

Work in Thermodynamics

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The expression for mechanical work obtained in the expansion of a gas commonly used in physical chemistry textbooks is critically examined. The mathematical form of the first law of thermodynamics is arrived at by a procedure that is consistent with the common definition of mechanical work. The treatment is extended to explain the concept of reversible and irreversible work.

Key Words: Thermodynamics, Work, Heat.

INTRODUCTION

When physical chemistry textbooks^{1–6} develop the concept of work as part of their introduction to the first law of thermodynamics, they almost invariably start with the definition of work with which that the students are familiar. This definition, namely, the magnitude of mechanical work equals force multiplied by the distance through which the force acts, is one of the first concepts that the students have learned previously in a physics course.

However, when the books apply this definition to the expansion of a gas contained in a cylinder with a piston, they use the opposing pressure rather than the pressure of the gas. The textbooks' development of the expression for the work of expansion goes along these lines: For a gas expanding against a frictionless piston and the piston moving from a position a to b , against an opposing force F_{ex} , the work is

$$-\int_a^b F_{\text{ex}} dx = -\int_a^b (F_{\text{ex}}/A)A dx,$$

where A is the area of cross-section of the cylinder. Now, since $F_{\text{ex}}/A = P_{\text{ex}}$ and $A dx = dV$, where P_{ex} is the *external* pressure, and V the volume of the gas, one gets the relation:

$$W = -\int_a^b P_{\text{ex}} dV$$

Most accounts emphasize that the pressure in the formula is the one *against* which work is done; in other words it is the *opposing* pressure. In an expansion, when the volume of the gas is expanding, the opposing pressure is the outside pressure and one gets the above expression for work.

However, for a compression process, where the opposing pressure is clearly the pressure of the gas, the textbooks still use the external pressure. This is done without explanation, which must be a source of confusion for an inquiring student.

There have been attempts to address this anomaly, although the fundamental incompatibility with the accepted definition of work remains unresolved. Bertrand⁷ in a recent article gives a lively account of the discussion that took place over 40

years ago and summarizes four protocols that emerged from it. These are: (i) use the opposing pressure in each case (P_g for compression and P_{ex} for expansion); (ii) use P_{ex} when the process is stopped by factors in the system, otherwise use P_{ex} ; (iii) use P_{ex} in all cases; and (iv) use P_g in all cases. The matter remains unresolved to this day. Bauman⁸ while pointing out that for a compression process the pressure of the gas, P_g , should be used in the expression for work, still leaves in place the definition of work in terms of the force opposing the motion. Kivelson and Oppenheim⁹ use P_g in the expression for work for expansion and P_{ex} for compression in an irreversible process, although the arguments leading to this implicitly assume the validity of the first law of thermodynamics. It has been pointed out by Canagaratna¹⁰ that using the first law to introduce the concept of work and then using this work to explain the law, introduces circularity in pedagogy. This is obviously unsatisfactory.

Other attempts to explain this and other anomalies have resulted in authors defining various types of work. Thus "thermodynamic work" has been presented as a distinct quantity from classical mechanical work, which is the result of all the forces acting on the piston¹¹. Several other types of work, such as internal work, macroscopic work, pseudo work, conservative work, among others, have been devised. These are reviewed by Mallinckrodt and Leff¹², who list at least eight different types of work.

It makes a difference whether pressure of the gas or the external pressure is used to define work for a process where the two pressures are not the same, *i.e.*, for an irreversible expansion. As is shown below the difference between the two expressions equals the kinetic energy of the piston and weights supported by it. However, the expression for the change in internal energy can be shown to be the same irrespective of which definition of work is used, provided heat is appropriately and differently defined in each case.

Definition of Work in Mechanics: If we adhere to the accepted definition of work, we can resolve the inconsistency in the prevailing treatments, which define work in terms of opposing pressure, but still use the external pressure when it is not the opposing pressure (as in a compression). Work as defined in mechanics, has nothing to do directly with the opposing force, although the work done by the two forces is related by the principle of conservation of energy. The two quantities, however, are not always equal. Even when they are equal, defining the work of the system *via* the work of the surroundings, implicitly assumes the validity of the first law, leading to the above-mentioned circularity.

