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Joule-Thomson Coefficients of Argon-Carbon Dioxide Mixtures

Adiabatic Joule-Thomson coefficients are presented for argon and two argon-carbon dioxide mixtures (46.4% CO_2 and 75.4% CO_2) in the single-phase part of the range: $-120 < T < 110°C$, $P < 190$ atm. Results are analyzed in terms of the virial equation (including terms to account for the quadrupole moment of CO_2), several forms of the Redlich-Kwong equation, and the Benedict-Webb-Rubin equation. In general, the best results were obtained by the Redlich-Kwong equation as modified by Barner et al. (1966).

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SCOPE

Methods of predicting the thermodynamic properties of mixtures, and thus phase and chemical equilibria, are essential if design work on new systems is not to remain tied to specific laboratory studies. The Joule-Thomson coefficient, which is zero for ideal gases, is a particularly rigorous test of predictive theories. This coefficient μ is defined as $(\partial T/\partial p)_H$; it is usually determined by the numerical differentiation of experimental curves of temperature vs. pressure obtained by the expansion of a gas to successively lower pressures through an adiabatic valve or porous plug. Precise measurements of ΔT and Δp make it possible to avoid the inherently inaccurate numerical or graphical differentiation by doing the experiment differentially. The pressure drop is confined to less than two atmospheres, for which ΔT is typically about one degree Celsius.

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CONCLUSIONS AND SIGNIFICANCE

The experimental methods used here have produced results that are more accurate than most others from the literature. They confirm the observations of others that the classical work of Roebuck (1934) has considerable systematic error in the important low-temperature region.

An evaluation of several equations of state indicates that methods based on the Barner modification (1966) of the equation of Redlich and Kwong are remarkably accurate without introducing excessively complicated calculations. On the molecular scale, it is evident that an intermolecular potential having a third parameter (the quadrupole moment) to account for orientation effects is necessary for a nonspherical molecule like carbon dioxide.

The significance of the work lies not only in the possibility of its direct application to the design of low-temperature systems involving Ar and CO_2, but also as a source of accurate data against which more elaborate predictive methods can be tested as they develop.

The apparent simplicity of the Joule-Thomson experiment—only temperatures and pressures need be measured—has attracted the interest of workers for nearly 120 years. The usefulness of accurate Joule-Thomson data has also long been recognized. Enthalpies, specific heats, and volumes can be easily calculated from Joule-Thomson coefficients. These properties are of great utility for the engineer involved in the design of low temperature separation plants. Joule-Thomson data are also a useful alternative to *P-V-T* or enthalpy data for testing the applicability of equations of state. The Joule-Thomson coefficient is a differential property and tends to magnify any disagreements. A nonzero Joule-Thomson coefficient is direct evidence of molecular interaction, and values extrapolated to zero pressure can be used in the same way as virial coefficients to obtain information about such interactions. Intermolecular potentials can be tested and force constants determined. Joule-Thomson coefficients, in fact, are somewhat more sensitive to the potential than are second virial coefficients (Kielich, 1961).

Many adiabatic and isothermal Joule-Thomson devices have been constructed. Good surveys of the experimental literature are available elsewhere (Sherwood, et al., 1966; Johnston and White, 1948; Yesavage et al., 1967; Mason and Spurling, 1969). The two coefficients are related through $\phi = -\mu C_p$. For the isothermal method, a heater is used to maintain the outlet temperature of the gas equal to the inlet temperature. This method appears to eliminate heat leak since the temperature is constant. However, between the points where the temperatures are measured, large temperature changes can occur if the gas is brought to a high velocity. This usually occurs at the point where the gas is throttled (the seat of a valve). Nonisothermal conditions can also occur near the heater. The isothermal method also requires accurate measurement of the gas flow rate. This can be quite a problem, especially in a closed-loop system. For these reasons, an adiabatic apparatus was constructed for the present work.

The throttling is usually created by a porous plug or a valve. The porous plug used by J. R. Roebuck and coworkers (1925, 1934, 1940, 1942) is well known and is a good example of this type of throttling device. Gas flows radially inward through a thimble-shaped ceramic plug. The downstream thermometer is located inside the thimble and is thus thermally isolated. Any heat leaking up the thimble is washed out by gas passing through the base of the thimble. The main disadvantage of this type of apparatus is that the pressure drop and flow rate can not be independently varied as they can be with a valve. Several plugs are usually necessary to cover the whole range of temperatures and pressures. Repeating the same experiment at a different flow rate also requires a plug change. Plugs of the proper porosity can be expensive and difficult to obtain.

A valve allows pressure drop and flow rate to be independently varied. The principal disadvantage is that heat leak is more of a problem. Experience and advances in low-temperature insulating techniques seem to have caused a recent renaissance of valve-type apparatuses; this design was also chosen for this work.

Data collection is generally accomplished for the adiabatic apparatus by an integral or by a differential method. For the integral method, the inlet pressure and temperature are held constant and the gas is throttled to a series of lower pressures and the resulting temperatures are measured. Since all downstream *T-P* points have the same enthalpy as the upstream point, these points define an isenthalp on a *T-P* plot. To obtain Joule-Thomson coefficients, the data must be differentiated numerically—a process which decreases their accuracy. This method was used by Roebuck with his porous plug and by most other workers.

For the differential method, small pressure drops are used and the ratio of $(\Delta T/\Delta P)_H$ is measured. If the pressure drop is sufficiently small, this can be equated to μ. Pressure drops of a few atmospheres are usually small enough. This method was used by Sage et al. (1936) with a porous plug. The differential method was employed for the work reported here.

A good deal of experimental Joule-Thomson data are available for pure components. The much smaller amount of mixture data available usually covers a limited temperature and pressure range or is not very accurate. Most of the available data are for mixtures containing hydrocarbon components. Data for nonhydrocarbon mixtures which are reasonably nonideal are quite limited. Such mixtures are frequently encountered and their nonideal behavior challenges existing predictive techniques.

Carbon dioxide was selected as one of the components because of its large quadrupole moment. Its intermolecular potential is not spherically symmetric and large nonidealities result, especially at low temperatures. Argon was chosen as a second component because it is monatomic and has a spherically symmetric potential. There is no quadrupole-quadrupole interaction between the Ar and CO_2 molecules, and the quadrupole-induced dipole contribution is quite small. This should cause the mixture to deviate from what one might expect from pure component data. Therefore, it was felt that this system should present a good challenge for existing equations of state but not be hopelessly complex.

Roebuck's μ data (1934, 1942) were available for each pure component for comparison and some values of

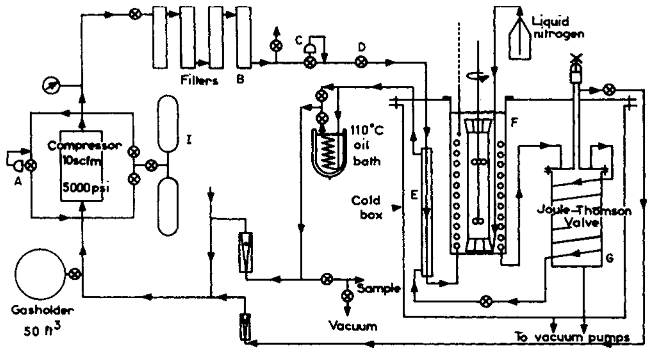

Fig. 1. Flow sheet for Joule-Thomson apparatus.

μ calculated from Michels' *P-V-T* data were also available for the pure components (Michels et al., 1950, 1958; Degroot and Michels, 1942). Isothermal Joule-Thomson coefficients covering a large temperature range were available for argon (Ishkin and Rogovaya, 1957) and for CO_2 (Charnley et al., 1953) over a limited temperature range. Virial coefficients for both pure components were available (Dymond and Smith, 1969) in addition to mixture virial coefficients over a small temperature range (Cottrell et al., 1956; Lichtenhaler and Schäfer, 1969).

APPARATUS DESCRIPTION

The apparatus was used over the temperature range $-120° < T < 110°C$ with pressures to 190 atm but was designed for a slightly larger range. Gas flows of 1 to 11 std. cu. ft./min. were used with a pressure drop of about 2 atm across the valve.

