

2.7 JOULE'S EXPERIMENT

Experimentation

The evaluation of the differential $(\partial U/\partial V)_T$ for gases, in principle, can be done with the help of Joule's experiment (Fig. 2.7.1). Two vessels A and B are connected via a stopcock. The vessel A is filled with a gas at a certain pressure and the vessel B is completely evacuated. The entire assembly is immersed in a large vat of water and is allowed to come to thermal equilibrium with the water. The stopcock is opened and the gas is allowed to expand till both the vessels are uniformly occupied. After some time, when the vessel has again come to thermal equilibrium, temperature of the water is recorded. The result shows that the temperature of water after the experiment is the same as that before the expansion.

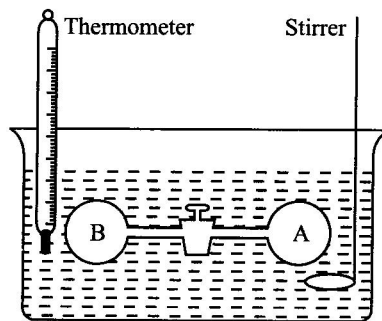


Fig. 2.7.1 Joule expansion experiment

Interpretation of the Results

Before expansion, the entire gas is present in the vessel A. On opening the stopcock, the boundary of the gas which always encloses the entire mass of gas expands against a zero opposing pressure. Such an expansion is called *free expansion*. Since $dw = -p_{\text{ext}} dV$, it is obvious that the work involved in the above expansion is zero. Now, according to the first law of thermodynamics $dU = dq + dw$, we have

$$dU = dq$$

Further, since there occurs no change in temperature of the bath, it follows that the heat dq involved must also be equal to zero. Thus, we conclude that

$$dU = 0$$

that is, Joule expansion is an isenergetic expansion.

Taking U to be a function to T and V , we write its differential as

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV$$

Since $dT = 0$ and $dU = 0$, we must have

$$\left(\frac{\partial U}{\partial V} \right)_T dV = 0$$

Now since $dV \neq 0$, it follows that

$$\left(\frac{\partial U}{\partial V} \right)_T = 0 \quad (2.7.2)$$

Equation (2.7.2) is known as Joule's law and it implies the following.

The change in energy of a gas with change in volume at a constant temperature is zero.

In other words, the energy of the gas is a function of temperature only. Mathematically, it is written as $U = f(T)$. Joule's law is strictly applicable only for ideal gases and not for real gases.

Joule Coefficient

The results of Joule's experiment involving any gas (either ideal or real) can be expressed in terms of Joule coefficient η , defined as

$$\eta = \left(\frac{\partial T}{\partial V} \right)_U \quad (2.7.3)$$

The Joule coefficient can be expressed in terms of the derivative $(\partial U / \partial V)_T$ by employing the first law of thermodynamics. Taking $U = f(T, V)$, we have

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV$$

Since, the Joule experiment is a process of constant energy, we have

$$0 = \left(\frac{\partial U}{\partial T} \right)_V \left(\frac{\partial T}{\partial V} \right)_U + \left(\frac{\partial U}{\partial V} \right)_T$$

Rearranging this, we get

$$\left(\frac{\partial U}{\partial V} \right)_T = - \left(\frac{\partial U}{\partial T} \right)_V \left(\frac{\partial T}{\partial V} \right)_U = -C_V \eta$$

$$\text{or} \quad \eta = - \frac{1}{C_V} \left(\frac{\partial U}{\partial V} \right)_T \quad (2.7.4)$$

Joule Coefficient in terms of Easily Determinable Derivatives

The Joule coefficient η can be expressed in terms of quantities obtainable from the equation of state of the gas by employing the thermodynamic equation of state, according to which (see Section 4.14), we have

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \quad (2.7.5)$$

$$\text{Therefore } \eta = -\frac{1}{C_V}\left(\frac{\partial U}{\partial V}\right)_T = -\frac{1}{C_V}\left\{T\left(\frac{\partial p}{\partial T}\right)_V - p\right\} \quad (2.7.6)$$

