A PROBLEM IN THERMODYNAMICS

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ERRATA

It has been pointed out by Mr. S.C. Chen (陳世昌) in a private communication that the discussion of the case (c) in my paper with the above title is wrong. Since in the case (c) there is an irreversible flow of heat from the gas at the higher temperature to the one at the lower temperature, the total entropy cannot remain constant as stated, but must have increased in the end of the process. As a consequence the formula (22) for the final pressure is wrong, and the whole discussion of the case (c) has to be rewritten. The following account appears, I believe, to be correct.

Case (c). Quasistatic 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 total internal energy of the gases will be decreased by doing work against the external agency. Since a quasistatic process is very slow, the temperatures of the two gases must have time to become equal before the piston moves. The whole process, therefore, consists of two stages. In the first stage there is an irreversible process of heat flow at constant volumes until the temperature is uniform throughout the whole system. In the second stage a reversible process of equalization of pressures in the two gases takes place, in which the total entropy is constant.

Let us denote the values for the intermediate state at the end of the first stage of the process by a star. We have

$$V_1^* = V_1, \quad V_2^* = V_2, \quad T_1^* = T_2^*.$$

Since the volumes V_1 and V_2 are kept constant in the first stage, no external work is done on the gases and the total internal energy remains unaltered, so that

$$(N_1+N_2)RT_1^*=p_1V_1+p_2V_2.$$

The values for the intermediate pressures are determined by the following equations

$$\frac{p_1^*V_1}{N_1}=\frac{p_2^*V_2}{N_2}=\frac{p_1V_1+p_2V_2}{N_1+N_2}.$$

The increase of entropy in the first stage of the process is

$$\Delta S=\frac{N_1R}{\gamma-1}\ln\frac{T_1^{*\gamma}p_1^{*1-\gamma}}{T_1^{\gamma}p_1^{1-\gamma}}+\frac{N_2R}{\gamma-1}\ln\frac{T_2^{*\gamma}p_2^{*1-\gamma}}{T_2^{\gamma}p_2^{1-\gamma}}$$

$$=\frac{N_1R}{\gamma-1}\ln\frac{T_1^*}{T_1}+\frac{N_2R}{\gamma-1}\ln\frac{T_2^*}{T_2}.$$

That ΔS is positive is easily seen by writing it in the form

$$\Delta S=\frac{R}{\gamma-1}\left[(N_1+N_2)\ln\frac{p_1V_1+p_2V_2}{N_1+N_2}-N_1\ln\frac{p_1V_1}{N_1}-N_2\ln\frac{p_2V_2}{N_2}\right].$$

In the second stage of the process the total entropy of the gases is constant. Since the piston is permeable to heat, eqs. (12) are still true, and the final volumes of the gases are the same as in the case (a). The condition for the constancy of the total entropy is, by (13),

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

$$=\frac{p_1V_1+p_2V_2}{N_1+N_2}\cdot\left(\frac{N_1+N_2}{V_1+V_2}\right)^{\gamma}\left(\frac{V_1}{N_1}\right)^{\frac{N_1(\gamma-1)}{N_1+N_2}}\left(\frac{V_2}{N_2}\right)^{\frac{N_2(\gamma-1)}{N_1+N_2}}$$

The final temperature is then given by

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

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

$$\Delta U = -(p_1V_1+p_2V_2-p_1'V_1'-p_2'V_2')/(\gamma-1).$$

That ΔU is negative can be proved by writing it in the form

$$\Delta U = -\frac{p_1V_1+p_2V_2}{\gamma-1}\left\{1-\left[\left(\frac{N_1+N_2}{V_1+V_2}\right)^{N_1+N_2}\left(\frac{V_1}{N_1}\right)^{N_1}\left(\frac{V_2}{N_2}\right)^{N_2}\right]^{\frac{\gamma-1}{N_1+N_2}}\right\}.$$

It may be noted that in the reversible adiabatic process in which the two gases having different pressures are in thermal communication with a common temperature T, we have

$$T(V_1^{N_1}V_2^{N_2})^{\frac{\gamma-1}{N_1+N_2}} = \text{const.}$$

instead of (7). This formula is true whether the total volume is kept constant or not. In the calculation of the final temperature we may use this law and obtain

$$T_1' = T_1^*\left[\left(\frac{V_1}{V_1'}\right)^{N_1}\left(\frac{V_2}{V_2'}\right)^{N_2}\right]^{\frac{\gamma-1}{N_1+N_2}}$$

If we define a mean volume V by

$$V^{N_1+N_2} = V^{N_1}V_2^{N_2},$$

then the law can be written in the form

$$T\,V^{\gamma-1} = \text{const.},$$

which is the same as the usual formula. If we also define a mean pressure p by

$$p^{N_1+N_2} = p_1^{N_1}p_2^{N_2},$$

then we can write the law in the form (7) or (8).

Numerical example.

For the initial values $p_1=5$, $V_1=100$, $T_1=250$, $N_1=2$; $p_2=1$, $V_2=300$, $T_2=300$, $N_2=1$ (the units being so chosen that $R=1$), we find

$$T_1^*=T_2^*=266.7,\ p_1^*=5.333,\ p_2^*=0.889;$$

$$p_1'=p_2'=1.715,\ T_1'=T_2'=228.7,\ V_1'=266.7,\ V_2'=133.3,$$

$$\Delta S=0.0282,\quad \Delta U=-284.5$$