A PROBLEM IN THERMODYNAMICS

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ABSTRACT

A simple problem in thermodynamics is considered with a view to emphasizing that the application of the adiabatic law $pV^\gamma = \text{const.}$ for a gas is permissible only when the process is quasistatic.

The problem. A cylinder is partitioned into two parts by a movable piston, and given quantities of a gas are placed in the two parts of the cylinder with different initial pressures, volumes and temperatures. The cylinder is then left to itself until a final state of equilibrium is reached. What is the final common pressure, and what are the final volumes and temperatures? Discuss the results according to whether the piston is permeable or impermeable to heat. Investigate the effect of an external agency to balance the difference of the pressures in the two volumes so as to make the motion quasistatic during the process of equalization of pressures in the two volumes.

General considerations

Let p_1 , V_1 and p_2 , V_2 be the initial values of the pressure and volume of the two gases, and let N_1 and N_2 be their respective mole numbers. We shall assume the gas to be a perfect gas, so that the temperatures T_1 and T_2 of the two gases are related to the pressures and volumes by

$$p_1 V_1 = N_1 R T_1, \quad p_2 V_2 = N_2 R T_2, \quad (1)$$

where R is the universal gas constant, having the value 8.314 joules per degree or 82.06 cm³ atm/deg.

Let p_1' , V_1' , T_1' and p_2' , V_2' , T_2' be the final values of the pressure, volume and temperature of the two gases. In the final state of equilibrium the pressure must be the same in the two gases, i.e.

$$p_1' = p_2'. \quad (2)$$

Since the total volume of the cylinder is unchanged during the process, we have

$$V_1 + V_2 = V_1' + V_2'. \quad (3)$$

Further, equations (1) are also applicable to the final state:

$$p_1' V_1' = N_1 R T_1', \quad p_2' V_2' = N_2 R T_2'. \quad (4)$$

For the sake of simplicity, we shall assume that the specific heat of the gas is constant. Then if we denote the ratio of c_p to c_v by γ , we obtain from the well-known relation $c_p - c_v = R$

$$c_v = R/(\gamma - 1), \quad c_p = R\gamma/(\gamma - 1).$$

The internal energy of N moles of the gas is

$$U = N c_v T = N R T / (\gamma - 1) = p V / (\gamma - 1), \quad (5)$$

and the entropy is

$$S = N c_p \ln T - N R \ln p + S_0 = \frac{N R}{\gamma - 1} \ln (T^\gamma p^{1-\gamma}) + S_0. \quad (6)$$

As the motion of the gas is adiabatic, one would be tempted to apply the well-known adiabatic law

$$p V^\gamma = \text{const.} \quad (7)$$

to the two parts of the gas, and would thus obtain an erroneous result. Now the law (7) requires

$$T^\gamma p^{1-\gamma} = \text{const.} \quad (8)$$

Then (6) show that the entropy is unchanged during the process, and consequently the process to which (7) is applicable must be reversible (quasistatic). In the case of an irreversible process the entropy is increased and (7) is no more applicable. The process can, however, be made reversible by applying an external agency to balance the difference between the pressures of the gas in the two volumes. Then the law (7) will be applicable to each volume if the piston is impermeable to heat (adiabatic), but will not be applicable when the piston is permeable to heat (diathermanous).

We shall divide the solution of the problem into four different cases.

Case (a). Irreversible process with diathermanous piston.

In the absence of external agency the process is irreversible without net external work. Since the process is also adiabatic, the total internal energy of the gas is unchanged. From (5) we obtain

$$p_1 V_1 + p_2 V_2 = p_1' V_1' + p_2' V_2'. \quad (9)$$

Substituting (2) and (3) into (9), we obtain the value of the final pressure

$$p_1' = p_2' = \frac{p_1 V_1 + p_2 V_2}{V_1 + V_2}. \quad (10)$$

Since the piston is diathermanous, the final temperature must be the same for the two gases. Then substituting (4) into (9), we obtain

$$T_1' = T_2' = \frac{p_1 V_1 + p_2 V_2}{(N_1 + N_2)R}. \quad (11)$$

The final volumes are easily obtained from (4). The result is

$$\frac{RT_1'}{p_1'} = \frac{V_1'}{N_1} = \frac{V_2'}{N_2} = \frac{V_1 + V_2}{N_1 + N_2}. \quad (12)$$

In this case the increase of the total entropy of the gas can be calculated from (6) with the result

$$\begin{aligned} \Delta S &= \frac{(N_1 + N_2)R}{\gamma - 1} \ln (T_1'^\gamma p_1'^{1-\gamma}) - \frac{N_1 R}{\gamma - 1} \ln (T_1^\gamma p_1^{1-\gamma}) - \frac{N_2 R}{\gamma - 1} \ln (T_2^\gamma p_2^{1-\gamma}) \\ &= \frac{(N_1 + N_2)R}{\gamma - 1} \ln \left[p_1' \left(\frac{V_1 + V_2}{N_1 + N_2} \right)^\gamma \right] - \frac{N_1 R}{\gamma - 1} \ln \left[p_1 \left(\frac{V_1}{N_1} \right)^\gamma \right] - \frac{N_2 R}{\gamma - 1} \ln \left[p_2 \left(\frac{V_2}{N_2} \right)^\gamma \right]. \end{aligned} \quad (13)$$

