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THEORETICAL STUDY OF JOULE - THOMSON
COEFFICIENT

by

Mohammad Riaz

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A Thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Engineering in Chemical & Petroleum Refining Engineering.

Signed: M. Riaz
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Date: September 29, 1970

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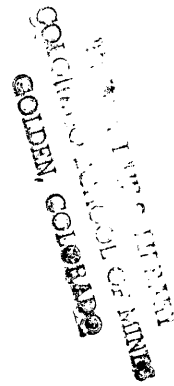
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A B S T R A C T

This work involves a theoretical study of the Joule-Thomson effect and an analysis of data available in the literature. Edmister(15) developed a correlation based upon the critical constants predicting the Joule-Thomson coefficient of pure gases and gas mixtures. This correlation is applicable in the range $0.85 \leq T_r \leq 4.0$ and $0.1 \leq P_r \leq 9.5$ for all gases and their mixtures except for the quantum gases. The values of the Joule-Thomson coefficient are calculated by using the Edmister correlation and are compared with experimental values. The results of the comparison appear satisfactory.

Actual critical temperature and critical pressure of the quantum gases, when used in the correlation as reducing parameters, fail to give reasonable values of the Joule-Thomson coefficients. Therefore, new effective critical temperature and critical pressure of these quantum gases are developed to make the correlation applicable to these gases.

The new effective critical constants are as follows:



Hydrogen

$$P_c = 15 \text{ atm.}$$

$$T_c = 37.8^\circ\text{K}$$

Helium

$$P_c = 5.226 \text{ atm.}$$

$$T_c = 13.88^\circ\text{K}$$

Effective critical temperatures of both hydrogen and helium are dependent upon the pressure at which the Joule-Thomson coefficient is to be determined.

Curves of pressure versus effective critical temperature are plotted for both hydrogen and helium.

The Joule-Thomson coefficient for hydrogen and helium and their mixtures with other gases were calculated by using modified constants in the Edmister correlation.

The results are in close agreement with the literature values.

D E D I C A T I O N

To my parents, wife, Tasneem, for her infinite
patience and my children, Farhana and Nadia.

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LIST OF SYMBOLS

| | |
|-------|------------------------------|
| A_0 | Beattie-Bridgeman constant |
| A_0 | Benedict-Webb-Rubin constant |
| B_0 | Beattie-Bridgeman constant |
| B_0 | Benedict-Webb-Rubin constant |
| C_0 | Benedict-Webb-Rubin constant |
| a | Beattie-Bridgeman constant |
| a | Benedict-Webb-Rubin constant |
| a | Redlich-Kwong constant |
| b | Beattie-Bridgeman constant |
| b | Benedict-Webb-Rubin constant |
| b | Redlich-Kwong Equation |
| c | Beattie-Bridgeman constant |
| c | Benedict-Webb-Rubin constant |

LIST OF SYMBOLS

| | |
|--------------------|--|
| E | Internal energy |
| Q | Heat term for unit quantity |
| W | Work term for unit quantity |
| H | Enthalpy |
| S | Entropy |
| P | Pressure |
| V | Volume |
| T | Temperature |
| C | Heat capacity |
| C_p | Heat capacity at constant pressure |
| R | Universal Gas constant |
| Δc_p | Isothermal pressure correction |
| K_2 | Constant(afunction of critical conditions) determines the dimension of ΔC_p . |
| Z | compressibility factor |
| $\Delta c_p^{(0)}$ | Heat capacity of ideal gas |
| $\Delta c_p^{(1)}$ | Heat capacity when departed from normal fluid |

LIST OF SYMBOLS

| | |
|-----------------|---|
| α | Residual volume |
| β | Benedict-Webb-Rubin constant |
| γ | Benedict-Webb-Rubin constant |
| λ | Benedict-Webb-Rubin constant |
| ϕ | Energy supplied (in isothermal method) |
| η | Entropy for unit mass used (in isothermal method) |
| μ | Joule-Thomson coefficient |
| ω | Acentric factor |
| Δ | Difference of initial and final value |
| subscripts | |
| c | Refers to critical property |
| r | Refers to reduced property |
| supersubscripts | |
| o | Refers to zero Pressure state. |

A C K N O W L E D G M E N T S

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I N T R O D U C T I O N

The thermodynamic function, "Joule-Thomson coefficient," is the partial derivative of the temperature of a fluid with respect to pressure at constant enthalpy. This function is widely used in refrigeration and liquefaction of gases.

Values of this function may be determined with the use of established experimental techniques or may be calculated from theoretical relationships (6,7,15,18,20,30).

The only generalized correlation for the Joule-Thomson coefficient is that of Edmister. This correlation (15) is based on the three parameters reduced temperature, reduced pressure, and acentric factor.

The objectives of this engineering report are three fold:

- 1) a) To test the correlation for all available gases and gas mixtures and to identify any limitations of its applicability.
- b) To compare the Joule-Thomson coefficient as predicted by this correlation with the available literature values.

- 2) To extend the correlation, if necessary, beyond its current limits to include all gases.
- 3) To survey and evaluate all available Joule-Thomson data for pure gases and gas mixtures. For this purpose the literature has been surveyed from 1900 to the present.

THERMODYNAMICS OF THE
JOULE-THOMSON EFFECT

When gas under pressure is forced through a porous plug or throttling valve, so that an appreciable pressure drop occurs the restriction, the temperature of the gas of the plug will differ when steady-state conditions prevail, provided that the system is substantially adiabatic (42, 12).

By the first law :

$$\begin{aligned} \Delta E &= Q - W & \text{Since } Q &= 0 \\ \Delta E &= - W & & (1) \end{aligned}$$

This shows that the change in internal energy of the gas must be equal to the work done by it. Since no net work is performed, in operating some sort of engine, the work done per mole of gas passing through the plug equals the difference between the work of expelling, 1 mole of the gas from the low pressure side of the plug, and the work done on the same quantity of gas in forcing it into the high pressure side. The net work done by 1 mole of the gas is therefore:

$$W = p_2 V_2 - p_1 V_1$$

subscripts 1 and 2 refer to conditions on the high and low pressure sides of the restriction respectively. Substituting this value for W in Eqn. (1) gives :

$$E_2 - E_1 = - (p_2 v_2 - p_1 v_1)$$

$$E_2 + p_2 v_2 = E_1 + p_1 v_1$$

$$H_2 = H_1$$

$$\Delta H = 0$$

That is, the Joule-Thomson expansion is an isenthalpic process, and called the fundamental equation of the Joule-Thomson effect.

As a quantitative measure of the behaviour of gases in the Joule-Thomson expansion, it is customary to employ the coefficient defined by the equation :

$$\mu =_{P \rightarrow 0} \frac{\Delta T}{\Delta P} = \left(\frac{\partial T}{\partial P} \right)_H$$

This represents the change in temperature per unit pressure drop, where the latter is differentially small.

μ is the ratio of thermodynamic point function, and is therefore, itself a point function.

DERIVATION OF DIFFERENTIAL EQUATION OF JOULE-THOMSON

COEFFICIENT

According to Dodge (12) differential equation in terms of measurable quantities is given as follows :

From the definition of H and S

Where H = Enthalpy

S = Entropy

$$dH = dE + PdV + VdP \quad \dots\dots\dots (i)$$

$$TdS = dE + PdV \quad \dots\dots\dots (ii)$$

Combining (i) and (ii)

$$TdS = dH - VdP \quad \dots\dots\dots(iii)$$

Dividing (iii) by dP at constant T

$$T\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T - V \quad (iv)$$

Differentiating Eq. (iv) with respect to T at constant pressure P :

$$T \frac{\partial^2 S}{\partial P \partial T} + \left(\frac{\partial S}{\partial P}\right)_T = \frac{\partial^2 H}{\partial P \partial T} - \left(\frac{\partial V}{\partial T}\right)_P \quad (v)$$

Since $dQ = C_p dT = TdS$ at constant P .

$$\text{or} \quad \left(\frac{\partial S}{\partial T}\right)_P = \frac{c_p}{T} \quad (a)$$

$$\text{But} \quad c_p = \left(\frac{\partial H}{\partial T}\right)_P \quad (b)$$

$$\text{Therefore} \quad T\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P \quad (c)$$

$$\text{and hence} \quad T \frac{\partial^2 S}{\partial T \partial P} = \frac{\partial^2 H}{\partial T \partial P} \quad (vi)$$

Making this substitution in Eq. (v)

$$\left(\frac{\partial S}{\partial P}\right)_T = - \left(\frac{\partial V}{\partial T}\right)_P \quad (vii)$$

Since S is a property

$$dS = \left(\frac{\partial S}{\partial T}\right)_P \cdot dT + \left(\frac{\partial S}{\partial P}\right)_T \cdot dP \quad (viii)$$

By inserting the values from (a) and (viii), Eq. (viii)

can be written as

$$dS = c_p \cdot \frac{dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P \cdot dP \quad (ix)$$

Putting this value in Eq.(iii) an analogous equation for H is obtained:

$$dH = c_p \cdot dT + \left[V - T \left(\frac{\partial V}{\partial T} \right)_P \right] dP \quad (x)$$

At constant H it will become:

$$\mu = \left(\frac{\partial T}{\partial P} \right)_H = \frac{T(\partial V/\partial T)_P - V}{c_p} \quad (A)$$

If the term $T \left(\frac{\partial V}{\partial T} \right)_P$ is larger than V , the term $\left(\frac{\partial H}{\partial P} \right)_H$ is positive, and a decrease in pressure will also decrease the temperature. The gas (41) will cool on expansion.

If $T \left(\frac{\partial V}{\partial T} \right)_P$ is equal to V , a free expansion will cause no temperature change. If $T \left(\frac{\partial V}{\partial T} \right)_P$ is less than V , the gas will heat up during a free expansion.

It can be shown also if the numerator and denominator of Eq. (A) are both divided by T :

$$\text{Then } \mu = \left(\frac{\partial T}{\partial P} \right)_H = \frac{(\partial V/\partial T)_P - V/T}{c_p/T}$$

the three cases $\left(\frac{\partial V}{\partial T} \right)_P \gtrless V/T$

are illustrated graphically.

Fig.(1) represents a plot of V versus T at constant pressure.

For ideal gas:

$$PV = RT$$

$$\left(\frac{\partial V}{\partial T} \right)_P - \frac{V}{T} = 0$$

Therefore, the ideal gas is represented by line (B) in figure (1) where $(\frac{\partial V}{\partial T})_P = \frac{V}{T}$ and thus the Joule-Tomson coefficient is zero.

Therefore, an ideal gas cannot be cooled by free expansion.

In curve (A) of Fig. (1) the instantaneous slope is greater than the average slope,

$$(\frac{\partial V}{\partial T})_P > V/T$$

and therefore, $(\frac{\partial V}{\partial T})_P$ is greater than zero. The gas will cool on expansion. For a non-ideal gas $PV = ZRT$ and $V = (Z)(\frac{R}{P})(T)$, thus compressibility factor Z must increase with T at the constant pressure in question in order for the curve to have a continually increasing slope. Mathematically:

$$(\frac{\partial Z}{\partial T})_P > 0$$

Likewise, if $(\frac{\partial Z}{\partial T})_P$ is less than zero, the plot of V versus T at constant pressure will be similar to curve C of Fig.(1). Therefore, $(\frac{\partial T}{\partial P})_H$ will be negative and gas will heat up on expansion.

There are two other possibilities which may occur. A plot of V versus T may have an increasing slope initially, but may have an inflection and pass through a point where the instantaneous slope is equal to the average slope, (V/T) , and then become less than the average slope, or it may start out with a decreasing slope which later increases until $(\frac{\partial V}{\partial T})_P$

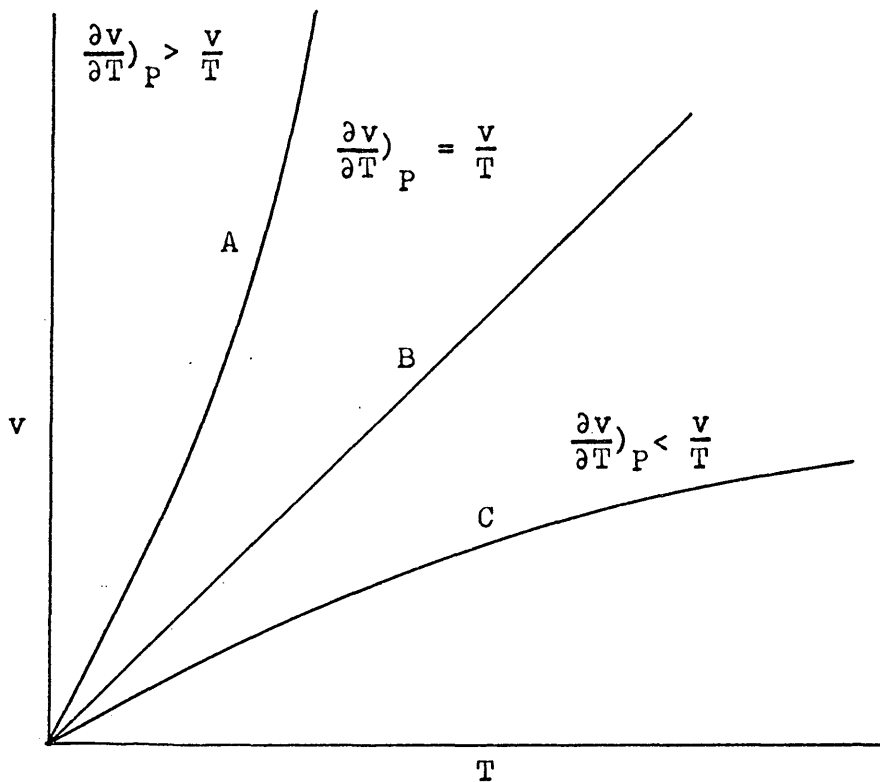


Figure 1.

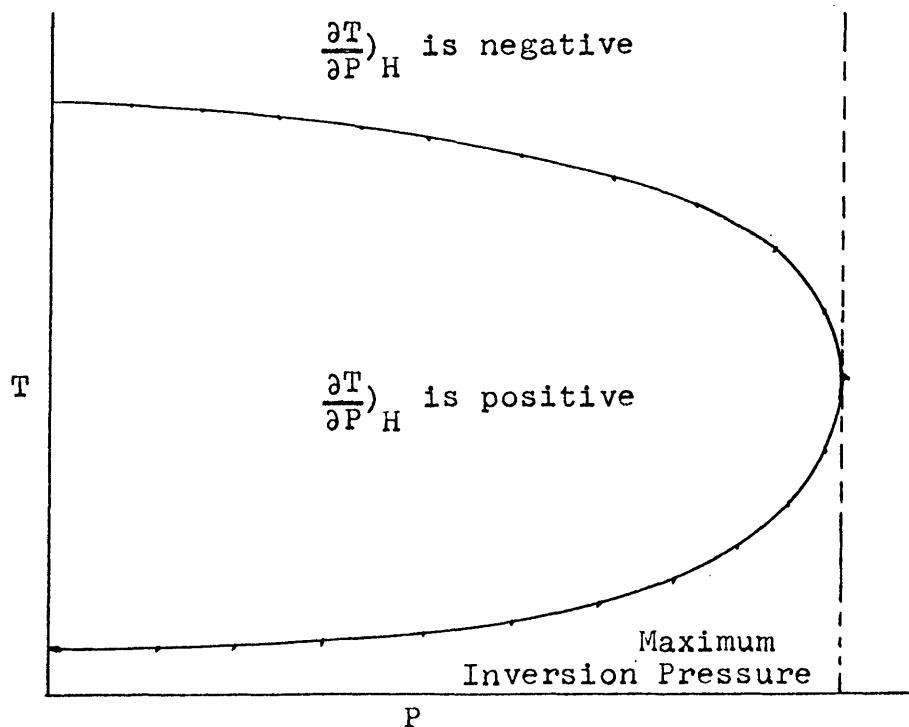


Figure 2.

is greater than (V/T) .

In either case the point on the curve where $(\frac{\partial V}{\partial T})_p$ becomes equal to (V/T) is called the inversion point. It is the point where the Joule-Thomson coefficient changes sign.

The inversion temperature for a gas is the temperature at a given pressure, at which the Joule-Thomson coefficient changes sign. Fig. (2) is a plot of inversion temperature versus pressure. For each pressure below the maximum there are two inversion temperatures. The area inside the curve is the region of positive coefficient, and outside the curve is of negative coefficient. This shape of the curve is general for all actual gases.

HISTORY

A complete historical review of past Joule-Thomson experiments is not summarized here, but reference will be given and annotated so that such a review may be made conveniently.

Joule and Thomson performed(1) the original classical experiment in the years 1852-1862, and included work on air, oxygen, nitrogen, carbondioxide, hydrogen and a mixture of two of more of these. They performed the experiment with the porous plug form of apparatus.

Accuracy of this type of apparatus was doubtful because of heat-transfer effects and thermal eapacity.

Buckingham(6) in 1903 suggested that the effects of heat leakage could be eliminated by supplying a precisely measured electrical heat input to the porous plug-the exact amount needed, to prevent temperature drop. He also suggested that arrangement of the flow into two concentric paths would contribute toward a reduction in heat leakage.

In 1910 Burnett(7) proposed a radial-flow plug, which Hoxton (44) also adopted in 1915.

The radial-flow plug is in the form of a hollow cylinder that is closed at one end. It is made of ceramic porous, unglazed material with a very low thermal conductivity. The gas being tested enter the plug approximately in a radial fashion. As the gas flows over the interior surface, it maintains them at a temperature very nearly equal to that of downstream gas.

True-blood(45) in 1917 investigated experimentally the effects of heat transfer in both axial-flow and radial flow plugs. He

found that heat leakage effects were less in the radial than in the axial plug.

The most extensive and accurate measurements of the Joule-Thomson effect on inorganic gases has been that carried on at University of Wisconsin by Roebuck and co-workers(30-36). During the period of 1930-1934, they investigated air, nitrogen, carbondioxide, helium and argon by use of a radial-plug apparatus.

Keyes and Collins(46), in 1932 measured some data on both carbon dioxide, nitrogen and ammonia. These data were taken with an isothermal expansion type of apparatus.

Most reliable studies on Joule-Thomson effect on hydrocarbon gases have been done by Sage and Lacey in California Institute of Technology(2,3,4,5,38,18,58,59,60).

They used apparatus with the radial-flow porous plug and obtained data on propane, n-butane, n-pentane, methane, ethane-also on mixtures of methane and ethane, methane and butane and of methane and propane.

In 1954 Charnley, Rowlinson, Sutton, and Townley(43) measured the Joule-Thomson coefficient at zero pressure for the four gas mixtures(Carbon dioxide-nitrogen oxide, carbon-dioxide-ethylene, and nitrous oxide-nitrogen). Like Keyes and Collins, they used the isothermal approach for their investigation.

Grossman(16) in 1965 conducted a study of Joule-Thomson

coefficients for the system nitrogen-carbon dioxide with a new porous plug apparatus, operating at as low pressure drops. The Beattie-Bridgeman and Benedict-Webb-Rubin equations were used to predict the Joule-Thomson coefficient of the mixture. Deviation was only 4 percent of the experimental value.

In 1967 Sabnis(37) in his work at Lehigh University studied Joule-Thomson effects in nitrogen and two ternary mixtures consisting of helium, nitrogen, methane and hydrogen, nitrogen, methane, respectively. A circulating system employing a throttling valve was used to measure the Joule-Thomson effects. These coefficients were compared with predicted Joule-Thomson coefficients from several empirical equations of state. The average deviation was found to be 6 percent value.

DEVELOPMENT OF APPARATUS

There are two experimental techniques for the measuring of the Joule-Thomson coefficient.

- (i) Adiabatic method
 - (a) Expansion valve
 - (b) Porous plug with axial flow
 - (c) Porous plug with radial flow.
- (ii) Isothermal method

(i) Adiabatic Method

(a) Expansion Valve:

Joule Thomson (49) performed their initial experiments by measuring the temperature change which accompanies direct expansion through a needle valve. They were unable to obtain reproduceable results in these experiments and quickly abandoned the method in favor of the porous plug.

The difficulties with this method were clarified by the experimental work of Bradley and Hale(47). These difficulties arise from heat flow along the valve exaggerated by the influence of the so-called "Kinetic-Jet" effect, which is associated with the high-velocity gas stream, and they also arise from errors of temperature measurement on the downstream side of the valve, likewise due to the high gas velocity. Because of these difficulties the method was generally abandoned after 1909.

Johnston and co-workers overcame these difficulties with a valve of new design(48) and obtained good results on hydrogen and deuterium down to 64 deg K.

(b) Porous Plug with Axial Flow

The porous plug used by Joule and Thomson, and by most late workers, owes its advantages to the low thermal conductivity of the ceramic material from which it is usually fabricated. The gas (20) flows through capillary pores in the material was paralleled to the axis of the cylinder. This form of porous plug is referred to as "porous plug with axial flow".

The very first attempt made by Joule and Thomson to determine μ experimentally was done in the following way:

An air pump supplied air at pressure ranging from 2 to 5 atmospheres through a coil immersed in a constant-temperature water bath; from the coil outlet, the air passed through a porous resistance and then back to the air pump.

Figure 3 shows the porous plug assembly.

Cotton or silk was enclosed in a ring of rubber and contained between an upper and a lower perforated metal disc. A compression screw was provided in such a way that by varying the density of the silk or wool, varying resistances to flow were obtained. It was assumed that the upstream gas was at a temperature equal to that of the water bath. The water-bath and down stream gas temperature were measured with mercury-in-glass-thermometers

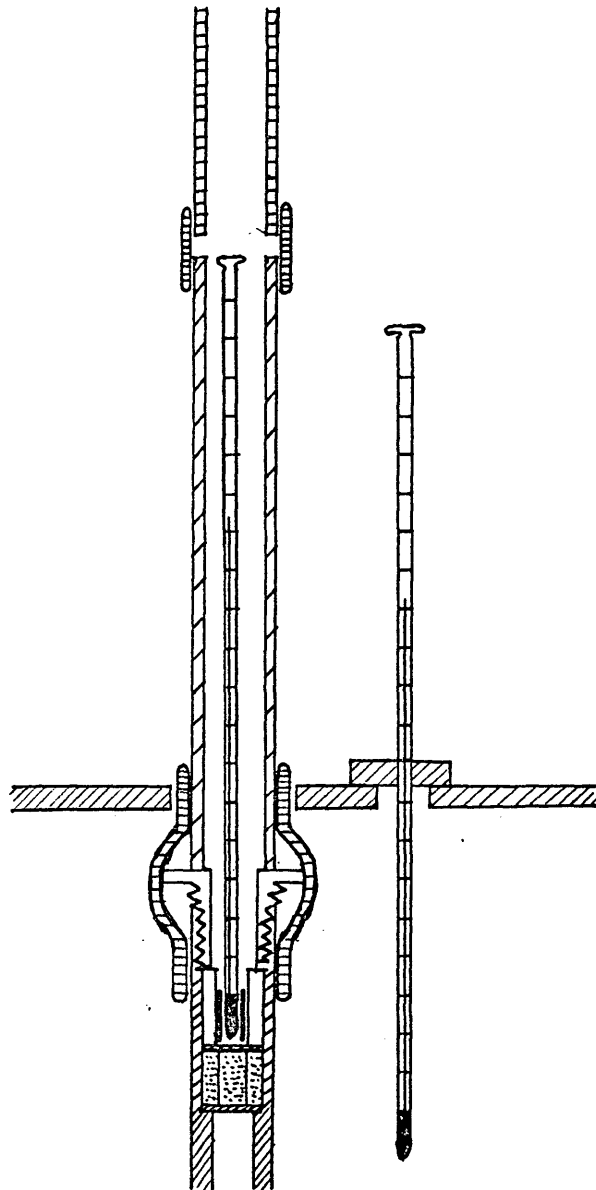


Figure 3. Axial Flow

Some important features of the apparatus shown in figure (3) are:

(1) The down stream portion of the plug-holding device is surrounded by the bath medium. Since the throttled gas and the bath medium are at different temperatures, heat transfer occurs and will produce an effect upon the reading of the downstream thermometer.

(2) Conduction heat transfer can occur along the piping which is external to the bath itself. This heat transfer will also be effective in altering the thermometer reading.

(3) Since the thermometer itself is not located in an isothermal region relative to its bulb, considerable heat transfer may occur along the thermometer stem.

(4) The mass of the thermometer bulb is so large that its thermal capacity is large relative to that of the flowing fluid. Thus considerable time lag in the thermometer reading must exist.

(5) The size of the thermometer bulb is large relative to the area available for fluid flow. Thus some sort of average temperature, as constrained to temperature at a point, was measured.

In presenting the results, Joule and Thomson reported the ratios of finite difference in pressure and temperature.

For example, if P_1 and P_2 represent upstream and downstream pressure, and T_1 and T_2 represents the corresponding temperatures, the value would be

$$\mu = \left(\frac{T_1 - T_2}{P_1 - P_2} \right)_{H} = \left(\frac{\Delta T}{\Delta P} \right)_{H}$$

In this experimental method, Joule and Thomson varied pressure drop across the porous resistance in very small amounts. For sufficiently small pressure changes, one may write:

$$\lim_{\Delta P \rightarrow 0} \left(\frac{\Delta T}{\Delta P} \right)_H = \left(\frac{\partial T}{\partial P} \right)_H$$

However, since a small ΔP results in a small ΔT the accuracy of this method is subject to question, particularly in view of the heat transfer effects and thermal capacity and physical size of the thermometer bulb.

c) RADIAL-FLOW POROUS PLUG

In the ordinary form of porous plug, the flow is continuous and linear; the most serious errors arise from the complicated radiation and conduction losses unavoidably involved with any temperature gradient between the points at which the temperature are measured.

Burnett(7) suggested an experimental arrangement in which these errors are minimized by the use of a RADIAL FLUID FLOW. The accompanying radial temperature gradient is generally free from all detrimental heat interchange.

A brief description of its equipment follows.

The fluid being tested is brought to any desired initial temperature, and maintained there by passing through a coil immersed in a bath controlled by a suitable thermostat. After passing through the coil its temperature is measured by a thermometer immersed in the fluid; under these conditions the thermometer, the fluid and walls being continuously at the same

temperature, radiation and conduction errors are avoided.

The next part of the apparatus which may be described as the Radial Flow portion constitutes the essential improvement. It is situated in the bath but thermally insulated from it.

Figures 4 and 5 represent diagrammatically the principal features of the expansion chamber. In the porous plug form this consists of a round-ended porous tube of suitable non-conducting material (usually porcelain). The fluid is let toward the outer surface of these non-conducting tubes, flows radially through them, gathers within, and is led away through a passage preferably insulated from the bath. The second temperature is measured within the porous tube by a thermometer whose stem is thus protected by the outflowing fluid.

Two cases are to be distinguished, first when the fluid passes through the porous partition with a rise, and second with a fall of temperature. In the first case, the conduction of heat by the porous walls is opposed to the flow of fluid and only very small flows would be necessary to completely offset this minute conduction; as a consequence, both outer and inner surfaces of the plug would be exactly at the temperature of the fluid, and thus both radiation and conduction losses would be entirely avoided. In the second case, the conduction takes place in the same direction as the flow, but conduction from the outside can carry heat only from the fluid entering to the fluid leaving the walls and therefore cannot influence the thermometer readings. Its total effect will be to shift slightly the temperature of

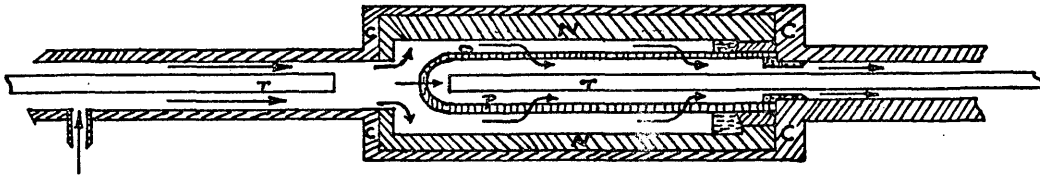


Figure 4

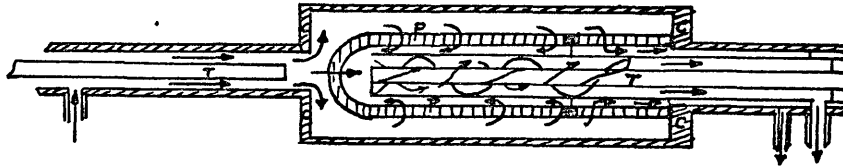


Figure 5

Radial Flow

plug surfaces from that of the passing fluid, and so might give rise to appreciable radiation errors. The minute conductivity of porous material and the intimate contact of the fluid with the wall render this error negligible in most cases. Insulation of the porous tube from its container in the bath by suitable non-conducting materials and confining the fluid flow to the region adjacent to the porous wall, will minimize any possible radiation loss from the plug. In both cases the support of the porous tube should be arranged to prevent radiation to or from the second thermometer. The effect of axial conduction along the porous wall from its support is without influence on the second thermometer reading because the fluid which passes close to the support does not come in contact with the bulb of the thermometer. In a guard-ring two independent concentric plugs are employed. If, in the steady state, both plugs are giving similar results, it is sure that the inner plug is not subject to any thermal leakage from outside. It is easy to distribute thermometer coils in the various places where difference temperatures are to be expected, and so test the uniformity of temperatures throughout the apparatus; and such differential measurement may give a very high degree of sensitiveness.

(ii) Isothermal Method

The weak point of the original method seems to lie in the fact that the passage through the plug was not strictly adiabatic.

Buckingham(6) suggested that adiabatic passage should be made isothermal. Instead of the fall of temperature we then have to

measure the energy which must be supplied to keep the temperature from falling. It means that effects of heat leakage could be eliminated by supplying a measured electrical heat input to the porous plug. This would be made exactly sufficient to offset the Joule-Thomson cooling; that is, the process would be isothermal and the isothermal coefficient, C_T , would be obtained directly.

As a further precaution, we may also use the guard-ring principle. That the arrangement of the flow into the concentric paths would contribute toward a reduction in heat leakage.

The fundamental equation of the plug experiment performed in a manner, outlined above, assumes a particularly simple form:

Let V , P and E be the specific volume, the pressure and the specific internal energy of the gas, before the passage through the plug; and let V' , P' , and E' be the corresponding values after the passage. Let ϕ be the energy supplied per unit mass of gas to keep the process isothermal when the fall of pressure is δP . For a finite fall of pressure we shall then have

$$E' = E + PV - P'V' + \int_{P'}^P \phi dP$$

or for an infinitesimal fall of pressure

$$\delta E = -\delta(PV) - \phi \delta P$$

Let T represent the absolute temperature, and η the entropy of unit mass, we have, for any reversible change of state,

$$\delta E = T\delta\eta - P\delta V$$

The passage through the plug is not reversible, but since E and

η are functions only of the coordinates which define the instantaneous state of the system, the change of entropy and energy of the mass of gas are the same as if the process had been reversible. We may apply the formulae for reversible processes to the case in hand equating the two values of δE , we have

$$\delta(PV) - \phi\delta P = -T\delta\eta + P\delta V$$

$$-T\delta\eta = V\delta P - \phi\delta P$$

$$-T \left(\frac{\partial\eta}{\partial P}\right)_T = V - \phi$$

Since we know the following thermodynamics relation

$$\left(\frac{\partial\eta}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

Whence, by comparison with the last equation, we obtain

$$T \left(\frac{\partial V}{\partial T}\right)_P = V - \phi$$

$$\text{or } \log \frac{T_2}{T_1} = \int_{V_1}^{V_2} \frac{\delta V}{V - \phi}$$

where T_2 and T_1 are absolute temperatures.

We have thus a relation between the absolute temperature and the temperature measured by a constant pressure thermometer filled with the gas under investigation. It will be noted that neither j (Joule equivalent) nor C_p enters into this equation, their place being taken by λ , the measured value of which depends upon the electrical units.

This method is not applicable to any gas above its inversion temperature.

CALCULATION OF THE JOULE-THOMSON COEFFICIENT

Joule-Thomson coefficients can be computed with the use of empirical equations of state and by generalized function based on critical constants.

1) Empirical Equations of State

The chore of expressing and differentiating data can be greatly simplified through the use of an equations of state that will accurately represent the data. To obtain an accurate calculation of the Joule-Thomson coefficients requires an extremely accurate representation of P-V-T data by the equation of state.

There are several equations of state out of which Beattie-Bridgman, Benedict-Webb-Rubin and Redlich-Kwong equations are briefly discussed here. Selection was based on the accuracy of prediction as a function of the number of arbitrary constants in the equation of state.

a) Beattie-Bridgman Equation:

Beattie and Bridgman(50) proposed a five-constants equation of state, whose constants were not derivable from the critical constants alone. The P-V-T data of the substance must be available, to obtain these constants and the stagewise procedure to obtain these constants has been outlined in the literature(51).

The state expression in a form explicit to pressure and substituted in the thermodynamic function for heat capacity and the Joule-Thomson coefficient is given as follows(37)

EXPRESSIONS FOR HEAT CAPACITY AND THE JOULE-THOMSON COEFFICIENTBeattie-Bridgman

$$P = \frac{RT}{V} + \frac{B_0 RT}{V^2} - \frac{B_0 b RT}{V^3} - \frac{cR}{V^2 T^2} - \frac{B_0 c R}{V^3 T^2} + \frac{B_0 bc R}{V^4 T^2} - \frac{A_0}{V^2} + \frac{A_0 a}{V^3}$$

$$c_P = c_P^0 - R + \frac{6cR}{VT^3} + \frac{3B_0 c R}{V^2 T^3} - \frac{2B_0 bc R}{V^3 T^3}$$

$$+ \frac{\frac{R}{V} + \frac{B_0 R}{V^2} - \frac{B_0 b R}{V^3} + \frac{2cR}{V^2 T^3} + \frac{2B_0 c R}{V^3 T^3} - \frac{2B_0 bc R}{V^4 T^3}}{\frac{R}{V^2} + \frac{2B_0 R}{V^3} - \frac{3B_0 b R}{V^4} - \frac{2cR}{V^3 T^3} - \frac{3B_0 c R}{V^4 T^3} + \frac{4B_0 bc R}{V^5 T^3} - \frac{2A_0}{V^3 T} + \frac{3A_0 a}{V^4 T}}$$

$$\mu_{c_P} = \frac{B_0 RT - \frac{2B_0 b RT}{V} - \frac{4cR}{T^2} - \frac{5B_0 c R}{VT^2} + \frac{6B_0 bc R}{V^2 T^2} - 2A_0 + \frac{3A_0 a}{V}}{-RT - \frac{2B_0 RT}{V} + \frac{3B_0 b RT}{V^2} + \frac{2cR}{VT^2} + \frac{3B_0 c R}{V^2 T^2} - \frac{4B_0 bc R}{V^3 T^2} + \frac{2A_0}{V} - \frac{3A_0 a}{V^2}}$$

b) Benedict-Webb-Rubin Equation:

Benedict-Webb-Rubin (52) proposed an 8-constant equation of state, which was developed by considering the properties of hydrocarbons; this equation is traditionally associated with these compounds. However this can be applied to non-hydrocarbons as well. A large amount of accurate data is required to evaluate the eight B-W-R constants. Values of these constants are available in the literature(53). The expression for heat capacity and the Joule-Thomson coefficient is given as follows(37).

