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# EVIDENCE OF ASSOCIATION IN CARBON DIOXIDE FROM THE JOULE-THOMSON EFFECT

BY FREDERICK G. KEYES

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## Introduction

There has recently appeared an important paper by Burnett[1] dealing with the experimental determination of the Joule-Thomson effect for carbon dioxide. The measurements extend from about —24° to 120° in temperature and cover a pressure range of 20 to 75 atmospheres. By means of empirical equations these data, together with the data of Jenkins and Pye,[2] have been correlated by Burnett and yield values of the Joule-Thomson effect at temperatures from 220°K. to 400°K. for the constant pressure of one atmosphere. These values have been selected for the present contribution to the theory of the Joule-Thomson effect since at low pressures the effect tends to become a function of the temperature alone.

In a previous paper dealing with the Joule-Thomson effect for air[3] it was shown that the pressure-volume-temperature data of all observers were in conformity with the measurements existing for the Joule-Thomson effect for air as well as with the specific-heat data for air.

In the case of carbon dioxide the $p,v,T$ data due to Andrews as corrected by Ramsay[4] have been shown[5] to indicate that for the range of the experiments the pressure-temperature relation at constant volume is linear. The constant-volume specific-heat measurements of Joly,[6] for carbon dioxide, however, indicate that the pressure is not linear with temperature at constant volume. The work of Burnett which supplies Joule-Thomson data also indicates that the constant-volume pressures are not strictly linear with temperature.

The data have heretofore not been available[7] for examining to what extent the assumption of association in a gas may be of service in providing an explanation of certain apparent inconsistencies in the general properties of a fluid. For example, the linearity of the constant-volume increase of pressure with temperature in the case of carbon dioxide is, as has been stated, at variance, in the inferences deduced therefrom, with the Joly

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[1] Burnett, *Phys. Rev.*, **22**, 590 (1923).

[2] Jenkins and Pye, *Phil. Trans.*, **213A**, 67 (1914); **214A**, 353 (1915).

[3] THIS JOURNAL, **43**, 1452 (1921).

[4] Ramsay, *Z. physik. Chem.*, **1**, 433 (1887).

[5] *J. Am. Soc. Ref. Engineers*, **3**, 17 (1917).

[6] Joly, *Proc. Roy. Soc.* (London), **41**, 352 (1886); *Phil. Trans.*, **182A**, 73 (1891); **185A**, 943 (1894).

[7] The recent specific-heat data of the Bureau of Standards for ammonia furnish additional data for examining further the validity of the ideas presented in this paper.

specific-heat measurements and with the recent Joule-Thomson measurements of Burnett. It was foreseen a number of years ago that the existence of a very small fraction of polymerized molecules could exercise a pronounced influence on both the specific heats and the Joule-Thomson effect and yet hardly be detectable from measurements of $p$, $v$ and $T$.

## Theoretical Treatment

The Andrews data for carbon dioxide have been shown to be represented[8] by the equation of state of form (see Table I)

$$p = \frac{RT}{v - \beta e^{-\alpha/v}} - \frac{A}{(v + l)^2} \tag{1}$$

TABLE I

ANDREWS' DATA FOR CARBON DIOXIDE COMPARED WITH PRESSURES COMPUTED BY EQUATION OF STATE

| Temp. °C. | 30 cc. Obs. | 30 cc. Calc. | 25 cc. Obs. | 25 cc. Calc. | 20 cc. Obs. | 20 cc. Calc. | 15 cc. Obs. | 15 cc. Calc. |
|---|---|---|---|---|---|---|---|---|
| 0.0 | 15.074 | 15.102 | 17.695 | 17.690 | 21.224 | 21.333 | 26.670 | 26.723 |
| 6.1 | 15.488 | 15.503 | 18.200 | 18.192 | 21.871 | 21.979 | 27.573 | 27.627 |
| 31.1 | 17.221 | 17.232 | 20.315 | 20.295 | 24.579 | 24.683 | 31.355 | 31.407 |
| 48.1 | 18.396 | 18.396 | 21.745 | 21.719 | 26.413 | 26.515 | 33.916 | 33.968 |
| 64.0 | 19.495 | 19.484 | 23.084 | 23.051 | 28.129 | 28.228 | 36.312 | 36.363 |
| 100.0 | 21.982 | 21.950 | 26.116 | 26.066 | 32.013 | 32.107 | 41.736 | 41.785 |