That $\Delta S > 0$ can be proved by using the inequality

$$a^\alpha b^\beta < \left(\frac{\alpha a + \beta b}{\alpha + \beta} \right)^{\alpha + \beta}$$

First, putting $a = V_1/N_1$, $b = V_2/N_2$, $\alpha = N_1$, $\beta = N_2$, we obtain

$$\left(\frac{V_1}{N_1}\right)^{N_1} \left(\frac{V_2}{N_2}\right)^{N_2} < \left(\frac{V_1+V_2}{N_1+N_2}\right)^{N_1+N_2}.$$

Next putting $a = p_1 V_1 / N_1$, $b = p_2 V_2 / N_2$, $\alpha = N_1$, $\beta = N_2$, we obtain

$$\left(\frac{p_1 V_1}{N_1}\right)^{N_1} \left(\frac{p_2 V_2}{N_2}\right)^{N_2} < \left(\frac{p_1 V_1 + p_2 V_2}{N_1 + N_2}\right)^{N_1 + N_2} = \left(\frac{p_1 (V_1 + V_2)}{N_1 + N_2}\right)^{N_1 + N_2}.$$

Multiplying this by the $(\gamma - 1)$ -th power of the first, we obtain

$$\left[p_1 \left(\frac{V_1}{N_1}\right)^\gamma\right]^{N_1} \left[p_2 \left(\frac{V_2}{N_2}\right)^\gamma\right]^{N_2} < \left[p_1 \left(\frac{V_1 + V_2}{N_1 + N_2}\right)^\gamma\right]^{N_1 + N_2}.$$

Taking logarithm of both sides and multiplying by $R/(\gamma - 1)$, we find $\Delta S > 0$.

Case (b). Irreversible process with adiabatic piston.

In this case equations (9) and (10) are still true, but (11) and (12) no more hold. Since the piston is impermeable to heat, each gas has undergone an adiabatic process with an increase of entropy. The increase of the entropy of the first gas is

$$\Delta S_1 = \frac{N_1 R}{\gamma - 1} \ln \frac{T_1'^\gamma p_1^{1-\gamma}}{T_1^\gamma p_1^{1-\gamma}}. \quad (14)$$

The condition $\Delta S_1 > 0$ gives a lower limit T_{1e}' for T_1' :

$$T_{1e}' = T_1 (p_1' / p_1)^{1-\frac{1}{\gamma}}. \quad (15)$$

Similarly for the second gas we have

$$\Delta S_2 = \frac{N_2 R}{\gamma - 1} \ln \frac{T_2'^\gamma p_2^{1-\gamma}}{T_2^\gamma p_2^{1-\gamma}} \quad (16)$$

and

$$T_{2e}' = T_2 (p_2' / p_2)^{1-\frac{1}{\gamma}}. \quad (17)$$

We can obtain an upper limit T_{1u}' for T_1' and an upper limit T_{2u}' for T_2' from (9). We have

$$p_1 V_1 + p_2 V_2 = N_1 R T_1' + N_2 R T_2' > N_1 R T_{1u}' + N_2 R T_{2e}',$$

whence

$$T_1' < (p_1 V_1 + p_2 V_2 - N_2 R T_{2e}') / N_1 R = T_{1u}'. \quad (18)$$

Similarly we have

$$T_2' < (p_1 V_1 + p_2 V_2 - N_1 R T_{1e}') / N_2 R = T_{2u}'. \quad (19)$$

The final volumes also lie within limits V_{1e}' , V_{1u}' and V_{2e}' , V_{2u}' , given by

$$V_{1e}' = N_1 R T_{1e}' / p_1', \quad V_{1u}' = N_1 R T_{1u}' / p_1', \quad \text{etc.} \quad (20)$$

Since

$$N_1 R T_{1e}' + N_2 R T_{2u}' = N_1 R T_{1u}' + N_2 R T_{2e}' = p_1 V_1 + p_2 V_2,$$

it follows that

$$V_{1e}' + V_{2u}' = V_{1u}' + V_{2e}' = V_1 + V_2. \quad (21)$$

It should be verified that

$$N_1 R T_{1e}' + N_2 R T_{2e}' < p_1 V_1 + p_2 V_2$$

in order that $V_{1e}' < V_{1u}'$ and $V_{2e}' < V_{2u}'$. By (15) and (17) this inequality can be written in the form

$$p_1 V_1 (p_1' / p_1)^{1-\frac{1}{\gamma}} + p_2 V_2 (p_2' / p_2)^{1-\frac{1}{\gamma}} < p_1 V_1 + p_2 V_2.$$

This is a consequence of Hölder's inequality

$$a_1^\alpha b_1^{1-\alpha} + a_2^\alpha b_2^{1-\alpha} < (a_1 + a_2)^\alpha (b_1 + b_2)^{1-\alpha},$$

if we put $a_1 = p_1 V_1$, $a_2 = p_2 V_2$, $b_1 = p_1' V_1$, $b_2 = p_2' V_2$, $\alpha = 1/\gamma$.

