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# Evaluation of a cation isotopic substitution technique in conjunction with a high temperature gas pycnometer for determining the stoichiometry of materials

Michael Clair Graves

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EVALUATION OF A CATION ISOTOPIC SUBSTITUTION TECHNIQUE  
IN CONJUNCTION WITH A HIGH TEMPERATURE GAS PYCNOMETER  
FOR DETERMINING THE STOICHIOMETRY OF MATERIALS

BY

MICHAEL CLAIR GRAVES, 1947-

A THESIS

Presented to the Faculty of the Graduate School of the

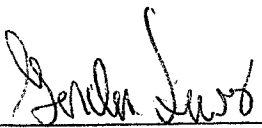

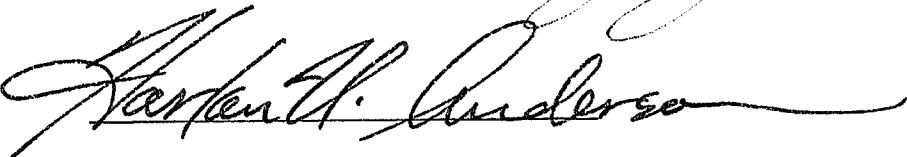
UNIVERSITY OF MISSOURI-ROLLA

In Partial Fulfillment of the Requirements for the Degree

MASTER OF SCIENCE IN CERAMIC ENGINEERING

1971

Approved by

 \_\_\_\_\_ (Advisor)  \_\_\_\_\_  


## PUBLICATION THESIS OPTION

This thesis has been prepared in the style utilized by the Journal of the American Ceramic Society. Pages 1 to 30 will be presented for publication in that journal. Appendices F and G have been added for purposes normal to thesis writing.

## ABSTRACT

This study was concerned with the evaluation of a high temperature gas pycnometer, used in conjunction with a cation isotopic substitution technique, for determining the stoichiometry of materials. Three methods were investigated for determining the correction factors for the thermal gradient effects in the gas pycnometer. The correction factors were shown to be dependent on the temperature, the sample volume, and the height of the sample in the sample chamber. Under the conditions of these experiments, the correction factors were shown to be essentially independent of sample grain size and pycnometer atmosphere. The determination of the stoichiometry of cadmium oxide proved inconclusive because the compositional range is such that the change in density is less than the propagated error of the system. The isotope exchange method of stoichiometry determination could prove useful as a complementary method in determining stoichiometry and defect type.

## ACKNOWLEDGEMENTS

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## I. INTRODUCTION

This study is concerned with the evaluation of a method for determining the defect structure of crystalline solids. The method utilizes a high temperature gas pycnometer and thermogravimetric analysis. The weights and volumes determined are used in calculating the densities of the materials. The densities are used in conjunction with a cation isotopic substitution technique to establish the feasibility of this technique in determining the defect structure of the material.

Experimentalists throughout the years have obtained density data from experiments conducted on materials which have been quenched from high temperature to room temperature. Some of the external or internal reactions which took place in attaining the equilibrium at high temperature must be frozen in upon cooling to room temperature, thus the quenched material is in a metastable state of equilibrium when investigated. The method used in this study will allow measurements to be taken at high temperatures under equilibrium conditions.

## II. EXPERIMENTAL

### A. Equipment

The high temperature gas pycnometer is shown schematically in Figure 1 and is similar to that used by Atlas, Schlehman, and Readey<sup>(1)</sup>. The furnace (1) was wound with Kanthal A-1 wire and could be operated up to 900°C. The sample chamber (2) was a 1/2 inch O.D. Coors AD 998 Alumina Tube. The vacuum coupling (3) used to connect the sample chamber with the glass system was a Cajon ultra-torr reducing union. This was protected from the hot zone of the furnace by a water-cooled copper coil (6). A Gilmont microburette (4) was used to produce a change in the volume of the pycnometer. The corresponding change in pressure was measured with a Texas Instruments precision pressure gage with micron gearing (5).

Furnace temperatures were maintained with a Leeds and Northrup low-level set point unit and a current-adjusting type temperature controller. A chromel-alumel thermocouple was used to determine the temperature of the furnace and sample. The temperature profile of the furnace was obtained at each temperature. The furnace was placed around the sample chamber so that the sample was in a zone (3-1/2 inches in length) with a temperature variation of  $\pm 10^\circ\text{C}$ . This variation made it unnecessary to calibrate the chromel-alumel thermocouple.