Pressures in atms. of 76 cm. of Hg; vol. in cc. per gram.

$$p = \frac{1.865}{v - \delta}T - \frac{3219}{(v - 0.055)^2}; \log_{10}\delta = 0.4650 - \frac{0.7065}{v}$$

This equation was deduced[9] for an unchanging or constant molecular species. Table I indicates the degree of approximation with which it reproduces the Andrews data and the agreement is believed to be all that may be expected. If polymerization exists it must be judged to be small in amount and incapable of exercising appreciable influence on the accuracy of the constants of the equation.

Assuming therefore that the constants of the equation are relatively accurate, the equation to be used in examining the effect of the presence of a small fraction of double molecules may be obtained by applying for the calculation of derived quantities the equation,

$$p = \frac{R(1 - y/2)T}{v - \delta} - \frac{A}{(v + l)^2} \tag{2}$$

Since this equation is to be used for low pressures it will suffice if $\alpha$ and $l$ are considered negligible and there results

$$p = \frac{R(1 - y/2)T}{v - \beta} - \frac{A}{v^2} \tag{3}$$

The fraction associated, $y$, is in this instance considered to be so small as not to affect the values of $\beta$ or $A$. There is evidence to show that $\beta$

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[8] Ref. 4, p. 445.

[9] *Proc. Nat. Acad. Sci.*, **3**, 323 (1917).

for any value of $y$ is $\beta(1-y/2)$. In the case of carbon dioxide on the other hand, at one atmosphere and 0° $\beta$ is required to be known with an accuracy of only 3% for pressures to one part in 5000. A value of 0.001 for $y$ would, therefore, be negligible. A similar statement may be made with regard to $A$. The fraction associated enters, therefore, at low pressures only through the term $R(1-y/2)$.

Forming the derivative $\left(\frac{\partial v}{\partial T}\right)_p$ from (3) there results,

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{v-\beta}{T}\,\frac{1-\dfrac{T}{2(1-y/2)}\left(\dfrac{\partial y}{\partial T}\right)_p}{1-\dfrac{2A}{RT}\dfrac{(v-\beta)^2}{v^3}\dfrac{1}{1-y/2}} = \frac{v-\beta}{T}\,\frac{1-\dfrac{T}{2}\left(\dfrac{\partial y}{\partial T}\right)_p}{1-\dfrac{2A}{RT}\dfrac{(v-B)^2}{v^3}} \qquad (4)$$

When Equation 4 is substituted in the general thermodynamic equation for the Joule-Thomson effect where $\omega$ represents $v-\beta$ there results

$$C_p\mu = C_p\frac{\mathrm{d}T}{\mathrm{d}p} = T\left(\frac{\partial v}{\partial T}\right)_p - v = \frac{2A}{RT}\left(\frac{\omega}{v}\right)^2 - \beta - \frac{\omega T}{2}\left(\frac{\partial y}{\partial T}\right)_p$$

Considering $\left(\frac{\omega}{v}\right)^2$ as substantially equal to unity and assuming $\omega = v$ in $\frac{\omega T}{2}\left(\frac{\partial y}{\partial T}\right)_p$ the equation becomes

$$\mu C_p = \frac{2A}{RT} - \beta - \frac{vT}{2}\left(\frac{\partial y}{\partial T}\right)_p \qquad (5)$$

The application of thermodynamics to a gaseous reaction of the type, $CO_2 = {}^1/_2(CO_2)_2$, leads to the following equation where $y$ is small and $C$ a constant, $\Delta U^0$ being the heat of reaction at absolute zero for one mole or 44 g. of carbon dioxide:

$$y = C\,e^{\frac{2\Delta U^0}{RT}}\frac{R}{v}\frac{1}{T^{3/2}} = C\,e^{\frac{2\Delta U^0}{RT}}\frac{p}{T^{5/2}} \qquad (6)$$

From this equation there results, where $\Delta H_p$ is the heat of reaction at $T$ and constant pressure,

$$\left(\frac{\partial y}{\partial T}\right)_p = -2y\frac{\Delta H_p}{RT^2} \qquad (7)$$

