A note on irreversible adiabatic cyclic process and role of time in thermodynamics

Radhakrishnamurty Padyala
282, DMLO, Yelhanka, Bangalore – 560064, India.
Email: padyala1941@yahoo.com

Abstract

Irreversible adiabatic cyclic process of an ideal gas is an important thermodynamic process. It offers a method of analysis of second law without involving any heat interactions. We show in this note that the impossibility of an irreversible adiabatic cyclic process is equivalent to the assertion that time plays no role in thermodynamic predictions.

Key words: Irreversible adiabatic cyclic process, Second law of thermodynamics, Role of time in thermodynamics.

Introduction

"Classical thermodynamics", says Nash[1], "a discipline of immense generality, is also one of immense reliability". Thermodynamics is not understood properly by many, it is even misunderstood by some. As time passes, the proportion of those who misunderstand is going up.

One of the major misunderstandings of classical thermodynamics concerns the role of *time* in thermodynamics. Time plays no role in thermodynamics. To quote Nash[1], "Classical thermodynamics is concerned with the *equilibrium states of systems NOT* with the *paths* by which different states may be connected; and *NOT* with the *rates* at which the paths may be traversed and the states attained". However, as ever, efforts are on to demonstrate, using modern tools, that the slower a process is carried out the more reversible it becomes[2]. This is against the very spirit of thermodynamics.

Given two equilibrium states of a system, A, B, thermodynamics predicts whether a process connecting them is possible or impossible. The validity of the prediction is unquestionable! The thermodynamic prediction is based on the criterion of change of entropy of the universe, ΔS_{Univ}, the process brings about. If ΔS_{Univ} is negative, the process is deemed to be impossible and if ΔS_{Univ} is positive, then the process is deemed to be spontaneous or *irreversible*. Finally, if $\Delta S_{Univ} = 0$, the process is considered reversible. This truth is not conditional or subject to any conditions whatever. More specifically, the time rate at which the process connecting A and B is carried out is immaterial; it could be infinitely fast bordering on instantaneous to infinitely slow – it matters little in deciding whether the process is irreversible or not.

Irreversible thermodynamic process

An irreversible thermodynamic process according to Planck[3] is described thus: "*A process which can in no way be completely reversed is termed irreversible, all other processes reversible. That a process may be irreversible it is not sufficient that it cannot be directly reversed. This is the case with many mechanical processes which are not irreversible. The full requirement is, that it be impossible even with* *the assistance of all agents in nature, to restore everywhere the exact initial state when the process has once taken place*".

Planck mentions[3] expansion of an ideal gas without performance of external work or absorption of heat as one among the three characteristic examples of irreversible processes, the other two being process of conduction of heat and the process of generation of heat by friction.

To develop the second law of thermodynamics, Caratheodory[4] had taken up the adiabatic process. According to his formulation[4], the second law may be stated as: "In every arbitrarily close neighborhood of a given state there exist states that cannot be reached arbitrarily closely by adiabatic process".

With this background we take up the analysis of the process of irreversible adiabatic expansion. For this purpose, we choose the simplest system – the ideal gas.

Ideal gas system

Thermodynamically, ideal gas is defined as a system whose internal energy E, is a function of temperature only. $E = f(T)$, $E \neq f(V, P)$. It is governed by a simple equation of state: $PV = nRT$. The symbols P, V, T, n have their usual significance. Therefore, ideal gas is the simplest system.

Reversible adiabatic process of an ideal gas

Additional simplicity would accrue by choosing an adiabatic process. Since here, heat interactions are eliminated and we need to consider only work interactions. Elimination of heat interactions makes $\Delta S_{Surr} = 0$. Therefore, we need to consider only the entropy change suffered by the system, in our analysis.

Reversible adiabatic expansion of an ideal gas is governed by the equation: PV^{γ} = constant, where γ is the ratio of specific heat at constant pressure to that at constant volume. The process can be depicted on a P-V graph as shown in figure 1.

Fig. 1 Reversible adiabatic curve of an ideal gas with two states A and B marked on it

According to second law of thermodynamics, reversible adiabatic processes are isentropic, that is, S_{sym} = constant. A reversible adiabatic process takes the system from one point A on a reversible adiabatic (isentropic) curve to another point B, on the same curve as shown in figure 1.

Irreversible adiabatic expansion process of an ideal gas

An irreversible adiabatic process takes the system from a point A on one reversible adiabatic curve (S_1) to a point B' on a different reversible adiabatic curve (S_2) located to the right of S_1, as shown by the dashed line, in figure 2. That is, the initial and final states of a closed system of an ideal gas in an irreversible adiabatic process lie on different reversible adiabatic curves. Stated differently, it is impossible for the initial and final states of a closed system of an ideal gas to lie on one and the same reversible adiabatic curve when the system suffers an irreversible adiabatic process. It is important to keep this in mind in understanding any discussion of an irreversible adiabatic process that a system undergoes. It is also important to keep in mind the second important point that since the heat interaction is zero in an adiabatic process, the entropy change suffered by surroundings, $\Delta S_{surr} = 0$. Therefore, $\Delta S_{Univ} = (\Delta S_{surr} + \Delta S_{Sym}) = \Delta S_{sym}$.

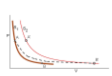

Figure 2. AB' (dotted line) depicts irreversible adiabatic expansion of ideal gas. AB (S_1) and A'B' (S_2) show reversible adiabatics. There are infinite number of reversible adiabatics between S_1 and S_2

It is clear from the figure that the initial and final states of irreversible adiabatic expansion of an ideal gas do not lie on one and the same adiabatic curve. Irreversible expansion process of an ideal gas takes the system across reversible adiabatics from one to another.

