THE SPECIFIC HEATS OF GASES AND VAPORS

A CRITICAL REVIEW OF METHODS AND RESULTS

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NOTATION

If we designate by c_p, c_v the heat capacity per gram at constant pressure and at constant volume, respectively, and by C_p and C_v the corresponding quantities per gram-mole, we have

$$C_p = Mc_p \text{ and } C_v = Mc_v$$

where M is the molecular weight of the gas. The normal calorie (15°) is assumed as the heat unit and temperatures are referred to the normal centigrade scale (hydrogen thermometer) but few authors take precautions in this connection on account of the moderate accuracy claimed for the result.

We can also write

$$\gamma = \frac{C_p}{C_v} = \frac{c_p}{c_v} \text{ and } \delta = c_p - c_v \tag{1}$$

It is obvious that it suffices to determine two of the four quantities c_p, c_v, γ and δ in order to find the others but knowledge of a third offers a valuable check.

FUNDAMENTAL QUANTITIES

The quantities γ and c_p are usually considered as the primary ones because c_v presents greater difficulties in experimental determination and the methods for calculating δ are unsatisfactory.

For example, to take the most favorable case, that of air, the values of c_p at one atmosphere obtained by different investigators for the same temperature interval exhibit differences greater than one per cent and the values obtained over a temperature range can be fitted only by an undulating curve, as shown in Table 1. Furthermore while the values of γ for dry CO_2-free air at atmospheric pressure in the neighborhood of 20° are sufficiently concordant to permit averaging (1.400 to 1.405), the values obtained at other temperatures and pressures exhibit discrepancies which can be characterized only as enormous. It is necessary, therefore, to consider the possibilities of calculating δ.

TABLE 1

t	−181	−75	+20	25	59	60	*ca.*230	*ca.*410
c_p	0.249	0.243	0.240	0.241_2	0.237	0.241_5	0.237	0.243

METHODS

1. Calculation of δ

In certain special cases precise values are available for the two coefficients of expansion

$$\alpha = \frac{1}{v_0}\frac{\partial V}{\partial T} \text{ and } \beta = \frac{1}{p_0}\frac{\partial p}{\partial T}$$

and for such cases δ is readily obtained from the classical relation

$$\delta = \frac{T}{J}\frac{\partial p}{\partial T}\frac{\partial v}{\partial T}$$

in which all terms are known for 0° and 1 atm., and are comparatively easy to determine in general.

$\frac{\partial v}{\partial T}$ and $\frac{\partial p}{\partial T}$ may be computed in a general way from an appropriately selected equation of state; but it is first necessary to eliminate all equations, such as that of Van der Waals, which yield a value of β (and consequently of the internal pressure) which is independent of T.

A recent examination (1) of the behavior of the internal pressure as a function of p and T has led to the expression[1] (CGS Units)

$$Mpv = RT\left[\left(\frac{v}{v + \mathrm{a}}\right)^2 - 3.160_5\,\frac{\mathrm{a}\;v}{(v - \mathrm{a})^2}\,(4^x - 1)\right] \tag{2}$$

in which x is the reciprocal of the reduced temperature $\left(x = \frac{T_c}{T}\right)$; $\alpha = 0.0463\,\frac{RT_c}{Mp_c}$; $R = 8.316 \times 10^7$ and $T_o = 273.1°$.

For our present purposes this equation is somewhat inconvenient on account of the complexity of the calculations which it involves. Others have been suggested based more or less upon that of Van der Waals and upon the principle of corresponding states. One of these, proposed by D. Berthelot, yields results of sufficient accuracy, except close to the critical point, but cannot be used in the region of saturation. Another due to Callendar yields errors in the opposite direction. For example, for saturated steam at 100° and 1 atm.

$$M\delta = \begin{cases} 2.070 \text{ Equation of Berthelot} \\ 2.198 \text{ Equation of Callendar} \end{cases}$$

The mean 2.134 is not far from the true value 2.12.

