

JOULE-THOMSON EXPANSION OF A NON-DEGENERATE GAS.

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Various properties of degenerate and non-degenerate matter have been investigated in recent years and these results have found numerous applications in various physical (1) and astrophysical (2) problems. Kothari (3) has calculated the Joule-Thomson effect and adiabatic change in degenerate gas (degenerate in the sense of Fermi-Dirac statistics) and finds that the Joule-Thomson expansion of degenerate gas leads to heating. It will be interesting to investigate this effect in non-degenerate gas and compare it with the effect calculated for a degenerate gas. This is done in the present paper.

According to classical thermodynamics the Joule-Thomson effect is given by the relation

$$\left(\frac{\partial T}{\partial p}\right)_H = \frac{T \left(\frac{\partial V}{\partial T}\right)_p - V}{C_p}, \quad \dots \quad (1)$$

where $\left(\frac{\partial T}{\partial p}\right)_H$ denotes the Joule-Thomson effect and C_p the specific heat of the gas per N molecules ($N =$ Avogadro number). We have to calculate the right-hand side in equation (1) for a non-degenerate gas.

The usual expressions for the energy E and pressure p of a non-degenerate non-relativistic gas are the following ¹ :—

$$E = \frac{3}{2} NkT \left[1 + \frac{\beta}{2^{5/2} f} + \dots \right] \quad \dots \quad (2)$$

$$p = nkT \left[1 + \frac{\beta}{2^{5/2} f} + \text{terms in higher powers of } \frac{1}{f} \right] \quad \dots \quad (3)$$

where $n = \frac{N}{V}$; $\frac{1}{f} = \frac{nh^3}{g(2\pi mkT)^{3/2}}$

$\beta = +1$ for gas obeying Fermi-Dirac statistics

$\beta = -1$ „ „ „ Bose-Einstein „

¹ See Saha and Srivastava, *A Treatise on Heat*, (2nd ed.), p. 723.

We shall neglect quantities containing squares and higher powers of $\frac{\beta}{f}$ since in this case $f \gg 1$. Thus to a first approximation we have

$$\begin{aligned} C_V &= \left(\frac{\partial E}{\partial T} \right)_V = \frac{3}{2} Nk - \frac{1}{2} \frac{3 Nk\beta}{2 \cdot 2^{5/2}} \frac{nh^3}{g(2\pi mk)^{3/2} T^{3/2}} \\ &= \frac{3}{2} Nk \left[1 - \frac{1}{2} \frac{\beta}{2^{5/2} f} \right] \dots \dots \dots \dots \dots \quad (4) \end{aligned}$$

To find C_p we use the well-known thermodynamical relation

$$C_p - C_V = T \left(\frac{\partial p}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_p \dots \dots \dots \quad (5)$$

Using (3) we get

$$\left(\frac{\partial p}{\partial T} \right)_V = nk \left[1 - \frac{1}{2} \frac{\beta}{2^{5/2} f} \right] \dots \dots \dots \quad (6)$$

$$\begin{aligned} \left(\frac{\partial p}{\partial V} \right)_T &= \frac{\partial}{\partial V} \left[\frac{NkT}{V} \left\{ 1 + \frac{\beta}{2^{5/2} f} \right\} \right] \\ &= - \frac{NkT}{V^2} \left\{ 1 + \frac{\beta}{2^{5/2} f} \right\} - \frac{NkT}{V} \cdot \frac{\beta}{2^{5/2} f V} \\ &= - \frac{NkT}{V^2} \left[1 + \frac{2\beta}{2^{5/2} f} \right] \dots \dots \dots \quad (7) \end{aligned}$$

