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REVERSIBILITY AND DEFINITION OF WORK

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Abstract. The article points out a fundamental discrepancy between the definition of work from elementary mechanics, and how the expression for work is developed in most of the courses in chemical thermodynamics. A method of correcting this is suggested. This discrepancy is used as a heuristic tool to develop an easy to understand explanation of what the difference is between reversible and irreversible expansion of a gas, as well as transfer of heat. The explanation leads to a definition of reversible processes.

Keywords: thermodynamics, work, reversibility/irreversibility

Introduction

Students learn in their physics courses that mechanical work is the product of the force on a moving boundary multiplied by the distance moved in the direction of force (Serway & Jewett, Jr., 2004). The agency applying the force loses an amount of energy equal to the work. This is acknowledged by affixing a negative sign to the expression of work when the agency is doing the work. Later, in their thermodynamic courses this concept is applied to the process of expansion of a gas. To treat the expansion of gas, the product of force and distance is replaced by its equivalent, pressure x change in volume. In conventional treatments in physical chemistry, the original definition of work is not followed and without explanation it is replaced by another in which instead of the pressure of the gas, the pressure of the external agent, or the *opposing pressure*, is used. But, while treating the opposite process, that of compression or a decrease in volume, the opposing pressure is no longer used but instead it is the pressure causing the net movement that is used. This internal inconsistency and contradiction with the fundamental definition of work can be used as a heuristic tool to develop an easy to understand treatment of the nature of reversible and irreversible processes.

Work of expansion

Consider the system in Fig. 1. The system is the gas along with the inside surfaces of the cylinder and the piston with which the gas is in contact. The rest is the surroundings. Also any transfer of heat between the system and the surroundings can be measured by a calorimeter which is in contact with the system but thermally insulated otherwise.

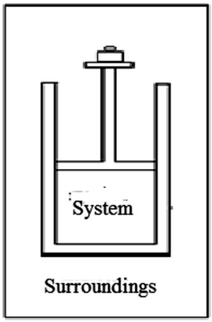

Fig. 1. System and surroundings to illustrate reversible and irreversible expansion

For the system described, the pressure (and hence the force) on the inside surface of the cylinder applied by the gas is always outwards – away from the bulk of the gas. Moreover for the movement of the piston, only two directions are possible: away from the bulk of the gas (outwards) or towards the gas (inwards). For the movement of the piston in either direction, the force can be along the direction of the motion of the piston, or in the opposite direction. The piston can move in a direction opposite to that of the force exerted by the gas if there is a greater force exerted by an external agency in the opposite direction. In such a case the volume of the gas decreases, and the process is said to be that of compression. If the pressure of the gas is higher than the outside pressure, it expands pushing the piston out.

If the piston moves outward, then the gas is said to be doing the work equal to the force multiplied by the distance that the piston moves in the direction of the force. The energy of the gas decreases by this amount. If the piston is moving inwards decreasing the volume of the gas, the gas will gain energy, since the force being applied is now in the opposite direction to the direction of the motion.

Applying the definition of work given earlier, it can be shown that

$$w = -\int P_g \mathrm{d}V \tag{1}$$

The limits of integration are the initial and the final volume of the gas. For an infinitesimal process then, $\mathrm{d}w = -P_g\mathrm{d}V$.

So far this is in accordance with the way the topic is represented in most textbooks (Laidler et al., 2003; Raff, 2001; Atkins & de Paula, 2001; Engel & Reid, 2010; Klotz & Rosenberg, 2000). From this point on, however, the books start using a different definition from the one given above without explanation. Instead of using the force doing the work, i.e., the pressure of the gas, they use the external or opposing pressure against which the work is being done. Because the two pressures are different (as evidenced by the motion of the piston) the two values of work are necessarily different. For expansion, since $P_{gas} > P_{ext}$, the magnitude of the work done by the system, and hence the decrease in energy of the system, is greater than the increase in the energy of the surroundings if the above definition of work is used.

In conventional treatments by the textbooks, however, the work, which appears *outside* is then equated to the decrease in the energy of the gas (assuming no heat exchange), whereas according to Eq. (1) this is not true. Eq. (1) uses the pressure of the *gas*, since it is the gas that exerts the force on the moving boundary and consequently undergoes a change in its energy.

Only when the process is reversible, i.e., when the external pressure and the pressure of the gas are equal, can we assume that work calculated using the external pressure is in accordance with the fundamental definition. The First Law of thermodynamics states that the balance of heat loss or gain by the *system* and the work done by or on the *system* determines the change in the internal energy of the *system*. Yet the way it is commonly stated, the Law effectively says that for an expansion of a gas, the change in energy of the *system* is equal to the balance of the work received by the *surroundings* and the heat received by the *system*. This statement of the law is circular in that it first assumes that energy is conserved before asserting that the energy is conserved.

