

Study Material - Sem. 3 - Kinetic

Theory of Gases - Dr. T. Kerr

C6T - Class 7

Joule's Experiment

In the year 1840, Joule devised a simple experiment with gases: whether there is any change of internal energy of an ideal gas when it is allowed to expand against zero external pressure. The apparatus consists of two identical glass spheres A and B, which are connected by a narrow tube provided with a stop cock [Fig. 1].

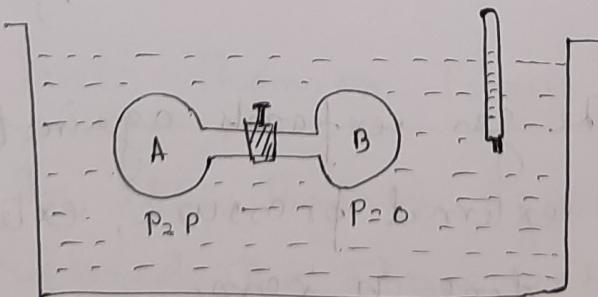


fig. 1

This set up is kept immersed in a vessel containing water. The sphere A is filled with air at a pressure of about 22 atmosphere and the sphere B is empty. When the whole system comes in thermal equilibrium, the stop cock is suddenly opened. Air from A immediately fills the vessel B. After expansion of the gas it is found that temperature of water in the vessel does not change. It remains constant. The experiment proves that:

- (a) when an ideal gas expands, it does not perform any work against intermolecular force.
- (b) As the gas expands against zero external pressure, external work done is zero.

So, Joule comes to the conclusion that internal energy of a perfect gas does not depend on its volume.

Unfortunately, he did not notice any change in temperature. Thermal capacity of the vessels and water being very large than that of air, accurate results could not be expected from an experiment of this nature.

Later Joule and Thomson jointly devised the famous porous plug experiment. This experiment being more accurate, it was conclusively established the existence of intermolecular attraction in gases.

Joule-Thomson Porous Plug Experiment

In 1852, Thomson together with Joule replaced the above experiment performed by Joule in a modified

form when a slight temperature change could be measured accurately and succeeded in detecting a change of temperature during expansion of a gas through a porous plug. The experiment is commonly known as Joule - Thomson's porous plug experiment.

Principle: The main principle of the experiment is to allow a compressed real gas to pass through a porous plug. Substances like cotton, wool, silk etc. which has numerous pores can act as porous plugs and the pores will act as a number of narrow orifices in parallel. As a result of passage of the gas through the pores, an appreciable difference of pressure between the ends of the pores will be observed; the ~~pressure~~ pressure at the entrance being much higher than that at the exit.

Such a flow of gas through the pores is called throttling process. The gas is said to be throttled, i.e., the molecules go further apart.

As the gas is throttled, its temperature either decreases or increases depending on the initial temperature of the gas. So, internal energy of the gas as it passes through the process also decreases or increases. The experiment was performed to study the variation of internal energy of real gases with volume.

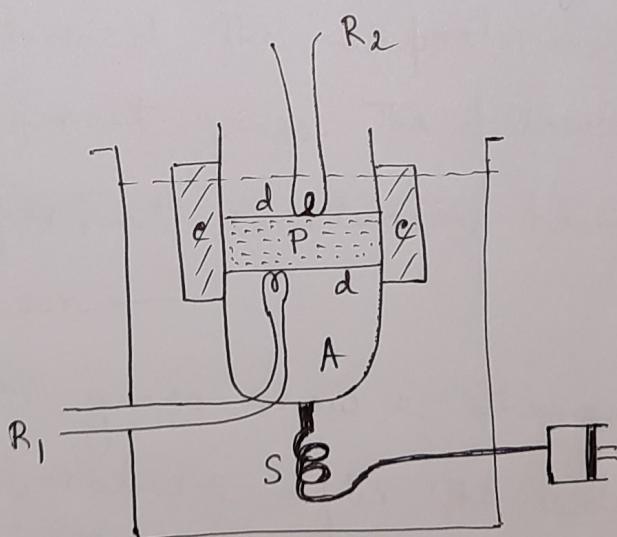


Fig. 2

Experiment: The experimental arrangement

are shown in fig. 2. The gas under pressure is passed through a copper spiral S immersed in a constant temperature water bath at a slow and uniform rate. The gas then enters into copper tube A. In this tube, porous plug P made of cotton or wool or silk is kept. The plug is kept in position by two porous brass plates d. A vessel (c) full of wool and cotton surrounds the tube A. Vessel c acts as a good insulator. This makes the porous plug and its adjacent region

Thermally isolated from the surroundings. Consequently, the gas will undergo adiabatic expansion through the pores. The system is immersed in a water bath upto the top of cc. Two sensitive thermometers R_1 and R_2 are placed on the two sides of the porous plug in order to measure accurately the temperature of the gas before and after throttling.

