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Manometer Report IV: Internal Manometric Volume Ratio Calibrations During 1974

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Manometer Report IV:

Internal Manometric Volume Ratio Calibrations

During 1974

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for the

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I. Introduction

Calibrations were carried out in 1974 to check the volume ratios of the constant volume manometric system previously determined by expansion of CO_2 gas within the system. To calibrate the large manometer one 4000 cc flask, normally part of one of the 5000 cc chambers, was temporarily detached and calibrated with water. This chamber and additional 1000 and 5000 cc chambers were then calibrated by gas expansion or gas transfer using CO_2. To calibrate the 4 cc chamber of the small manometer separate auxiliary glass plenums were calibrated with mercury and their volumes compared to that of the 4 cc chamber by gas transfer using CO_2 gas.

As a further check on the accuracy of previous calibrations by expansion, the validity of the virial coefficients of CO_2 and N_2 at low pressure was tested. This was done by expanding nitrogen and argon as well as CO_2 from the calibrated 4000 cc flask to the 5000 cc chamber of the large manometer.

The new calibration of volumes is not entirely in satisfactory agreement with the earlier volume ratio determinations. The 5000 cc/4 cc volume ratio based on the new calibrations is about two parts per thousand higher than three concordant volume ratio determinations made in 1959, 1961, and 1972 by expanding gas. This leads to a 0.5 ppm discrepancy in the absolute calibration of CO_2 reference gases in the range of 300 to 350 ppm. The uncertainty in absolute calibration may be still greater and cannot be reduced without further work using either still another method of calibration

or by directly calibrating the intermediate chambers of the manometric system.

II. Experimental Procedure

The procedure for making measurements with the manometric system is fully described in Manometer Report III. The following discussion emphasizes special gas handling procedures followed in the new calibrations. Afterwards the volume calibration data will be presented and discussed.

A. Large Manometer Sample Chamber Calibrations

Table 1 presents the original experimental data for all the large manometer volume calibrations done in 1974. The column number identifies the large manometer sample column on which the measurement was made. Column number 5 was used for the reference gas calibrations reported in Manometer Report III and in previous work. Column 6 is the adjacent column to the right of column 5. The vacuum column height was measured at column 8. Column 7 was not used in this study.

1. Absolute Calibrations of the Large Manometer Sample Chambers

In Table 1, experiments number 1, 2, and 12 refer to volume calibrations of columns 5 and 6 using CO_2 gas. Experiments number 3 through 8 refer to volume calibrations of column 6 using nitrogen and argon gases. These measurements served as a check on the virial coefficients used in calculating earlier results.

The procedure in the experiments using CO_2 was as follows. First, column 6 was filled at a very slow rate to a pressure of

about 60 cm of mercury with CO_2 gas from a commercial cylinder (supplied by the Matheson Company) after passage through several traps cooled to dry ice temperature to remove water vapor. In experiments 1 and 2 five U-traps were used. In experiment 12 the CO_2 gas was introduced to the associated vacuum line at the reference gas entry point so as to pass it through a thimble trap. The thimble trap and six U-traps in the path of the gas were cooled to dry ice temperature. In all of the calibrations, water vapor was later found in all the traps.

After filling was complete, the CO_2 was frozen out by cooling the 1000 cc flask in column number 6 to liquid nitrogen temperature. Then the residual non-condensable gas was pumped away. This operation was performed twice to make sure that all the non-condensable gas was removed. About 1% by volume of the dried gas from the CO_2 cylinder was found to be non-condensable gas.

Finally, further checks were made to detect and remove any remaining water vapor from the CO_2 gas. In experiments 1 and 2, this was done by allowing the system to stand for about thirty minutes with the 1000 cc flask cooled to dry ice temperature so that any remaining water vapor would freeze out. Then the 4000 cc flask was cooled to liquid nitrogen temperature to freeze out the CO_2. The 4000 cc flask stopcock was closed, and the 1000 cc bulb was thawed and then evacuated. No deflection of downstream vacuum gauges was noticed, indicating that very little water vapor remained

in the sample. In experiment 12, a dry ice sublimation of the CO_2 from the 1000 cc bulb in column number 6 to the 1000 cc bulb in column number 5 was accomplished in the following way. First, the gas was frozen in the 1000 cc flask in column 6 with liquid N_2, then liquid N_2 was placed around the 1000 cc flask in column 5. Finally a dry ice dewar flask was placed around the 1000 cc flask in column 6. This sublimation went on for about 80 minutes. Afterward there appeared to be no gas left in column 6 as determined by the absence of a deflection on the downstream vacuum gauges when column 6 was thawed and then opened to the vacuum pump.

It was concluded that the treatment described above effectively removed water vapor and non-condensable gas from the CO_2 gas taken from the cylinder.

The first measurement to be made was of the pressure of the entire sample enclosed in the nominally 5000 cc chamber of column 6. The usual precautions and procedures for a large manometer measurement were followed as outlined in Manometer Report III. In Table 1 this measurement is reported on the first line of data for experiments 1, 2, and 12. This measurement determines the pressure and thus the number of moles of gas present in the calibrated 4000 cc flask of column 6. It was this flask that had been volume calibrated using water. Immediately after the mercury height measurements and temperature readings had been made, the manometric system cabinet door was opened and the stopcock on the 4000 cc flask quickly closed to confine the CO_2

present in the flask. The gas remaining in the 1000 cc portion of column 6 was then pumped away until the pressure read at the first downstream vacuum gauge was less than 1 millitorr. The main stopcock of column 6 was then closed and the 4000 cc flask stopcock opened to expand the gas contained in the calibrated 4000 cc flask into the nominally 5000 cc chamber of column 6. After temperature equilibration, the pressure was again measured. This measurement is reported on the second line of data for experiments 1, 2, and 12 on Table 1. The true volume of column 6 can thus be determined knowing the volume of the 4000 cc flask.

To calibrate the nominally 5000 cc chamber of column 5, the sample was transferred from column 6 to column 5 by placing a liquid nitrogen dewar flask on the 1000 cc flask of column 5, which had been well evacuated, and then opening the stopcocks between the two columns. The pressure measurement of the sample in the nominally 5000 cc chamber of column 5 was then made. This measurement is reported on the third line of data for experiments 1, 2 and 12 on Table 1. The volume of column 5 can thus be determined when this measurement is combined with the first measurement of the experiment and with the volume of the calibrated 4000 cc flask in column 6. Finally the CO_2 was transferred back to column 6 and its pressure measured again as a check on whether quantitative transfer of the CO_2 between the two sample chambers had been effected. This measurement is reported on the fourth line

of data on Table 1 for experiments 1, 2, and 12.

The procedure for experiment numbers 3 through 8, using N_2 and Ar gases, was simpler because no sublimations were made. The gases were flowed into column 6 using the normal procedure for filling the large manometer sample chamber with reference gases as described in Manometer Report III. The infrared analyser zero control was set for a vacuum trace to monitor CO_2 content of the N_2 or Ar flowing through the lines. Using N_2 gas, liquid nitrogen was placed around the thimble trap and two U-traps in the path of the gas to freeze out any water vapor, CO_2 or other condensable gases. In experiment number 5 using Ar gas, liquid nitrogen temperature traps were also attempted but the Ar partially froze out. This sample was apparently contaminated during the filling process. Possibly lower pressure in the delivery line caused room air to be sucked into the system. For subsequent experiments using Ar gas (numbers 6 and 7) the traps were cooled to dry ice temperature. Once column 6 was brought to full pressure with dried N_2 or Ar, the pressure measurement was made for the determination of the number of moles of gas to be confined in the calibrated 4000 cc flask. This measurement is reported on the first line of data in Table 1 for experiments 3 through 8. The 4000 cc flask stopcock was then closed, the extra gas pumped away, the main stopcock of column 6 closed, the 4000 cc sample expanded into the nominally 5000 cc chamber and the volume calibrating pressure measurement made.