Further

$$\begin{aligned} \left(\frac{\partial V}{\partial T} \right)_p &= - \left(\frac{\partial p}{\partial T} \right)_V / \left(\frac{\partial p}{\partial V} \right)_T \\ &= \frac{nk \left[1 - \frac{1}{2} \frac{\beta}{2^{5/2} f} \right]}{\frac{NkT}{V^2} \left[1 + \frac{2\beta}{2^{5/2} f} \right]} \\ &= \frac{V}{T} \left[1 - \frac{5}{2} \frac{\beta}{2^{5/2} f} \right] \text{ approx.} \dots \dots \quad (8) \end{aligned}$$

Hence equation (5) yields

$$\begin{aligned} C_p - C_V &= T \left[nk \left\{ 1 - \frac{1}{2} \frac{\beta}{2^{5/2} f} \right\} \right] \frac{V}{T} \left\{ 1 - \frac{5}{2} \frac{\beta}{2^{5/2} f} \right\} \\ &= Nk \left[1 - \frac{3\beta}{2^{5/2} f} \right] \text{ approx.} \dots \dots \quad (9) \end{aligned}$$

Hence

$$C_p = \frac{3}{2} Nk \left[1 - \frac{1}{2} \frac{\beta}{2^{5/2} f} \right] + Nk \left\{ 1 - \frac{3\beta}{2^{5/2} f} \right\}$$

$$= \frac{5}{2} Nk \left[1 - \frac{3}{2} \frac{\beta}{2^{5/2} f} \right] \dots \dots \dots (10)$$

Substituting these values in equation (1) we get

$$\left(\frac{\partial T}{\partial p} \right)_H = \frac{-\frac{5}{2} \frac{\beta}{2^{5/2} f}}{\frac{5}{2} nk \left[1 - \frac{3}{2} \frac{\beta}{2^{5/2} f} \right]} = -\frac{\beta}{2^{5/2} f nk} \text{ approx.} \dots (11)$$

Hence

$$\left(\frac{\partial T}{\partial p} \right)_H = \frac{1}{2^{5/2} f nk}, \text{ i.e. positive for a gas obeying Bose-Einstein statistics.}$$

$$\left(\frac{\partial T}{\partial p} \right)_H = -\frac{1}{2^{5/2} f nk}, \text{ i.e. negative for a gas obeying Fermi-Dirac statistics.}$$

Thus the Joule-Thomson expansion leads to cooling for a gas obeying Bose-Einstein statistics and to heating for a gas obeying Fermi-Dirac statistics.

From equation (11) we have, on substituting the value of f ,

$$\left(\frac{\partial T}{\partial p} \right)_H = -\beta \frac{h^3}{g(2\pi m)^{3/2} k^{6/2} 2^{5/2} T^{3/2}} \dots (12)$$

Hence we get the interesting result that the Joule-Thomson effect for a non-degenerate gas is independent of the molecular concentration n or the pressure p of the gas, and varies inversely as $T^{3/2}$.

Kothari (3) has shown that the Joule-Thomson effect for a degenerate electron gas (degenerate in the sense of Fermi-Dirac statistics) is given by the relation

$$\left(\frac{\partial T}{\partial p} \right)_H = -\frac{g}{\pi k n} \left(\frac{3}{4\pi f} \right)^{2/3}$$

$$= -\frac{3^{2/3}}{2^{7/3}} \frac{h^2}{\pi^{8/3} m k^2} \cdot \frac{g^{1/3}}{T n^{1/3}}$$

$$= -\frac{3}{8k^2 T} \left[\frac{4gh^{12}}{15\pi^{14} m^6 p} \right]^{1/6} \dots (13)$$

Thus we see that for a fixed value of T , the Joule-Thomson effect for a gas obeying Fermi-Dirac statistics varies as $p^{-1/6}$ for the degenerate state and

becomes constant (independent of p) when the gas becomes non-degenerate. The Joule-Thomson effect at different pressures has been calculated for *electron gas* at 5°K . and the values so obtained have been plotted in Fig. 1, where the ordinate denotes the Joule-Thomson effect in degrees/dyne and the abscissa the pressure of the gas. The degenerate state extends to the right of the vertical line A and the non-degenerate state to the left of A . In the neighbourhood of A , however, the shape of the actual curve will differ appreciably from the