A schematic of the flow system is shown in Figure 1. A four-stage oil-lubricated compressor compresses the gas to about 15 atm above operating pressure. The compressor outlet pressure is regulated with a back pressure regulator (A) which recycles the unused portion of the gas back to the inlet of the compressor. The gas then passes through a filtering train (B) to remove oil vapors and any water in the system. The first filter is a trap for large drops; it has a tangential inlet. The other filters are packed with glass wool and various adsorbents. The composition of the gas was determined at each experimental point chromatographically and periodic small additions of CO_2 were made to compensate for its removal in the filters.

A Hoke two-stage regulator (C) then drops the pressure to the desired level. Very fine adjustment of the pressure is made with a needle valve (D). The gas then enters the cold box, which is a large cylindrical tank (about 50 gallons) containing the constant temperature bath, the Joule-Thomson valve, heat exchangers, and various valves. It is filled with a low temperature powder insulation (50% by weight Cab-O-Sil M5 and 50% fine aluminum powder) which was continuously evacuated to below 0.2 torr. The thermal conductivity of the powder is about 2.3×10^{-6} watts/cm°K (Hunter et al., 1960).

The gas is precooled by passing through a double-tube heat exchanger (E) where it countercurrently exchanges heat with the exiting gas stream. The gas then passes through about 70 ft. of copper tube with an inside diameter of about ⅛ in. which is in the constant temperature bath. The bath is filled with various cryostat fluids for different temperature ranges (Kanolt, 1925). At high temperatures, silicone oil is used. When necessary, cooling is provided by blowing liquid nitrogen through an evaporator in the bath or by a small Freon-12 refrigerator. The bath fluid is circulated around a draft tube. A Bayley proportional temperature controller is used to maintain a constant bath temperature. This temperature did not drift more than 0.05°C/3 hours.

From the bath, the gas passes to the Joule-Thomson valve where it is throttled by a Δ P of about 2 atm. A small portion (~0.3 std. cu. ft./min.) of the gas is bled up through the valve handle extension tube to wash out any heat leaking down these metal parts. The valve is located inside a metal heat-shield can (G) which is also filled with the powder insulation and separately evacuated to about 0.06 torr. The gas leaving the valve passes through a coil of tubing soldered to this can. Thus, the valve is surrounded by walls which are brought close to the operating temperature. The gas then encounters a throttle valve. It can be throttled down to a few atmospheres before entering the heat exchanger, causing a large temperature drop. This often caused enough cooling of the incoming gas so that no additional refrigeration was required for operation at temperatures down to $-20°C$. Frequently, the throttled stream would be well into the two-phase region. This caused no flow instabilities unless solid CO_2 was formed. In this case, the gas was not throttled until after it left the cold box and was heated to about 110°C by passing through a coil in an oil bath.

Flow rates are monitored with a rotameter (H) before the gas returns to the compressor. A sampling system allows samples to be taken at this point which are stored in small cylinders.

A Wiggins gasholder floats on the compressor inlet to regulate the inlet pressure and compensate for changes in the volume of gas in the system because of pressure changes. The gas is returned to high pressure storage tanks (I) after each day's running.

The Joule-Thomson valve is shown in Figure 2. The metal parts are all type 304 stainless steel with welded joints. The interior parts of the valve are Kel-F and Teflon. Kel-F was used where rigidity was required such as for the stem and seat. This limits the upper operating temperature to about 175°C.

Gas enters the upper chamber of the valve from the gas inlet tube and flows upward and around the upper part of the supporting sleeve. At heat leak into this annular section is absorbed by the gas prior to measurement of the upstream temperature. The gas then flows downward and over 16 thermocouple junctions (T_1). At the seat, the gas undergoes a two-atm. drop in pressure. The stem angle is 30° and the seat

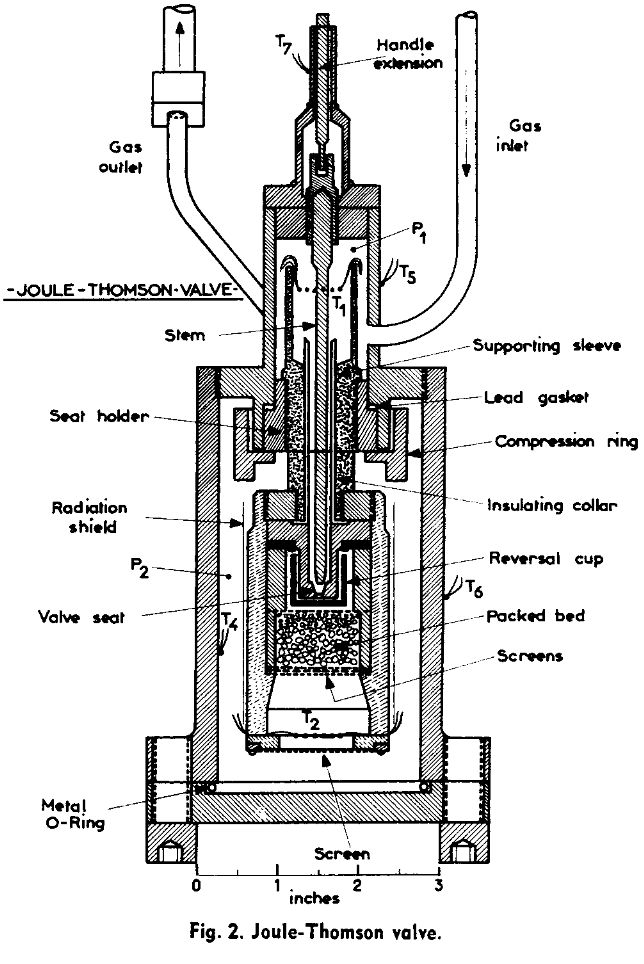

Fig. 2. Joule-Thomson valve.

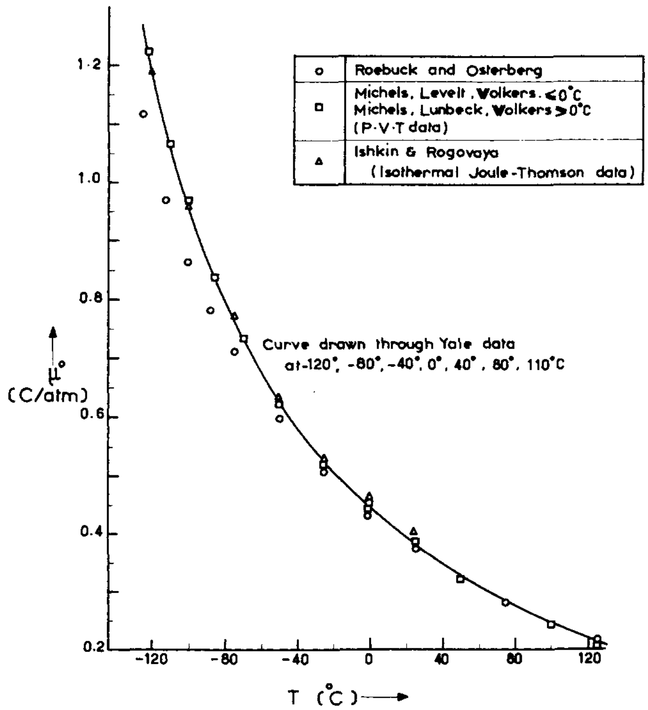

Fig. 3. Comparison of various experimental Joule-Thomson coefficients at zero pressure for argon.

orifice is 3/32 in. This allows reasonably fine adjustments of the valve to be made. The gas then flows upward between the seat and flow reversal cup to the top of the cup where it leaves through a series of small holes. This design thermally isolates the seat. At first, the seat was located just above the retainer ring and relatively large errors due to heat leak to the seat occurred. Calculations showed that the temperature of the gas in the seat region could drop by 30°C owing to the velocity increase. As the gas stagnates at the walls, it does not fully recover its temperature, and the seat wall can be 3°C below the upstream or downstream temperatures. A heat leak results which causes the data to fall low at low pressures. The calculations showed that the error would be nearly independent of flow rate. This was found to be the case. Isolation of the seat in the flow reversal cup eliminated the possibility of this kind of error by making the conduction path long and tortuous.