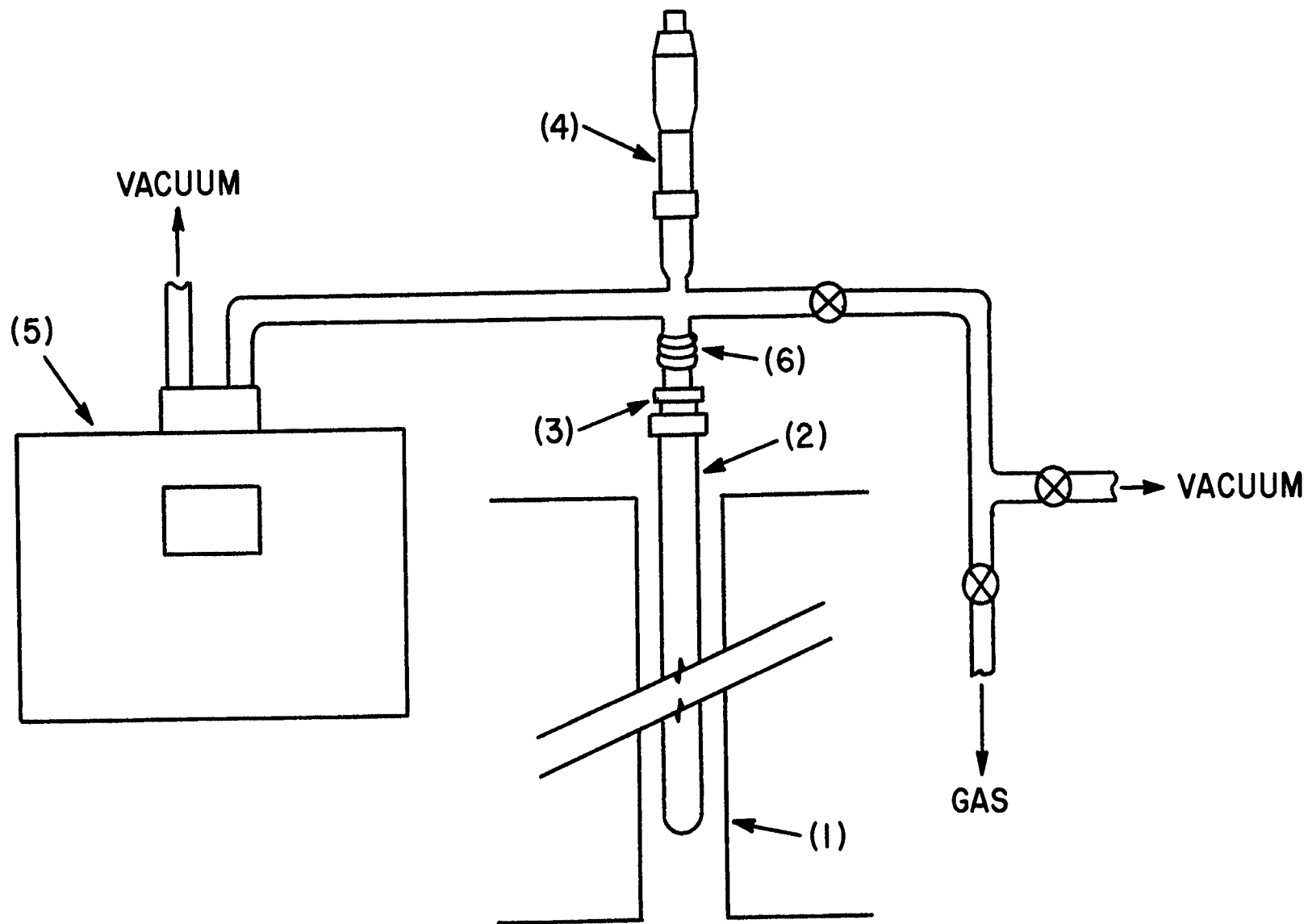


Figure 1. High Temperature Gas Pycnometer

A Mettler Thermoanalyzer, used in the thermogravimetric mode, was used to investigate the change in sample weight with time as the gaseous atmosphere was changed from oxidizing to neutral at the selected temperatures.

## B. Materials

Cadmium oxide was used in the present study, because of its availability in isotopically enriched form. The high vapor pressure of the cadmium oxide and the transport of the material under reducing conditions made it necessary to do a thermogravimetric analysis of the material. Two samples were used;  $\text{Cd}^{112.40}_0$  which will be referred to as the natural sample, and  $\text{Cd}^{112.74}_0$  as the enriched sample. The natural  $\text{Cd}_0$  was 'Baker analyzed' reagent grade material. The enriched  $\text{Cd}_0$  sample was prepared by combining known amounts of the natural,  $\text{Cd}^{112.40}_0$ , and an enriched sample,  $\text{Cd}^{114.00}_0$ , obtained from Oak Ridge National Laboratory. Data are given in Table I on the isotopic analysis of each sample. The two components, prior to mixing, were treated by heating to  $850^\circ\text{C}$  in an oxygen atmosphere (0.724 atm.)

Two alumina samples were used in the calibration runs, a sample of Norton's alundum and a sample from Fisher Scientific of particle size less than 250 micron and less than 44 micron respectively. The reported density of the samples was  $3.98^{(4)} \text{ g/cm}^3$ . This value was used in calculating the initial volume of each sample from a weighed quantity of the material.

TABLE I

ANALYSIS OF  $\text{Cd}^{112.74}\text{O}$  SAMPLEWeight of  $\text{Cd}^{112.40}\text{O}$  = 4.2123gWeight of  $\text{Cd}^{114.00}\text{O}$  = 1.1335gYields 5.3458g  $\text{Cd}^{112.74}\text{O}$ 

## Isotopic Composition

## Atomic Percent

Isotope	$\text{Cd}^{112.40}\text{O}^{(2)}$	$\text{Cd}^{114.0}\text{O}^{(3)}$
106	1.22	<0.02
108	0.88	<0.02
110	12.39	0.04
111	12.75	0.06
112	24.07	0.18
113	12.26	0.25
114	28.86	99.38
116	7.58	0.08

The gases used in the pycnometer were Linde's high purity, dry argon (99.996%) and oxygen (99.5%). No additional purification of the gases was made prior to flowing into system.

### C. Procedure\*

The data were taken as a function of gas atmosphere, temperature and sample material. The total pressure of the gas in the pycnometer was maintained at 0.724 atm., because this was the highest initial pressure possible to operate in the range of the pressure gage after heating. The four system atmospheres used were oxygen and argon, each at 0.724 atm. and two mixtures of oxygen and argon having oxygen partial pressures of  $10^{-1}$  and  $10^{-2}$  atm. respectively and total pressures of 0.724 atm. (see Table II). The two component atmospheres were prepared by backfilling with oxygen to the correct partial pressure, then with argon to obtain the correct total pressure. These atmospheres were chosen to provide different oxygen activities while maintaining a constant total system pressure.

The 500°, 600°, 700° and 800°C. temperatures were chosen because the Mettler thermograms indicated that cadmium oxide was unreactive below 500°C, and that above 800°C., vaporization and transport became significant.

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\* A detailed experimental procedure can be found in Appendix A, Masters Thesis by Michael C. Graves, University of Missouri-Rolla, 1971.

TABLE II  
PYCNOMETER ATMOSPHERES

Atmosphere (atm)	$P_p^*$ Argon (atm)	$P_p^*$ Oxygen (atm)	Total (atm)
Oxygen 0.724	-----	0.724	0.724
Oxygen $10^{-1}$	0.624	0.100	0.724
Oxygen $10^{-2}$	0.714	0.010	0.724
Argon 0.724	0.724	-----	0.724

\* Partial Pressures

The weights of both cadmium oxide samples at the selected temperatures and atmospheres were used together with the corresponding calculated volumes to obtain the densities of the samples. The weights were determined by thermogravimetric analysis on a representative sample of each material using the Mettler Thermoanalyzer. The weight gain or loss per gram of sample was determined and used to correct the weights of the cadmium oxide samples used in the pycnometer.



### III. RESULTS AND DISCUSSION

The working principle of the high temperature gas pycnometer is based upon the perfect gas law in the form<sup>(1)</sup>:

$$V_s = V_p - \frac{\Delta V_B}{1 - \gamma(P_1/P_2)} \quad (1)$$

where:

$V_s$  = the net volume of the sample

$V_p$  = the net volume of the pycnometer

$\Delta V_B$  = the change in the microburette volume  
(2.500 cm<sup>3</sup>)

$\gamma$  = an empirical correction factor for thermal  
gradient effects

$P_1$  = the initial pressure

$P_2$  = the final pressure

One of the characteristics of the above equation, using  $\gamma = 1$ , was an apparent decrease in pycnometer volume with increasing temperature. The decreasing pycnometer volumes are given in Table III together with the net volumes of the pycnometer at the elevated temperatures. Figure 2 shows graphically the apparent volume effect versus temperature. The net volumes were calculated from the experimental room temperature volume (no thermal gradient effect) and the increase in volume resulting from the thermal expansion

TABLE III  
PYCNOMETER VOLUMES

Temp. (°C)	Experimental* $V_p$ (cm <sup>3</sup> )	Net $V_p$ (cm <sup>3</sup> )
25	30.335	30.335
500	23.157	30.408
600	22.605	30.424
700	22.041	30.445
800	21.517	30.465

