

7.17: Free Expansion of a Gas

To develop the theory of thermodynamics, we must be able to model the thermodynamic properties of gases as functions of pressure, temperature, and volume. To do so, we consider processes in which the volume of a gas changes. For the expansion (or compression) of a gas to be a reproducible process, the exchange of heat between the system and its surroundings must be controlled. There are two straightforward ways to do this. We can immerse the system in a constant temperature bath whose temperature is the same as that of the system; in this case, $\Delta T = 0$, and we can say that the process is isothermal.

Alternatively, we can isolate the system so that it cannot exchange heat with the surroundings; in this case $q = 0$, and the process is said to be adiabatic. In §7 we find that the work done on a system when its volume changes by dV under the influence of an applied pressure, P_{applied} , is

$$dw = -P_{\text{applied}}dV.$$

Any expansion of a system in which the applied pressure is less than the system pressure can be called a **free expansion**. In [Section 10.14](#) we consider the adiabatic expansion of a real gas against a constant applied pressure—a process known as a **Joule-Thomson expansion**. We find that we must introduce a new parameter—the Joule-Thomson coefficient—in order to describe the behavior of a real gas in a free expansion. The Joule-Thomson coefficient varies with pressure and temperature.

Literally, an **isothermal process** is one in which the temperature of the system remains the same throughout the process. However, we often use the term to mean merely that the process occurs while the system is in thermal contact with constant-temperature surroundings. The free expansion of a gas is an irreversible process; in principle, the temperature of a gas undergoing a free expansion is not a meaningful quantity. When we talk about an isothermal free expansion of a gas, we mean that the final temperature is the same as the initial temperature.

Here we consider the behavior of ideal gases, and we begin by considering the limiting case of a free expansion in which the applied pressure is zero. Physically, this corresponds to the expansion of a system into a (very large) evacuated container. Under this condition, $dw = 0$, and the energy change is $dE = dq$. For one mole of any substance, $C_V = (\partial E / \partial T)_V$. If only pressure–volume work is possible and the applied pressure is zero, we have $dE = dq = C_V dT$, and

$$\Delta E = q = \int_{T_1}^{T_2} C_V dT$$

where T_1 and T_2 are the temperatures of the substance before and after the expansion, respectively.

At ordinary temperatures, C_V changes only slowly as the temperature changes. Over a short temperature range, it is usually a good approximation to assume that C_V is constant. We have

$$\Delta E = q = C_V (T_2 - T_1)$$

(one mole of any gas or other substance)

For a monatomic ideal gas, the energy change is exactly

$$\Delta E = q = \frac{3}{2}R(T_2 - T_1)$$

(one mole of a monatomic ideal gas)

The enthalpy change for any process is $\Delta H = \Delta E + \Delta(PV)$. If the system is one mole of an ideal gas, we have, because $\Delta(PV) = R\Delta T = R(T_2 - T_1)$,

$$\Delta H = C_V (T_2 - T_1) + R(T_2 - T_1) = (C_V + R)(T_2 - T_1) = C_P (T_2 - T_1)$$

(one mole of any ideal gas)

For an isothermal free expansion against an applied pressure of zero, we have $\Delta T = 0$, and so neither the energy nor the enthalpy of the gas changes. Since also $dw = 0$, there can be no exchange of heat with the surroundings. We have

$$w = q = \Delta T = \Delta E = \Delta H = 0$$

(free expansion, ideal gas)

For an adiabatic free expansion, we have $dq = 0$ and $dw = 0$, and it follows again that $w = q = \Delta T = \Delta E = \Delta H = 0$. We see that the isothermal and adiabatic expansions of an ideal gas into a vacuum are equivalent processes. If the expansion is opposed by a non-zero applied pressure, the two processes cease to be equivalent.

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