Substituting in (5) gives, where $C_p\mu_0$ represents $\frac{2A}{RT} - \beta$ and $v$ is taken to be equivalent to $\frac{RT}{p}$

$$C_p\mu = C_p\mu_0 + \frac{y}{p}\,\Delta H_p \qquad (8)$$

From Equation 6, $y$ is seen to vary as the pressure, and since $\Delta H_p$ is a function of the temperature alone it is clear that the effect of the term, $\frac{y}{p}\,\Delta H_p$, diminishes with temperature increase, but is independent of the pressure. It appears then that the Joule-Thomson effect, in a gas containing a small fraction of associated molecules, consists of the normal effect due to the deviation from the perfect gas laws for the single molecular species, to which must be added a change in temperature with pressure due to a small shift in the molecular species.

This is an important conclusion, if true, since it provides a means of obtaining the constants of the association Equation 6 which should enable values of the pressure coefficient of the specific heat at constant volume to be calculated and these latter are very much affected where the association is appreciable because of the large value of $\Delta H_p$ as compared with the small value of the heat capacity of the unassociated molecules *per se.* Conversely, it is important to be able to obtain, from the measurements at definite pressures and various temperatures of the apparent specific-heat capacities of gases, the heat capacities of single species types of molecules. Indeed, until this is possible little progress can be made in the development of a sound theory of the dependence of internal energy of single molecular species on temperature.

Substituting the value of $y$ from (6) in Equation 8 there results

$$C_p\mu = \frac{2A}{RT} - \beta + \frac{C e^{\frac{2\Delta U^0}{RT}}}{T^{5/2}} \Delta H_p \qquad (9)$$

In this equation $C_p\mu$ represents the product of the measured value of the Joule-Thomson effect with the specific heat at the pressure to which the effect corresponds. Evidently at high temperature $C_p\mu$ considered as a function of $1/T$ would be expected to approach linearity since the third term of the right hand member becomes evanescent. Air, for example, at temperatures above zero (and at one atmosphere) gives values of $C_p\mu$ which are linear in $1/T$, and values at low temperatures (—100°) would be most interesting to supplement the measurements above zero.

## The Numerical Data

The results obtained by Burnett for the Joule-Thomson effect at one atmosphere and temperatures from 220°K. to 400°K. have been multiplied by the value of $C_p$ at one atmosphere corresponding to the temperature for each datum.

The equation of state constants have also been used to compute for the round temperatures from 220° to 400° the value of $\mu_0 C_p$ or $\frac{2A}{RT} - \beta$. By subtracting the latter from $\mu C_p$, the Burnett Joule-Thomson coefficients for carbon dioxide multiplied by the constant-pressure heat capacity per mole in cc./atm., there remains the last term of (8) or $\frac{y}{p}\Delta H_p$ for the one atmosphere pressure.

It is clear that if the logarithms of these differences increased by $\frac{5}{2}\log T$

and denoted by log $(\Delta \mu C_p T^{5/2})$ are used to construct a rectangular diagram with $1/T$ a straight line should result, the slope of which is approximately $2\Delta U^0/2.3R$ and the intercept of value $(\log C + \log \Delta H_p)$. The latter quantity is of course not constant, because $\Delta H_p$ is a function of the temperature, $\Delta H_p = \Delta U^0 + \frac{5}{4} RT$. However, since the slope gives the approximate value of $\Delta U^0$ or therefrom $\Delta H_p$, a second plotting of $\log \frac{\Delta \mu C_p T^{5/2}}{\Delta H_p}$ and $\frac{1}{T}$ will give the true value of $\Delta U^0$ and the constant $C$ in the dissociation equation based on the assumption that the difference in the specific heats of one mole of $CO_2$ and $^1/_2$ mole of $(CO_2)_2$ is $^3/_4 R$ independent of temperature. This latter assumption is not exactly correct but the resulting approximation is the best compromise in the present state of our knowledge of the specific heats of gases.

