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$\begin{array}{c} Comparative \ evaluation \ of \ the \ Joule-Thomson \ coefficient \ for \ CO_{2(g)} \ and \ N_{2(g)} \\ distributed \ by \ air \ liquide \ PLC, \ Onitsha \ Anambra \ State, \ Nigeria \end{array}$

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ABSTRACT

In this research, the Joule-Thomson (JT) coefficient, μ_{JT} for $CO_{2(g)}$ and $N_{2(g)}$ distributed by Air Liquide was measured at high pressures (psig): 90,75, 65, 50 and 40 using the Joule-Thomson cell. The gauge pressures above were converted to atmosphere (atm) after taking readings of the voltage (μ V) and converting to temperature (K). Plots of temperature (T) against pressure (P_p) obtained over time for the two gases were made with slopes (μ_{JT}) evaluated to be -107.14 and -125Katm⁻¹ for CO₂ and N₂ respectively. However, from literature, the JT coefficient for CO₂ and N₂ were 10.9 and 2.15k.MPa⁻¹ respectively. This disparity is expected since μ_{JT} is a function of P_p and ΔP_p , for a small pressure decrease originating at 1atm pressure. There is also a concordance in JT coefficient variation for the two gases as CO₂ (-107.14Katm⁻¹) has a higher value than N₂ (-125katm⁻¹) as contained in literature: CO₂ (10.9kMPa⁻¹) and N₂(2.15kPa⁻¹).The research confirms the behaviour of a real gas at high pressure with respect to the values of Joule- Thomson coefficient obtained.

Keywords: Joule-Thomson coefficient, Carbon dioxide, Nitrogen, Real gases

INTRODUCTION

The enthalpy of an ideal gas depends only on the temperature and not on the pressure because of the absence of intermolecular forces. In real gases, however, for which such forces cannot be neglected, the enthalpy is pressure-dependent, and this property has many practical consequences.

One famous direct experimental study of intermolecular attractions was reported by Joule and Thomson (later Lord Kelvin) in 1853. Phenomenologically, it is the change in temperature accompanying the expansion of a gas that is measured in this experiment. This effect is of great practical importance and has many industrial applications. It is relevant not only in the liquefaction of gases (an ultimate consequence of intermolecular attractions) but also in the operation of the refrigerator and the heat pump [1].

Fig. 1 examines the theoretical background of this work. The gas, initially at the temperature (T_1) , enters an insulated cylinder at a constant pressure (P_1) . Under these conditions, the gas has a molar volume (V/n), V_{m1} . The gas is driven through a porous plug (which acts as a throttle) and then emerges at a lower (constant) pressure, P_2 . The outflowing gas therefore has a larger molar volume, V_{m2} . The equilibrium temperature of the exiting gas is T_2 ; for a real gas, $T_2 \neq T_1$. The dashed lines in Fig. 1 indicate the imaginery boundary of *one mole* of flowing gas. It is thus represented that $V_2 > V_1$. This expansion is carried out at constant enthalpy (isenthalpically). Fig. 1 also shows the pressure profile assumed in the system.

Because the entire system is insulated, q = 0 (no heat is exchanged with the surroundings



Figure 1: Gas flowing through an insulated tube containing a porous obstruction. The entering gas is at temperature and pressure T_1 and P_1 and has molar volume V_{m1} ; the exiting gas is characterized by T_2 , P_2 , and V_{m2} , $P_2 > P_1$.

The work, w_1 , involved in pushing an arbitrary volume of gas (e.g., v_1) through the plug is given by [2,3].

$$w_1 = -\int_{v_1}^{o} P_1 dV = P_1 V_1 \tag{1}$$

where it is assumed that the driving pressure, P_1 , is constant throughout the entire left-hand part of the tube. In eq. (1) $w_1 > 0$, because work is done on the gas ($\Delta V < 0$, and work is absorbed). The work done by the same quantity of gas as it emerges in the right-hand side of the tube is:

$$w_2 = -\int_0^{v_2} P_2 dV = P_2 V_2 \tag{2}$$

where it is again assumed that the low pressure, P_2 , is constant throughout the low-pressure region. Note that in equation (2) $w_2 < 0$ ($\Delta v > 0$) and hence work flows from the system. In the overall expansion, the net work, w, accompanying the flow of 1 mole of gas is

$$w = w_1 + w_2 = P_1 V_1 - P_2 V_2 \tag{3}$$

Using equation (3) and the fact that q = 0, the change is the internal energy (per mole) of flowing gas becomes

$$\Delta U = q + w = U_2 - U_1 = P_1 V_1 - P_2 V_2 \tag{4}$$

Equation (4) can be rearranged to give

$$U_2 + P_2 V_2 = U_1 + P_1 V_1, (5)$$

Since enthalpy, H, is defined as U +PV, it follows that $H_2 = H_1$ and $\Delta H = 0$; therefore, we see that the process is carried out at *constant enthalpy*. The gas can be said to undergo an irreversible, *isenthalpic, adiabatic expansion* [4].