It can be seen from figure 2 that an irreversible adiabatic process takes the system from one isoentrope, S_1 to another isoentrope S_2 at higher entropy, located to the right of S_1. It is also evident that a reversible adiabatic process cannot take the system from one adiabat to another. This is because it needs a shift from S_1 to S_2 which a reversible adiabatic process is incapable of achieving. That the initial and final states of a system that undergoes an irreversible adiabatic process lie on different isentropes S_1 and S_2 is not subject to the rate at which the process is brought about. The process connecting A and B' may be very fast or may be very slow – it makes no difference. It is an issue of thermodynamics – not of kinetics.

Caratheodory's postulate[4] of the second law of thermodynamics says, it is impossible to take the system from the state B' to the initial state A by an adiabatic process, whether reversible or irreversible. Therefore it follows that it is impossible to bring about an irreversible adiabatic cyclic process.

It is easy to understand this. Let us try a reversible adiabatic process to take the system from final state B' to the initial state A, to complete the cycle. We find this impossible because B' and A lie on different isentropes and a reversible adiabatic process is incapable of taking the system from one reversible adiabat S_2 to another reversible adiabat S_1.

What about employing an irreversible adiabatic process to bring the system from B' on S_2 to A on S_1?

Let us assume, we are able to bring the system back to its initial state A on S_1 by an irreversible adiabatic process (whether fast or slow), from the final state B' on S_2. This process entails $\Delta S_{Sym} < 0$. Since $\Delta S_{Univ} = \Delta S_{Sym}$ for an adiabatic process, we get $\Delta S_{Sym} = \Delta S_{Univ} < 0$. Such a result violates the Clausius' statement of the second law. Therefore, it is impossible to bring the system back to its initial state A on S_1 by an irreversible adiabatic process, from the final state B' on S_2 without violating the second law.

Irreversible adiabatic compression process of an ideal gas

Just as irreversible expansion process of an ideal gas took the system from state A on S_1 to a higher entropy state B' on S_2 located to the right of S_1, an irreversible compression process (whether fast or slow) takes the system from state B' on S_2 to a higher entropy state A" on S_3 located to the right of S_2 as shown in figure 3.

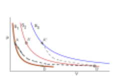

Figure 3. B'A" (dotted line) depicts irreversible adiabatic compression of ideal gas. S_1, S_2, and S_3 show reversible adiabatics. It is clear from the figure that irreversible adiabatic compression from state B' takes the system to an isentrope at a higher entropy S_3 located to the right of S_2 but not to isentrope S_1. Even a reversible adiabatic compression from state B' takes the system to a A' on the same isentrope but not to a point on S_1.

Thus it is clear that when once an ideal gas closed system undergoes an irreversible adiabatic process, there exists no adiabatic process - whether reversible or irreversible, or whether fast or slow - to bring the system back to initial state. In other words it is impossible to take a system through an irreversible adiabatic cyclic process (rates of processes play no role in this conclusion). In short, an irreversible adiabatic cyclic process is impossible.

Therefore, once a system suffers an irreversible an adiabatic process, it is impossible to bring the system to its initial state using another adiabatic process. This is, after all what is to be expected because, when the process is adiabatic, surroundings suffer no entropy change and since the process is cyclic, system suffers no entropy change. Consequently, at the end of an irreversible adiabatic cyclic process universe suffers no entropy change. But that is the characteristic of a reversible cyclic process. Thus an irreversible adiabatic cyclic process leads to a paradox and is therefore an impossible process. This is a form of statement of the second law of thermodynamics. We know that the laws of thermodynamics are not subject to any concept involving time. This applies to all processes whether reversible or irreversible, whether cyclic or non-cyclic.

Role of time in thermodynamics

Time played no role in our analysis above. In other words, we did not use any argument where the time rate of change of the process entered the scene – any description that involved whether a process is fast, or slow, or infinitely slow or instantaneous etc. Therefore, the thermodynamic result that an irreversible adiabatic cyclic process is an impossible process is independent of the time rate at which the processes that are involved in the cycle are carried out. The equation: PV^{γ} = constant, does not involve any quantity that is a function of time. *Even an infinitely slow adiabatic process, cannot connect two states of a system lying on different isentropes*. If it were possible, then it would be possible to achieve an irreversible adiabatic cyclic process. Similarly, a very fast reversible process cannot take the system from one isentrope to a different isentrope. For example, a very rapid ideal mechanical motion (no friction) does not qualify to be an irreversible process. It is considered a reversible process, in spite of the fact that it was assumed to be a rapid (fast) process.

The impossibility of an irreversible adiabatic cyclic process proves the assertion that time plays no role in thermodynamic predictions.

This is the characteristic of any and every thermodynamic process: The result is independent of the rate at which the process is carried out. Time plays no role in thermodynamics.

Acknowledgement

I thank Mr. Arunmozhi Selvan Rajaram, Davis Langdon KPK India Pvt Ltd, Chennai, India, for his constant support and encouragement of my research pursuits in every possible way.

References

1. L. K. Nash, ‘ELEMENTS OF *Chemical Thermodynamics*’, Addison-Wesley series in the Principles of Chemistry, Addison-Wesley Pub. Co., Inc. Reading, MS, (1962), p. 2.
2. Carmen Alwarez-Rua and Javier Borge, J. Chem. Educ., ***93*** (2016) 2110-2116.
3. Max Planck, *Treatise on Thermodynamics*, Part III, Tr. by A. Ogg, Dover Pub. Inc., N. Y. (1969).
4. C Caratheodory, *The Second Law of Thermodynamics, Benchmark papers on Energy / 5, DH&R Inc Penn (1976), p.220.*