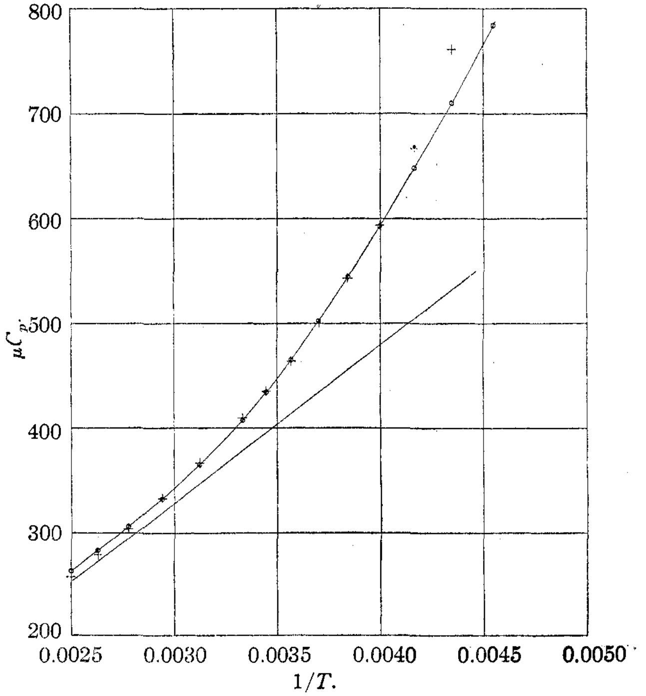

Fig. 1.

In Fig. 1 there are represented the measured values of $\mu C_p$, the $\mu_0 C_p$ computed from the equation of state and corresponding to $y = 0$, and in Fig. 2, log $\frac{\Delta \mu C_p T^{5/2}}{\Delta H_p}$, all of which quantities are plotted with $1/T$ as independent variable. The latter data for the temperatures —53°, —43° and

—33° are seen to tend away from the straight line drawn through the majority of the data. These are data which are extrapolated from the values at higher temperatures and in any case should be measured with particular care since the physical assumption underlying the whole of the present thought is that equilibrium among the single and double molecules is instantaneously attained in the Joule-Thomson measurements. The coördinates corresponding to the highest temperatures are obtained as the differences between large numbers and cannot be expected to correlate exactly with the data more favorably computed.[10]

It is of interest to compute the $\mu C_p$ values using the equation of state together with the equation for the association now obtained. The crosses in the diagram represent the computed values and Burnett's curve is seen to be very well represented with the exception of the three lowest temperature points.

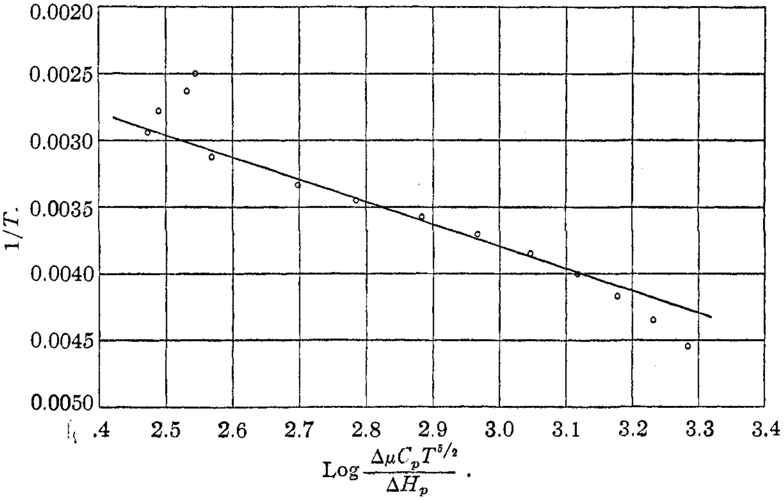

Fig. 2.

Table II presents all the data employed together with the values of $y$ corresponding to each temperature. Col. 12 gives the computed $\mu$ values corresponding to the crosses in the diagram.

The values of $y$ are seen to be very small corresponding to 1 double molecule in 500 at —53° and 1 in 20,000 at 127°. The values are undoubtedly only approximate since the $\beta$ and $A$ constants of the carbon dioxide molecules are not final but to be regarded as tentative until new $p,v,T$ data are available. The Burnett curve is seen to be straightening out at high temperatures with a slope close to that of the equation of state line cor-

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[10] The equation for log $y$ is: $\log_{10} y = 0.715 + \frac{603}{T} - 5/2 \log_{10} T + \log_{10} p$.

responding to no association. This is as it should be if associated molecules really are a factor in the Joule-Thomson effect.