As mentioned above, in this experiment one measures the temperature change $(T_2 - T_1)$ accompanying an isenthalpic expansion between known initial and final pressures. Thus, the Joule-Thomson (JT) (sometimes called Joule-Kelvin) coefficient, μ_{JT} , which is defined as

$$\mu_{JT} \equiv \lim_{\Delta P \to 0} \left(\frac{\Delta T}{\Delta P} \right)_{H} = \left(\frac{\partial T}{\partial P} \right)_{H}, \quad (6)$$

where $\Delta T = T_2 - T_1$ and $\Delta P = P_2 - P_1$, can be evaluated. If a gas *cools* in a JT expansion, $T_2 < T_1$ and the JT coefficient is *positive* (since $P_2 < P_1$). Alternatively, if the gas warms, μ_{JT} is negative. As will be mentioned below, the JT coefficient is a function of both *T* and *P*, and therefore a gas that heats in a JT expansion under certain conditions can be made to cool if the temperature and/or pressure of the expansion are appropriately changed.

It is desirable to relate μ_{JT} to thermodynamically useful expression. To this end, we express the enthalpy change in terms of differentials of *T* and *P*:

$$dH = \left(\frac{\partial H}{\partial T}\right)_{H} dT + \left(\frac{\partial H}{\partial P}\right)_{T} dP = C_{p} dT + \left(\frac{\partial H}{\partial P}\right)_{T} dP, \quad (7)$$

where C_p , the constant pressure heat capacity, is introduced. For an isenthalpic process dH = 0, and $(\partial T/\partial P)_H$ is expressed from (7) as

$$\left(\frac{\partial H}{\partial T}\right)_{H} = \mu_{JT} = \frac{-(\partial H/\partial P)_{T}}{(\partial H/\partial T)_{P}} = \frac{-(\partial H/\partial P)_{T}}{C_{P}}$$
(8)

As mentioned above, $\mu_{JT} = 0$ for an ideal gas. Because $C_p \neq 0$, the JT coefficient is zero only if $(\partial H/\partial P)_T = 0$. We can understand this derivative to imply something about the nature of intermolecular interactions. At high pressures where the average intermolecular distance is smaller, the presence of intermolecular forces will result in a change in energy (in this case, enthalpy). For example, if inter-molecular *attractions* dominate, the enthalpy is lower at high pressure and heat is *absorbed* ($\Delta H > 0$) when the pressure is decreased ($\Delta P < 0$), as weakly attracted molecules are separated from each other (assuming T is kept constant). Thus in this case, $(\partial H/\partial P)_T < 0$, and from (8), $\mu_{JT} > 0$. On the other hand, if intermolecular (or atomic) *repulsions* are more significant, a decrease in pressure is accompanied by a *liberation* of energy and $\Delta H < 0$ for $\Delta P < 0$. Under these circumstances, $(\partial H/\partial P)_T < 0$ and $\mu_{JT} > 0$ [1,5].

The relationship between attractive and repulsive molecular forces and their effect on the sign (and magnitude) of the JT coefficient can be obtained from the equation of state of the gas, e.g., the van der Waals equation. This will be illustrated below (see equation 16).

Since both μ_{JT} and C_P are measurable, the quantity, $(\partial H/\partial P)_T$ can be determined quantitatively. Because the latter reflects the nature and magnitude of intermolecular interactions, it allows the correctness of an equation of state for a real gas to be evaluated. Knowledge of $(\partial H/\partial P)_T$ is also important in correcting the enthalpies of gases at high pressures to standard conditions. This is used in *bomb calorimetry*.