EXPRESSIONS FOR HEAT CAPACITY AND THE JOULE-THOMSON COEFFICIENTBenedict-Webb-Rubin

$$P = \frac{RT}{V} + \frac{B_0 RT}{V^2} - \frac{A_0}{V^2} - \frac{C_0}{V^2 T^\beta} + \frac{bRT}{V^3} - \frac{a}{V^3} + \frac{a\lambda}{V^6} + \frac{c}{V^3 T^2} + \frac{c\gamma}{V^5 T^2} \exp(-\gamma/V^2)$$

$$c_P = c_P^0 - R + \frac{\beta(\beta+1)C_0}{V(T)^{\beta+1}} - \frac{6c}{\gamma T^3} + \frac{6c}{\gamma T^3} + \frac{3c}{V^2 T^3} \exp \frac{-\gamma}{V^2}$$

$$+ \frac{R/V + \frac{B_0 R}{V^2} + \frac{bR}{V^3} + \frac{\beta C_0}{V^2 T^{\beta+1}} - \frac{2c}{V^3 T^3} - \frac{2c\gamma}{V^5 T^3} \exp\left(\frac{-\gamma}{V^2}\right)^2}{\frac{R}{V^2} + \frac{2B_0 R}{V^3} - \frac{2A_0}{TV^3} - \frac{2C_0}{V^3 T^{\beta+1}} + \frac{3bR}{V^4} - \frac{3a}{TV^4} + \frac{6a\lambda}{TV^7} + \frac{3c}{V^4 T^3} + \frac{3c\gamma}{V^6 T^3} - \frac{2c\gamma^2}{V^8 T^3} \exp(-\gamma/V^2)}$$

$$\mu_{c_P} = \frac{B_0 RT - 2A_0 - \frac{2C_0}{T^\beta} - \frac{\beta C_0}{T^\beta} + \frac{2bRT}{V} - \frac{3a}{V} + \frac{6a\lambda}{V^4} + \frac{5c}{VT^2} + \frac{5c\gamma}{V^3 T^2} - \frac{2c\gamma^2}{V^5 T^2} \exp\left(\frac{-\gamma}{V^2}\right)}{-RT - \frac{2B_0 RT}{V} + \frac{2A_0}{V} + \frac{2C_0}{VT^\beta} - \frac{3bRT}{V^2} + \frac{3a}{V^2} - \frac{6a\lambda}{V^5} - \frac{3c}{V^2 T^2} + \frac{3c\gamma}{V^4 T^2} - \frac{2c\gamma^2}{V^6 T^2} \exp\left(\frac{-\gamma}{V^2}\right)}$$

c) Redlich-Kwong Equation

Redlich and Kwong(54) published a two-constant equation of state based on several theoretical and practical considerations. The equation is rather empirical in nature, and no rigorous justification can be made in its presentation.

The equation is

$$P = \frac{RT}{v - b} - \frac{a}{T^{0.5}v(v+b)}$$

where the constants are

$$a = 0.4278 R^2 T_c^{2.5} / P_c$$

$$b = 0.0867 RT_c / P_c$$

Shah and Thodos(55) compared this equation with thirteen other equations, for the representation of PVT properties of argon and n-butane. Their findings indicate that this relatively simple equation was found to be outstanding and possesses a combination of advantages in simplicity and accuracy over wide ranges of temperature and pressure.

Expression for heat capacity and the Joule-Thomson coefficient is as follows(37).

EXPRESSIONS FOR HEAT CAPACITY AND THE JOULE-THOMSON COEFFICIENTRedlich-Kwong

$$P = \frac{RT}{V-b} - \frac{a}{T^{0.5}V(V+b)}$$

$$c_p = c_p^o - R + \frac{0.75a}{T^{1.5}b} \ln\left(\frac{V+b}{V}\right) - T \frac{R}{V-b} + \frac{0.5a}{T^{1.5}(V+b)V} \\ - \frac{RT}{(V-b)^2} + \frac{2a}{T^{0.5}(V+b)^2V} + \frac{ab}{T^{0.5}V^2(V+b)^2}$$

$$\mu_{c_p} = \frac{-\frac{RT}{V-b} - \frac{0.5a}{T^{0.5}(V+b)V} + \frac{RTV}{(V-b)^2} - \frac{2a}{T^{0.5}(V+b)^2} - \frac{ab}{T^{0.5}(V+b)^2V}}{-\frac{RT}{(V-b)^2} + \frac{2a}{T^{0.5}(V+b)^2V} + \frac{ab}{T^{0.5}V^2(V+b)^2}}$$

2) Correlation Employing Reduced Properties
Based on Critical Constants

The only generalized correlation for the Joule-Thomson coefficient is that of Edmister. In a discussion of this correlation for C_p and Joule Thomson coefficient and to see how it was developed, it is necessary to form an equation showing the isothermal effect of pressure on C_p . A knowledge of the acentric factor is also required for this purpose.

a) Effect of Pressure on C_p

When heat is added at constant pressure, the heat(14,II) absorbed is equal to the increase in the enthalpy.

$$C_p = \left(\frac{\delta H}{\delta T} \right)_P \quad \dots\dots(1)$$

By the second law, $dQ = TdS$ $\dots\dots(2)$ for a reversible process

When heat flows between two systems of different temperatures, the process is reversible more nearly as the temperature difference is smaller. If a system with heat

capacity C , (14, III) absorbs heat from a reservoir of infinitesimally higher temperatures and thus rises through the temperature interval dT so that

$$dQ = cdT \dots (3)$$

In combination with (2)

$$dS = CdT/T \dots (4)$$

Since entropy is a property, and heating occurs either at constant volume or at constant pressure,

$$dS = C_v dT/T; \text{ or}$$

$$\left(\frac{\delta S}{\delta T}\right)_P = C_p/T \quad (5)$$

On combination with (1) and (5)

$$\left(\frac{\delta S}{\delta T}\right)_P = C_p/T = 1/T \left(\frac{\delta H}{\delta T}\right)_P$$

Differentiating with respect to P gives the following relationship:

$$\frac{\delta^2 S}{\delta T \delta P} = \frac{1}{T} \left(\frac{\delta C_p}{\delta P}\right)_T = \frac{1}{T} \frac{\delta^2 H}{\delta T \delta P} \quad (6)$$

By the first law of thermodynamics

$$dE = TdS - pdV \dots (7)$$

The equation for the enthalpy

$$dH = dE + pdV + v dP \dots (8)$$

On combination of this equation with (7)

$$dH = TdS + v dP \dots (9)$$

When this equation (9) is divided through by dP and the temperature is kept constant

$$v = -T \left(\frac{\delta S}{\delta P}\right)_T + \left(\frac{\delta H}{\delta P}\right)_T \quad (10)$$

on differentiation with respect to temperature with pressure constant

$$\left(\frac{\delta V}{\delta T}\right)_P = -T \frac{\delta^2 S}{\delta P \delta T} - \left(\frac{\delta S}{\delta P}\right)_T + \frac{\delta^2 H}{\delta P \delta T}$$

.....(11)

Therefore from Equation (6)

$$\left(\frac{\delta S}{\delta P}\right)_T = -\left(\frac{\delta V}{\delta T}\right)_P$$

.....(12)

The isothermal effect of pressure on C_p may be obtained by differentiating equation (12) with respect to temperature with pressure constant:

$$\frac{\delta^2 S}{\delta P \delta T} = -\left(\frac{\delta^2 V}{\delta T^2}\right)_P$$

.....(13)

On combination of (13) & (6)

$$\left(\frac{\delta C_p}{\delta P}\right)_T = -T \left(\frac{\delta^2 V}{\delta T^2}\right)_P$$

.....(14)

This equation is very useful in computing the effect of pressure on the heat capacity.

For the expression of this equation in terms of residual volume, the compressibility factor is defined as

$$Z = \frac{PV}{RT} \quad \dots\dots(15)$$

and the "Residual Volume" is the difference between the ideal and actual gas volume and is denoted by α (14,xi) where α is function of P and T.

then

$$\alpha = \frac{RT}{P} - V \quad \dots\dots(16)$$

The first derivative of volume with respect to temperature with pressure constant is found by differentiating equation (15) and (16) giving:

$$\left(\frac{\delta V}{\delta T}\right)_P = \frac{ZR}{P} + \frac{RT}{P} \left(\frac{\delta Z}{\delta T}\right)_P \quad \dots\dots(17)$$

and

$$\left(\frac{\delta V}{\delta T}\right)_P = \frac{R}{P} - \left(\frac{\delta \alpha}{\delta T}\right)_P \quad \dots\dots(18)$$

The second derivative of volume with respect to T, with pressure constant is found by differentiating equation 17 and 18, giving

$$\left(\frac{\delta^2 V}{\delta T^2}\right)_P = \frac{2R}{P} \left(\frac{\delta Z}{\delta T}\right)_P + \frac{RT}{P} \left(\frac{\delta^2 Z}{\delta T^2}\right)_P \quad \dots\dots(19)$$

$$\left(\frac{\delta^2 V}{\delta T^2}\right)_P = -\left(\frac{\delta^2 \alpha}{\delta T^2}\right)_P \quad \dots\dots(20)$$

The isothermal effect of pressure on the heat capacity at constant pressure can be found by combining 14,19,2

$$\left(\frac{\delta C_p}{\delta P}\right)_T = -\frac{2RT}{P} \left(\frac{\delta z}{\delta T}\right)_P - \frac{RT^2}{P} \left(\frac{\delta^2 z}{\delta T^2}\right)_P$$

....(21)

and

$$\left(\frac{\delta C_p}{\delta P}\right)_T = T \left(\frac{\delta^2 \alpha}{\delta T^2}\right)$$

....(22)

For the value of C_p at any conditions, equation (21) and (22) must be integrated from the ideal gas(zero pressure) state.

In terms of reduced conditions

$$\left(\frac{\partial C_p}{\partial P_r}\right)_{T_r} = \frac{P_c \alpha_c}{T_c} T_r \left(\frac{\partial^2 \alpha_r}{\partial T_r^2}\right)_{P_r}$$

....(23)

This equation is more convenient for the isothermal effect of pressure on C_p .

The generalized thermodynamic functions evaluated for (14,xii) the vapor phase for specific heat is given as follows:

$$C_p = C_p^0 + \Delta C_p$$

....(23A)

where

$$\Delta C_p = \frac{P_c \alpha_c T_r}{T_c} \int_0^{P_r} \left(\frac{\partial^2 \alpha_r}{\partial T_r^2}\right)_{P_r} dP_r$$

.....from (23)

$$C_p^0 = \text{Sp. heat at } P = 0 \text{ (ideal gas state heat capacity)}$$

and

$$\frac{P_c \alpha_c}{T_c} = K_2 \quad \alpha_c = \text{(critical residual volume)}$$

where K_2 , a function of critical conditions, determines the dimension of ΔC_p .

The units of K_2 are usually Btu/lb^oF. Values of K_2 have been calculated to be 1.44 for all gases(14) Therefore the equation for Δc_p becomes

$$\Delta C_p = 1.44 \int_0^{P_r} \left(\frac{\partial^2 \alpha_r}{\partial T_r^2} \right)_{P_r} dP_r \dots(24)$$

where ΔC_p is the isothermal pressure correction to C_p in Btu/lb mole deg R.

Edmister(14,xiii) has developed a graph, showing the generalized isothermal pressure correction to heat capacity at constant pressure. The coordinates are $\frac{\Delta c_p}{K_2}$ and P_r with T_r as a parameter.

Since the numerical value of K_2 is already known, Δc_p can be directly calculated.

The caluves of C_p are then calculated by the relation (23A)

b) Acentric Factor

Pitzer and his coworkers(21,26) have worked on improving the accuracy of the most familiar equation of state the ideal gas law. The ideal gas law is applicable only within a limited range of pressure and temperature.

The ideal gas law and corresponding states theory produced the following relation: $PV = ZRT$, where Z = compressibility factor.

When computed values of Z are plotted as a function of T_r and P_r , it is found that the values of Z for most gases fall almost on the same curve.

$$PV/RT = f(P_r, T_r) \dots(B) \text{ where } f \text{ is a universal function.}$$

Z is correlated with the two variables T_r and P_r , which in turn depends upon T_c and P_c .

T_c characterizes the intermolecular interaction energy, and P_c characterizes the intermolecular distance.

This relation (B) works very well for simple fluids such as inert gases, but for more complex molecules it does not work well.

Pitzer, et al (26) have introduced a third parameter (w), called the acentric factor, which measures the deviation of the intermolecular potential from that of a simple fluid. This third parameter is required because the intermolecular force in complex molecules is a sum of interactions between various parts of the molecules and not just their centre hence, the name "acentric factor". The acentric factor is mathematically defined by the reduced vapor pressure at $T_r = 0.7$ as follows.

$$W = \left[\log(P_r^0)_{T_r=0.7} + 1.00 \right]$$

This method of defining 'w' (28) results from the fact that for spherically symmetric molecules (as argon) for value of P_r^0 at a T_r of 0.7 is very nearly 0.1; thus 'w' is zero.

The reduced vapor pressure is almost precisely 0.1 at a reduced temperature of 0.7. This point is well removed from the critical yet above the melting point for almost all substances. Consequently, it is convenient to take 0.7 as our standard value of reduced temperature for the determination of the acentric factor.

The slope of the vapor pressure curve is of course related to the entropy of vaporization. Thus the acentric factor may be regarded as a measure of the increase in the entropy of vaporization over that of a simple fluid.

The acentric factor depends upon the core radius of a globular molecule, the length of an elongated molecule, or the dipole moment of a slightly polar molecule.

With the use of this parameter, the equation of state becomes

$$Z = PV/RT = f(T_r, P_r, w)$$

By expanding the compressibility factor function as a power series in the acentric factor.

$$Z = Z^0 + wZ^1 + w^2Z^2 \dots \dots \dots (b)$$

where

Z^0 = compressibility factor for simple fluid.

Z^1 = compressibility factor correction for deviation from simple fluid.

Both Z^0 and Z^1 are functions of T_r and P_r .

In the almost all regions the first two terms in equation (b) are sufficient. The quadratic term $z^{(2)}$ was evaluated for the small region in which it appeared to be significant. The resulting values of Z^2 showed such irregular behaviour as functions of T_r and P_r that the validity becomes doubtful. Consequently, no values of Z^2 are reported and equation (b) is

$$Z = Z^0 + wZ^1 \dots \dots \dots (b)$$

Pitzer, Lippmann and others (26) plotted the values of Z^1 and Z^0 as function of T_r and P_r .

Values of w for different important gases are given(53) below.

| <u>Substance</u> | <u>w</u> |
|------------------|----------|
| Methane | 0.0104 |
| Ethane | 0.0986 |
| Propane | 0.1524 |
| n-Butane | 0.2010 |
| i-Butane | 0.1848 |
| n-Pentane | 0.2539 |
| i-Hexane | 0.2825 |
| i-Pentane | 0.2223 |
| n-Hexane | 0.3007 |
| n-Heptane | 0.3498 |
| Ethylene | 0.0868 |
| Propylene | 0.1405 |
| i-Butylene | 0.1951 |
| Benzene | 0.2125 |
| Ammonia | 0.2550 |
| Argon | -0.0180 |
| CO ₂ | 0.2310 |
| Helium | |
| Nitrogen | 0.0450 |
| Freon-12 | 0.2030 |
| Hydrogen | |

By applying T_c, P_c , and the atmospheric boiling point, Edmister(28) has devised a way for finding 'w' where the required vapor pressure data are not available.

A plot of $\log P_r$ versus reciprocal T_r is almost a straight line.

$$\log Pr^0 = m(1 - 1/Tr)$$

$$\text{where } m = \frac{\log (pc/14.7)}{T_c/T_B - 1} \quad T_B = \text{atm. B.P.}$$

on Combination of these equation with equation (C),

$$w = \frac{3}{7} \left(\frac{\log(P_c/14.7)}{T_c/T_B - 1.0} \right) - 1.0$$

c) Edmister Correlation for C_p

The isothermal effect of pressure (as described before equation 23A) on the heat capacity is defined as follows:

$$C_p = \Delta C_p + C_p^0$$

With the introduction of acentric factor C_p can be determined more accurately and in a simple manner. According to Edmister(15) it may be evaluated from derivative eompressibility factors.

The compressibility factor is defined as $Z = PV/RT$ and is correlated in terms of the reduced parameter T_R , P_R and 'w'. From these correlations it is possible to estimate a value of Z for most gases under a given set of conditions.

For the determination of isothermal variations in the common energy funations, the derivatives $\left. \frac{\partial V}{\partial T} \right|_P$ and $\left. \frac{\partial V}{\partial P} \right|_T$ are then required. By defining two new factors (29) Z_p and Z_T .

$$Z_p = Z - P_R (\partial Z / \partial P_R)_{T_R} \quad (25)$$

$$Z_T = Z + T_R (\partial Z / \partial T_R)_{P_R} \quad (26)$$

$$\left(\frac{\partial V}{\partial T} \right)_P = \frac{\partial}{\partial T} (2RT/P)_P = \frac{RZ_T}{P} \quad \text{From 25. \& 26.} \quad (27)$$

$$\left(\frac{\partial V}{\partial P} \right)_T = \frac{\partial}{\partial P} (ZRT/P) = - \frac{RT}{P^2} Z_p \quad (28)$$

Equations (27) and (28) may be used to calculate derivative functions after Z_p and Z_T values are obtained.

In determining the relation of Z_p and Z_t to reduced properties, Pitzer(26) correlated Z also with T_r and P_r and used the acentric factor as a third parameter. He also prepared tables, for the calculation of Z_p and Z_T .

Pitzer also showed that for molecules that are not strongly polar Z is also linearly related to "w" for each T_r and P_r .

$$Z = Z^{(0)} + wZ^{(1)} \dots \dots \dots (29)$$

where Z^0 is the value of Z for non associating unimolecular gases and

$$Z^{(1)} = \left(\frac{\partial Z}{\partial w} \right)_{T_r, P_r}$$

Both Z^0 and Z^1 have been published as tabulated functions of T_r and P_r (26,28).

In terms of the new parameter(29) $Z_T = Z_T^{(0)} + wZ_T^{(1)} \dots (30)$

where

$$Z_T^{(0)} = Z^{(0)} + T_r \left(\frac{\partial Z^{(0)}}{\partial T_r} \right) P_r$$

$$Z_T^{(1)} = Z^{(1)} + T_r \left(\frac{\partial Z^{(1)}}{\partial T_r} \right) P_r$$

and

$$Z_p = Z_p^{(0)} + wZ_p^{(1)}$$

where

$$Z_p^{(0)} = Z^{(0)} - P_r \left(\frac{\partial Z^{(0)}}{\partial P_r} \right) T_r$$

$$Z_p^{(1)} = Z^{(1)} - P_r \left(\frac{\partial Z^{(1)}}{\partial P_r} \right) T_r$$

Again from the equations, which Edmister derived in terms of residual volume.

$$\Delta C_p = \frac{P_c \alpha_c}{T_c} T_r \int_0^{P_r} \left(\frac{\partial^2 \alpha_r}{\partial T_r^2} \right)_{P_r} dP_r \quad (23)$$

where $\alpha_r \Big|_{P_r} = \frac{RT_r}{P_r} (1-Z) \Big|_{P_r} \quad (31)$

Differentiating with respect to T_r and P_r constant

$$\frac{\partial \alpha_r}{\partial T_r} \Big|_{P_r} = \left[\frac{R}{P_r} - \frac{R}{P_r} \left(T_r \frac{\partial Z}{\partial T_r} + Z \right) \right]_{P_r} \quad (32)$$

Second time differentiating

$$\frac{\partial^2 \alpha_r}{\partial T_r^2} = \left[0 - \frac{R}{P_r} \left(T_r \frac{\partial^2 Z}{\partial T_r^2} + \frac{\partial Z}{\partial T_r} \right) + \frac{\partial Z}{\partial T_r} \right]_{P_r}$$

Since $Z_T = Z + T_r \left(\frac{\partial Z}{\partial T_r} \right)_{P_r}$

Differentiating with respect to T_r

$$\frac{\partial Z_T}{\partial T_r} = \frac{\partial Z}{\partial T_r} + \left[T_r \left(\frac{\partial^2 Z}{\partial T_r^2} \right) + \frac{\partial Z}{\partial T_r} \right]_{P_r} \quad (33)$$

From (32) and (33)

$$\frac{\partial Z_T}{\partial T_r} = - \frac{\partial \alpha_r^2}{\partial T_r^2} \frac{P_r}{R}$$

Therefore equation (23) may be written as

$$\Delta C_p = -R \int_0^{P_r} \frac{T_r}{P_r} \left(\frac{\partial Z_T}{\partial T_r} \right)_{P_r} dP_r \quad \dots\dots\dots(34)$$

In terms of acentric function Δc_p can be expressed as follows:

$$\Delta C_p = \Delta C_p^{(0)} + w \Delta C_p^{(1)} \quad \dots\dots\dots(34A)$$

where $\Delta C_p^{(0)}$ = Heat capacity of normal fluid(ideal gas)
 $\Delta C_p^{(1)}$ = Heat capacity when departed from normal
 fluid(Real gas)

and

$$\Delta C_p^{(0)} = -R \int_0^{P_r} \frac{T_r}{P_r} \left(\frac{\partial Z_T^{(0)}}{\partial T_r} \right)_{P_r} dP_r \quad (35)$$

$$\Delta C_p^{(1)} = -R \int_0^{P_r} \frac{T_r}{P_r} \left(\frac{\partial Z_T^{(1)}}{\partial T_r} \right)_{P_r} dP_r \quad (36)$$

Where $Z_T = Z_T^0 + w Z_T^{(1)} \dots\dots\dots(37)$ in terms of
 acentric factor.

where

$$Z_T = Z + T_r \left(\frac{\partial Z}{\partial T_r} \right)_{P_r} \quad (26)$$

$$Z_T^{(0)} = Z^0 + T_r \left(\frac{\partial Z^{(0)}}{\partial T_r} \right)_{P_r} \quad (38)$$

$$Z_T^{(1)} = Z^{(1)} + T_r \left(\frac{\partial Z^{(1)}}{\partial T_r} \right)_{P_r} \quad (39)$$

In order to determine Z_T from Equation (37) the Pitzer tables were used and the derivatives in (38) and (39) were obtained by graphical techniques.

Values of $Z^{(0)}$, $Z^{(1)}$, $Z_T^{(0)}$ and $Z_T^{(1)}$ have been tabulated in the region T_r 0.8 to 4.0 and P_r 0.1 to 9.0(26,29). This region was selected due to the interesting behaviour near the critical point and covers the area of greatest practical interest. Outside of this region data becomes too sparse to give a good test.

Edmister(15) has prepared graphs correlating the values of equations 35 and 36 ($\Delta c_p^{(0)}$ and $\Delta c_p^{(1)}$) and T_r with parameter P_r and determined the values of C_p as follows:

$$C_p = C_p^{(0)} + \Delta C_p$$

where Δc_p is defined in equation (34A)

d) EDMISTER CORRELATION FOR JOULE THOMSON COEFF.

The general equation for the Joule Thomson effect is

$$\mu = \frac{T(\delta V/\delta T)_P - V}{C_p} = \frac{(\delta H/\delta P)_T}{C_p} \quad (40)$$

A generalized equation of state using the compressibility factor may be written as follows:

$$Z = \frac{PV}{RT} = \frac{P_c V_c}{T_c R} \cdot \frac{P_r V_r}{T_r} \quad (15)$$

The ideal gas volume is RT/P and the actual gas volume V , giving $V = RT/P - \alpha$ (16)

As before from equation (15) and (16)

$$\left(\frac{\delta V}{\delta T}\right)_P = \frac{Z_r}{P} + \frac{RT}{P} \left(\frac{\partial Z}{\partial T}\right)_P \quad \dots(17)$$

$$\left(\frac{\delta V}{\delta T}\right)_P = \frac{R}{P} - \left(\frac{\delta \alpha}{\delta T}\right)_P \quad \dots(18)$$

μ can now be expressed in terms of PVT correlations and the heat capacity, using equation (40) with (15) and (17) or with (16)

and (18) $\mu = \frac{RT^2}{P} \left(\frac{\partial Z}{\partial T} \right)_P$ (41)

and

$$\mu = \frac{\alpha - T(\delta\alpha/\delta T)_P}{C_p} \quad (42)$$

In these two equations for the Joule-Thomson coefficient the terms are evaluated at the P and T condition, involved. Equation (41) may be written in terms of compressibility factor as

$$\mu = \frac{RT_c/P_c \left(\frac{\partial Z}{\partial T_r} \right)_{P_r}}{C_p} \quad (41a)$$

or

$$\mu = \frac{\alpha_c \alpha_r - T_r \left(\frac{\partial \alpha_r}{\partial T_r} \right)_{P_r}}{C_p} \quad (42a)$$

in terms of reduced residual volume

define $P_c \alpha_c / T_c = K_2$

Since $C_p = C_p^0 + \Delta C_p$

μ can be written as

$$\mu = \frac{1.44 \frac{T_c}{P_c} \alpha_r - T_r \left(\frac{\partial \alpha_r}{\partial T_r} \right)_{P_r}}{C_p^0 + \Delta C_p} \quad (43)$$

Equation (43) shows that J.T.C. is a function of two generalized functions:

$$\Delta C_p \quad \text{and} \quad \alpha_r - T_r \left(\frac{\partial \alpha_r}{\partial T_r} \right)_{P_r}$$

One Specific function, C_p^0 , and a characteristic constant, T_c/P_c .

The equation can be written in dimensionless form as follows:-

$$\frac{P_c}{T_c} \mu C_p = 1.44 \alpha_r - T_r \left(\frac{\partial \alpha_r}{\partial T_r} \right)_{P_r} \quad (44)$$

$$\mu = \left(\frac{\partial T}{\partial P} \right)_H = \frac{T(\partial V / \partial T)_{P-V}}{C_p} = - \frac{(\partial H / \partial P)_T}{C_p} \quad (40)$$

$$\text{Since } T \left(\frac{\partial V}{\partial T} \right)_P = \frac{RZ_T}{P}$$

$$V = \frac{ZRT}{P}$$

$$\begin{aligned} \therefore \mu &= T \left(\frac{RZ_T}{P} \right) = \frac{RZ_T}{P} \\ &= \frac{T_r}{P} \frac{(Z_T - Z)}{C_p} \end{aligned}$$

$$\mu C_p = \frac{RT}{P} (Z_T - Z) \quad \text{Multiply both sides by } P_c/T_c$$

$$\frac{P_c}{T_c} (\mu C_p) = \frac{RT}{P} \frac{P_c}{T_c} (Z_T - Z)$$

$$\frac{P_c}{RT_c} (\mu C_p) = \frac{T_r}{P_r} (Z_T - Z) \quad (45)$$

Since Z_T and $Z = f(T_r, P_r, \text{ and } w)$. Therefore, according to Edmister (15) eq. 45 may be written as follows:

$$\frac{P_c}{RT_c} (\mu C_p) = \left[\frac{P_c}{RT_c} (\mu C_p) \right]^{(0)} + w \left[\frac{P_c}{RT_c} (\mu C_p) \right]^{(1)} \quad (46)$$

$$\text{where } \left[\frac{P_c}{RT_c} (\mu C_p) \right]^{(0)} = \frac{T_r}{P_r} (Z_T^{(0)} - Z^{(0)}) \quad (47)$$

$$\text{and } \left[\frac{P_c}{RT_c} (\mu C_p) \right]^{(1)} = \frac{T_r}{P_r} (Z_T^{(1)} - Z^{(1)}) \quad (48)$$

The right hand side of equations (47) and (48) are easily evaluated by combining the derivative compressibility factors of Reid and Valbert (29) with the compressibility factor of Pitzer et. al. (21).

Edmister (15) has prepared graphs correlating the values of $P_c/RT_c(\mu C_p)$ and T_r with parameter P_r for the simple fluid and for the real fluid.

$(P_c/RT_c)(\mu C_p)$ then be found with the relation(46)

C_p can be obtained with the relations discussed previously. The numerical value of μ according to Edmister is then calculated as follows.

$$\mu = \left[\frac{P_c}{RT_c} \mu C_p \right] \left(\frac{R}{C_p} \right) \frac{T_c}{P_c}$$

This is the generalized correlation for the product of the Joule-Thomson coefficient and heat capacity and may be used to predict the Joule-Thomson coefficient of gases and gas mixtures within the following P-T limits.

$$0.1 \leq P_r \leq 9.5$$

$$0.80 \leq T_r \leq 4.0$$

COMPARISON OF CALCULATED VALUES OF THE JOULE
THOMSON COEFFICIENT, THROUGH THE USE OF THE
EDMISTER CORRELATION WITH THE EXPERIMENTAL
AND THEORETICAL VALUES AS REPORTED IN THE
LITERATURE

The Joule Thomson coefficient for the pure components and their mixtures are calculated with the use of the Edmister correlation(15). These values are compared with those of the literature values.

The pressure and temperature range covered by different workers for the determination of μ values of gases and gas mixtures are presented. The data obtained in the common range of temperature and pressure of various workers are compared.

The following section may be divided into three parts.

- (i) Pure gases
- (ii) Pure gas mixtures
- (iii) Quantum gases and their mixtures.

PURE GASES

(i) In this part the predicted values of Joule-Thomson coefficients of different gases based on Edmister correlation were compared with the experimental Joule-Thomson coefficients.
(sample calculation in Appendix 1)

METHANE

The Joule Thomson coefficient data on methane have been determined experimentally, by R.A. Budenholzer, B.H. Sage, and W.N. Lacey(58), four years prior to these measurements John H. Perry and Carl V. Herrmann(24) calculated the Joule-Thomson coefficient with the Beattie and Bridgeman equation of state. Perry covered a greater range of pressure and temperature as shown in Fig 1A.

Fig 1.B represents a comparison of the overlapping data of the experimental measurements with Perry and Herrmann from pressure-volume-temperature measurements.

It is noticed that at the higher pressure the experimentally determined Joule-Thomson coefficient decreases with an increase in pressure, and this effect is more pronounced at the lower temperatures.

The values calculated by Perry and Herrmann are consistently lower than the experimental values except at pressures in the vicinity of atmospheric.

The Joule-Thomson coefficient of methane was obtained from the Edmister(15) correlation and compared with the experimental data in Table 1. The calculated values are in very good agreement with the experimental values.

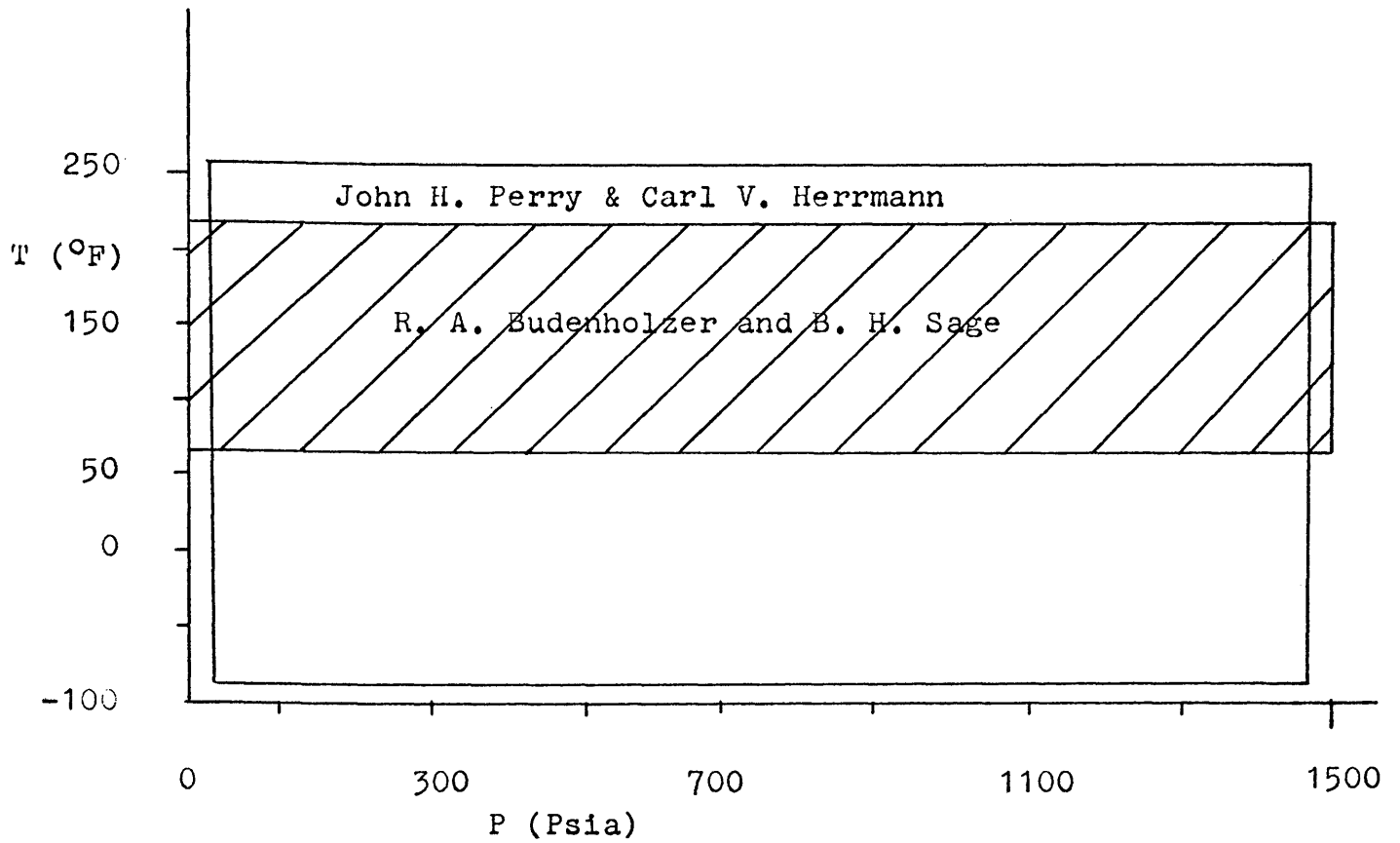


Figure 1A. Pressure-temperature range covered for Joule-Thomson coefficient (Methane).