Whenever a force, F (or pressure), is being applied to a moving boundary, work is said to be done because of this applied force. This work equals $F dx$ where dx is the distance the boundary moves in the direction of the force. Any opposing force is doing its own work. The other important concept from mechanics is that the agent applying the force (and hence doing the work) undergoes a change in its energy equal to the work.

Work of opposing forces: To make the above point clear, let us consider the setup in the diagram, where two opposite but unequal forces are acting on a body in opposite directions (Fig. 1). The forces are assumed to be constant for the duration being considered. The body is assumed to have a mass, but is in frictionless contact with the ground.

Suppose the force acting in the $+x$ direction was 4 N, and the opposing force, the one in the $-x$ direction, was 3 N. Suppose the distance that the body moved in the $+x$

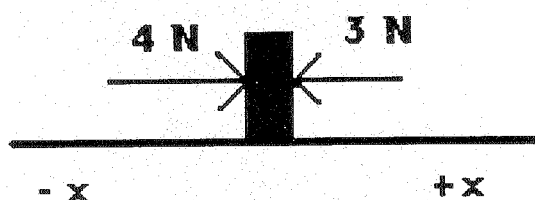


Fig. 1. Two forces acting on a body in opposite directions. Each force does its own work independently of the other.

direction under the resultant force was 2 m. Then the work done by the 4 N force would be 4 N times 2 m, or 8 J. The work done by the other force would be 3 N times $(-2x)$, or -6 J. The minus sign arises because the displacement is in a direction opposite to the force. Whatever agent was exerting the 4 N force would have lost 8 J of energy, and whatever agent was exerting the 3 N force would lose -6 J, or in other words gain $+6$ J of energy. From this example, it is clear that each force has its own work associated with it, independent of the opposing force. Overall, the resultant work done by both the forces in the setup will equal the resultant force in the x -direction $(4 - 3)$ N multiplied by the displacement of the body in that direction (2 m), which is 2 J. This work of 2 J will appear as kinetic energy of the body. However, if our interest were limited to the agent applying the 4 N force (in other words, if that agent were our *system*), we would state that the system has lost 8 J of energy.

System: In order to apply this argument to the expansion of a gas, we first define a system. We consider a gas in a cylinder fitted with a frictionless vertical piston, capable of supporting weights (Fig. 2). The gas forms the system. The cylinder and piston are placed in a vacuum so that the movement of the piston does not encounter any air resistance. The weights supported by the piston are not part of the system. The cylinder is assumed to be sufficiently tall so that the piston is not pushed out of the cylinder during an expansion process before equilibrium is reached. The system is in thermal contact with a calorimeter, which is itself thermally isolated from the rest of the surroundings. The temperature of the calorimeter at the beginning of the process can be chosen to suit the process. Thus for an isothermal expansion, the calorimeter will need to be at a higher temperature than the system, whereas it will be at a lower temperature for an isothermal compression. The thermal contact between the calorimeter and the system can be broken when desired, *e.g.*, for an isothermal process, the contact is maintained for as long as is necessary to maintain the temperature of the system at the desired value.

Heat: The energy that is transferred by means other than by movement of the walls separating the system from the surroundings is called heat. Thus heat, q , is defined as the thermal energy that flows into the system across the boundary from the calorimeter and is determined from the change in the temperature of the calorimeter during the process.

Isothermal compression: Let us consider an isothermal process. Initially the system is at equilibrium; the pressure of the gas is balanced by the weights supported by the piston. If the weights on the piston are increased, the piston starts moving down and the gas starts getting compressed. When the pressure of the gas again becomes equal to the outside pressure, the process ends and the system attains

equilibrium again. The question concerning us is: "What was the work of the *system* in this process?" We answer this by invoking the definition of work and apply that definition to this process. Since it is the system that is of concern to us, we need to consider the force on the system side of the moving boundary.