A third relation proposed by Leduc may be expressed thus

$$Mpv = RT\varphi \tag{3}$$

which may be regarded as a definition of the relative molal volume φ, in terms of that of a perfect gas.

However, instead of taking for φ, the expression between brackets in equation 2, it may be treated as a function of T and p and the equation written in the form

$$C_p - C_v = M\,\delta = \frac{RT^2}{\mathrm{J}}\,\alpha'\,\beta'\,\varphi = \frac{\left(\varphi + T\,\frac{\partial \varphi}{\partial T}\right)^2}{\varphi - p\,\frac{\partial \varphi}{\partial p}} \tag{4}$$

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[1] A. Leduc, Thermodynamique, Doin, (1924), p. 192; and Compt. rend. **176**, 1132 (1923). This equation reproduces very closely Amagat's data for CO_2 almost up to saturation and as high as 200 atm. and 100°, for example. It also faithfully reproduces the isotherms of O_2 up to 500 atm. but with significant departures at 1000 atm. doubtless because the variation of the co-volume is not properly taken care of by the equation.

with $\alpha' = \frac{1}{v}\frac{\partial v}{\partial T}$ and $\beta' = \frac{1}{p}\frac{\partial p}{\partial T}$. If p is of the order of 1 atmosphere (or if the reduced pressure $\pi \leq 0.1$), φ is given with sufficient accuracy by the expression

$$\varphi = 1 - mp - np^2 \tag{5}$$

in which m and n are functions of T and in most cases (normal gases) functions of the reduced temperature τ or better of its reciprocal $x, \left(= \frac{T_c}{T}.\right)$

If we put $z = mp_c$ and $u = np_c^2$ equation 4 may be written

$$M\,\delta = \frac{R}{J}\frac{\left(\varphi - x\frac{\partial \varphi}{\partial x}\right)^2}{\varphi - \pi\frac{\partial \varphi}{\partial \pi}} = \frac{R}{J}\frac{\left[1 + \pi\left(x\frac{\partial z}{\partial x} - z\right) + \pi^2\left(x\frac{\partial u}{\partial x} - u\right)\right]^2}{1 + \pi^2 u} \tag{4a}$$

For the pressure range under consideration and for $\tau \leq 0.9$, $\pi^2 u$ is negligible.

For normal gases z is given by

$$z = 0.1\sqrt{2x}\,[2x^3 + 1.45x\,(2 - x) - 1]$$

and within the pressure limits under consideration we may assume[2] (2)

$$u = 2x^3\,(x-1)$$

The values of δ employed in Table IV have been calculated by means of the above equations. The error in the values so calculated apparently should not exceed 0.2 per cent.

It should be noted that the partical derivatives, $\frac{\partial p}{\partial T}$ and $\frac{\partial v}{\partial T}$, apply to the same state of the gas, the calculation of δ in this way is not applicable to mean specific heats.

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[2] A. Leduc, Compt. rend., **148,** 548 (1909) and Thermodynamique, pp. 109 and 113, in which the case of the "abnormal" gas is also discussed.

2. *Velocity of sound*

The best method for determination of the specific heat ratio γ appears still to be that known as the "velocity of sound method" based upon the formula of Laplace

$$V = \sqrt{Ev} = v\sqrt{-\gamma \frac{\partial p}{\partial v}}$$

It is, however, not safe to assume the equation of state of a perfect gas in using the Laplace formula, a precaution not observed by many investigators, including some modern ones. In this manner for example (3) Wüllner (1878) found for CO_2 at 0°, $\gamma = 1.31131$ while the correct calculation gives 1.320.

TABLE 2

H_2	1.0006	CO_2	0.993	C_2H_6	0.988
N_2	0.9995	N_2O	0.9925	NH_3	0.9856
CO	0.9994	C_2H_4	0.992	Cl_2	0.983
O_2	0.9991	HCl	0.992	CN	0.978
NO	0.9990	PH_3	0.991	SO_2	0.9773
CH_4	0.998	H_2S	0.990		

The Van der Waals equation would obviously give a better result. It is, however, necessary to determine the constants of the equation from experimental data on the gas in the same region of pressures and temperatures.