This measurement is reported on the second line in Table 1 for experiments 3 through 8. Experiment numbers 3 and 4 used the same sample of N_2 gas. All other experiments used separate samples of gas.

An error in procedure or in reading the cathetometer was apparently made in experiment number 6 since the volume determined from the expansion was very far off. One likely procedural error might have been that, after the first measurement, the mercury column was set into motion before the 4000 cc flask stopcock was closed. This was done on another calibration but caught by the operator just after doing it.

2. 5000 cc/1000 cc Volume Ratio Determinations using N_2

Three measurements of the 5000 cc/1000 cc volume ratio in column 5 were carried out by expansion using N_2 gas to afford a comparison with determinations made in 1959, 1961 and 1972 using CO_2 gas. The data are reported as experiment numbers 9, 10 and 11 in Table 1. The procedure followed was to evacuate column 5 to less than 1 millitorr pressure and then close the 4000 cc flask stopcock. The remaining 1000 cc portion of column 5 was then filled with N_2 gas to between 60 to 65 cm of mercury pressure by passing the cylinder gas through three traps cooled to liquid N_2 temperature. After waiting for temperature equilibration to be achieved, the pressure was determined at the column 5 pointer. Then the 4000 cc flask stopcock was opened to expand the sample into the 5000 cc chamber, and a second pressure measurement was

made at the column 5 pointer after temperature equilibration. The results of these two measurements were combined, as discussed below, to find the 5000 cc/1000 cc volume ratio.

B. Small Manometer Sample Chamber Calibrations

Table 2 presents experimental data obtained from the small chamber calibrations carried out in 1974. Experiment number 5 is a 16 cc/4 cc volume ratio determination by expansion. The other experiments are determinations of the volume of the nominally 4 cc sample chamber with reference to plenums whose volumes were determined using mercury.

1. Volume Calibration of the 4 cc Chamber

The basic procedure for these calibrations was to place a known amount of CO_2, contained in a volume calibrated plenum, into the small manometer sample chamber and to measure its temperature and pressure at the 4 cc pointer. Specifically, the first step was to fill the plenums with CO_2. This part of the calibration was carried out by Adams on the extraction vacuum line in Rm. 2328, Ritter Hall. The plenums were filled to ambient pressure and brought to constant temperature while immersed in a water bath. The first line in Table 2 lists the data for each such experiment. Here the Vacuum Column Height refers to the reading of a wall barometer. The sample column height is, by definition, zero in this case. One of the two readings listed under temperature refers to the temperature of the mercury barometer measured by its attached

thermometer, and the other refers to the temperature of the water bath in which the plenums were immersed. For the volume calibrations through experiment 13, the plenums were prepared in pairs, using the largest and smallest plenums, numbers 7 and 1 respectively. The four plenums used in experiments 14 to 17 were all filled at one time with CO_2.

The plenums were attached to the (yellow) sample tube manifold. The CO_2 sample from each plenum was transferred into the small manometer in two steps using two dry ice sublimations, first at the plenum and then at U-trap R4 of the (red) vacuum line. The pressure measurement procedure was exactly the same as described in Manometer Report III. Usually, two separate mercury approaches to the 4 cc pointer were made for each calibration. The usual precautions were taken for temperature equilibration.

The results for the first five volume calibrations show considerable scatter. In the first four calibrations, the volume of the 4 cc chamber with referenee to the small plenum was significantly smaller than the volume with reference to the large plenum. A possible explanation for the discrepancy lies in the way the plenum samples were handled. Soon after they were filled the CO_2 was frozen in the plenums by surrounding them with a liquid N_2 bath. It is hypothesized that CO_2 may have dissolved in the plenum stopcock grease during filling of the plenums. When the CO_2 was later frozen, this CO_2 evolved out of the grease, adding CO_2 to the sample beyond

the calibrated amount. This effect would lower the volume of the 4 cc chamber obtained using the small plenum more than the volume obtained using the large plenum as observed. Beginning with experiment number 6 the sample was no longer frozen in the plenum. The hypothesis assumes that CO_2 will come out of the stopcock grease only quite slowly; otherwise, it would also come out when the sample was transferred from the plenum into the manometer by vacuum sublimations.

A second possible problem came to light after experiment number 6 was run. In this case the CO_2 was transferred from the plenum into the manometer without using dry ice in the first transfer to U-trap R4. The transfer from U-R4 into the manometer, however, was accomplished using a dry ice-liquid N_2 sublimation transfer. Testing the pressure of the contents of trap U-R4 after the transfers were complete revealed that considerable water vapor remained. The volume found for the 4 cc chamber was high for experiment number 6 possibly due to the presence of a significant amount of water vapor in the plenum. Since the water vapor was frozen out in U-R4 the sample reaching the manometer had less than the calibrated amount of gas.

To solve the water vapor problem Adams made a number of changes in his procedure. For experiment numbers 1 to 7, the CO_2 had been prepared from solid Na_2CO_3 by acidification and extraction. There was, of necessity, considerable water vapor in the extraction vacuum line. Beginning with experiment number 8, Adams obtained the CO_2

from a commercial gas cylinder. The second change was to place another trap in the extraction vacuum line system so that he could sublime the CO_2 back and forth and separate it from H_2O vapor more efficiently. Finally, all the CO_2 prepared in the first six experiments was frozen out in one of the plenums, usually number 7, before it was expanded into both plenums via the connecting lines. Plenum 7 would therefore retain most of the H_2O when the plenum was thawed as not enough time was allowed for diffusion of the H_2O to the other plenum. To avoid this situtation, Adams installed on the extraction vacuum line a dummy plenum into which the CO_2 was frozen before it was expanded into the calibrating plenums.

For all the volume calibrations after experiment 7 the CO_2 was not stored frozen in the plenums. Transfer of the plenum samples into the small manometer sample chamber was, however, still accomplished using dry ice sublimations. After the transfers were complete and the traps thawed, the vacuum line was checked for residual pressure with the vacuum gauges. No evidence of water vapor was detected in any experiment. In experiment number 17 the sample was again kept frozen in the small plenum, in an attempt to bring back the early anomalies, but no effect on the results was detected.

2. 16 cc/4 cc Volume Ratio Determination Using CO_2

A volume ratio determination was made by expansion using the plenum CO_2 sample prepared for the volume calibration in experiment

number 4. This is listed as experiment 5 in Table 2. The pressure and temperature measurements made for the 4 cc chamber were combined with measurements for the expanded sample in the 16 cc chamber. The mercury approach to the 16 cc pointer was not as easy as the approach to the 4 cc pointer. The main problem lay in the difficulty of seeing the point of contact of the pointer with the mercury. Three 4 cc chamber measurements and five 16 cc chamber measurements were made.