\* Results from Equation (1) with  $\gamma \equiv 1$  and  $V_s \equiv 0$

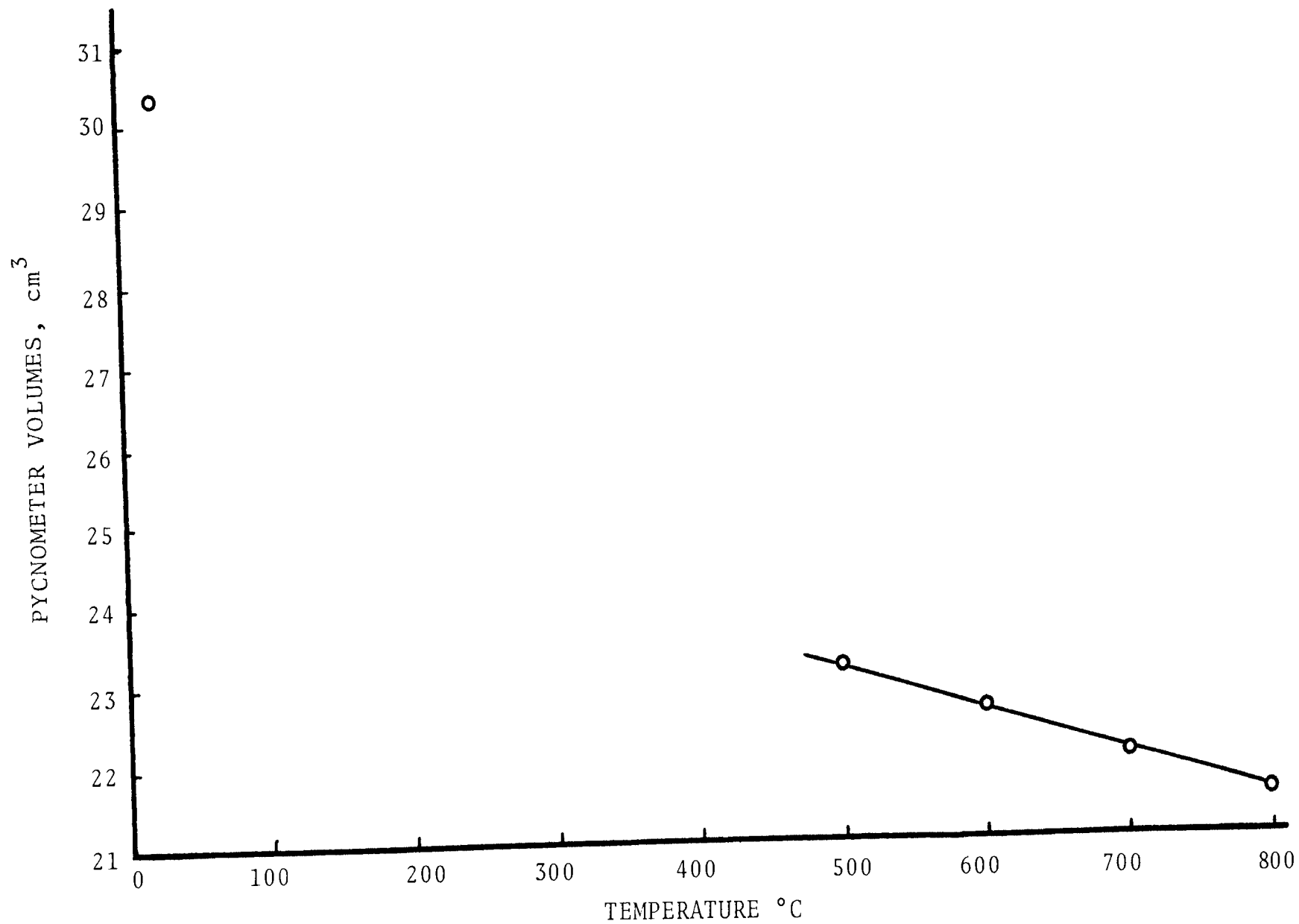


Figure 2. Experimental Pycnometer Volumes

of the alumina sample chamber upon heating. The apparent decrease in the pycnometer volumes is due to the fact that only a portion of the total pycnometer system is being heated. Thus the changing thermal gradient necessitates calibration of the pycnometer system.

The calibration was accomplished using data obtained with an empty pycnometer and with the pycnometer filled with three different volumes of alumina. The calibration data were taken in an oxygen atmosphere of 0.724 atm., Table IV. The sample heights are  $\pm 1/4$  inch. The net  $V_s$  is the volume of the sample including the increase due to the thermal expansion of the material.

The correction factors obtained from the calibration data were found to be dependent on the temperature, sample volume and height in the sample chamber as shown in Figure 3. In the analysis of the parameters that influence the correction factors, it was noted that the grain size of the material (sample volume of 1.44  $\text{cm}^3$  had a grain size of less than 250 micron and the material having a sample volume of 2.73  $\text{cm}^3$  had a grain size of less than 44 micron) and the atmosphere in the pycnometer (Figure 4) had little or no apparent effect on the thermal gradient.

TABLE IV  
CALIBRATION DATA

Temp. (°C)	Sample	Sample Height (in)	Net V <sub>S</sub> (cm <sup>3</sup> )	$\frac{P_1}{P_2}$ Exp.	$\frac{P_1}{P_2}$ Calc.	$\frac{1}{\bar{\gamma}}$	$\gamma'^{**}$	$\Delta V_B(\text{con})$	F <sup>+</sup>
25	None	0	0	0.917586	0.917586	1.00000	12.145	2.500	1.0898
500			0	0.892041	0.917785	0.97195	12.514	2.500	1.0896
600			0	0.889405	0.917828	0.96903	12.559	2.500	1.0895
700			0	0.886575	0.917885	0.96589	12.608	2.500	1.0895
800			0	0.883813	0.917939	0.96282	12.657	2.500	1.0894
25	Alumina Powder ( $<250\mu$ )	1	0.609	0.915958	0.915958	1.00000	11.890	2.4471	1.0897
500			0.618	0.893928	0.916079	0.97582	12.211	2.5447	1.0934
600			0.620	0.890197	0.916119	0.97171	12.269	2.5186	1.0923
700			0.622	0.888914	0.916172	0.97025	12.295	2.5593	1.0939
800			0.624	0.887204	0.916223	0.96833	12.327	2.5852	1.0948
25	Alumina Powder ( $<250\mu$ )	3	1.441	0.913599	0.913477	1.00013	11.556	2.3743	1.0895
500			1.462	0.891077	0.913632	0.97531	11.872	2.4467	1.0923
600			1.466	0.887620	0.913668	0.97149	11.923	2.4555	1.0927
700			1.472	0.885073	0.913713	0.96865	11.964	2.4632	1.0929
800			1.476	0.882866	0.913760	0.96619	12.001	2.4772	1.0934
25	Alumina 60 Mesh ( $<44\mu$ )	3	2.726	0.909581	0.909450	1.00014	11.042	2.2587	1.0891
500			2.766	0.889061	0.909558	0.97747	11.312	2.4059	1.0953
600			2.774	0.886338	0.909584	0.97444	11.350	2.4243	1.0961
700			2.784	0.883807	0.909620	0.97162	11.388	2.4328	1.0964
800			2.793	0.882009	0.909656	0.96961	11.418	2.4569	1.0974

$$* \frac{1}{\bar{\gamma}} = \frac{P_1/P_2 \text{ Exp.}}{P_1/P_2 \text{ Calc.}} \pm 0.000001$$

