done is given by:

$$w_2 = -(1)\ (V-0) = (1\ V)\ \text{L. atm.}$$

Looking at the energy balance during the compression (with the accompanying condensation of the vapor) and the expansion (with the resultant evaporation), we see that a net amount work equal to [(1.1 V) – (1V)] L. atm work has been done during the cyclic process. This difference in work must equal the heat dissipated, as required by the First Law. Hence it has been shown that during the irreversible cyclic process, some heat has been dissipated. In the above treatment, it has been assumed that the enthalpy of vaporization of water at 1 atm is nearly equal to its value at 1.1 atm.

Conclusion

The above examples have shown that to restore a system to its original state after it has undergone an irreversible process some energy has to be dissipated to the surroundings in the form of heat. A corollary is that if any part of a cyclic process is irreversible, the process will involve some energy being dissipated to the surroundings as heat. This can make the concept of irreversibility clearer.

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