**Background**

This experiment has been in existence since before 1819. A gas is compressed \((P_1)\) in a large vessel and allowed to equilibrate to ambient temperature \((T_1)\). The gas is suddenly released to expand at atmospheric pressure \((P_2)\), and is quickly re-closed before an appreciable amount of heat transfer between the system and the surroundings can occur. The temperature of the gas instantaneously drops \((T_2)\), but quickly begins to return to the ambient temperature. [It is physically impossible to insulate against this heat transfer between the walls of the vessel and the gas.] While we have instruments today that can measure this instantaneous drop in temperature, this was certainly not possible in 1819. This experiment uses an ingenious way to calculate the temperature at the point in time at which the container was re-closed. At this point, the vessel contains \(n\) moles of the gas in a volume \((V)\) at atmospheric pressure \((P_2)\) and some unknown temperature \((T_2)\). As the gas warms to the ambient temperature \((T_1)\) at constant \(n\) and \(V\), the pressure increases \((P_3)\) according to the approximate relationship:

\[
\frac{T_2}{P_2} = \frac{T_1}{P_3}
\]

Therefore, if the initial pressure is known \((P_2 = P_{\text{atm}})\), and the final condition \((T_1 = T_{\text{ambient}}, P_3)\) is measured, the unknown temperature \((T_2)\) may be calculated.

The actual changes occurring in the system are controlled by the First Law of Thermodynamics:

\[
dU = DQ + DW = DQ - P_{\text{op}}dV
\]

The instantaneous expansion of the gas may be considered an adiabatic process \((DQ = 0)\). The operating pressure \((P_{\text{op}})\) has been the subject of some debate. Historically, the process has been considered reversible, such that the operating pressure may be replaced with the pressure of the gas \((P_{\text{op}} = P = nRT/V)\), approximated as ideal. Bertrand and McDonald have pointed out that the process is actually an irreversible expansion against the constant pressure of the atmosphere \((P_{\text{op}} = P_{\text{atm}} = P_2)\). Continuing the ideal gas approximation, the energy of an ideal gas (by definition) depends only on temperature, and for this adiabatic situation:

\[
dU = nC_{v,m}dT = - P_{\text{op}}dV
\]

in which \(C_{v,m}\) is the molar constant-volume heat capacity of the gas. If the operating pressure is constant, this integrates to:

\[
\Delta U = nC_{v,m}(T_2 - T_1) = - P_2(V_2 - V_1),
\]

and substituting for the volumes,

\[
nC_{v,m}(T_2 - T_1) = - P_2(nR)(T_2/P_2 - T_1/P_1) = - (nR)(T_2 - T_1P_2/P_1)
\]

By eliminating the number of moles and doing a bit of algebra, this can be rearranged to

\[
(C_{v,m} + R)(1 - T_2/T_1) = R(1 - P_2/P_1).
\]
For an ideal gas, the molar constant-volume heat capacity is related to the molar constant-pressure heat capacity:

\[ C_{p,m} = C_{v,m} + R = R(1 - P_2/P_1)/(1 - T_2/T_1) \]  
(7i)

and on substituting Eq (1),

\[ C_{p,m} = R(1 - P_2/P_1)/(1 - P_2/P_3) . \]  
(8i)

**Equation (8i) is used to calculate the heat capacity of the gas.**

If the process is reversible, Eq (3) becomes

\[ dU = nC_{v,m}dT = -PdV = -nRT(dV/V) \]  
(3r)

which integrates to

\[ nC_{v,m}\ln(T_2/T_1) = -nR\ln(V_2/V_1) \]  
(4r)

and substituting for the volumes gives

\[ nC_{v,m}\ln(T_2/T_1) = -nR \ln(T_2/T_1) + nR \ln(P_2/P_1) \]  
(5r)

which rearranges to

\[ C_{p,m}\ln(T_2/T_1) = R \ln(P_2/P_1) \]  
(6r)

and

\[ C_{p,m} = R \{\ln(P_2/P_1)/\ln(T_2/T_1)\} . \]  
(7r)

On substituting Eq (1),

\[ C_{p,m} = R \{\ln(P_1/P_2)/\ln(P_3/P_2)\} \]  
(8r)

Clearly, the equations for the reversible and irreversible cases are not equivalent. However, as a practical matter, if \( P_1 \) is not substantially greater than \( P_2 \) the differences between the equations for the two cases is minute.

In this experiment, several gases will be compared in terms of their temperature drops for comparable adiabatic expansions, and the data will be used to estimate the constant-pressure heat capacities for comparison to accepted values.
EXPERIMENTAL

Gases: Argon, Nitrogen, Carbon Dioxide

1. Make sure ALL clamps on hoses leading to and from the carboy are OPEN, especially the exit hose (D).
2. Open gas cylinder by turning the tank valve (A) counter-clockwise while the reducing valve (B) is closed (turned counter-clockwise until loose).
3. Open the needle valve (C) and slowly turn the reducing valve (B) clockwise until a gentle wind can be felt from the open hose.
4. Let system purge for about 15 minutes.
5. Close the needle valve (C).
6. Close valve on the open hose (D). Make sure the stopper is securely in place.
7. SLOWLY open the needle valve (C) while watching the oil levels in the manometer. When the oil levels are about 60 cm apart (2 feet), shut the valve.

IF YOU OPEN THE NEEDLE VALVE TOO QUICKLY OR WAIT TOO LONG BEFORE CLOSING IT, YOU WILL SPEND AN HOUR CLEANING UP THE OIL THAT COMES SPILLING OUT OF THE MANOMETER.

8. If the oil levels do not stabilize within a minute or two, re-tighten the clamp on the open hose (D) and make sure the stopper is secure. Repeat step 7.
9. When the oil levels remain constant, record the values. This pressure difference (converted to torr) is added to the barometric pressure to obtain the initial pressure (P₁).
10. Pull the stopper out of the carboy (about 4” high) and quickly replace it. The oil levels in the manometer will approach each other, then start to separate again.
11. Record the oil levels when they stabilize - this may take several minutes. This difference (converted to torr) is added to the barometric pressure to obtain the final pressure (P₃).

Obtain 2 replicate sets of data by repeating steps 5-11. It is not necessary to purge again unless you have allowed air to get into the system.

12. Repeat steps 1 - 11 with two other gases.
13. Record the barometric pressure (P₂) and the ambient temperature in the laboratory.
PRESSURE CONVERSIONS:
The pressure exerted by a column of fluid is: \( P = gdh \), in which \( g \) is the gravitational constant, \( d \) is the density of the fluid, and \( h \) is the height of the column.
Mercury: \( d = 13.55 \text{ g/cm}^3 \)  
Dibutylphthalate (oil): \( d = 1.046 \text{ g/cm}^3 \)  
1 torr \( \sim 1 \text{ mm Hg} \)

CALCULATIONS
Present in Tabular Form:
The pressure change for each experiment.
The temperature change for each experiment.
The molar constant-pressure heat capacity calculated for each experiment.
The “best” experimental value for \( C_P \) of each gas and its uncertainty.
Compare your results to accepted values (handbook, thermochemical tables, etc.).
Comment on any errors or spurious observations.

References

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