Heat Capacity Ratio of a Gas by Adiabatic Expansion

A Physical Chemistry Experiment with an Erroneous Assumption

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This experiment apparently dates back to 1819 (1) as cited by Partington (2). It is cited and discussed by Rayleigh (3), and appears in at least three laboratory manuals (4–6). Problems based on variations of this experiment appear in two chemical thermodynamics texts (7, 8).

The experiment is performed by pressurizing a gas ($P_1$) in a large vessel at ambient temperature ($T_1$), then releasing the gas at atmospheric pressure ($P_2$) and quickly reclosing before an appreciable amount of heat transfer between the system and the surroundings has occurred. The vessel and remaining gas are then allowed to return to ambient temperature ($T_1$) at constant volume, and the final pressure ($P_3$) is measured. The heat capacity ratio ($C_P/C_V$) for the gas is then calculated from the three pressures. An idealized version of this experiment would have the pressurized gas ($P_1, T_1$) insulated and confined by a weightless, frictionless piston expanding against the resistance of the atmosphere ($P_2$). After the gas has reached a uniform temperature ($T_2$) and pressure (equal to the atmospheric pressure, $P_2$), following this adiabatic expansion to some volume ($V_2$), a volume of the gas equal to the initial volume ($V_1$) is trapped and allowed to return at constant volume to the initial temperature ($T_1$) and a new pressure ($P_3$).

In every discussion we have found, this process is treated as an adiabatic reversible process, in some cases explicitly and in other cases by referring to an isentropic process. The process is not truly reversible, however, due to a finite difference between the pressure ($P_2$) within the system and the pressure ($P_3$) operating in the surroundings (see Moore (9)). Modifications of the experiment, such as slowing the escape of the gas (7) or actually measuring the temperature of the gas immediately after expansion (8,10,11), do not alter the irreversible nature of this process.

The idealized version of this experiment is an irreversible, adiabatic expansion at constant opposing pressure (atmospheric). The actual process differs from the idealized version in that the insulation is not perfect, and the escaping gas mixes with the surrounding atmosphere. The actual experiment will also suffer from the fact that the gas cannot be trapped at the precise instant at which the remaining gas would adiabatically equilibrate to atmospheric pressure. If precisely performed, however, the mixing of the escaping gas with the atmosphere will have little effect on the remaining gas. Failure to meet the truly adiabatic condition is a common flaw whether the process is considered to be reversible or irreversible but, because of the quickness of the process, should contribute little error.

Based on these considerations, the experiment is more realistically considered as an irreversible adiabatic expansion at constant opposing pressure than as an adiabatic reversible process. Application of the first law of thermodynamics to an adiabatic process involving only $P$-$V$ work gives:

$$dU = -P_{op}dV$$ (1)

In the special case of an ideal gas (which will be assumed throughout this derivation), the change in energy ($dU$) depends only on the change in temperature, the number of moles of gas ($n$), and the molar constant-volume heat capacity ($C_v$):

$$nC_v dT = -P_{op} dV$$ (2)

At constant opposing pressure ($P_2$), this integrates to

$$nC_v (T_2 - T_1) = -P_2 (V_2 - V_1)$$ (3)

Substituting for initial and final volumes using the equation of state of an ideal gas:

$$nC_v (T_2 - T_1) = -P_2 (nRT_2 / P_2 - nRT_1 / P_1)$$ (4)

The number of moles ($n$) refers to the original amount in the idealized experiment. However, it is common to both sides of eq 4, and removal leaves only intensive properties of the gas in the initial and final states. The difference between the constant-pressure and constant-volume heat capacities of an ideal gas ($C_p - C_v = R$) is substituted for the gas constant:

$$C_v (T_2 - T_1) = -(C_p - C_v) (T_2 - T_1) / P_2$$ (5)

which rearranges to

$$C_v (P_2 / P_1) = C_p (P_2 / P_1) - T_2 / T_1$$ (6)

The temperature after the adiabatic expansion is unknown but may be calculated from the final pressure after the trapped gas returns to the initial temperature ($T_1$):

$$T_2 / P_2 = T_1 / P_3$$ (7)

and substituted in eq 6 to give

$$C_p = (P_2 / P_1) - 1$$ (8)

The final expression derived for the adiabatic reversible process is (4)

$$C_p = \ln(P_2 / P_1)$$ (9)

While eq 9 is based on the incorrect assumption of a reversible process, calculations of the heat capacity ratio for nearly ideal gases using this equation are normally found to agree quite well with literature data. If this were not the case, the
experiment would have been discarded long ago, or the theoretical development would have been corrected. The correct results are obtained because, for the recommended conditions of this experiment, the mathematical difference between eqs 8 and 9 is actually quite small. For an initial pressure \( P_1 \) of about 600 mm of oil above atmospheric pressure, the ratio \( P_1/P_2 \) is approximately 1.07, and the ratio \( P_1/P_3 \) lies between this value and unity. Expansion of the logarithmic terms of eq 9 gives

\[
\frac{C_v}{C_p} = \frac{(P_1/P_2 - 1)\left[1 - (1/2)(P_1/P_2 - 1) + (1/3)(P_1/P_2 - 1)^2 - \ldots\right]}{(P_1/P_3 - 1)\left[1 - (1/2)(P_1/P_3 - 1) + (1/3)(P_1/P_3 - 1)^2 - \ldots\right]}
\]

(10)

and will reduce to eq 8 for pressure ratios approaching unity (in the limiting case, the process would actually be reversible). For an ideal monatomic gas under the recommended experimental conditions, eq 9 gives a heat capacity ratio that is 1.1% lower than the value calculated with eq 8, and the difference becomes even smaller for more complex ideal gases. This error is small compared to the effects of errors due to gaseous nonideality, imperfect insulation, and the great difficulty in actually performing the experiment to match the idealized conditions.

In view of the almost negligible correction we propose, our criticism may appear to be trivial. However, the existing explanation of this experiment presents an additional stumbling block to students trying to understand the complexities of reversibility versus irreversibility. This discussion should add considerably to the teaching potential of this experiment. The derivation presented above is actually less complex mathematically (it could be presented in terms of \( \Delta T \) and \( \Delta V \), rather than differential quantities, without loss of precision) than is the derivation for the reversible case.

**Literature Cited**

(10) Lummmer, O.; Pringsheim, R. Ann. Physik 1898, 64 (3), 582.