Heat Capacity of Gases by the Adiabatic Expansion Method

Thesis by E. J. Burcik

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Introduction

Introduction

In 1911 Bjerrum showed how gaseous heat capacities could be calculated if the normal vibrational frequencies of a molecule are known. Accurate experimental values of gaseous heat capacities have then a two fold interest. Not only are they useful in calculating thermodynamic equilibria but they also serve as a valuable check on the spectroscopically determined vibrational frequencies. Unfortunately, for many years, little could be done in correlating the spectroscopic and experimental heat capacities. This was due either to the lack of knowledge regarding the internal molecular motions of the molecules or to the lack of accurate experimental heat capacity data. In the past few years both these difficulties have been removed. The spectroscopist succeeded in determining the vibrational frequencies of a large number of molecules and improved methods of determining the heat capacity of gases have been devised.

Probably the most accurate method available for the determination of gaseous heat capacities is the adiabatic expansion method of Lummer and Pringsheim. Using this method the heat capacities of a number of gases were determined at various temperatures. Data for oxygen, carbon dioxide, sulphur dioxide, ethylene, boron trifloride, cyanogen, dichlorodifloromethane and trichloromonofloromethane will be reported in this thesis. The purpose of this research was principally to verify the analysis of the Infra red and Raman spectra of the substances. However, the thermodynamic interests are not overlooked. Data on the heat capacities of oxygen and carbon dioxide are included principally to give an indication of the accuracy of the method used, for supposedly there is little doubt concerning the veracity of the spectroscopically determined frequencies.

Theory

Theory

From the first law of thermodynamics we have

$$dE = dQ - dW$$

where E is the internal energy of the system, Q is the heat absorbed by the system and W is the work done by the system. If we consider an expansion which is adiabatic no heat enters or leaves the system. Hence all the work done by the system is done at the expense of the internal energy of the gas. If the process is reversable, that is, if the expansion takes place infinitely slowly, the internal pressure will be essentially equal to the external pressure at all times. Therefore

$$dE = -pdv \qquad (1)$$

In general $dE = (\frac{\partial H}{\partial T})_p dT + (\frac{\partial H}{\partial p})_T dp - pdv - vdp$, where H is the heat content of system as defined by H = E + pv. Equation (1) becomes:

$$C_p = \frac{V - (\frac{\partial H}{\partial p})_T}{(\frac{\partial T}{\partial p})_{q=0}} \qquad (2)$$

The coefficient $(\frac{\partial H}{\partial p})_T$ is the amount of heat which would be absorbed, per unit difference in pressure, if the expansion had been conducted at constant temperature and not in a thermally insulated vessel. Since the measurement of this coefficient is rather inconvenient ~~then~~ it is desirable to obtain an expression for it in terms of more easily measurable quantities. With the aid of the second law of thermodynamics we find

$$(\frac{\partial H}{\partial p})_T = V - T\ (\frac{\partial V}{\partial T})_p$$

Hence equation (2) becomes:

$$C_p = \frac{T(\frac{\partial V}{\partial T})_p}{(\frac{\partial T}{\partial p})_s} \qquad (3)$$

In order to integrate this equation we assume that the equation of state for the gas under consideration is of the form:

$$P = \frac{RT}{V-B}$$

If we assume that $\frac{dB}{dT}$ and C_p are constants over the small range of temperature and pressure involved, equation (3) becomes on integration

$$C_p = \frac{R \ln \frac{p_1}{p_2}}{\ln \frac{T_1}{T_2}} - \frac{\Delta P \frac{dB}{dT}}{\ln \frac{T_1}{T_2}} \qquad (4)$$

where C_p is the heat capacity at the mean temperature and pressure of the experiment.

The heat capacities calculated from spectroscopic data are the heat capacities of the gas at infinitely low pressures, whereas the experimentally determined values are for pressures equal to the mean pressure of the adiabatic expansion. In order to correlate results the usual practice is to convert the experimental heat capacity to heat capacity at infinite attenuation. To do this one has recourse to the thermodynamic relation

$$(\frac{\partial C_p}{\partial P})_T = - T\ (\frac{\partial^2 V}{\partial T^2})_p \qquad (5)$$

With the assumption that the equation of state is again of this form

$$P = \frac{RT}{V-B}$$

and that $\left(\frac{\partial^2 B}{\partial T^2}\right)_p$ is a constant over the pressure range, equation (5) integrates to

$$C_p - C_p^o = T \left(\frac{\partial^2 B}{\partial T^2}\right)_p P \qquad (7)$$

where C_p^o is the calculated value of the heat capacity, C_p is the experimentally determined value, P is the mean pressure and T is the mean temperature.

In equations (5) and (7) the quantities $\frac{dB}{dT}$ and $\frac{d^2 B}{dT^2}$ appear so that in order to calculate accurate heat capacity values the equation for B as a function of temperature must be known. It has been found experimentally that the temperature dependence of B can be expressed quite satisfactorily by an equation of the form:

$$B = \beta - \frac{A}{T} - \frac{C}{T^3} \qquad (8)$$

where β, A, and C are constants. Equations of this type have been developed for a number of the more common gases. However, when there is no existing data for the gas under consideration one is forced to make an estimate of the magnitude of $\frac{dB}{dT}$ and $\frac{d^2 B}{dT^2}$ Keyes found that by writing equation (8) in the form:

$$\frac{BP_c}{T_c} = \beta_\theta - \frac{A_\theta}{\theta} - \frac{C_\theta}{\theta^3}$$

(P_c = critical pressure, T_c = critical temperature, $\theta = \frac{T}{T_c}$) the calculated values of the constants β_θ, A_θ and C_θ were each very nearly equal for a large number of non polar substances. This is shown in Table I. The average value of β_θ, A_θ and C_θ are 13.29, 34.9 and 5.47 respectively so that to a first approximation for all non polar substances

$$\frac{B\,P_c}{T_c} = 13.29 - \frac{34.9}{\theta} - \frac{5.47}{\theta^3}$$

This equation was used in this research to calculate the gas corrections for substances whose true equation of state was unknown. It must be remembered that values of B obtained in this way may be in error by as much as 20 per cent.

Table 1 Equation of State Constants.

Substance	β_θ	A_θ	C_θ
He	6.08	21.74	6.00
Ne	12.48	35.34	6.99
A	12.52	33.24	5.57
H_2	8.08	27.95	5.31
N_2	13.42	34.57	5.58
O_2	14.89	37.93	4.21
Air	12.96	33.65	5.24
CO_2	25.14	48.13	5.63
CH_4	13.39	34.82	4.41
C_2H_4	21.88	47.72	1.80
C_2H_6	15.04	37.54	5.07
$(C_2H_5)_2O$	34.54	62.04	0.25
Average	13.29	34.9	5.47

We have succeeded in developing an expression by means of which an experimental value for the heat capacities of a gas can be determined. We are now ready to consider the process by which the heat capacity can be calculated from spectroscopic data.

The heat capacity of the ideal gas is made up of a number of component parts. We can write to a first approximation:

$$C_v^o = C_{translational} + C_{rotational} + C_{vibrational}$$

C_p^o being equal to C_v^o + R

All molecules have a translational heat of 3/2 R calories; R/2 calories for each translational degree of freedom. This classical value holds even if quantum statistical mechanics is applied to the translational motion of the molecules. For monatomic gases no heat other than the 3/2 R can be absorbed and C_p is simply equal to 3/2 R + R. In the case of diatomic and polyatomic gases additional heat can be absorbed with the production of other types of motion. The classical value of R/2 for each rotational degree of freedom is already fully developed at room temperatures. In other words the rotational heat is R and 3R/2 for diatomic and polyatomic molecules respectively. The increase of heat capacity above room temperatures is due to the vibration of atoms and atom groups within the molecule. This vibratory motion of the atoms may be resolved into one or more component vibrational degrees of freedom, each of which has R as its limiting value at high temperatures. Diatomic molecules have one vibrational degree of freedom while polyatomic molecules possess (3n - 6) (n = number of component atoms). For the special case of linear polyatomic molecules the number of vibrational degrees of freedom is (3n - 5). Except for a small positive correction arising from the stretching of the valence bonds with an accompanying increase in potential energy, no other types of motion are possible.

The increase of vibrational heat with rising temperature is given quite accurately by the Planck-Einstein equation for the heat absorbed by a linear harmonic oscillator.

$$C_{\text{vibrational}} = R\left(\frac{hv}{kT}\right)^2 \frac{e^{\frac{hv}{kT}}}{\left(e^{\frac{hv}{kT}} - 1\right)^2}$$

v is the vibrational frequency as deduced from Raman and Infra Red spectra,h is Planck's Constant, k is Boltzmann's Constant, and T is the absolute temperature., $\frac{hv}{k}$ has the dimensions of temperature and is therefore known as the characteristic temperature. If we denote this characteristic temperature by θ we can formally write:

$$C_{\text{vibrational}} = P\left(\frac{\theta}{T}\right)$$

Hence for a diatomic molecule with one vibrational degree of freedom we have:

$$C_p^o = \frac{7}{2} R + P\left(\frac{\theta}{T}\right)$$

In the case of polyatomic molecules where several vibrational frequencies are involved a separate Planck Einstein term may be used for each different frequency. Therefore in general C_p for linear molecules is given by:

$$C_p^o = \frac{7}{2} R + \sum_{i=1}^{3n-5} P\left(\frac{\theta i}{T}\right)$$

And for nonlinear molecules:

$$C_p^o = \frac{8}{2} R + \sum_{i=1}^{3n-6} P\left(\frac{\theta i}{T}\right)$$

It should be mentioned that to facilitate the calculation of $C_{\text{vibration}}$ tables have been drawn up listing $C_{\text{vibration}}$ versus $\frac{\theta}{T}$ so that it is a relatively simple matter to calculate the vibrational contribution of the heat capacity.