Equation (2) is much more reliable; but the calculation is very laborious and for pressures of the order of one atmosphere it is more convenient to employ equations (3) and (5) which give

$$v\frac{\partial p}{\partial v} = -\frac{p\varphi}{1 + np^2}$$

and since np^2 is negligible (4)

$$V = \varphi\sqrt{\frac{RT}{M}\gamma}$$

Having calculated γ with the aid of the perfect gas law, it is now corrected by multiplying it by the factor $\frac{1}{\varphi^2}$ if the law of Avogadro has been assumed or by the factor $\frac{1}{\varphi}$ if an experimental value for the density has been utilized. Table 2 gives the values of φ_0 at 0° and 1 atm. ($\pm$0.0002 where the fourth decimal is given).

The correction for departure from the perfect gas law amounts, therefore, to 5 per cent of γ for SO_2, and to 4 per cent in the case of benzene at 100° and 1 atm.

The determination of V by the method of Kundt also requires certain precautions. The formula of Kirchoff

$$V_{\text{obs.}} = V\left[1 - \frac{K}{d\sqrt{\pi N}}\right]$$

in which V is the velocity in free air, K is a constant and N is the frequency, is not valid according to some authorities (Lord Rayleigh, Helmholtz) unless the diameter, d, of the measuring tube $\geq$ 5 cm. K is usually taken as 0.65. Now most investigators have employed tubes of much smaller diameters and the various devices which have been used to eliminate K by using two or three different tubes are not valid since such an elimination itself assumes the validity of Kirchoff's equation. Moreover K is a function of certain properties of the gas (e.g., the viscosity, which varies with T) and also of the nature of the tube, and it is probable that the proportionalities assumed are inexact. The correction is, therefore, unsatisfactory unless it is small; that is, unless the tube is wide and N is large.[3]

3. *Method of Clement-Desormes*

We shall pass over the grave difficulties created by the oscillations of Cazin which have not yet been satisfactorily resolved. The usual procedure is to produce a sudden expansion ($\nless$ 5 cm. Hg) and it is necessary to calculate γ by the logarithmic formula (5).

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[3] If $d = 5$ cm. and $N = 435$ the correction amounts to 35×10^{-4} which is in the case of air 1.20 m/sec. This means that an error of 10 per cent in the correction is scarcely allowable since it is a systematic error.

Wüllner, with $d = 3$ cm. and $N = 2539$, failed to make any correction thus introducing an error of 0.5 per cent in γ for CO_2. If the true value for N is 2535, Wüllner's CO_2 was not, as he supposed, free from air. Thus two errors were present, the first of which $\geq$ 0.3 per cent and the second possibly a little greater but impossible to evaluate. These two must have partially compensated the other one.

Even with an expansion equivalent to 10 cm. Hg for CO_2 at 0°, the error introduced by failure to correct for departure from the perfect gas law amounts to $\frac{\Delta\gamma}{\gamma} = -2.6 \times 10^{-4}$, which is negligible because a precision of 0.1 per cent is, at present, illusory. The correction is still small but necessary in the case of SO_2 at 0°, for example. It has been suggested that a series of expansions of decreasing magnitude be made and that the curve of values of γ thus obtained be extrapolated to zero expansion. This method, however, is of no value because of the increasing uncertainty in γ with decreasing expansion. This is the case, for example, in the experiments of Maneuvrier (formula of Reech).

4. Method of Lummer and Pringsheim

This method has been perfected by numerous investigators, and most recently by Partington. The correction for departure from the perfect gas law is especially large in this method: 0.5 per cent for CO_2 and 1.8 per cent for SO_2 at 15°. It is easily made with the aid of the relations discussed above. With the aid of an extra fine bolometric filiament (Wollaston wire, $d \leq 2\mu$) and a rapid and sensitive galvanometer, Partington and Howe have sought to reproduce by means of the oscillations of the galvanometer mirror, those which occur within the gas.