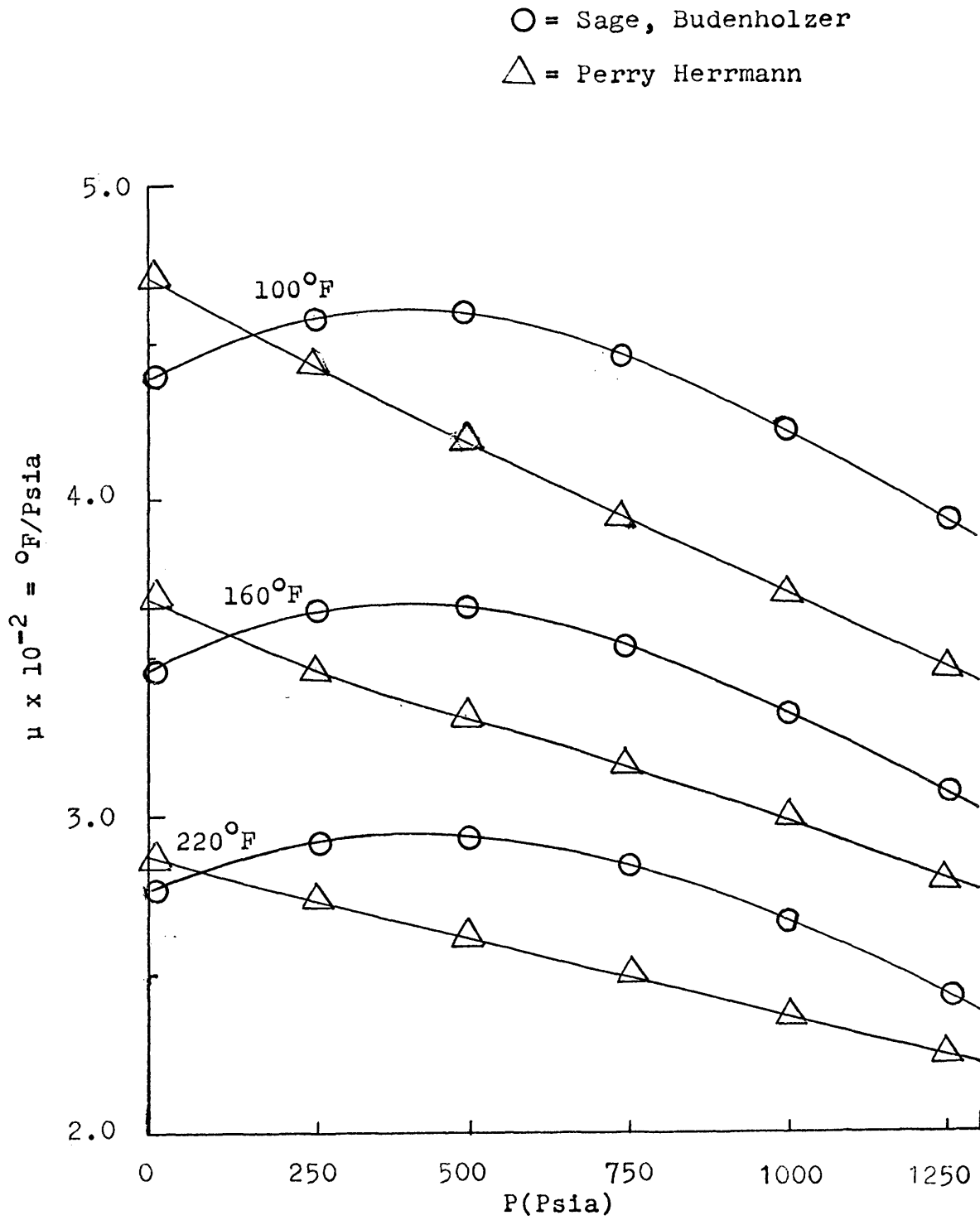


Figure 1B. Comparison of Joule-Thomson Coefficients (Methane).

TABLE NO.1

COMPARISON OF CALCULATED VALUES
OF Methane (APPENDIX I) WITH THE
LITERATURE VALUES (58)

$$\mu = \text{°F/Psia}$$

| P(Psia) | Temp deg F | | | | | |
|---------|------------|--------|--------|--------|--------|-----------------------|
| | 70 | 100 | 130 | 160 | 190 | 220 |
| 0 | | | | | | |
| *0 | 0.0496 | 0.0440 | 0.039 | 0.0347 | 0.0310 | 0.0278 |
| 250 | 0.0501 | | 0.0411 | 0.0361 | | 0.0296 |
| *250 | 0.0520 | 0.0459 | 0.0408 | 0.0365 | 0.0327 | 0.0293 |
| *500 | 0.0520 | 0.0461 | 0.0409 | 0.0366 | 0.0328 | 0.0295 |
| 500 | | 0.0464 | | | 0.0326 | 0.0296 ⁽¹⁾ |
| 750 | 0.0506 | | 0.0394 | 0.0350 | | |
| *750 | 0.0502 | 0.0447 | 0.0397 | 0.0355 | 0.0317 | 0.0285 |
| 1000 | | 0.0426 | | | 0.0294 | 0.0267 |
| *1000 | 0.0477 | 0.0424 | 0.0375 | 0.0333 | 0.0298 | 0.0268 |
| 1250 | | 0.0415 | 0.0340 | | 0.0285 | |
| *1250 | 0.0443 | 0.0394 | 0.0348 | 0.0308 | 0.0278 | 0.0244 |
| 1500 | 0.0403 | 0.0349 | | 0.0273 | | 0.0222 |
| *1500 | 0.0407 | 0.0360 | 0.316 | 0.0280 | 0.0248 | 0.0220 |

* literature values

(1) Appendix 1

ETHANE

Sage, Webster, and Lacey(59) investigated the Joule-Thomson coefficient of Ethane. More recently Alan L. Stockelt(40) determined experimentally the Joule-Thomson data on the same gas. Pressure and temperatures range covered by these two investigators is shown in fig 2A.

Calculated values for the Joule-Thomson coefficient have been obtained from the Edmister correlation and compared with the experimental data of Sage, Webster, and Lacey in Table 2.

From the values in Table 2 it is evident that almost all calculated values agree with the experimental values from 6 to 10%.

Fig 2B represents a comparison of the overlapping data of Sage and Stockelt values.

It is noticed that with an increase in temperature Sage's values decrease rapidly. This effect is slightly more at higher pressure.

Stockelt's values are consistently lower than the Sage's value except at lower temperatures. This is especially true at high pressure. At lower pressure this effect is just opposite.

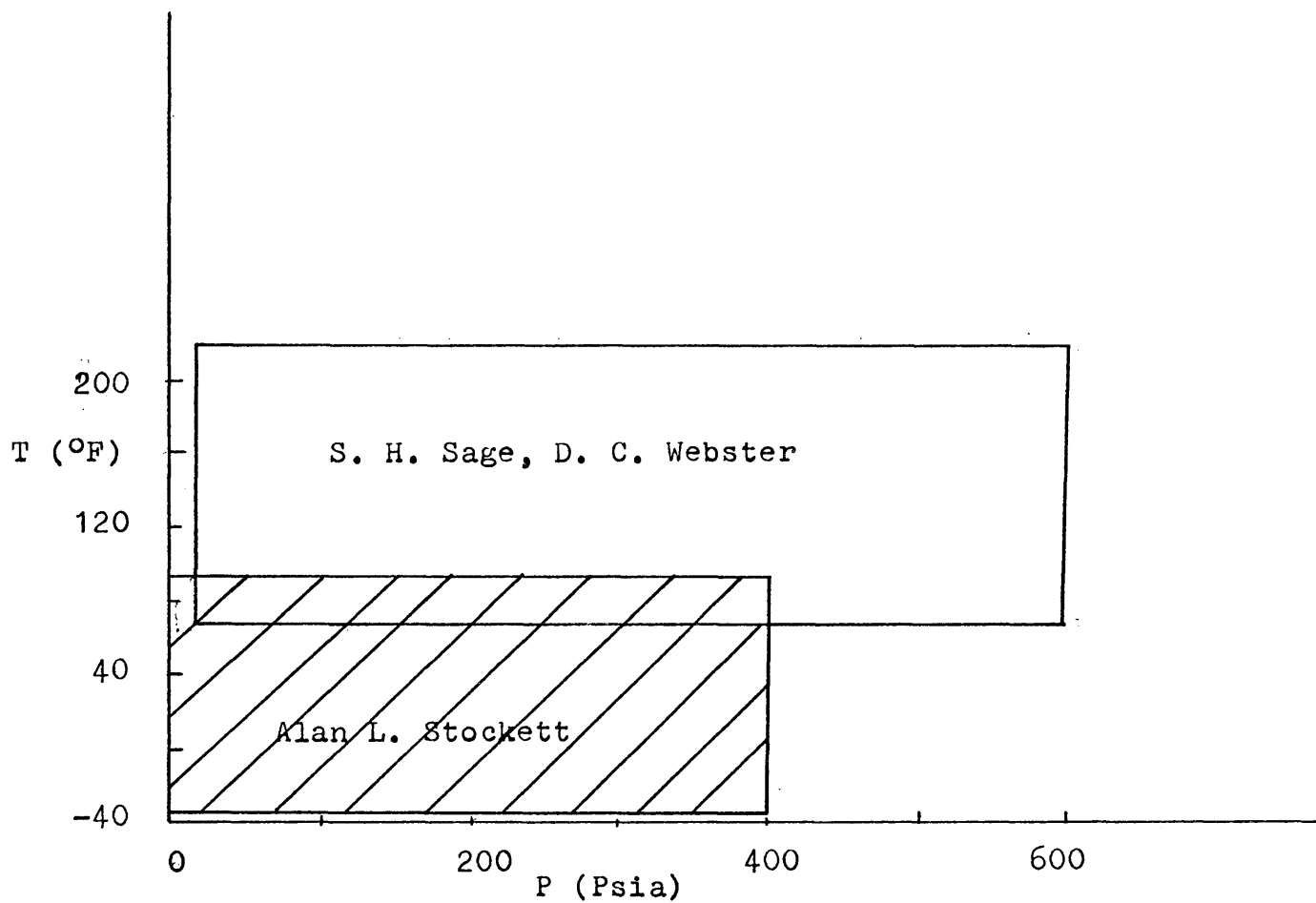


Figure 2A. Pressure-temperature range covered for Joule-Thomson coefficient (Ethane).

TABLE No. 2

COMPARISON OF CALCULATED VALUES OF ETHANE WITH LITERATURE VALUES(59)

$$\mu = \text{ }^{\circ}\text{F}/\text{Psia.}$$

| P/ ^o F | 70 | 100 | 130 | 160 | 190 | 220 |
|-------------------|-------|-------|--------|--------|--------|--------|
| 14.7 Psi. | | | | | | |
| *14.7 | 0.117 | 0.103 | 0.0913 | 0.0812 | 0.0712 | 0.0614 |
| 100 | 0.141 | 0.123 | 0.099 | | | 0.0702 |
| *100 | 0.129 | 0.112 | 0.0983 | 0.0852 | 0.0751 | 0.0640 |
| 200 | 0.155 | | 0.114 | 0.0921 | 0.0793 | |
| *200 | 0.142 | 0.122 | 0.105 | 0.0903 | 0.0782 | 0.0673 |
| 300 | | 0.146 | | 0.0972 | | 0.0726 |
| *300 | 0.158 | 0.132 | 0.112 | 0.0953 | 0.0821 | 0.0712 |
| 400 | | 0.153 | 0.126 | | 0.0863 | |
| *400 | 0.174 | 0.142 | 0.118 | 0.100 | 0.0850 | 0.073 |
| 500 | 0.194 | | | 0.113 | | 0.0742 |
| *500 | 0.190 | 0.152 | 0.124 | 0.104 | 0.0871 | 0.073 |
| 600 | | | 0.135 | | 0.0886 | 0.077 |
| *600 | | 0.162 | 0.130 | 0.106 | 0.0875 | 0.073 |

*Literature values.

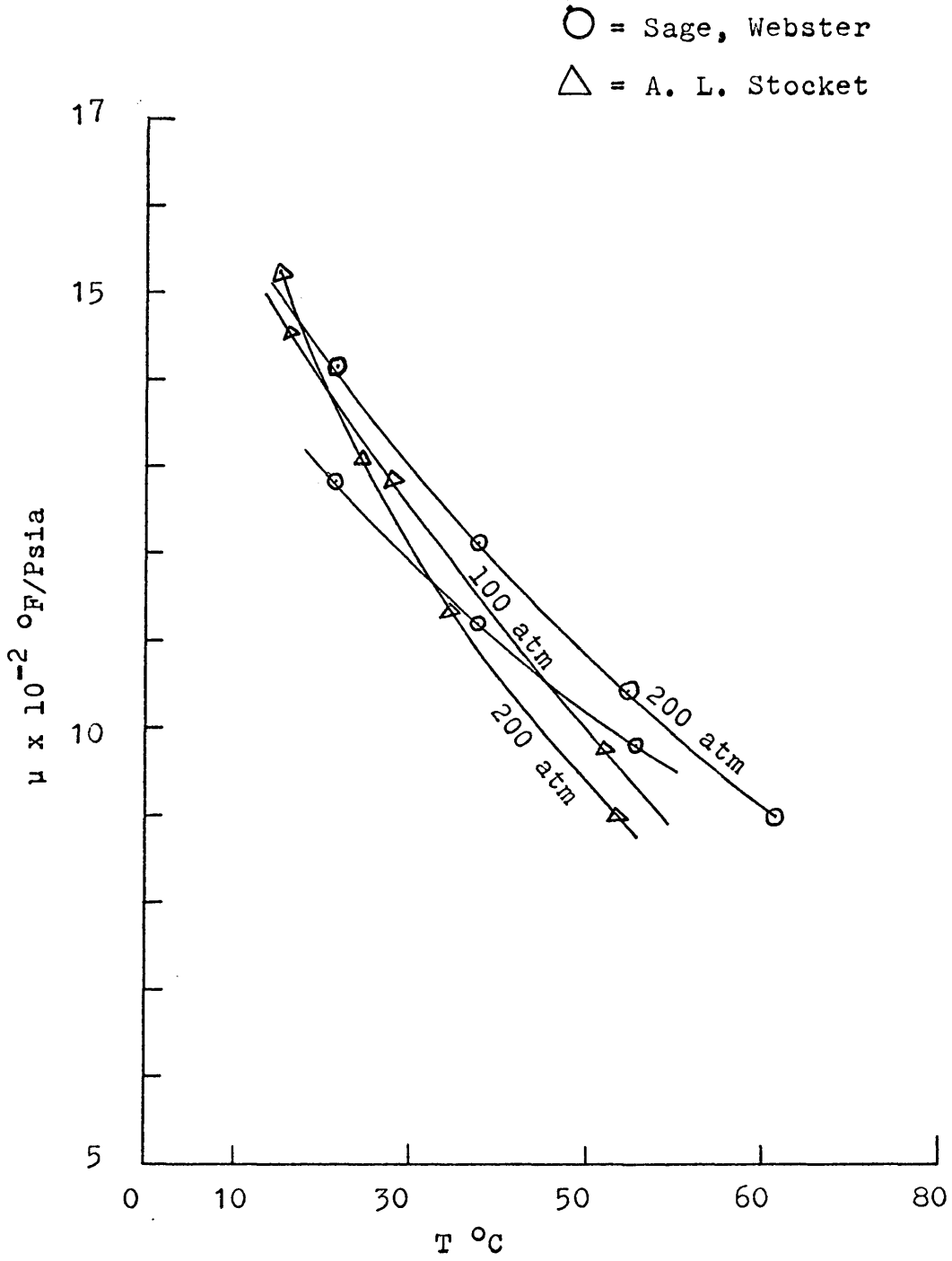


Figure 2B. Comparison of Joule-Thomson Coefficients (Ethane).

PROPANE

B.H. Sage, E.R. Kennedy, and W.N. Lacey(5) measured the Joule-Thomson coefficient of propane. The experimental values are compared with values from the Edmister correlation in Table 3. Pressure and temperature covered in the investigation are shown in fig 3A. Joule-Thomson coefficient at pressure of 50 psia and less could not be compared as at this pressure P_r came out to be less than 0.10, and as mentioned earlier the Edmister correlation does not work for P_r less than 0.1. These are the only data on propane and they are in good agreement.

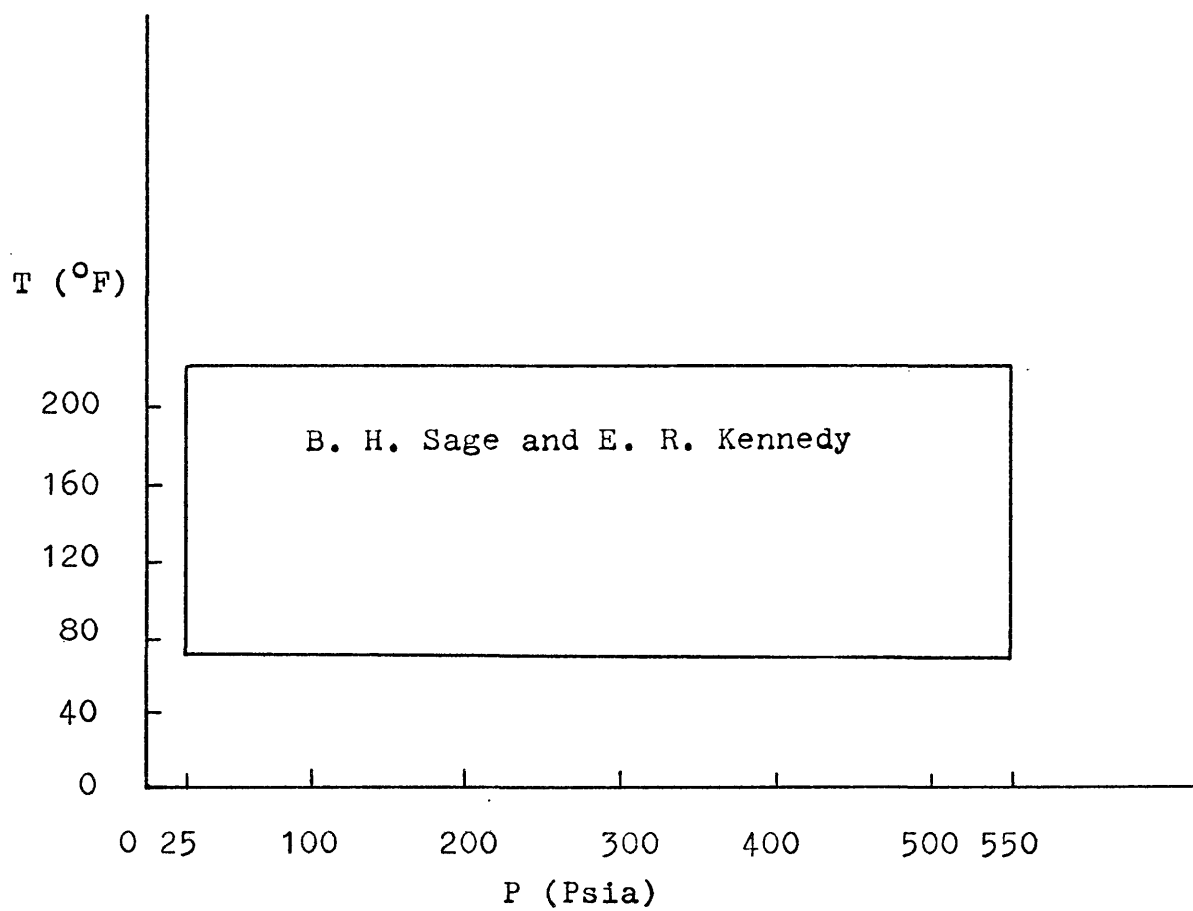


Figure 3A. Pressure-temperature range covered for Joule-Thomson coefficient (Propane).

TABLE No. 3

PROPANE (5)

$$\mu = \text{°F} / \text{Psia.}$$

| P/°F Psia. | 70 | 100 | 130 | 160 | 190 | 220 |
|---------------|--------|--------|--------|--------|--------|--------|
| 25 | | | | | | |
| *25 | 0.2150 | 0.1824 | 0.1542 | 0.1339 | 0.116 | 0.100 |
| 50 | | | | | | |
| *50 | 0.2409 | 0.1995 | 0.1658 | 0.1433 | 0.1232 | 0.1040 |
| 100 | 0.274 | | 0.191 | | | 0.118 |
| *100 | 0.2831 | 0.2242 | 0.1862 | 0.1589 | 0.1340 | 0.1100 |
| 150 | | 0.255 | 0.200 | | 0.1417 | |
| *150 | | 0.2475 | 0.2052 | 0.1732 | 0.1436 | 0.1158 |
| 200 | | | | 0.1871 | | 0.1236 |
| *200 | | | 0.2252 | 0.1853 | 0.1506 | 0.1225 |
| 250 | | | | | 0.150 | |
| *250 | | | 0.2468 | 0.1986 | 0.1575 | 0.1288 |
| 300 | | | | 0.208 | | 0.143 |
| *300 | | | | 0.2152 | 0.1653 | 0.1343 |
| 350 | | | | 0.249 | | |
| *350 | | | | 0.2353 | 0.1735 | 0.1410 |
| 400 | | | | | 0.1825 | 0.153 |
| *400 | | | | | 0.1818 | 0.1458 |
| 450 | | | | | | |
| *450 | | | | | 0.1925 | 0.1500 |
| 550 | | | | | | 0.150 |
| *550 | | | | | | 0.1557 |

* Literature values.

n-BUTANE AND n-PENTANE

B.H. Sage, E.R. Kennedy, and W.N. Lacey (60) investigated the Joule-Thomson coefficient of these two gases. The temperature and pressure range covered for these gases is shown in figs 4A and 5A.

Values determined from the Edmister correlation are compared with the experimental values in Table 4 and Table 5. Agreement is fair for both cases.

In the case of both n-butane and n-pentane numerical values of Joule-Thomson coefficient could not be calculated at pressure of 40 psia and less as Pr came out to be less than 0.1

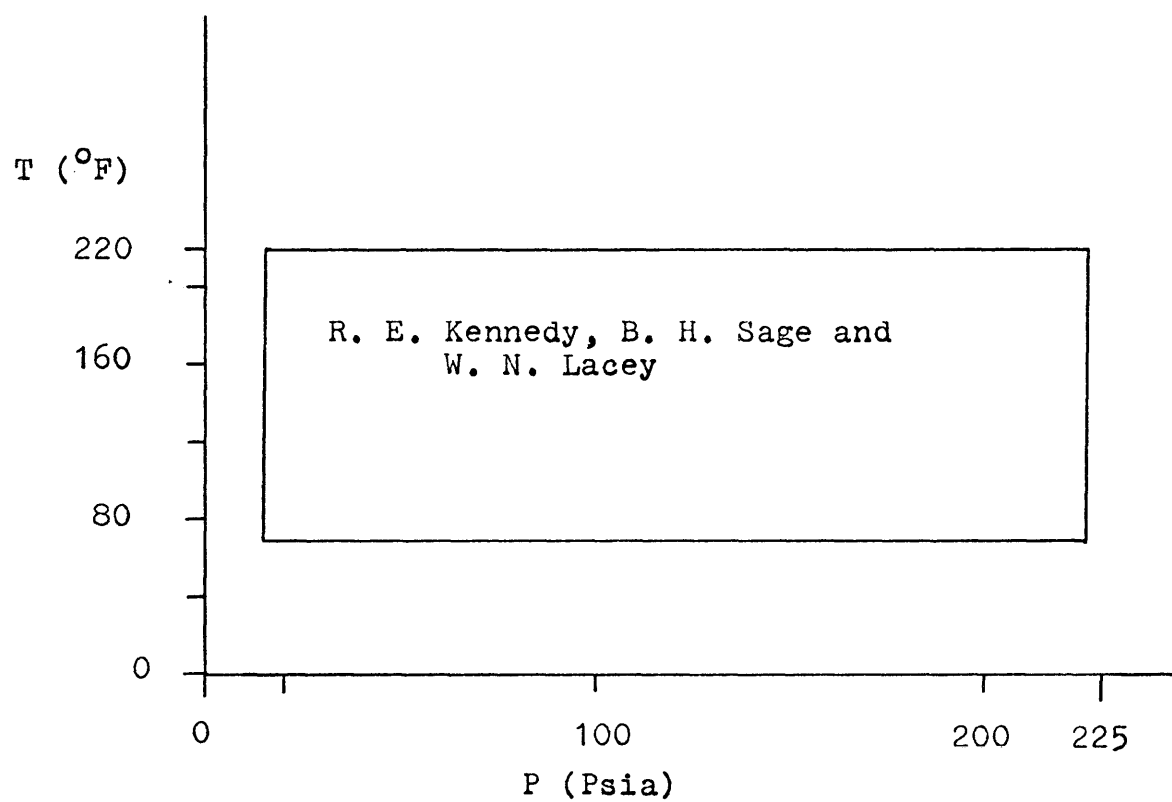


Figure 4A. Pressure-temperature range covered for Joule-Thomson coefficient (N-Butane).

TABLE No. 4

n - BUTANE (60)

 $\mu = \text{°F/Psia.}$

| P/°F Psia. | 70 | 100 | 130 | 160 | 190 | 220 |
|------------|--------|--------|--------|--------|--------|--------|
| | 0.2900 | 0.2343 | 0.1996 | 0.1708 | 0.1430 | 0.1173 |
| 20 | | | | | | |
| *20 | 0.3164 | 0.2486 | 0.2086 | 0.1772 | 0.1472 | 0.1200 |
| 40 | | | | | | |
| *40 | | 0.3012 | 0.2410 | 0.1988 | 0.1634 | 0.1310 |
| 60 | | | 0.2790 | | 0.1690 | 0.160 |
| *60 | | | 0.2706 | 0.2184 | 0.1778 | 0.1412 |
| 80 | | | 0.301 | 0.244 | 0.204 | |
| *80 | | | 0.2954 | 0.2362 | 0.1910 | 0.1512 |
| 100 | | | | 0.248 | | 0.1679 |
| *100 | | | | 0.2526 | 0.2032 | 0.1608 |
| 125 | | | | | 0.225 | |
| *125 | | | | | 0.2176 | 0.1720 |
| 150 | | | | | | 0.1866 |
| *150 | | | | | 0.2330 | 0.1830 |
| 175 | | | | | 0.249 | |
| *175 | | | | | 0.2476 | 0.1947 |
| 200 | | | | | | |
| * 200 | | | | | | 0.2069 |
| 225 | | | | | | 0.2199 |
| * 225 | | | | | | 0.2188 |

* Literature values.

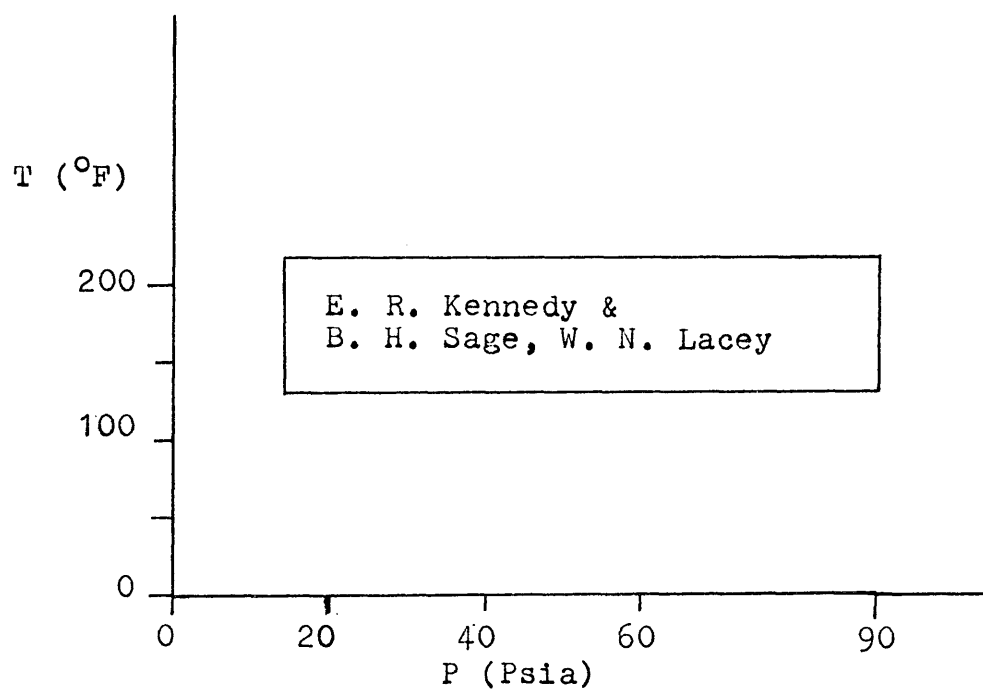


Figure 5A. Pressure-temperature range covered for Joule-Thomson coefficient (N Pentane).

TABLE No. 5

n-PENTANE (60)

 $\mu = ^\circ\text{F}/\text{Psia.}$

| P/ ^o F Psia. | 130 | 160 | 190 | 220 |
|-------------------------|--------|--------|--------|--------|
| Atm. | | | | |
| *Atm. | 0.2838 | 0.2288 | 0.1952 | 0.1720 |
| 20 | | | | |
| *20 | 0.3168 | 0.2470 | 0.2068 | 0.1802 |
| 30 | | | | |
| *30 | | 0.2810 | 0.2284 | 0.1950 |
| 40 | | | | |
| *40 | | 0.3134 | 0.2496 | 0.2090 |
| 50 | | | 0.274 | 0.225 |
| *50 | | | 0.2684 | 0.2214 |
| 60 | | | 0.294 | 0.243 |
| *60 | | | 0.2858 | 0.2328 |
| 70 | | | | 0.240 |
| *70 | | | | 0.2432 |
| 80 | | | | 0.246 |
| *80 | | | | 0.2528 |
| 90 | | | | 0.252 |
| *90 | | | | 0.262 |

* Literature values.

AMMONIA

J.A. Beattie(57) calculated the Joule-Thomson coefficient of ammonia employing the Beattie-Bridgeman equation of State. The pressure and temperature range covered by him for his calculation is shown in fig6. The critical pressure of ammonia gas is 111 atm, therefore only at one point(that is at 10.41 meter of Hg and 110.05°C) μ could be calculated with the Edmister correlations. This value came out to be $1.54^{\circ}\text{C}/\text{meter}$ of Hg against $1.70^{\circ}\text{C}/\text{meter}$ of Hg. as from the equation of state. The deviation is about 10% as shown in the Table 6.

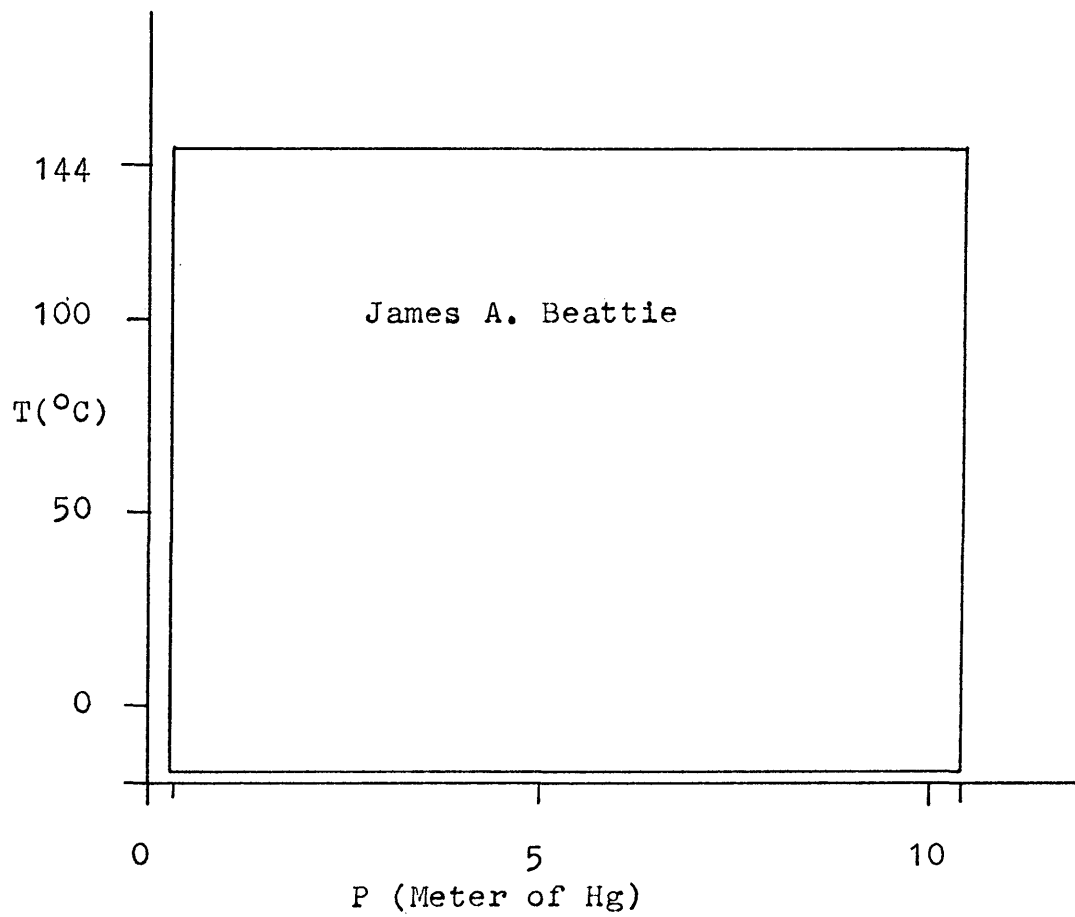


Figure 6. Pressure-temperature range covered for Joule-Thomson coefficients (Ammonia).

Table No.6
 $\mu = \text{°C/meter of Hg.}$
 Ammonia (57)

| P(meter of Hg.) | T(°C) | °C/meter of Hg. |
|--------------------|---------|-----------------|
| 0.392 | -5.0 | 5.392 |
| 0.394 2 | -18.22 | 6.81 |
| 0.752 | +144.95 | 1.25 |
| 1.303 | 52.50 | 2.70 |
| 1.512 | 110.05 | 1.71 |
| 1.513 | 70.05 | 2.41 |
| 1.527 | 30.15 | 3.39 |
| 10.41 | 110.05 | 1.70 |
| *10.41 | 110.05 | 1.54* |

*Calculated values

FREON-12

Freon-12(dichlorodifluoromethane) is a very important chemical for mechanical refrigeration. A. Schmidtke(39) investigated the Joule-Thomson Coefficient of this gas. The temperature and pressure range covered by him is shown in fig.7.

The Edmister correlation could not be applied in the pressure range covered by Schmidtke, as within that pressure range Pr came out to be less than 0.1. However, Schmidtke presented a graph in the same article from which it is possible to read a numerical value of Joule-Thomson coefficient at 52.5 Psia. At this pressure Pr came out to be 0.09. On the assumption that this value is nearly 0.1 the Joule-Thomson coefficient was obtained from the Edmister correlation at the two different temperatures 200F and 300F. The agreement is quite good as shown in table 7.

It is difficult to say anything about the reliability of the data as there are no other data for comparison.