C. Meniscus Corrections

Table 3 presents the meniscus corrections made for this phase of the 1974 manometric calibration. These measurements actually refer to observed mercury levels which are affected by any deviation from horizontal in the swing of the cathetometer telescope as well as meniscus effects. Measurements were made as described in Manometer Report III: with vacuum above both mercury columns for the 4 cc and 16 cc pointers in the small manometer sample chamber and for the large manometer column number 6 pointer and with about 2 cm pressure of N_2 above the mercury columns for the large manometer column number 5 pointer. The average Applied Correction, as listed, is to be added to the measured difference between the vacuum column and sample column heights found during an experiment.

III. Calculations and Summary of Results

A. Volumes of Independently Calibrated Vessels

Table 4 lists the volumes of auxiliary vessels independently

calibrated by direct methods. The 4000 cc flask in column 6 of the large manometer was removed from its position in the manometric system cabinet, and its volume was calibrated by weighing it both empty and filled with water. All of the large manometer calibrations reported here are referred to this volume. The five small volume plenums were calibrated by weighing them empty and filled with mercury. Most of the 4 cc chamber calibrations are referred to the largest and smallest plenums, number 7 and number 1 respectively, with one calibration referred to each of the other three plenums. Details of these independent volume calibrations are given in Volumetric Report I. The calibrations were carried out by A. Adams.

B. Temperature Readings in Manometric System Cabinet

During the calibrations of the large manometer readings of all the thermometers in the manometric cabinet were made. These are reported in Table 5 as deviations from the reading of thermometer No. 6112. The readings in Table 5 are corrected to reflect a 1968 calibration of the thermometers including No. 6112. Temperatures listed in Table 1 for large manometer measurements are the uncorrected readings of thermometer No. 6112 averaged over the measurements. These latter temperatures were always within .03°C of the readings of thermometer No. 6112 shown in Table 5. The average deviations from thermometer No. 6112 shown at the end of Table 5 indicate that the maximum difference in temperature existing in the manometric system cabinet during

the large manometer volume calibrations was, on average, .04°C.

For discussion of earlier temperature studies, see Manometer Report III.

C. 4 cc Chamber Volume Calibrations

The equation of state used in this study to calculate moles of gas is expressed in the implicit form:

$$PV = nRT\ (1 + \frac{n}{V} B\ (T) + \ldots) \qquad (1)$$

where P, V, and T are the measured pressure, volume and absolute temperature, and n is the calculated moles of the gas. R denotes the gas constant and B (T) the temperature dependent second virial coefficient in the expansion of the compressiblity factor PV in powers of the density 1/V. Higher order terms in 1/V are neglected.

The volume calibration calculations are carried out in two steps. First, rearranging (1) as a quadratic in n, the number of moles of CO_2 contained in the plenum sample is computed by the positive root:

$$n = \frac{V\left(\sqrt{1 + \frac{4PB}{RT}} - 1\right)}{2B} \qquad (2)$$

where specifically:

P = the pressure of the gas when the plenum was filled, in dynes/cm^2

V = the calibrated volume of the plenum, in cc

T = the temperature of the gas when the plenum was filled, taken as the temperature of the constant temperature water bath, in °K

B = the second virial coefficient for CO_2 at T, in cc/mol.

R = 8.31436×10^7 ergs/mol.°K.

The pressure P was calculated from the height of a mercury column supported by the atmosphere as measured on a mercury barometer by the equation:

$$P = h \cdot \rho_{Hg}(T) \cdot g \tag{3}$$

where

h = the observed height of the mercury column in the barometer at the time the plenum was filled, in cm.

$\rho_{Hg}(T)$ = the density of the mercury in the barometer at the observed temperature of the column, in g/cc (g/ml ÷ 1.000027)

g = the acceleration of gravity at 32°52'N taken to be 979.558 cm^2/sec^2

In the second step of the calculation the volume in cc of the 4 cc chamber of the small manometer is obtained from the measured pressure and temperature of the gas, in the manometer, and the number of moles of gas calculated from equation (2):

$$V = \frac{2nB}{\sqrt{1 + \frac{4PB}{RT}} - 1} \tag{4}$$

where:

In equation (3) h is replace by Δh, the observed manometric mercury height difference in cm; $\rho_{Hg}(T)$ is the density of mercury at the temperature of measurement, in grams/cc

T = temperature of manometric measurement, in °K

n = number of moles of CO_2 in the plenum

B = second virial coefficient of CO_2 for the temperature of the manometric measurement, in cc/mol.

R and g are as defined previously

Values of the second virial coefficient of CO_2 gas were obtained from the values listed in Table 2 of Manometer Report III by a linear Lagrangian interpolation. See the discussion in Section III A of Manometer Report III.

Table 6 summarizes the results of the volume calibrations of the 4 cc chamber. All the variable quantities used to calculate the results are listed in the table except for the plenum volumes, which are listed in Table 4. For each experiment, the first corrected mercury height difference listed in Table 6 refers to the barometric reading; succeeding values refer to differences between the sample mercury column number 4 of the small manometer and the vacuum mercury column 2 after applying appropriate meniscus corrections shown in Table 3. Two temperatures are listed for the barometric measurements since the temperature of the barometer column and of the CO_2 gas were separate readings.

As discussed in section IIB.1 above, problems were encountered with the first six volume calibration runs. The only run which can be catagorically thrown out on the basis of experimental observations, however, is experiment number 6 where considerable water vapor was detected in the plenum sample. If experiment number 3 is also omitted because it is more than three standard deviations from the average of the remaining experiments, the standard deviation

is decreased from .0014 to .0007 cc. If all of the first five determinations are omitted, the standard deviation decreases to .0005. In this case the average is not changed even in the fifth place.

A precision in the calibrated volume of .0005 cc is one part in 8000, which seems to be quite a reasonable lower limit when possible sources of error are considered. An error of 0.1 mm, which is the least count for the barometer measurement, would lead to an error of .0005 cc in the computed volume. If we assume a random error of .05 mm, about half of the observed error is already accounted for. The manometer pressure reading could be in error by as much as 50 microns of mercury since the vacuum column measurements before and after contact of mercury with the glass pointer differ by as much as 100 microns. This error causes an error of .0004 cc and .0007 cc for the largest and smallest plenum, respectively. A more reasonable estimate for this random error is about 25 microns, which would account for the remaining half of the observed error. The other likely source of random error is temperature. The temperature reading of the plenum sample in the water bath might reasonably be in error by .01°C, leading to an error of .0001 cc. The temperature reading in the manometric system cabinet is probably determined within .02°C, leading to an error of .0002 cc. In conclusion, even fairly conservative estimates of errors in the measurements exceed the observed error in the result.

Possible systematic errors are not easily estimated. The

estimated accuracy of the plenum volumes is .0002 cc; and this causes a systematic error in the calibrated volume of ±.0006 cc for the smallest plenum P1. One might be able to notice this systematic error in differences among the volumes of the 4 cc chamber obtained with reference to different plenum volumes. However, the six good calibrations using plenum number one average 3.7973 cc and the five good calibrations using plenum number seven average 3.7974 cc. The true systematic error might reasonably be greater than the stated precision, perhaps .0010 cc or about one part in four thousand.