Case (c). Reversible process with diathermanous piston.

In the presence of an external agency the motion of the piston can be made quasistatic by adjusting the external force to balance the difference of pressures in the two gases. The internal energy of the gas will be decreased by doing work against the external agency. On the other hand, the process is reversible and the total entropy of the gases remains constant. Since the piston is permeable to heat, eqs. (12) are still true, and the final volumes of the gas are the same as in the case (a).

The condition for the constancy of the total entropy is, by (13),

$$p_1' = \left(\frac{N_1 + N_2}{V_1 + V_2} \right)^\gamma \left[p_1 \left(\frac{V_1}{N_1} \right)^\gamma \right]^{\frac{N_1}{N_1 + N_2}} \left[p_2 \left(\frac{V_2}{N_2} \right)^\gamma \right]^{\frac{N_2}{N_1 + N_2}} \quad (22)$$

Substituting into (12), we obtain the final temperature

$$T_1' = \frac{p_1' (V_1 + V_2)}{(N_1 + N_2)R}$$

The decrease of the total internal energy by doing work against the external agency is, by (5),

$$\Delta U = -(p_1 V_1 + p_2 V_2 - p_1' V_1' - p_2' V_2')/(\gamma - 1). \quad (23)$$

That $\Delta U < 0$ can be proved in the same way as for $\Delta S > 0$ in the case (a).

Case (d). Reversible process with adiabatic piston.

If the piston is adiabatic, then each gas undergoes a reversible adiabatic process without change of entropy. Hence $\Delta S_1 = 0$ and $\Delta S_2 = 0$. we have, from (14) and (16),

$$T_1' = T_1 (p_1' / p_1)^{1-\frac{1}{\gamma}}, \quad T_2' = T_2 (p_2' / p_2)^{1-\frac{1}{\gamma}} \quad (24)$$

The final pressures being equal, we have

$$p_1' = \frac{N_1 R T_1'}{V_1} = \frac{N_2 R T_2'}{V_2} = \frac{N_1 R T_1' + N_2 R T_2'}{V_1 + V_2} \quad (25)$$

Eliminating T_1' and T_2' from (24) and (25), we obtain

$$p_1' = \left(\frac{p_1^{\frac{1}{\gamma}} V_1 + p_2^{\frac{1}{\gamma}} V_2}{V_1 + V_2} \right)^{\gamma} \quad (26)$$

This result can be more easily obtained from (7) as follows:

$$(p_1')^{\frac{1}{\gamma}} V_1' + (p_2')^{\frac{1}{\gamma}} V_2' = p_1^{\frac{1}{\gamma}} V_1 + p_2^{\frac{1}{\gamma}} V_2.$$

Substituting the value of p_1' obtained from (26) into (24), we obtain the final temperatures. The final volumes are then determined by (25). They can also be calculated from (7), thus

$$V_1' = V_1 (p_1/p_1')^{\frac{1}{\gamma}}, \quad V_2' = V_2 (p_2/p_2')^{\frac{1}{\gamma}}. \quad (27)$$

The decrease of the total internal energy is again given by (23). That $\Delta U < 0$ can be proved by using Hölder's inequality with $a_1 = p_1 V_1$, $a_2 = p_2 V_2$, $b_1 = V_1$, $b_2 = V_2$, $\alpha = 1/\gamma$.

Numerical example.

For simplicity we shall choose our units of pressure and volume such that $R=1$. This can be achieved, for instance, by choosing the normal atmosphere (1013250 dyne/cm²) as our unit of pressure and 82.06 cm³ as our unit of volume.

Suppose initially we have $p_1=5$, $V_1=100$, $N_1=2$; $p_2=1$, $V_2=300$, $N_2=1$. We shall assume $\gamma=1.4$, which is the value for air. The initial values of the temperatures calculated from (1) are $T_1=250$, $T_2=300$.

For the case (a), we have $p_1'=p_2'=2$, $T_1'=T_2'=266.7$, $V_1'=266.7$, $V_2'=133.3$, $\Delta S=1.179$.

For the case (b), we have $p_1'=p_2'=2$, $192.4 < T_1' < 217.15$, $365.7 < T_2' < 415.2$, $192.4 < V_1' < 217.15$, $182.85 < V_2' < 207.6$.

For the case (c), we have $p_1'=p_2'=1.709$, $T_1'=T_2'=227.9$, $V_1'=266.7$, $V_2'=133.3$, $\Delta U=-291$.

For the case (d), we have $p_1' = p_2' = 1.829$, $T_1' = 187.6$, $T_2' = 356.5$, $V_1' = 205.1$, $V_2' = 194.9$, $\Delta U = -171$.

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