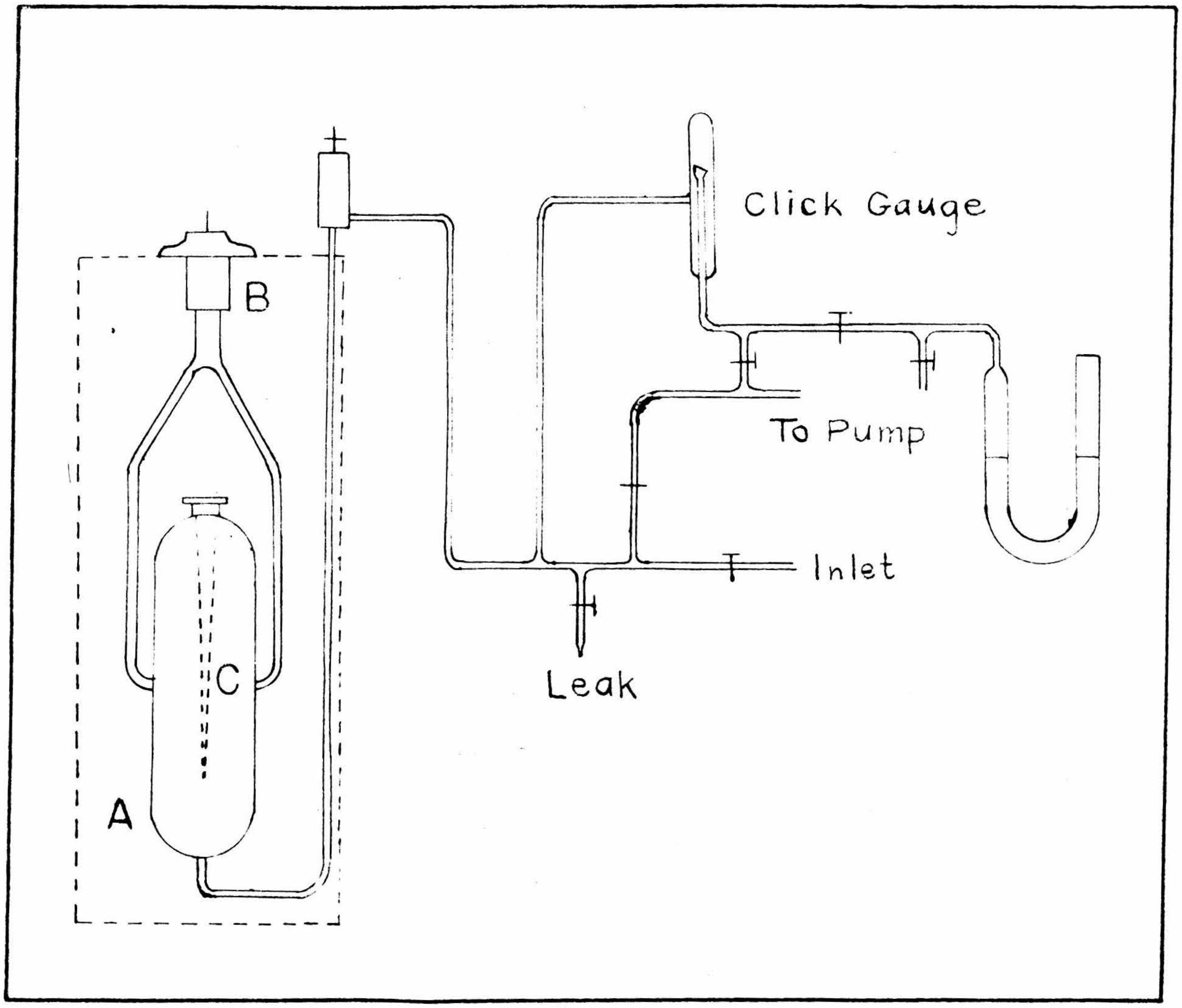
Apparatus

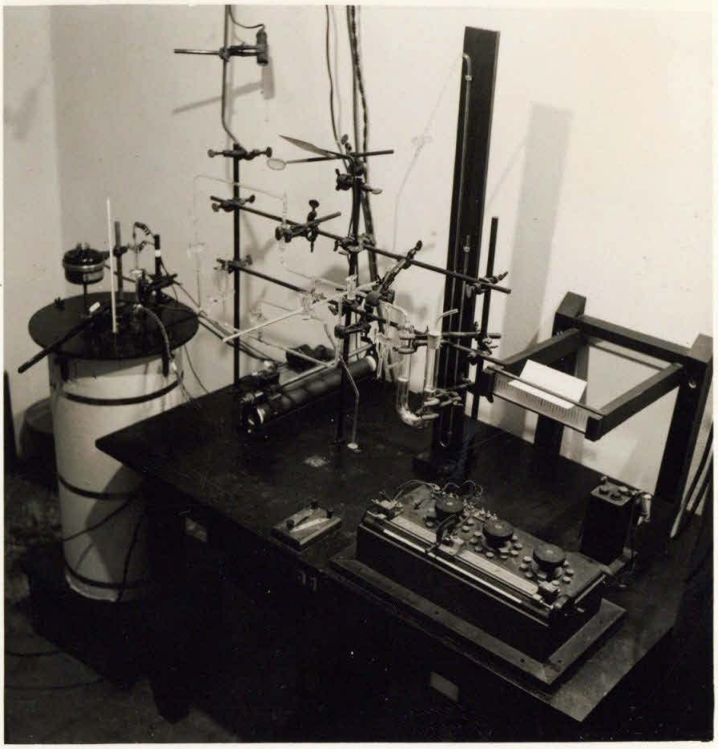
Apparatus

Figure 1 is a diagram of the apparatus developed for this research. The gas which is to be investigated is confined in the expansion chamber A. This chamber has a capacity of approximately two liters. The vessel itself is constructed entirely of copper and brass, all joints being hard soldered. Four symmetrically placed tubes, arranged so that turbulence during expansion was a minimum, connected the expansion chamber to the expansion valve B. This valve was designed so that a large orifice could be opened rapidly. The change in temperature of the gas, due to the adiabatic expansion was measured by means of a platinum resistance thermometer C. This was constructed of 0.001 inch diameter annealed platinum wire and was suspended freely along the axis of the expansion chamber. A small glass bead on the lower end afforded the necessary tension to keep the wire taut. The entire expansion chamber was inclosed in an insulating container or thermostat whose temperature could be controlled by heating coils in conjunction with a mercury thermal regulator.

The platinum resistance thermometer C forms one arm of a wheatstone bridge circuit. A variable resistance whose resistance could be accurately determined by means of a White double potentiometer formed another arm. A fixed ratio completed the bridge circuit. All resistance coils were constructed of Manganin wire to reduce any temperature effects. A sensitive galvanometer with a period of only 1.7 seconds was used in the bridge circuit. The current was supplied by means of number DA-2-1 Willard low

Fig. 1



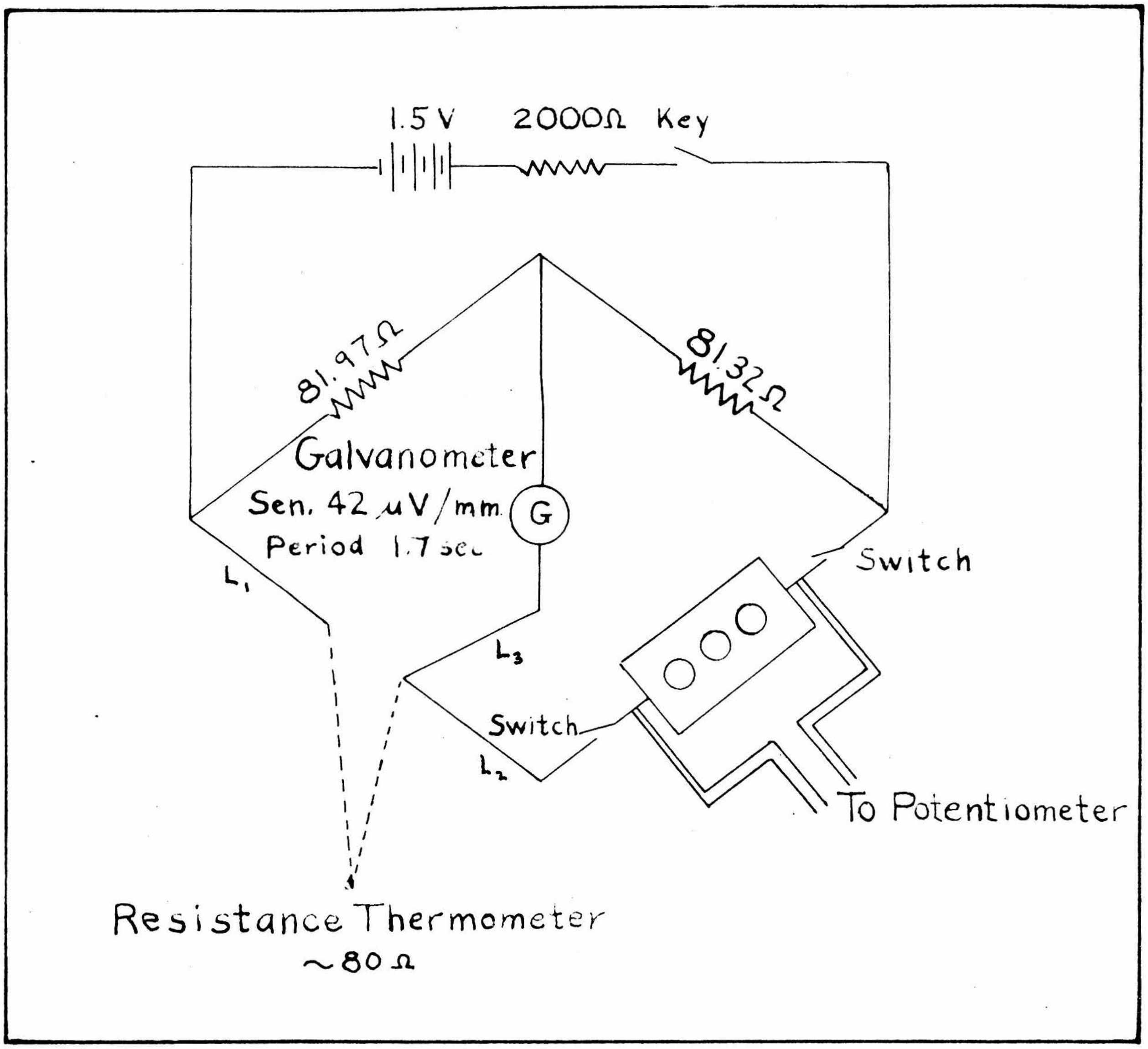


Photograph of Apparatus: The expansion chamber is inclosed in the constant temperature bath on the left. The lever arrangement for rapid opening of expansion valve can also be seen. The variable resistance and the galvanometer scale are visible on the right.

discharge storage cell in series with a high resistance; a current of about 7.5 x 10^{-4} amps being employed. The bridge was of the open circuit type, the current flowing only during the short time necessary for measurement. With this arrangement no heating effects of the resistance wire could be detected. Figure 2, a diagram of the electrical circuit used, shows the actual magnitude of the resistances used. It will be noted that all resistances in the wheatstone bridge circuit were constructed to be approximately equal so as to insure maximum sensitivity of the galvanometer. Furthermore by running the leads L_1 and L_2 parallel to one another and by attaching lead L_3 directly to the resistance thermometer small changes in Resistance due to changes in external temperature will be compensated.

