Elementary remarks on the ambiguous explanation of pressure in chemical thermodynamics

Yukio Kobayashi

Department of Information Systems Science
Faculty of Engineering
Soka University
Tokyo 192-8577, Japan.
koba@t.soka.ac.jp

(Submitted 28-08-2014)

Abstract

At the collegiate level of chemical thermodynamics, action-reaction pairs are not explicitly described, which results in an ambiguous explanation of the procedures to vary the volume of a system. Pedagogically, it is essential to specify not only the magnitude of forces, but also the object that applies the force and the object that experiences the force. The physical meanings of some of the equations in thermodynamics should be explained in terms of elementary mechanics. From these viewpoints, it is indispensable to combine physics education and chemical education at an elementary level of science teaching.

---

1 Introduction

In standard physical chemistry textbooks for undergraduate students [1, 2, 3], some papers on physics education [4], and some papers on chemical education [5], the work performed in varying the volume of a system is explained at an elementary stage, but the descriptions are unexpectedly ambiguous. From a pedagogical standpoint, the physical meanings of some quantities in chemical thermodynamics should be explained on the basis of elementary mechanics. Many textbooks, however, give confusing descriptions of the work done on the system, because the action-reaction pairs are not explicitly described, as seen from Figure 1.

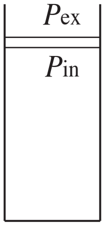

Figure 1: The pressure of a gas inside the cylinder is P_{in} and the external pressure is P_{ex}.

To examine this circumstance, the following elementary problem is given from the standpoint of mechanics.

> Consider the gas inside of a cylinder with a piston area S (Figure 2). The internal pressure exerted on the piston by the gas is P and the external pressure exerted on the piston by the surroundings (e.g., the atmosphere and/or an external agent such as the hands of a person) is P_{ex}. The volume swept during an infinitesimal expansion is denoted as dV, where $dV = Sdx$ and dx is the displacement of the piston. Does PdV, $-PdV$, or $-P_{\text{ex}}dV$ represent the work done on the system (i.e., the gas in the cylinder)?

This problem is difficult to solve for some students, because PdV, $-PdV$, and $-P_{\text{ex}}dV$ are frequently confused with one another due to the ambiguous descriptions in the above-cited physical chemistry textbooks and papers. These quantities should be distinguished according to elementary mechanics. The system does not experience pressure directly from the surroundings, but rather via the piston [6]. If we consider the work done on the system to be $-P_{\text{ex}}dV$ following the above textbooks, the equation for the equilibrium of the piston, $PS + (-P_{\text{ex}}S) = 0$, is essentially meaningless, as shown in the Section 4.

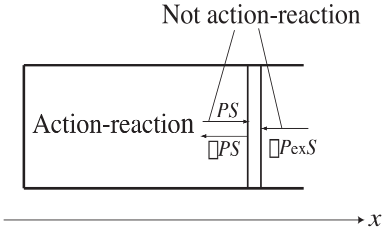

Figure 2: Internal pressure and external pressure. PS is the force exerted on the piston by the gas. $-PS$ is the force exerted on the gas by the piston. $-P_{\text{ex}}S$ is the force exerted on the piston by the surroundings. PS and $-PS$ constitute an action-reaction pair. PS and $-P_{\text{ex}}S$ act on the piston in a state of equilibrium.

2 Representation of the Work Done on the System

The object that performs the work should be described to avoid confusion with the three quantities PdV, $-PdV$, and $-P_{\text{ex}}dV$. It is important to distinguish the following quantities: the work done on the system by the piston ($-PdV$), the work done on the piston by the system (PdV), and the work done on the piston (not on the system) by the surroundings ($-P_{\text{ex}}dV$) as shown in Figure 2. During a quasistatic process, these quantities are equal in magnitude. For this reason, some textbooks state that the work done on a system is $-P_{\text{ex}}dV$ [1], but according to elementary mechanics [7, 8], this description is not necessarily accurate. Irrespective of whether the piston is in equilibrium or not, $-P_{\text{ex}}dV$ and $-PdV$ are conceptually different quantities.