D. 5000 cc Chamber Volume Calibrations

Equations identical in form to (2) and (4) were also used to calculate the 5000 cc chamber volumes. In applying equation (2) V refers to the independently calibrated volume of the nominally 4000 cc flask in column number 6, 3947 cc (see Table 4). The pressure P is calculated from the observed mercury height difference of the large manometer, after the meniscus correction is applied, for the measurement with column number 6 filled with calibrating gas. The temperature, T is as listed in Table 1 and discussed in section III-B.

Equation (4) is applied to the measurements made after expansion of gas from the calibrated 4000 cc flask into the 5000 cc chamber of column 6 or transfer into column 5.

Values of the second virial coefficients for carbon dioxide, nitrogen and argon were obtained by linear Lagrangian interpolation

of the data listed in Table 2 of Manometer Report III.

Table 7 summarizes all the 5000 cc volume calibrations made. Experiment Nos. 1, 2 and 12 with CO_2 gas, and 3,4 and 8 made with N_2 gas, are deemed satisfactory. Of three calibrations made using Ar gas, the first two are rejected owing to procedural errors, leaving only number 7 as probably valid.

In Table 7 the first line of data for each calibration refers to the pressure measurement of the original sample of gas in the nominally 5000 cc column number 6 and to the moles of gas contained in the calibrated 4000 cc flask at that pressure. The second line of data refers to the pressure measurement after expansion from the 4000 cc flask into the nominally 5000 cc volume. The third line for the CO_2 calibrations refers to the measurement made after the gas has been transferred from column 6 into column 5. The final line for the CO_2 calibrations is for the measurement made after transfer back into column 6. The corrected mercury height difference is the observed difference in mercury heights between the mercury vacuum column (number 8) and the mercury sample column (5 or 6) after applying the appropriate meniscus corrections from Table 3. The density of mercury at the temperature of the run is obtained by interpolation of data listed in the Handbook of Chemistry and Physics, Edition 45, p. F5.

The average volume of column 5 for three determinations with CO_2 is 5015.09 cc with a standard deviation of 0.16 or about one

part in 30,000. This level of scatter is probably mostly due to the error in the measurement of temperature. The results are very insensitive to the distance of the sample mercury column from the pointer for these measurements. Normally the mercury is brought to within 0.300 mm of the pointer. The volume of the portion of the chamber between the mercury and the pointer under these conditions is only about 0.1 cc.

The results for column 6 exhibit about twice the imprecision of those for column 5. This probably reflects a more realistic estimate of the true experimental standard deviation based on a larger number of replicate experiments (12 instead of 3). The three calibrations using N_2 taken separately have a standard deviation of 0.27 cc but they are also about 0.7 cc, or about 1 part in seven thousand, lower on average than the calibration results using CO_2 gas. This difference may reflect errors in the virial coefficients, but the difference is too small to be sure that it is significant. The single good Ar result is close to the CO_2 results. Taken altogether, the results show that no serious errors are introduced by using CO_2 as a calibrating gas with respect to the more ideal gases, N_2 and Ar.

Comparison of the column 6 volumes calculated from measurements made before and after transfer of the CO_2 gas sample out of column number 6 (in experiment numbers 1, 2 and 12) reveals an average difference of +0.33 cc in the result. This may reflect a small

loss of CO_2 in transfer; but the scatter, with a standard deviation of 0.36 cc, indicates that the loss is hardly significant.

The estimated error in the independently calibrated volume of the nominally 4000 cc flask in column number 6 is slightly more than ±1 cc. The precision in volume of the 5000 cc chamber is thus much less than the likely systematic error.

E. Volume Ratios by Expansion

Table 8 summarizes the determinations of volume ratios by expansion made for comparison with previous measurements made in 1959, 1961 and 1972. Part I presents one set of expansions done on the 16 cc and 4 cc chambers of the small manometer using a sample of CO_2 gas. Part II presents three expansions done on the 5000 cc and 1000 cc chambers of the large manometer column number 5 using N_2 gas. The results are calculated from the manometric pressure and temperature measurements by the following rearrangement of equation (1) in terms of the specific molar volume V/n:

$$\frac{V}{n} = \frac{2B}{\sqrt{1 + 4\frac{PB}{RT}} - 1} \qquad (5)$$

where the quantities are as defined for equation (4). The ratio V/n is expressed in cc/mole; it is calculated for each pressure measurement and a ratio of the results for two contiguous chambers is then computed to obtain the volume ratio of the two chambers. The other quantities listed in Table 8 are as in Tables 6 and 7.

The average result for the 16 cc/4 cc volume ratio, 4.2062, compares very well with the determinations made in 1961 and 1972 (4.2058 and 4.2068); the result for 1959 (4.2013) appears now to be too low. The scatter of individual values of V/n, however, continues to be high. The standard deviation for the 4 cc chamber measurement is about one part in 8700 for three measurements, a quite satisfactory imprecision similar to that for reference gas calibration measurements. The standard deviation for the 16 cc measurements is however about one part in 3800 for five measurements. The combination of these two standard deviations yields about one part in 3500 for the determined volume ratio. As discussed in Part IIB.2 of this report, there are experimental difficulties in making measurements at the 16 cc pointer. An error in approach of the sample mercury column to the pointer, in terms of a given distance from the pointer, represents about the same proportion of the volume of the chamber for both the 4 cc chamber and the 16 cc chamber. This is because the tube diameter at the 4 cc pointer is about 1/2 that at the 16 cc pointer. Only with the larger chambers (64 cc and larger) does this error decrease. The difficulty in approaching the 16 cc volume pointer reproducibly leads to a relatively large error in measurements made there in comparison to measurements made at the 4 cc volume pointer.

The average of the three 5000 cc/1000 cc volume ratios determined

with N_2 gas, 4.9045, agrees quite well with previous determinations using CO_2 gas (4.9034 in 1959, 4.9056 in 1961 and 4.9058 in 1972). The standard deviation of .0012 also is similar to that of the 1972 results, which was .0011 for three measurements in the 1000 cc chamber and two in the 5000 cc chamber made on a single sample of CO_2 gas. This error is about one part in 4000 and is probably due mostly to the greater importance of temperature errors in large manometer determinations. No effect from changing from CO_2 gas to N_2 gas can be seen.

IV. Conclusions. New 5000 cc/4 cc Volume Ratio

The primary purpose of the manometric volume calibrations was to redetermine the 5000 cc/4 cc volume ratio in the manometric system. Using the best value for the volume of the 4 cc chamber, 3.7974 cc, and the best value for the volume of the 5000 cc chamber, 5015.09 cc, one calculates a 5000 cc/4 cc volume ratio of 1320.66 with a composite standard deviation of 0.18 calculated from the following equation:

$$\sigma_{5000\ cc/4\ cc} = 1320.66 \sqrt{\left(\frac{\sigma}{V}\right)^2_{4\ cc} + \left(\frac{\sigma}{V}\right)^2_{5000\ cc}} \qquad (6)$$

In Table 9 the above result is compared with previous determinations of the 5000 cc/4 cc volume ratio made by the expansion method. In the latter method five adjacent volume ratios, 16 cc/4 cc, 64 cc/16 cc, 250 cc/64 cc, 1000 cc/250 cc, and 5000 cc/1000 cc are multiplied together to obtain the overall volume ratio. As

shown in Table 9, the new result is different from the previous results by about two parts per thousand, leading to a difference of about 0.5 ppm between reference gas determinations calculated using the two volume ratios of 1318.2 and 1320.6. The origin of this discrepancy is unknown at this time, but the expansion determinations are suspect and will be investigated further. As shown in Table 9, the individual volume ratios determined in 1959, 1961 and 1972 show considerable scatter, leading to a composite standard deviation of 1.52 in the overall volume ratio, yet the three overall ratios have a range of variation of only 0.2. Similarly, the composite standard deviation for the 1972 ratios, obtained by combining the standard deviations for each adjacent volume ratio determination, is 0.88. Fortuitous cancellation of errors may be hiding a more realistic scatter in the overall volume ratio. The maximum volume ratio calculated from the 1959, 1961 and 1972 data is 1320.3, very close to the recently determined value. The minimum calculated volume ratio is 1315.0.