The gas then passes through a packed bed to break up any jets and to produce a uniform temperature distribution. The packing is 1/16-in. round aluminum pellets. A series of one coarse and two fine screens below the bed further reduces jets to fined-grained turbulence. No jets could be detected 2 mm from the bed (fine screens removed) with a pitot tube and inclined water manometer with high flows a atmospheric pressure.

After this bed the gas flows over the downstream thermocouple junctions (T_2) and then up the annular section between the walls and the packed bed. A radiation shield surrounds the packed bed. Heat leaking in through the downstream walls is absorbed by the gas in this section and is carried out with it. The gas then leaves through two exit tubes.

The valve is assembled through the bottom flange which is sealed with a teflon-covered hollow metal O-ring.

INSTRUMENTATION AND ERRORS

The temperature drop (usually less than 1°C) was measured with a 30-junction (15 junctions each side) thermopile. It was made of 30-gauge copper and constantan wires. The leads passing between the upstream and downstream sides were sealed into four holes in the seat holder with epoxy.

The thermopile was calibrated in a differential manner against a calibrated platinum resistance thermometer at six temperature levels extending to −130°C. The 52 calibration points were represented very well by an equation

$$E = (a_1 + 2a_2 T + 3a_3 T^2 + 4a_4 T^3) \cdot \Delta T - (a_2 + 3a_3 T + 6a_4 T^2) \cdot \Delta T^2 + (a_3 + 4a_4 T) \cdot \Delta T^3 - a_4 \cdot \Delta T^4 \quad (1)$$

The four independent constants were determined by least squares; the calibration introduces a maximum error of $0.6\mu V$, or ±0.001°C/atm in μ. Calibrated absolute thermocouples were used to measure the upstream and downstream temperatures ($T1$ and $T2$, Figure 2). Skin temperatures were also monitored at several locations. EMF's were measured with a Leeds and Northrup type K-3 potentiometer.

Two large Heise Bourdon tube gauges indicated the upstream and downstream pressures, $P1$ and $P2$. A calibrated deadweight gauge of the simple free-piston type developed by Keyes was actually used to measure and set $P1$.

Pressure drop was measured with a high pressure differential mercury manometer. It is a modification of a manometer described by Barnett et al. (1963). The mercury level was observed to within ±0.2 mm in a moveable cell with a view window. A differential Bourdon tube gauge (Midwest Instruments) was used to indicate the ΔP so that a given pressure drop could easily be set.

The largest measurement error was the chromatographic composition determination. The composition could be established to within 0.3% CO_2. Six calibration gases were used (3 for each mixture) to attain this accuracy. This could result in a maximum error in μ of 0.2 to 0.3%. The method of propagation of errors using maximum errors for each measurement shows that the maximum error in μ attributable to the instrumentation is ±(0.001°C/atm + 0.53%) for the mixtures and ±(0.001°C/atm + 0.22%) for argon. Remaining errors are attributable to instabilities in the experimental conditions, impurities, corrections applied to the data, and errors associated with nonisenthalpic conditions—heat leaks, jets, etc.

Instability of the inlet temperature and pressure was quite small and did not cause any significant error in μ. The ΔP would often cycle over a range of ± 0.3 torr and occasionally went as high as ± 10 torr for some of the high pressure points. These fluctuations produced cycles in ΔT of ± 0.5 μv to as high as ± 2 or 3 μv. The cycling was in phase and frequent simultaneous readings were made to improve the accuracy. The maximum error in μ due to instabilities is estimated to be ± (0.0005°C/atm + 0.13%). When operating in the two-phase region these fluctuations were quite large. Composition variations are also quite likely in this region. For these reasons, the 2-phase data are not presented.

High purity argon (Air Products Inc.) and Coleman Instrument grade carbon dioxide (Matheson) were used. They contain no stated impurities which could be of any significance. This was confirmed by chromatographic analysis. N_2 and O_2 gradually entered the system by diffusion through the rubber seal of the gasholder. When analysis revealed 0.1 to 0.2% total impurities, the gas was discarded. These small impurities can safely be counted as argon since their properties are similar to those of argon.

Variation in the CO_2 concentration was usually below 0.5%. The data were interpolated to the average composition. Also, small interpolations were made to correct the average temperature to even values of T(40°, 0°, −40°, etc.). The total of these corrections was generally less than 0.5% and any reasonable errors in the estimation of the corrections will not contribute significantly to error in μ.

A change in elevation occurs as the gas passes between the upstream and downstream thermocouples. The change in gravitational potential can be neglected; however, the head change causes a slight compression of the gas. This compression is isentropic (rather than isenthalpic) and typically causes an error in ΔT of 0.2 to 0.8%. Corrections applied to the data for this effect were estimated from the Barner et al. (1966), modification of the Redlich-Kwong equation (See Analysis of Results section). Any resulting error in μ can be neglected.

Errors caused by nonisenthalpic conditions can only be estimated from the data themselves. Some scatter of the data in the low density region was noticed. It seemed that the magnitude of the scatter varied inversely with the density of the gas, increasing at low pressure and high temperature. It was

Table 1. Estimated Accuracy of the Data
(Expressed as percent of μ°)

	Argon		Ar-CO$_2$ Mixtures	
Low density	Raw	Smoothed	Raw	Smoothed
(30 atm, 40°C)	±5%	±2%	±2.5%	±1%
High density	±1%	±0.75%	±1%	±0.75%

Table 2. Joule-Thomson Coefficients (°C/atm)
Argon

P(atm) T(°C)	110	80	40	0	−40	−80	−120
0	0.231	0.276	0.349	0.444	0.584	0.798	1.190
10	0.2240	0.2677	0.338	0.432	0.568	0.782	1.163
20	0.2174	0.2593	0.328	0.419	0.550	0.758	1.122
40	0.2043	0.243	0.308	0.392	0.513	0.697	0.970
60	0.1917	0.227	0.287	0.365	0.471	0.617	0.226
80	0.1794	0.2123	0.266	0.336	0.426	0.524	0.100
120	0.1557	0.1840	0.229	0.280	0.332	0.312	0.042
160	0.1340	0.1572	0.192	0.226	0.245	0.170	0.012
200	0.1148	0.133	0.162	0.178	0.172	0.101	0.000

Table 3. Joule-Thomson Coefficients (°C/atm)
46.4% CO$_2$-53.6% Ar

P(atm) T(°C)	110	80	40	0	−20	−40
0	0.384	0.458	0.604	0.808	0.962	1.157
10	0.376	0.449	0.592	0.792	0.937	1.129
20	0.368	0.440	0.576	0.773	0.910	1.097
40	0.350	0.420	0.544	0.723	0.847	—
60	0.333	0.397	0.509	0.664	—	—
80	0.315	0.373	0.472	0.589	—	—
120	0.277	0.321	0.388	0.401	—	—
160	0.239	0.269	0.300	0.246	0.161	0.081
200	0.202	0.220	0.220	0.153	0.097	0.045

not noticed above 40 atm. for argon and was almost imperceptible in the mixture data. The scatter in the argon data was less than ±5% for the worst low pressure point. The scatter was even higher for some preliminary data taken for nitrogen. The density of nitrogen at the same conditions is lower than for argon and its Joule-Thomson coefficient is smaller and both effects magnify the scatter. The scatter showed no clear dependence on flow rate in the range 1 to 9 std.cu. ft./min. In the liquid and high-density gas regions (where fluctuations are maximum) the reproducibility was quite good—within the limits of accuracy of the measuring instruments.

The cause of the scatter is not known. Jets in the downstream side will make μ too high. Heat leak will cause low values. Scatter both above and below the proper value must be caused by some more complex phenomenon such as a vortex in the downstream side. Points where the error was large usually showed an error in the downstream thermocouple reading of several tenths of a degree. This thermocouple measures temperature at a single point rather than the average of 15 points indicated by the thermopile and is thus more sensitive to nonuniformity in T$_2$.