$dw = (\text{force exerted on the boundary by the system}) \times (\text{differential displacement of the boundary in the direction of the force}) = P_g \times \text{area of the moving boundary} \times dl = P_g dV.$

Here dl , the differential displacement of the boundary, is positive for expansion (being in the same direction as the force), and negative for compression. The infinitesimal quantity of work is denoted by the symbol dw to emphasize that w is not a property of the system and dw is not an exact differential⁶. The lower case w is

used to denote work resulting from the force exerted by the system, while W denotes work due to the forces external to the system. Thus the two symbols distinguish the present treatment (in terms of P_g) from the treatment using P_{ex} . The above expression for work is a specific case of the general definition, according to which work is the product of a generalized force and a generalized coordinate. The coordinate in this case is the variable length of the cylinder containing the gas, and the force is a function of this length. The classic article by Redlich¹³ deals with the concept of generalized force and coordinates and describes how the system is influenced by the surroundings only through the coordinate.

Since the pressure of the gas is always outwards, $P_g dV$ is a positive quantity for expansion, and negative for compression. As outlined earlier, if the motion of the boundary is in the direction of the force, the energy of the system applying the force decreases and vice versa.

Just as $P_g dV$ is the work done by the system and affects its energy, $P_{ex} dV$ is the work done by the external forces (in this case weights on the piston), and affects the energy of the surroundings. An analysis of the process of compression outlined above is instructive. Since during the compression, there is a net downward force on the piston, the piston acquires acceleration, in accordance with Newton's Second Law. The piston acquires kinetic energy, which, following our example of the mass being acted on by two opposite forces in Fig. 1, equals $\int (P_g - P_{ex}) dV$. This is a positive quantity for this process, since $P_g < P_{ex}$ and $dV < 0$. This kinetic energy, KE, is dissipated within the gas. The piston eventually stops moving as a result of P_g becoming equal to P_{ex} . We can write

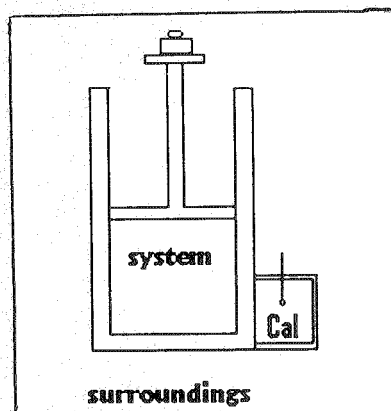


Fig. 2. The system comprising the gas contained in a cylinder. The cylinder is in thermal contact with a calorimeter (labelled Cal in the diagram), which is a part of the surroundings, but is thermally insulated from the rest of the surroundings.

$$\int (P_g - P_{ex})dV = KE$$

whence,

$$\int P_g dV - \int P_{ex} dV = KE \quad (1)$$

Isothermal expansion: The dissipation of the kinetic energy of the piston as heat is visualized easily in the case of compression treated above, but the same argument applies to the case where the gas expands and the piston moves outwards in the vacuum. The system is assumed to be initially at equilibrium, with the pressure of the gas being equal to the external pressure at the outset. Some weights are then removed from the piston and the gas starts expanding, progressively decreasing the pressure of the gas. Eventually, the pressure of the gas becomes equal to the external pressure. Since the piston is frictionless and the expansion is in vacuum, the piston continues to move outwards in accordance with Newton's First Law. Any further expansion, however, also results in the outward force (due to the pressure of the gas) becoming smaller than the opposing force (due to gravity), so that a net downward force results, causing a reversal in the direction of the motion. The result is oscillatory movement causing a damping of the motion, eventually bringing the piston to a halt. The kinetic energy is again dissipated within the gas as thermal energy, since outside the system a vacuum exists, and the gas presents the only medium with friction. The situation is analogous to a stone being thrown vertically up (assuming no friction with air), and eventually returning to earth, with its kinetic energy dissipated as heat on contact with the ground. Eq. 1 is thus valid for both compression and expansion. For this case, too,

$$\int (P_g - P_{ex}) dV > 0,$$

since now

$$P_g > P_{ex} \quad \text{and} \quad dV > 0.$$

Adiabatic volume change: The treatment above also applies to adiabatic processes, where there is no heat transfer between the system and surroundings; the only heat is that generated by the damping of the motion. As long as the only possible medium for the dissipation of the kinetic energy is the gas, the only heat generated is within the gas. Eq. (1) is valid in this case too.