Discussions of the results of the experiment: Joule and Thomson performed the experiment with different gases. The following important conclusions have been drawn —

- All gases show a change in temperature after the adiabatic throttling process.
- The temperature change is proportional

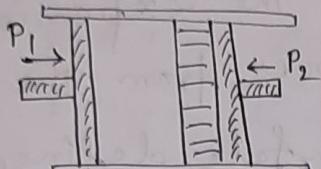
VIII

To The difference in pressure
on the two sides of The porous
plug.

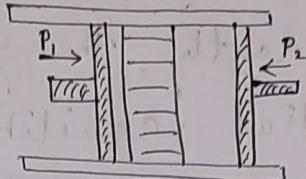
(c) At ordinary temperature, all permanent gases except hydrogen and helium, show cooling effect. For hydrogen and helium, there is a rise in temperature due to adiabatic Throttling process at room temperature.

Later experiments reveal that for every gas there is a particular temperature known as temperature of inversion below which the gas shows a cooling effect. As the inversion temperatures of hydrogen and helium are much below 0°C , they show heating effect at the ordinary temperature.

Theory of Porous Plug Experiment



(a)



(b)

Fig. 3

We consider a thermally insulated cylinder, provided with two non-conducting pistons on opposite sides of a porous plug. Between the left-hand piston and the plug, there is a gas at a pressure P_1 , volume V_1 and internal energy U_1 , and the right-hand piston is in contact with the plug. So, no gas can pass through the plug to the right. Now, the left piston is moved slowly towards the plug keeping its pressure fixed at P_1 . The gas passes through the plug pushing the right-hand piston to the right on which the pressure is maintained at a constant value P_2 . This process is continued till all the gas is pushed to the right side of the plug.

Let P_2 , V_2 and U_2 be the pressure, volume and internal energy of the gas respectively after the expansion. Evidently, the gas passes from the initial equilibrium state defined by (P_1, V_1) to the final equilibrium state defined by (P_2, V_2) .

Now, we apply first law of Thermodynamics to the process. As the system is thermally insulated, heat added to the system is zero, i.e., $\Delta Q = 0$.

$$\text{Work done on the gas} \Rightarrow \int_0^{V_1} P_1 dV = P_1 V_1$$

$$\text{Work done by the gas} \Rightarrow \int_0^{V_2} P_2 dV = P_2 V_2$$

$$\therefore \text{Net work done by the gas} = P_2 V_2 - P_1 V_1$$

$$\text{Now, } \Delta Q = \Delta U + \Delta W$$

$$\therefore 0 = (U_2 - U_1) + (P_2 V_2 - P_1 V_1)$$

$$\therefore U_1 + P_1 V_1 = U_2 + P_2 V_2 \rightarrow ①$$

$$\therefore V_1 - V_2 = P_2 V_2 - P_1 V_1 \rightarrow ②$$

Total heat function, enthalpy

$H = U + PV$ of the system remains

constant in the Throttling process [eq. (1)].
The process is also termed as isenthalpic process. It is to be noted that this process is irreversible one, because it passes through non-equilibrium states on its way from the initial equilibrium state to final equilibrium state. From eq. (2), we get the following information —

- (a) If $P_2 V_2 > P_1 V_1$, then $U_1 > U_2$. So, there is a decrease in internal energy of the system, producing fall in temperature of the gas. This is positive J-T effect.
- (b) If $P_2 V_2 < P_1 V_1$, then $U_1 < U_2$. So, internal energy of the system increases, producing rise in temperature. This is negative J-T effect.

Discussions

- For all permanent gases either cooling or heating effect is produced. So, we can infer that none of these

gases obey Boyle's law at ordinary temperature. This is also supported by Andrew's experiment. The reason is: Boyle's law holds good only in the case of ideal gases, wherein there is no intermolecular attraction.

But in all real gases, the inter-molecular attraction cannot be altogether neglected. So, Boyle's law is not expected to hold good in their cases.