The estimated accuracy of the data is shown in Table 1. It is expressed as percent of the zero pressure value of μ for that isotherm since percent error is not meaningful when μ is small (as it usually is at high pressure).

RESULTS—EXPERIMENTAL DATA

The smoothed μ values for argon and two argon-carbon dioxide mixtures of 46.4 and 75.4% CO$_2$ are given in Tables 2 to 4. The smoothing was done graphically. Raw data appear in Figures 4 to 10.

A comparison of the −120° argon isotherm with the μ values of Roebuck and Osterberg (1934) and the values of μ calculated by Michels et al. (1950) from their very precise P-V-T data is shown in Figure 6. The correction factor of 0.9677 due to an error in pressure measurement (Roebuck and Osterberg, 1940) was applied to the Roebuck Osterberg (1934) data. The agreement between the Michels data and those presented here is excellent. Roebuck's data differ by as much as 20% near 30 atm. The same discrepancy is also evident for the −80° and −40° isotherms, where Roebuck's data appear to differ by a maximum of 4% at low pressure. At the highest pressure, Roebuck's data fall above other sets of data for almost all isotherms. This is probably a result of his numerical differentiation technique.

A comparison of μ values extrapolated to zero pressure

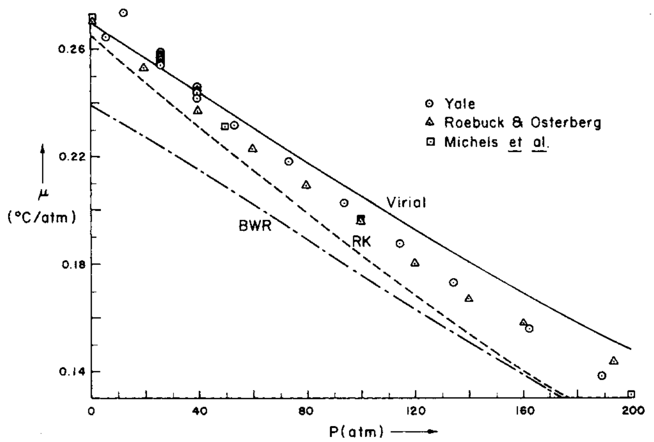

Fig. 4. Joule-Thomson coefficients for argon at 80°C.

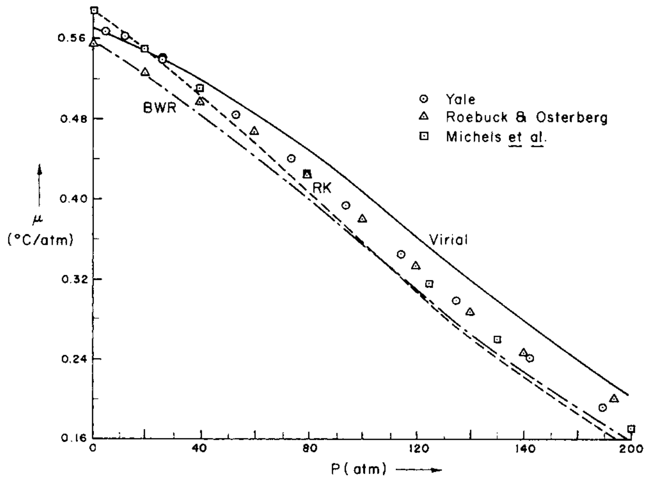

Fig. 5. Joule-Thomson coefficients for argon at −40°C.

TABLE 4. JOULE-THOMSON COEFFICIENTS (°C/ATM)
75.4% CO_2-24.6% Ar

P(atm)	T(°C) 110	80	40	0	−40
0	0.504	0.615	0.811	1.113	1.655
10	0.497	0.604	0.798	1.105	1.632
20	0.489	0.595	0.784	1.093	—
40	0.468	0.570	0.752	1.043	—
60	0.447	0.541	0.710	0.928	—
80	0.423	0.509	0.652	0.590	—
120	0.321	0.434	0.454	0.150	0.0093
160	0.311	—	0.264	0.072	0.0015
200	0.243	—	0.163	0.049	−0.0036

TABLE 5. A_{12} (CM³/MOLE)

T, °C	From 45.4% CO_2 mixture	From 75.4% CO_2 mixture	Weighted average
110	95 ± 6	94 ± 13	95 ± 8
80	111 ± 7	122 ± 17	114 ± 10
40	148 ± 9	166 ± 23	153 ± 13
0	196 ± 12	241 ± 34	209 ± 18
−40	259 ± 16	309 ± 43	275 ± 23

for argon is shown in Figure 3. In addition to the data of the other workers mentioned previously, the data of Ishkin and Rogovaya (1957) are also shown. They were calculated from their experimental Φ values. A slight extrapolation from $P = 1$ atm to $P = 0$ was required for each set of data. Again, the agreement with Michels et al. is quite good. Roebuck's data fall low by up to 10% at low temperatures. Agreement with Ishkin and Rogovaya is excellent at low temperature, but their data appear to be too high by about 5% at their upper temperature of 24°C.

The apparent error in Roebuck's low temperature argon data was noted by Ishkin and Rogovaya. Ishkin and Kaganer (1957) also found disagreement of Roebuck's air data with their own by 10 to 15% below − 100°C and disagreement of 15 to 20% with his nitrogen data at low temperatures. It is hard to imagine the cause of the error in Roebuck's data. In view of the confirmation that this work gives to the conclusion of Ishkin and Rogovaya about Roebuck's data, any conclusions based on his data must be suspect.

Values of $A_{12} = (\mu\ C_p)^0{}_{12}$, the nonlike interaction constant, in $A_{\text{mix}} = \sum_i \sum_j x_i x_j A_{ij}$ were calculated using Roebuck's μ values for CO_2 (1942) and are shown in Table 5. The weighted average of the values calculated for each mixture is shown along with error estimates assuming ±1.5% for the data presented here and ±2% for Roebuck's data. Agreement between A_{12} values calculated from each mixture value, although within error limits, is not good. It is likely that Roebuck's μ values for CO_2 are in error. In fact, if the CO_2 values are adjusted upward to near that predicted by Barner's (1966) and by Grey's (1969) modifications of the Redlich-Kwong equation, and by the B-W-R equation, the A_{12}'s come into good agreement. It is unfortunate that a breakdown of our equipment terminated data collection before pure CO_2 could be studied.

For comparison of accuracies of experimental values of nonlike interaction constants it is noted that the B_{12} determined by Cottrell et al. (1956) for this system at 30°C differs from the value of Lichtenhaler and Schäfer (1969) by about 7%. The 95% confidence limits for Cottrell's B_{12}'s are somewhat larger than the estimated accuracies in Table 5.

If the $\mu - x$ curves are viewed from the argon side, where they are not dependent on the pure CO_2 data, they are clearly concave upward (negative excess A).

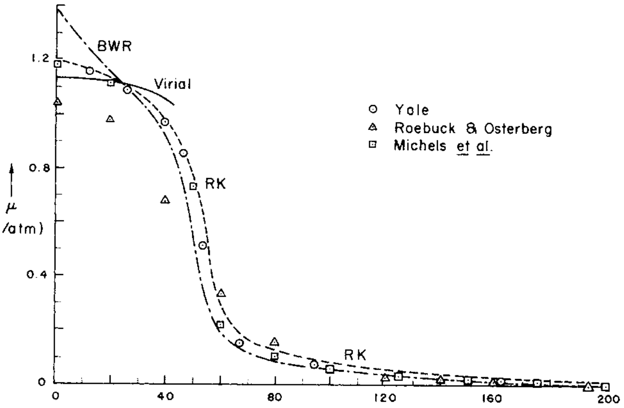

Fig. 6. Joule-Thomson coefficients for argon at −120°C.