If ΔT and ΔV are small, Joule coefficient can be written as

$$\eta = \left(\frac{\partial T}{\partial V}\right)_U \approx \frac{(\Delta T)_U}{(\Delta V)_U} \quad (2.7.7)$$

Substituting this in the previous expression, we get

$$(\Delta T)_U = \frac{1}{C_V}\left[p - T\left(\frac{\partial p}{\partial T}\right)_V\right]\Delta V \quad (2.7.8)$$

Joule Coefficient for an Ideal Gas

For an ideal gas $p = nRT/V$, therefore

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V}$$

This implies that

$$\eta = -\frac{1}{C_V}\left\{T\left(\frac{\partial p}{\partial T}\right)_V - p\right\} = -\frac{1}{C_V}\left(\frac{nRT}{V} - p\right) = -\frac{1}{C_V}(p - p) = 0 \quad (2.7.9)$$

that is, Joule coefficient for an ideal gas is zero.

Joule Coefficient for a Real Gas

For a real gas, the sign of η depends on the relative magnitudes of p and $(\partial p/\partial T)_V$ as can be seen from Eq. (2.7.6). Thus we have

(i) When $p > T(\partial p/\partial T)_V$ then η is positive. Since dV is always positive in Joule's experiment, it follows from Eq. (2.7.3) that $(\partial T)_U$ is positive, that is, there occurs an increase in temperature of the gas. In this case, as can be seen from Eq. (2.7.4), $(\partial U/\partial V)_T$ will have a negative sign.

(ii) When $p < T(\partial p/\partial T)_V$ then η is negative. Hence, it follows that $(\partial T)_U$ is negative, that is, there occurs a decrease in temperature of the gas. In this case, $(\partial U/\partial V)_T$ will have a positive sign.

The fact that $(\partial U/\partial V)_T$ is negative at very high pressures and is positive at ordinary pressures may be explained on the basis that the energy U actually consists of two types of energies, namely, kinetic energy and potential energy. When the volume is increased at constant temperatures, the kinetic energy remains constant but potential energy varies. At ordinary pressures where the attractive molecular forces predominate, the potential energy increases on expansion and hence $(\partial U/\partial V)_T$ is positive. At very high pressures, where the excluded volume plays the dominating role, the potential energy decreases on expansion with the result that $(\partial U/\partial V)_T$ is negative.

2.8 JOULE-THOMSON EXPERIMENT

Experimentation

The Joule-Thomson experiment involves the expansion of a gas from one fixed pressure to another fixed pressure under adiabatic conditions. The apparatus for the Joule-Thomson experiment is shown in Fig 2.8.1. It consists of a cylinder divided into two parts by a porous plug, a needle valve or any other throttling device. A fixed quantity of gas is contained in the cylinder by frictionless pistons placed on either sides of the porous plug. The entire apparatus is surrounded by an adiabatic wall. The gas to the left of the porous plug is at a high pressure p_1 and that to the right is at a low pressure p_2 ($p_1 > p_2$). The gas is allowed to pass through the porous plug from left to right, maintaining the pressures p_1 and p_2 at constant values. This can be achieved by removing the left-hand and right-hand pistons to the right quasi-statically.