The following description is ambiguous from the standpoint of elementary mechanics.

> The force exerted on the piston by the surroundings is $-P_{\text{ex}}S$. When the system expands through a distance dx, the system moves the piston against the force $-P_{\text{ex}}S$. The work done on the surroundings by the system is $P_{\text{ex}}dV$.

The phrase 'on the surroundings by the system' seems to indicate that the system exerts the force directly on the surroundings. From a pedagogical standpoint, this explanation contains a jump in logic, which can be described as follows. Although the forces PS and $-P_{\text{ex}}S$ act in opposite directions and have the same line of action, they do not constitute an action-reaction pair. Both forces act on the same body (the piston), whereas an action and its reaction act on separate bodies according to Newton's third law of motion. When a piston is in equilibrium, the forces PS and $-P_{\text{ex}}S$ are equal in magnitude. Even when a piston is not in equilibrium, the force exerted on the system by the piston and the force exerted on the piston by the system are equal in magnitude. The system exerts a force PS on the piston and the piston exerts a force $P_{\text{ex}}S$ on the surroundings. The forces $P_{\text{ex}}S$ and $-P_{\text{ex}}S$ constitute an action-reaction pair, because $P_{\text{ex}}S$ is the force exerted on the surroundings by the piston and $-P_{\text{ex}}S$ is the force exerted on the piston by the surroundings. It is important to distinguish the forces shown in Figure 2, although $-PdV$ and $-P_{\text{ex}}dV$ are equal in magnitude.

Table 1 Forces on what by what

Force	On	By
PS	piston	system
$-P_{\text{ex}}S$	piston	surroundings
$P_{\text{ex}}S$	surroundings	piston

The following is another example from physics education. A weigh scale indicates not the gravitational force exerted on a body, but the force exerted on the weigh scale by the body, although these two forces are in equilibrium (they have equal magnitudes). If these two forces are not separately identified, it will be impossible to understand the meaning of the value from the weigh scale during accelerated motion. This value is different from that of a weigh scale at rest. The value is determined by the force exerted on the weigh scale by the body. This force is not equal in magnitude to the gravitational force during accelerated motion. Physics educationists should specify not only the magnitude of a force, but also the object that applies the force and the object that experiences the force.

3 Remarks on the First Law of Thermodynamics

The interpretation of the physical or chemical significance of an equation depends on the form that is used to express it. For example, the equation for the equilibrium of a body in statics, $m\boldsymbol{a} - \boldsymbol{F} = \boldsymbol{0}$, has a different physical significance from the equation of motion based on Newton's second law of motion in dynamics, $m\boldsymbol{a} = \boldsymbol{F}$, despite these equations being algebraically equivalent [9, 10]. The term $m\boldsymbol{a}$ in the equation of equilibrium is recognized as an inertial force, whereas the equation of motion indicates that the acceleration determined by the mass of the body results from the sum of the exerted forces, $\boldsymbol{F}$. Unfortunately, some educationists are not necessarily convinced that $m\boldsymbol{a} - \boldsymbol{F} = \boldsymbol{0}$ has a physical significance that is different from that of $m\boldsymbol{a} = \boldsymbol{F}$.

Analogously, the meaning of the first law of thermodynamics depends on how it is expressed algebraically. The change in the total energy of a system du is equal to the sum of the energy added to the system in the form of absorbed heat $d'q$ and the work done on the system $d'w$:

$$du = d'q + d'w. \tag{1}$$

In Eq. (1), $d'w = -PdV$ (see the previous section), although some textbooks give $d'w = -P_{\mathrm{ex}}dV$ [1, 2]. In contrast, the heat absorbed by a system $d'q$ yields the energy change of the system du and the work done on the piston by the system $-d'w$:

$$d'q = du + (-d'w), \tag{2}$$

in which $-d'w = PdV$.