The temperature drop due to the adiabatic expansion must be measured within a few seconds after the expansion due to the rapid exchange of heat from the walls to the cooled gas. The time available is dependent on the gas involved but is usually of the order of one to two seconds. Because of the short time available the variable resistance in the bridge circuit must be set closer and closer to the correct resistance in a series of successive expansions for which the initial and final pressures and the initial temperature are the same. For this reason a click gauge was convenient for the pressure measurements. In this research pressure drops of approximately 3.5 to 8 cm. of mercury were used, the results obtained with various pressure drops agreeing within the experimental error.

Fig. 2


1.5 V
2000Ω
Key
81.97Ω
81.32Ω
Galvanometer
Sen. 42 μV/mm.
Period 1.7 sec
G
L_1
L_3
L_2
Switch
Switch
To Potentiometer
Resistance Thermometer
~80 Ω

Experimental Procedure

Experimental Procedure

A brief description of the actual experimental technique will now be given. The gas to be examined is slowly introduced into the evacuated expansion chamber until the click gauge responds. Since one side of the click gauge is open to the atmosphere, the gas in the expansion chamber is at a pressure greater than atmospheric by an amount equal to or greater than the upper click constant of the gauge. The gas is then allowed to escape very slowly through a fine capillary until the pressure difference is equal to the lower click constant as is shown by the second response of the gauge. The expansion chamber was then cut off from the remainder of the apparatus by means of a stopcock. A period of about a minute was allowed before the expansion so that the system could attain equilibrium. The gas, in escaping through the capillary, was cooled slightly but the increase in pressure when the gas warmed up to the temperature of the thermostat was entirely negligible. When equilibrium is obtained, the expansion valve is rapidly opened by means of a lever arrangement and shortly thereafter the switch controlling the bridge current was closed. If the bridge is in balance the galvanometer will remain at rest on the zero point for a short time before moving off due to the warming up of the expanded gas. However, if the bridge is out of balance the galvanometer will come to rest momentarily at some point other than the zero position. By noting the magnitude and direction of the deflection the variable resistance can be set closer and closer to the correct resistance. Usually a series of about six expansions are sufficient to determine the correct setting of the variable resistance. Employing the galvanometer as a null instrument in this manner avoided the use of complicated photographic recording equipment.

After the Wheatstone bridge is balanced the variable resistance is measured by means of a White double potentiometer. In this way the actual calibration of the variable resistance is unnecessary. Next the resistance is measured with the gas in an unexpanded condition, that is, with the temperature of the gas equal to that of the thermostat. In this way the resistance drop due to the expansion was determined, and knowing the temperature coefficient of resistance of platinum, the temperature drop can readily be calculated. An exact value for the temperature coefficient of resistance is unnecessary due to the relative nature of the experiment. In this research the tabulated value for annealed platinum wire of .00392 ~~ohms~~ per degree was used. Relatively large changes in this value could be made without appreciably changing the final results.

In this research pure nitrogen was used as the standard gas. It was obtained from the Linde Air Products Company and probably contained less than .1 per cent impurities. These impurities, being largely oxygen, afforded little source of error as far as the heat capacity of nitrogen was concerned. The vibrational frequency of nitrogen is rather high (2330 cm^{-1})

whence the contribution of the vibrational heat capacity at low temperatures is neglig~~a~~ible. Over the temperature range used in this research C_p^o (at zero pressure) remained constant at 7/2 R or 6.955 cal. per mol. per degree.

The unknown gas was always bracketed between two determinations of nitrogen, the standard gas. The temperature drop for nitrogen was taken as the average of the two determinations. In this way, any errors caused by a slow drift in external pressure and temperature during the course of the experiment were eliminated.

Method

Method

In the derivation of equation (4) it was necessary to make the assumption that the expansion was both adiabatic and reversible. Obviously neither of these assumptions is strictly true when applied to the actual expansion process. There are certainly heat interchanges between the system and its surroundings, and the process is hardly reversible, for although the expansion chamber was designed for minimal turbulence and frictional losses, they are not entirely absent. Therefore, in view of these facts it is inadvisable to attempt to make the method absolute, but instead to calibrate the instrument with a gas of known heat capacity. This method, although it has the disadvantage of being dependent on the value of the heat capacity assigned to the standard gas, avoids a number of experimental difficulties which we believe can not be entirely overcome by an absolute method.

It is probably worthwhile to discuss the non adiabatic and irreversible nature of the process in greater detail and to demonstrate more precisely why a relative method overcomes the difficulties encountered in an absolute method. A number of corrections concerning the non adiabatic and irreversible nature of the process are so small that they can easily be neglected, others are removed by the compensating nature of the relative method, while still others, while not completely eliminated, are reduced in magnitude. The following factors which contribute to irreversibility and non adiabatic nature of the actual expansion will be discussed:

1. The finite heat capacity of the resistance thermometer.
2. Radiation corrections.
3. Gas conduction corrections.
4. End effects of the resistance thermometer including conduction and radiation.
5. Turbulence and frictional losses.

Because of the finite heat capacity of the resistance wire an error may be introduced due to the fact that the gas in the immediate vicinity of the wire does not change in temperature as much as an isolated sample. It is impossible to make quantitative calculations regarding this effect because the actual volume of gas effected by the resistance thermometer is unknown. However, that this correction is small is shown by the following experimental fact. When resistance thermometers constructed of different size wires are employed no change in the final result is noticeable. This fact seems to indicate that no corrections for the finite heat capacity of the resistance thermometer are necessary.

After the gas has expanded the temperature of even an infinitely small wire will be slightly higher than that of the surroundings due to the radiation it receives from the walls of the containing vessel. In general we may write:

$$A(T_W - T_R) = B(T_R - T_G)$$

where A is the heat transferred from the wall to the resistance wire under a temperature gradient of one degree and B represents the heat transferred from the wire to the gas under similar conditions. T_W is the temperature of the wall, T_R is the temperature of the resistance wire, and T_G is the temperature of the gas. Rearranging this equation we obtain:

$$(T_R - T_G) = (T_W - T_R)\frac{A}{B}$$

In other words the difference in temperature between the resistance thermometer and the gas due to radiation from the walls is equal to the temperature difference existing between the walls and the wire times the ratio of the heat conductivities from the wire in vacuum and in the gas at atmospheric pressure. The ratio $\frac{A}{B}$ depends on the nature of the gas involved and the temperature. For annealed platinum wires this ratio is exceedingly small as is shown by experimental determinations of Kistiakowsky and Rice[1]. For most gases at zero degrees the ratio has the value of approximately 10^{-3}. This makes the radiation corrections so small that they can be entirely neglected.

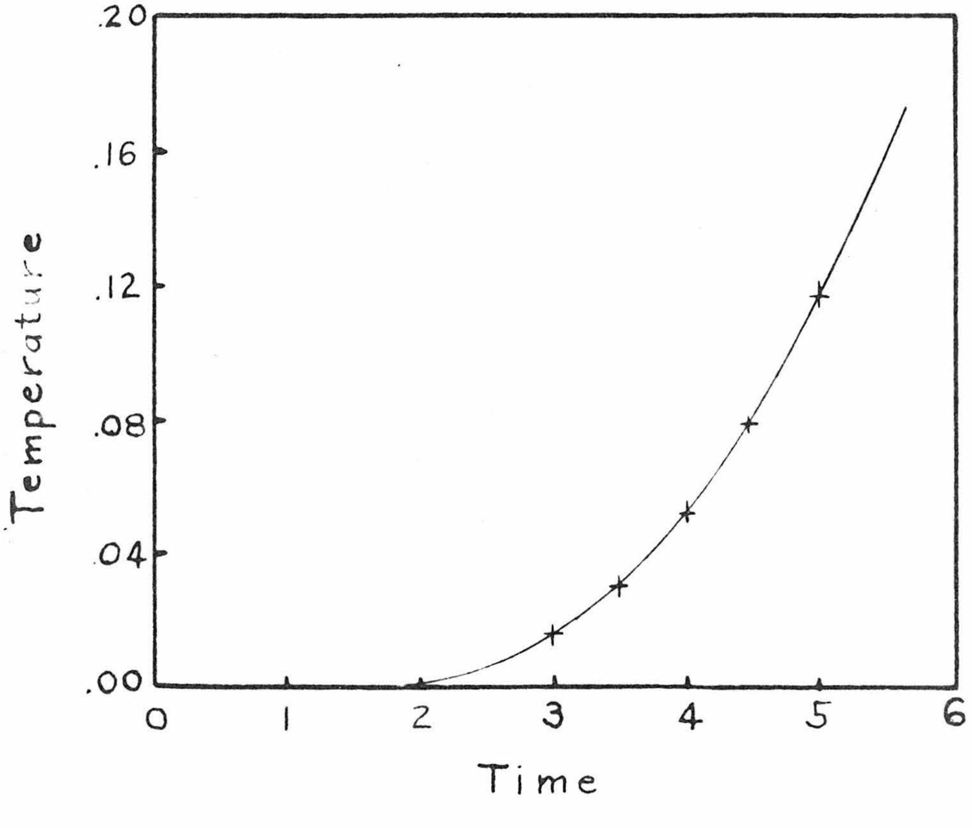
The warming of the resistance wire by conduction through the gas is not appreciable. The conduction of heat through a gas requires a finite time. The time interval after expansion before the effects of conduction of heat from the walls to the wire became noticeable was found in these experiments to be of the order of from one to two seconds. Hence, if the measurement of resistance is made during this short interval no correction is necessary for the conductional heat interchange.

