



An Ideal Gas Indeed Does Work in Expansion into Vacuum

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Author's contribution

The sole author designed, analysed, interpreted and prepared the manuscript.

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ABSTRACT

Basic thermodynamics is able to treat an actual (non-equilibrium) process as well as the corresponding equilibrium process. An example of such a pair of processes is familiar to every chemical engineer; namely, (Joule) free expansion of a gas and the corresponding equilibrium expansion [1]. Formerly, we thought that an ideal gas does no work in expansion into vacuum. It is shown that such a gas does work. This result is confirmed by experiments.

Keywords: Ideal gas; real gas; Clément Desormes method; adiabatic expansion.

1. INTRODUCTION

Formerly, it was supposed that an ideal gas does no work in expansion into vacuum [2]. Almost all authors, assumed that an expanding gas does the following work:

$$\Delta A = \int P_{\text{ext}} dV, \quad (1)$$

where P_{ext} is the external pressure opposing the expansion. If the gas expands into vacuum, then $P_{\text{ext}} = 0$ and the work of expansion is zero. Some authors assumed that the work of expansion is the following:

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$$\Delta A = \int P_{\text{gas}} dV \quad (2)$$

where P_{gas} is the pressure of the gas in the vessel [3,4], and $P_{\text{gas}} > P_{\text{ext}}$. In [4], it was shown using experimental data that Eq. (2) is correct and Eq. (1) is incorrect. Equation (2) is valid only when a gas expands in a quasistatic process. But Clement-Desormes experiment allows to model such quasistatic expansion,

In the theory of an ideal gas there is a paradox [1]: an ideal gas that expands into vacuum should produce no work, and therefore, it must exhibit no temperature change. However, experiments show that an ideal gas cools or warms in expansion [3,6]. The experiments were performed with real gases, but real gases behave with high accuracy like an ideal gas [4,7].

2. THEORY

There is a modified Clément-Desormes method for determining the heat capacities of gases [4]:

“A gas is maintained in a closed bottle, fitted with a stopcock and a manometer, at room temperature T_1 and at a pressure P_2 above atmospheric pressure P_1 . When the stopcock is opened, the gas expands almost adiabatically to atmospheric pressure. During this expansion the gas cools from T_1 to T_2 . Then the stopcock is closed again and the gas is allowed to return to thermal equilibrium with surroundings. To determine the heat capacity one can measure P_1 , P_2 , and T_1 , and T_2 .”

In adiabatic expansion the gas does the following work:

$$P_1(V_2 - V_1) = -C_A(T_2 - T_1) \quad (3)$$

(where C_A is the heat capacity in the adiabatic process). Or the following one:

$$P_2(V_2 - V_1) = -C_A(T_2 - T_1). \quad (4)$$

Equations (3) and (4) are very non strict but these equations are the equations of the Clement-Desormes experiment, and all equations which describe Clement-Desormes experiment. are very not strict.

In [8] it was shown that $C_A = C_V$. Introducing the expressions for the volumes of an ideal gas into Eqs(3) and (4), one obtains:

$$P_2(RT_2/P_1 - RT_1/P_2) = -C_A(T_2 - T_1), \quad (5)$$

$$P_1(RT_2/P_1 - RT_1/P_2) = -C_A(T_2 - T_1) \quad (6)$$

There is another paradox in the Joule expansion (TYPICALLY a doubling of volume with no addition of heat OR work [1,5,9,10]: for such an expansion, the change in the internal energy $\Delta U = 0$, and consequently, the change in the entropy $\Delta S = 0$. However, from the fundamental thermodynamic relation:

$$TdS = dU + PdV \quad (7)$$

It follows that:

$$TdS = +PdV, \quad (8)$$

and $\Delta S = R(\ln 2)$.

So, the explanation of the paradox is the following: In the fundamental thermodynamic relation, P in PdV is the pressure in the gas but not the external pressure, which is zero. It was proven in my paper [4].

First of all, it is necessary to note that there is the fourth Maxwell relation, and according to it, the entropy of a substance changes during its deformation, even in an adiabatic process. According to [11], the first law of thermodynamics for gas expansion in the Clément Desormes method can be written as:

$$V\Delta P = -P\Delta V - \Delta U \quad (9)$$

and according to [12]: $-\Delta U = \Delta Q$.

Here, ΔQ is the quantity of heat that appears in the system due to the adiabatic process. In Section 2 (Theory), it was shown, that $P\Delta V$ is not equal to zero. Consequently, in Eq. (9), $V\Delta P = V(P_2 - P_1)$ is not equal to zero, and then ΔU is also not equal to zero even for an ideal gas. Using experimental results given in (Table 4 in [4]) and the references therein, and introducing the adiabatic heat capacity $C_A = V_1(P_2 - P_1) / (T_2 - T_1)$

one can calculate with Eq. (9) that $C_A = 3.6R$, $C_P = -P_2(V_2 - V_1) / (T_2 - T_1) = 2.6R$, and $-\frac{\Delta U}{T_2 - T_1} = R$;

therefore, $\left(\frac{\partial U}{\partial T}\right)_A = R$, where subindex A denotes

adiabatic and subindex P denotes isobaric. This agrees with [8], where it was also found that

$$\left(\frac{\partial U}{\partial T}\right)_A = R.$$

The calculations which produced $C_A=3.6R$ and $C_P=2.6R$ are very approximate and one may not expect that they will produce the results which strictly agree with [8].

3. CONCLUSION

Some paradoxes of Joule expansion are explained. It is shown that in such an expansion, the changes in the internal energy and in the entropy of an ideal gas are not zero, as it was formerly supposed. Some results obtained agree with the previous results of the author. Other authors also obtained that the work of isothermal expansion of an ideal gas is not zero [13].

COMPETING INTERESTS

Author has declared that no competing interests exist.

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