$$** \text{ Equation (3)}$$

$$+ \text{ Equation (4)}$$

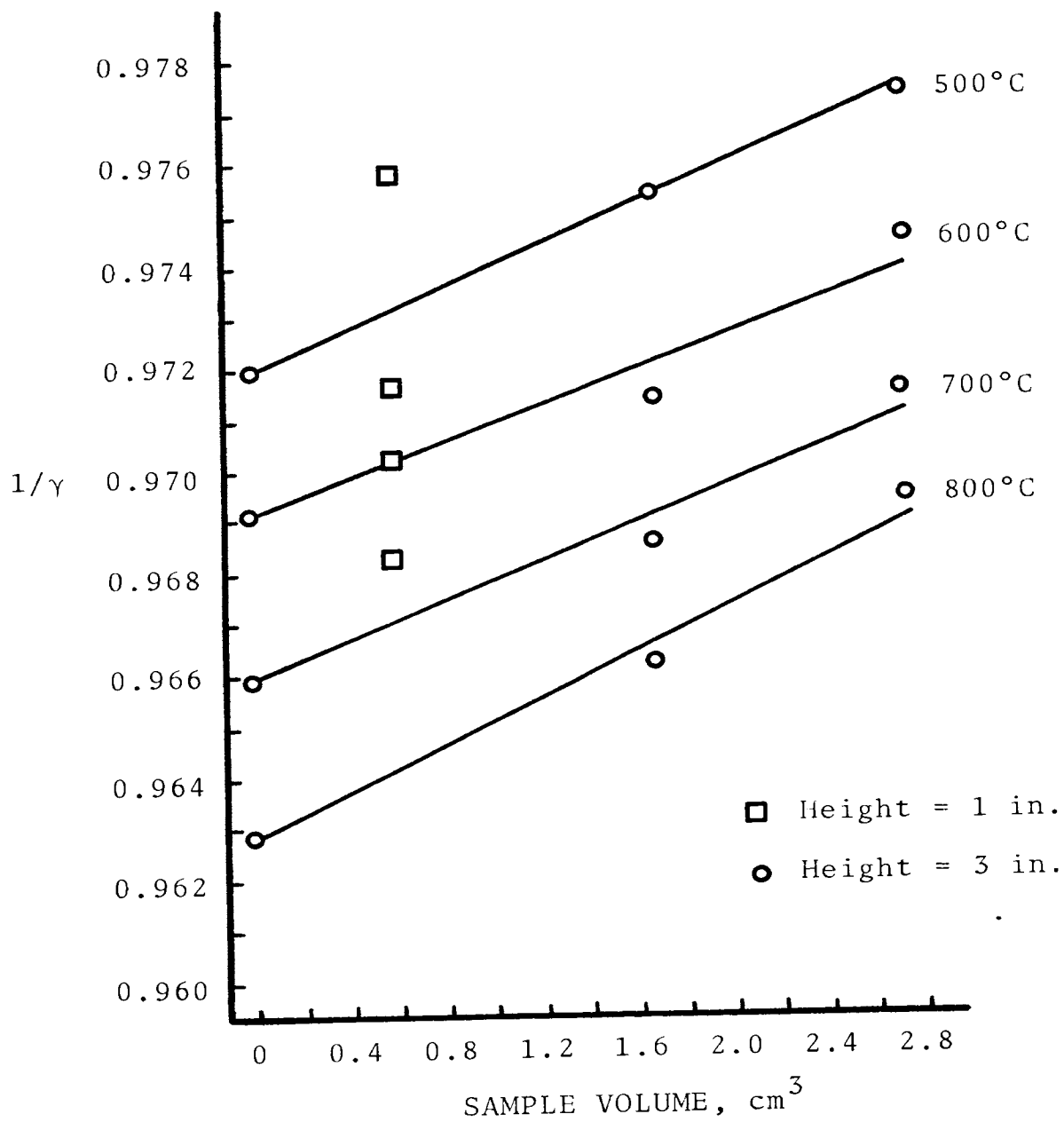


Figure 3. Volume Effect on Correction Factors

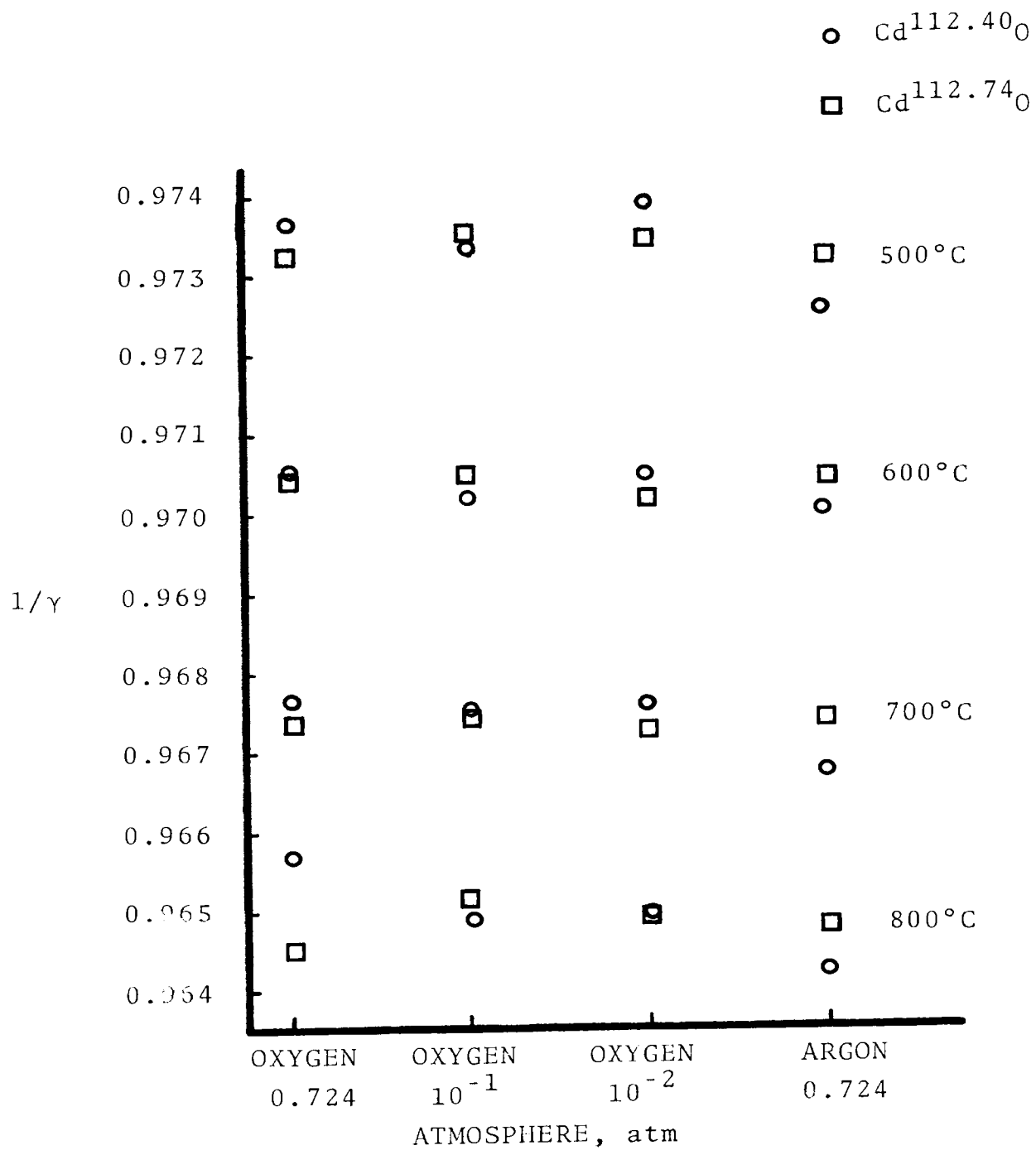


Figure 4. Effect of Atmosphere on the Correction Factors

The  $\gamma$  factor\* in Equation (1) is the inverse of the ratio of the experimental  $P_1/P_2$  to the calculated  $P_1/P_2$ . The calculated  $P_1/P_2^\dagger$  was determined by solving Equation (1) for  $P_1/P_2$ ,  $\gamma = 1$ , and then evaluating it using the calibration data. The reciprocal  $\gamma$  factors are listed in Table IV together with the experimental and calculated  $P_1/P_2$  ratios.