It is possible to calculate the change in temperature of the resistance wire due to the conduction of heat from the walls of the expansion chamber if a few simplifying assumptions are made. The temperature at the center of an infinite cylinder of still gas of radius R at time t provided that at a time zero the gas in the cylinder is at a uniform temperature T_0 and the walls of the cylinder are at a temperature $T_0 +$ T is given by the following expression[1]:

$$T = T_0 + \Delta T_0 \left[1 - 2 \sum_{N} \frac{e^{-\frac{k}{R^2(\alpha_n R)^2 t}}}{J_1(\alpha_n R)(\alpha_n R)} \right]$$

where k is the ratio of thermal conductivity of the heat capacity of the gas times its density. T is the temperature at the center of the cylinder at time t. The temperature of the walls $(T_0 + \Delta T)$ was assumed to remain constant. $(\alpha_n R)$ is the n^{th} root of the equation $J_0(\alpha R) = 0$, $J_1(\alpha_n R)$ is the Bessel function of the 1^{st} order. Fig. 3 shows a typical change of resistance wire temperature after expansion. It will be noted that the effects of conduction of heat from the walls do not become appreciable until two or three seconds after expansion. In actual practice this period will be somewhat shortened due to the fact that there is some turbulence and the gas is not still as was assumed in the simplified discussion above. Nevertheless, if the resistance of the resistance thermometer is measured immediately after expansion the effects of conduction are negligible. The time available for the measurement of the resistance is dependent on the gas involved, being rather short for light gases such as hydrogen and helium but becoming greater as the thermal conductivities of the gases decrease.

Fig. 3



At the ends of the resistance wire heat is conducted to the wire by the heavy metal lead in wires. Hence after expansion has taken place the entire wire will not be at the same temperature but rather a temperature gradient will exist along the wire. It will now be shown that at a given time after expansion the measured temperature drop will be directly proportional to the initial temperature drop and hence the correction will compensate itself due to the relative nature of the experiment. Consider a wire of length 1 and of uniform cross-section, the ends of whichare attached to two heavy metal wires whose temperature remains constant at T_b. Assume that immediately after expansion the resistance wire is lowered uniformly to the temperature T_a. The equation for linear conduction of heat without radiation is:

$$\frac{\partial T}{\partial t} = K\frac{\partial^2 T}{\partial^2 x}$$

where T = temperature, t = time, K = conductivity/$C_p\rho$ and x is the distance along the wire. The boundary conditions are

$$\left.\begin{aligned} T &= T_b \text{ when } x = 0 \\ T &= T_b \text{ when } x = l \end{aligned}\right\} \text{ for all values of } t$$

$$T = f(x) = T_b - T_a \text{ for } t = 0 \qquad T \neq \infty \text{ for } t = \infty$$

The solution of this differential equation is

$$f(xt) = \quad b_m e^{-K(\frac{m\pi}{l})^2 t} \sin\frac{m\pi x}{l} \text{ , } b_m = \frac{2}{l}\int_0^l f(x) \sin\frac{m\pi x}{l}\, dx$$

Since $f(x) = (T_b - T_a)$ b_m becomes

$$b_m = \frac{4(T_b-T_a)}{m\pi} \qquad \text{for m odd}$$

$$b_m = 0 \qquad \text{for m even.}$$

Hence at $t = t_o$ the average value of $\overline{f(xt)}$ which is $\overline{(T_b-T_a)}$ becomes

$$\overline{f(xt)} = \sum b_m e^{-K\left(\frac{m\pi}{\ell}\right)^2 t_o} \overline{\sin\frac{m\pi x}{\ell}}$$

$$= \frac{8(T_b-T_a)}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} e^{-K\left(\frac{(2n+1)}{\ell}\pi\right)^2 t_o}$$

where $m = (2n+1)$ and where we have substituted for $\overline{\sin\frac{m\pi x}{\ell}}$ its value of $\frac{2}{m\pi}$.

It will readily be seen that the sum in the above equation is a constant for a given value of t_o and we can write:

ΔT (observed) = $C\,\Delta T$ actual.

We have considered the case of heat conduction along the wire but we have neglected the heat lost by the wire due to radiation. In this more general case the differential equation for variable linear flow with radiation is as follows.

$$\frac{\partial T}{\partial t} = K\frac{\partial^2 T}{\partial^2 x} - bT$$

where $b = \frac{\epsilon p}{c\rho\sigma}$, ϵ = emissivity, p = the perimeter of the wire c = the specific heat of the wire, ρ, its density, and σ = the cross-sectional area. If we make the substitution $T = \phi e^{-bt}$ the above differential equation becomes:

$$\frac{\partial^2 \phi}{\partial x^2} = K \frac{\partial \phi}{\partial t}$$

It will be noted that this equation in ϕ has exactly the same form as the original differential equation for heat flow without radiation. Hence, we obtain the same final result that the observed temperature drop will be directly proportional to the actual temperature drop.

$$\Delta T \text{ (observed)} = K' \Delta T \text{ (actual)}$$

where $K' = C\, e^{-bt_o}$.

It is possible to consider the still more general case of heat lost by the wire not only by radiation but by conduction as well. Our equation becomes

$$\frac{\partial T}{\partial t} = K\frac{\partial^2 T}{\partial x^2} - bT - k(T - T_a)$$

where $T - T_a$ is the temperature difference between the wire and the surrounding gas, and k is a constant depending on the particular gas in question. Previously the constant of proportionality between the actual temperature drop and the observed temperature drop was dependent only on the constants of the resistance wire, and was independent of the nature of the surrounding gas. Now considering the loss of heat by gas conduction this will no longer be true. Fortunately the heat lost by the wire by conduction is a relatively small amount. It is a well known fact that the conductivity of gases in comparison to metals is very small indeed. Therefore we will assume that the heat lost by the wire is negligible.

Even though this is not true the effects of this loss will at any rate tend to cancel out in the relative method.

Since ΔT (observed) = $K'\Delta T$ (actual) it is evident that dt (observed) = K'dt (actual). If we substitute the value of dt (actual) in equation (3) we have

$$C_p = \frac{T\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial t(ob)}{K'\partial P}\right)_s}$$

Hence on integration we obtain:

$$C_p = \frac{K'R \ln\frac{P_1}{P_2}}{\ln\frac{T_1}{T_2}} - \frac{K'\Delta P \frac{\partial B}{\partial t}}{\ln\frac{T_1}{T_2}}$$

T (observed) is not very much less than T (actual). Actual experiments with gases of known heat capacity have shown the observed temperature drop is about 90 per cent of the actual drop. Hence in the last term of the above equation, which is actually a small correction term, we can set K' equal to one with no great loss in accuracy.

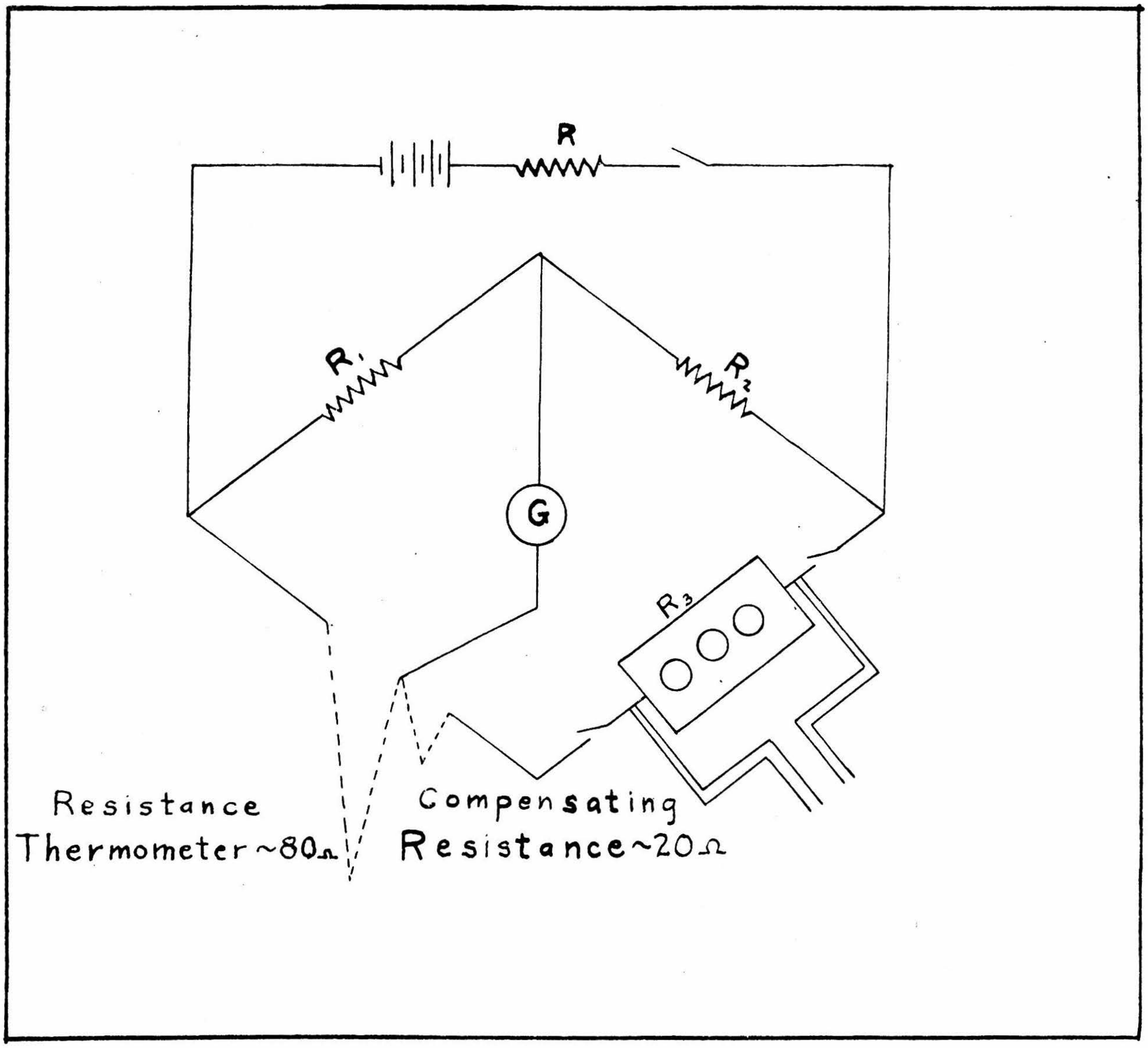
The above discussion concerning the end effects of the resistance thermometer is necessarily only qualitative in nature. In actual practice the phenomena are much more complicated and an exact treatment is impossible. That the final result is valid is shown quite conclusively by the fact that experimental results for carbon dioxide and oxygen are in agreement with calculated theoretical values. In order to remove any uncertainty these end effects were largely removed in later experiments (see Phosphorus trifluoride page 60). A short compensating resistance wire, connected to the opposing arm of the Wheatstone bridge, was suspended beside the main resistance thermometer as shown in Fig. 4. In this way any end effects on the large thermometer would be balanced by an equal effect on the small compensating resistance.