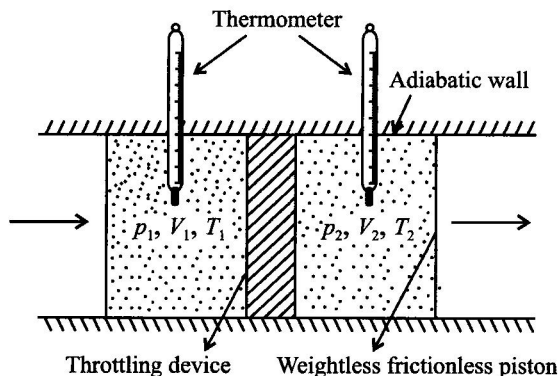


Fig. 2.8.1 Joule-Thomson Experiment

Nature of Joule-Thomson Expansion

Suppose a certain amount of gas is passed through the porous plug. We then have

$$\text{Change in volume on the left hand side} = -V_1$$

$$\text{Work involved on the left hand side} = p_1 V_1$$

$$\text{Change in volume on right hand side} = V_2$$

$$\text{Work involved on the right hand side} = -p_2 V_2$$

$$\text{Net work involved in the system} = -p_2 V_2 + p_1 V_1$$

Because the process is adiabatic, $dq = 0$, and thus from the first law, we have

$$\Delta U = w$$

$$\text{or } U_2 - U_1 = -p_2 V_2 + p_1 V_1$$

$$\text{or } U_2 + p_2 V_2 = U_1 + p_1 V_1$$

$$\text{or } H_2 = H_1 \quad (2.8.1)$$

that is, the enthalpy of the gas which has moved across the porous plug remains unchanged and thus the *Joule-Thomson expansion is an isenthalpic process*.

The measured change in temperature $-\Delta T$ and the measured change in pressure $-\Delta p$ are combined in the ratio

$$\left(\frac{-\Delta T}{-\Delta p} \right)_H = \left(\frac{\Delta T}{\Delta p} \right)_H$$

Joule-Thomson Coefficient

The Joule-thomson coefficient μ_{JT} is defined as the limiting value of this ratio as Δp approaches zero

$$\mu_{JT} = \lim_{\Delta p \rightarrow 0} \left(\frac{\Delta T}{\Delta p} \right)_H = \left(\frac{\partial T}{\partial p} \right)_H \quad (2.8.2)$$

Example 2.8.1

At 573 K and pressures of 0 – 6.0 MPa, the Joule-Thomson coefficient of $N_2(g)$ can be represented as

$$\mu_{JT}/K \text{ MPa}^{-1} = 0.140 - 2.533 \times 10^{-2} (p/\text{MPa})$$

Assuming this equation to be temperature-independent near 573 K, find the temperature drop which may be expected in the Joule-Thomson expansion of the gas from 6.0 MPa to 2.0 MPa pressure.

Solution

Since $\mu_{JT} = (\partial T / \partial p)_H$, therefore

$$dT = \mu_{JT} dp$$

$$= (0.140 \text{ K MPa}^{-1}) dp - (2.533 \times 10^{-2} \text{ K MPa}^{-1}) (p/\text{MPa}) dp$$

Integrating within the limits of pressure, we get

$$\Delta T = (0.140 \text{ K MPa}^{-1})(p_2 - p_1) - (2.533 \times 10^{-2} \text{ K MPa}^{-1}) \left(\frac{p_2^2}{2 \text{ MPa}} - \frac{p_1^2}{2 \text{ MPa}} \right)$$

Substituting the given values of p , we get

$$\begin{aligned} \Delta T &= (0.140 \text{ K MPa}^{-1}) (2.0 \text{ MPa} - 6.0 \text{ MPa}) - (2.533 \times 10^{-2} \text{ K MPa}^{-1}) \\ &\quad \times \left(\frac{(2.0 \text{ MPa})^2}{2 \text{ MPa}} - \frac{(6.0 \text{ MPa})^2}{2 \text{ MPa}} \right) \end{aligned}$$

$$= -0.560 \text{ K} + 0.405 \text{ K}$$

$$= -0.155 \text{ K}$$

4.11 THE CLAUSIUS INEQUALITY

A Characteristic of Entropy Function

Since S is a state function, it follows that $\oint dS = 0$. If the cyclic process involves going from A to B and then coming back to A, then

$$\oint dS = \int_A^B dS + \int_B^A dS = 0$$

$$\text{or} \quad \int_A^B dS = - \int_B^A dS \quad (4.11.1)$$

that is, the entropy change in going B to A is equal but of opposite sign to that in going from A to B, for only then the addition of these two will be zero.