The  $\gamma$  factors in Table V were determined for both cadmium oxide samples by interpolation from Figure 3, at the respective 25° volume of each sample. These were used in Equation (1) to calculate the volumes of the cadmium oxide samples. Sample densities were obtained using these calculated volumes, (column 4) Tables VI and VII and the corresponding weights. A calculation of the expected precision of the density measurements\*\* ( $\pm 0.5 \text{ g/cm}^3$ ), which is based on experimental errors in the volume and mass data, shows that the range of densities obtained is far greater than the method should generate. Examination of Equation (1) indicates that a small error in the  $\gamma$  factor propagates a much larger error in the calculated volume. A change of 0.0001 in the  $\gamma$  factor used in calculating the volume of natural

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\*  $\gamma$  factor calculation can be found in Appendix B, Masters Thesis by Michael C. Graves, University of Missouri-Rolla, 1971.

† A sample calculation of  $P_1/P_2$  calculated can be found in Appendix C, Masters Thesis by Michael C. Graves, University of Missouri-Rolla, 1971.

\*\* An error analysis can be found in Appendix D, Masters thesis by Michael C. Graves, University of Missouri-Rolla, 1971.



TABLE V  
SUMMARY OF CORRECTION FACTORS

Temp (°C)	Sample	$\gamma^*$	$\gamma, \dagger$
25	Cd <sup>112.40</sup> O	1	11.882
500		1.027	12.235
600		1.031	12.281
700		1.034	12.327
800		1.037	12.371
25	Cd <sup>112.74</sup> O	1	11.895
500		1.028	12.249
600		1.031	12.295
700		1.034	12.342
800		1.037	12.386
*	$\pm$ 0.04		
†	$\pm$ 0.001		

TABLE VI

CALCULATED VOLUMES AND DENSITIES OF Cd<sup>112.40</sup><sub>0</sub>

Temp. (°C)	Atm. (atm)	Sample Weight (g)	Equation (1)		Equation (3)	
			V <sub>s</sub> * (cm <sup>3</sup> )	ρ (g/cm <sup>3</sup> )	V <sub>s</sub> + (cm <sup>3</sup> )	ρ (g/cm <sup>3</sup> )
25	Oxygen 0.724	5.1800	0.577	8.98	0.622	8.33
500		5.1621	0.513	10.06	0.626	8.25
600		5.1620	0.554	9.32	0.629	8.21
700		5.1617	0.523	9.87	0.625	8.26
800		5.1615	0.189	27.31	0.601	8.59
25	Oxygen 10 <sup>-1</sup>	5.1576	0.586	8.80	0.626	8.24
500		5.1579	0.616	8.37	0.635	8.12
600		5.1579	0.654	7.89	0.635	8.12
700		5.1582	0.561	9.20	0.628	8.21
800		5.1579	0.463	11.14	0.624	8.27
25	Oxygen 10 <sup>-2</sup>	5.1566	0.521	9.90	0.620	8.32
500		5.1563	0.433	11.91	0.620	8.32
600		5.1561	0.534	9.66	0.627	8.22
700		5.1560	0.534	9.66	0.626	8.24
800		5.1558	0.457	11.28	0.623	8.28
25	Argon 0.724	5.1566	0.562	9.18	0.624	8.26
500		5.1561	0.874	5.90	0.657	7.85
600		5.1561	0.693	7.44	0.640	8.06
700		5.1557	0.814	6.33	0.649	7.94
800		5.1555	0.688	7.49	0.642	8.03
		* ± 1.2 cm <sup>3</sup>	+ ± 0.04 cm <sup>3</sup>			

TABLE VII

CALCULATED VOLUMES AND DENSITIES OF  $\text{Cd}^{112.74}_0$ 

Temp (°C)	Atm. (atm)	Sample Weight (g)	Equation (1)		Equation (3)	
			$V_s^*$ ( $\text{cm}^3$ )	( $\text{g}/\text{cm}^3$ )	$V_s^+$ ( $\text{cm}^3$ )	( $\text{g}/\text{cm}^3$ )
25	Oxygen 0.724	4.9281	0.504	9.78	0.590	8.35
500		4.9217	0.590	8.34	0.604	8.15
600		4.9216	0.495	9.94	0.595	8.27
700		4.9214	0.541	9.10	0.597	8.24
800		4.9213	0.532	9.25	0.600	8.20
25	Oxygen $10^{-1}$	4.9215	0.524	9.39	0.591	8.33
500		4.9151	0.500	9.83	0.596	8.25
600		4.9150	0.467	10.53	0.593	8.29
700		4.9151	0.512	9.60	0.505	8.26
800		4.9150	0.304	16.17	0.581	8.46
25	Oxygen $10^{-2}$	4.9125	0.488	10.07	0.588	8.35
500		4.9096	0.509	9.65	0.597	8.22
600		4.9093	0.587	8.91	0.603	8.14
700		4.9092	0.582	8.44	0.601	8.17
800		4.9090	0.401	12.24	0.589	8.33
25	Argon 0.724	4.9090	0.459	10.70	0.586	8.38
500		4.9045	0.579	8.47	0.603	8.13
600		4.9052	0.478	10.26	0.593	8.27
700		4.9049	0.552	8.89	0.598	8.20
800		4.9048	0.475	10.24	0.592	8.29

\*  $\pm 1.2 \text{ cm}^3$ +  $\pm 0.04 \text{ cm}^3$

cadmium oxide at 500°C in an oxygen atmosphere (0.724 atm.) yields a change in volume of 0.09 cm<sup>3</sup>. The expected density of cadmium oxide is 8.15 g/cm<sup>3</sup> (5).

The next method used the approximation:

$$\frac{1}{1-x} = 1 + x \quad (2)$$

where:

$$x \equiv \gamma P_1/P_2.$$

This approximation, substituted into Equation (1) gives:

$$V_s = V_p - \Delta V_B (1 + \gamma' P_1/P_2) \quad (3)$$

The values of  $\gamma'$  were obtained from the calibration data, and are presented in Table IV. The graphical representation of the  $\gamma'$  factors versus sample volume, Figure 5, shows the same dependence on temperature, sample volume, and sample height as shown in Figure 3. The interpolated  $\gamma'$  factors for the cadmium oxide data, summarized in Table V, were used in Equation (3) to obtain volumes of the samples (column 6, Tables VI and VII). The volumes obtained using this method, as well as the calculated densities, fall within expected error limits (8.15 g/cm<sup>3</sup>  $\pm$  0.5 g/cm<sup>3</sup>). Additional support for this calculation is provided by comparing the thermal expansion of cadmium oxide with that obtained from Figure 6 where the volume of the natural cadmium oxide samples in three oxygen atmospheres was plotted versus temperature. The linear thermal expansion was found to be