As $-d'w$ in Eq. (2) is represented by a force exerted on the piston by the system PS, $d'w$ in Eq. (1) transformed by Eq. (2) can be determined by the force exerted on the system by the piston $-PS$. However, some textbooks describe $d'w$ in Eq. (1) as the force exerted on the piston by the surroundings $-P_{\mathrm{ex}}S$, because P and P_{ex} are equal in magnitude. Consequently, students will be confused if they fail to understand that PS and $-P_{\mathrm{ex}}S$ constitute an action-reaction pair of forces, if the piston is ignored, during a quasistatic process (see the end of the next section).

4 Physical Meaning of the Internal Pressure

The equation of state for an ideal gas is taught in the form $PV = nRT$, where n is the amount of gas at temperature T, P is the internal pressure exerted on a piston by the system with a volume V, and R is the gas constant. The meaning of the internal pressure becomes clear when the equation is transformed from $PV = nRT$ to $P = (n/V)RT$. The internal pressure depends on the number density and the temperature of the system. The internal pressure does not need to be generated by a piston in the following, but it is easier to consider that the pressure is generated via a piston. The internal pressure is largely determined by the average number of strokes performed by the piston. The number density and the temperature of the system can be adjusted to maintain a constant internal pressure, as expressed by $dP = d(n/V)RT + (n/V)RdT$.

The external pressure is the sum of the pressure exerted on the piston by the atmosphere and the pressure due to an external agent, such as the hands of a person. The external pressure is independent of the number density and the temperature of the system, although the external pressure has the same magnitude as the internal pressure when a piston is in equilibrium. Measuring $-P_{\mathrm{ex}}$ is the only way to determine the magnitude of P (or $-P$). We can obtain the work done on the system as $d'w = -PdV$ by using Newton's third law of motion; this expression is independent of $P_{\mathrm{ex}}S$. This equation can be applied to a piston in equilibrium, $PS + (-P_{\mathrm{ex}}S) = 0$, to determine P in $d'w = -PdV$. If P and P_{ex} are not distinguished, the equation for the equilibrium of the piston cannot be written. During a quasistatic process, the piston enables us to measure P through P_{ex} and to calculate the work done on the piston by the surroundings from the displacement of the piston by expressing $d'w$ as $-P_{\mathrm{ex}}dV$.

There is another view in standard textbooks on chemical thermodynamics as follows. When a piston is in equilibrium, we can also consider that the piston transmits a force from the surroundings to the system and vice versa. The role of the piston is frequently interpreted as follows: PS exerted on the piston by the system (the gas) equals $-P_{\mathrm{ex}}S$ exerted on the piston by the surroundings in magnitude, because the piston is in equilibrium. As $-PS$ exerted on the system (the gas) by the piston is always equal in magnitude to PS according to Newton's third law of motion, in this special case of equilibrium, $-PS$ also equals $-P_{\mathrm{ex}}S$; that is, the force exerted on the system by the piston is equal to the force exerted on the piston by the surroundings. The piston is thus considered to transmit the total force exerted on the piston by the surroundings to the system. If we adopt this point of view, it is not necessary to consider the piston itself; thus, we can also consider that the surroundings exert a force $-P_{\mathrm{ex}}S$ directly on the system. The reaction to this force is the force exerted by the system on the surroundings when the piston is not taken into consideration. We can also write $-P_{\mathrm{ex}}S$ for the inner surface of the system (the gas) while not taking the piston into consideration. However, it is inconsistent to refer to the piston only for the measurement of the internal pressure exerted on the piston by the gas, P, to calculate $-PdV$, when only the gas and the surroundings are taken into consideration instead of the system (the gas), the piston, and the surroundings.

The same approach is also applied to the following mechanics problem in some textbooks on elementary physics [7, 8]. Two blocks are connected by a light inextensible string and are placed on a smooth horizontal table. The force exerted on the first block due to the string running to the second block constitutes an action-reaction pair with the force exerted on the second block due to the string running to the first block. This interpretation is false. If the mass of the string is not negligible compared to the mass of the blocks, these two forces will not be equal in magnitude and thus they do not constitute an action-reaction pair. Newton's third law of motion is independent of the mass of the string [11]. Even if the string is light, the former force is applied to the first block by the string, whereas the latter force is applied to the second block by the string.