The deflection was found to assume a constant value during a period of time varying with the nature of the gas, in some cases amounting to 10 seconds but not exceeding 2 seconds in the case of hydrogen.

It is difficult to follow the authors in their conclusion that this condition corresponds to a permanent equilibrium. It is rather an apparent or mobile equilibrium (Prevost) resulting from the fact that the heat supplied to the filiament by radiation from its surroundings compensates for a short time, that which it loses to the gas cooled by the expansion. As a consequence the degree of cooling, and likewise the value of γ, is underestimated. This effect evidently increases with the diameter of the wire and it is on this account that Makower, using a wire of 30 μ diameter found for saturated steam at $100°\gamma = 1.303$, while the cyclic method (Leduc *v.* infra) based upon the latent heat of vaporization and the vapor pressure gives $\gamma = 1.373$ and the experiments of Neyreneuf lead to the value 1.368 for the slightly superheated vapor. Aside from all other considerations, it is, therefore, necessary to increase slightly all values obtained by this method with very fine wires and to reject all those obtained with wires whose diameter attains 20 to 30 μ, for example. On the basis of these considerations it may be remarked that the great mobility of the hydrogen molecules favoring the exchange of heat between the wire and the gas would account for the decrease in the apparent equilibrium period.

One investigator has obtained a value for γ independent of the rate of the expansion employed. It is, however, difficult to see how a slow expansion could be adiabatic.

The substitution of a thermocouple for a bolometric wire (Moody) does not appear to offer any advantages.

5. Direct experimental determination of C_p

a. Method of mixtures (e.g., Regnault) and method of circulation (Delaroche and Bèrard, E. Wiedemann, etc.). In this method the quantity of heat furnished to a calorimeter by a supposedly known mass of gas preheated to a known temperature is measured. The accurate determination of the mass of the gas is very difficult. The error in determining the fall in temperature of the gas is relatively unimportant, this fall being usually large.

The current of gas is necessarily rapid, which results in a significant pressure drop through the calorimeter even with the arrangement used by Regnault and especially with those employed in modern investigations (3). As a result an expansion takes place within the calorimeter resulting in an absorption of heat amounting in the case of air (according to two blank experiments by Regnault) to 1/160 of the heat carried by the gas when employing a preheat to 180° and a flow of 18 liters per minute. Since we are concerned here only with the order of magnitude of the heat effect due to the expansion of the gas it suffices to add a correction of 1/160 for experiments of this character. In this way we obtain for air, $c_p = 0.239$ and it is noteworthy that this is precisely the value obtained by Wiedemann using a rate of flow of only 3 liters per minute but with a different type of apparatus.

It is obvious that this correction should increase with the velocity of flow. It should be very large, for example, in the experiments of Knoblauch and Jakob on the vapor of water in which a flow of 750 grams per minute was employed.

b. Constant flow. In the method of Callendar and Barnes on the other hand, the quantity measured is the heat which must be supplied to the gas by an electric current in order to heat it from t_1 to t_2, while it is flowing at high velocity and consequently undergoing an expansion. The quantity of heat obtained is therefore too large. The values obtained by the method of constant flow are in fact larger than those obtained by the method of mixtures. The estimation of the exact magnitude of this error in either case is unfortunately difficult on account of the simultaneous presence of other errors. One is consequently reduced to averaging the results obtained by the two methods when similarly applied to the same gas.