Entropy Changes in a Reversible Process

If we assume that the surroundings always transfer heat reversibly, then the entropy change in any process carried out reversibly will be the negative of the entropy change of the surroundings, i.e.

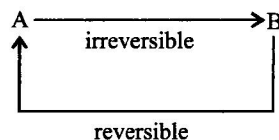
$$\Delta S(\text{system}) = - \Delta S(\text{surroundings})$$

$$\text{or} \quad \Delta S(\text{total}) = \Delta S(\text{system}) + \Delta S(\text{surroundings}) = 0 \quad (4.11.2)$$

Thus, the sum of entropy changes for the system and of the surroundings will always be zero. Hence, it may be concluded that in reversible processes entropy is merely transferred between the system and surroundings and that the total entropy change is zero.

Expression of Clausius Inequality

Now let us consider what happens when the process $A \rightarrow B$ is irreversible. No matter what the nature of this process might be, we can assume that the reverse process $B \rightarrow A$ is carried out reversibly. Then we have the following cycle.



Now
$$\oint \frac{dq(\text{irr})}{T} = \int_A^B \frac{dq(\text{irr})}{T} + \int_B^A \frac{dq(\text{rev})}{T}$$

Making use of Eq. (4.11.1), we have

$$\oint \frac{dq(\text{irr})}{T} = \int_A^B \frac{dq(\text{irr})}{T} - \int_A^B \frac{dq(\text{rev})}{T}$$

Now, according to Eq. (4.10.2), we have

$$\oint \frac{dq(\text{irr})}{T} < 0$$

Thus, it follows that

$$\int_A^B \frac{dq(\text{irr})}{T} < \int_A^B \frac{dq(\text{rev})}{T}$$

Using Eq. (4.9.11), this becomes

$$\int_A^B \frac{dq(\text{irr})}{T} < \int_A^B dS$$

or
$$\int_A^B \frac{dq(\text{irr})}{T} < \Delta S_{AB} \quad (4.11.3)$$

where ΔS_{AB} is the change of entropy of the system in going from A to B.

The expression of Eq. (4.11.3) is known as *Clausius inequality* which is a fundamental requirement for a real transformation. The inequality of Eq. (4.11.3) enables us to decide whether or not, some proposed transformation will occur in nature. We will not use this expression as such, but will manipulate it to express the inequality in terms of properties of the state of a system rather than in terms of path property such as $dq(\text{irr})$.

Clausius Inequality Applied to an Isolated System

For any change in an isolated system

$$dq(\text{irr}) = 0$$

and the inequality of Eq. (4.11.3) becomes

$$0 < \Delta S_{AB} \quad \text{or} \quad \Delta S_{AB} > 0 \quad (4.11.4)$$

Thus, the requirement for a real transformation in an isolated system is that ΔS be positive, i.e. the entropy of the system increases whenever a natural change is occurring within an isolated system. The entropy continues to increase so long

as changes occur in it. When the changes cease, the system is in equilibrium, and the entropy has reached a maximum value.

Thus the condition of equilibrium in an isolated system is that the entropy has a maximum value.

Clausius Inequality Applied to System and Surroundings

We can always imagine that system I and its surroundings form a larger system called system II, which is isolated from its surroundings. Consequently, no matter what the interaction between system I and its surroundings in the irreversible process might be, the entropy of system II always increases. We, therefore, have

$$\Delta S_{\text{sys}}(\text{II}) = \Delta S_{\text{sys}}(\text{I}) + \Delta S_{\text{surr}}(\text{I}) > 0 \quad (4.11.5)$$

Clausius assumed that the entire universe could be considered as an isolated system, in which all naturally occurring processes are irreversible. This is the basis for his often quoted statement:

The energy of the universe is constant, the entropy of the universe always tends toward a maximum.