The turbulence and frictional losses in an actual expansion will depend largely on the pressure drop. By making the method relative and using the same pressure drop for the standard substance and the unknown substance the error caused by the irreversibility will tend to compensate itself. Due to the irreversibility of the expansion the PV work done will be less than PdV as was assumed in equation (1). We will now make the assumption that this frictional loss is approximately the same for all gases. Strictly speaking this assumption is false, for the frictional loss for a given gas will depend on its viscosity and its density as well as the velocity of expansion. However, in any case the losses will at least be of the same order of magnitude and will tend to cancel out in the relative process. The important point is to design the apparatus in such a way as to minimize these losses and this way reduce the error to as small a value as possible. That the frictional losses tend to cancel in the relative process can be seen in the following manner. Equation (1) becomes

$$dE = - (PdV - K'')$$

Carrying this through as before and integrating using, of course,

Fig. 4


R
R₁
R₂
G
R₃
Resistance
Thermometer ~80Ω
Compensating
Resistance ~20Ω

the previous result that dt (observed) = K'dt (actual), we have as the complete equation, including the correction for the end effects of the wire

$$C_p = \frac{K'R \ln\frac{P_1}{P_2}}{\ln\frac{T_1}{T_2}} - \frac{\Delta P\frac{dB}{dT}}{\ln\frac{T_1}{T_2}} + \frac{K'K''\Delta P}{\ln\frac{T_1}{T_2}}$$

Therefore, by calculating the quantity $K'R \ln\frac{P_1}{P_2} + K'K''\Delta P$ for the standard gas we can substitute it back into the equation for the unknown gas and calculate the heat capacity of the unknown substance.

1. G. B. Kistiakowsky and W. W. Rice, J. of Chem. Phys., Vol. 7, No. 5, 281 (1939).

Experimental

Results

Oxygen and Carbon Dioxide

Tables 2 and 3 give the results for oxygen and carbon dioxide; C^o_p being the values of the heat capacity at constant pressure for the gas at infinite attenuation.

Table 2 (Oxygen)

Temperature °A	C^o_p observed cal./deg.	C^o_p calculated cal./deg.	% deviation from theory
269.8	7.01 ± .01	6.99	+.29
299.0	7.03 ± .01	7.02	+.14
320.0	7.03 ± .01	7.04	-.14

Table 3 (Carbon dioxide)

Temperature °A	C^o_p observed cal./deg.	C^o_p calculated cal./deg.	% deviation from theory
271.8	8.63 ± .02	8.60	+.35
298.7	8.95 ± .01	8.91	+.44
299.7	8.96 ± .01	8.92	+.44
324.7	9.22 ± .00	9.19	+.33

The values reported here are the averages of two or more separate determinations. (Detailed experimental data for all gases investigated in this research are tabulated in Table 13). Both gases were supplied by the Linde Air Products Company, each containing less than 0.5 per cent impurities. Statistical values of the heat capacities were obtained by the usual formulas for harmonic oscillators from vibrational data given in Sponer's *Molekülspektr~~a~~en*. For oxygen ν_1 was taken to be 1556 cm^{-1} and for carbon dioxide $v_1 = 2350\ cm^{-1}$, $v_2 = 1285\ cm^{-1}$ and $v_3 = 667\ cm^{-1}$ (2).

In the case of oxygen and carbon dioxide there can be little doubt as to the correctness of the vibrational frequencies. Also the values of the virial coefficients and their derivatives are certainly correct to within five per cent. We believe then, justified by the above experiments, that the heat capacities to be reported are accurate to within 0.5 per cent. Our claim is further justified by the fact that other investigators obtain results which are in essential agreement with those reported above. In Table 4 the theoretical heat capacities, the results obtained in this research, and the results obtained by other investigators are listed for comparison purposes.

Table 4 C_p^o for O_2 and CO_2

Temperature °A	C_p^o Theoretical	C_p^o This Research	C_p^o K and R[1]	C_p^o E and L[2]
Oxygen				
269.8	6.99	7.01		6.93
299.0	7.02	7.03		6.97
320.0	7.04	7.03		7.00
Carbon Dioxide				
271.8	8.60	8.63	8.61	8.53
298.7	8.91	8.95	8.88	8.84
324.7	9.19	9.22	9.16	9.15

1. G. B. Kistiakowsky and W. W. Rice, J. of Chem. Phys. 7, 281 (1939).

2. A. Eucken and K. v Lüde, Z. für Phys. Chem. B5 413 (1929).

Boron Trifloride

Two separate samples of Boron Trifloride were prepared by the thermal decomposition of phenyldiazonium fluoroborate[1] ($C_6H_5N_2BF_4$) previously obtained from diazotized aniline and fluoroboric acid. The product was purified by careful distillation. We have obtained data at only one temperature, namely at 271.6 °A. The average experimental value of C_p^o was found to be 11.60 ± .02 cal./deg., being in good agreement with the statistical value of 11.54 cal./deg. calculated from the vibrational assignment of Yost, De Vault, Anderson, and Lassettre[2]. The assignment given by these investigators is as follows. v_1 (1) = 888 cm^{-1}, v_2 (1) = 722 cm^{-1} and 694 cm^{-1}, v_3 (2) = 1448 cm^{-1} and 1501 cm^{-1}, v_4 (2) = broad band from 439 cm^{-1} to 513 cm^{-1}.

The doubly degenerate frequency which occurs in the Raman spectrum as a band from 439 cm^{-1} to 513 cm^{-1} was taken to be the average at 481 cm^{-1}. This was confirmed by the infra red studies of Gage and Barker[3] who found this frequency to be a doublet with maxima at 480.5 cm^{-1} and 482.1 cm^{-1}. For those vibrations in which the boron atom moves appreciably the Raman lines appear double due to the two isotopes of boron. In other words every frequency, except the symmetrical swelling frequency at 888 cm^{-1} should occur as a doublet. In the calculation of the theoretical heat capacities it was assumed that the relative abundance of Boron isotopes was 80 per cent B^{11} and 20 per cent B^{10}.

(1) G. Balz and G. Schiemann, Berl. 60 1186 (1927).

(2) D. M. Yost, D. DeVault, T. F. Anderson and E. N. Lassettre, J. of Chem. Phys. 6 424 (1938).

(3) Gage and Barker, J. Of Chem. Phys. 7 455 (1939).

Cyanogen

Two different samples of cyanogen were used, each of which was prepared from copper sulphate and potassium cyanide by the usual method. Care was taken to free the gas from hydrogen cyanide, water, and carbon dioxide. In Table 5 the experimental molal heat capacities at constant pressure, obtained at three different temperatures, are given. The values of C_p^o are those for the gas at infinite attenuation.

Table 5 Heat Capacities of Cyanogen

Temperature °A	C_p^o observed (cal./deg.)	C_p^o calculated (cal./deg.)	Per cent deviation from theory
271.3	13.14 ± .02	13.14	.00
295.4	13.46 ± .02	13.51	-.37
325.9	13.96 ± .02	13.93	+.22

In Table 6 the results of this research and those of other investigators are compared.

Table 6 C_p^o for $(CN)_2$

Temperature °A	C_p^o Theoretical	C_p^o This Research	C_p^o F.S.[7]	C_p^o E and B[5]
271.3	13.14	13.14	13.40	10.00
295.4	13.51	13.46	13.90	10.35
325.9	13.93	13.96	14.55	10.75

The theoretical heat capacities in column three of Table 5 were calculated from the vibrational frequency assignment of Woo and Badger[1] which gives the following values for the frequencies:

v_1, 860 cm^{-1}, v_2, 2150 cm^{-1}, v_3 = 2336 cm^{-1}, $2s_1$ = 230 cm^{-1}, and $2s_2$ = 512 cm^{-1}. This assignment is in accord with the entropy data of Ruehrwein and Giauque[2], and as pointed out by Stevenson[3], the frequency v_1 is in agreement with the electron diffraction studies of Pauling, Springall, and Palmer[4]. Eucken and Bertram[5], as a result of their heat capacity measurements by the "hot wire" method, assigned a value of 740 cm^{-1} to the $2s_1$ vibration, but this value is certainly too high. The lower value 230 cm^{-1}, has been confirmed recently by the work of Bailey and Carson[6] on the infrared spectrum of the gas.

It must be remembered that the values of B for cyanogen were obtained by the approximate Keye's equation and hence may be in error by as much as 20 per cent. This may well account for a part of the small discrepancies between the experimental and calculated values at the higher temperatures.