This point has been discussed in detail elsewhere (Ahmad & Ddamba, 2006). How can this obvious discrepancy be reconciled? The answer is that in non-reversible (spontaneous) expansion, the difference in the work done by the system (as defined using the fundamental definition) and the work appearing outside (calculated using the external pressure) is just the kinetic energy of the piston, which will be non-zero for a spontaneous expansion. This kinetic energy then appears as heat and when it is accounted for in the balance of heat received by the system, the discrepancy disappears. The fact that this discrepancy gets resolved is no justification, however, for using an incorrect definition of work, or for the subtle circularity of the statement of the First Law.

Reversible and irreversible expansion

Our purpose here is to use this discrepancy as a heuristic tool to arrive at an understanding of reversibility of a process. As noted earlier when during a process the external pressure is infinitesimally smaller than the pressure of the gas, the expansion is reversible. The condition can be stated mathematically as $\lim P_{ext} \rightarrow P_{gas}$, $w = w_{rev.}$ Under this condition, the piston will not have any kinetic energy and there will be no heat generated as a result of dissipation of this kinetic energy. This can be succinctly stated as:

An expansion process is reversible during which no part of the system has any kinetic energy.

This straightforward definition allows students to understand the otherwise demanding concept of reversibility.

We can see how this criterion of reversibility applies to a process of compression of the gas. Now the direction of motion of the piston is opposite to the direction in which the gas is applying the force, so according to the aforementioned definition, the gas gains energy. For this process, $P_{ext} > P_g$. This implies that the work done by the surroundings, and consequently the decrease in energy of the surroundings is greater than what is received by the system if we were to use Eq. (1). The discrepancy is made up by considering the kinetic energy of the piston, which gets dissipated as heat in the system.

For a reversible process, there would be no kinetic energy, and $P_{ext} = P_g$.

Reversible and irreversible heat transfer

So far we have considered only the process where expansion takes places without any transfer of heat. The criterion developed so far (i.e. reversible process is where there is no kinetic energy) can be extended to the transfer of heat as well. In a properly constructed system irreversible process will result in kinetic energy, while it would be absent during a reversible process.

We now consider a different system, where we replace the gas in the cylinder considered above with some water at its boiling point (Fig. 2). The cylinder is immersed in a thermo stated bath whose temperature can be controlled. When the temperature of the bath is equal to the boiling point of water and the cylinder is at thermal equilibrium with the surroundings (the bath), the following equilibrium is attained: $H_2O(l) \rightleftharpoons H_2O(g)$

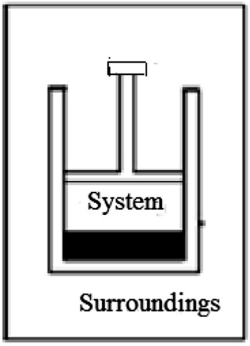

Fig. 2. System and surroundings to illustrate reversible and irreversible transfer of heat

Shaded area shows liquid water, and clear area above it represents water vapour. The amounts of liquid water and water vapor remain unchanged with time. Now if the temperature of the bath is raised infinitesimally, some liquid will change to vapor, the additional vapor will cause the pressure of the vapor to increase, which will push the piston outward to maintain the pressure equal to the outside pressure. Since the increase in temperature is infinitesimally small, the amount of additional vapor is infinitesimal too and the movement of the piston is similarly infinitesimal and so the piston moves at infinitesimally small speed. The kinetic energy is zero in the limit, and by our definition above, the process is reversible.

An irreversible process, by contrast, would be where the temperature of the thermostat is changed by any non-infinitesimal value and non-infinitesimal heat is transferred to the system. The amount of additional vapor would then be non-zero and the piston would move up with some kinetic energy. By the definition above the process would be non-reversible. Irreversible transfer of heat, then, is when the transfer takes place between objects at different temperatures. We thus arrive at the following definition of reversible transfer of heat:

> *A transfer of heat between two objects is reversible when the temperature of one differs only infinitesimally from the other initially and during the transfer; otherwise it is irreversible.*

The reverse of the process could also be envisaged. If the system is at equilibrium (its temperature is the same as the surroundings), and if the external pressure applied on the piston is raised by an infinitesimal amount, then the piston moves inwards, decreasing the volume of the system and consequently raising the pressure of the vapor infinitesimally. This causes the vapor to condense to liquid water to maintain the equilibrium vapour pressure. This releases heat as a result since condensation is an exothermic process. The heat released is transferred to the surroundings. The process goes infinitesimally slowly. Since there is no kinetic energy for the process, the process is reversible. Thus when the temperature of the two objects remains the same, the heat transfer takes place reversibly.

If, on the other hand, the pressure on the piston were increased by a finite amount, the piston would move at a finite speed and hence will possess a finite kinetic energy. The pressure of the vapour would increase, causing it to condense and release heat which is transferred to the surroundings. Now since in the process the piston has kinetic energy, it would be deemed to be irreversible.

Conclusion

The discrepancy between the basic definition of work in physics and its application to thermodynamics as well as internal inconsistency between the definitions used for expansion and compression has been used to develop a treatment of reversibility of processes. A process of expansion of a gas is irreversible if some part of the system has non-zero kinetic energy. Similarly transfer of heat is irreversible if it takes place between two systems in thermal contact that are at different temperatures.

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