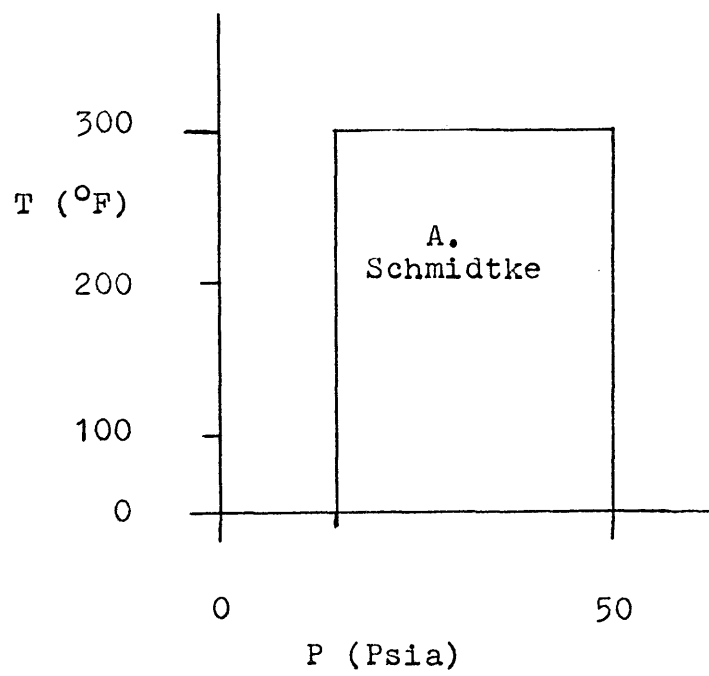


Figure 7. Pressure-temperature range covered for Joule-Thomson coefficient (Freon-12).

Table No.7FREON -12(39)

$$\mu = \text{°F/Psia}$$

| P/T Psia | 100 F | 140 F | 180 F | 200 F | 260 F | 280F | 300 F |
|-------------|-------|-------|-------|-------|-------|-------|--------|
| 15 | 0.144 | 0.112 | 0.092 | 0.088 | 0.082 | 0.080 | 0.077 |
| 25 | 0.194 | 0.158 | 0.138 | 0.133 | 0.120 | 0.117 | 0.112 |
| 35 | 0.213 | 0.181 | 0.162 | 0.157 | 0.143 | 0.139 | 0.135 |
| 50 | 0.229 | 0.198 | 0.183 | 0.177 | 0.168 | 0.164 | 0.160 |
| *52.5Atm | | | | 0.186 | | | *0.168 |
| *52.5Atm | | | | 0.180 | | | 0.160 |

*
calculated value

ETHYLENE

S.R. Degroot and M. Geldermann(10) calculated the Joule-Thomson coefficient of ethylene. They used the published values of C_p and PV as functions of temperature and pressure to calculate μ from the following formula:

$$\mu = \frac{1}{C_p} \left(\frac{\partial V}{\partial T} \right)_P - V$$

The pressure and temperature range covered by them is shown in the fig(8).

The values of the Joule-Thomson coefficient of ethylene were obtained from the Edmister correlation and compared with Degroot and Geldermans' values in Table 8. It is found that upto 200 atm. pressure the agreement is fair, but at higher pressures the deviation goes up to 20 to 35%. Therefore data may not be reliable at higher pressure.

In this case the numerical values of ethylene could not be compared at pressure atmosphere, as at this pressure P_r came out to be less than 0.1

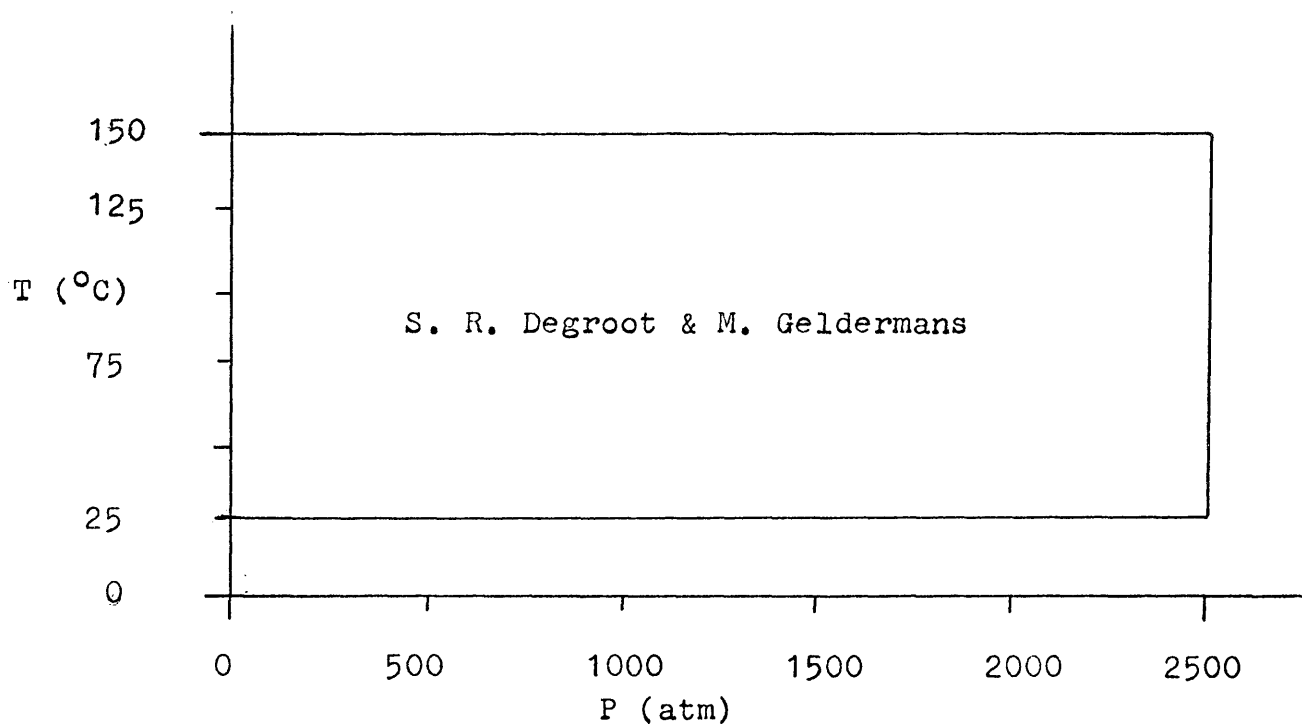


Figure 8. Pressure-temperature range covered for Joule-Thomson coefficients (Ethylene).

Table No.8

ETHYLENE(10) $\mu = ^\circ\text{C}/\text{atm.}$

| P/T atm | 25 C | 50 C | 75 C | 100C | 125 C | 150 C |
|------------|---------|----------|---------|---------|---------|--------|
| *1 | 1.022 | 0.843 | 0.691 | 0.581 | 0.490 | 0.379 |
| 50 | 1.2138 | | | 0.580 | | 0.397 |
| *50 | 1.349 | 0.870 | 0.711 | 0.571 | 0.481 | 0.401 |
| 100 | | 0.435 | | 0.488 | | 0.364 |
| *100 | 0.1832 | 0.426 | 0.533 | 0.470 | 0.412 | 0.355 |
| 200 | 0.0257 | | 0.116 | | 0.190 | 0.20 |
| *200 | 0.0269 | 0.0656 | 0.1119 | 0.1543 | 0.1814 | 0.1811 |
| 300 | -0.0058 | 0.00897 | | 0.0454 | 0.0542 | 0.067 |
| *300 | -0.0078 | 0.00975 | 0.0281 | 0.0473 | 0.0639 | 0.078 |
| 400 | -0.0206 | | -0.0014 | 0.00702 | | 0.0200 |
| *400 | -0.0243 | -0.01273 | -0.0023 | 0.00807 | 0.01819 | 0.0264 |

* literature values.

ARGON

J.R. Roebuck and H. Osterberg(35) determined the Joule-Thomson coefficients of argon.

A. Michels, J.M. Leveet and G.V. Wokers (23) calculated the Joule-Thomson Coefficient by experimental PVT data and covered more range of pressure as shown in fig9. However, the temperature range was only 0 to -140C, whereas Roebuck and Osterberg covered from 300C to -170C.

Figure 9B represents a comparison of the overlapping data of the experimental measurements with Michels measurements. It is noticed that at lower temperatures μ falls very rapidly with the increase of pressure. This effect is more pronounced from 0 to 60-atm. pressure. At higher pressure that is from 100 to 200-atm. this effect is considerably reduced, At higher temperatures (0°C, and -25°C) decrease in μ value is smooth with the rise of pressure.

The values calculated by Michels and co-workers consistently follow the experimental values at higher temperatures and at all pressure, except at 20 atm and 0°C, where the deviation is about 21%. Data are most uncertain at lower temperature (-100 to -125C) and at low pressure (0 to 80 atm.)

The Joule-Thomson coefficients of argon were obtained from the Edmister correlation and compared with the Roebuck and Osterberg data in Table 9. The agreement is good.

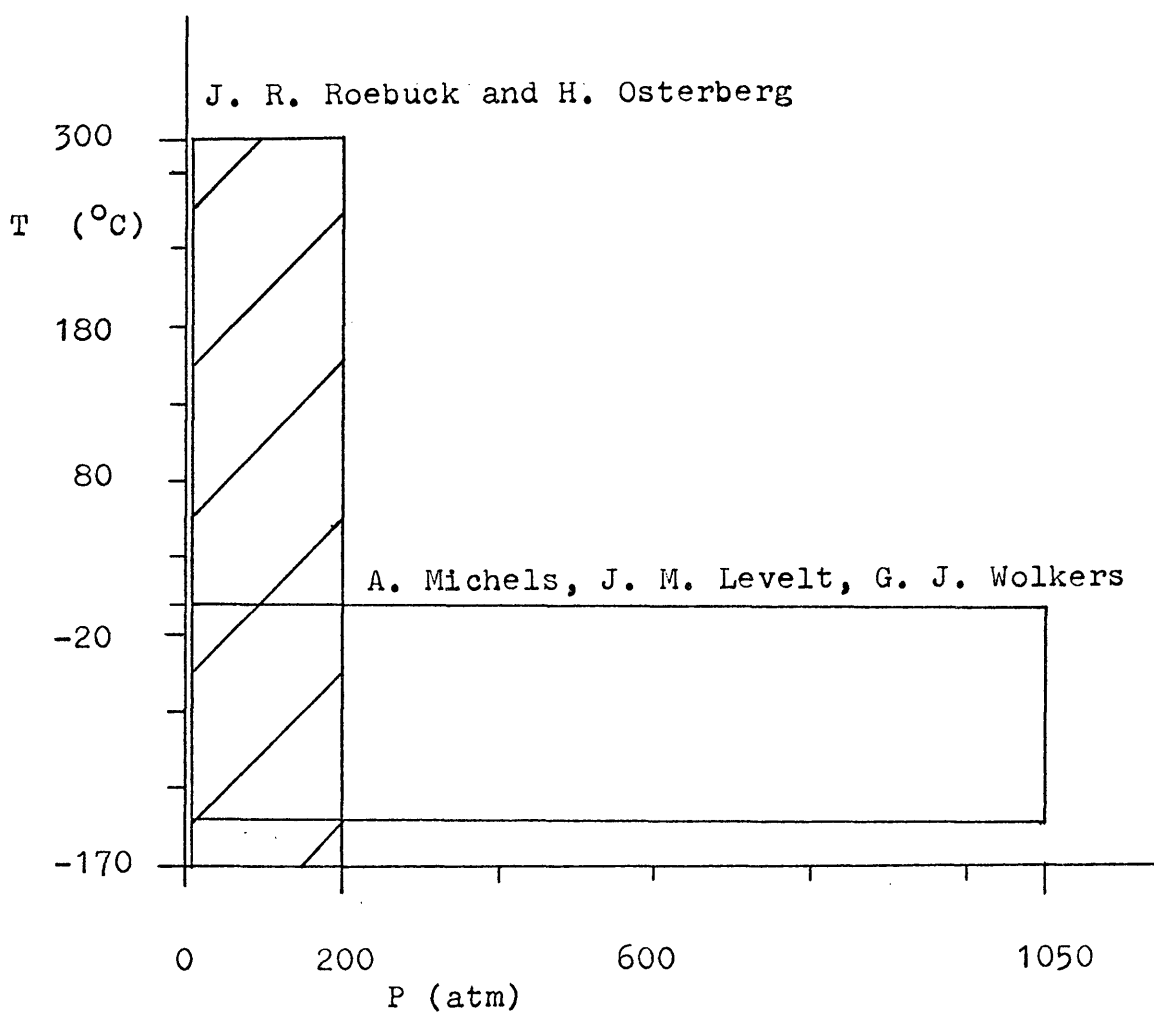


Figure 9. Pressure-temperature range covered for Joule-Thomson coefficients (Argon).

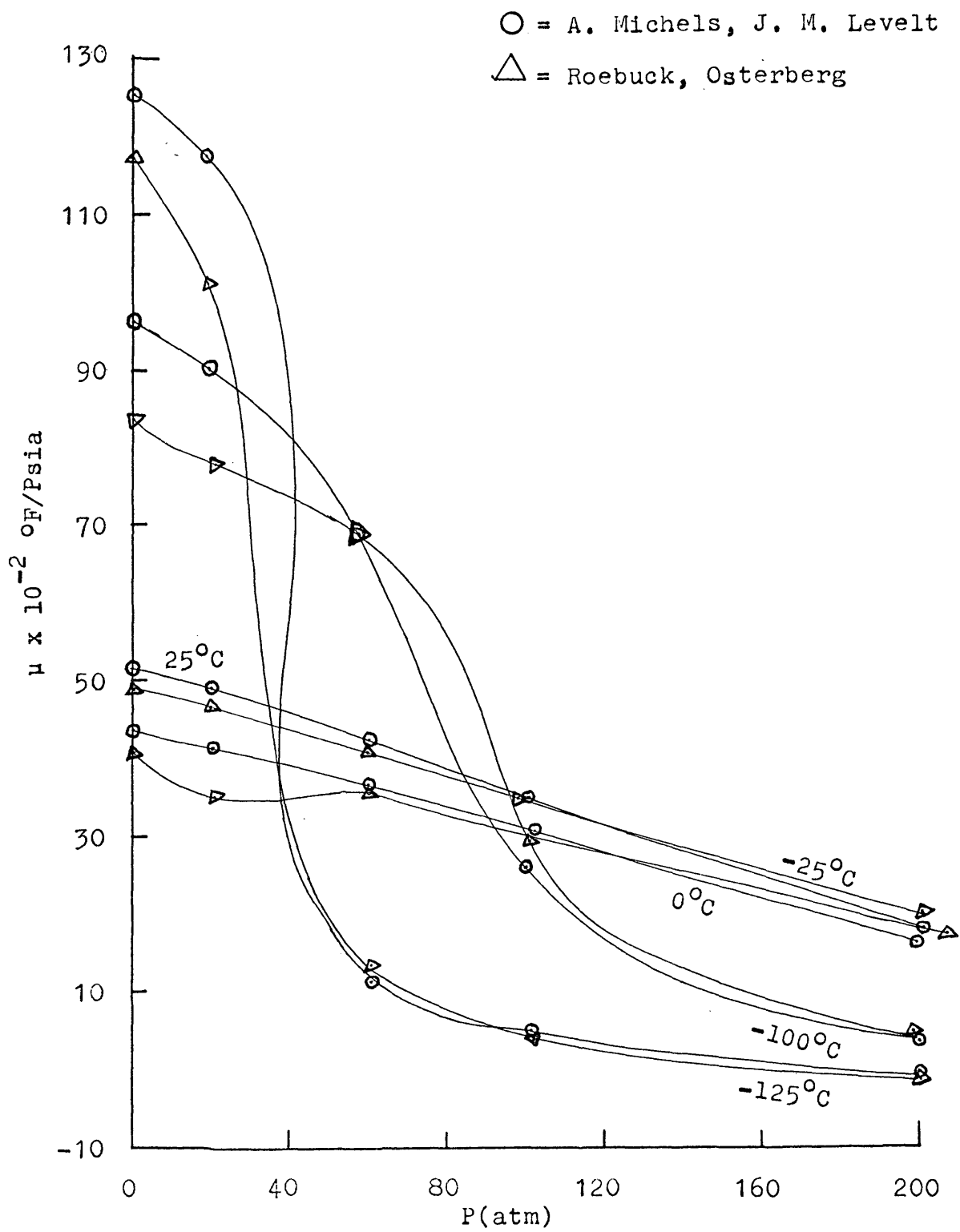


Figure 9B. Comparison of Joule Thomson Coefficients (Argon).

Table No.9

ARGON (35)

 $\mu = ^\circ\text{C}/\text{atm.}$

| P/T atm. | 300C | 200C | 100C | 0C | -50 ^o C | -100 C | -125C |
|-------------|--------|--------|--------|--------|-----------------------|--------|---------|
| *1 | 0.0620 | 0.133 | 0.2340 | 0.4170 | 0.5765 | 0.8335 | 1.0765 |
| 20 | 0.0576 | | | 0.405 | | | 1.136 |
| *20 | 0.0580 | 0.1235 | 0.218 | 0.344 | 0.5450 | 0.7780 | 1.0155 |
| 60 | | 0.115 | | 0.352 | | 0.700 | |
| *60 | 0.0522 | 0.1080 | 0.1927 | 0.3498 | 0.4878 | 0.6810 | 0.1277 |
| 100 | 0.0429 | | 0.168 | | 0.401 | | 0.0439 |
| *100 | 0.0445 | 0.0935 | 0.1715 | 0.2995 | 0.3934 | 0.2970 | 0.0430 |
| 140 | | 0.0818 | | 0.251 | | 0.120 | |
| *140 | 0.0375 | 0.0802 | 0.1480 | 0.2475 | 0.290 | 0.1227 | 0.0077 |
| 180 | | | 0.130 | | 0.220 | | -0.0063 |
| *180 | 0.0319 | 0.0714 | 0.1312 | 0.2048 | 0.2110 | 0.0592 | -0.0058 |
| 200 | 0.0277 | | | 0.1866 | | | -0.0116 |
| *200 | 0.0280 | 0.0680 | 0.1260 | 0.1871 | 0.1877 | 0.0425 | -0.011 |

* literature values

NITROGEN

J.R. Roebuck and H. Osterberg(34) measured the Joule-Thomson coefficient of nitrogen. One year prior to these measurements, John H. Perry and Carl V. Herrmann(24) calculated the Joule-Thomson coefficient with the Beattie and Bridgeman equation of state.

The temperature and pressure range covered by these investigators is shown in the fig10A.

Fig 10B represents a comparison of the overlapping data of the experimental measurements with Perry and Herrmann from pressure volume-temperature measurements.

It is noticed that μ values decrease with the rise of temperatures and this effect is significant at lower temperatures.

The values calculated by Perry and Herrmann follow the experimental values. The deviation in μ values is low at higher temperatures. The data are more reliable at 100 atm. and at all temperatures.

The Joule-Thomson coefficient of nitrogen was obtained from the Edmister correlation and compared with the Roebuck and Osterberg data in Table 10. The agreement is good.

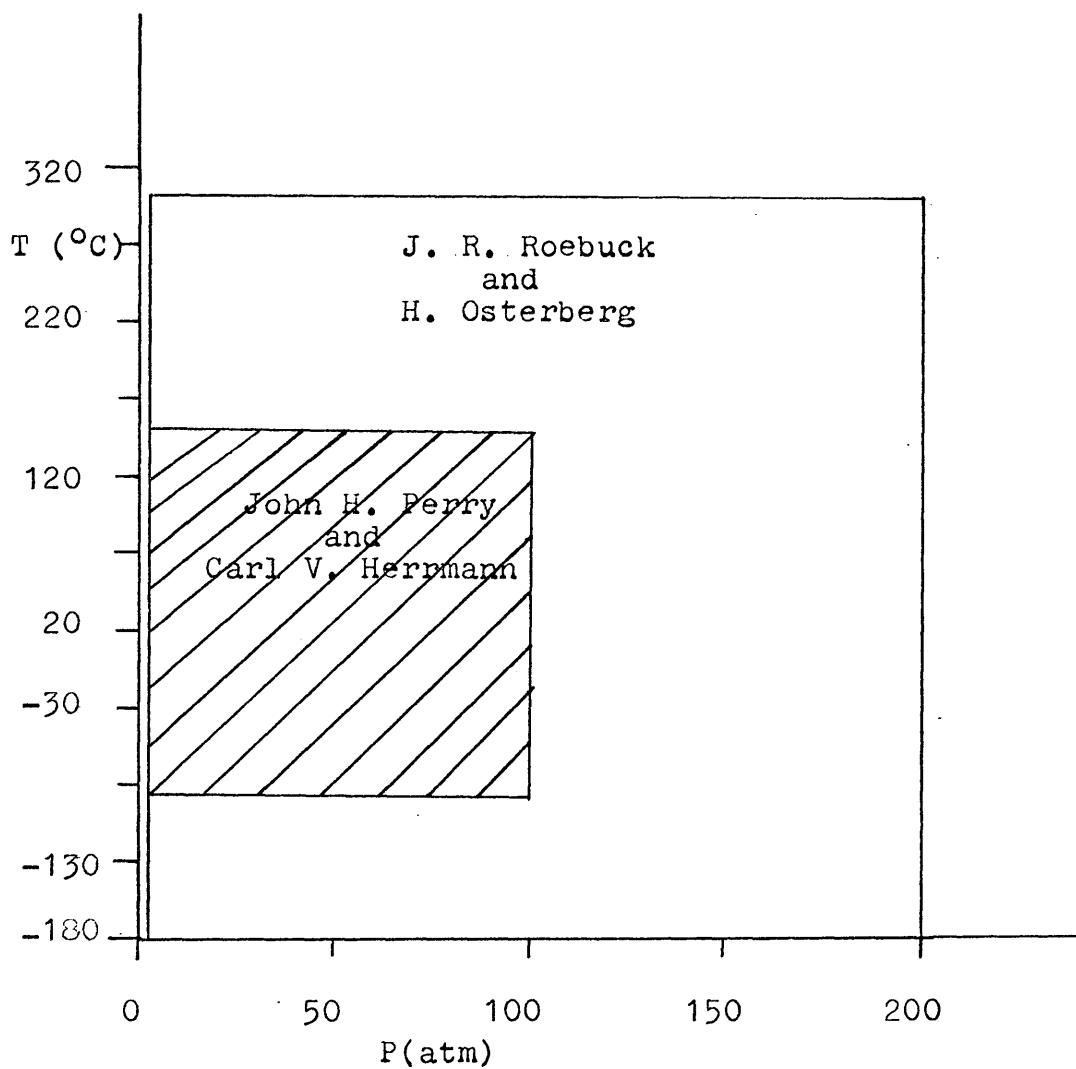


Figure 10A. Pressure-temperature range covered for Joule-Thomson coefficient (Nitrogen).

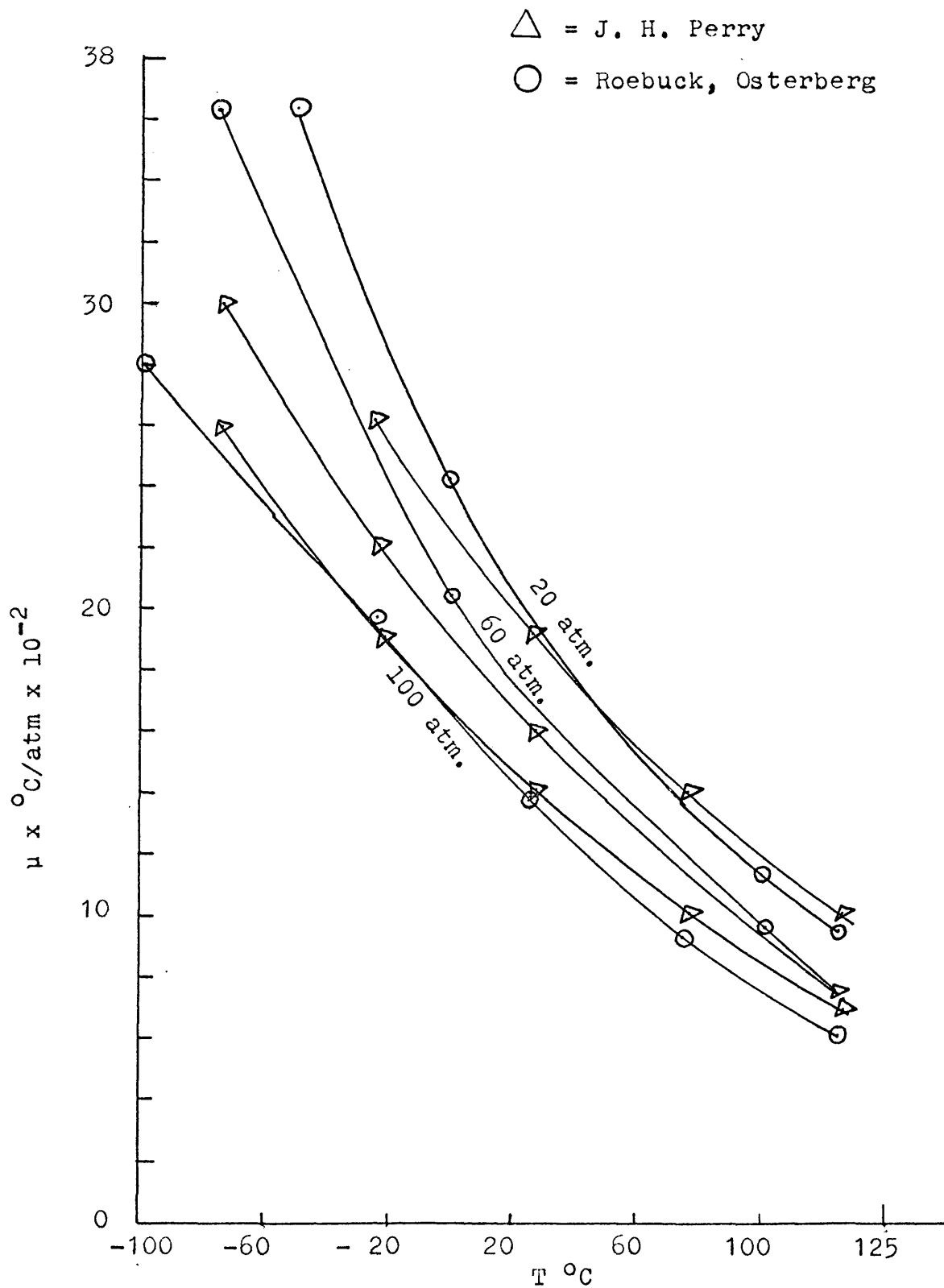


Figure 10B. Comparison of Joule-Thomson Coefficients (Nitrogen).

TABLE NO.10

NITROGEN(34)

$\mu = \text{°C/atm.}$

| P/°C atm. | 200C | 100C | 0C | -100C | -150C |
|--------------|--------|--------|--------|--------|---------|
| 200 | 0.0473 | 0.123 | 0.251 | 0.559 | 1.124 |
| *200 | 0.0460 | 0.114 | 0.242 | 0.5785 | 1.097 |
| 60 | 0.0359 | 0.104 | 0.213 | 0.462 | 0.065 |
| *60 | 0.0365 | 0.0955 | 0.2040 | 0.443 | 0.062 |
| 100 | 0.0272 | 0.0782 | 0.177 | 0.292 | 0.0220 |
| *100 | 0.0260 | 0.076 | 0.1660 | 0.281 | 0.0215 |
| 140 | 0.0161 | 0.063 | 0.140 | 0.151 | -0.0026 |
| *140 | 0.0170 | 0.058 | 0.1310 | 0.142 | -0.0025 |
| 200 | 0.0078 | 0.0427 | 0.102 | 0.059 | -0.0247 |
| *200 | 0.0075 | 0.0415 | 0.09 | 0.062 | -0.0255 |

*LITERATURE VALUES

CARBON DIOXIDE

J.R. Roebuck, T.A. Murrell, and E.E. Miller (30) determined the Joule-Thomson coefficients of Carbon dioxide in 1942. Six years after their investigation S.R. Degroot and A. Michels(9) calculated the carbon dioxide data. The method of their calculation was similar to that of S.R. Degroot and M. Geldermans which they employed for the calculation of Ethylene(10). However, S.R. Degroot and A. Michels used the following equation for the determination of C_p

$$C_p = \left(\frac{\partial H}{\partial T}\right)_P$$

In 1956, Donna Price (27) calculated the Joule Thomson coefficient of Carbon dioxide as follows

$$\mu = \frac{1}{PC_p} \cdot T \left(\frac{\partial(PV)}{\partial T}\right)_P - PV$$

The pressure and temperature range covered ~~for~~ these investigations is shown in fig. 11A.

Fig 11B represents a comparison of the overlapping data of the experimental measurements of Roebuck-Murrell with theoretically determined values of Degroot and Dona Price. It is noticed that at higher pressure, the experimentally determined Joule-Thomson coefficient decreases very sharply with an increase of pressure. This effect is more evident at lower temperatures. The values calculated by Degroot and Donna follow closely the experimental values except at higher temperature and in the vicinity of atmosphere.

The Joule-Thomson coefficient of carbon-dioxide obtained from the Edmister correlation and compared with the experimental data in table 11. These calculated values are in good agreement with the experimental values.

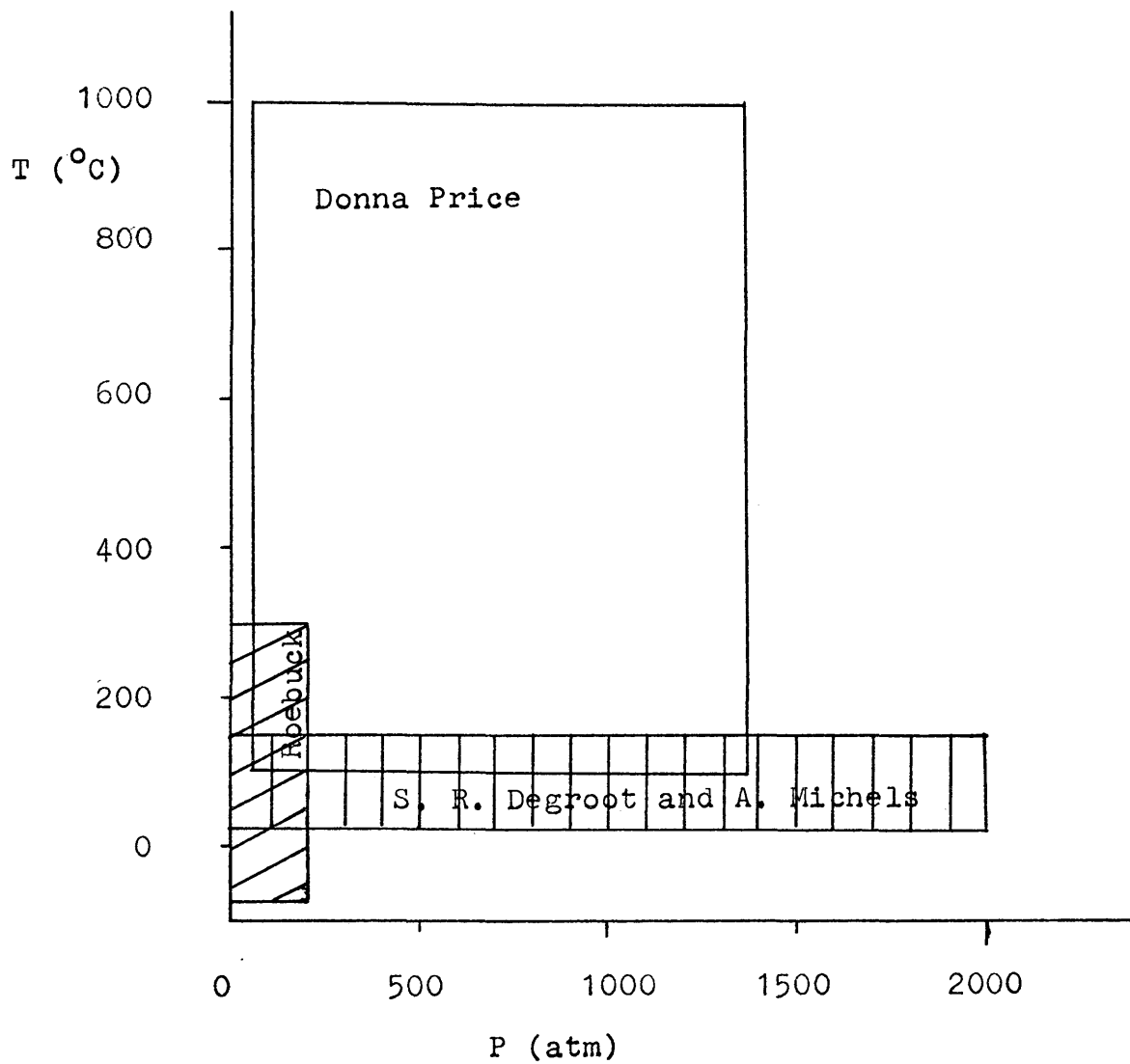


Figure 11A. Pressure-temperature range covered for Joule-Thomson coefficients (Carbon dioxide).

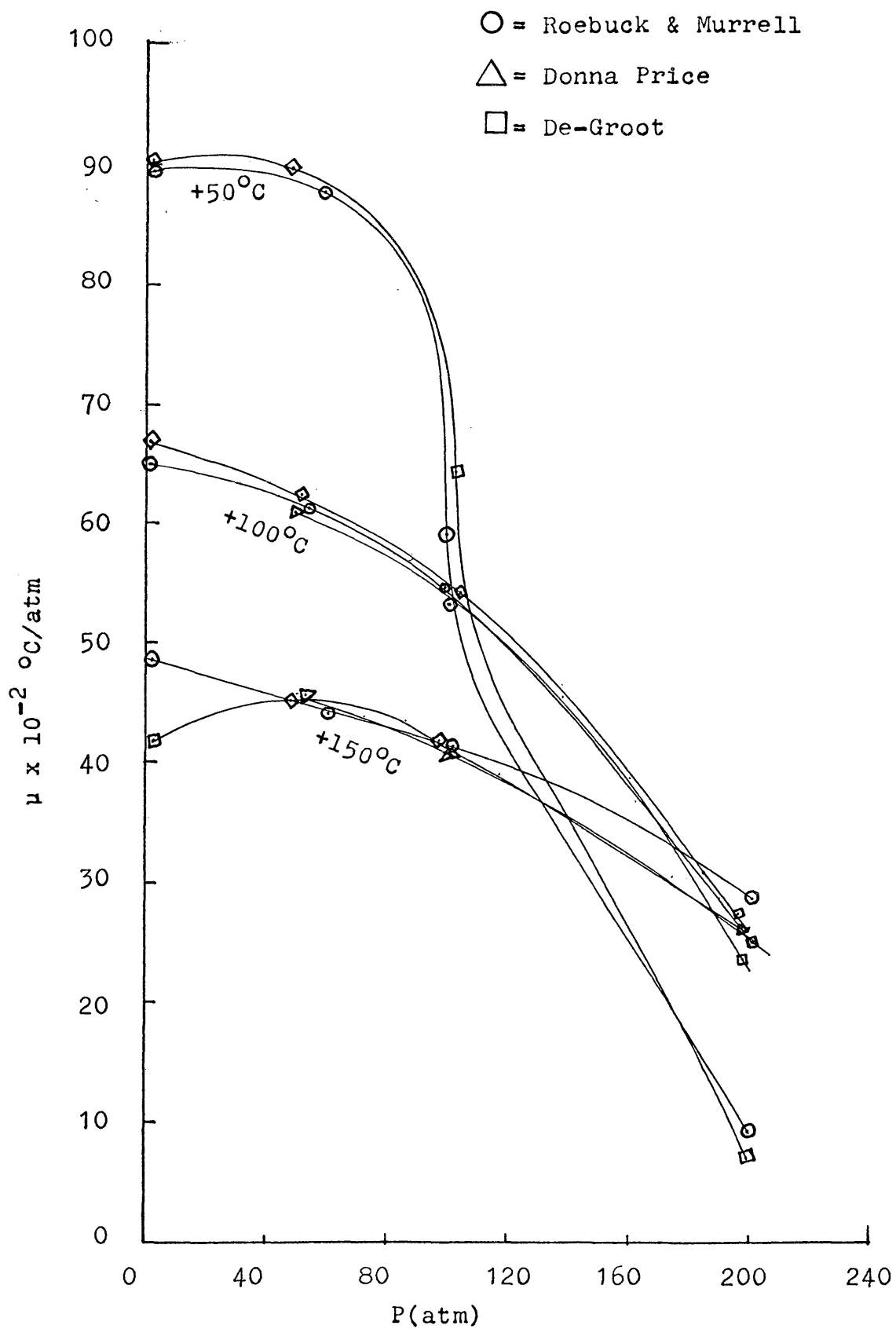


Figure 11B. Comparison of Joule-Thomson Coefficients (Carbon dioxide).