Recently Stitt[7] has communicated values of C_V^o for cyanogen as obtained by an improved "hot wire" thermal conductivity method. His values are from two per cent to four per cent higher than those predicted by theory, but, like those presented here, they are in essential agreement with the theoretically predicted heat capacities. The values of C_V^o obtained by Eucken and Bertram on the other hand, are over 20 per cent less than those reported by Stitt and by us, and a frequency of $2s_1$ = 740 cm^{-1} rather than 230 cm^{-1} was required to get agreement with theory.

1. S. C. Woo and R. M. Badger, Phys. Rev. 39 432 (1932).
2. R. A. Ruehrwein and W. F. Giauque, J. Am. Chem. Soc. 61 2940 (1939).

3. D. P. Stevenson, J. Chem. Phys. 7 171 (1939)

4. Linus Pauling, H. D. Springall, and K. J. Palmer, J. Am. Chem. Soc. 61, 927 (1939)

5. A. Eucken and A. Bertram, Zeits. f. physik. Chemie, B31, 361 (1935).

6. C. R. Bailey and S. C. Carson, J. Chem. Phys. 7, 859 (1939).

7. F. B. Stitt, J. Chem. Phys. 7, 1115 (1939).

Sulfur Dioxide

The experimental results for sulfur dioxide are not in agreement with those calculated from spectroscopic data but are from two to five per cent higher depending on the magnitude of the gas corrections used. Two samples of sulfur dioxide gas were used, one being supplied by the Great Western Electrochemical Supply Company (99.5 per cent SO_2), the other being carefully prepared from sodium bisulphite and sulphuric acid. Both samples gave consistent results.

Virial coefficients and their derivatives, calculated from the coefficient of expansion[1] and the gas density[2] gave values of the heat capacity which differed from the theoretical value by as much as five per cent. Virial coefficients calculated from pressure, volume, temperature data[3] give results inconsistent among themselves. Keyes' has developed an equation for polar gases similar to the one for non polar substances described previously on page 7. However, the data available on polar substances is so meager and the values of the β_{θ} A_{θ},C_{θ} differ so widely from gas to gas that the results obtainable are practically worthless. Surprisingly enough the virial coefficients calculated with Keyes' equation give results for the heat capacities which are in better agreement with theory than those calculated from experimental pressure, volume, temperature data. Still the results differ by about 2.5 per cent, an amount which can hardly be attributed to experimental error.

The experimentally determined heat capacities as determined by other investigators show little agreement, either among themselves, or with the results of this research.

Table 7 lists a few of the results obtained by other workers. C_p is the heat capacity of the gas at atmospheric pressure and at 273.16°. These values were taken from Mellor's <u>Comprehensive Treatise on Inorganic and Theoretical Chemistry</u>.

Table 7 C_p' for SO_2 as determined by other investigators

Investigator	C_p' cal./mol.
A. Masson	9.834
J. R. Partington	9.476
R. Frustenau	9.18
B. Bernkis	9.00

Theory

That accurate data concerning the physical properties of so common a substance as sulfur dioxide are not available is surprising.

On the other hand the analysis of the Raman and infra-red spectra are probably correct. The theoretical heat capacities were calculated from the vibrational frequency assignment of Bailey and Cassie[4] who give the following values for the frequencies: $v_1 = 524\ cm^{-1}$, $v_2 = 1152\ cm^{-1}$ and $v_3 = 1361\ cm^{-1}$. These are entirely in agreement with the analysis of the Raman spectrum made by Gerding and Nijveld[5]. As a matter of fact the Raman spectrum of sulfur dioxide was redetermined in this laboratory with the hope of finding a possible error in the previous work, but the results obtained were identical with those of Gerding and Nijveld. It seems improbable that the anomal~~l~~y between theory and experiment can be attributed to an incorrect assignment of frequencies.

In view of these facts we believe that the error lies wholly in the virial coefficients. In order to bring our results into a agreement with statistical values, $\frac{dB}{dT}$ and $\frac{d^2B}{dT}$ should be of the same order of magnitude as the corresponding quantities for carbon dioxide. This is quite possible due to the abnormally high virial coefficients of carbon dioxide (see Table 1).

Because of the uncertainty involved in the virial coefficients we report our experimental results in the following form:

$$C_p^o\ (270.9^\circ) = 9.335 + .1425\ B'_{(270.9^\circ)} - 6.559\ B''_{(270.9^\circ)}$$

$$C_p^o\ (295.2^\circ) = 9.626 + .1309\ B'_{(295.2^\circ)} - 7.146\ B''_{(295.2^\circ)}$$

$$C_p^o\ (300.0^\circ) = 9.619 + .1457\ B'_{(300.0^\circ)} - 7.262\ B''_{(300.0^\circ)}$$

$$C_p^o\ (324.8^\circ) = 9.819 + .1525\ B'_{(324.8^\circ)} - 7.864\ B''_{(324.8^\circ)}$$

where C_p^o is the gaseous heat capacity at zero pressure, B' is $\frac{dB}{dT}$ and $B'' = \frac{d^2B}{dT^2}$. It is hoped that accurate values of the virial coefficients will be available in the near future.

1. Leduc Ann. Chem. Phys. 15, 1 (1898).

2. Baume J. Chim. Phys. 6, 1 (1908).

3. K. Wohl, Zeit. fur Phy. Chem. 133, 305 (1928).

4. C. R. Bailey and A. B. D. Cassie, Proc. of the Royal Soc. of Lon. 140, 605 (1933).

5. H. Gerding and W. J. Nijveld, Nature, 137, 1070 (1936).

Ethylene

The ethylene gas used in this investigation was supplied by the Ohio Chemical Manufacturing Company of Cleveland. Its purity, by the bromine absorbtion test was given as 99.8 per cent ethylene. The experimental results obtained for the heat capacity are listed below in Table 8.

Table 8 C_p^o for ethylene

Temperature °A	C_p^o experimental cal./deg.
270.7	9.74
300.0	10.39
320.7	10.99

No calculated values are listed for the heat capacity, for of the twelve vibrational frequencies of ethylene only eight are known with certainty as is shown in Table 9[1].

Table 9 Normal modes of vibration of the ethylene molecule.

(Frequencies listed in brackets are uncertain)

v_1	1626 cm^{-1}
v_2	3020
v_3	1343
v_4	2988
v_5	1444
v_6	3107
v_7	(1020)
v_8	(3075)
v_9	(1030)
v_{10}	950

v_{11}	943
v_{12}	(700)

One frequency, v_{12} involving the twisting of the CH_2 groups with respect to each other is forbidden both in the infra red and Raman spectra. To calculate this forbidden frequency from the experimental heat capacity data is impossible until at least two of the remaining uncertain frequencies have been verified.

A number of other investigators have determined the heat capacity of ethylene by various methods. From Table 10 it can be seen that the results of this research are in essential agreement with those of other investigators.

Table 10 Comparison of experimental heat capacity data of this research with those of other investigators

Temperature °A	This research C_p^o	E and P[2] C_p^o	H[3] $°C_p$
270.7	9.74	9.74	9.64
300.0	10.39	10.44	10.38
320.7	10.99	10.96	-----

---

1. G. K. T. Conn and G. B. B. M. Sutherland, Proc. of the Royal Soc. of Lon., 172, 172 (1939).
2. A. Eucken and A. Parts, Z. Phy. Chem. B20, 184 (1933).
3. W. Heuse, Ann. Physik, 59, 86 (1919).

Dichlorodifluoromethane (Freon-12)

A tank of pure dichlorodifluoromethane, or Freon-12 as it is known in industry, was supplied for this research by the Kinetic Chemicals, Inc. of Wilmington, Delaware. This compound, because of its non-corrosive, non-toxic, non-inflammable nature has found extensive practical use as a refrigerant. It is commercially prepared by treating carbon tetrachloride with antimony trifluoride, using antimony pentafluoride as a catalyst.

Our experimental results are reported in Table 10.

Table 10 (Dichlorodifluoromethane)

Temperature °A	C^o_p observed cal./deg.	C^o_p calculated cal./deg.	% deviation from theory
271.7	16.79 ± .01	16.73	+ .36
300.5	17.76 ± .12	17.57	+1.1
320.9	18.18 ± .03	18.12	+ .33

As before the corrections for gas imperfections were obtained from the Keye's relation. The theoretical heat capacities were calculated using the vibrational frequency assignment of C. A. Bradley[1] who gives $v_1 = 1082\ cm^{-1}$, $v_2 = 1147\ cm^{-1}$, $v_3 = 664\ cm^{-1}$, $v_4 = 455\ cm^{-1}$, $v_5 = 260\ cm^{-1}$, $v_6 = 433\ cm^{-1}$ and $v_7 = 320\ cm^{-1}$. Bradley also observed a frequency at 887 cm^{-1} which he believed to be a combination frequency ($v_4 + v_6$), but according to Mecke[2] this too is a fundamental. Eucken and Bertram[3] determined the remaining frequency to be 408 cm-1 from low temperature "hot wire" heat capacity measurements. However, at higher temperatures his measurements indicated a much lower value for the frequency. Our results, shown on Table 10 are in fair agreement with theoretical heat capacities calculated on the basis that v_8 = 887 and

$v_9 = 408$. That $v_9 = 408$ cm^{-1} is in agreement with a prediction of Bradley who believed the missing frequency to be in the neighborhood of 440 cm^{-1}.

Our experimental results would seem to indicate that a slightly lower value of 375 cm^{-1} would give better agreement than the assumed value of 408 cm^{-1}. However, since the gas corrections due to their empirical nature, are somewhat uncertain, such a correction is unwarranted.

As mentioned before Eucken and Bertram have also made some measurements on the heat capacity of dichlorodifluoromethane by the hot wire method. Their results are compared with the results of this research in Table 11. Our results are in good agreement with those of Buffington and Fliesher[4] who used the flow method to determine the heat capacity. The results of these investigators are also included in Table 11.