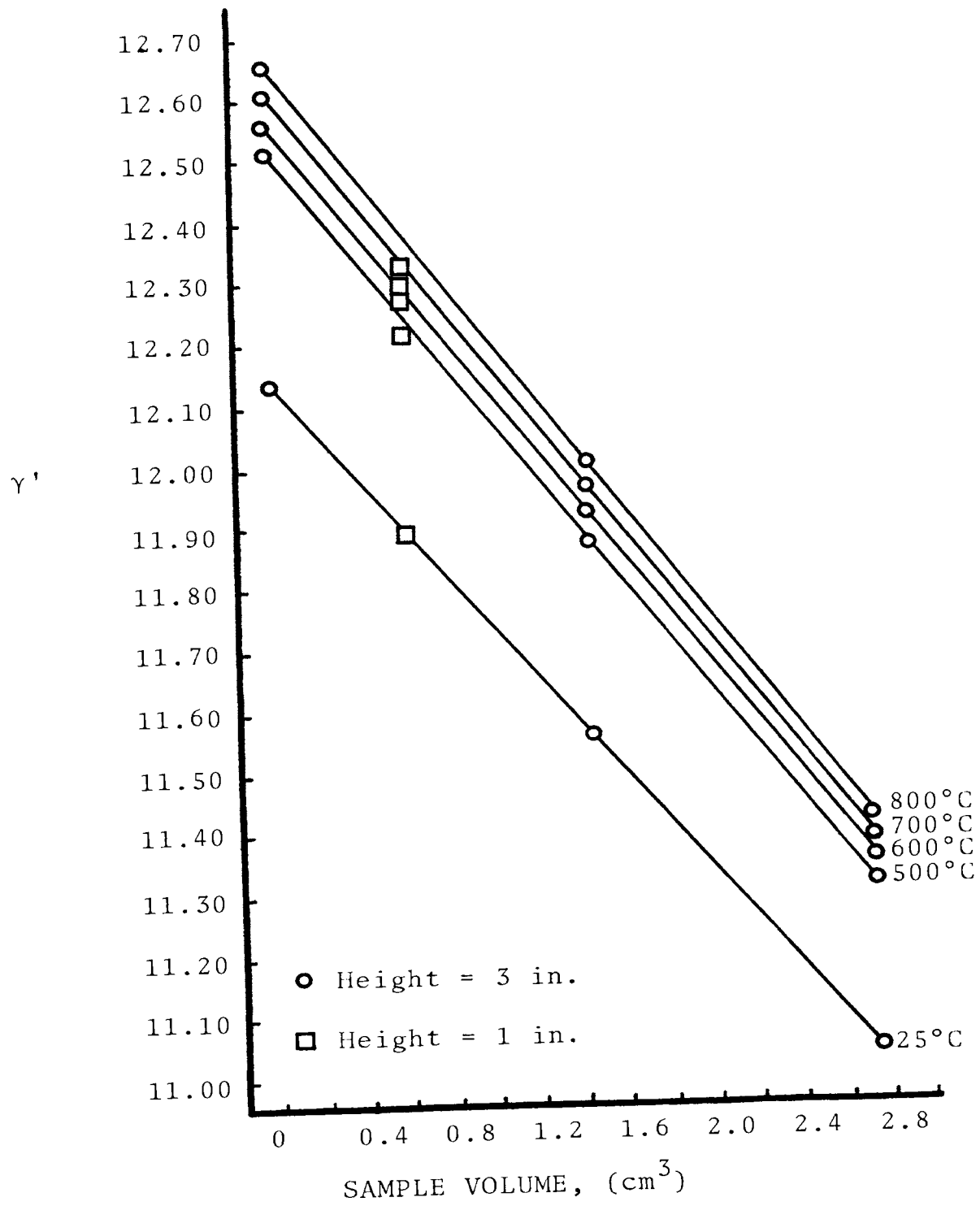


Figure 5. Correction Factors Utilizing Approximation

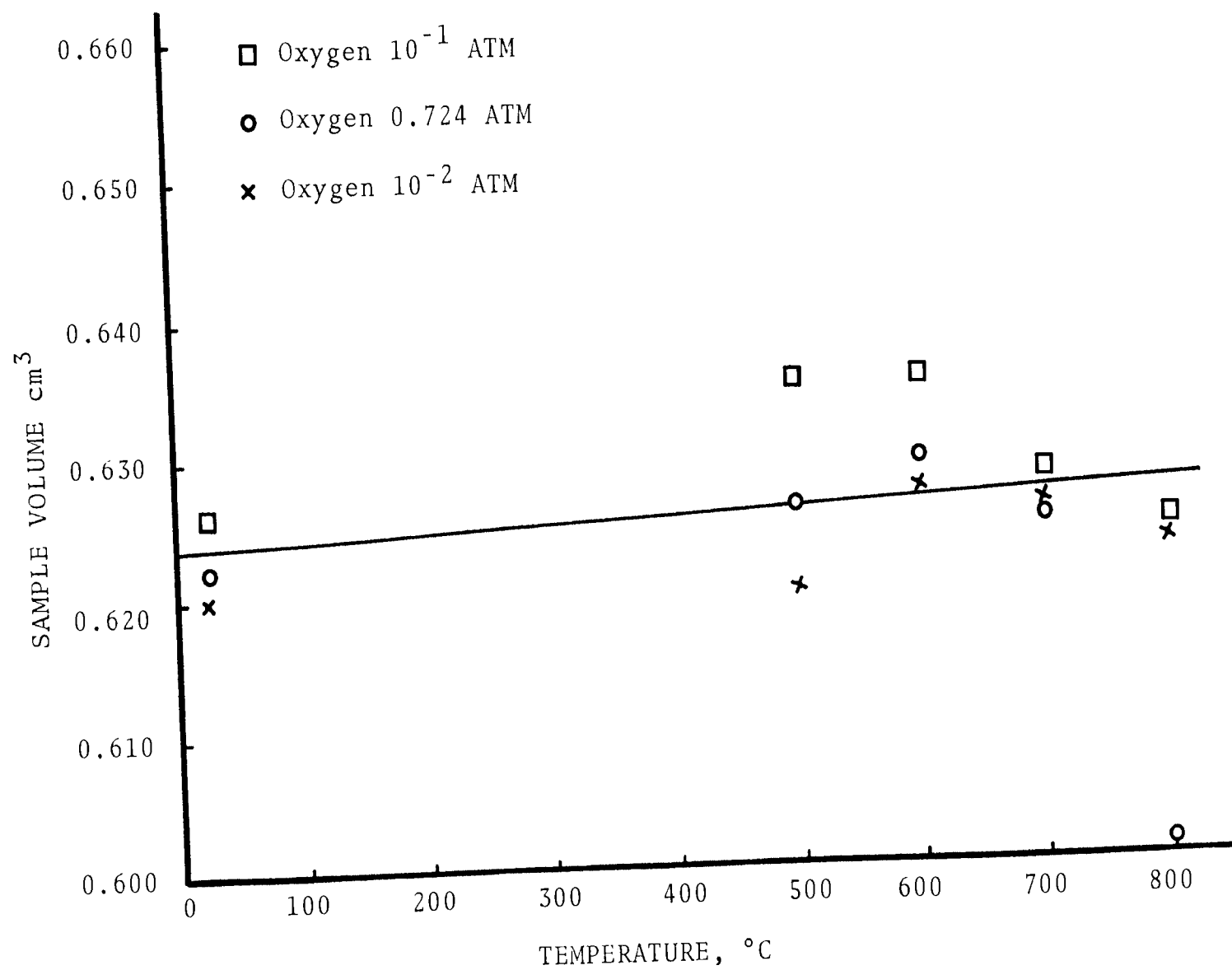


Figure 6. Thermal Expansion of Cd<sup>112.400</sup>.