## The Constant-Volume Specific Heat

Joly, employing his steam calorimeter for measuring the constant-volume specific heat of carbon dioxide, obtained data which he represented by the following equation where $\rho$ is the density: $C_v = 0.1650 + 0.2125\rho + 0.3400\rho^2$. This equation refers to the average temperature between 16° and 100°.

TABLE II

NUMERICAL DATA AND STEPS IN THE CALCULATIONS

| $T$ | Obs. $\mu^{\text{deg.}}/_{\text{atm.}}$ Burnett | $C_p^{\text{cal.}}/_{\text{mole}}$ | $C_p \frac{\text{cc. atm.}}{\text{mole}}$ | Obs. $\mu C_p$ Burnett | Calcd. $\mu_0 C_p$ Eq. state | $\Delta\mu C_p$ obs. |
|---|---|---|---|---|---|---|
| 200 | .... | 8.10 | 334.5 | ... | ... | ... |
| 220 | 2.3035 | 8.24 | 340.3 | 784.0 | 562.0 | 177.6 |
| 230 | 2.0700 | 8.31 | 343.1 | 710.2 | 532.0 | 178.2 |
| 240 | 1.8700 | 8.39 | 346.5 | 648.0 | 504.6 | 143.4 |
| 250 | 1.6954 | 8.48 | 350.0 | 593.0 | 479.2 | 113.8 |
| 260 | 1.5405 | 8.56 | 353.5 | 544.6 | 456.0 | 88.6 |
| 270 | 1.4060 | 8.65 | 357.2 | 502.2 | 434.2 | 68.0 |
| 280 | 1.2900 | 8.74 | 361.0 | 465.7 | 413.8 | 51.9 |
| 290 | 1.1900 | 8.83 | 364.7 | 434.0 | 395.7 | 38.3 |
| 300 | 1.1045 | 8.93 | 368.8 | 407.2 | 378.0 | 29.2 |
| 320 | 0.9665 | 9.15 | 377.9 | 365.2 | 346.3 | 18.9 |
| 340 | .8595 | 9.35 | 386.2 | 332.0 | 318.7 | 13.3 |
| 360 | .7750 | 9.55 | 394.2 | 305.7 | 293.5 | 12.2 |
| 380 | .7045 | 9.73 | 401.8 | 283.1 | 271.1 | 12.0 |
| 400 | .6440 | 9.89 | 407.5 | 262.4 | 251.3 | 11.1 |

| $T$ | $\text{Log}_{10}$ $\Delta\mu C_p T^{5/2}$ | $\text{Log}_{10}$ $\frac{\Delta\mu C_p T^{5/2}}{\Delta H_p}$ | $\frac{10^4}{T}$ | Calcd. $\Delta\mu C_p$ | Calcd. $\mu$ | $y$ |
|---|---|---|---|---|---|---|
| 200 | ..... | ..... | ... | ... | ... | ...... |
| 220 | 8.10549 | 3.18668 | 45.45 | 329.8 | 2.623 | 0.0040 |
| 230 | 8.15524 | 3.25106 | 43.48 | 229.0 | 2.219 | .0027 |
| 240 | 8.10708 | 3.17759 | 41.67 | 162.0 | 1.925 | .0019 |
| 250 | 8.05099 | 3.11626 | 40.00 | 116.6 | 1.702 | .0014 |
| 260 | 7.98486 | 3.04516 | 38.46 | 87.1 | 1.536 | .0010 |
| 270 | 7.91091 | 2.96589 | 37.04 | 65.9 | 1.400 | .00075 |
| 280 | 7.83307 | 2.88319 | 35.71 | 50.5 | 1.286 | .00057 |
| 290 | 7.73920 | 2.78412 | 34.48 | 39.4 | 1.193 | .00045 |
| 300 | 7.65818 | 2.69835 | 33.33 | 31.1 | 1.110 | .00034 |
| 320 | 7.53734 | 2.56875 | 31.25 | 20.3 | 0.970 | .00023 |
| 340 | 7.45255 | 2.47348 | 29.41 | 13.8 | .860 | .00014 |
| 360 | 7.47711 | 2.48892 | 27.78 | 9.7 | .769 | .00010 |
| 380 | 7.52863 | 2.53150 | 26.31 | 7.1 | .692 | .000071 |
| 400 | 7.55047 | 2.54441 | 25.00 | 5.3 | .630 | .000052 |