Further investigation of the volume ratio discrepancy will involve redetermining the individual volume ratios by expansion as well as volume calibration of the intermediate chambers with reference to the volumes of containers calibrated by weighing mercury or water. It is hoped that these investigations will resolve the discrepancy between the 5000 cc/4 cc volume ratios obtained by the two methods.

Table 1. Large Manometer Volume Calibrations - Experimental Data

Experiment Type and No.	Date	Nominal Volume of Chamber (cc)	Gas	Column No.	Vacuum Column Height (mm)	Sample Column Height (mm)	Temp. °C
Calibration of Large Manometers using CO_2	18 JUN 74	5000	CO_2	6	810.640	175.898	20.60
	19 JUN 74			6	683.068	175.932	20.74
1	19 JUN 74			5	673.488	173.240	20.72
	19 JUN 74*			6	682.962	175.976	20.66
2	20 JUN 74	5000	CO_2	6	795.622	175.996	20.62
	20 JUN 74			6	670.431	176.032	20.40
	20 JUN 74			5	661.175	173.304	20.47
	21 JUN 74*			6	670.600	176.046	20.50
Virial Coefficient Checks	25 JUN 74	5000	N_2	6	805.025	176.223	19.72
3	25 JUN 74			6	678.364	176.236	19.91
4	25 JUN 74	5000	N_2	6	677.970	176.194	19.72
	25 JUN 74			6	576.830	176.213	19.84
5	26 JUN 74**	5000	Ar	6	811.601	176.336	20.28
	26 JUN 74**			6	681.714	176.289	20.02
6	27 JUN 74+	5000	Ar	6	797.918	176.297	19.97
	27 JUN 74+			6	668.499	176.324	19.90
7	2 JUL 74	5000	Ar	6	796.262	176.301	20.19
	2 JUL 74			6	670.616	176.238	20.00
8	3 JUL 74	5000	N_2	6	809.618	176.274	20.18
Determinations of 5000 cc/1000 cc Volume Ratio	3 JUL 74			6	681.227	176.272	19.94
	3 JUL 74	1000	N_2	5	807.150	173.492	20.18
9	3 JUL 74	5000		5	302.568	173.444	19.81
10	5 JUL 74	1000	N_2	5	824.080	173.458	24.83
	5 JUL 74	5000		5	306.417	173.530	25.18
11	9 JUL 74	1000	N_2	5	820.726	173.443	20.62
	9 JUL 74	5000		5	305.826	173.504	21.07
Calibration of Large Manometers using CO_2	13 AUG 74	5000	CO_2	6	804.851	176.442	19.76
	13 AUG 74			6	677.720	176.380	19.47
	13 AUG 74			5	668.720	173.688	19.74
12	14 AUG 74*			6	678.161	176.531	19.67

* Repeat after transfers
** Filling problems - sample probably contaminated
\+ Probable error in procedure made

Table 2. Small Manometer Volume Calibrations - Experimental Data

Experiment Type and No.	Date	Chamber	Vacuum Column Height (mm)	Sample Column Height (mm)	Temperature °C
Volume Calibrations	20 JUN 74	Plenum 7	761.4	---	Hg 20.8; CO_2 20.78
1	21 JUN 74	4 cc	827.298	370.618	20.54
	21 JUN 74	4 cc	826.917	370.566	20.40
2	20 JUN 74	Plenum 1	761.4	---	Hg 20.8; CO_2 20.78
	21 JUN 74	4 cc	631.725	370.605	20.28
	21 JUN 74	4 cc	631.515	370.580	20.07
3	26 JUN 74	Plenum 1	760.8	---	Hg 20.5; CO_2 20.75
	26 JUN 74	4 cc	631.522	370.838	19.76
	26 JUN 74	4 cc	631.485	370.820	19.73
4	26 JUN 74	Plenum 7	760.8	---	Hg 20.5; CO_2 20.75
	27 JUN 74	4 cc	826.306	370.820	19.97
	27 JUN 74	4 cc	826.096	370.792	19.90
	28 JUN 74	4 cc	826.475	370.830	20.13
Determination of 16 cc/4 cc Volume Ratio	27 JUN 74	4 cc	826.306	370.820	19.97
	27 JUN 74	16 cc	418.110	309.656	19.84
	27 JUN 74	16 cc	418.100	309.654	19.88
5	27 JUN 74	4 cc	826.096	370.792	19.90
	27 JUN 74	16 cc	418.070	309.648	19.86
	28 JUN 74	4 cc	826.475	370.830	20.13
	28 JUN 74	16 cc	418.079	309.650	19.92
	28 JUN 74	16 cc	418.062	309.650	19.92
Further Volume Calibrations	9 JUL 74*	Plenum 7	763.8	---	Hg 20.7; CO_2 20.77
6	9 JUL 74*	4 cc	827.928	370.798	20.87
	9 JUL 74*	4 cc	827.923	370.804	20.83
7	9 JUL 74	Plenum 1	763.8	---	Hg 20.7; CO_2 20.77
	10 JUL 74	4 cc	633.268	370.806	20.91
	10 JUL 74	4 cc	633.304	370.818	20.91
8	29 JUL 74	Plenum 7	761.7	---	Hg 21.2; CO_2 20.75
	29 JUL 74	4 cc	826.286	370.798	19.60

Table 2. Small Manometer Volume Calibrations - Experimental Data

Experiment Type and No.	Date	Chamber	Vacuum Column Height (mm)	Sample Column Height (mm)	Temperature °C
9	29 JUL 74	Plenum 1	761.7	---	Hg 21.2; CO_2 20.75
	30 JUL 74	4 cc	630.979	370.822	19.28
	30 JUL 74	4 cc	630.953	370.818	19.20
10	30 JUL 74	Plenum 1	763.4	---	Hg 20.4; CO_2 20.75
	30 JUL 74	4 cc	631.683	370.800	19.39
	30 JUL 74**	4 cc	631.513	370.800	19.31
11	30 JUL 74	Plenum 7	763.4	---	Hg 20.4; CO_2 20.75
	30 JUL 74	4 cc	826.460	370.788	19.06
	30 JUL 74	4 cc	826.322	370.791	19.02
12	1 AUG 74	Plenum 7	763.1	---	Hg 20.2; CO_2 20.77
	1 AUG 74	4 cc	827.544	371.094	19.73
	1 AUG 74	4 cc	827.421	371.064	19.64
13	1 AUG 74	Plenum 1	763.1	---	Hg 20.2; CO_2 20.77
	1 AUG 74	4 cc	631.828	371.018	19.47
	2 AUG 74	4 cc	631.954	371.058	19.52
14	7 AUG 74	Plenum 3	760.8	---	Hg 20.3; CO_2 20.75
	7 AUG 74	4 cc	699.303	371.073	19.96
	7 AUG 74	4 cc	699.182	371.074	19.87
15	7 AUG 74	Plenum 5	760.8	---	Hg 20.3; CO_2 20.75
	8 AUG 74	4 cc	738.966	371.084	19.72
	8 AUG 74	4 cc	738.667	371.076	19.55
16	7 AUG 74	Plenum 4	760.8	---	Hg 20.3; CO_2 20.75
	8 AUG 74	4 cc	719.972	371.044	19.03
	8 AUG 74	4 cc	719.888	371.036	18.98
17	7 AUG 74	Plenum 1	760.8	---	Hg 20.3; CO_2 20.75
	9 AUG 74	4 cc	631.340	371.070	19.60
	9 AUG 74	4 cc	631.257	371.060	19.59