Table No.11

CARBON DIOXIDE (30)

$$\mu = \text{°C/atm.}$$

| P/T | 300 C | 200 C | 100 C | 50 C | 0 C |
|------|--------|--------|--------|--------|---------|
| 20 | 0.2328 | 0.3510 | 0.631 | 0.882 | 1.389 |
| *20 | 0.2425 | 0.3575 | 0.6375 | 0.8950 | 1.402 |
| 60 | 0.212 | 0.352 | 0.618 | 0.89 | 0.038 |
| *60 | 0.2080 | 0.3400 | 0.6080 | 0.88 | 0.037 |
| 100 | 0.193 | 0.3195 | 0.552 | 0.548 | 0.0209 |
| *100 | 0.1872 | 0.3150 | 0.5405 | 0.5570 | 0.0215 |
| 140 | 0.173 | 0.292 | 0.438 | 0.169 | 0.0119 |
| *140 | 0.1700 | 0.2890 | 0.4320 | 0.1720 | 0.0115 |
| 200 | 0.1529 | 0.246 | 0.247 | 0.099 | 0.00449 |
| *200 | 0.1505 | 0.2455 | 0.2555 | 0.093 | 0.0045 |

*literature values

A I R

J.R. Roebuck(36) investigated the Joule-Thomson coefficient of air in 1925. Four years prior to his measurements Frederick G. Keyes (19) presented his own equation of State and at low pressure calculated the data on air based on the measurements of pressure, volume and temperature by Amagat(61). In 1930 James A. Beattie(57) calculated the Joule-Thomson coefficient of air, employing the Beattie-Bridgeman equation of state. The pressure and temperature range covered by these investigators is shown in fig.12A.

Fig 12B. represents a comparison of the overlapping data of the experimental measurements with Beattie A. James values. It is noticed that at all temperatures experimental values of μ decrease with the increase of temperature, and this is significant at lower pressure.

The values calculated by James A. Beattie consistently follow the experimental values except at higher pressure. At 220 atm. and at 50C, deviation is about 20%.

The Joule-Thomson coefficient of air was obtained from the Edmister correlation and compared with the Roebuck data in Table 12. From the table it is seen that the deviation is about 9-18%. This increased deviation may be due to the fact that the acentric factor of nitrogen is used in place of that of air, since the acentric factor of air is not calculable. Secondly air is a mixture of different gases, but in these calculations it is treated as a single gas(nitrogen). However, the critical constants are taken as those of air(8).

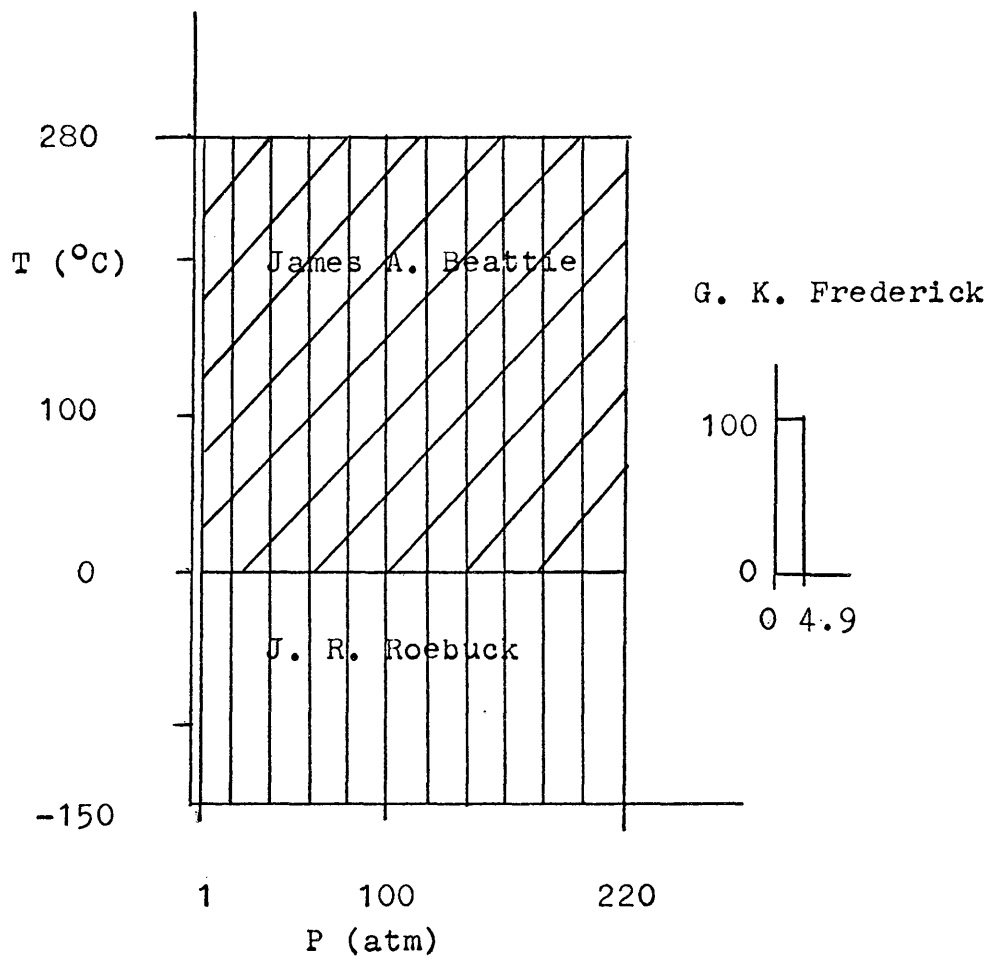


Figure 12A. Pressure-temperature range covered for Joule-Thomson coefficients (Air).

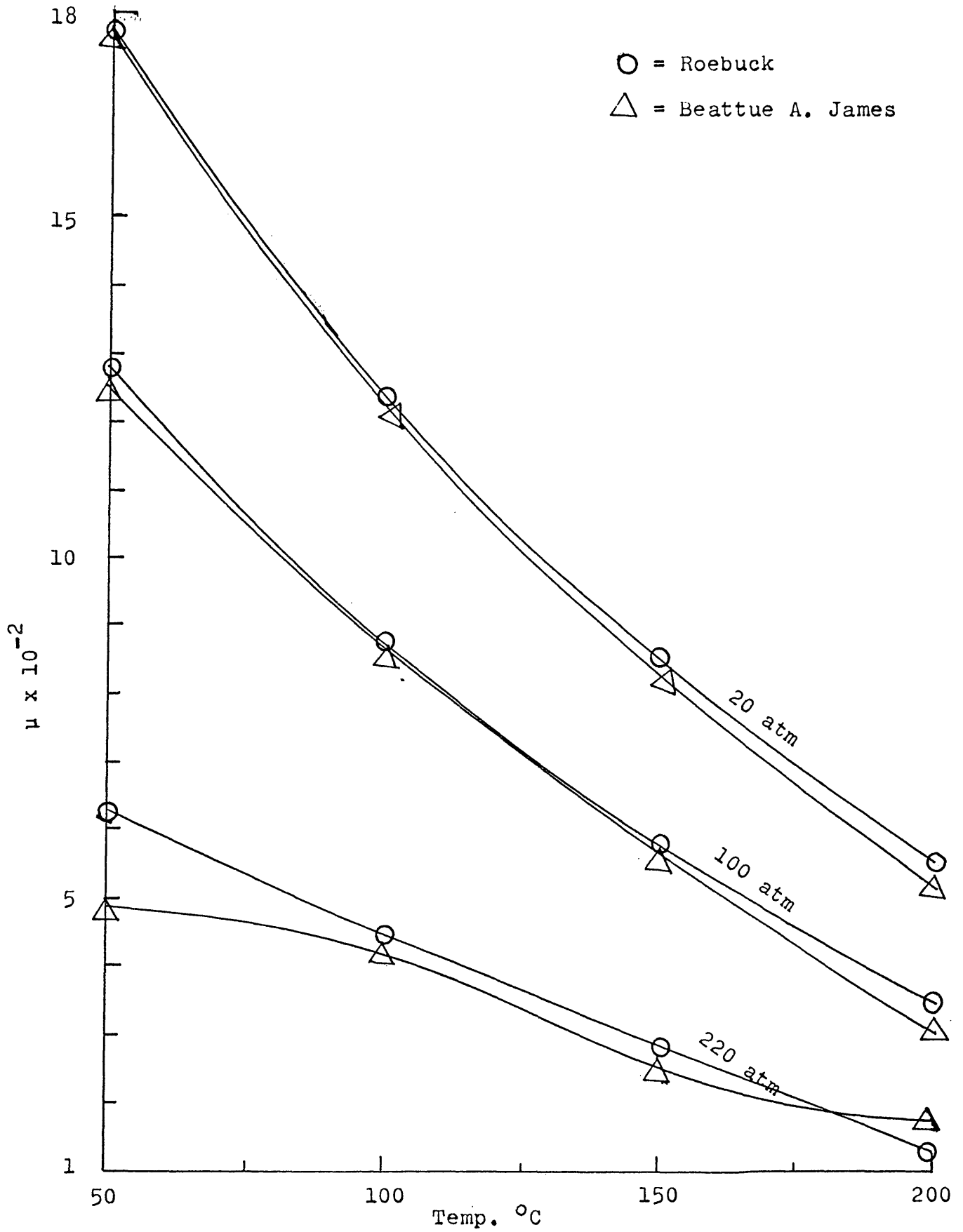


Figure 12B. Comparison of Joule-Thomson Coefficients (Air).

Table No.12

AIR (36)

$$\mu = \text{oC/atm.}$$

| P/T atm. | 250C | 100C | 25C | 0C | -25C | -100C | -150C |
|-------------|---------|--------|--------|--------|--------|--------|---------|
| *1 | 0.0402 | 0.1327 | 0.2269 | 0.2663 | 0.3160 | 0.5750 | |
| 20 | 0.0280 | | 0.238 | | | 0.505 | |
| *20 | 0.0340 | 0.1244 | 0.2116 | 0.2494 | 0.2965 | 0.5535 | |
| 60 | | 0.120 | 0.210 | 0.250 | 0.283 | | 0.0482 |
| *60 | 0.0251 | 0.1057 | 0.1815 | 0.2143 | 0.2540 | 0.4700 | 0.044 |
| 100 | 0.0139 | 0.0802 | | | 0.239 | | 0.022 |
| *100 | 0.0164 | 0.0890 | 0.1517 | 0.1782 | 0.2115 | 0.2845 | 0.019 |
| 140 | | 0.0763 | | 0.161 | | 0.169 | |
| *140 | 0.0093 | 0.0723 | 0.1237 | 0.1445 | 0.1640 | 0.1415 | -0.003 |
| 180 | | | | 0.129 | 0.109 | | |
| *180 | 0.0027 | 0.0578 | 0.0974 | 0.1125 | 0.1250 | 0.0745 | -0.0215 |
| 220 | -0.0016 | | 0.0770 | | | 0.0352 | -0.0362 |
| *220 | -0.0020 | 0.0452 | 0.0718 | 0.0812 | 0.0975 | 0.0310 | -0.0385 |

* Literature values

ii) PURE GAS MIXTURES

The Joule-Thomson coefficient of different gas mixtures are calculated through the use of the Edmister correlations. The linear averaging rule for mixing is used in these calculations (sample calculations in Appendix II). These values are compared with the literature values.

METHANE - ETHANE MIXTURE

R.A.Budenholzer, B.H.Sage, and W.N.Lacey (4) determined experimentally the Joule-Thomson coefficient of methane - ethane gas mixture at various mixture compositions. The temperatures pressure range covered for each composition is shown in fig. 13.

The Joule-Thomson coefficient of this mixture using the linear averaging mixing rule was obtained from Edmister correlation and compared with the experimental data in Table 13. The calculated values are in good agreement with the experimental values.

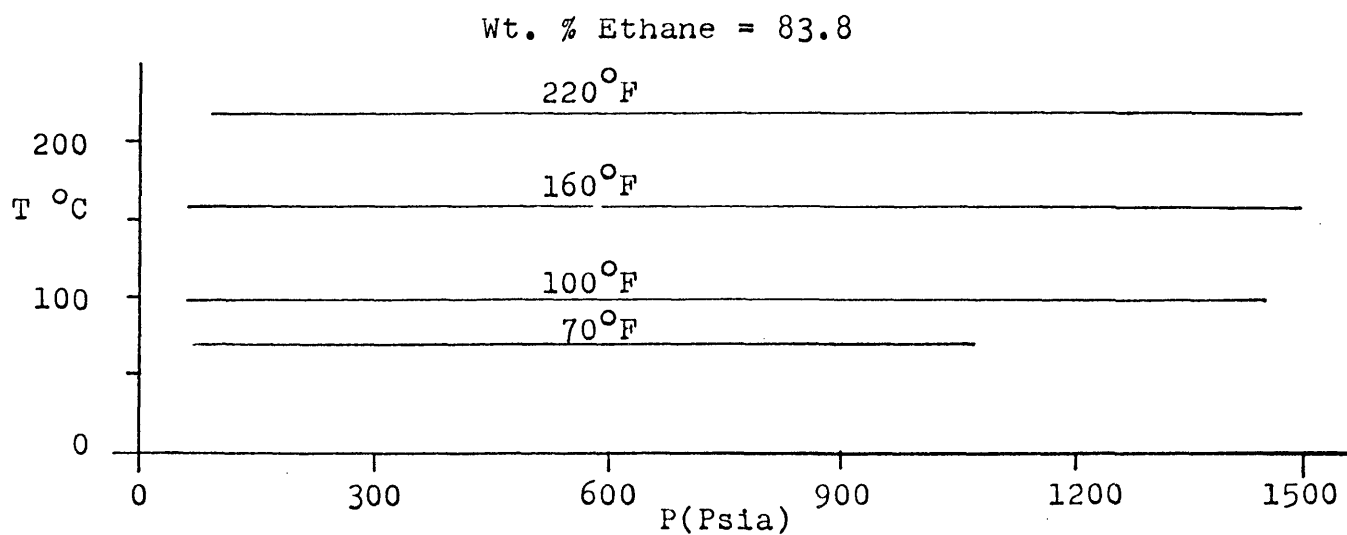
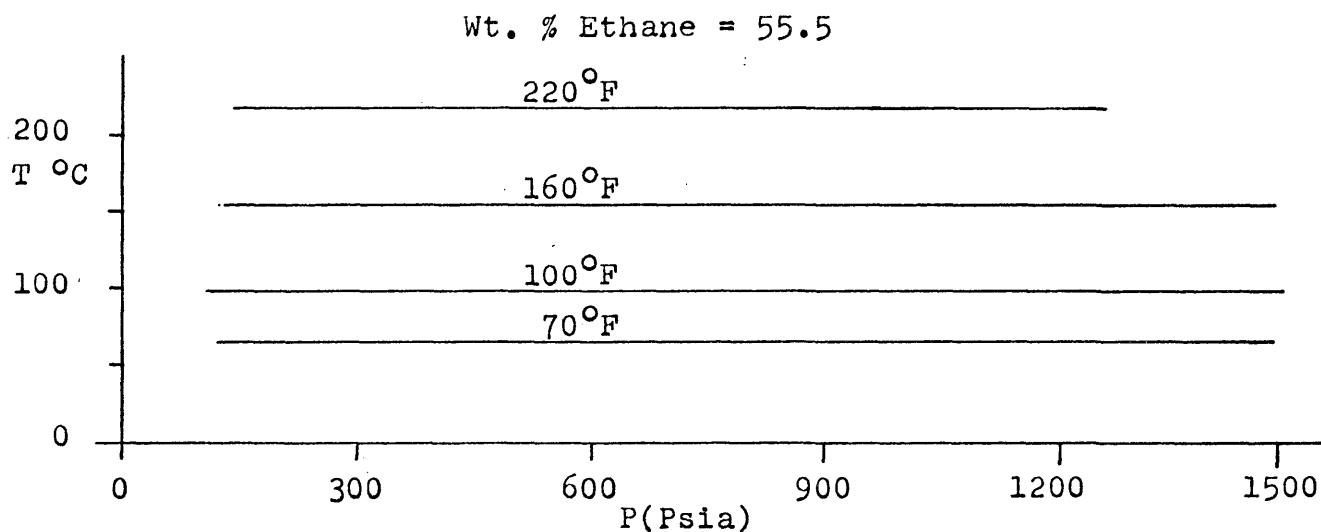
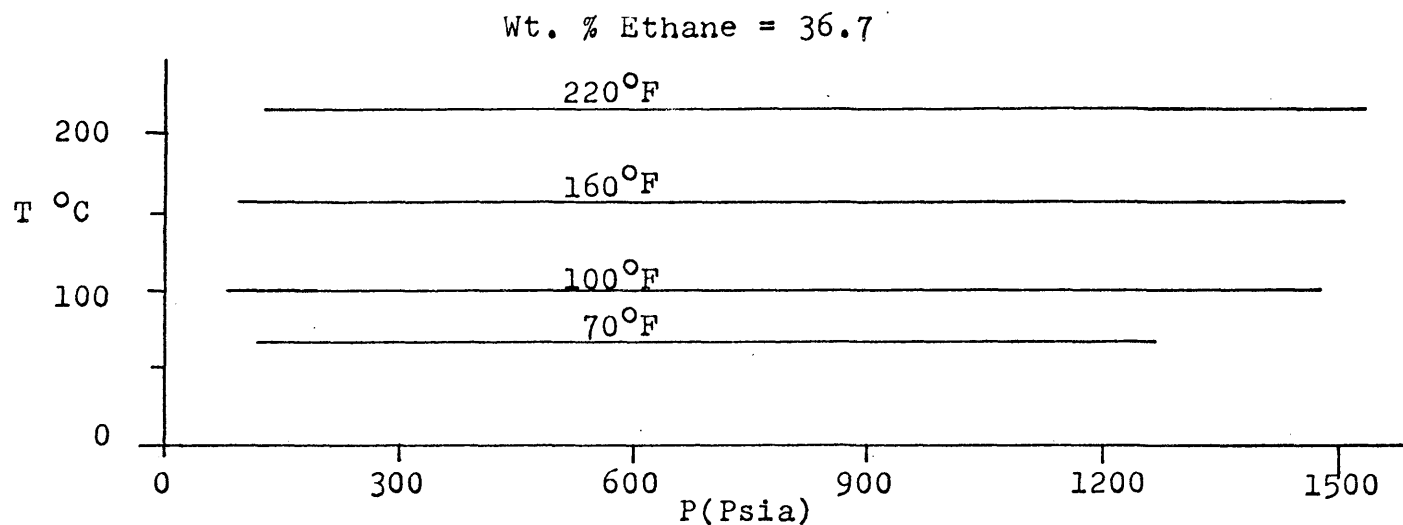


Fig. 13. Pressure-temperature range covered for Joule-Thomson Coefficient (Methane-Ethane Mixture).

Table No. 13

METHANE-ETHANE MIXTURE(4)

$$\mu = \text{°F/Psia}$$

Mixture Comp.

- (1) Ethane = 40% by mole
 (2) Methane = 60% by mole

| Pressure Psia | Temp 70F | |
|------------------|-----------|---|
| 113 | 0.0730 | calculated |
| | 0.0802 | experimental |
| 450 | 0.0807 | calculated |
| | 0.0857 | experimental |
| 1482 | 0.0539 | calculated |
| | 0.0519 | experimental |
| | Temp 220F | |
| 127 | 0.0418 | calculated |
| | 0.0442 | experimental |
| 222 | 0.0409 | calculated |
| | 0.0440 | experimental |
| 1252 | 0.0369 | calculated |
| | 0.0400 | experimental |
| | | (1) Ethane = 23.6% by mole (2) Methane = 76.4% by mole |
| | Temp 70F | |
| 110.5 | 0.0600 | calculated |
| | 0.067 | experimental |
| 463.0 | 0.0606 | calculated |
| | 0.0700 | experimental |
| 1259.0 | 0.0514 | calculated |
| | 0.0576 | experimental |

Table No. 13 contd.

| Pressure in Psia | Temp 220F | |
|---|-----------|--------------|
| 113 | 0.0322 | calculated |
| | 0.0359 | experimental |
| 507 | 0.0334 | calculated |
| | 0.0376 | experimental |
| 1544 | 0.0357 | calculated |
| | 0.0313 | experimental |
| Methane = 26.7%by mole Ethane = 73.3%by mole | | |
| Temp 220F | | |
| 218.3 | 0.612 | calculated |
| | 0.0585 | experimental |
| 613 | 0.0645 | calculated |
| | 0.0600 | experimental |
| 1484 | 0.0480 | calculated |
| | 0.0511 | experimental |
| Temp 70F | | |
| 126.7 | 0.109 | calculated |
| | 0.1124 | experimental |
| 575 | 0.1398 | calculated |
| | 0.1274 | experimental |
| 1062 | 0.061 | calculated |
| | 0.0680 | experimental |

METHANE-PROPANE MIXTURE

R.A. Budenholzer, D.F. Botkin, B.H. Sage and W.N. Lacey(2) determined the Joule Thomson coefficients of the methane-propane system. They performed the measurements for three different compositions. The composition, pressure, and temperature range covered by them is presented in fig.14.

The Joule-Thomson coefficient of this mixture using the linear averaging mixing rule was obtained from the Edmister correlation and compared with the experimental data in Table 14. The calculated values are in fair agreement with the experimental values.

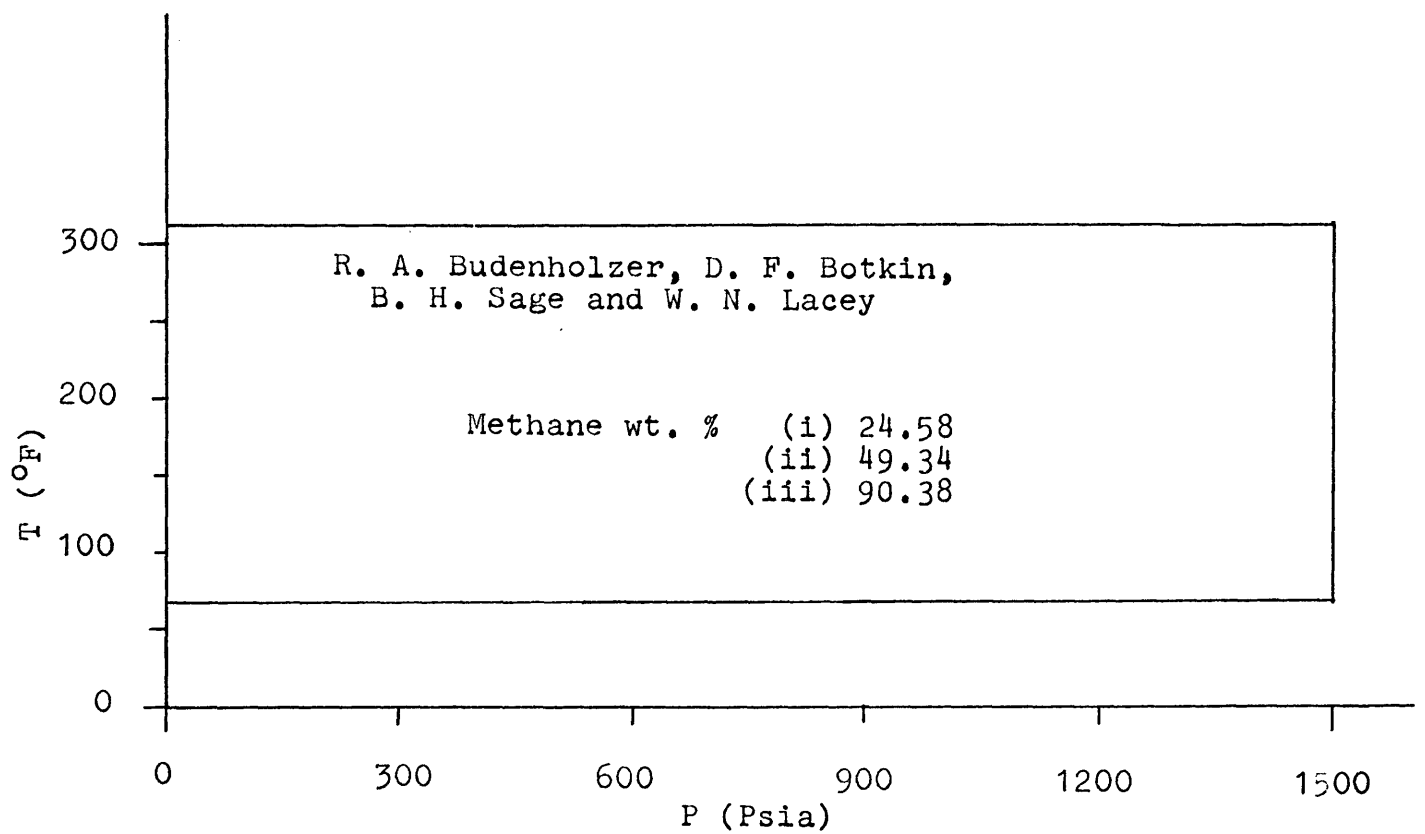


Figure 14. Pressure-temperature range covered for Joule-Thomson coefficient (Methane-Propane Mixture).

Table No. 14METHANE-PROPANE MIXTURE(2)

$$\mu = \text{deg } \overset{\circ}{\text{F}}/\text{Psia}$$

| Temp deg F | Absolute Pressure Psia | Wt. percent Methane | | |
|---------------|------------------------------|---------------------|--------|--------|
| | | 24.58 | 49.34 | 75.52 |
| 70 | 200 | 0.121 | 0.105 | 0.0592 |
| | *200 | 0.143 | 0.0939 | 0.0694 |
| | 800 | | | 0.0638 |
| | *800 | | | 0.0678 |
| | 1500 | | | 0.0580 |
| | *1500 | | | 0.0604 |
| 190 | 200 | 0.0792 | 0.0530 | 0.0409 |
| | *200 | 0.0812 | 0.0562 | 0.0428 |
| | 800 | 0.0800 | 0.0510 | 0.0390 |
| | *800 | 0.0822 | 0.0532 | 0.0414 |
| | 1500 | 0.0460 | 0.0430 | 0.0310 |
| | *1500 | 0.0480 | 0.4160 | 0.0342 |
| 310 | 200 | 0.0417 | 0.0324 | 0.0257 |
| | *200 | 0.0480 | 0.0355 | 0.0278 |
| | 800 | 0.0521 | 0.0308 | 0.0250 |
| | *800 | 0.0498 | 0.0344 | 0.0270 |
| | 1500 | 0.0470 | 0.0255 | 0.0239 |
| | *1500 | 0.0453 | 0.0284 | 0.0217 |

*Literature values

METHANE-n-BUTANE MIXTURE

R.A. Budenholzer, B.H. Sage, and W.N. Lacey(3) measured the Joule-Thomson coefficient of the mixture for four different compositions. The pressure and temperature range covered by them is shown in fig 15.

By using the Edmister correlation, Joule-Thomson coefficients for this mixture were determined at various points and compared with the experimental values in Table 15. The calculated values are in very good agreement, with the experimental values.

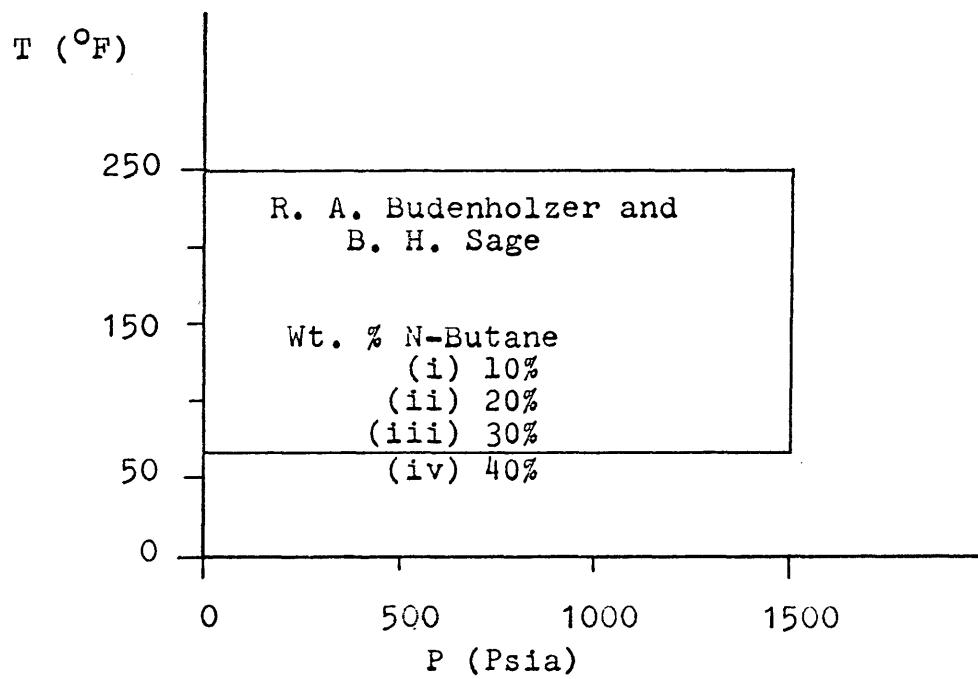


Figure 15. Pressure-temperature range covered for Joule-Thomson coefficient (Methane-N-Butane Mixture).

Table No. 15

METHANE -n-BUTANE (3)

$$\mu = \text{ }^{\circ}\text{F/Psia}$$

| Temp deg F | Absolute Pressure lb/sq.in. | Wt% of n-Butane | | |
|---------------|-----------------------------------|-----------------|--------|--------|
| | | 10 | 30 | 50 |
| 70F | 250 | 0.0558 | 0.0656 | |
| | *250 | 0.0546 | 0.0668 | |
| | 750 | 0.0524 | | |
| | *750 | 0.0535 | | |
| | 1500 | 0.0403 | | |
| | *1500 | 0.0414 | | |
| 190 | 250 | 0.0332 | 0.0423 | |
| | *250 | 0.0342 | 0.0414 | 0.0534 |
| | 750 | 0.0345 | 0.0400 | 0.0532 |
| | *750 | 0.0336 | 0.0408 | 0.0525 |
| | 1500 | 0.0280 | 0.0319 | 0.0433 |
| | *1500 | 0.0271 | 0.0327 | 0.0442 |
| 310 | 250 | 0.0223 | 0.0257 | 0.0320 |
| | *250 | 0.0208 | 0.0266 | 0.0340 |
| | 750 | 0.0213 | 0.0268 | 0.0323 |
| | *750 | 0.0203 | 0.0261 | 0.0334 |
| | 1500 | 0.0197 | 0.0223 | 0.0277 |
| | *1500 | 0.0170 | 0.0218 | 0.0282 |

*literature values

NATURAL GAS

B.H. Sage, D.F. Botkin, and W.N. Lacey(38)
 measured the Joule-Thomson coefficient for two natural
 gas mixtures. The composition of the two gases is as
 follows:

| | A | B |
|------------------|--------|--------|
| Carbon dioxide | 0.009 | 0.0420 |
| Methane | 0.8255 | 0.838 |
| Ethane | 0.0901 | 0.0637 |
| Propane | 0.0462 | 0.0374 |
| Isobutane | 0.0074 | 0.0039 |
| n-Butane | 0.0126 | 0.0095 |
| Iso-Pentane | 0.0032 | 0.0016 |
| n-Pentane | 0.0022 | 0.011 |
| Hexane & Heavier | 0.0038 | 0.0023 |

The temperature and pressure range covered for
 these two gases is shown in the fig 16.

The Joule-Thomson coefficient of gas A (taking only
 the higher percentage, i.e. CO_2 , CH_4 , C_2H_6 , C_3H_8 and $n\text{C}_4\text{H}_{10}$)
 by using linear averaging mixing rule, was obtained from
 the Edmister correlation and compared with the experimental
 values in Table 16. The deviation is 4 to 11%, which is
 reasonable.