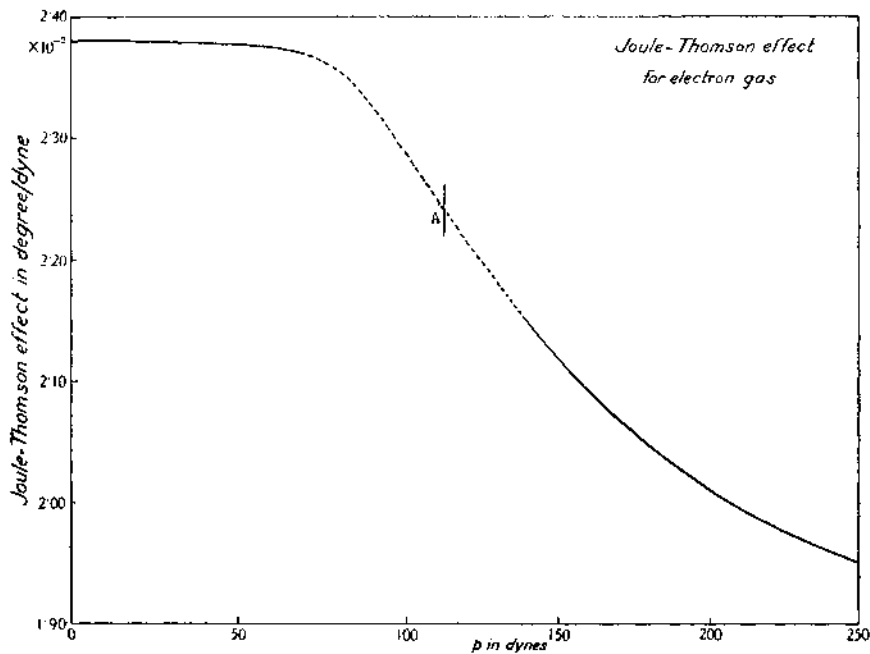


FIG. 1.

asymptotic formulæ [equation (12) for non-degenerate and equation (13) for degenerate state] and therefore this region is made dotted to indicate the general trend.

It will be of great interest to examine if the Joule-Thomson expansion can possibly afford an experimental test of the statistics obeyed by a gas. The only possible gas for which a test is possible is helium, since it is the only substance to remain in a gaseous state to very near the absolute zero in which region alone the Joule-Thomson effect due to statistical deviation becomes appreciable. But the thermal effect observed in a Joule-Thomson process is due not only to the statistical deviation from the classical perfect gas discussed above but also due to van der Waals' correction terms. We shall evaluate numerically the magnitude of these effects for helium.

Supposing helium gas obeys Bose-Einstein statistics (which we know to be a fact from band spectra data) we have

$$\begin{aligned}
 (\Delta T)_{\text{statis.}} &= \frac{(6.55 \times 10^{-27})^3 \times 1.01 \times 10^6}{T^{3/2} (2\pi \times 4 \times 1.66 \times 10^{-24})^{3/2} (1.37 \times 10^{-16})^{5/2} 2^{5/2}} \text{ per atmos.} \\
 &= \frac{0.847}{T^{3/2}} \text{ degree/atmos.} \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (14)
 \end{aligned}$$

Calculation shows that at $T = 5^\circ\text{K.}$ and $p = 1$ atmos., $f = 10$, hence helium would remain almost non-degenerate. Hence at this temperature and pressure $(\Delta T)_{\text{statis.}} = 0.076^\circ$.

For a van der Waals' gas the expression for cooling, to a first approximation, is given by

$$\Delta T = \frac{1}{C_p} \left[\frac{2a}{RT} - b \right] \Delta p \quad \dots \quad \dots \quad \dots \quad (15)$$

Substituting the values of a and b for helium, viz. $a = 0.0341 \times 10^6$ atmos., $b = 23.7$ c.c. we get for $T = 5^\circ\text{K.}$, $\Delta T = 0.68^\circ$ per atmos.