* Considerable water vapor found in plenum sample
** Premature contact - discard

Table 3. Meniscus Corrections

Date	Approx. Distance From Hg to Pointer (mm)	Pointer Reading (mm)	No. of Det'ns	Average Sample Column Height (mm)	Average Vacuum Column Height (mm)	Applied Correction (mm)	Comments
4cc Pointer in Small Manometer (Col. #4 [sample] vs. Col. #2 [vacuum])							
31 MAY 74	0.18	370.642	10	370.457	370.808	-0.351	Hg not bulging toward pointer.
28 JUN 74	0.23	370.844	10	370.618	370.999	-0.381	Hg slightly bulging toward pointer.
					Average	-0.366	
16cc Pointer in Small Manometer							
28 JUN 74	0.28	309.676	10	309.392	309.406	-0.014	Hg slightly bulging toward pointer.
Pointer in Large Manometer Sample Column No. 5 (Col. #5 [sample] vs. Col. #8 [vacuum])							
31 MAY 74	0.24	173.440	10	173.202	173.270	-0.068	Hg not bulging toward pointer.
14 AUG 74	0.22	173.870	10	173.647	173.775	-0.128	Hg not bulging toward pointer.
					Average	-0.098	
Pointer in Large Manometer Sample Column No. 6 (Col. #6 [sample] vs. Col. #8 [vacuum])							
21 JUN 74	0.40	176.240	10	175.838	175.919	-0.081	Hg not bulging toward pointer.
28 JUN 74	0.31	176.390	10	176.080	176.199	-0.119	Hg not bulging toward pointer.
					Average	-0.100	

Table 4. Volumes of Independently Calibrated Vessels

Description of Vessel	Determined Volume* (cc)	Comments
4000 cc flask in large manometer column 6	3947 ±1	Used for large volume calibrations (calibrated by weighing water)
Plenum 1	1.2978±0.0002	Used for small volume calibrations (calibrated by weighing mercury)
Plenum 3	1.6359±0.0002	
Plenum 4	1.7457±0.0002	
Plenum 5	1.8359±0.0002	
Plenum 7	2.2732±0.0002	

* All volumes calibrated by A. Adams (For details see Volumetric Report I).

Table 5. Readings of Thermometers in Manometric System Cabinet

Experiment Number - Large Manometer Volume Calibrations	Date	Corrected Deviations of Thermometers from No. 6112 in °C						
		6114	6113	6111	6112	6115	6117	6116
1	18 JUN 74	-.01	--	+.01	20.60	.00	-.01	+.01
	19 JUN 74	-.01	-.03	+.01	20.75	-.01	-.03	.00
	19 JUN 74	-.02	-.04	.00	20.73	.00	-.03	+.01
	19 JUN 74	-.01	-.05	.00	20.68	-.01	-.03	.00
2	20 JUN 74	.00	--	+.01	20.62	.00	-.03	+.01
	20 JUN 74	.00	-.04	+.01	20.40	.00	-.03	+.01
	20 JUN 74	-.01	-.04	+.01	20.47	.00	-.02	+.02
	21 JUN 74	+.01	-.03	+.01	20.50	.00	-.04	+.02
3	25 JUN 74	.00	-.01	+.01	19.73	-.02	-.03	+.03
	25 JUN 74	+.01	-.01	+.02	19.92	-.01	-.02	+.03
4	25 JUN 74	+.01	-.01	+.01	19.75	-.02	-.02	+.03
	25 JUN 74	+.02	-.01	+.02	19.86	-.01	-.02	+.04
5	26 JUN 74	+.02	-.02	+.02	20.28	.00	-.02	+.04
	26 JUN 74	+.02	-.02	+.02	20.02	-.01	-.03	+.03
6	27 JUN 74	+.01	-.02	+.01	19.98	-.02	-.03	+.03
	27 JUN 74	+.01	-.02	+.01	19.91	-.01	-.03	+.03
7	2 JUL 74	+.03	-.03	+.02	20.18	-.01	-.04	+.04
	2 JUL 74	+.02	-.02	+.01	20.00	.00	-.01	+.05
8	3 JUL 74	+.01	-.03	+.01	20.18	.00	-.03	+.03
	3 JUL 74	+.01	-.02	+.01	19.96	-.02	-.02	+.03
9	3 JUL 74	+.02	-.01	+.02	19.82	-.01	-.03	+.04
10	5 JUL 74	-.03	+.02	.00	24.86	-.02	.00	.00
	5 JUL 74	-.03	+.02	.00	25.21	-.02	.00	+.01
11	9 JUL 74	-.01	-.01	+.01	20.65	-.01	.00	+.03
	9 JUL 74	+.01	-.01	+.01	20.08	.00	-.01	+.03
12	13 AUG 74	+.02	--	+.01	19.74	-.01	-.04	+.04
	14 AUG 74	+.02	-.03	.00	19.68	-.02	-.03	+.03
Average Deviation from No. 6112		.00	-.02	+.01		-.01	-.02	+.02
Standard Deviation of Deviation		$.01_6$	$.01_7$	$.00_6$		$.00_8$	$.01_2$	$.01_4$

Table 5. Readings of Thermometers in Manometric System Cabinet

Notes: (1) Temperatures are observed thermometer readings plus the following corrections determined by Elliot Atlas in September, 1968 (Book II, part 3, page 29 of manometric calibrations notebook):

#6114	-0.03°C	#6112	+0.01°C	#6117	-0.03°C
#6113	+0.02°C	#6115	+0.03°C	#6116	-0.03°C
#6111	0.00°C				

(2) 3 of 5 air circulating fans on (Mid and Intermediate fans) at 40 volts on control rheostat.

(3) #6112 reading always within 0.03°C of temperature recorded for measurement.