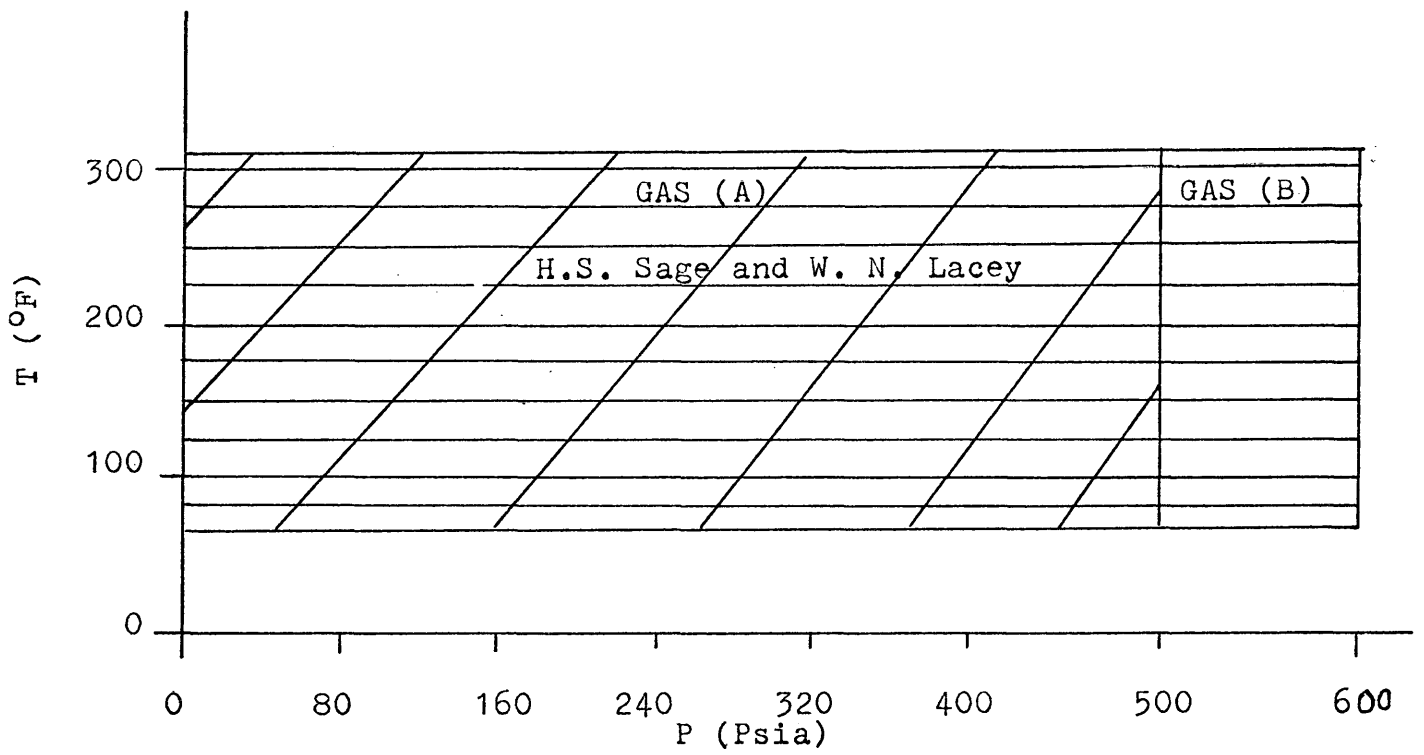


Figure 16. Pressure-temperature range covered for Joule-Thomson coefficient (Natural gas).

TABLE NO. 16

NATURAL GAS A (38)

 $\mu = \text{deg F/Psia}$

| Pressure Psia | Temp deg F | | | | |
|------------------|------------|--------|--------|--------|--------|
| | 70 | 130 | 190 | 250 | 310 |
| * 0 | 0.068 | 0.0549 | 0.0436 | 0.0346 | 0.0273 |
| 200 | 0.0621 | 0.620 | 0.0412 | 0.0310 | 0.0262 |
| *200 | 0.0697 | 0.0567 | 0.0458 | 0.0364 | 0.0284 |
| 400 | 0.078 | 0.0530 | 0.0408 | 0.0345 | 0.0250 |
| *400 | 0.0701 | 0.0575 | 0.0464 | 0.0367 | 0.0287 |
| 500 | 0.0640 | 0.062 | 0.0439 | 0.0400 | 0.0254 |
| *500 | 0.0698 | 0.0575 | 0.0461 | 0.0365 | 0.0286 |

* literature values

NITROGEN-METHANE MIXTURE

John H. Perry and Carl V. Herrmann(24) calculated the Joule-Thomson coefficient of nitrogen-methane mixture with the Beattie Bridgeman equation of state. They used linear combination mixing rule for their calculations. The temperature and pressure range covered and the compositions of the mixture are shown in the fig 17.

The Joule-Thomson coefficient of methane of this mixture was obtained from the Edmister correlation and compared with the Perry and Herrmann data in table 17. The agreement is good.

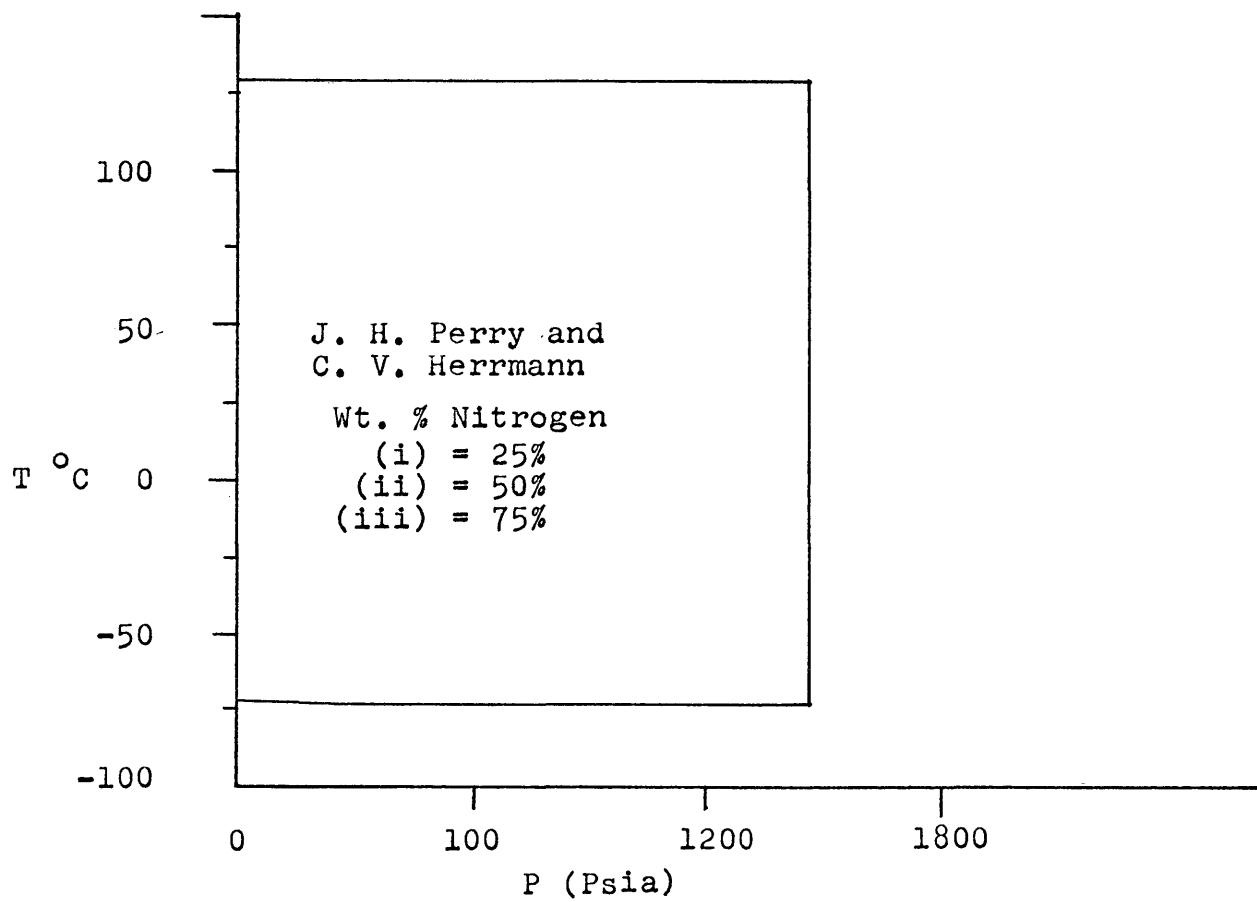


Figure 17. Pressure-temperature range covered for Joule Thomson coefficients (Nitrogen-Methane mixture).

Table No.17
 NITROGEN-METHANE MIXTURE (24)
 μ =deg C/atm.

| Pressure Atm. | Temp deg Kelvin | | |
|--------------------|-----------------|-------|-------|
| | 200 | 300 | 400 |
| Wt% Nitrogen 25 | | | |
| 5 | 0.708 | 0.362 | 0.228 |
| *5 | 0.74 | 0.35 | 0.19 |
| 25 | 0.628 | 0.344 | 0.199 |
| *25 | 0.65 | 0.33 | 0.18 |
| 50 | 0.572 | 0.285 | 0.160 |
| *50 | 0.55 | 0.30 | 0.17 |
| 100 | 0.445 | 0.265 | 0.168 |
| *100 | 0.41 | 0.25 | 0.15 |
| Wt% Nitrogen 50 | | | |
| 5 | 0.69 | 0.33 | 0.182 |
| *5 | 0.64 | 0.30 | 0.16 |
| 25 | 0.59 | 0.239 | 0.170 |
| *25 | 0.56 | 0.26 | 0.15 |
| 50 | 0.433 | 0.243 | 0.129 |
| *50 | 0.48 | 0.26 | 0.14 |
| 100 | 0.33 | 0.230 | 0.100 |
| *100 | 0.37 | 0.21 | 0.12 |
| Wt % Nitrogen = 75 | | | |
| 5 | 0.563 | 0.220 | 0.116 |
| *5 | 0.53 | 0.25 | 0.13 |
| 25* | 0.47 | 0.23 | 0.13 |
| *25 | 0.51 | 0.210 | 0.109 |
| 50 | 0.45 | 0.232 | 0.10 |
| *50 | 0.41 | 0.21 | 0.11 |
| 100 | 0.347 | 0.158 | 0.11 |
| *100 | 0.32 | 0.17 | 0.09 |

*literature values

NITROGEN-ETHANE MIXTURE

Alan L. Stocket(40) measured the Joule- Thomson coefficient of this mixture at various temperatures and pressures by using different compositions, as shown in fig 18.

The Joule-Thomson coefficient of nitrogen-ethane mixture was obtained from the Edmister correlation and compared with the experimental data in Table 18. The deviation is 5 to 11% which is reasonable.

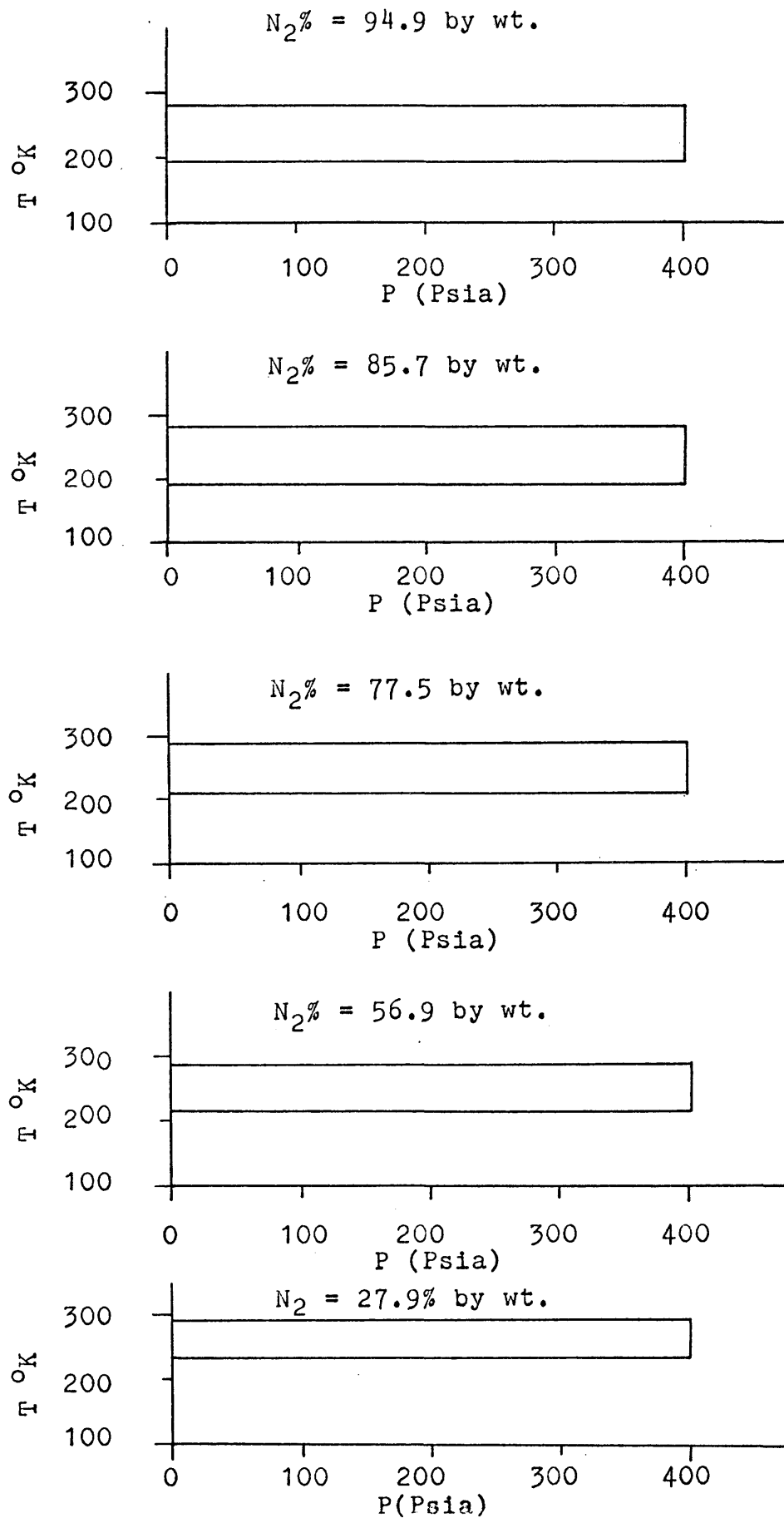


Figure 18. Comparison of Joule-Thomson Coefficients (Nitrogen-Ethane Mixture).

Table No. 18
NITROGEN-ETHANE (40)

| | | μ =deg C/atm. | wt%Nitrogen = 85.7 | |
|----------------------|-----------------------|-------------------|----------------------------|--|
| Pressure Psia | Temperature deg C. | | | |
| 100 | 12.22 | 0.352 0.330 | calculated experimental | |
| 800 | 25.77 | 0.250 0.239 | calculated experimental | |
| 1200 | 20.09 | 0.231 0.219 | calculated experimental | |
| 1600 | 17.04 | 0.181 0.193 | calculated experimental | |
| 2400 | 25.55 | 0.136 0.126 | calculated experimental | |
| Wt% Nitrogen = 77.5% | | | | |
| 100 | -24.86 | 0.582 0.561 | calculated experimental | |
| 400 | 11.28 | 0.369 0.387 | calculated experimental | |
| 800 | 20.77 | 0.330 0.311 | calculated experimental | |
| 2400 | 1.90 | 0.180 0.208 | calculated experimental | |
| Wt% Nitrogen = 56.9% | | | | |
| 100 | -27.9 | 0.808 0.858 | calculated experimental | |
| 400 | 20.53 | 0.490 0.454 | calculated experimental | |
| 1600 | 20.38 | 0.300 0.334 | calculated experimental | |

(iii) QUANTUM GASES AND THEIR MIXTURES

The quantum gases such as helium, hydrogen and neon are described by quantum rather than statistical mechanics. Therefore the characteristics of these gases are different than those of other gases, when the actual critical constants are used as the reducing parameters.

The Joule-Thomson coefficients of the above-mentioned gases could not be calculated by using actual critical constants in the Edmister correlation, and therefore no comparison could be made at this stage. However, new effective critical constants of quantum gases are defined in the next chapter. These constants made the Edmister correlation applicable for these gases and their mixtures. At that stage μ values are calculated and compared with the literature values.

The different experimenters who have worked with hydrogen and helium and mixtures containing hydrogen and helium, and the pressure-temperature ranges they covered, are shown in fig 19 to 24.

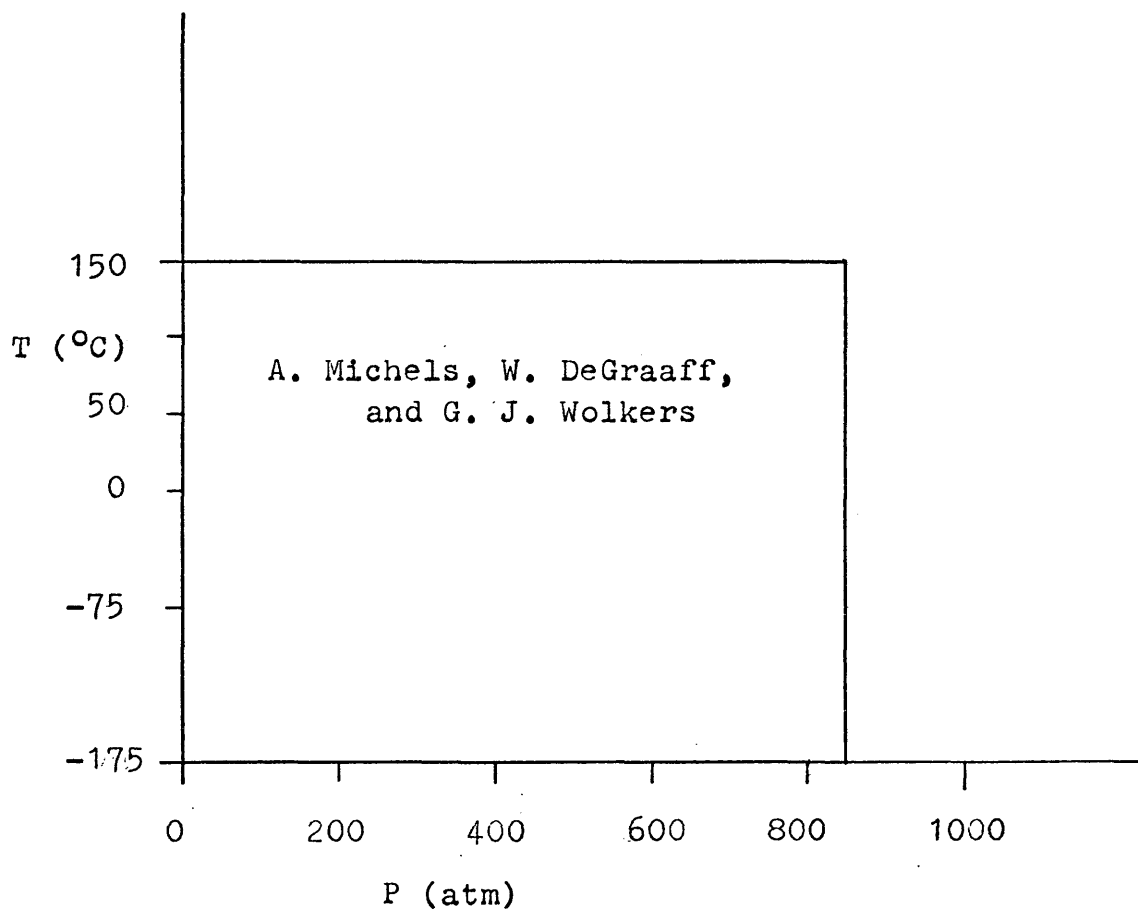


Figure 19. Pressure-temperature range covered for Joule-Thomson coefficient (Hydrogen).

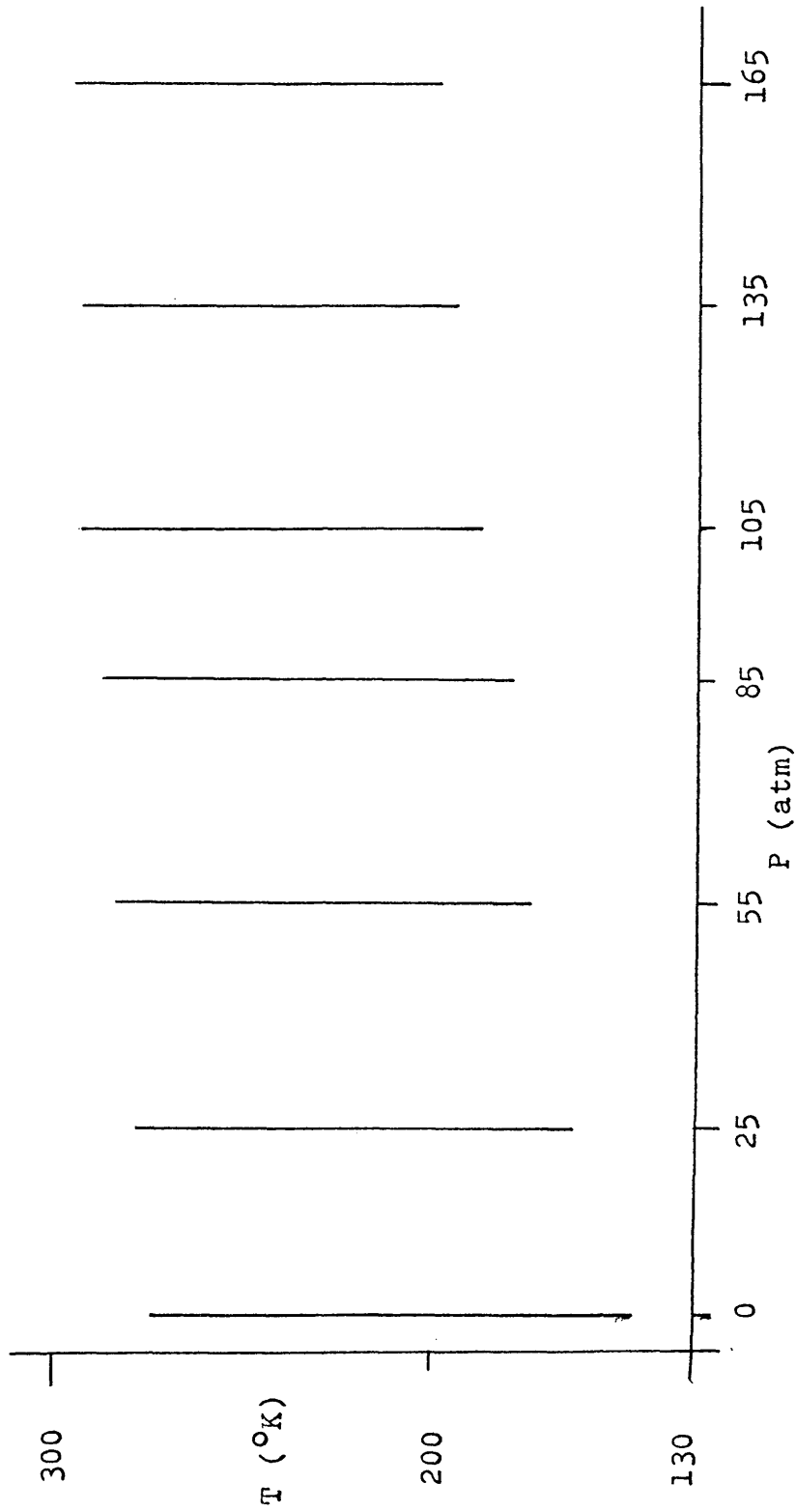


Figure 20. Pressure-temperature range covered for Joule-Thomson coefficients (Hydrogen-Nitrogen-Methane Mixture), 33 mole %.

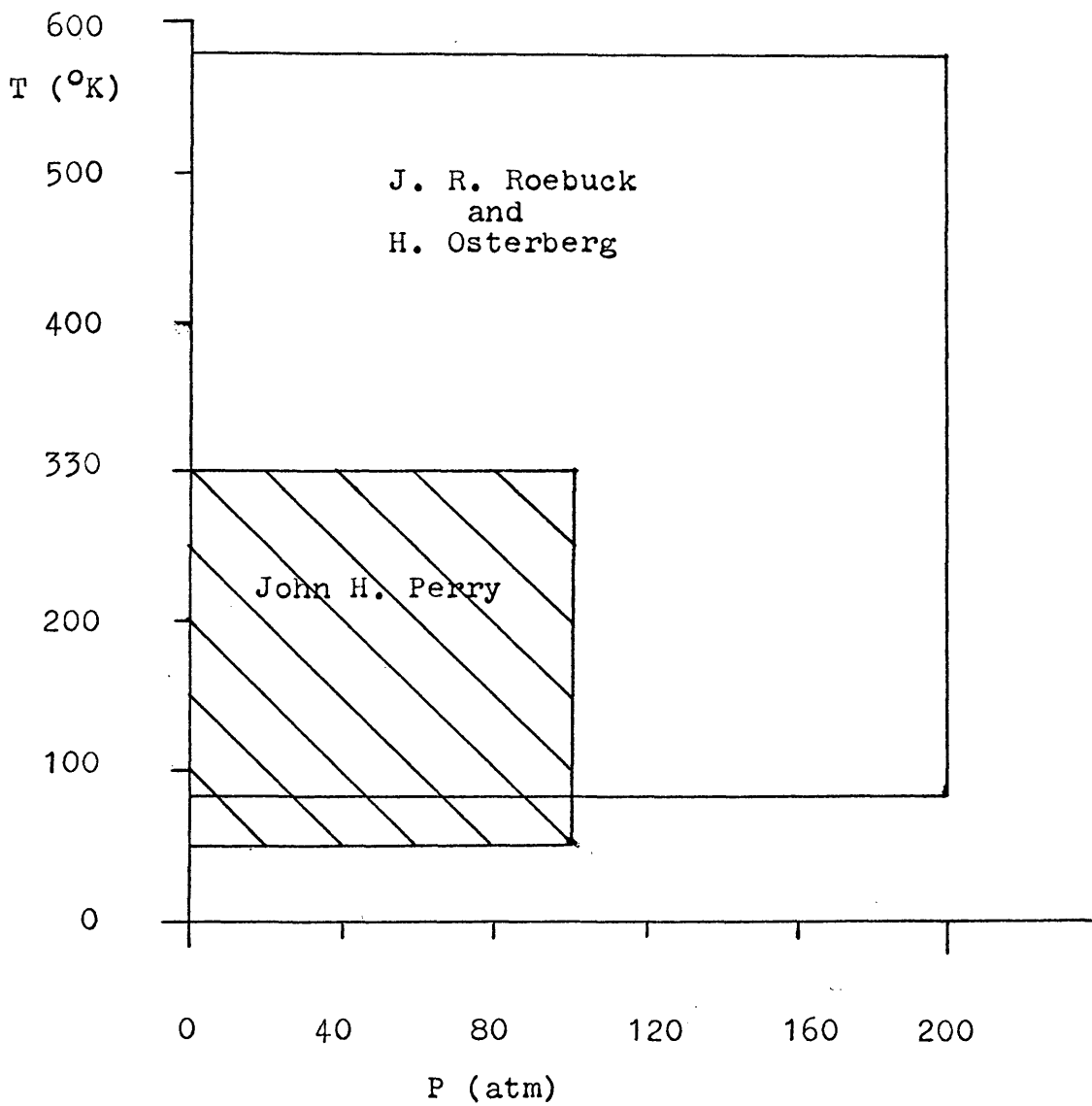


Figure 21. Pressure-temperature range covered for Joule-Thomson coefficients (Helium).

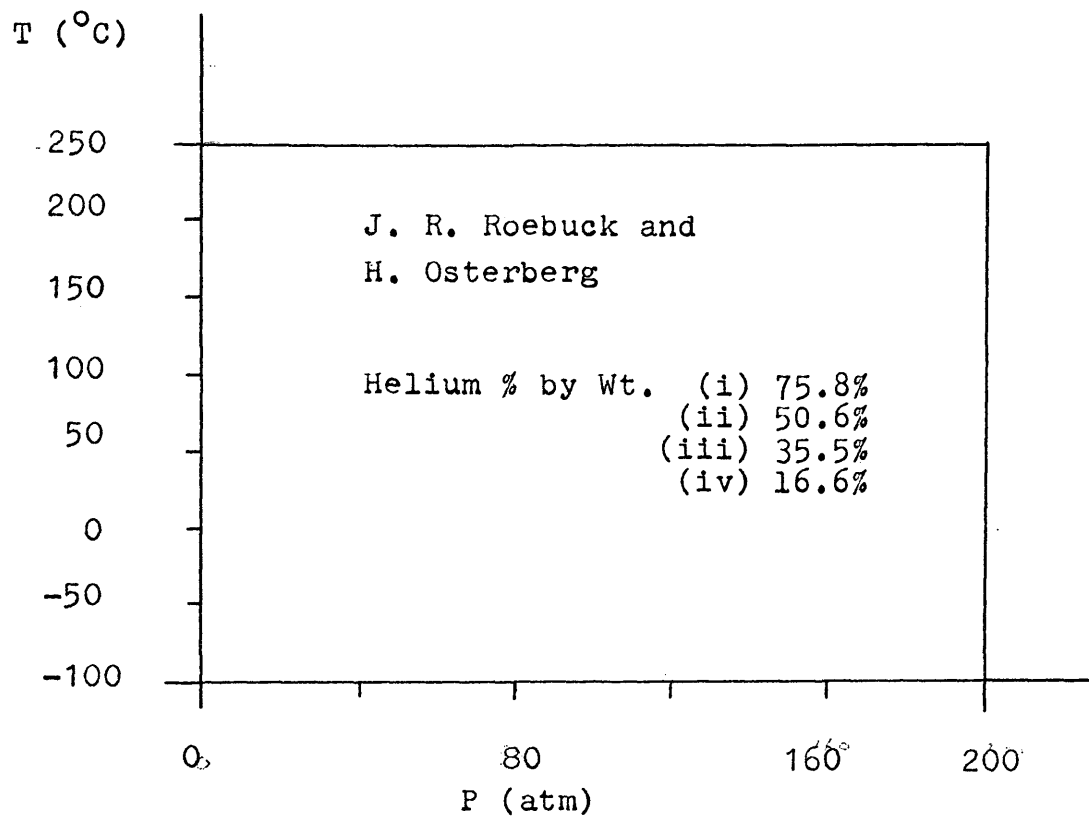


Figure 22. Pressure-temperature range covered for Joule-Thomson coefficient (Helium-Argon Mixture).

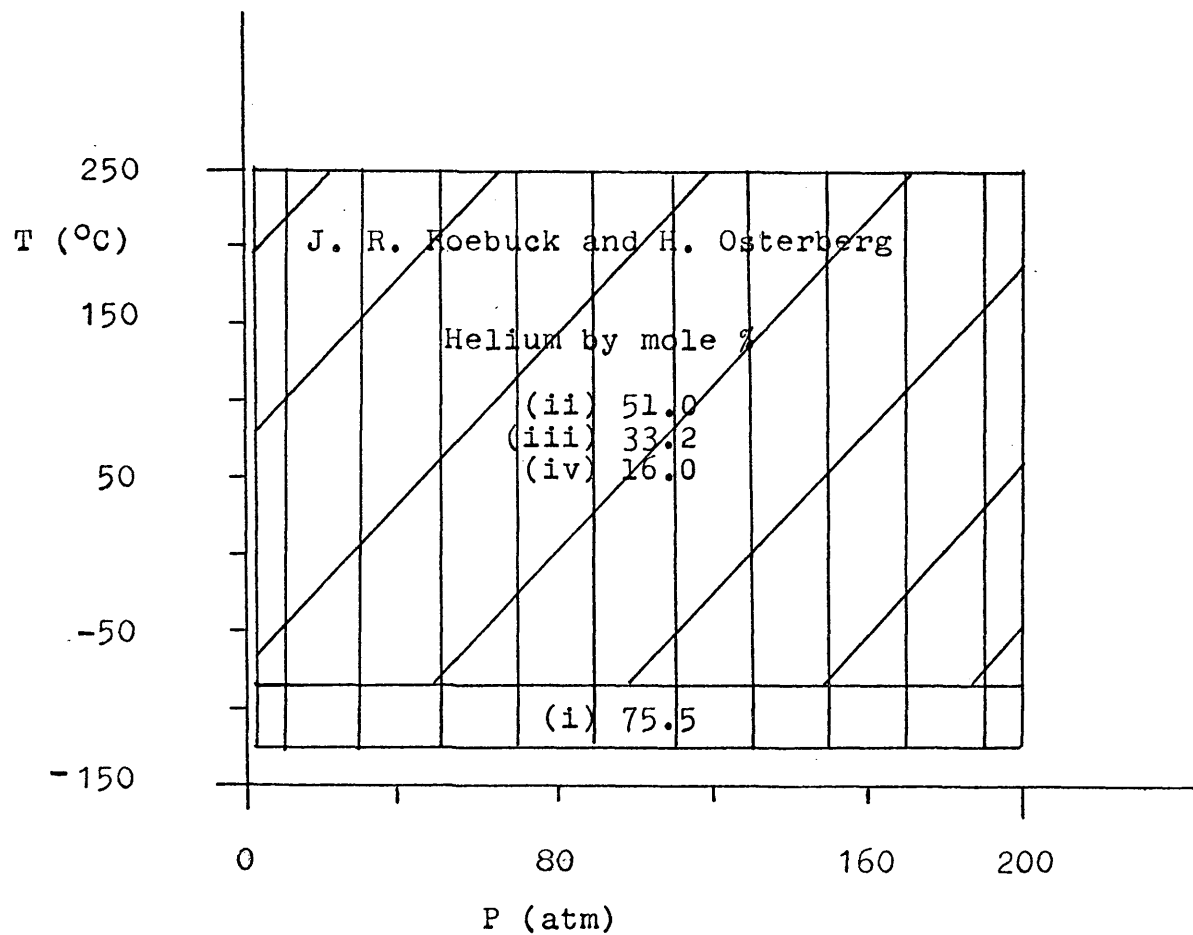


Figure 23. Pressure-temperature range covered for Joule-Thomson coefficient (Helium-Nitrogen Mixture).

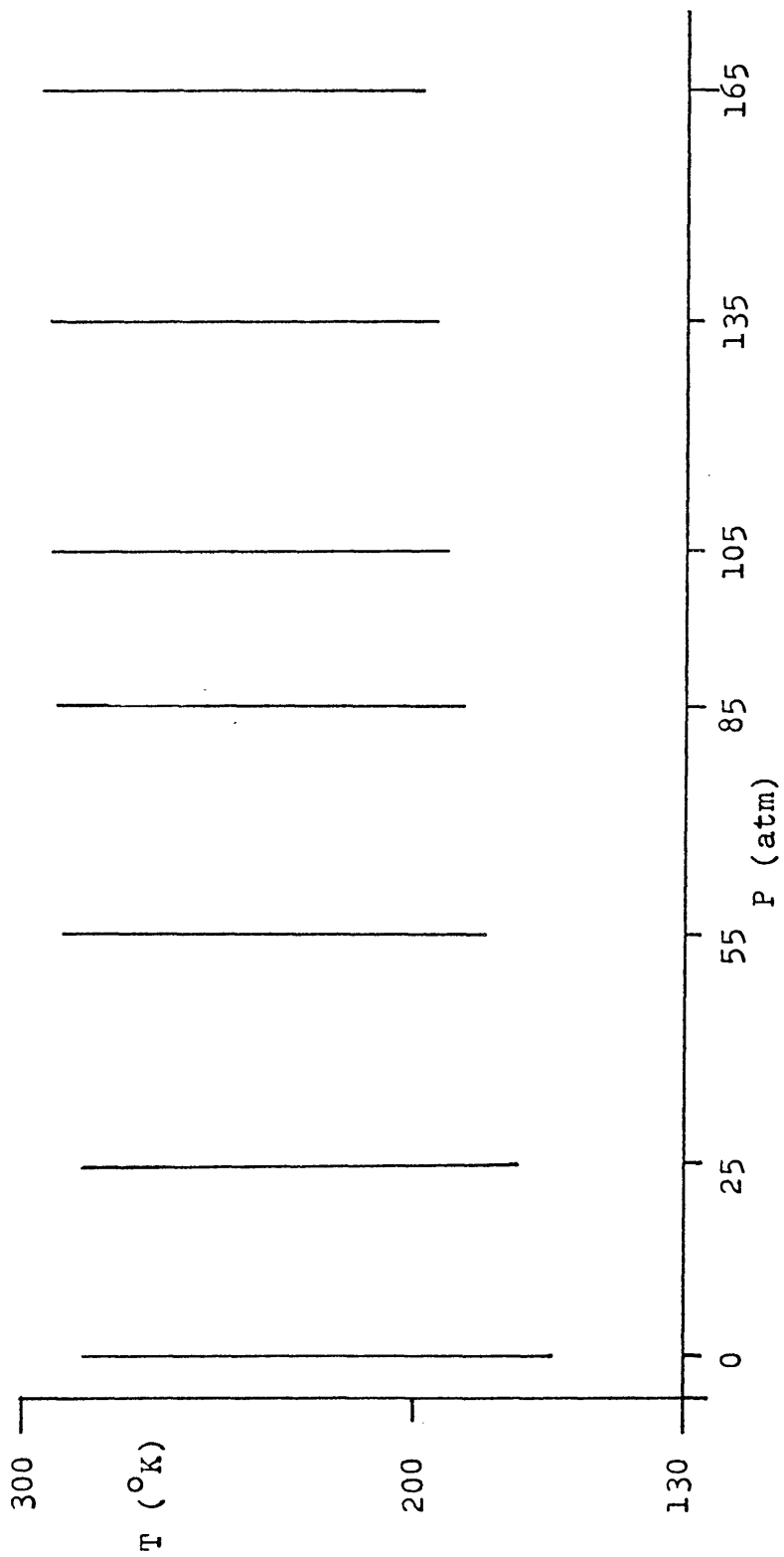


Figure 24. Pressure-temperature range covered by Joule-Thomson coefficients (Helium-Nitrogen-Methane Mixture), 33 mole %.