Using the more accurate expression, viz. :—

$$\Delta T = \frac{1}{C_p} \left[\frac{2a}{RT} - b - \frac{6ab}{R^2 T^2} p \right] \Delta p \quad \dots \quad \dots \quad (16)$$

and

$$C_p = C_{p_0} + \frac{2a}{RT^2} p - \frac{3ab}{R^2 T^3} p^2$$

we get for $T = 5^\circ\text{K.}$ and $p = 1$ atmosphere

$$\Delta T = 0.57^\circ \text{ per atmos.}$$

As van der Waals' equation may not hold in this region we shall calculate the Joule-Thomson effect by utilizing that equation of state which is found experimentally to hold in this region. Using Kamerlingh Onnes' equation ¹

$$pV = RT \left\{ 1 + \frac{B}{V} + \frac{C}{V^2} \right\} \quad \dots \quad \dots \quad \dots \quad (17)$$

¹L. Gropper (4) has developed the quantum theory of the equation of state at low temperatures and has deduced an expression for the second virial coefficient. For a gas obeying Bose-Einstein statistics he finds that approximately at low temperatures

$$B = -\frac{N\pi^{3/2}\lambda^3}{2} - \frac{h^2}{\pi mkT} Nf(0) - \pi Nf''(0) - \dots$$

where $\lambda^2 = h^2/4\pi^2 mkT$. The evaluation of the function f however cannot be done without recourse to experimental data and even then the values are not free from uncertainties, and hence it is best at the present stage to use directly Kamerlingh Onnes' equation.

we can deduce, correct to small quantities of the second order, that

$$p \left(\frac{\partial V}{\partial T} \right)_p = R \left(1 + \frac{B}{V} + \frac{C}{V^2} \right) + RT \left[\frac{1}{V} \frac{dB}{dT} - \frac{B}{V^2} \left(\frac{\partial V}{\partial T} \right)_p \right. \\ \left. + \frac{1}{V^2} \frac{dC}{dT} - \frac{2C}{V^3} \left(\frac{\partial V}{\partial T} \right)_p \right]$$

$$\text{or} \quad \left(\frac{\partial V}{\partial T} \right)_p = \frac{R \left(1 + \frac{Bp}{RT} - \frac{B^2 p^2}{R^2 T^2} + \frac{Cp^2}{R^2 T^2} \right) + p \frac{dB}{dT} - \frac{Bp^2}{RT} \frac{dB}{dT} + \frac{p^2}{RT} \frac{dC}{dT}}{p + \frac{p^2}{RT} B + \frac{2Cp^3}{R^2 T^2} - \frac{2B^2 p^3}{R^2 T^2}}$$

$$= \frac{R}{p} \left[1 + \frac{p}{R} \frac{dB}{dT} + \frac{p^2}{R^2 T^2} \left\{ B^2 - 2BT \frac{dB}{dT} - C + T \frac{dC}{dT} \right\} \right]$$

$$\therefore T \left(\frac{\partial V}{\partial T} \right)_p - V$$

$$= \frac{RT}{p} \left[1 + \frac{p}{R} \frac{dB}{dT} + \frac{p^2}{R^2 T^2} \left\{ B^2 - 2BT \frac{dB}{dT} - C + T \frac{dC}{dT} \right\} \right]$$

$$- \frac{RT}{p} \left[1 + \frac{Bp}{RT} - \frac{B^2 p^2}{R^2 T^2} + \frac{Cp^2}{R^2 T^2} \right]$$

$$= T \frac{dB}{dT} - B + \frac{p}{RT} \left\{ 2B^2 - 2BT \frac{dB}{dT} - 2C + T \frac{dC}{dT} \right\} \dots \quad (18)$$