Table 6. 4 cc Chamber Volume Calibrations - Results

Experiment Number - Small Manometer	Plenum No.	Corr. Hg. Height Diff. cm	Temperature °C	Temperature °K	Second Virial Coeff. of CO_2 cc/mol.	Density of Hg, g/cc	Calc. No. of Moles of CO_2	Calc. Volume cc	Run Average Volume cc
1	7	76.14	Hg 20.8	CO_2 293.94	-127.2	13.5439	.000094458		
		45.6314		293.70	-127.4	13.5445		3.7978_3	3.7982
		45.5985		293.56	-127.6	13.5448		3.7986_6	
2	1	76.14	Hg 20.8	CO_2 293.94	-127.2	13.5439	.000053927		
		26.0754		293.44	-127.7	13.5451		3.7959_7	3.7959
		26.0569		293.23	-127.9	13.5456		3.7957_9	
3	1	76.08	Hg 20.5	CO_2 293.91	-127.2	13.5446	.000053893		
		26.0318		292.92	-128.2	13.5464		3.7928_0	3.7927
		26.0299		292.89	-128.2	13.5465		3.7926_6	
4	7	76.08	Hg 20.5	CO_2 293.91	-127.2	13.5446	.000094398		
		45.5120		293.13	-128.0	13.5459		3.7975_5	3.7980
		45.4938		293.06	-128.1	13.5461		3.7981_0	
		45.5279		293.29	-127.8	13.5455		3.7984_3	

Table 6. 4 cc Chamber Volume Calibrations - Results

Experiment Number - Small Manometer	Plenum No.	Corr. Hg. Height Diff. cm	Temperature °C	Temperature °K	Second Virial Coeff. of CO_2 cc/mol.	Density of Hg, g/cc	Calc. No. of Moles of CO_2	Calc. Volume cc	Run Average Volume cc
6	7	76.38	Hg 20.7	CO_2 293.93	-127.2	13.5441	.000094762		
		45.6764		294.03	-127.1	13.5437		3.8108_4	3.8106
		45.6753		293.99	-127.2	13.5438		3.8103_8	
7	1	76.38	Hg 20.7	CO_2 293.93	-127.2	13.5441	.000054101		
		26.2096		294.07	-127.1	13.5436		3.7972_8	3.7971
		26.2120		294.07	-127.1	13.5436		3.7969_4	
8	7	76.17	Hg 21.2	CO_2 293.91	-127.2	13.5429	.000094498		
		45.5122		292.76	-128.4	13.5468		3.7964_6	3.7965
9	1	76.17	Hg 21.2	CO_2 293.91	-127.2	13.5429	.000053950		
		25.9791		292.44	-128.7	13.5476		3.7979_2	3.7975
		25.9769		292.36	-128.8	13.5478		3.7971_4	
10	1	76.34	Hg 20.4	CO_2 293.91	-127.2	13.5448	.000054079		
		26.0517		292.55	-128.6	13.5473		3.7978_9	3.7979
		26.0347		292.47	-128.6	13.5475		3.7992_8*	

Table 6. 4 cc Chamber Volume Calibrations - Results

Experiment Number - Small Manometer	Plenum No.	Corr. Hg Height Diff. cm	Temperature °C	Temperature °K	Second Virial Coeff. of CO_2 cc/mol.	Density of Hg, g/cc	Calc. No. of Moles of CO_2	Calc. Volume cc	Run Average Volume cc
11	7	76.34	Hg 20.4	CO_2 293.91	-127.2	13.5448	.000094724		
		45.5306		292.22	-128.9	13.5481		3.7965_4	3.7968
		45.5165		292.18	-128.9	13.5483		3.7971_4	
12	7	76.31	Hg 20.2	CO_2 293.93	-127.2	13.5453	.000094683		
		45.6084		292.89	-128.2	13.5465		3.7976_3	3.7974
		45.5991		292.80	-128.3	13.5467		3.7971_7	
13	1	76.31	Hg 20.2	CO_2 293.93	-127.2	13.5453	.000054056		
		26.0444		292.63	-128.5	13.5471		3.7984_4	3.7982
		26.0530		292.68	-128.4	13.5470		3.7978_7	
14	3	76.08	Hg 20.3	CO_2 293.91	-127.2	13.5451	.000067936		
		32.7864		293.12	-128.0	13.5459		3.7970_5	3.7971
		32.7742		293.03	-128.1	13.5461		3.7972_4	
15	5	76.08	Hg 20.3	CO_2 293.91	-127.2	13.5451	.000076241		
		36.7516		292.88	-128.2	13.5465		3.7971_2	3.7975
		36.7225		292.71	-128.4	13.5469		3.7978_0	

Table 6. 4 cc Chamber Volume Calibrations - Results

Experiment Number - Small Manometer	Plenum No.	Corr. Hg. Height Diff. cm	Temperature °C	Temperature °K	Second Virial Coeff. of CO_2 cc/mol.	Density of Hg, g/cc	Calc. No. of Moles of CO_2	Calc. Volume cc	Run Average Volume cc
16	4	76.08	Hg 20.3	CO_2 293.91	-127.2	13.5451	.000072495		
		34.8562		292.19	-128.9	13.5482		3.7978_7	3.7979
		34.8486		292.14	-129.0	13.5484		3.7980_0	
17	1	76.08	Hg 20.3	CO_2 293.91	-127.2	13.5451	.000053895		
		25.9904		292.76	-128.4	13.5468		3.7967_9	3.7973
		25.9831		292.75	-128.4	13.5468		3.7977_3	

Summary:

Average of All Calibrations but No. 6	3.7971	σ = .0014 (of 15).
Average of All Calibrations but No. 3 & No. 6	3.7974	σ = .0007 (of 14).
Average of Calibrations Numbers 7 - 17	3.7974	σ = .0005 (of 11).

Notes: Calibrations 1 - 7 with CO_2 extracted from Na_2CO_3; calibrations 8 - 17 with CO_2 from gas cylinder.

* Discarded-premature contact of pointer in manometric measurement

Table 7. 5000 cc Chamber Volume Calibrations - Results

Experiment Number - Large Manometer	Gas	Corr. Hg Height Diff. cm	Temp. °K	Second Virial Coeff. cc/mol	Density of Hg, g/cc	Calc. No. of Moles of Gas	Calc. Vol. of Column No. 5, cc	Calc. Vol. of Column No. 6, cc
1	CO_2	63.4642	293.76	-127.4	13.5444	.136674		
		50.7036	293.90	-127.3	13.5440			4947.3_1
		50.0150	293.88	-127.3	13.5441		5015.2_8	
		50.6886	293.82	-127.3	13.5442			4947.3_4*
2	CO_2	61.9526	293.78	-127.4	13.5443	.133394		
		49.4299	293.56	-127.6	13.5448			4947.3_5
		48.7773	293.63	-127.5	13.5447		5015.0_2	
		49.4454	293.66	-127.5	13.5446			4947.5_7*
3	N_2	62.8702	292.88	-6.1	13.5465	.135251		
		50.2028	293.07	-6.1	13.5460			4946.5_1
4	N_2	50.1676	292.88	-6.1	13.5465	.107920		
		40.0517	293.00	-6.1	13.5462			4946.2_0
5	Ar	63.5165	293.44	-17.0	13.5451	.136419		
		50.5325	293.18	-17.1	13.5458			4957.1_0+
6	Ar	62.1521	293.13	-17.1	13.5459	.133636		
		49.2075	293.06	-17.1	13.5461			4984.6_4++
7	Ar	61.9861	293.35	-17.1	13.5454	.133174		
		49.4278	293.16	-17.1	13.5458			4947.0_6
8	N_2	63.3244	293.34	-6.0	13.5454	.136004		
		50.4855	293.10	-6.1	13.5459			4946.7_4
12	CO_2	62.8309	292.92	-128.2	13.5464	.135717		
		50.1240	292.63	-128.5	13.5471			4946.8_2**
		49.4934	292.90	-128.2	13.5465		5014.9_7	
		50.1530	292.83	-128.3	13.5466			4947.5_5*

* Rerun after transfers

** Column No. 6 possibly changed in volume due to breakage and repair.

\+ Experimental Problems - Ar gas froze in liquid N_2 during filling, resulting in probable contamination.