T-1329

IMPROVED CORRELATION FOR THE
QUANTUM GASES

The charts prepared by Edmister are not applicable for Hydrogen, Helium and neon for predicting J.T.C.

However, the Edmister correlation would be applicable provided new effective critical constants for the quantum gases were used.

To determine the effective critical constants was quite a difficult and time consuming, as there is no relationship or equation given in the literature with which one can find new constant under various conditions. Some effective constants are found in the literature but all have a specific applications.

A major goal of this work was to find new constants for hydrogen, helium and neon, which could be used to predict Joule-Thomson coefficients for these gases with the help of the Edmister correlation, and if possible to prepare new charts for these gases.

For this purpose there should be enough Joule Thomson data available so that calculated values could be compared with the experimental values over a wide range of pressure and temperature.

There is not sufficient neon data for this purpose, as experimentally little work has been done on this. However, data on helium and hydrogen and their mixtures are readily available in the literature.

H Y D R O G E N

The actual P_c and T_c of hydrogen are 12.8 atm. and 33.3°K respectively. When these actual constants were used as reducing parameters in the Edmister correlation to find the Joule-Thomson coefficient of hydrogen, the agreement was extremely poor (66 - 80% deviation), as shown in the fig 27.

The data of A. Michels, W. DeGraff and G.J. Wolkers(22) of hydrogen were used to calculate the critical constants (T_c and P_c) of hydrogen. It was noticed that a single T_c is not sufficient to determine values of the Joule-Thomson coefficients of hydrogen, and it was also noted that T_c depends upon the pressure in a simple manner.

After doing calculations for the Joule-Thomson coefficient of hydrogen, through the use of the Edmister correlation, at various temperatures and pressures - 75°C was selected as the most appropriate temperature to use in determining the new effective T_c and P_c .

It was found that new effective constants for hydrogen are as follows:

$$P_c = 15 \text{ atm.}$$

$$T_c = 37.8^\circ\text{K}$$

As mentioned before, T_c varies with the pressure; thus a correction factor (hydrogen correction factor) of 0.01125 was applied. The correction factor means that with the rise of each atm. T_r will decrease by a value of 0.001125.

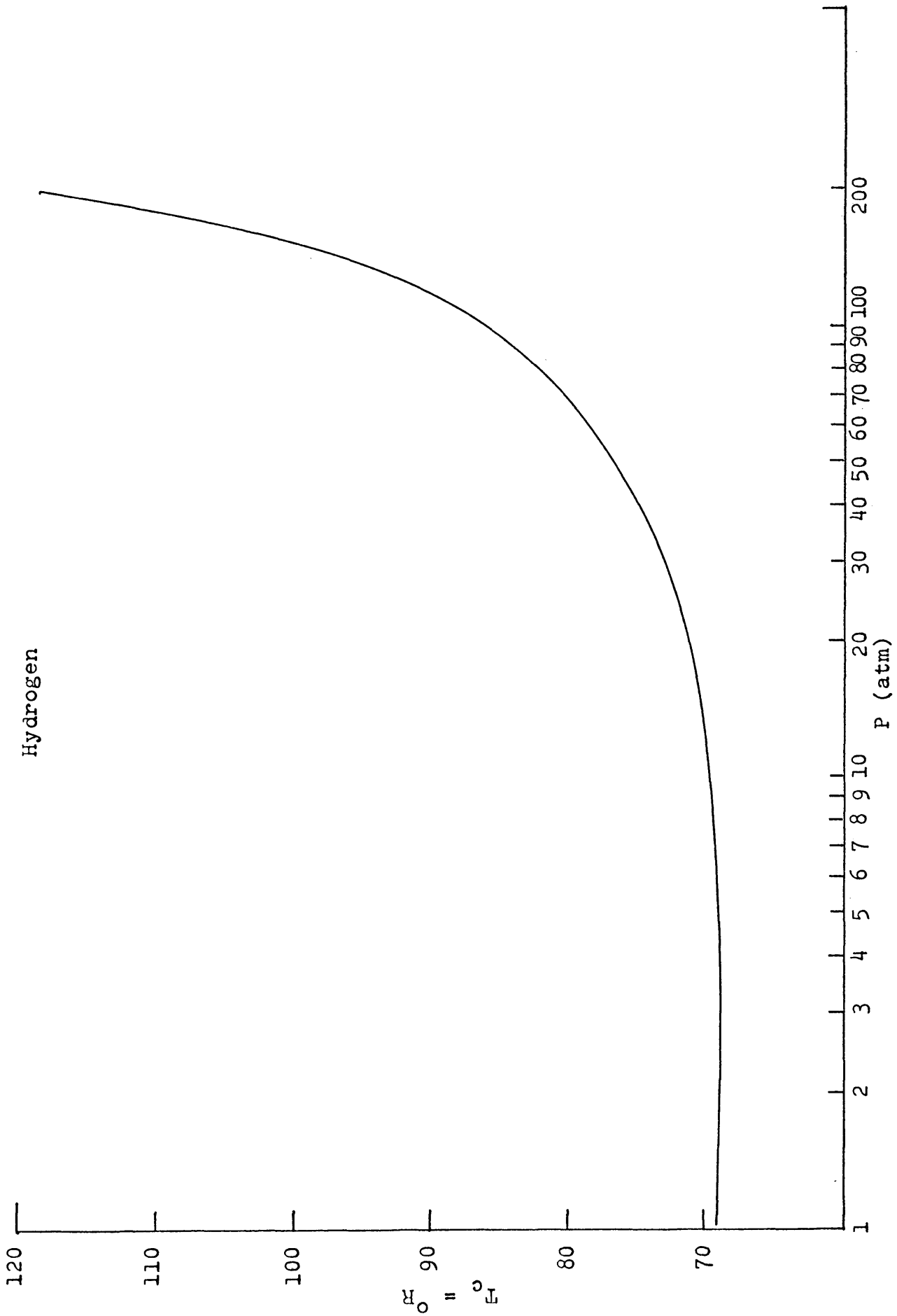


Figure 25.

This T_r will be based upon -75°C . In summary a graph is prepared (fig.25) from which T_c can be directly taken for any pressure desired. In other words, effective P_c for Hydrogen(15 atm.) is constant, but effective T_c for hydrogen(37.8°K) is at 1 atm., and it increases as the pressure, at which Joule-Thomson coefficient, is to be determined, increases(fig 25).

A new chart suitable for hydrogen has been prepared as follows:

The equation Edmister(15) presented is

$$\frac{P_c}{RT_c} (\mu C_p) = \left[\frac{P_c}{RT_c} (\mu C_p) \right]^{(0)} + w \left[\frac{P_c}{RT_c} (\mu C_p) \right]^{(1)} \quad (A)$$

The 2nd term on right had side is for the real fluid, being multiplied with the acentric factor 'w', which is to measure the deviation of the intermolecular potential from that of a simple fluid. Since 'w' for hydrogen is zero, this term can be eliminated. Hence equation A can be written as

$$\frac{P_c}{RT_c} (\mu C_p) = \left[\frac{P_c}{RT_c} (\mu C_p) \right]^{(0)} \quad (B)$$

This equation(B) has been plotted in fig.26 with lines of constant reduced pressure instead of reduced temperature as in the original Edmister article, since T_c is not constant in this case.

μ is calculated as follows:

$$\mu = \frac{P_c}{RT_c} (\mu C_p) \times \left(\frac{R}{C_p} \right) \frac{T_c}{P_c} \quad (C)$$

The value of $\frac{P_c}{RT_c} (\mu C_p)$ can be read directly from the prepared chart(fig26).

C_p is determined as

$$C_p = C_p^0 + \Delta C_p$$

and

$$\Delta C_p = \Delta C_p^{(0)} + w(\Delta C_p) \quad (1)$$

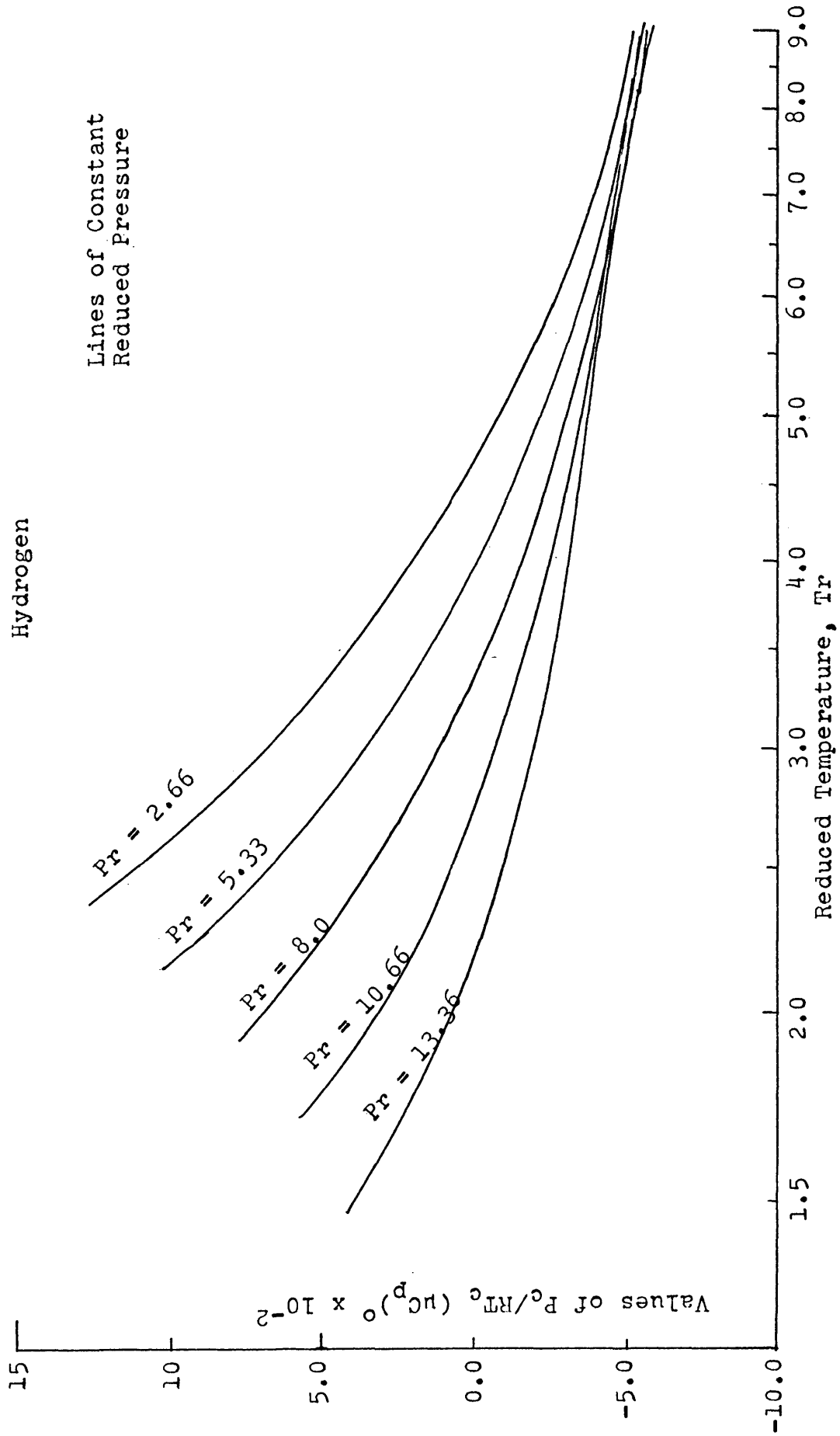


Figure 26.

As 'w' is zero

$$\Delta C_p = \Delta C_p^{(0)}$$

Therefore

$$C_p = C_p^{(0)} + \Delta C_p^{(0)}$$

This $\Delta C_p^{(0)}$ can be found from the chart of heat capacity for the simple fluid as given in the article by Edmister(15). Therefore μ values for hydrogen can easily be calculated from equation C.

COMPARISON OF THE CALCULATED VALUES OF
HYDROGEN, EMPLOYING NEW CONSTANTS, WITH
THE LITERATURE VALUES.

Calculated values for the Joule-Thomson coefficient of Hydrogen have been obtained from the Edmister correlation using actual and new effective constants and compared with the experimental data of A. Michels and his coworkers(21) in Table 19. The temperature and pressure range covered by A. Michels is shown in fig. 19.

Fig 27 represents the same values of Table 19 in graphical form, where Joule-Thomson coefficient has been plotted as a function of pressure with temperature as constant. It should be noted that the calculated values of Joule-Thomson coefficient through the use of the Edmister correlation and employing new effective constants are in very good agreement with the experimental values of A. Michels and his co-workers. Agreement is especially very good at lower temperature.

The agreement between the experimental and calculated values, using the actual constants is extremely poor.

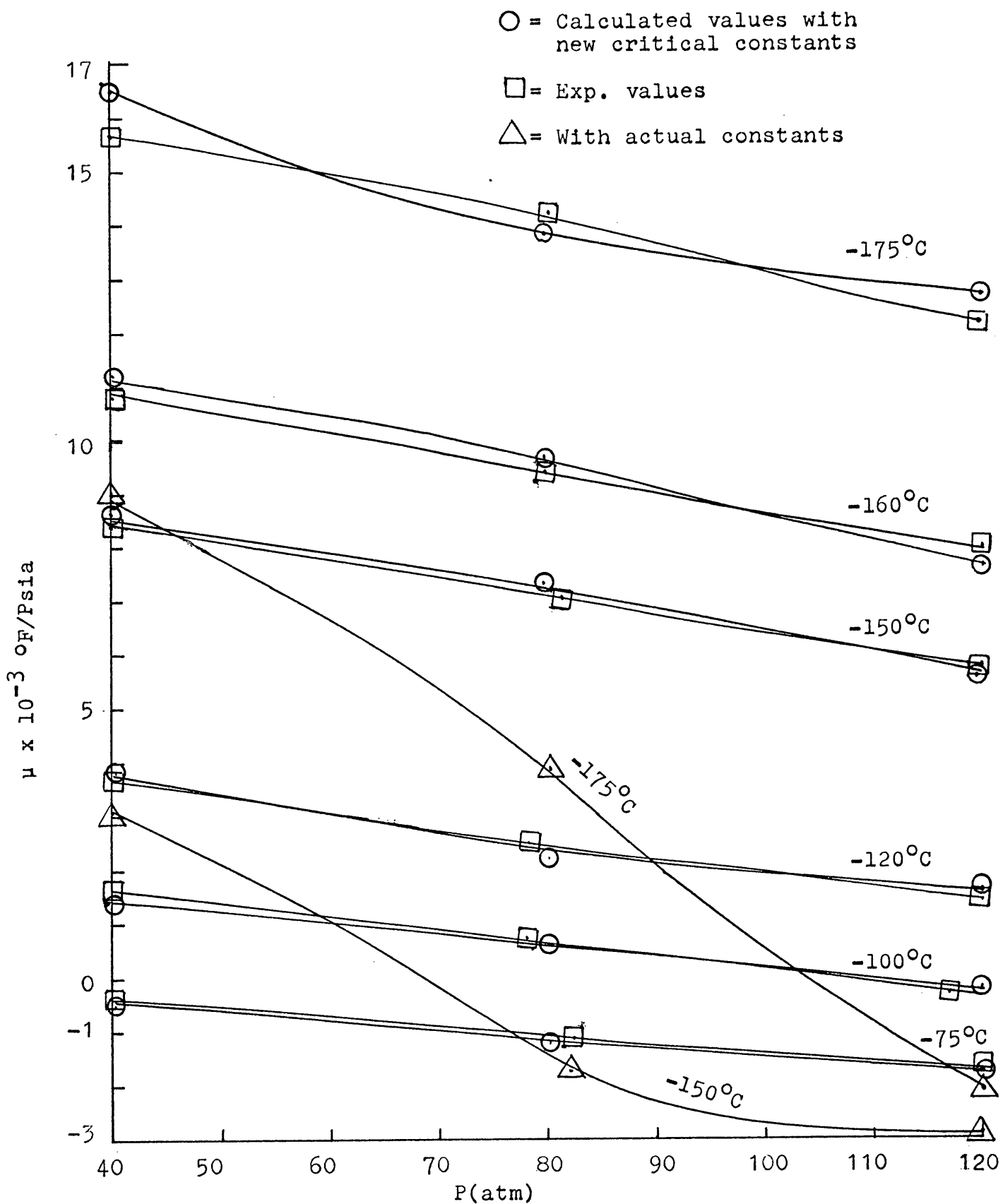


Figure 27. Comparison of Joule-Thomson Coefficients (Hydrogen).

TABLE No. 19

COMPARISON OF THE CALCULATED VALUES OF
HYDROGEN EMPLOYING NEW COSTANTS WITH
THE LITERATURE VALUES. (22)

$$\mu = \text{ }^{\circ}\text{F} / \text{Psia.}$$

| P atm./ [*] F | -175 | -160 | -150 | -120 | -100 | -75 |
|------------------------|---------|---------|----------|----------|-----------|-----------|
| 40 | 0.0165 | 0.0112 | 0.00852 | 0.00381 | 0.001526 | -0.000321 |
| *40 | 0.0157 | 0.0109 | 0.00851 | 0.00373 | 0.001627 | -0.000318 |
| **40 | 0.00894 | - | 0.00307 | - | - | - |
| 80 | 0.0138 | 0.00964 | 0.00727 | 0.002407 | 0.000657 | -0.00111 |
| *80 | 0.0142 | 0.00943 | 0.00712 | 0.00255 | 0.0006609 | -0.00105 |
| **80 | 0.00396 | - | 0.00061 | - | - | - |
| 120 | 0.01273 | 0.00768 | 0.00562 | 0.00162 | -0.000188 | -0.00177 |
| *120 | 0.01224 | 0.00796 | 0.00575 | 0.00153 | -0.000195 | -0.00172 |
| **120 | 0.0001 | - | -0.00099 | - | - | - |

* Literature values.

** Calculated values using actual constants.

COMPARISON OF THE CALCULATED VALUES OF THE JOULE-THOMSON COEFFICIENT OF A TERNARY MIXTURE ($H_2 + N_2 + CH_4$) THROUGH THE USE OF THE EDMISTER CORRELATION, EMPLOYING NEW EFFECTIVE CRITICAL CONSTANTS, WITH THE EXPERIMENTAL VALUES.

S.T. Sabnis(37) in his Ph.D. work at Lehigh Universit determined the Joule-Thomson coefficient of a ternary mixture of hydrogen-nitrogen-methane at various temperatures and pressures. The pressure and temperature range covered by him is already shown in fig.20.

The Joule-Thomson coefficient of this ternary mixture is calculated by using new effective critical constants and is compared with the Sabnis data in Table20.

Fig 28. represents the same values of Table 20 in graphical form, where Joule-Thomson coefficients of this mixture have been plotted as a function of temperature with pressure as constant.

It is noticed that the calculated values of this mixture employing new effective critical constants are in fair agreement with the Sabnis values. Agreement is better at high pressure.

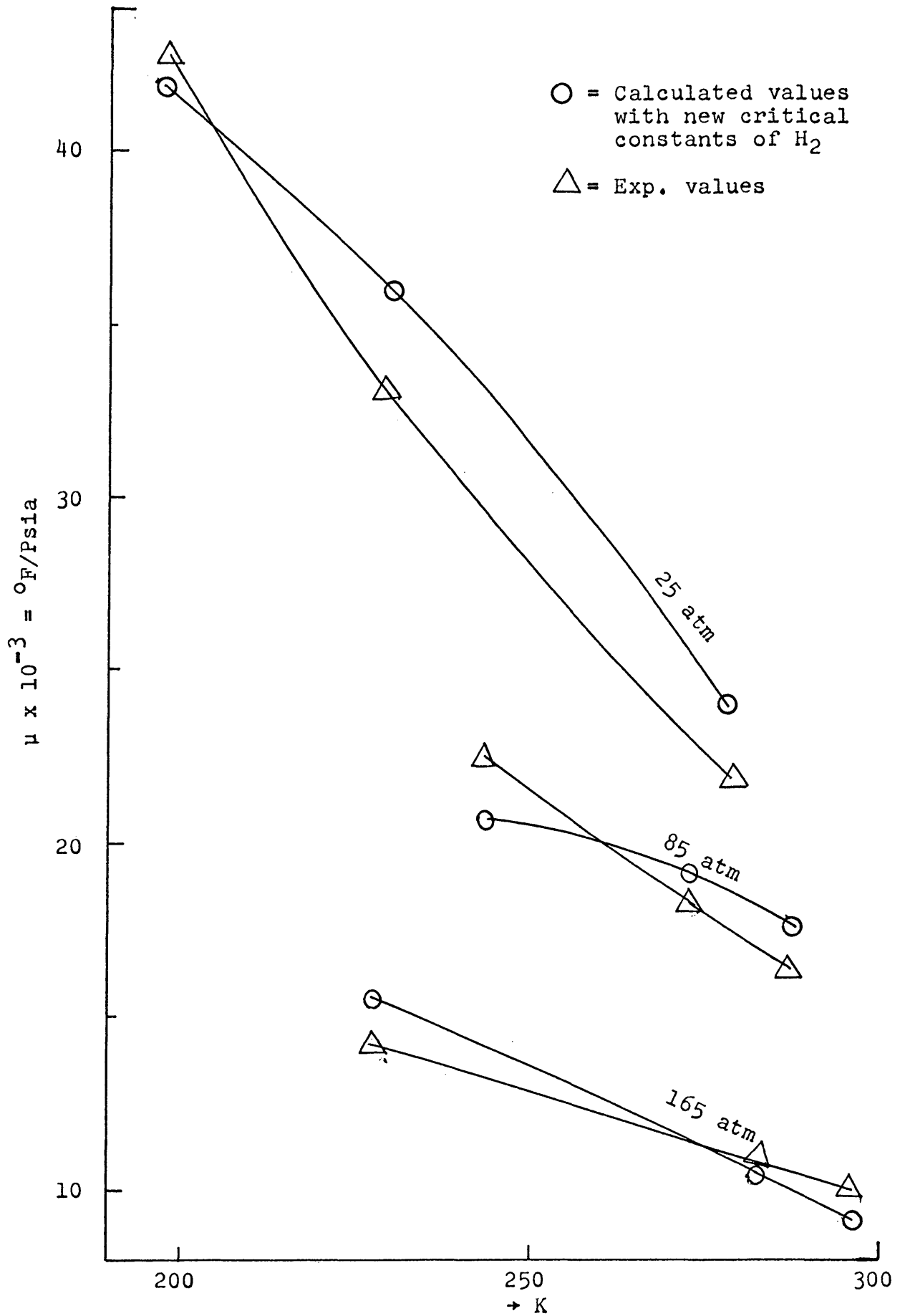


Figure 28. Comparison of Joule-Thomson Coefficients (Hydrogen-Nitrogen-Methane Mixture).

Table No.20

Hydrogen-Nitrogen-Methane Mixture (37)

$$\mu = \text{deg} / \text{Psia}$$

A) Composition 33 mole% each.

Temp. in Kelvin

| | | |
|--------|------------|---------------------|
| 230.21 | at 25 atm. | 0.036 calculated |
| | | 0.033 experimental |
| 278.31 | at 25 atm. | 0.024 calculated |
| | | 0.022 experimental |
| 198.28 | " | 0.0419calculated |
| | | 0.0427experimental. |

B) Composition 33 mole% each

| | | |
|--------|------------|---------------------|
| 243.75 | at 85 atm. | 0.0207 calculated |
| | | 0.0226 experimental |
| 287.80 | at 85 atm. | 0.0176 calculated |
| | | 0.0164 experimental |
| 273.56 | at 85 atm. | 0.0193 calculated |
| | | 0.0182 experimetal |

c) Composition 33 mole% each.

| | | |
|--------|--------------|---------------------|
| 227.65 | at +165 atm. | 0.0155 calculated |
| | | 0.0142 experimental |
| 282.91 | at +165 atm. | 0.01048 calculated |
| | | 0.0089 experimental |
| 296.34 | at +165 atm. | 0.0092 calculated |
| | | 0.0100 experimental |

HELIUM

Effective critical constants for Helium gas determined in a manner similar to that for hydrogen are as follows:

$$P_c = 5.2263 \text{ atm.}$$

$$T_c = 13.88 \text{ K}$$

These constants are based on 50K and 1 atm. In this case T_c also varies with pressure; Thus a correction factor (Helium correction factor) of 0.00816 was applied which means that, with the rise of each atm., T_r will increase by a factor of 0.00816. This T_r will be based upon 50K. A graph (fig 29) showing T_c as a function of pressure is prepared for helium gas.

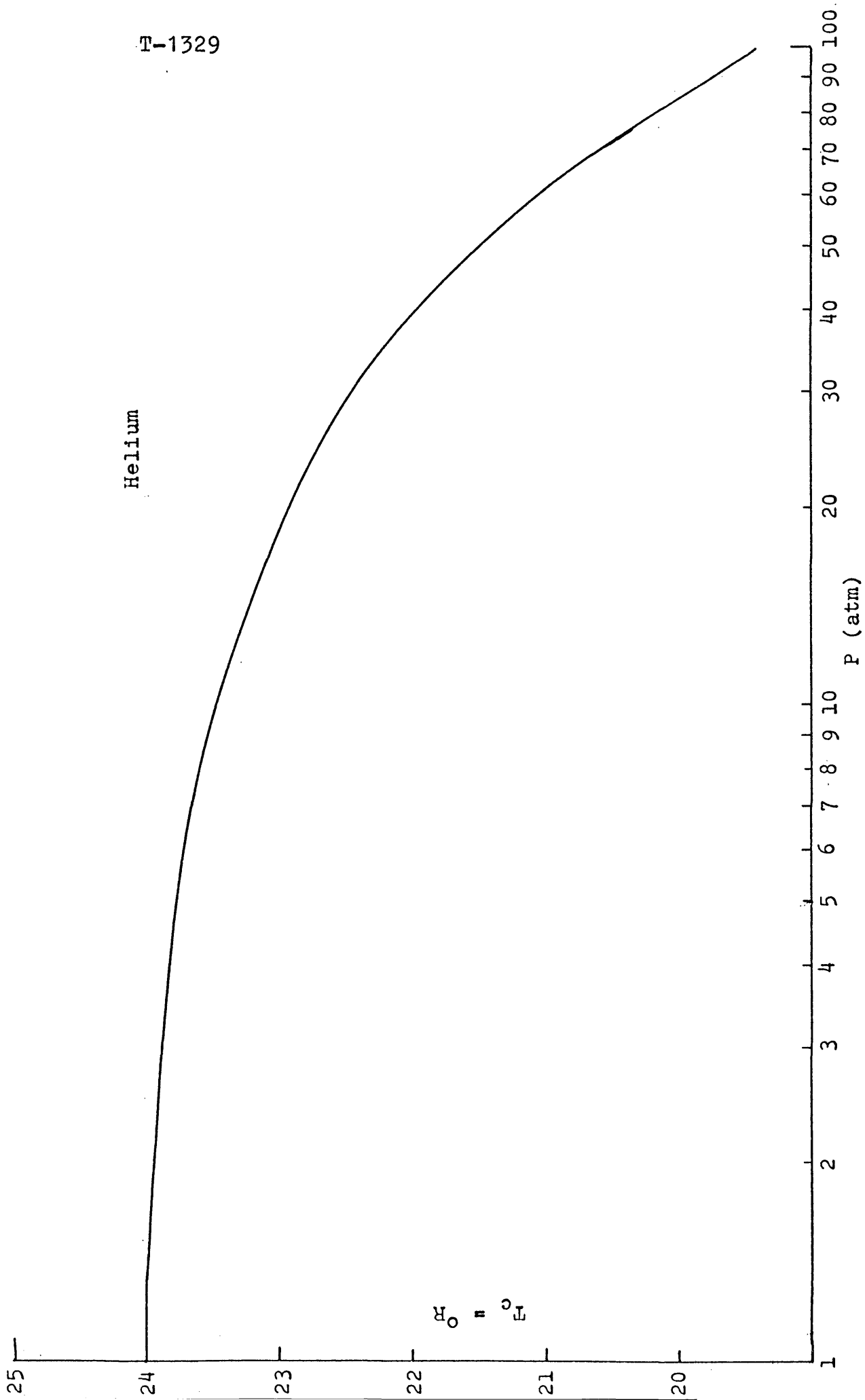
A new chart (fig 30), which is a generalized correlation of the product of Joule-Thomson coefficient and the heat capacity for helium gas, and which can be used to predict the Joule-Thomson coefficient of helium, has been prepared.

New effective critical constants and John. H. Perry (25) data were used to prepare this chart.

The acentric factor 'w' is also zero for helium, and therefore the same procedure as in case of hydrogen may be followed to calculate the numerical value of Joule-Thomson coefficient of helium.

T-1329

Helium



$T_c = T_0$

Figure 29.

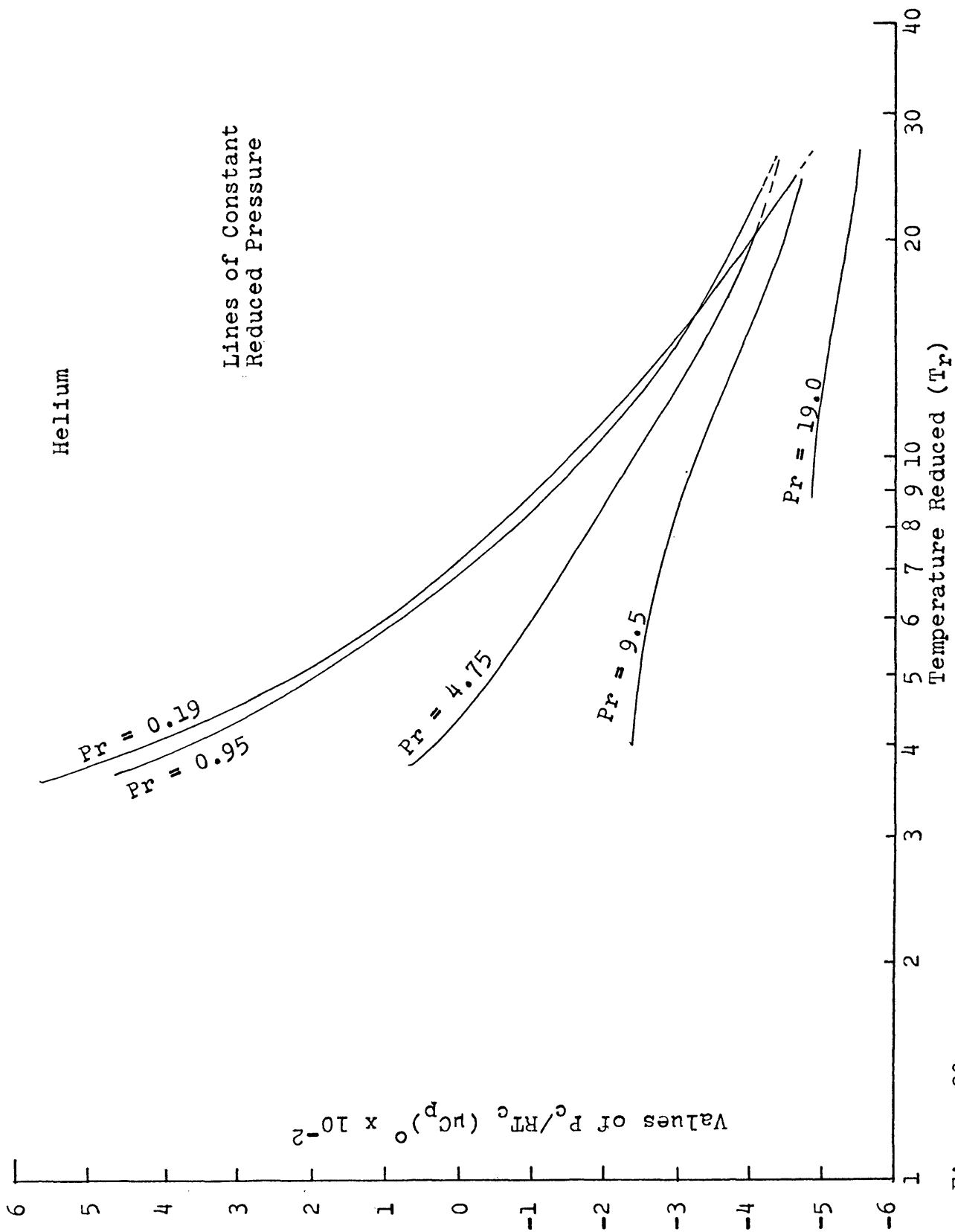


Figure 30.

COMPARISON OF THE CALCULATED VALUES OF THE JOULE-THOMSON COEFFICIENT OF HELIUM THROUGH THE USE OF THE EDMISTER CORRELATION EMPLOYING NEW EFFECTIVE CRITICAL CONSTANTS WITH THE LITERATURE VALUES.

John. H. Perry(25) calculated the Joule Thomson coefficient of helium, and his computations are based on equation of state of the Keyes type(62).