6. Determination of C_v

a. Method of condensation of vapor. This method suggested by Bunsen has given in the hands of Joly a few very interesting results notably a variation of C_v with density which is confirmed by means of the equation of state. These results will be discussed below:

b. Velocity of sound. Dixon and his coworkers in their recent work do not claim to have bettered the precision of their predecessors at low or moderate temperatures, but they do claim to find the true value c_t, instead of the mean value $c_{t_1}^{t_2}$ sought by previous investigators, usually with very discordant results. Dixon determines the time required for sound to travel the length of a long tube (straight or coiled) of lead, steel or silica according to the temperature. He found first that a tube 25-mm. diameter gave the same result when straight as when coiled. Using Kirchoff's correction, he found for air at 0°, $V = 331.8$ m/sec as compared with the accepted value 331.5. This concordance is reassuring. γ was computed and then C_p and C_v with the aid of Berthelot's equation.[4]

In spite of the great difficulties connected with such experiments at very high temperatures, the results appear to be more reliable than those obtained by the following method.

7. *The explosion method*

In this method the explosive mixture receives a supposedly known amount of heat which suffices to raise the final system to a certain pressure which can be assumed to be a simple function of T if the composition of the final mixture is known at the moment of attaining the maximum temperature.

In reality this composition varies in an unknown manner with time, and though the mean heat capacity of the mixture is approximately known, it is not possible to calculate with any feeling of security the heat capacity of each gas in the mixture. This state of affairs justifies the attempts of Pier to *measure* the actual maximum temperature with the aid of a bolometer instead of attempting to calculate it from the measured pressure. Ingenious instruments were devised for correcting for the loss of heat (e.g., by an automatic pressure recorder) so that even though the values found for the specific heats of the gases are not satisfactory for the purposes of the scientist, they do make it possible to calculate the temperature and pressure developed in an analogous explosive mixture of the same gases in different proportions which has certain useful applications in ballistics.

8. *Examination of the specific heat data*

Atmospheric air under ordinary conditions and dry air at 0°. It is not possible to determine accurately the so-called normal

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[4] The question has been asked as to whether the perfect gas law may be safely employed under conditions of high pressure if the temperature is also high. Application of equation (4a) gives for CO_2 at 1000° ($x = 0.24$) and 1 atm., $C_p - C_v = \frac{R}{J} \times 1.0003$ that is practically $= \frac{R}{J}$. At 100 atm., however, we would have approximately $C_p - C_v = 2.05$ the same as for CO_2 at 0° and 1 atm. The error would be still greater at 2000° under 2000 atm.

velocity of sound; that is, the velocity in open air. Measurements in large tubes are much more accurate. The Violle correction for the tube diameter may be regarded as reliable but the humidity correction according to the formula of Regnault

$$V = V_{\mathrm{Dry}}\left(1 + A\frac{f}{H}\right)$$

with $A = 0.1875$ is very inaccurate.

In 1913, Violle accepted $A = 0.16$ and obtained $V_0 = 331.36$ m/sec.

In practice it is convenient to employ Leduc's equation for gas mixtures (6).

$$\frac{K_{\mathrm{Mix}}}{\gamma - 1} = \Sigma \frac{k_\alpha\, r_\alpha}{\gamma_\alpha - 1}$$

in which r_α is the richness of the mixture in the gas α and k_α the value (for this gas) of the expression

$$K = \frac{(\beta\, T)^2\,(1 + np^2)}{\varphi}$$

This is equivalent to the use of Regnault's equation with $A = 0.15$. It is necessary in addition to make two smaller corrections for CO_2 and for the mercury-in-glass temperature scale, which gives finally

$$V_0 = 331.5 \pm 0.1 \text{ m/sec.}$$

Equation (5) then gives $\gamma_0 = 1.402_7$ which may be compared with

1.403	Guéritot 1912
1.403_2	(17°) Partington 1913
1.402_9	(20°) Miss Schields 1917
1.403_1	(0°) Hebb 1919

On the basis of the best values we may take $\gamma_0 = 1.403$ and $\gamma_{100} = 1.401$, the latter being based upon an assumed linear variation with t and being therefore less certain. The coefficients of expansion α and β are accurately known and lead to