Pedagogically, it is essential to always interpret the physical meaning of the internal pressure by following elementary mechanics. A comparison between the dynamical system of a massless spring connected to a particle and the thermodynamic system helps students understand the internal energy of the system, as well as the action-reaction pair of forces. A particle and the spring correspond to the piston and the gas, respectively.

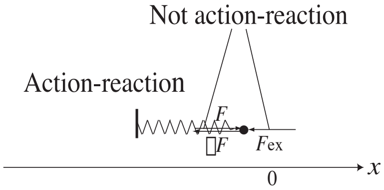

Figure 3: A massless spring connected to a particle. In this figure, the spring is compressed. Compare this figure to Figure 2.

It is important to distinguish the following three forces: F, the force exerted on the particle by the spring; $-F$, the force exerted on the spring by the particle; and F_{ex}, the force exerted on the particle by an external agent such as the hands of a person. The internal energy of the gas is comparable to the energy stored in the spring. During a quasistatic process to compress the spring, the work done on the particle by the agent is cancelled exactly by the work on the particle by the spring, and thus the energy is not stored in the particle. The spring, however, stores the energy by the work on the spring by the particle. Similarly, the piston transmits the energy from the surroundings to the gas and thus the same amount of energy is stored in the gas.

5 Concluding Remarks

According to some textbooks on elementary chemical thermodynamics, the forces PS and $-P_{\mathrm{ex}}S$ constitute an action-reaction pair by regarding the piston, the atmosphere, and the hands of a person as the surroundings. In this approach, $-P_{\mathrm{ex}}S$ is exerted on the system by the surroundings. However, it is difficult to consider that the magnitude of $P_{\mathrm{ex}}S$ is equal to the magnitude of the force exerted on a piston by the atmosphere and the hands of a person. The work done on the piston by its surroundings differs physically from the work done on the system by the piston. These textbooks employ ambiguous reasoning to derive the work done on a system, because they do not explicitly introduce the concept of an action-reaction pair. Following the standard textbook [12], we must specify the *force on what by what* and the *work on what by what* when the force and work are discussed.

Through the problem discussed in this article, it is pedagogically essential to combine physics education and chemical education at an elementary level when teaching science. The basic notion of an action-reaction in elementary mechanics at the high school level is not fully reflected in chemical education. Reconsidering the chemical thermodynamics from a physics standpoint helps educationists and students understand the basic mechanism of the dynamical process.

References

[1] P. W. Atkins. Physical Chemistry (Freeman, 1994)

[2] D. Eisenberg and D. Crothers. Physical Chemistry with Application to Life Science (Benjamin, 1979)

[3] E. B. Smith. Basic Chemical Thermodynamics (Oxford Science Publications, 1990)

[4] A. Kinoshita (2007). J. J. Appl. Phys. Educ. 31, 25-29

[5] G. L. Bertand (2005). J. Chem. Educ. 82, 874-877

[6] I. Sakama, T. Tani, and Y. Yamamoto. Daigaku Nyushi Hissyu Butsuri (Sundaibunko, 1980) [in Japanese]

[7] J. A. Richards, F. W. Sears, M. R. Wehr, and M. W Zemansky. Modern University Physics (Addison-Wesley, 1960)

[8] F. W. Constant. Fundamental Laws of Physics (Addison-Wesley, 1963)

[9] Y. Kobayashi (2008). Eur. J. Phys. 29, 599-606

[10] Y. Kobayashi (2012). Phys. Educ. 28, 6

[11] K. Tomiyama. Butsurigaku heno Michi (Iwanami, 1974) [in Japanese]

[12] C. Kittel, W. D. Knight, and M. A. Ruderman. Berkeley Physics Course Vol. 1, Mechanics (McGraw-Hill, 1973)