++ Error in procedure probably made.

(cont. on page 2.)

Table 7. 5000 cc Chamber Volume Calibrations - Results

		Calc. Vol. of Column No. 5, cc	Calc. Vol. of Column No. 6, cc	Standard Deviation of Measurement
Summary:	Average of 3	5015.0_9		$\sigma = 0.16$
	Average for CO_2 before transfer (of 3)		4947.1_6	$\sigma = 0.30$
	Average for CO_2 after transfer (of 3)		4947.4_9	$\sigma = 0.36$
	Average for N_2 (of 3)		4946.4_8	$\sigma = 0.27$
	Average for Ar (of 1)		4947.0_6	

Table 8. Volume Ratio Determinations by Expansion - Results

Nominal Volume of Chamber (cc)	Corr. Hg Height Diff (cm)	Temp. (°K)	Second Virial Coeff. (cc/mol.)	Density of Hg, (g/cc)	V/n (cc/mol.)	Summary of Results
I. Experiment Number 5 - Small Manometer Volume Calibrations 16 cc/4 cc Volume Ratio Determination Using CO_2						
4	45.5120	293.13	-128.0	13.5459	40229.2	Average (V/n) (of 3) = 40234.2 cc/mol σ=4.64
16	10.8440	293.00	-128.1	13.5462	169173.	4 cc
16	10.8432	293.04	-128.1	13.5461	169210.	
4	45.4938	293.06	-128.1	13.5461	40235.0	
16	10.8408	293.02	-128.1	13.5461	169236.	Average (V/n) (of 5) = 169234. cc/mol σ=44.7
4	45.5279	293.29	-127.8	13.5455	40238.4	16 cc
16	10.8415	293.08	-128.1	13.5459	169262.	
16	10.8398	293.08	-128.1	13.5459	169288.	Average 16 cc/4 cc = 4.2062 σ = .0012*
II. Experiment Numbers 9, 10 and 11 - Large Manometer Volume Calibrations 5000 cc/1000 cc Volume Ratio Determinations in Column Number 5 Using N_2						
1000	63.3560	293.34	-6.0	13.5454	29006.8	5000 cc/1000 cc = 4.9046
5000	12.9026	292.97	-6.1	13.5463	142267.	
1000	65.0524	297.99	-5.1	13.5340	28723.3	5000 cc/1000 cc = 4.9057
5000	13.2789	298.34	-5.0	13.5332	140907.	
1000	64.7185	293.78	-5.9	13.5443	28441.0	5000 cc/1000 cc = 4.9033
5000	13.2224	294.23	-5.8	13.5432	139456.	

Average of 3 Determinations = 4.9045 σ = .0012

* σ of $V_{16\text{ cc}/4\text{ cc}} = 4.2062 \sqrt{\left(\frac{\sigma}{V/n}\right)^2_{4\text{ cc}} + \left(\frac{\sigma}{V/n}\right)^2_{16\text{ cc}}}$

Table 9. Manometric System Volume Ratio Summary

Nominal Volumes	Year of Measurement 1959	1961	1972	1974	Average[1]	Standard Deviation[1]
16cc/4cc	4.2013	4.2058	4.2068	4.2062	4.2046	.0029
64cc/16cc	3.9641	3.9619	3.9586		3.9615	.0028
250cc/64cc	5.1174	5.1124	5.1168		5.115	.0027
1000cc/250cc	3.1544	3.1544	3.1539		3.1542	.0003
5000cc/1000cc	4.9034	4.9056	4.9058	4.9045[2]	4.9049	.0013
5000cc/4cc overall ratio	1318.2_3	1318.2_1	1318.4_1	1320.6_6[3]	1318.2_3[1]	1.52[1,4]

1. Not including 1974 determinations
2. Using N_2 instead of CO_2
3. Ratio of Calibrated Volumes (5015.09 cc/3.7974 cc)
4. Computed by the formula:

$$(\sigma/R)_{\text{overall}} = \sqrt{\sum_{i=1}^{5} \left(\sigma_i/R_i\right)^2}$$

where R_i denotes the i^{th} volume ratio

Appendix 1. Large Manometer Volume Calibrations-Pointer Heights

Experiment No.	Date	Large Manometer Column No.	Pointer Height, mm
1	18 JUN 74	6	176.206
	19 JUN 74	6	176.230
	19 JUN 74	5	173.430
	19 JUN 74	6	176.188
2	20 JUN 74	6	176.210
	20 JUN 74	6	176.206
	20 JUN 74	5	173.400
	21 JUN 74	6	176.240
3	25 JUN 74	6	176.484
	25 JUN 74	6	176.420
4	25 JUN 74	6	176.460
	25 JUN 74	6	176.410
5	26 JUN 74	6	176.460
	26 JUN 74	6	176.470
6	27 JUN 74	6	176.416
	27 JUN 74	6	176.410
7	2 JUL 74	6	176.450
	2 JUL 74	6	176.420
8	3 JUL 74	6	176.434
	3 JUL 74	6	176.410
9	3 JUL 74	5	173.662
	3 JUL 74	5	173.610
10	5 JUL 74	5	173.632
	5 JUL 74	5	173.640
11	9 JUL 74	5	173.644
	9 JUL 74	5	173.600
12	13 AUG 74	6	176.670
	13 AUG 74	6	176.640
	13 AUG 74	5	173.870
	14 AUG 74	6	176.670

Appendix 2. Small Manometer Volume Calibrations-Pointer Heights

Experiment No.	Date	4cc Pointer Height or 16cc Pointer Height* mm
1	21 JUN 74	370.640
	21 JUN 74	370.608
2	21 JUN 74	370.600
	21 JUN 74	370.590
3	26 JUN 74	370.862
	26 JUN 74	370.830
4	27 JUN 74	370.816
	27 JUN 74	370.810
	28 JUN 74	370.840
5	27 JUN 74	370.816
	27 JUN 74	309.670*
	27 JUN 74	309.642*
	27 JUN 74	370.810
	27 JUN 74	309.648*
	28 JUN 74	370.840
	28 JUN 74	309.666*
	28 JUN 74	309.660*
6	9 JUL 74	370.805
	9 JUL 74	370.788
7	10 JUL 74	370.812
	10 JUL 74	370.830
8	29 JUL 74	370.840
9	30 JUL 74	370.834
	30 JUL 74	370.820
10	30 JUL 74	370.810
	30 JUL 74	370.820
11	30 JUL 74	370.810
	30 JUL 74	370.806
12	1 AUG 74	371.100
	1 AUG 74	371.084
13	1 AUG 74	371.040
	2 AUG 74	371.094
14	7 AUG 74	371.080
	7 AUG 74	371.100
15	8 AUG 74	371.108
	8 AUG 74	371.091
16	8 AUG 74	371.040
	8 AUG 74	371.060
17	9 AUG 74	371.070
	9 AUG 74	371.083