$$(c_p - c_v)_0 = 0.0689_5$$

whence $(c_p)_0 = 0.240_0$ and $(c_v)_0 = 0.171_1$. For a molecular weight of 28.98 these correspond to $(C_p)_0 = 6.95_5$ and $(C_v)_0 = 4.95_8$.. It is to be noted that the method of mixtures gives at 25°$c_p = 0.237$ (e.g., Scheel and Heuse, Eggert) instead of 0.241 by the constant flow method (Swann, Scheel and Heuse). This confirms previous observations. We must conclude, therefore, that the value of Swann $(c_p)_{100} = 0.243$ and that of Thibaut, $(c_p)_{350} = 0.245$, are too large. Volume V of International Critical Tables gives a tabulation of the results of various investigators between − 185° and + 280°, and for pressures up to 220 atm. Within this region the data show that

$$\frac{\partial c_p}{\partial p} > 0 \text{ and } \frac{\partial c_p}{\partial T} > 0$$

We may note further that c_p (Witkowsky) and c_v (Bennewitz and Splitberger) (7) each becomes infinity at the critical point.

It may be noted further that the values calculated by Lussana are in general much larger than the experimental values of other investigators. Thus for 100° and 100 atm. Lussana gives $c_p = 0.395$ instead of 0.265.

As regards γ, while at 0° Witkowsky and Koch find that it varies almost linearly with the pressure between 25 and 200 atm. ($\gamma = 1.83$), Koch finds that at −79.4° it passes through a maximum at 150 atm. ($\gamma = 2.47$) and falls again to 2.33 at 200 atm.

Various gases at 15° and 1 atm. The value of γ is rarely known to 0.001 and in some cases the value is not known beyond the second decimal. Even in such cases, however, calculation through γ and δ is to be recommended. One obtains in this way table 3.

Molal heat capacity at 15° and 1 atm. Calculated from γ and δ. At very low temperatures it is best to utilize the experimental C_p values at atmospheric pressure as determined by Scheel and Heuse and others, and to calculate δ from equation (4). The second decimal is here uncertain on account of experimental difficulties.

According to the data of those authors the specific heats for certain gases decrease with increase in temperature in the region

$-180°$ to $-50°$, while above 0° we have in nearly all cases $\frac{\partial c_p}{\partial T} > 0$ and $\frac{\partial c_v}{\partial T} > 0$ at atmospheric pressure. Such a result would ordinarily be attributed to important experimental errors; but the phenomenon appears also in the case of CO_2 at ordinary temperatures and high pressures, according to Lussana (e.g., $c_p = 1.47$ at 13.2° and 0.386 at 114.9° under a pressure of 20.5 atm.). According to Knoblauch and Mollier the same is true for water vapor.

TABLE 3

GAS	$M\delta = c_p - c_v$	γ	c_p	c_v
A	1.994	1.66_8	5.00	3.00
H_2	1.987	1.410	6.83	4.84
N_2	1.995	1.404	6.94	4.94
O_2	1.995	1.401	6.97	4.97
NO	1.996	1.400	6.99	4.99
CO	1.995	1.404	6.94	4.94
CH_4	2.004	1.31	8.47	6.47
CO_2	2.041	1.304	8.75	6.71
N_2O_2	2.050	1.303	8.82	6.77
C_2H_4	2.057	1.255	10.07	8.03
HCl	2.057	1.41	7.07	5.02
C_2H_2	2.057	1.26	9.97	7.91
C_2H_6	2.086	1.22	11.6	9.5
H_2S	2.092	1.32	8.63	6.54
NH_3	2.108	1.31	8.91	6.80
Cl_2	2.135	1.35_5	8.15	6.0_1
CN	2.170	1.25_6	10.6_5	8.4_8
SO_2	2.18_3	1.29	9.7_1	7.5_3

In spite of the satisfactory nature of the curves obtained, it seems justifiable to question these results on account of the enormous gas velocities employed, the flow amounting to more than 750 g./min. This appears to be the more justifiable in the light of Holborn and Henning's values at atmospheric pressure which fail to exhibit any minimum. It might be objected that these latter experiments do not extend below 250° while the minimum to be expected is not very pronounced and should lie at about 190°. But it should be noted that at a given temperature the experimental values are uncertain to 2 per cent which is the difference found between 100° and 190°.