VIRIAL EQUATION

The virial equation of state in Leiden form was truncated after the term C/V^2. Inclusion of higher order terms would little affect the results since it was found that the largest discrepancies occur at low pressure. Joule-Thomson coefficients were calculated from

$$\mu = \frac{1}{C_p}\left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right]$$

$$= \frac{1}{C_p}\ \frac{\left(B - T\dfrac{dB}{dT}\right) + \dfrac{1}{v}\left(2C - T\dfrac{dC}{dT}\right)}{1 + \dfrac{2B}{v} + \dfrac{3C}{v^2}} \tag{2}$$

The real roots of this cubic equation were determined from the exact solution of the cubic equation. This method avoids locating the improper root as can happen with the usual Newton-Raphson method.

The value of C_p at high pressures was also calculated with the truncated virial equation. $C_p{}^0$ for argon was taken as 5/2 R and spectroscopic values of $C_p{}^0$ were used for CO_2 (Gratch, 1949).

Second virial coefficients for the mixture were calculated from $B_{\text{mix}} = \sum_i \sum_j x_i x_j B_{ij}$. Third virials were calculated using $C_{\text{mix}} = \sum_i \sum_j \sum_k x_i x_j x_k\ C_{ijk}$.

The Lennard-Jones (6, 12) potential was chosen to calculate virial coefficients. Corrections to B to account for the angle dependent part of the potential for CO_2 were included (Pople, 1954b; Buckingham and Pople, 1955; Kielich, 1961). The CO_2 molecule contains a large quadrupole which causes large nonidealities. The second virial coefficient is represented as

$$B = B(\text{central}) + B(Q\text{-}Q) + B(Q\text{-ind}\ \mu) + B\ (\text{anis}) + B\ (\text{shape}) \tag{3}$$

The quadrupole-quadrupole interaction, $B(Q\text{-}Q)$, is the strongest noncentral (or angle dependent) interaction. The anisotropic dispersion contribution B(anis) and the quadrupole-induced dipole $B(Q\text{-ind}\ \mu)$ contributions are smaller but are still significant. The shape term, a contribution to the repulsive part of the potential due to anisotropy, was omitted because the shape factor for CO_2 computed by Spurling and Mason (1948) was not realistic (wrong sign).

To calculate these angle dependent contributions, the following reduced quantities are defined:

$$B_{ij}{}^{*} = \frac{B_{ij}}{b_0} = \frac{B_{ij}}{(2/3)\pi N \sigma_{ij}{}^{3}} \quad Y_{ij} = 2\left(\frac{\epsilon_{ij}}{kT}\right)^{1/2}$$

$$\overline{\alpha}^{*}{}_{ij} = \left(\frac{\overline{\alpha}_i\,\overline{\alpha}_j}{\sigma_{ij}{}^{6}}\right)^{1/2} \qquad Q^{*}{}_{ij} = \frac{Q_i\,Q_j}{\epsilon_{ij}\,\sigma_{ij}{}^{5}} \tag{4}$$

Then the angle dependent B_{ij}'s for the nonlike interaction as first derived by Kielich (1961, 1962) are

$$B^{*}{}_{ij}(Q\text{-}Q) = -\frac{7}{320}Q^{*}{}_{ij}{}^{2}\left\{H_{10}(Y_{ij}) - \frac{18}{343}H_{15}(Y_{ij})\right\}$$

$$B^{*}{}_{ij}(Q\text{-ind}\,\mu) = \frac{3}{32}\left\{(\overline{\alpha}^{*}{}_{ii}Q^{*}{}_{jj} + \overline{\alpha}^{*}{}_{jj}Q^{*}{}_{ii})H_8(Y_{ij}) - \frac{24}{25}Q^{*}{}_{ij}\left[\kappa_i\kappa_j H_{11}(Y_{ij}) + \frac{5}{28}(\overline{\alpha}^{*}{}_{ii}\kappa_i Q_{jj} + \overline{\alpha}^{*}{}_{jj}\kappa_j Q^{*}{}_{ii})H_{13}(Y_{ij})\right]\right\}$$

$$B_{ij}(\text{anis}) = -\frac{1}{40}\left[\kappa_i^2 + \kappa_j^2 + \frac{38}{10}\kappa_i^2\kappa_j^2\right]H_{12}(Y_{ij}) \tag{5}$$

The H functions (and their derivatives, where necessary) derived by Pople (1954a, 1954b) and tabulated by Buckingham and Pople (1955) were calculated by expansion of the infinite series. For CO_2, the values of $\overline{\alpha} = 2.925$ Å^3 and $\kappa = 0.257$ were used (Orcutt, 1963). For argon, $\overline{\alpha} = 1.63$ Å^3 was used (Euken, 1950).

Force constants for the nonlike interaction were determined from the usual combining rules, $\epsilon_{ij} = (\epsilon_i\epsilon_j)^{1/2}$, $\sigma_{ij} = (\sigma_i + \sigma_j)/2$.

Third virial coefficients were calculated for the Lennard-Jones (6, 12) potential from the tables in Hirschfelder et al. (1954). Although nonadditive (Sherwood et al., 1966) and quadrupole and anisotropic contributions (Levine and MacQuarrie, 1956) have been computed, they were not included because the added complexity did not seem justified. Of the several methods for calculating $C_{ijk}(T)$ for nonlike interactions (Hirschfelder et al. 1954; Connolly, 1961; Orentlicher and Prausnitz, 1967; Rowlinson et al., 1954) the approximation used by McHenry (1968) was used. For this method, pseudo-force constants are calculated for the nonlike interaction by extension of the combining rules for binary interactions. Again, since it was found that the largest discrepancies occur at low pressure, small corrections to $C(T)$ should not greatly affect the results.

DETERMINATION OF FORCE CONSTANTS AND QUADRUPOLE MOMENT

Determination of quadrupole moments from second virial coefficient (B) data, particularly for CO_2, has interested several workers primarily bcause they are difficult to determine by other methods. A good summary of available methods is given by Buckingham (1959). Values of Q for CO_2 determined spectroscopically (microwave) range from 1.7×10^{-26} to 5.9×10^{-26} esu with the more recent value of 4.4×10^{-26} esu (Maryott and Kryder, 1964) being perhaps the most reliable. Buckingham and Dish (1963) developed a method to determine Q and its sign by determining the birefringence induced in gaseous CO_2 in an inhomogeneous electric field. This method gives $Q \cdot (\alpha_{\parallel} - \alpha_{\perp})$ from which a value of $Q = -4.1 \times 10^{-26}$ esu was calculated. This is the only method which gives the sign of Q.

The Buckingham method (1938) is often used to calculate force constants from second virial coefficient data. The quantities log X and log Y defined by

$$\log X = \log\left[\frac{3\,B(T)}{2\pi N}\right] - \log B^{*}(T) \tag{6}$$

$$\log Y = \log T - \log T^{*}$$

are plotted for several B^*, T^* values at each experimental B, T point. This results in a series of points, one for each B-T pair, which intersect (hopefully) at one point. The coordinates of this point then determine the force constants at one point. The coordinates of this point then determine the force constants since $\log X = 3 \log \sigma$ and $\log Y = \log \epsilon/k$. If the curves intersect in an area rather than at a point, the data are inaccurate or the potential cannot adequately represent the gas in question. This procedure can be extended to a 3-parameter potential by making several plots, one for each value of the third parameter. At the optimal value the intersection will be smallest. Pople (1954b) used this technique to estimate Q from the B-data of MacCormack and Schneider. Only the central and quadrupole-quadrupole terms were included in the analysis and only first order terms were included. He obtained the rather high value of $Q = 5.73 \times 10^{-26}$ esu. Butcher and Dadson (1964) and Dadson et al. (1967) used the same technique on their own data and determined $Q = 3.3\ 10^{-26}$ esu.

Spurling and Mason (1967) have used a refinement of Orcutt's technique (1963) to calculate Q for several gases. This method is based on the observation that transport properties are much less sensitive to the orientation dependent parts of the potential. Thus, central force constants (σ and ϵ/k) are calculated from viscosity data. Values of B (central) are then calculated from these force constants. The difference between the calculated and experimental values is then used to calculate Q. Spurling and Mason included a small correction to the viscosity data for the quadrupole interaction obtained using an initial estimate of Q. Anisotropic and induced interactions and higher order terms in the expansion were not omitted. Shape (steric) factors were also calculated. A value of $Q = 4.1 \times 10^{-26}$ esu with a shape factor $D = -0.1$ was obtained for CO_2. The shape factor is somewhat unreasonable since its sign should be positive for CO_2. Data from three sources were used. It is perhaps coincidental that their value coincides with the Buckingham-Dish value.