J.R. Roebuck and H. Osterberg(33) discussed the Joule-Thomson coefficient of helium but did not calculate the numerical value of $J.T.C.$. The pressure and temperature range covered by these investigators is shown in fig21. The Joule-Thomson coefficient of this gas is calculated by using new effective critical constants and is compared with the John. H. Perry in Table 21.

Fig 31 represents the same values of Table 21 in graphical form, where the Joule-Thomson coefficient has been plotted as a function of pressure at constant temperature. It is noticed that the calculated values of this gas employing new effective critical constants are in very good agreement with the Perry values.

TABLE No. 21

COMPARISON OF THE CALCULATED VALUES
 OF HELIUM EMPLOYING NEW EFFECTIVE
 CONSTANTS WITH THE LITERATURE VALUES(25).

$$\mu = \text{ }^{\circ}\text{F} / \text{Psia}$$

| P (atm.) | T in Kelvin. | | | |
|----------|--------------|-----------|-----------------------|-----------|
| | 50 K | 75 K | 100 K | 200 K |
| 1 | 0.00714 | 0.0027 | Difficult to read. | - 0.00381 |
| *1 | 0.00722 | 0.0023 | - 0.0000367 | - 0.00372 |
| 5 | 0.00593 | 0.00188 | - 0.000337 | - 0.00392 |
| *5 | 0.00590 | 0.00176 | - 0.00040 | - 0.00383 |
| 25 | 0.000698 | -0.000825 | - 0.00203 | - 0.00419 |
| *25 | 0.000790 | -0.000844 | - 0.00199 | - 0.00426 |
| 50 | - 0.00248 | -0.0032 | - 0.00355 | - 0.00483 |
| *50 | - 0.00276 | -0.00300 | - 0.00342 | - 0.00473 |
| 100 | - | - | - 0.00502 | - 0.00538 |
| *100 | - | - | - 0.00511 | - 0.00544 |

*Literature values.

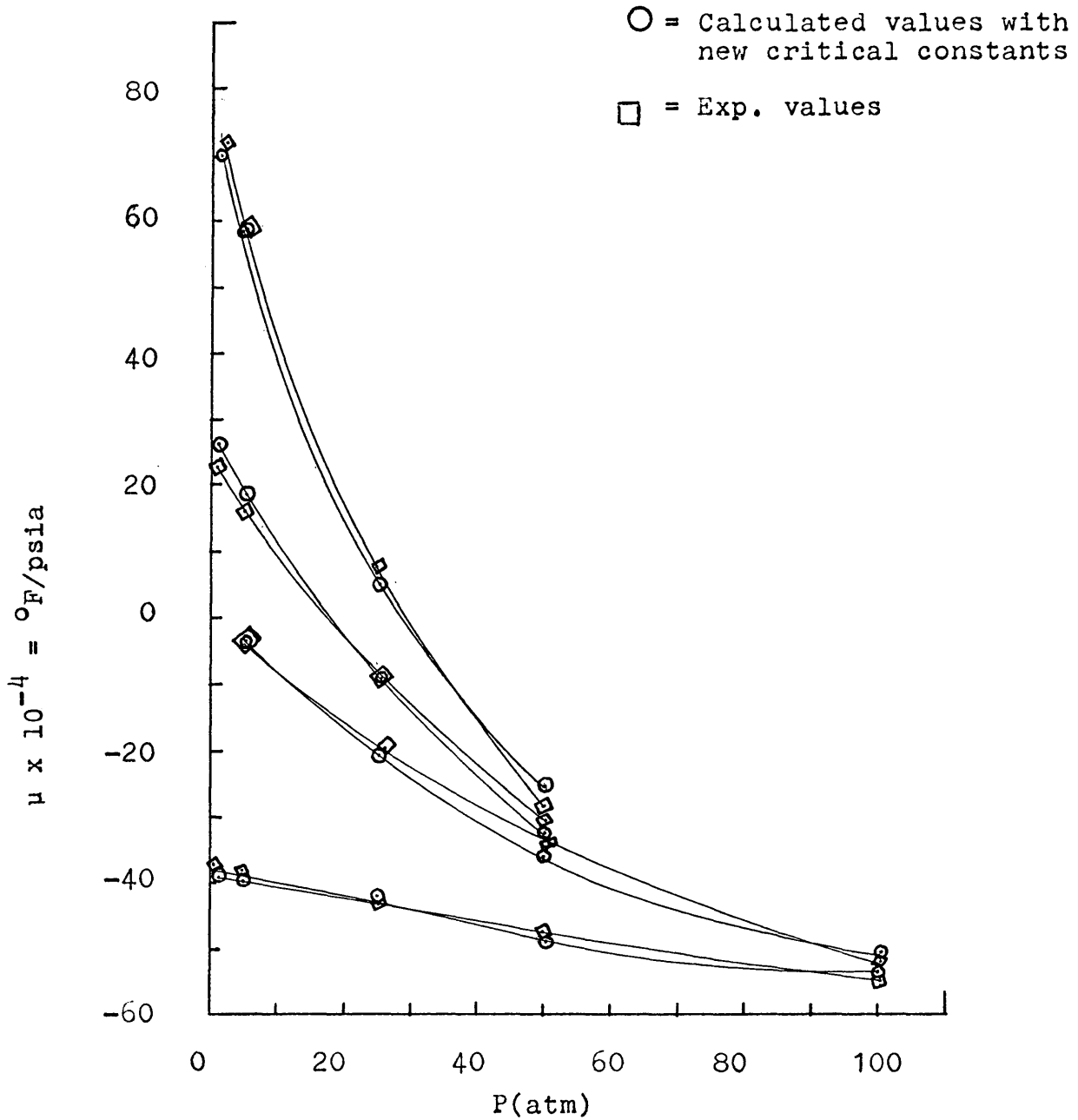


Figure 31. Comparison of Joule Thomson Coefficients (Helium)

COMPARISON OF THE CALCULATED VALUES OF THE JOULE-THOMSON
COEFFICIENT OF A BINARY MIXTURE(He+A) THROUGH THE USE OF
THE EDMISTER CORRELATION EMPLOYING NEW CRITICAL CONSTANTS
WITH THE LITERATURE V A L U E S

J.R. Roebuck and H. Osterberg(32) investigated the Joule Thomson coefficient of helium-Argon gas mixture at various mixture compositions. The composition, pressure, and temperature range covered by them is shown in fig.22.

The Joule-Thomson coefficient of this mixture (at one composition) by using the linear averaging mixing rule was obtained from the Edmister correlation by using new effective critical constants and is compared with the Roebuck and Osterberg values in Table 22.

Fig.32 represents the same values of Table 22. in graphical form, where the Joule-Thomson coefficient has been plotted as a function of pressure when temperature was constant.

It is noticed that the calculated values of this gas mixture employing new effective critical constants are in good agreement with the experimental values.

Agreement is especially good at higher temperatures and pressure, and at all temperatures, both values are almost identical.

TABLE No. 22

Helium - Argon Mixture (32)

Composition : He = 50.6 mole %
 A = 49.4 mole %
 μ = $^{\circ}\text{F}$ / Psia

| Temp/P $^{\circ}\text{C}$ | 20 atm | 60atm | 100 atm | 200 atm |
|------------------------------|---------|---------|---------|----------------|
| -50 | 0.0188 | 0.0141 | 0.01050 | 0.00460 |
| *-50 | 0.0154 | 0.0125 | 0.00996 | 0.004444 |
| 0 | 0.00835 | 0.00693 | 0.00553 | 0.00221 |
| *0 | 0.00880 | 0.00674 | 0.00504 | 0.00192 |
| -100 | - | 0.0240 | 0.0202 | 0.0072 |
| *-100 | - | 0.0217 | 0.0173 | 0.0066 |
| 50 | 0.00460 | 0.00342 | 0.00211 | -0.00012 (Appo |
| *50 | 0.00448 | 0.0029 | 0.00170 | -0.000085 |

* Literature values.

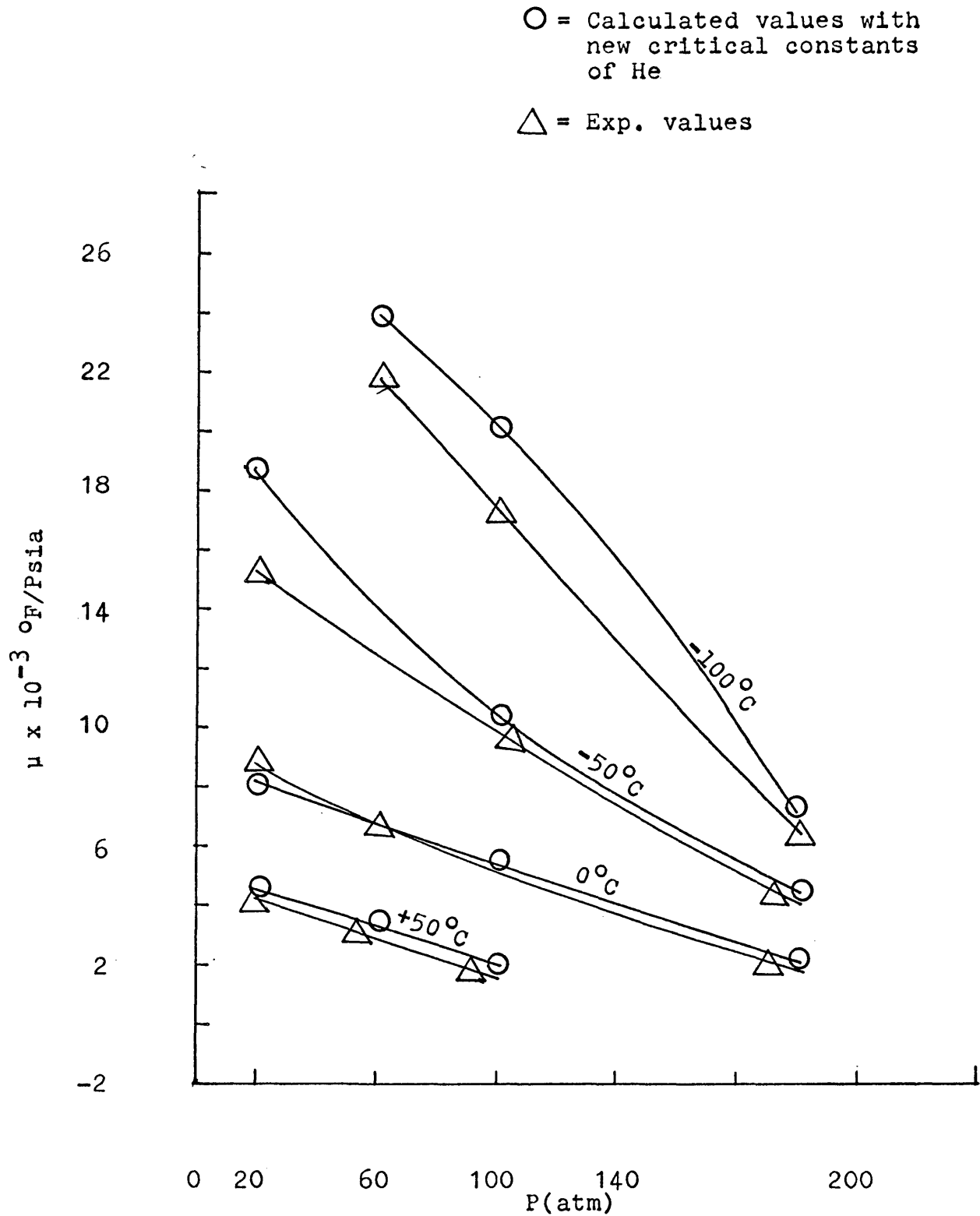


Figure 32. Comparison of Joule-Thomson Coefficients (Helium-Argon Mixture).

COMPARISON OF THE CALCULATED VALUES OF THE JOULE-
THOMSON COEFFICIENT OF A BINARY MIXTURE(He+N₂)
THROUGH THE USE OF THE EDMISTER CORRELATION EMPLOYING
NEW EFFECTIVE CRITICAL CONSTANTS WITH THE LITERATURE
VALUES

J.R. Roebuck and H. Osterberg(31) investigated the Joule-Thomson^{coefficient} of helium-nitrogen gas mixture at various mixture compositions. The composition, pressure and temperature range covered by them is shown in fig23.

Calculated values for the Joule-Thomson coefficients of He-N₂ mixture have been obtained from the Edmister correlation by using both actual and new effective critical constants and are compared with the experimental data of Roebuck and Osterberg in Table 23.

Fig 33. represents the same values of Table 23 in graphical form, where the Joule Thomson coefficient has been plotted as a function of pressure when temperature was constant.

It should be noticed that the calculated values of the Joule-Thomson coefficient through the use of the Edmister correlation and employing new effective constants are in good agreement with the experimental values. But the agreement between the experimental and calculated values, using the actual constants is poor, especially very poor at higher pressure.

TABLE No. 23

Helium - Nitrogen Mixture (31)

Composition : He = 51.0 mole %
 N₂ = 49.0 mole %
 μ = °F/Psia

| Temp / P °C | 20 atm | 60 atm | 100 atm | 140 atm |
|----------------|---------|---------|---------|----------|
| 0 | 0.00404 | - | 0.00162 | - |
| *0 | 0.00417 | - | 0.00154 | - |
| -50 | 0.0099 | 0.00742 | 0.00443 | 0.00331 |
| *-50 | 0.00882 | 0.00707 | 0.00489 | 0.00320 |
| ** -50 | 0.0072 | 0.00633 | 0.00346 | 0.000965 |
| -87.5 | 0.0148 | 0.01210 | 0.00782 | 0.00500 |
| *-87.5 | 0.0140 | 0.0111 | 0.00820 | 0.00589 |
| ** -87.5 | 0.0135 | 0.0100 | 0.00701 | 0.0024 |

*Literature values.

** Calculated values using actual constants.

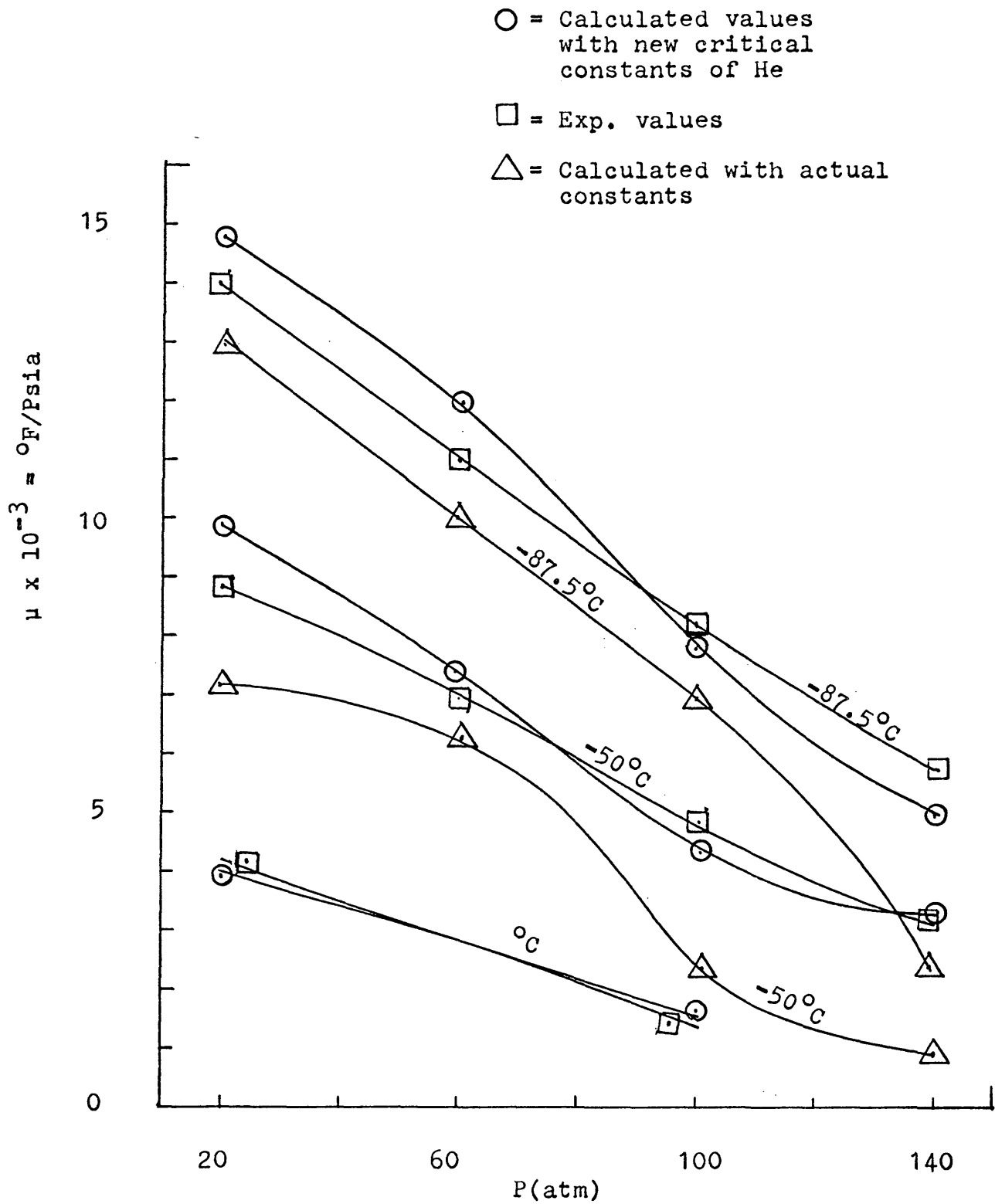


Figure 33. Comparison of Joule-Thomson Coefficients (Helium-Nitrogen Mixture).

COMPARISON OF THE CALCULATED VALUES OF THE JOULE-
THOMSON COEFFICIENT OF A TERNARY MIXTURE(He+N₂+CH₄)
THROUGH THE USE OF THE EDMISTER CORRELATION EMPLOYING
NEW EFFECTIVE CRITICAL CONSTANTS, WITH THE EXPERIMENTAL
VALUES

S.T. Sabnis(37) also determined the Joule-Thomson coefficient of a ternary mixture of helium-nitrogen-methane at various temperatures and pressures. The pressure and temperature range covered by him is shown in fig.24.

The Joule-Thomson coefficient of this ternary mixture is calculated by using the new effective critical constants and is compared with the Sabnis data in Table 24.

Fig.34 represents the same values of table 24 in graphical form, where the Joule -Thomson coefficient of this mixture have been plotted as a function of temperature when pressure was constant.

It is noticed that the calculated values of this mixture employing new effective critical constants are in good agreement with the experimental values.

Table No.24

Helium-Nitrogen- Methane Mixture(37)

Composition 33 mole% each.

| Temp in K | $\mu = \text{°F/Psia}$ | |
|-----------|------------------------|----------------------|
| 174.27 | at 25 atm. | 0.0430 calculated |
| | at 25 atm. | 0.0383 experimental |
| 207.65 | at 25 atm. | 0.0330 calculated |
| | at 25 atm. | 0.0281 experimental |
| 238.59 | at 25 atm. | 0.025 calculated |
| | at 25 atm. | 0.0229 experimental |
| 218.86 | at 85 atm. | 0.0206 calculated |
| | at 85 atm. | 0.0181 experimental |
| 247.76 | at 85 atm. | 0.0163 calculated |
| | at 85 atm. | 0.0150 experimental |
| 276.78 | at 85 atm. | 0.0130 calculated |
| | at 85 atm. | 0.0121 experimental |
| 199.03 | at 165 atm. | 0.01234 calculated |
| | at 165 atm. | 0.01138 experimental |
| 227.8 | at 165 atm. | 0.0120 calculated |
| | at 165 atm. | 0.0104 experimental |
| 255.32 | at 165 atm. | 0.00989 calculated |
| | at 165 atm. | 0.00893 experimental |

 &

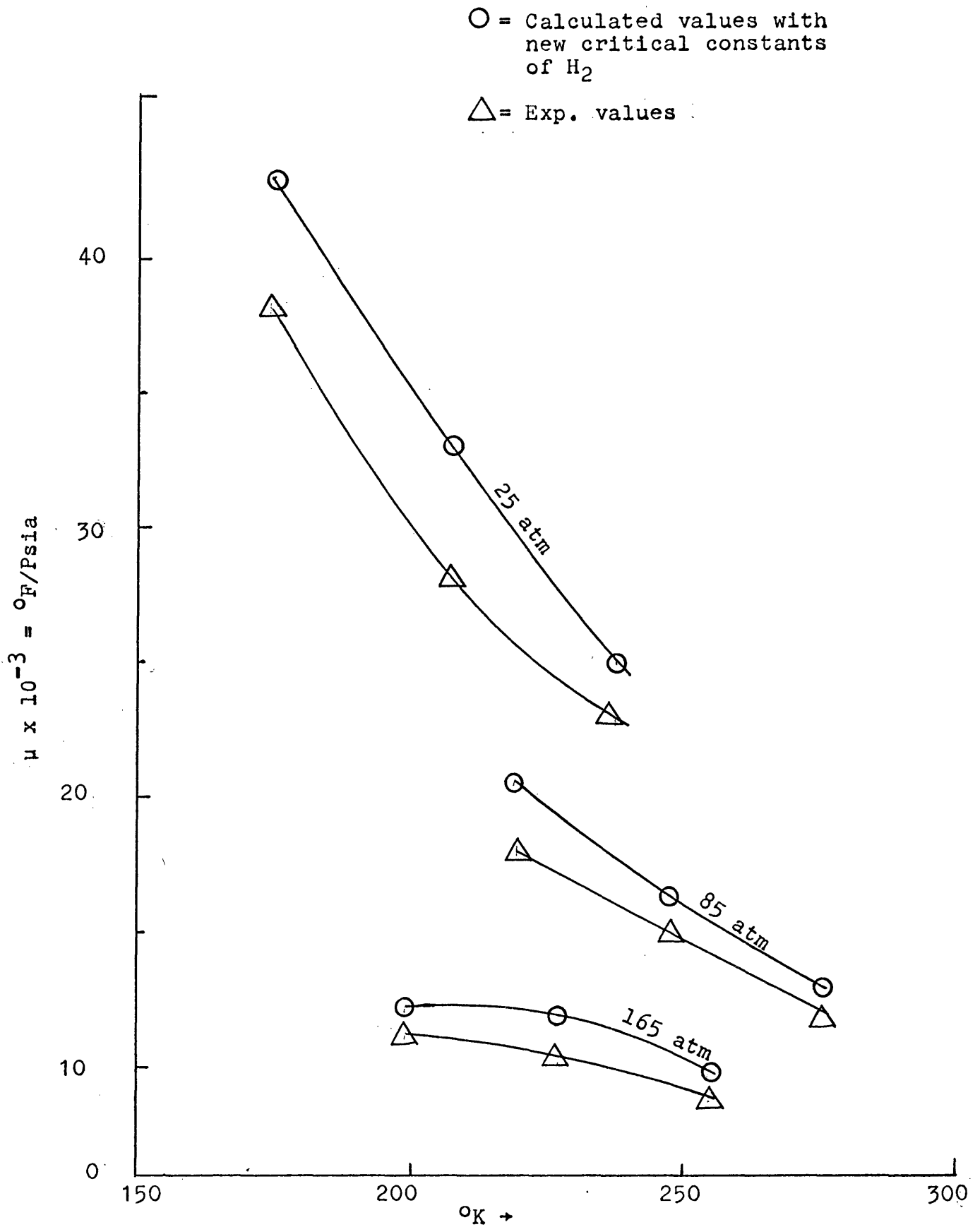


Figure 34. Comparison of Joule-Thomson Coefficients (Helium-Nitrogen-Methane Mixture).

DISCUSSION OF RESULTS

Experimentally determined Joule-Thomson coefficients for gases and mixtures of gases afford a satisfactory means of checking the accuracy of the Edmister correlation.

All available data on gases and gas mixtures were collected to investigate the reliability of the correlation. It is seen that the correlation, which was primarily evaluated for hydrocarbon gases can be used for the prediction not only of inorganic gases but also for all binary, ternary and higher mixtures.

Generally the experimental results agree well with the values calculated by the Edmister correlation. In the case of ethylene, it is seen that, up to 200 atmospheres, the calculated data agree well with the experimental values; but beyond this pressure the deviation is 20 to 24 percent, a deviation that arouses doubts about the data at higher pressure.

The pressure and temperature range covered by J.A. Beattie to determine the μ values of ammonia is such that Edmister correlation could not be applied except at 10.41 meter of Hg. At this pressure, the calculated value deviates about

10 percent from the Beattie's value, and there are no other data for comparison. Therefore it can be said that data on ammonia may or may not be reliable.

On the same basis it may be inferred that A. Schmidtke's data on freon-12 may not be reliable.

For the purposes of comparison overlapping data on methane, ethane, argon, nitrogen, carbon dioxide, and air have been plotted in fig 1.B, 2.B, 9.B, 10.B, 11.B, and 12.B. One of the objectives of this report was to improve the generalized correlation of Edmister so that it would be applicable to the quantum gases and their mixtures.

The following observations are made:

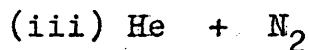
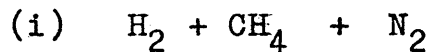
1. For use with the Edmister correlation, the critical temperature of hydrogen and helium are dependent upon the pressure. Overall, the relationship between the critical temperature and the pressure is a relatively smooth curve, with T_c increasing with pressure for hydrogen, but decreasing with pressure for helium. (fig 25 & 29).
2. Charts in figures 26 and 30 which use new effective constants to predict the Joule-Thomson coefficients for hydrogen and helium, have the following significance:

a) For hydrogen this new chart(fig26) can be used in the range $1.5 \leq T_r \leq 9.0$ as compared to $0.85 \leq T_r \leq 4.0$ in the case of the Edmister correlation, and $2.66 \leq P_r \leq 13.36$ as compared to $0.1 \leq P_r \leq 9.5$ for the Edmister correlation.

b) For helium, this new chart(fig.30) can be used in the range $4.0 \leq T_r \leq 20.0$ as compared to the original $0.85 \leq T_r \leq 4.0$, and $0.9 \leq P_r \leq 19.0$ as compared to the original $0.1 \leq P_r \leq 9.5$

In other words, at least for these two gases, this is a significant extension of the parameter used in the Edmister correlation.

3) In order to evaluate the performance of the modified critical constants, a comparison was made with the following gas mixtures:



Unfortunately there is not enough data for gas mixtures containing hydrogen. The only work is

that of S.T. Sabnis, who measured the Joule-Thomson coefficient for the two ternary mixtures $H_2 + CH_4 + N_2$ and $He + CH_4 + N_2$. For helium gas however, there are two other mixtures with argon and nitrogen.

New effective critical constants for hydrogen are verified as follows:

Joule-Thomson coefficients of hydrogen are calculated through the use of the Edmister correlation employing both actual and new effective critical constants. Results are given together with the literature values in Table 19 and are presented in graphical form in fig.27. It is seen that μ values calculated with the new effective constants follow the literature values, whereas values calculated with the actual constants deviate about 80 percent.

A revealing test for the evaluation of the modified effective critical constants for hydrogen is the calculation of the values for equimolar ternary mixture of $H_2 + CH_4 + N_2$. These values, together with the literature values, are given in Table 20, and are graphically presented in fig.28. It is noticed that maximum deviation is about 10 percent.

Similarly, the new effective critical constants for helium are tested by comparing the values of Joule-Thomson coefficient for helium, calculated through the use of the Edmister correlation by using the new constants with the literature values. Results are given in Table 21. and fig 31. Deviation is negligible.

Joule-Thomson coefficients of He + N₂ mixture are calculated through the use of the Edmister correlation by using both actual and new effective critical constants. Results are given together with the literature values in Table 23 and are presented graphically in fig. 33. It is seen that values calculated with the new effective critical constants follow within ± 10 percent of the literature values, whereas the values calculated with the actual constants deviate 50 to 60 percent at high pressure.

The average deviation in the case of He + A (Table 22, fig 32) is about 8 percent. Maximum deviation of the order of 15 percent is found in the case of ternary mixture of He + CH₄ + N₂ (Table 24, fig 34).

C O N C L U S I O N

The Edmister correlation is quite satisfactory for the prediction of the Joule-Thomson coefficient for pure gases and gas mixtures except for the quantum gases (H_2 , He and Ne). The calculated results for methane, ethane, propane, butane, pentane, nitrogen, carbon dioxide, argon, air, methane-ethane, methane-propane, methane-butane, and nitrogen methane agree within $\pm 2 - 12$ percent with the experimental values.

The calculated values of the Joule-Thomson coefficient of ethylene, at pressure more than 200 atm., deviate 20 to 24 percent from the experimental values.

The values of ammonia and freon-12 could not be calculated except at one or two points because their investigators covered a range of pressure and temperature that was not sufficient for use in the Edmister correlation.

The new effective critical constants for hydrogen and helium determined are as follows:

Hydrogen

$$T_c = 37.8 \text{ }^\circ\text{K} \quad P_c = 15 \text{ atm.}$$

Helium

$$T_c = 13.88 \text{ }^\circ\text{K} \quad P_c = 5.2263 \text{ atm.}$$

Critical temperatures of hydrogen and helium are found to ^{be} dependent upon pressure (Figs 25 and 29).

These constants extended the Edmister Correlation to these gases. The calculated results for hydrogen, helium, hydrogen-methane-nitrogen, helium-argon, helium-nitrogen, and helium-nitrogen-methane agree within ± 4 percent in the case of pure hydrogen and helium gases, ± 10 percent in the cases of hydrogen-methane-nitrogen and helium-nitrogen, and within ± 8 percent in the case of helium-argon. A maximum deviation 15 percent was observed for the helium-nitrogen-methane mixture.

APPENDIX 1

Calculation of the Joule-Thomson coefficient of methane(58) at 220F and 500 Psia by using the Edmister correlation(15).

Critical constants of methane

$$P_c = 673.26 \text{ Psia}$$

$$T_c = 343.8^{\circ}\text{R.}$$

$$\text{Therefore } T_r = \frac{220 + 460}{343.8} = 1.97$$

$$P_r = 500/673.26 = 0.74$$

Ideal gas state heat capacity at 220 F is C_p^0 (63) = 0.605 $\frac{\text{Btu}}{\text{lb F}}$.

The effect of pressure on the heat capacity from figs 28.1 and 28.2(15)

$$\Delta C_p = \Delta C_p^{(a)} + w(\Delta C_p^{(b)})$$

$$\text{where } w(53) = 0.0104$$

$$\Delta C_p^{(a)} = 0.025 \text{ Btu/lb F from fig 28.1}$$

$$\Delta C_p^{(b)} = 0.00775 \text{ Btu/lb F from fig 28.2}$$

$$\begin{aligned} \text{Therefore } \Delta C_p &= 0.025 + 0.0104(0.00775) \\ &= 0.02508 \text{ Btu/lb F.} \end{aligned}$$

$$\begin{aligned} C_p &= C_p^{(a)} + \Delta C_p \\ &= 0.605 + 0.02508 \\ &= 0.630 \text{ Btu/lb F.} \\ &= 10.08 \text{ Btu/lb mole F.} \end{aligned}$$

According to Edmister correlation (15).

$$\frac{P_c}{RT_c} (\mu C_p) = \left[\frac{P_c}{RT_c} (\mu C_p) \right]^{(0)} + w \left[\frac{P_c}{RT_c} (\mu C_p) \right]^{(1)}$$

from figs 28.3 and 28.4 (15)

$$\left[\frac{P_c}{RT_c} (\mu C_p) \right]^{(0)} = 0.295 \quad \text{from fig 28.3}$$

$$\left[\frac{P_c}{RT_c} (\mu C_p) \right]^{(1)} = -0.08 \quad \text{from fig 28.4}$$

$$\text{Therefore } \left[\frac{P_c}{RT_c} (\mu C_p) \right] = 0.295 \times 0.0104(-0.08)$$

and

$$\begin{aligned} \mu &= \left[\frac{P_c}{RT_c} (\mu C_p) \right] \left(\frac{R}{C_p} \right) \frac{T_c}{P_c} \\ &= \frac{0.294 \times 1.987 \times 343.8}{10.08 \times 673.26} \\ &= 0.0296 \end{aligned}$$

where Experimental value = 0.0295

APPENDIX II

Calculation of the Joule-Thomson coefficient of natural gas A(38) at 70F and 200 Psia by using the Edmister correlation(15).

Natural gas is a mixture of different gases. Selecting the gases of higher compositions(CO_2 , CH_4 , C_2H_6 , C_3H_8 , and $n\text{C}_4\text{H}_{10}$) and mixing these gases by linear averaging rule.

| | CO_2 | CH_4 | C_2H_6 | Propane | n-Butane |
|-----------------------------|---------------|---------------|------------------------|---------|----------|
| Wt%Comps. | 0.009 | 0.8255 | 0.0901 | 0.0462 | 0.0126 |
| Mole% | 0.00356 | 0.9204 | 0.0535 | 0.01873 | 0.00374 |
| T_c in $^{\circ}\text{R}$ | 547.2 | 343.8 | 550.8 | 666 | 765 |
| P_c in Psia | 1071.63 | 673.26 | 708.54 | 617 | 551.25 |
| w | 0.231 | 0.0104 | 0.0986 | 0.1524 | 0.201 |
| Mol.wt. | 44 | 16 | 30 | 44 | 58 |

$$\begin{aligned} \text{Mean } T_c &= (0.00356 \times 547.2) + (0.9204 \times 343.8) + \\ &\quad (0.0535 \times 550.8) + (0.01873 \times 666) + \\ &\quad (0.00374 \times 765) \\ &= 1.948 + 316.4 + 29.467 + 12.474 + 2.86 \\ &= 363.15 \text{ } ^{\circ}\text{F}. \end{aligned}$$

$$\text{Similarly Mean } P_c = 675.0 \text{ Psia.}$$

$$\text{Mean } w = 0.026$$

$$\text{Therefore } T_r = 530/363.15 = 1.459$$

$$P_r = 200/675 = 0.296$$

C_p at 70 F and 200 Psia(38) = 8.848 Btu/lb moleF.

According to Edmister correlation

$$\frac{P_c}{RT_c} (\mu C_p) = \left[\frac{P_c}{RT_c} (\mu C_p) \right]^{(0)} + w \left[\frac{P_c}{RT_c} (\mu C_p) \right]^{(1)}$$

From fig 28.3 and 28.4 (15)

$$\left[\frac{P_c}{RT_c} (\mu C_p) \right]^{(0)} = 0.51 \text{ from fig 28.3}$$

$$\left[\frac{P_c}{RT_c} (\mu C_p) \right]^{(1)} = 0.15$$

$$\left[\frac{P_c}{RT_c} (\mu C_p) \right] = 0.51 + 0.026 \times (0.15) = 0.5139$$

$$\mu = \left[\frac{P_c}{RT_c} (\mu C_p) \right] \left(\frac{R}{C_p} \right) \frac{T_c}{P_c}$$

$$= \frac{0.5139 \times 1.987 \times 363.15}{8.848 \times 675.0}$$

$$= 0.0621$$

where Experimental value = 0.0697

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