There are practical aspects to the JT expansion. It is the basis of the Linde method of gas liquefaction. In this process, a gas is compressed to a reasonably high pressure and the heat liberated thereby is removed. The temperature is then low enough that $\mu_{JT} > 0$. The cooled, pressurized gas is then expanded adiabatically through a nozzle, and if the pressure drop is sufficiently large for the particular gas, it will cool so much that the final temperature is below its boiling point, and the gas liquefies. The liquid is drawn off and stored in heavy-walled containers. When the liquid warms (i.e., to ambient temperature), the pressure in the container can be significant. In addition, the JT effect is the basis of operation of the refrigerator and the device that operates in the reverse sense, the heat pump, and also determines the efficiency of a gas as a fire extinguisher.

It is desirable to obtain $(\partial H/\partial P)_T$ from any particular equation of state. To achieve this, we write the fundamental Gibbs equation for dH.

$$dH = T \, dS + V \, dP \tag{9}$$

Constructing $(\partial H/\partial P)_T$ from (9)

$$\left(\frac{\partial H}{\partial P}\right)_{H} = T\left(\frac{\partial S}{\partial P}\right)_{T} + V, \qquad (10)$$

 $(\partial S/\partial P)_T$ can be expressed in terms of measurable by using the Maxwell relation implied in dG = - S dT +V Dp, namely,

$$\left(\frac{\partial S}{\partial P}\right)_{T} = -\left(\frac{\partial V}{\partial T}\right)_{P}$$
(11)

Substituting this result into equation (10) provides the relation

$$\left(\frac{\partial H}{\partial P}\right)_{T} = V - \left(\frac{\partial V}{\partial T}\right)_{P}$$
(12)

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which can be directly applied to an equation of state, V = f(T, P).

Since many equations of state relate P = f(T,V), it is useful to recast equation (12) accordingly. We can use the cyclic relation:

$$\left(\frac{\partial V}{\partial T}\right)_{P} = \frac{-(\partial P/\partial T)_{V}}{(\partial P/\partial V)_{T}}$$
(13)

Express the JT coefficient as

$$\mu_{JT} = \frac{-1}{C_P} \left[V + \frac{T(\partial P / \partial T)_V}{(\partial P / \partial V)_T} \right]$$
(14)

Eq. (14) can be used to estimate μ_{JT} from an equation of state that is of the form P = f(T,V). Alternatively, the adequacy of an equation of state can be tested by using its ability to predict μ_{JT} values using (14) [3,6].

Calculation of μ_{JT} from Equations of State:

THE VAN DER WAALS (vdW) EQUATION: The vdW equation of state can be expressed as

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2},\qquad(15)$$

where *a* and *b* are parameters that can be obtained from the critical constants of a gas. If eq. (14) is applied to the vdW equation, one obtains a result in which μ_{JT} is a function of T and V_m (or pressure). This is observed to be the case, although the pressure dependence of μ_{JT} is rather small (except at very high pressures). At low pressures (a few tens of atmospheres, i.e., large molar volumes), the expression obtained from eq. (14) and (15) is

$$C_P \mu_{JT} = \frac{2a}{RT} - b \quad (vdW \ gas), \qquad (16)$$

and the temperature dependence of μ_{JT} in the low-pressure regime can be obtained from eq. (16). Generally, in applying this eq. (16), the temperature dependence of C_P should be taken into account [7, 8].

MATERIALS AND METHODS

The procedure followed in this experiment involved the direct temperature change that accompanies the expansion of a gas under nearly isenthalpic conditions. Thus ΔT and ΔP values were measured and used to compute the JT coefficient. The inlet pressure of the gas was measured and connected to a Bourdon gauge. The temperature change of the gas after expansion was determined directly from a pair of matched thermocouples connected in series. One thermocouple was placed in the high-pressure gas stream, and the other, located in the emerging, low-pressure, gas. See Figs. 2.

Apparatus

A diagram of the experimental apparatus is shown in Fig 2. The JT cell was constructed from stainless-steel fittings. Stainless steel was used because of its relatively low thermal conductivity; this helps to keep the process adiabatic. The whole system is made of metal so that it can withstand the pressure used in this experiment (up to 6 atm).

The heart of the apparatus, the porous plug (throttle), is a 3/8-in.-diameter stainless-steel frit having a porosity of about 2μ m. The entire apparatus is insulated by a layer of glass wool to keep it as adiabatic as possible. Gas at high pressure is forced through the cell. It expands through the frit and is then released at ambient pressure (into the atmosphere). The high-pressure side of the cell was monitored by a pressure gauge. The thermocouple that sense the temperature of the flowing, high-pressure gas was mounted in the center of the stainless-steel cross. This thermocouple junction is rather small (ca. 0.5 mm diameter) and thus has a very small thermal mass; it can react very rapidly to any change and the temperature of the exiting low-pressure gas was monitored by an identical thermocouple.