In this connection, it is interesting to compare (table 4) some values by Knoblauch and Mollier with those of Holborn and Henning. The existence of such a minimum is furthermore inconsistent with the calculations of Leduc (8) for saturated and superheated vapor between 100° and 160° and for pressures up to 4 atm. based upon the vapor pressure data of Holborn and Henning up on the latent heat values of Henning, and upon the curves of compressibility (in reduced coördinates) of the vapor up to the saturation point (see equations 3, 5, etc.). It should be noted that the values of γ calculated by the same method (the cycle method) are materially greater than those ordinarily accepted. Thus at 100° $\gamma_s = 1.373$ in good agreement with the value deduced from the velocity of sound according to Neyreneuf (9) by means of equation (5), namely, $\gamma = 1.368$ for the slightly superheated vapor.

TABLE 4

	KNOBLAUCH AND MOLLIER	HOLBORN AND HENNING
100°	0.48_2	
200°	0.47_1	0.46_5 (extrapolated)
400°	0.49_0	0.47_3

In conclusion, even if we reject the more doubtful series of measurements as well as those involving the most serious experimental difficulties, it is scarcely possible to be certain of a precision better than 1 part in 200 for pressures other than atmospheric at very high or very low temperatures.

For c_v the uncertainty is even greater whether the values are obtained by the explosion method or deduced from γ or c_p by combination with δ.

Partington and Shilling (10) have constructed specific heat-temperature curves from the best available data in particular the c_p data of Knoblauch and Mollier and the c_v data of Pier between 2000° and 2500° as recalculated and materially modified by Siegel.

It should be pointed out that the values of c_p being for 1 atm. this will also be the case for the values of c_v calculated by equation

(1), while the c_v values obtained by the explosion method correspond to a wide variation in pressure.

It is, therefore, not justifiable to deduce c_p values from these c_v values unless they are expressed as a function of T and p. It is possibly for this reason that the curves obtained for water vapor have such a peculiar form, since the high temperature values are deduced from the explosion data. Dissociation is, however, also doubtless a factor, since the curves for CO_2 computed from similar data do not exhibit the same character.

9. *Variation of c_v with density*

The experiments of Joly (11) using with a high degree of perfection the method of vapor condensation suggested by Bunsen deserve special mention. The values shown in table 5 were obtained for the mean specific heat (at substantially constant volume) of CO_2 between 12° and 100°. Joly represents his data by the following formula:

TABLE 5

d, g/cm^3	0.0387	0.077	0.118	0.144
c_v	0.171_4	0.184	0.194	0.202

$$(c_v)_{12}^{100} \pm 1\% = 0.165 + 0.2125\, d + 0.340\, d^2$$

Now, if we use the classical equation

$$\frac{\partial c_v}{\partial v} = \frac{T}{J} \frac{\partial^2 p}{T^2}$$

together with equation (2), we obtain

$$\frac{\partial c}{\partial d} = \frac{12.07}{M} x^2 \times 4^x \frac{a}{1 + a\, d}$$

whence on integrating

$$c = c_0 + 0.274\, x^2\, 4^x \frac{a\, d}{1 + a\, d}$$

where c_0 corresponds to $d = 0$.

The calculation gives for $d_1 = 0.05$ and $d_2 = 0.15$, $c_2 - c_1 = 0.030$.

Now experiment gives $c_1 = 0.176$ and $c_2 = 0.204$. The difference, 0.028, shows satisfactory agreement with the calculated value and it is safe to assume that the function $c = F(d)$ is a hyperbola at least up to $d = 0.15$ and probably further.

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