2. Calculation of T-T effect

We can define T-T coefficient, μ , as the change in temperature per unit change in pressure under the condition of the experiment, i.e.,

$$\mu = \left(\frac{\partial T}{\partial P} \right)_H$$

In T-T effect, enthalpy $H = U + PV$ remains constant.

$$\begin{aligned} \therefore dH &= dU + PdV + VdP \\ &= (dQ - PdV) + PdV + VdP \\ &= Tds + Vdp \rightarrow ① \end{aligned}$$

$dQ = dU + PdV$ $dQ = Tds$

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Since enthalpy remains constant,

$$dH = 0$$

$$\therefore Tds + vdp = 0 \rightarrow (2)$$

Now, $S = f(T, P)$

$$\therefore ds = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dp$$

$\therefore Tds = T \left(\frac{\partial S}{\partial T}\right)_P dT + T \left(\frac{\partial S}{\partial P}\right)_T dp$

$$= C_p dT + T \left(\frac{\partial S}{\partial P}\right)_T dp$$

$$= C_p dT - T \left(\frac{\partial v}{\partial T}\right)_P dp$$

$$\boxed{\begin{matrix} S & P \\ V & T \end{matrix}}$$

$\hookrightarrow (3)$

From eq. (2), we get,

$$C_p dT - T \left(\frac{\partial v}{\partial T}\right)_P dp + v dp = 0$$

$\therefore C_p dT = [T \left(\frac{\partial v}{\partial T}\right)_P - v] dp$

$\therefore \left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_p} [T \left(\frac{\partial v}{\partial T}\right)_P - v] = \mu$

$\hookrightarrow (4)$

Case 1. If $T \left(\frac{\partial v}{\partial T}\right)_P > v$, then μ is positive

- J-T effect is positive. As $P_2 < P_1$, dp is negative. So μ to be positive, dT will be negative i.e., cooling will occur.

Case 2. If $T \left(\frac{\partial V}{\partial T} \right)_P < V$ Then μ is negative — J-T effect is negative.
 As $P_2 < P_1$, dP is negative and μ to be negative dT should be positive, i.e., heating will occur.

Case 3. If $T \left(\frac{\partial V}{\partial T} \right)_P = V$, J-T effect is zero. The temperature at which J-T effect is zero is called temperature of inversion. $V_0 = T_{inversion}$

J-T effect for a perfect gas

for a perfect gas, $PV = RT$ (for 1 mole)

$$\therefore V = \frac{RT}{P}$$

$$\therefore \left(\frac{\partial V}{\partial T} \right)_P = \frac{R}{P}$$

$$\therefore \mu = \frac{1}{C_P} \left[T \left(\frac{\partial V}{\partial T} \right)_P - V \right]$$

$$= \frac{1}{C_P} \left[\frac{TR}{P} - V \right] = \frac{1}{C_P} [V - V]$$

$$= 0$$

J-T effect for a Real Gas

Let us consider one mole of real gas obeying van der Waals' equation of state.

$$\left(P + \frac{a}{V^2} \right) (V - b) = RT \rightarrow \textcircled{1}$$

Differentiating eq. \textcircled{1} w.r.t T, we get,

$$\left[\left(-\frac{2a}{V^3} \right) (V - b) + \left(P + \frac{a}{V^2} \right) \right] \left(\frac{\partial V}{\partial T} \right)_P = R$$

$$\begin{aligned} \text{or } \left(\frac{\partial V}{\partial T} \right)_P &= \frac{R}{\left(P + \frac{a}{V^2} \right) - \frac{2a}{V^3} \cdot (V - b)} \\ &= \frac{R(V - b)}{\left(P + \frac{a}{V^2} \right)(V - b) + \frac{2a(V - b)^2}{V^3}} \\ &= \frac{R(V - b)}{RT - \frac{2a(V - b)^2}{V^3}} \end{aligned}$$

$$\begin{aligned} &= \frac{R(V - b)}{R \left[T - \frac{2a(V - b)^2}{RV^3} \right]} \\ &= \frac{(V - b)}{T \left[1 - \frac{2a(V - b)^2}{RTV^3} \right]} \end{aligned}$$

$$\therefore T \left(\frac{\partial V}{\partial T} \right)_P = (V - b) \left[1 - \frac{2a(V - b)^2}{RTV^3} \right]^{-1}$$