The thermocouples are constructed of very fine gauge wire in order to minimize heat transfer between the system and the surroundings. The thermocouple pair used is copper-constantan, which produces a potential of $39\mu V$ per C^o (at ambient temperature)



Figure 2: Cutaway view of the Joule-Thomson cell.

The junctions were connected in series (the copper wire of one thermocouple was connected to the constantan wire of the other), and thus the pair directly measures the temperature *difference* between the high-and low-pressure sides of the JT cell. The thermocouples were well matched and produce a negligible voltage when the two junctions are equilibrated at a common temperature. The thermocouple pair was attached directly to a microvoltmeter (having a bipolar meter) that indicates the voltage difference between the two junctions. With this particular apparatus, a meter deflection to the right (positive voltage) indicates that the high-pressure-sensing thermocouple (gas inlet) is at a higher temperature than the low-pressure-sensing thermocouple (gas outlet). A negative deflection indicates the opposite situation.

The pressure of the gas entering the JT apparatus was read from a Bourdon-type pressure gauge, a mechanical device capable of adequate accuracy. The gas first passes through a length of 1/4 –in. copper tubing so that it is equilibrated to ambient temperature before it enters the JT cell.

RESULTS AND DISCUSSION

The micrometer readings at varying gauge pressures for CO_2 and N_2 are shown in Tables 1 and 2.

 Table 1:
 Micrometer readings at varying pressures for CO2

p/psig	90	75	65	50	40
V/µV	3	18.5	29.3	45.1	55.7

Table 2: Micrometer readings at varying pressures for N₂

p/psig	90	75	65	50	40
V/µV	3.6	22.7	35.4	54.6	67.5

The voltage generated above were converted to temperature and presented in Tables 3 and 4 for CO_2 and N_2 respectively.

Table 3:	Voltage –	Temperature	Conversion for	: CO2
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V/µV	3	18.5	29.3	45.1	55.7
T/K	21	131	205	316	390

$Table \ 4: \quad Voltage - Temperature \ Conversion \ for \ N_2.$

V/µV	3.6	22.7	35.4	54.6	67.5
T/K	25	159	248	382	472

A Plot of temperature (K) vs Pressure (atm) for CO_2 and N_2 are contained in Figs 3 and 4 respectively.



Fig 3: A plot of temperature against pressure for CO₂



Fig 4: A plot of temperature against pressure for $N_{\rm 2}$

It should be noted that the behavior of real gases depends on the temperature and pressure upon expansion. It was observed from Table 3 and 4 that as pressure reduces the temperature of the gas increases. Joule Thomson coefficients as evaluated from the slope of the plot of temperature against pressure gave values ($-107.14 \text{ Katm}^{-1}$) for CO₂ and (-125Katm^{-1}) for N₂ gas. These values were found to be lower than the values reported in the literature. The variations observed in JT coefficient for both gases when compared with literature forms the basis of this research as JT coefficients are pressure dependent, deviating measurably at higher pressures.

For all gases JT coefficient may be positive, negative and/or zero. For a positive JT coefficient, change in pressure must be negative suggesting a fall in temperature on expansion; for a negative JT coefficient, the change in pressure must be negative and change in temperature must be positive, suggesting that the gas warms on expansion; For JT coefficient to be zero, change in temperature must be zero,

suggesting that neither cooling nor warming is observed [9]. This confirms the difference in behavior of real gases from ideal gases, as ideal gases neither cools nor warms on expansion.

All real gases have an inversion point at which JT coefficient changes sign. The temperature at this point, the Joule-Thomson inversion temperature depends on the pressure of the gas before expansion [9]. This clearly indicates that JT Coefficients are pressure dependent, deviating measurably at high pressure. This result of our findings suggests that both gases can function as fire extinguisher if expanded at high pressure or cooled before expansion.

CONCLUSION

JT coefficients for CO_2 (-107.14 Katm⁻¹) and N_2 (-125 Katm⁻¹) gas by Air Liquide was successfully measured. The variations observed in JT coefficient for both gases when compared with literature suggests that JT coefficients are pressure dependent, deviating measurably at higher pressures. This confirms the difference in behavior of real gases from ideal gas upon expansion at constant enthalpy. The result of this experiment suggests that both gases can function as fire extinguishers in expanded at higher pressure.

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