Table 11 (Freon-12)

Temperature	This Research C_p^o	E and B[3] C_p^o	B and F[4] C_p^o
271.74	16.79	15.10	16.79
300.54	17.76	15.70	17.59
320.91	18.18	-----	18.16

It should be mentioned that although the work of Eucken and Bertram is not in agreement with theory in the above temperature range, good agreement is obtained at lower temperatures. This is quite characteristic of the "hot wire" method because reasonable estimates of the accomodation coefficient of the "hot wire" can only be made at low temperatures.

1. C. A. Bradley, Phys. Rev. (2), 40, 908 (1932).
2. R. Mecke, Hand. u Jahrb. d. Chem. Physik, 9 II, 390 (1934)
3. A. Eucken and A. Bertram. Zeit. fur Phy. Chem., B31, 361 (1935-36)
4. R. M. Buffington and J. Fleisher, Ind. Eng. Chem. 23, 1290 (1931)

Trichloromonofluoromethane (Freon-11 or Carrene No. 2)

The vibrational frequencies when determined from the Raman spectrum of the substance by D. Osborn[1]. The results of his analysis, shown in Table 12, are in essential agreement with those of G. Glockler and G. R. Leader[2].

Table 12 (Normal vibrations of trichloromonofluoromethane)

	D.O.[1]		G and L[2]
v_1	351 cm^{-1}		349.5 cm^{-1}
v_2	246	(2)	243.7
v_3	536		535.3
v_4	838	(2)	833.2
v_5	1072		1067.2
v_6	398	(2)	397.5

The experimental heat capacity was found to be 19.72 ± .07 cal./mol. at 329.6 ° A. This is 1.4 % higher than 19.45 cal./mol., the value calculated from spectroscopic data. This error is somewhat higher than the usual experimental accuracy would seem to allow. However, it should be remembered that a gas like trichloromonofluoromethane is very different in nature from nitrogen, the standard comparison gas. It is quite probable that for gases which differ so with respect to heat capacity, heat conductivity and viscosity are unsuited for relative heat capacity measurements. Moreover there is still the uncertainty regarding the gas corrections, but it is improbable that they are the sole cause of the discrepancy between theory and experiment.

The trichloromonofluoromethane used in this research was supplied by the Kinetic Chemicals, Inc. of Wilmington, Delaware.

The commercial product was carefully dryed by passing it over phosphorus pentoxide.

1. D. Osborn, Thesis
2. G. Glockler and G. R. Leader, J. Chem. Phys. 7, 298 (1939).

Sulfuryl Fluoride.

The heat capacity of sulfuryl fluoride was determined at 271.6° A. C_p° at this temperature was found to be 15.16 cal./mol. The sulfuryl fluoride was prepared by H. Russell by the following series of reactions[1]:

$$H_2SO_4 + CaF_2 + 2SO_3 \longrightarrow 2HFSO_3 + CaSO_4$$

$$BaCl_2 + 2HFSO_3 \longrightarrow Ba(FSO_3)_2 + 2HCl$$

$$Ba(FSO_3)_2 \xrightarrow{heat} BaSO_4 + SO_2F_2$$

Since no data are available on the critical constants of the gas nor on its pressure, volume, temperature relations, the magnitude of the virial coefficients and its derivatives were assumed to be equal to those of dichlorodifluoromethane.

This work should be regarded merely as a preliminary experiment since only one determination of the heat capacity was made. Moreover, the sample of sulfuryl fluoride was of doubtful purity. However, for purpose of future reference these results are included in this thesis.

An analysis of the Raman spectrum of sulfuryl fluoride is now in progress in this laboratory[2]. However, final results are not available so that comparison of the theoretically calculated heat capacities with the experimentally determined heat capacities are not yet possible.

[1] W. T. Traube, I. Horening, F. Wunderlich, Berl. Ber. 52 II, 1272 (1919).

[2] H. Russell, Not yet published.

Experimental
Details

Table 13 lists all the experimental data necessary to calculate the results discussed in the previous section.

P_1 = atmospheric pressure

P = pressure drop employed

T_1 = temperature of gas before expansion

T = temperature drop due to expansion

$B' = \frac{dB}{dT}$

$B'' = \frac{d^2B}{dT^2}$

C'_p (exp.) = heat capacity in calories per mol. per degree at average temperature of experiment $(T_1 - \frac{\Delta T}{2})$ and at average pressure of experiment $(P_1 + \frac{\Delta P}{2})$

C°_p (exp.) = above heat capacity corrected to zero pressure

$C^\circ{}_p$ (calc.) = heat capacity calculated from spectroscopic data at average temperature of experiment $(T_1 - \frac{\Delta T}{2})$

Table 13

No.	Gas	P_1 m.m.	ΔP m.m.	T_1 °A	ΔT °A	B' cc/°A	B'' cc/°A/°A	C_p' exp.	C_p° exp.	C_p'' calc	Ave C_p° exp.	% error
1	O_2	745.0	82.9	273.16	6.727 6.678	.287 .270	.002 .002	7.02	7.00	6.99	7.01	+.29
2	O_2	"	"	"	6.703 6.642	"	"	7.03	7.02	"		
3	O_2	743.9	42.8	300.56	3.878 3.838	.235 .218	.002 .002	7.05	7.04	7.02	7.03	+.14
4	O_2	742.0	"	301.31	3.880 3.846	.231 .218	"	7.03	7.02	"		
5	O_2	740.0	"	321.76	4.144 4.104	.200 .184	.001 .001	7.03	7.02	7.04	7.03	−.14
6	O_2	740.9	"	322.06	4.123 4.078	"	"	7.04	7.03	"		
7	O_2	743.3	"	322.16	4.106 4.058	.199 .184	"	7.04	7.03	"		
8	CO_2	745.5	36.0	273.16	3.339 2.390	.287 1.174	.002 .011	8.70	8.63	8.60	8.63	+.35
9	CO_2	743.6	42.8	300.16	3.869 3.021	.233 .922	.002 .008	9.03	8.98	8.91	8.95	+.44
10	CO_2	742.9	"	"	3.869 3.034	"	"	8.99	8.94	"		
11	CO_2	742.6	"	"	3.866 3.031	"	"	8.99	8.94	"		
12	CO_2	741.9	"	301.26	3.875 3.032	.231 913	.002 008	9.01	8.96	8.92	8.96	+.44
13	CO_2	744.3	"	301.16	3.883 3.035	"	"	9.02	8.97	"		
14	CO_2	744.2	"	326.26	4.090 3.107	194 748	.001 .006	9.26	9.22	9.19	9.22	+.33
15	CO_2	744.4	"	326.26	4.103 3.117	"	"	9.26	"	"		
16	BF_3	745.0	82.9	273.16	6.704 4.065	.287 1.011	.002 .000	11.68	11.62	11.54	11.60	+.54
17	BF_3	744.4	42.8	273.16	3.488 2.117	"	"	11.64	11.58	"		
18	$(CN)_2$	745.0	82.9	"	6.685 3.638	.287 2.570	.002 .028	13.33	13.14	13.14	13.14	.00
19	$(CN)_2$	745.0	"	"	6.717 3.657	"	"	13.32	13.13	"		
20	$(CN)_2$	744.4	42.8	296.16	3.795 2.005	.240 2.018	.001 .020	13.66	13.44	13.51	13.46	−.37
21	$(CN)_2$	742.8	"	296.36	3.784 1.990	"	"	13.72	13.50	"		
22	$(CN)_2$	742.6	"	296.56	3.785 2.001	"	"	13.64	13.43	"		
23	$(CN)_2$	740.8	"	326.86	4.145 2.106	194 1.521	.001 .013	14.04	13.94	13.93	13.96	+.22
24	$(CN)_2$	740.7	"	326.96	4.159 2.104	"	"	14.09	13.99	"		
25	SO_2	745.0	82.9	273.16	6.736 5.015	.287 —	.002 —					
26	SO_2	"	"	"	6.721 5.006	"	"					
27	SO_2	"	"	"	6.709 5.019	"	"					
28	SO_2	742.6	42.8	301.36	3.878 2.810	.231 —	.002 —					
29	SO_2	742.8	"	301.36	3.883 2.802	"	"					
30	SO_2	743.6	"	326.26	4.101 2.907	.194 —	.001 —					
31	SO_2	743.8	"	326.26	4.095 2.898	"	"					
32	C_2H_4	745.0	82.9	273.16	6.714 4.843	.287 1.127	.002 .011	9.82	9.75		9.74	
33	C_2H_4	"	"	"	6.713 4.851	"		9.80	9.73			
34	C_2H_4	742.4	42.8	301.26	3.882 2.628	.231 .855	.002 .007	10.41	10.35		10.39	
35	C_2H_4	742.2	"	"	3.895 2.620	"	"	10.48	10.43			
36	C_2H_4	745.0	"	322.06	4.135 2.645	.200 .721	.001 .006	11.01	10.97		10.99	
37	C_2H_4	"	"	322.01	4.129 2.629	"	"	11.05	11.01			
38	CCl_2F_2	"	82.9	273.16	6.737 2.910	.287 3.380	.002 .037	17.01	16.77	16.73	16.79	+.36
39	CCl_2F_2	"	"	"	6.700 2.891	"	"	17.04	16.80	"		
40	CCl_2F_2	742.9	42.8	301.36	3.884 1.570	.231 2.540	.002 .024	17.91	17.74	17.57	17.76	+1.1
41	CCl_2F_2	743.9	"	"	3.878 1.578	"	"	17.79	17.62	"		
42	CCl_2F_2	744.6	"	301.46	3.901 1.570	"	"	18.10	17.93	"		
43	CCl_2F_2	745.9	"	301.26	3.869 1.553	"	"	18.04	17.87	"		
44	CCl_2F_2	745.0	"	301.26	3.874 1.565	"	"	17.91	17.74	"		
45	CCl_2F_2	745.1	"	301.21	3.867 1.554	"	"	18.01	17.84	"		
46	CCl_2F_2	745.0	"	321.71	4.124 1.619	.199 2.109	.001 .020	18.29	18.15	18.12	18.18	+.33
47	CCl_2F_2	"	"	"	4.106 1.607	"	"	18.35	18.21	"		
48	CCl_3F	748.8	36.0	330.16	3.937 1.433	.189 3.300	.001 .030	20.03	19.79	19.45	19.72	+1.4
49	CCl_3F	745.6	"	330.61	3.935 1.442	"	"	19.89	19.65	"		
50	CCl_3F	741.8	"	330.16	3.922 1.433	"	"	19.96	19.72	"		
51	SO_2F_2	745.0	82.9	273.16	6.701 3.196	287 ~3.0	.002 ~.03	15.40	15.16			

Sample Calculation

Sample Calculation

The following is a complete calculation of the heat capacity of carbon dioxide.