The method of nonlinear least squares was used here to calculate the force constants and quadrupole moment of CO_2 from second virial and Joule-Thomson data. This method has been previously used to calculate central force constants alone (Magasanik, 1963; Tee et al., 1966). The equations for B or A are linearized by expansion in a Taylor series about an initial estimate of the constants (σ, ϵ/k, Q). Derivatives higher than the first are dropped. The necessary derivatives ($\partial B/\partial\sigma$, $\partial B/\partial\epsilon/k$, $\partial B/\partial Q$) were calculated analytically by differentiating Equations (3) to (5). Corresponding equations were used for A. The derivatives of the H-functions were also calculated analytically. The method of least squares is applied to the linearized equation to calculate a new set of constants and the process is repeated until it converges.

Eight values of B for CO_2 from -10.5 to 200°C were selected from the data of Butcher and Dadson (1964) for the calculation of force constants for CO_2. These data are in good agreement with those of Dadson et al. (1967) obtained using a different experimental technique. There are large discrepancies in the B-data of different workers. The recent B-data of Lichtenhaler and Schäfer deviate from the Butcher-Dadson data by -5% at 15°C. Nine values

TABLE 6. FORCE CONSTANT SETS—CO_2

Set	Type of data	σ(A)	ϵ/k (°K)	$Q \times 10^{26}$ (esu)	How det.
1	η, Q	3.819	218.8	4.1	Calc. by Spurling and Mason (S&M) from η-data, Q from Buckingham-Dish
2	A	4.9458	160.00	0.00	from NLLS.* Q fixed at 0
3	A	3.6709	199.79	4.95	from NLLS
4	B	4.6593	167.07	5.24	from NLLS
5	B	4.7562	173.25	0	from NLLS, Q fixed at 0
6	η, B	3.8190	218.8	3.67	σ, ϵ from viscosity (S&M), Q from NLLS on B-data
7	B, Q	4.6993	169.70	4.10	Q from Buckingham-Dish; σ, ϵ from NLLS on B-data

* Nonlinear least squares.

TABLE 7. COMPARISON OF EXPERIMENTAL AND CALCULATED ZERO PRESSURE JOULE-THOMSON COEFFICIENTS

	Avg. |% dev|		
Force const. set	46.4% CO_2 53.6% Ar	75.4% CO_2 24.6% Ar	CO_2*
1	4.6	6.7	4.6
2	5.4	5.3	2.8
3	5.5	5.5	1.2
4	5.2	5.2	3.7
5	6.0	6.0	4.0
6	5.6	10.5	8.7
7	5.7	5.5	3.5

* Roebuck and Osterberg data.

of A for CO_2 calculated from Roebucks μ-data from 0 to 300°C and the C_p^0 data of Gratch (1949) were also selected for calculation of force constants. Data below 0°C were not included because they appeared to be in error.

Six σ, ϵ, Q sets were calculated from the B and A data by the method of nonlinear least squares. In several cases, σ and ϵ or Q were held fixed. The values of σ and ϵ with Q fixed at 0 correspond to the ordinary Lennard-Jones constants (in this case, κ was also fixed at zero). These sets are shown in Table 6, sets 2 through 7. The first set is the σ, ϵ determined from viscosity data by Spurling and Mason with the Buckingham-Dish experimental Q (which agrees with the value calculated by Spurling and Mason from B-data).

Set 5 (Q and κ fixed at 0) compares well with the values determined by Butcher and Dadson by the Buckingham method. The value of $Q = 3.67 \times 10^{-26}$ esu in set 6 is comparable to the value $Q = 4.1 \times 10^{-26}$ esu determined by Spurling and Mason using the modified Buckingham method in an analysis that included shape factors. Since Q is raised to the fourth power in the quadrupole-quadrupole term, this difference is not as small as it appears. The difference is, no doubt, largely due to the use of different B-data.

The A-data revealed an interesting phenomenon for the case of $Q = 0$. On a Buckingham plot, two intersections occur corresponding to two distinct sets of force constants. The new set is $\sigma = 2.6626$ A, $\epsilon/k = 479.04$°K. This new intersection is sharper than the other ($\sigma = 4.9458$, $\epsilon/k = 160.0$). As the quadrupole term was increased, however, the two intersections moved closer together.

An explanation for the double set of force constants for the case $Q = 0$ can be given. The angle averaged quadrupole-quadrupole interaction (Keesom's alignment potential) has a radial dependence of r^{-10}. This additional quadrupole energy (attractive) is produced in the pseudo-central potential by shifting the potential slightly upwards and to the right or by drastically lowering the potential and shifting it to the left. Joule-Thomson (and second virial coefficients) are most sensitive to the attractive region of the potential. Both potentials produce the required attractive branch. The discrepancy is a result of trying to represent a molecule with an angle-dependent potential with an angle-independent potential.

It can be seen that the spread in literature values of Lennard-Jones force constants is large for nonsimple molecules. If all the available values of σ and ϵ calculated from A and B data for CO_2 are plotted on a log-log plot, a straight line $\epsilon/k \cdot \sigma^{1.71} = 2048$) is seen to give a very good representation, with the exception of one point calculated from the B-data of MacCormack and Schneider. The two sets of σ, ϵ calculated here for the case $Q = 0$ also fall on the line. The relationship between σ and ϵ for values from different sources was noted by Reid (1968) for viscosity data. He also noted that similar trends were observed for constants from B-data. The spread is very small for the rare gases. (See also Reichenberg, 1973).

It is clear that the use of a two-parameter potential to represent a basically angle dependent interaction is quite empirical. These parameters can be used to reproduce the data from which they were derived but could lead to very erroneous results if other properties are calculated.

COMPARISON OF FORCE CONSTANT SETS

The seven sets of force constants for CO_2 in Table 6 were used to calculate zero pressure Joule-Thomson coefficients for both mixtures and for pure CO_2. In all cases the force constants for argon were taken from Magasinik (1963), who applied the method of least squares to the B-data of Michels and found $\sigma = 3.4044$ A, $\epsilon/k = 119.77$°K. The overall average deviations are shown in Table 7. Individual differences at the highest and lowest temperatures are about twice as large. The calculated values are always too low at low temperature.

The μ^0's predicted with set 1 are surprisingly good considering that they were not derived from thermodynamic data. If the quadrupole effect is not included the comparison is poor.

The values predicted with the second σ, ϵ pair calculated from A data ($\sigma = 2.6626$ A, $\epsilon/k = 479.04$°K, $Q = 0$) were, surprisingly, slightly better than set 2 or 3 for mixtures. These constants could not be used to calculate μ's at high pressures because the T^*'s calculated were so low that third virial coefficients could not be calculated.

With the exception of the μ^0's predicted with set six, all the average deviations are roughly comparable. Set six fails at low temperatures indicating that a higher value of Q, as in set 1, is necessary. If the B-values of Butcher and Dadson were lower at low temperatures, a higher Q value would result. This would bring their data closer to that of Lichtenhaler and Schäfer (1969). Set seven was chosen as the best set when due weight was given to error at the ends of the temperature range. Moreover, the Q value here is experimental. These constants were used to calculate μ-values at higher pressure with the virial equation.