$9.6 \times 10^{-6} \pm 9$  in/in/°C from a linear least squares fit of Figure 6, this is within an order of magnitude of that reported in the literature,  $14.33 \times 10^{-6}$  (6).

Atlas (7) used another method in the evaluation of the high temperature gas pycnometer, namely that:

$$V_s = \frac{V_p - F(V_p - \Delta V_B)}{1 - F} \quad (4)$$

where:

$$F \equiv \frac{T_i}{T_f} \frac{P_2}{P_1}$$

the experimental procedure differed from the present one in that a constant  $\Delta P$  was maintained and  $\Delta V_B$  was varied. Therefore, the data in this study had to be put in another form to employ the above equation. The data taken at various initial pressures were converted to a given initial pressure reading (205.0000) using:

$$\Delta P_{(\text{converted})} = (P_2/P_1 - 1) 205.0000 \quad (5)$$

The  $\Delta V_{B(\text{converted})}$  was obtained from:

$$\Delta V_{B(\text{converted})} = \Delta V_{B(\text{empty pycn.})} \times \frac{\Delta P_{(\text{converted})}}{\Delta P_{(\text{converted empty pycn.})}} \quad (6)$$

F factors were calculated using Equation (4) and the calibration data from Table IV. The cadmium oxide volumes obtained using the interpolated F factors from Figure 7 are given in Table VIII (column 6) together with the F

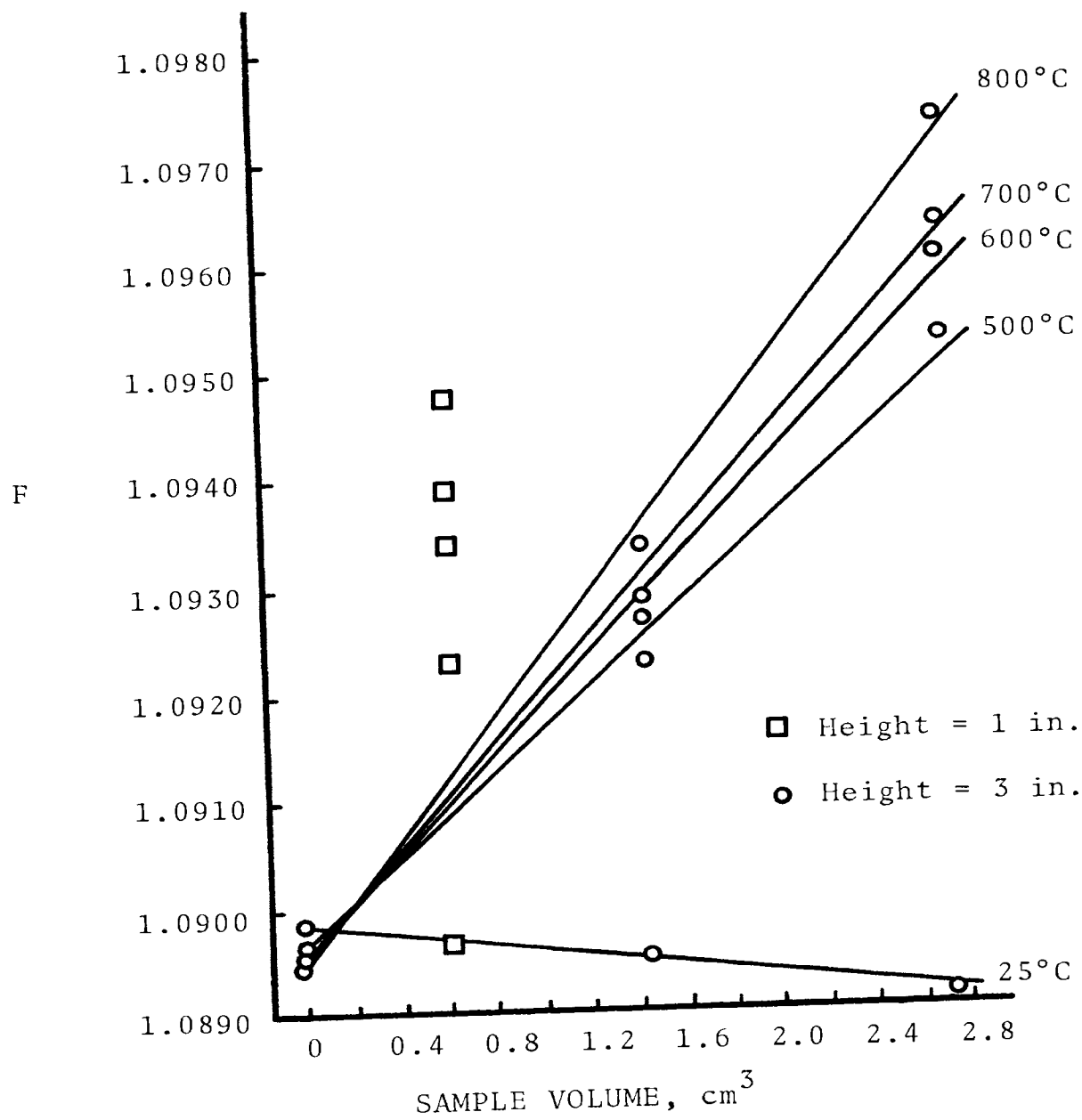


Figure 7. F Correction Factors



TABLE VIII

## RESULTS USING THE F CORRECTION FACTOR

Temp. (°C)	Sample	Atm. (atm)	$\Delta V_{B(\text{con})}$	F*	$V_s$ (cm <sup>3</sup> )	F calc.	$V_s$ (cm <sup>3</sup> )
25	Cd <sup>112.40</sup> <sub>0</sub>	Oxygen	2.4517	1.08965	0.536	1.08995	0.628
500		0.724	2.4973	1.09083	0.537	1.09153	0.628
600			2.4900	1.09093	0.550	1.09119	0.628
700			2.4978	1.09102	0.505	1.09143	0.628
800			2.5238	1.09118	0.264	1.09239	0.628

\*  
± 0.0001

factors calculated to give sample volumes of  $0.628 \text{ cm}^3$ . This corresponds to the calculated volume of the natural cadmium oxide at  $25^\circ\text{C}$  from the initial weight and the density of  $8.15 \text{ g/cm}^3$ . It can be seen from Table VIII, that a very small change in the F factor results in a very large one in the calculated volume. In other words, this method, like the first results in a large propagated error.

Therefore, it appears that the second method utilizing the approximation formula gives the best results of the three methods tried. It should be noted that the exact solution of the approximation formula used in the second method is:

$$\frac{1}{1-x} = 1 + x + x^2 + \dots \quad (7)$$

It was found that the first two terms were sufficient in determining the  $\gamma'$  factors.