First Law: The statement of the first law, applied to the case of a gas undergoing a change in volume and exchanging heat with the surroundings, is:

$$dU = \text{Heat supplied to the system} - \text{work done by the system} = q - w,$$

or for an infinitesimal change

$$dU = dq - dw \quad (2)$$

The internal energy, U , is a property of the system, which implies that dU is an exact differential. For the corresponding incremental quantity of heat the symbols dq is used, since heat (like work) is not an exact differential.

The negative sign before w is in recognition of the fact that the signs of energy change and work (as defined in mechanics) are opposite to each other, since if forces within a system produce (positive) work, then the energy of the system

decreases by an amount equal to the work done. In view of this treatment of work, the negative sign before w is more logical than the convention usually adopted at present, whereby a positive sign is used. The statement of the Law, moreover, asserts that internal energy also changes as a result of loss or gain of thermal energy by the system. For the processes discussed above, the kinetic energy always ends up in the system, and contributes positively to U .

The statement can be expressed in the integral form as:

$$U = q + KE - \int P_g dV \quad (3)$$

In view of our definition of heat (thermal energy transferred by means other than through the movement of the walls), the kinetic energy does not qualify as heat, so it must be considered part of work. Then,

$$\Delta U = q - w, \quad \text{where } w = -KE + \int P_g dV \quad (4)$$

Piston encountering external frictional resistance in an adiabatic process: What happens when the set up is modified and the system is placed not in a vacuum, but in air where the moving piston encounters air resistance during expansion? The system is also assumed to be enclosed within adiabatic walls; the only exchanged between the system and the surroundings (which include the calorimeter) is through the movement of the piston. The process, in other words, is adiabatic. Suppose the weights on the piston are decreased and $P_{ex} < P_g$ and the gas starts expanding. When the two pressures become equal, the expansion stops after oscillating. The kinetic energy is dissipated in the surroundings and the system because of this oscillation and the resulting friction. For simplicity, let us consider the limiting case where all of the kinetic energy ends up in the surroundings. The other extreme where all the kinetic energy ends up in the system has already been treated above. Clearly the magnitude of the work done, and the energy lost by the gas equals $\int P_g dV$. In other words,

$$\Delta U = -\int P_g dV \quad (5)$$

Correspondence between the two definitions of work: To see how Eq. (3) relates to the statement of the first law that uses P_{ex} , we combine Eq. (1) and Eq. (3) and introduce a quantity $Q = q + k.e.$, to get:

$$\Delta U = Q - \int P_{ex} dV = Q + W \quad (6)$$

This suggests that the two treatments give the same result (apart from the convention of sign of work), provided heat is defined differently from how it was defined for the purpose of Eq. (3). The use of different symbols, q and Q , is in recognition of this fact. Q is the total heat (comprising the thermal energy transferred between the system and the calorimeter plus the kinetic energy, which eventually gets dissipated as heat). Unlike q , this heat, Q , has a component that is transferred through the movement of the walls.

Let us examine the case when the system encounters external resistance (the treatment leading to Eq. (5)). Combining Eq. (5) with Eq. (3), we get

$$\Delta U = - \int P_{ex} dV - KE = W + Q$$

Here W is the work defined in terms of the external pressure and the kinetic energy is identified as heat, since it ends up increasing the temperature of some part of the surroundings, even though it would not be identified as heat if the definition above (for q) is used. This process is not "adiabatic" in the usual sense of the term, even though the system is enclosed in insulated walls.

Reversible and irreversible processes: It becomes simple to explain the concept of reversibility in the context of the treatment above. The processes where kinetic energy appears are irreversible, since the kinetic energy ends up as thermal energy and is dissipated. When no kinetic energy appears, the process is said to be reversible. This would be the case when the difference between P_{ex} and P_g is infinitesimally small and there is no net force to impart acceleration to the piston. This is a simpler and a far clearer way to introduce the otherwise difficult concept of reversible work during the expansion of a gas. A more comprehensive treatment of reversibility, which deals not only with isothermal, adiabatic expansion and compression, but also with temperature change at constant volume and constant pressure, is given by Battino *et al.*¹⁴.

Conclusion

It makes a difference whether work is defined in terms of the pressure of the gas or the external pressure in an irreversible expansion. The two treatments can be reconciled by appropriately defining heat and by taking into account the kinetic energy changes in irreversible expansion.

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