A. van Itterbeek (5) found that between 14.50° and 3.70°K., B is given by

$$B \times 10^3 = 0.7559 - \frac{19.64}{T} - \frac{3.79}{T^2} + \frac{34.94}{T^3}$$

in Kamerlingh Onnes' units. Multiplying this by 22.4×10^3 we get B in c.c. mole. The values of C are not very accurately known. In the lower temperature region the values of C given by Keesom and Kraak (6) may be taken, while at the higher temperature C may be neglected. C_p may be calculated with the help of the approximate formula

$$C_p = C_{p_0} - Tp \frac{d^2 B}{dT^2}$$

where $C_{p_0} = \frac{5}{2}R$ for helium. Making use of these results we get for $T = 5^\circ\text{K.}$ and $p = 1$ atmos.

$$\Delta T = 0.83^\circ \text{ per atmos.}$$

Calculations for $T = 10^\circ\text{K.}$ and $p = 5$ atmos. have also been made and are given in the following table together with the values for $T = 5^\circ\text{K.}$ and $p = 1$ atmos.

TABLE I.—Joule-Thomson effect (μ_J) IN °C. PER ATMOS.

	For $T = 5^\circ\text{K.}$ and $p = 1$ atmos.	For $T = 10^\circ\text{K.}$ and $p = 5$ atmos.
μ_J statistical	0.076°	0.027°
μ_J from van der Waals' equation (first approx.)	0.68	0.285
μ_J do. do. (second approx.)	0.57	0.262
μ_J from K. Onnes' experimental equation	0.83	0.375

These results clearly show that the Joule-Thomson effect due to statistical deviation amounts to about 10% of the total expected value for the gas at these temperatures; in other words, about 10% of the cooling is contributed by the statistical effect and the remainder by van der Waals' correction terms.¹

The experimental data on Joule-Thomson effect in helium are at present too meagre and cannot be utilized as a check to the conclusions arrived at above. The recent experiments of Roebuck and Osterberg (7) were not carried below 83°K. and thus at the temperatures of their experiment the statistical effect would be imperceptible.

Jacyna (8) in a number of papers has calculated the Joule-Thomson effect and the inversion curve for helium on the basis of his thermodynamic equation of state. He has however not given the values of μ_J in the range of temperatures discussed here. He finds that μ_J will be zero at all temperatures for $p \rightarrow 0$. We have seen here that due to the quantum statistical effect μ_J will not be zero even at $p \rightarrow 0$ as van der Waals' equation might suggest but will approach a limiting constant value, the value depending upon the temperature. For high temperatures the value is extremely small and hard to detect experimentally but at $T = 5^\circ$ or 10°K. it can possibly be detected. As already mentioned, no experiments in this region have yet been carried out.

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SUMMARY.

An expression for the Joule-Thomson effect in the case of a non-degenerate gas has been derived. According to this the Joule-Thomson expansion will

¹ Since the value of μ_J calculated from the experimental equation of state is always greater than that calculated from van der Waals' equation, it follows that the calculated values are perfectly consistent with the view that helium obeys Bose-Einstein statistics. Exact verification can only be done when the exact contribution of van der Waals' terms is separately known. This is not possible at present.

lead to cooling for a gas obeying Bose-Einstein statistics, while for a gas obeying Fermi-Dirac statistics it will produce heating. The magnitude of this effect varies as $T^{-3/2}$ and is independent of pressure. For the sake of comparison the Joule-Thomson effect has been calculated for helium at certain temperatures on the basis of van der Waals' equation and K. Onnes' experimental equation. It is found that at 5°K. the Joule-Thomson effect due to statistical deviation, i.e. deviation from the classical perfect gas state due to effect of quantum statistics, amounts to about 10% of that calculated from K. Onnes' experimental equation of state, while at 10°K. it is 8%. It is suggested that the Joule-Thomson expansion of helium gas at very low temperatures may afford an experimental test of the statistics obeyed by this gas.

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