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$$\therefore T \left(\frac{\partial V}{\partial T} \right)_P = (V - b) \left[1 - \frac{2a}{RTV} \right]^{-1} \quad [\because V \gg b]$$

$$= V \left(1 - \frac{b}{V} \right) \left[1 + \frac{2a}{RTV} \right]$$

$$= V \left[1 + \frac{2a}{RTV} - \frac{b}{V} - \frac{2ab}{RTV^2} \right]$$

$$= V \left[1 - \frac{b}{V} + \frac{2a}{RTV} \right]$$

$$= V - b + \frac{2a}{RT} \left(\frac{1}{V} - 1 \right)$$

$$\therefore T \left(\frac{\partial V}{\partial T} \right)_P - V = \frac{2a}{RT} - b \rightarrow ②$$

J.T. Coefficient,

$$\mu = \left(\frac{\partial T}{\partial P} \right)_H$$

$$= \frac{1}{C_P} \left[T \left(\frac{\partial V}{\partial T} \right)_P - V \right]$$

$$= \frac{1}{C_P} \left[\frac{2a}{RT} - b \right] \rightarrow ③$$

Thus, The cooling or heating in J-T effect is determined by The competition between The two van der Waals' constants b and a , i.e., terms characterising The finite size of gas molecules and intermolecular forces respectively.

So, three distinct situations may arise. These are —

- i) If intermolecular forces are very strong then, $a \gg b$.

Therefore, $\frac{2a}{RT} > b$ which makes $\mu > 0$ and The gas cools down.

- ii) If The intermolecular forces are weak and The volume correction term dominates Then $b > \frac{2a}{RT}$ which makes $\mu < 0$ and The gas warms up.

- iii) If $\frac{2a}{RT} = b$ Then $\mu = 0$ and There is neither cooling nor heating. Thus J-T effect changes sign at temperature $\frac{2a}{Rb}$. This temperature is known as inversion temperature, T_i , so,

$$T_i = \frac{2a}{Rb}$$

Relation between Boyle temperature, Critical temperature & Inversion temperature

Boyle temperature, $T_B = \frac{a}{bR}$

Critical temperature, $T_c = \frac{8a}{27bR}$

Inversion temperature, $T_i = \frac{2a}{Rb}$

$$\therefore T_i = 2T_B = \frac{27}{4} T_c$$

The validity of above relation necessarily depends on how accurate is the van der Waals equation of state for a gas under the given conditions.

$$J-T \text{ coefficient, } \mu = \frac{1}{C_p} \left[\frac{2a}{RT} - b \right]$$

$$= \frac{b}{C_p} \left[\frac{2a}{RTb} - 1 \right]$$

$$= \frac{b}{C_p} \left[\frac{T_i}{T} - 1 \right]$$

The above equation shows that J-T effect produces cooling (i.e., $\omega > 0$) provided the initial temperature, T of the gas is less than the inversion temperature T_i — a fact of paramount importance in the liquification of gases and studying the properties of gases at low temperatures. For hydrogen and helium, the inversion temperature is well below the room temperature, a fact that explains why these two gases withheld all attempts of liquification for a long time. They must be precooled below their inversion temperature for their successful liquification.

7.10. DIFFERENCE BETWEEN ADIABATIC COOLING AND JOULE-THOMSON COOLING

Adiabatic Cooling	Joule-Thomson Cooling
<ol style="list-style-type: none">1. Adiabatic expansion of a gas is so rapid that no heat exchange with the surroundings is possible within the small time interval.2. In this process entropy $\left(\sum \frac{dQ}{T} \right)$ is constant. So, the adiabatic process is isentropic.3. During adiabatic expansion, the gas performs work at the expense of its own energy. So, there is always a cooling effect during an adiabatic expansion. Even in the case of ideal gas, the cooling effect is expected.4. Adiabatic expansion always produces cooling effect. Only in the case of adiabatic compression heat is produced.5. It is a reversible process.	<ol style="list-style-type: none">1. Joule-Thomson throttling process is made artificially adiabatic in the sense that true heat exchange is practically stopped by proper thermal insulation.2. In Joule-Thomson cooling enthalpy ($H = U + PV$) remains constant. So, it is a isenthalpic process.3. In J-T effect work is done by the gas when it is real. Work is done against intermolecular force of attraction. This work is done at the expense of internal energy and so there is cooling. In the case of perfect gas, there being no intermolecular force, no work is done and hence no cooling is produced.4. Joule-Thomson expansion produces heating when the gas is above its inversion temperature.5. It is an irreversible process.