REDLICH-KWONG EQUATION

Several forms of the Redlich-Kwong (R-K) equation were tested. The original form (1949)

$$Z = \frac{v}{v - b} - \frac{a}{RT^{3/2} \cdot (v + b)} \tag{7}$$

with a and b related to critical constants and the modification developed by Barner, Pigford, and Schreiner (1966) were used to calculate Joule-Thomson coefficients at each of the experimental points. The modification suggested by Grey, Rent, and Zudkevitch (1969) was examined at zero pressure only. Both of these modifications are directed toward improvement of enthalpy (and volume) prediction through introduction of the acentric factor to account for nonideality and both aim at an improved fit to the Pitzer-Curl second virial coefficient expression. For zero acentric factor, the Barner et al. modification reduces to the original form while the more complex modification of Grey et al. does not. Neither equation was recommended for temperatures much above the critical or at high density. The following constants were used:

	CO_2	Ar
T_c:	304.19°K	150.72°K
P_c:	72.85 atm	48.01 atm
ω:	2.237	−0.002

The combining rules for the constants of the mixtures that were presented in the original papers were used.

BENEDICT-WEBB RUBIN EQUATION

The B-W-R equation (Benedict et al., 1940) was also examined at each of the experimental conditions with constants taken from several sources. The mixing rules suggested by these authors was used with Lorentz combination for B_0. The Stotler and Benedict (1953) mixing rule for A_0

$$A_0 = (\Sigma x_i \cdot A_{0i}{}^{1/2})^2 - 0.100 \cdot x_1 x_2 \tag{8}$$

where A_0 has units liter² · atm/(g mole)² was used. This lowering of A_0 by 0.100 x_1x_2 is now generally accepted (Tsonopoulos and Prausnitz, 1969).

The roots of the equation were located with a Newton-Raphson technique.

The B-W-R constants were calculated from PVT data by Zudkevitch and Kaufmann for Ar (1965) and by Cullen and Kobe for CO_2 (1955). A correlation of Su and Viswanath (1965) was also tested at zero pressure. This correlation effectively reduces the number of independent constants to two (T_c and P_c).

COMPARISON OF THE EQUATIONS OF STATE

The comparisons at zero pressure are shown in Tables 8 through 11. The force constants used in calculating virial coefficients is set 7, Table 6. Only the original Redlich-Kwong is shown for pure Ar since it gives results almost identical to the modifications in this case.

For pure Ar at $P = 0$, the virial equation gives the

TABLE 8. COMPARISON OF ZERO PRESSURE JOULE-THOMSON COEFFICIENTS FOR ARGON

Method	Source of data or consts.	$\mu°$ (°C/atm)						
		−120°	−80°	−40°	0°	40°	80°	110°C
Experimental	Yale (extrap. to $P = 0$)	1.190	0.798	0.584	0.444	0.349	0.276	0.231
Virial	Magasanik	1.133 [−4.8%]	0.780 [−2.3%]	0.573 [−1.9%]	0.437 [−1.6%]	0.341 [−2.3%]	0.270 [−2.2%]	0.228 [−1.3%]
Redlich-Kwong	T_c, P_c	1.202 [+1.0%]	0.816 [+2.3%]	0.589 [+0.9%]	0.441 [−0.7%]	0.339 [−2.9%]	0.265 [−4.0%]	0.222 [−3.9%]
BWR	Zudkevitch and Kaufmann	1.399 [+17.6%]	0.831 [+4.1%]	0.557 [−4.6%]	0.403 [−9.2%]	0.306 [−12.3%]	0.239 [−13.4%]	0.202 [−12.6%]
BWR	T_c, P_c (Su & Wiswanath correlation)	1.518 [+27.6%]	0.884 [+10.8%]	0.585 [+0.2%]	0.418 [−5.9%]	0.315 [−9.7%]	0.246 [−10.9%]	0.208 [−10.0%]

TABLE 9. COMPARISON OF ZERO PRESSURE JOULE-THOMSON COEFFICIENTS
46.4% CO_2-53.6% Ar

Method	Source of data or consts.	$\mu°$ (°C/atm)					
		−40°	−20°	0°	40°	80°	110°C
Experimental	Yale (extrap. to $P = 0$)	1.157	0.962	0.808	0.604	0.458	0.384
Virial	Table 6 Set 7	1.125 [−2.8%]	0.965 [+0.3%]	0.836 [+3.5%]	0.642 [+6.3%]	0.505 [+10.3%]	0.427 [+11.2%]
Redlich-Kwong	T_c, P_c	1.026 [−11.3%]	0.881 [−8.4%]	0.763 [−5.6%]	0.585 [−3.1%]	0.461 [+6.6%]	0.390 [+1.6%]
R-K (Barner)	T_c, P_c, ω	1.134 [−2.0%]	0.939 [−2.4%]	0.789 [−2.4%]	0.575 [−4.8%]	0.434 [−5.2%]	0.357 [−7.0%]
R-K (Grey)	T_c, P_c, ω	1.120 [−3.2%]	0.940 [−2.3%]	0.799 [−1.1%]	0.593 [−1.8%]	0.454 [−0.9%]	0.377 [−1.8%]
BWR	CO_2: Cullen & Kobe Ar:Zudkevitch & Kaufmann	1.278 [+10.5%]	1.038 [+7.9%]	0.858 [+6.2%]	0.613 [+1.5%]	0.459 [+0.2%]	0.378 [−1.6%]
BWR	T_c, P_c (Su & Viswanath correlation)	1.371 [+18.4%]	1.104 [+14.8%]	0.906 [+12.1%]	0.639 [+5.8%]	0.474 [+3.5%]	0.389 [+1.3%]

TABLE 10. COMPARISON OF ZERO PRESSURE JOULE-THOMSON COEFFICIENTS
75.4% CO_2—24.6% Ar

Method	Source of data or consts.	μ° (°C/atm) −40°	0°	+40°	+80°	+110°C
Experimental	Yale (extrap. to $P = 0$)	1.655	1.113	0.811	0.615	0.504
Virial	Table 6 Set 7	1.477 [−10.7%]	1.083 [−2.7%]	0.824 [+1.6%]	0.644 [+4.7%]	0.543 [7.7%]
Redlich-Kwong	T_c, P_c	1.305 [−21.1%]	0.964 [−13.4%]	0.736 [−9.2%]	0.578 [−6.0%]	0.489 [−3.0%]
R-K (Barner)	T_c, P_c, ω	1.716 [+3.7%]	1.143 [+2.7%]	0.805 [−0.7%]	0.593 [−3.6%]	0.482 [−4.4%]
R-K (Grey)	T_c, P_c, ω	1.633 [−1.3%]	1.120 [+0.7%]	0.807 [−0.5%]	0.603 [−2.0%]	0.495 [−1.8%]
BWR	CO_2: Cullen & Kobe Ar:Zudkevitch & Kaufmann	1.815 [+9.7%]	1.190 [+6.9%]	0.834 [+2.8%]	0.614 [−0.2%]	0.500 [−0.8%]
BWR	T_c, P_c (Su & Viswanath correlation)	1.963 [+18.7%]	1.263 [+13.5%]	0.872 [+7.5%]	0.635 [+3.3%]	0.514 [+2.0%]

TABLE 11. COMPARISON OF ZERO PRESSURE JOULE-THOMSON COEFFICIENTS FOR CARBON DIOXIDE

Method	Source of data or consts.	μ° (°C/atm) −40°	0°	40°	100°	200°C
Experimental	Roebuck (extrap. to $P = 0$)	1.992	1.284	0.957	0.650	0.378
Virial	Table 6 Set 7	1.709 [−14.2%]	1.291 [+0.5%]	0.976 [+2.0%]	0.676 [+4.0%]	0.404 [+6.9%]
Redlich-Kwong	T_c, P_c	1.545 [−22.4%]	1.134 [−11.7%]	0.862 [−9.9%]	0.603 [−7.2%]	0.369 [−2.4%]
R-K (Barner)	T_c, P_c, ω	2.298 [+15.3%]	1.491 [+16.1%]	1.029 [+7.5%]	0.643 [−1.1%]	0.344 [−9.0%]
R-K (Grey)	T_c, P_c, ω	2.237 [+12.3%]	1.485 [+15.6%]	1.043 [+9.0%]	0.664 [+2.1%]	0.360 [−4.8%]
BWR	Cullen & Kobe	2.303 [+15.6%]	1.488 [+15.8%]	1.030 [+7.6%]	0.651 [+0.2%]	0.396 [+4.8%]
BWR	T_c, P_c (Su & Viswanath correlation)	2.502 [+25.6%]	1.585 [+23.4%]	1.078 [+12.6%]	0.670 [+3.1%]	0.366 [−3.2%]

best representation. The B-W-R is remarkably poor with either set of constants. The B-W-R equation was originally developed to represent hydrocarbons, so its failure to represent an inert gas is not too surprising.