From the study of substances in the gaseous phase carried out in this Laboratory the conclusion at present is that for a single molecular species the pressure is strictly a linear function of the temperature. This implies directly that the constant-volume specific heat for a single molecular species depends on the temperature alone. This is a most important fact to ascertain and specific heat measurements made preferably at constant volume are now most urgently needed to provide a more precise insight into the properties of single molecular species. The Joule-Thomson data for carbon dioxide appear to substantiate the view that association in carbon dioxide actually exists and the equation for the fraction associated ($y$) may be used to compute the coefficient of the density for the specific heat between 16° and 100°.

A measured value of $C_v$ for a fluid containing a small fraction of associated molecules would be, where $C_v^0$ is the value for $y=0$,

$$C_v = C_v^0 + \Delta H_v \left(\frac{\partial y}{\partial T}\right)_v \tag{12}$$

In this equation $\left(\frac{\partial y}{\partial T}\right)_v$ must be computed as the mean value between 16° and 100° to correspond with the temperature interval employed by Joly. There is obtained $2.2 \times 10^{-3}\ \frac{1}{v}$. The heat of the reaction at constant volume for the temperature interval is 1880 cal. per mole or 44.7 cal. per g. The coefficient of $1/v$ or the density becomes, therefore, 0.094, and the constant-volume specific heat equation as far as the first term is, $C_v = C_v^0 + 0.094\rho$.

The coefficient is seen to be 0.094 as compared with 0.2125 of Joly or nearly 2½ times smaller. The agreement is not good and further work alone can resolve the discrepancy. Several comments are, however, at the moment apropos. The Joule-Thomson coefficient is necessarily obtained from measurements on a fluid in rapid motion. Equation 5, on the other hand, is deduced on the assumption that true chemical equilibrium exists at every instant of the measurement. It is, however, a well-known fact that in general a chemical reaction possesses a finite velocity increasing with rising temperature, which would preclude instantaneous adjustment. In the case of associating nitrogen dioxide, however, the adjustment of the single and double species is known to take place very rapidly. In any event until it can be assured that the equilibrium can actually adjust itself with sufficient rapidity the measurement of the Joule-Thomson effect for an associating gas presents peculiar difficulties.[11]

The specific heat measurement at constant volume is an experimental problem of particular difficulty. The copper spheres used by Joly re-

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[11] Professor A. B. Lamb, in conversation, made the very pertinent suggestion that experiments might be made with Joule-Thomson plugs in which catalysts were present, thus submitting to direct test the question of equilibrium attainment.

quired numerous corrections, one of which was briefly discussed in the paper on the Joule-Thomson effect for air. This is the change in heat capacity of the metal of the sphere due to tension produced by the gas inclosed. In addition to this effect there is also the heat due to stretching of the metal walls as the gas heats from 16° to 100°. Joly mentions this effect but dismisses it as of small magnitude. Another effect which may attain a magnitude sufficient to require consideration is the adsorption on the container walls and its shift with change in temperature. Heats of adsorption are enormous as compared with the heat capacity and, should such an effect exist, it would give a decided trend to the measured heat capacities.

## Summary

1. The equation for the Joule-Thomson effect is deduced for a gas containing a small fraction of associated molecules. The deduction is based on the assumption that true chemical equilibrium exists at every stage of the effect.

2. The equation is compared with the recent Joule-Thomson data of Burnett for one atmosphere and qualitatively found to be in agreement. Quantitatively, the fraction associated deduced from the observations at various temperatures is that function of the temperature which theory requires with the exception of the lowest three temperature data given by Burnett. The conclusion is that the Burnett data indicate the presence of association.

3. The numerical equation for the fraction associated for carbon dioxide from the Joule-Thomson data, when used to compute the density coefficient for the increase in constant-volume heat capacity of carbon dioxide, gives a number $2^1/_2$ times smaller than that given by Joly based on his measurements.

4. The value of the associated fraction of carbon dioxide at one atmosphere and 220°K. as obtained from Burnett's Joule-Thomson data is 0.004. At 270°K. it is 0.00075 and at 400°K., 0.000052.

CAMBRIDGE 39, MASSACHUSETTS