	ΔP	P_o	ΔR	R_o	ΔT	T_1	$\ln \frac{T_1}{T_2}$	B'
N_2	3.6 cm.	763.5	.8907	68.0845	3.3348	273.16	.012283	.2866
CO_2	3.6 cm.	763.5	.7229	68.0845	2.7064	273.16	.009957	1.1743

ΔP = pressure drop used in experiment

P_{Ave} = mean pressure of experiment (atmospheric + $\frac{\Delta P}{2}$)

ΔR = measured resistance drop.

R_o = resistance of resistance wire at 273.16°

ΔT = as calculated from $\Delta T = \frac{\Delta R}{R_o \alpha}$ α = coefficient of resistance of Pt = .003923. Since this is a relative method small differences in the value used for α will cause very little change in the final result)

$B' = \frac{dB}{dT}$ = as calculated from Keyes' relation

C_p = heat capacity at mean temperature ($T_1 - \frac{\Delta T}{2}$) and pressure of the experiment.

Hence using equation (7)

$$KR \ln \frac{P_1}{P_2} + KK' \Delta P = C_{p(N_2)} \left(\ln \frac{T_1}{T_2}\right)_{N_2} - .02421 \, \Delta P B'_{N_2}$$

$$= 6.970 \times .012283 - .000347$$

$$= .085266$$

$$C_{p_{CO_2}} = \frac{085266}{\left(\ln \frac{T_1}{T_2}\right)_{CO_2}} + \frac{.02421 \, \Delta P B'_{CO_2}}{\left(\ln \frac{T_1}{T_2}\right)_{CO_2}}$$

$$= \frac{.085266}{.009957} + \frac{.001422}{.009957}$$

$$= 8.563 + .143 = 8.706 \text{ cal./deg.}$$

This is C_p in Calories mol^{-1} deg^{-1} at 763.5 mm. pressure and at 271.81° A.

The calculation of the statistical heat capacity is carried out in the following manner:

$$C_p^o = C\ (\text{trans}) + C\ (\text{rotation}) + C\ (\text{vibration}) + R$$

$$= \frac{3}{2} R + R + \sum_{i=1}^{3n-6} P\left(\frac{\theta i}{T}\right) + R$$

For CO_2 the vibrational frequencies are $v_1 = 2350\ cm^{-1}$, $v_2 = 1285\ cm^{-1}$ and $v_3 = 667 cm^{-1}$ (2) where v_3 is doubly degenerate. At 271.81° A $\frac{kv}{kT}$ is equal to .0052905 v where v is now expressed in cm^{-1}. The values of the Planck Einstein term calculated for each vibrational frequency is given in the following table.

v_1		$\frac{kv}{kT}$	$\frac{C_v}{R}$
$v_1 = 2350$		12.433	.0000
$v_2 = 1285$		6.798	.0517
$v_3 = 667$	(2)	3.529	.3871

$$\frac{C_v}{R} \text{ total} = .0517 + (2 \times .3878) = .8273$$

Hence

$$C_p^o = \frac{7}{2} R + .8273\ R = 4.3275\ R = 8.599 \text{ cal./mol.}$$

This is the value of C_p^o at zero pressure and at 271.81° A. To correct the experimental value to zero pressure we subtract from it $.02421\ T_{Ave}\ P_{Ave} \frac{d^2P}{dT^2}$. For CO_2 this has the value .073.

Hence

$$C_p^o \text{ (experimental)} = 8.63$$

$$C_p^o \text{ (calculated)} = 8.60$$

Table of Constants used:

R (gas constant per mol)	1.9871 cal $deg^{-1}mol^{-1}$
h (Planck's constant)	6.624×10^{-27} erg. sec.
k (Boltzmann's constant)	1.3805×10^{-16} erg. $deg.^{-1}$
C (velocity of light)	2.99776×10^{10} cm. $sec.^{-1}$
Ice point	273.16° K

Phosphorus Trifluoride

Phosphorus Trifluoride

The heat capacity of phosphorus trifluoride was determined at two different temperatures. For these experiments an improvement was made in the apparatus. In previous experiments the measured temperature drop due to the adiabatic expansion is somewhat smaller than the actual temperature drop because of heat leaks at the ends of the resistance thermometer. It was shown that these end effects essentially cancel out due to the relative nature of the experiment but it is probably more precise to remove these effects entirely. This can be accomplished by suspending a shorter resistance thermometer beside the main thermometer in the expansion chamber. This compensating resistance is connected to the opposing arm of the Wheatstone Bridge together with the variable resistance. Any end effects in the main resistance thermometer will now be counter-balanced in the short compensating resistance thermometer and thus be eliminated.

This arrangement has still another advantage. Previous values of the heat capacity were reported at the mean temperature of the experiment. Since the measured temperature drop was always smaller than the actual drop this mean temperature was not known accurately. Although this difference was too small to be of serious consequence (the difference never amounting to more than 0.1 % in the final result) it is now removed and a more precise result is possible.

We have redetermined the heat capacity of gaseous carbon dioxide to obtain a check on the accuracy of this new method. The experimental molal heat capacities together with the theoretically calculated values are reported in table 14. It will be noted that the agreement of experiment with theory is of the same order of magnitude as previous experiments on carbon dioxide (see table 13).

Table 14

Temperature (°A)	C_p^o observed (cal./deg.)	C_p^o calculated (cal./deg.)	% deviation from theory
271.46	8.69	8.67	+ .23
292.39	8.95	8.91	+ .45

Phosphorus trifluoride was prepared by the method described by Ruff[1]. Phosphorus trichloride was allowed to react with arsenic trifluoride according to the following reaction:

$$PCl_3 + AsF_3 \longrightarrow PF_3 + AsCl_3$$

The resulting gas was passed through a cooling bath of dry ice and alcohol to remove any arsenic trifluoride and phosphorus trichloride present. The supposedly pure phosphorus trifluoride was finally condensed out in liquid air. Unfortunately the above proceedure did not yield pure phosphorus trifluoride for qualitative tests showed the presence of considerable quantities of partially fluorinated compounds such as $PClF_2$ and PCl_2F. These impurities were removed by bubbling the gases through a dilute solution of H_2SO_4($\sim$ .2 N) which removed the relatively more readily hydrolizable $PClF_2$ and PCl_2F. The gas was subsequently passed through sodium fluoride and phosphorus pentoxide to remove hydrogen fluoride and water. A second sample was purified by repeatedly bubbling the gases through a tower packed with glass beads and liquid arsenic trifluoride until the PCl_2F and $PClF_2$ were completely fluorinated. Both samples gave practically the same experimental result for the heat capacity.

The experimental results for phosphorus trifluoride are given in Table 15. These results are the averages of two or more separate experiments.

Table 15

Temperature (°A)	C_p^o observed (cal./deg.)	C_p^o calculated (cal./deg.)	% deviation from theory
272.16	13.77	12.77	+7.83
292.76	14.43	13.28	+8.68

The experimental data for both carbon dioxide and phosphorus trifluoride are given in Table 16. The symbols have here the same meaning as in Table 13.

It will be noted that the experimental values are about 8 % higher than those calculated from spectroscopic data. The vibrational frequencies of phosphorus trifluoride were obtained by Yost and Anderson[2] by an analysis of the Raman spectra and are probably correct. The reason for this discrepancy is at present unknown to the authors but it is hoped that further experiments will remove the difficulties.

1. Ruff, Die Chemie des Fluores P 28, Springer, Berlin, 1920
2. D. M. Yost and T. F. Anderson, J. Chem. Phys. 2, 264, 1934.

Table 16

No.	Gas	P_1 m.m.	ΔP m.m.	T_1 °A	ΔT °A	B' cc/°A	B'' cc/°A	C'_p exp.	C°_p exp.	$C^\bullet_p$ calc.	Ave. C°_p exp.	% error
52	CO_2*	744.8	42.8	273.16	4.181 3.395	.287 1.174	.002 .011	8.69	8.62	8.60	8.62	+.26
53	CO_2*	745.6	40.0	294.26	4.774 3.746	.244 .964	.002 .008	8.95	8.89	8.85	8.89	+.45
54	PF_3	743.8	42.8	273.16	3.858 2.002	.287 1.178	.002 .011	13.64	13.57	12 70	13.69	+7.83
55	PF_3	742.4	"	"	3.911 2.017	"	"	13.72	13.65			
56	PF_3*	7405	"	"	4.222 2.152	"	"	13.92	13.85			
57	PF_3*	744.2	"	293.86	4.436 2.188	.244 .973	.002 .008	14.31	14.25	13.21	14.37	+8.68
58	PF_3*	745.4	40.0	294.16	4.767 2.310	"	"	14.55	14.49			

* With Compensating Resistance

Abstract

The theory of adiabatic expansions is given and an apparatus for the measurement of gaseous heat capacities by this method is described. As here applied the method is relative, involving a comparison with a standard gas, nitrogen. The heat capacities of oxygen, carbon dioxide, boron trifluoride, cyanogen, sulfur dioxide, ethylene, difluorodichloromethane, fluorotrichloromethane, sulfuryl fluoride, and phosphorus trifluoride found at temperatures ranging from 0° to 57° are compared with those reported by earlier investigators and with those derived from molecular data. In general the agreement is good to within 0.5%, but for sulfur dioxide and phosphorus trifluoride there are discrepancies between the observed and calculated values of about 3% and 8%, respectively. The difficulty with sulfur dioxide may possibly arise from an error in the equation of state, but the phosphorus trifluoride discrepancy stands quite without explanation.