The results for mixtures show that the Grey et al. modification of the R-K equation gives excellent results—almost within the experimental error at every temperature for both mixtures. The Barner et al. modification is not as good, particularly at high temperature. Results for the virial equation are only fair. It is believed that the experimental values of Roebuck et al. for CO_2 are in error. This same trend was mentioned previously for other gases (Ar, N_2). Also, if the experimental values for CO_2 were close to those predicted by the Grey et al. modification, the A_{12}'s calculated for each mixture would give good agreement.

The virial, the Barner et al. modification of the R-K, and the B-W-R (constants from P-V-T data) were selected for comparison with the experimental μ data at pressures above zero. The Grey et al. equation did not give reasonable results at high pressures, no doubt owing to an error in the very complex equations that result, involving several numerical differentiations. Some of the results are shown graphically in Figures 4 to 10.

The μ's predicted from the virial equation for Ar show increasing deviations as pressure increases. This is due to the inability of the Lennard-Jones potential to accurately represent third virial coefficients, to the neglect of nonadditive contributions to C, and to the neglect of higher terms.

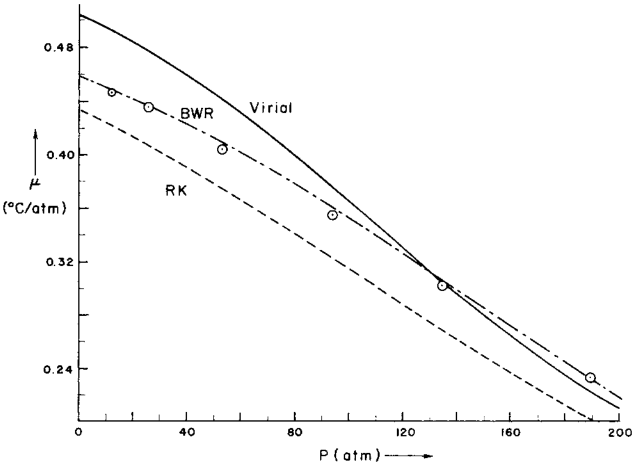

Fig. 7. Joule-Thomson coefficients for 46.4% CO_2—53.6% Ar at 80°C.

The μ's for Ar calculated with the modified R-K equation are in good agreement with the data at low pressure but deviate progressively as pressure increases. It is interesting that agreement is best at low temperatures and almost exact at −120°C.

The B-W-R isotherms for Ar are generally parallel to the data and displaced downward. At − 120°, only about

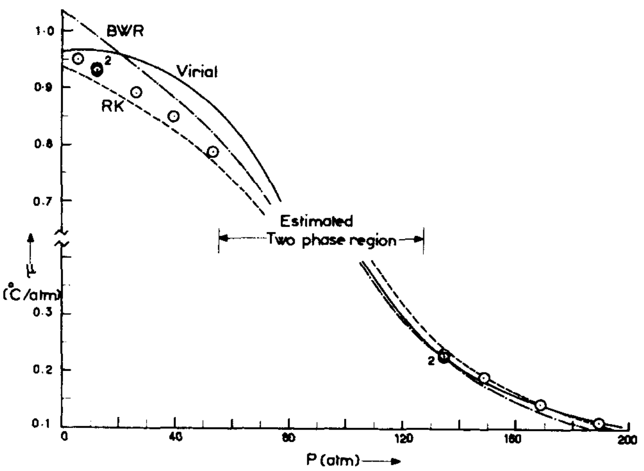

Fig. 8. Joule-Thomson coefficients for 46.4% CO_2—53.6% Ar at −20°C.

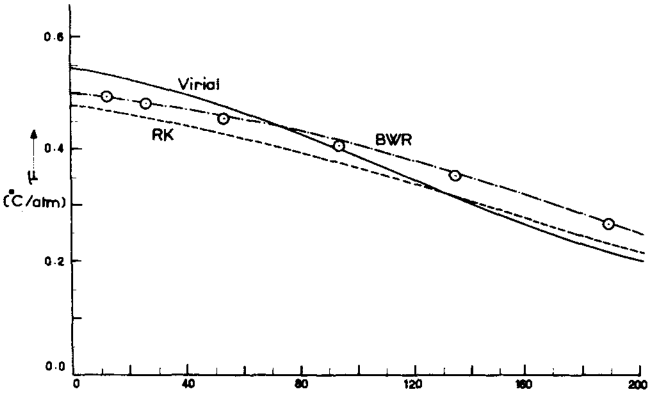

Fig. 9. Joule-Thomson coefficients for 75.4% CO_2—24.6% Ar at 110°C.

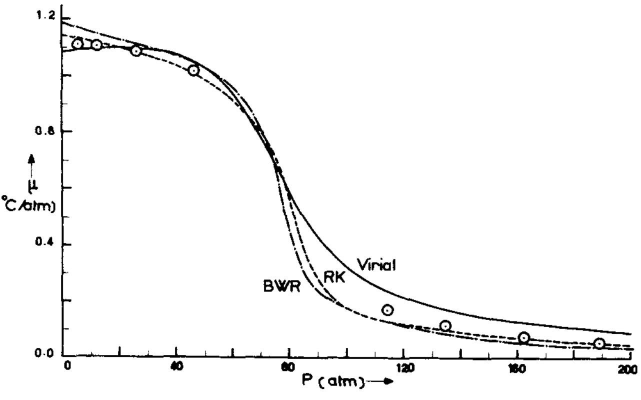

Fig. 10. Joule-Thomson coefficients for 75.4% CO_2—24.6 Ar at 0°C

2° above the critical, the low pressure error is very large. Zudkevitch and Kaufmann noted that a lowering of the C_0 constant was necessary near the critical and below. They suggested a linear temperature dependence for $T < T_c$. A lower value for C_0 would give a lower μ^0 and improve the agreement. The temperature dependence of other terms would also have to be altered to give better agreement at higher temperatures.

For mixtures, the virial equation is generally the least satisfactory. It is poorest in the low pressure, high temperature region, especially for the 46.4% CO_2 mixture.

The B-W-R equation gives better results for the mixtures than for argon. The Barner et al. modified R-K equation is best overall for mixtures, but it fails somewhat at high reduced temperatures.

The virial and modified R-K equations do surprisingly well in the liquid region.

NOTATION

T = temperature
P = pressure
H = enthalpy
H_{10}, H_{13}, etc. = functions of Pople (1954a, 1954b)
μ = Joule-Thomson coefficient $\left(\frac{\partial T}{\partial P}\right)_H$
E = EMF of thermopile
x_i = mole fraction
C_p = specific heat at constant pressure
V = volume
B = second virial coefficient
A = interaction constant $(\mu C_p)^0$ which is equal to $T\frac{dB}{dT} - B$
C = third virial coefficient
Q = quadrupole moment $\sum_i e_i(Z_i^2 - X_i^2)$
Y_{ij} = a reduced force constant
Y = plotting variable defined by Equation (6)
Z = compressibility factor $\frac{pv}{RT}$
Z_i = distance from center of mass to charge e_i parallel to the axis of symmetry
X = plotting variable defined by Equation (6)
X_i = distance from center of mass to charge e_i perpendicular to the axis of symmetry
R = gas constant
k = Boltzmann constant
a, b = constants in Redlich-Kwong equation
A_0, B_0 = constants in the B-W-R equation

Greek Letters

$\bar{\alpha}$ = mean polarizability
κ = anisotropic polarizability
ϵ, σ = constants in the Lennard-Jones (6-12) potential
ω = accentric factor
Φ = isothermal Joule-Thomson coefficient

Subscripts

ijk = refer to interactions of components i, j, k
c = critical condition
mix = refers to mixture properties

Superscripts

$*$ refers to reduced quantity
0 = at zero pressure

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