The exact nature of the defect structure of cadmium oxide is yet to be established, although oxygen vacancy models have been proposed by Koffyberg<sup>(8)</sup> and Haul and Just<sup>(9)</sup>, and cadmium interstitial models by Cimino and Marezio<sup>(10)</sup> and Engell<sup>(11)\*</sup>. The direct determination of the stoichiometry of cadmium oxide and hence the defect type using the high temperature gas pycnometer densities is

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\* A review of the literature on the defects in cadmium oxide can be found in Appendix E, Masters Thesis by Michael C. Graves, University of Missouri-Rolla, 1971.

impossible because the volumes at any temperature calculated from the pycnometer data are precise to only  $\pm 0.04 \text{ cm}^3$ . A defect structure resulting from the introduction of five percent oxygen vacancies would result in a change in volume of  $0.004 \text{ cm}^3$  using a five gram sample, a value too small to be observed considering the experimental error limits. If one assumed a five percent cadmium interstitial model, the volume change ( $0.026 \text{ cm}^3$ ) although larger, would still be less than the propagated error.

The indirect (isotope exchange) method of stoichiometry determination using a cation isotopic substitution technique is based on the equation:

$$\rho = \frac{n' M_c}{N_o V_s} + \frac{s' M_a}{N_o V_s} \quad (8)$$

where:

- $\rho$  = the density of the material
- $n'$  = the number of cations
- $M_c$  = the average cation atomic weight
- $N_o$  = Avogadro's number
- $V_s$  = the volume of the sample
- $s'$  = the number of anions
- $M_a$  = the anion atomic weight

Cation isotope substitution results in a change of the average atomic weight of the cation and leads to a change in sample density as a function of the atomic weight of the

cation. If Equation (8) were plotted, the slope of the line would yield the number of cations and the intercept would correspond to the product of the number of anions and the atomic weight of the anion. The isotope exchange method of stoichiometry determination, was inconclusive in this study because the difference in the densities of the two samples was not sufficiently large to observe an effect. In materials where either cationic or anionic isotope substitution is feasible to a high degree of enrichment, this method should prove to be a very important complementary tool in simultaneously establishing both stoichiometry and defect type.

#### IV. CONCLUSIONS

The volumes obtained from the high temperature gas pycnometer have been shown to be dependent on the changing thermal gradient. The thermal gradient is affected by temperature, sample volume and height. The grain size of the material and the atmosphere in the pycnometer have no apparent effect on the thermal gradient. It has been shown that both the direct and isotope exchange method of stoichiometry determination of cadmium oxide were inconclusive.

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## VITA

Born in Wellsville, New York on January 24, 1947, Michael Clair Graves received his primary and secondary education in the Scio Central School in Scio, New York. He attended the United States Air Force Academy from June 1965 to January 1967. He enrolled at Alfred University in February 1967 and received a Bachelor of Science Degree in Ceramic Engineering in June 1969. In September 1969 he enrolled in the Graduate School of the University of Missouri-Rolla and was a Research Assistant at the Graduate Center for Materials Research since that time.

APPENDIX A  
DETAILED EXPERIMENTAL PROCEDURE

The experiments to determine the volume of the samples were conducted in the following manner. The sample was placed in the sample chamber and the pycnometer was evacuated and backfilled with oxygen to a pressure of 0.724 atm. The sample was heated to 850°C, then cooled. This procedure was used as a pretreatment process before going to each different atmosphere. After cooling, the pycnometer was evacuated and filled with the selected gas. Two hours were required for equilibration to take place at temperature. The initial pressure reading was taken with the pressure gage in its manual mode. The volume was changed by 2.500 cm<sup>3</sup> utilizing a microburette. The  $\Delta V_B$  was standardized at this value throughout the experiment. Ten minutes elapsed between the initial and final pressure readings. The microburette was returned to its initial setting and another initial reading was taken again five minutes later. This was repeated until five sets of initial and final pressure readings were obtained. This was done at each temperature in each different gas atmosphere. In going from one temperature to the next, twenty minutes elapsed between the last pressure reading at the lower temperature and the first reading at the higher temperature. The pressure of the system was returned to 0.724 atm. and after ten minutes an initial pressure reading was again taken.



The experiments in the Mettler Thermoanalyzer were conducted in the same manner. The pretreatment was identical to that used in the pycnometer experiments. The weight gain or loss was recorded on a chart recorder at the different temperatures in the various atmospheres. The effect of buoyancy was considered when calculating the weight of cadmium oxide at temperature and atmosphere.

APPENDIX B  
 $\gamma$  FACTOR CALCULATION

$$(V_p - V_s)_{\text{exp}} = \frac{\Delta V_B}{1 - \gamma (P_1/P_2)_{\text{exp}}}$$

$$(V_p - V_s)_{\text{calc}}^* = \frac{\Delta V_B}{1 - (P_1/P_2)_{\text{calc}}^\dagger}$$

$$(V_p - V_s)_{\text{exp}} = (V_p - V_s)_{\text{calc}}$$

$$\frac{\Delta V_B}{1 - \gamma (P_1/P_2)_{\text{exp}}} = \frac{\Delta V_B}{1 - (P_1/P_2)_{\text{calc}}}$$

$$\gamma (P_1/P_2)_{\text{exp}} = (P_1/P_2)_{\text{calc}}$$

$$\gamma = \frac{(P_1/P_2)_{\text{calc}}}{(P_1/P_2)_{\text{exp}}}$$

\*  $(V_p - V_s)_{\text{calc}}$  is based on calibration data.

† Sample calculation of  $(P_1/P_2)_{\text{calc}}$  can be found in Appendix C.

APPENDIX C  
 SAMPLE CALCULATION OF  $(P_1/P_2)_{calc}$

$$(P_1/P_2)_{calc} = \frac{V_p - V_s - \Delta V_B}{V_p - V_s}$$

$$V_p = 30.408 \text{ cm}^3 \text{ from Table III @500}^\circ\text{C}$$

$$V_s = 0.618 \text{ cm}^3 \text{ from Table IV}$$

$$\Delta V_B = 2.500 \text{ cm}^3$$

$$(P_1/P_2)_{calc} = \frac{30.408 - 0.618 - 2.500}{30.408 - 0.618}$$

$$(P_1/P_2)_{calc} = 0.91608$$

Table IV Alumina  
 Powder @500°C  
 Sample Height = 1 inch

APPENDIX D  
DETAILED ANALYSIS OF ERRORS

	Relative Error	Source
$V_p$	$\pm 0.04$	Reproducibility
$\Delta V_B$	$\pm 0.001$	Manufacturer
P	$\pm 0.05$	Reproducibility
$\gamma^*$	$\pm 0.04$	Differentiation
$\gamma'^{**}$	$\pm 0.001$	Differentiation
$F^+$	$\pm 0.0001$	Differentiation
$V_s$ for calc. with $\gamma$	$\pm 1.2$	Differentiation
$V_s$ for calc. with $\gamma'$	$\pm 0.04$	Differentiation
$V_s$ for calc. with F	$\pm 0.06$	Differentiation
$\rho$	$\pm 0.5$	Differentiation

\* Equation (1)

$$\Delta\gamma = \frac{\frac{P_1}{P_2} \left( - \frac{(V_p - V_s) \Delta(\Delta V_B) - \Delta V_B (\Delta V_p - \Delta V_s)}{(V_p - V_s)^2} \right) - \left( 1 - \frac{\Delta V_B}{V_p - V_s} \right) \Delta \left( \frac{P_1}{P_2} \right)}{(P_1/P_2)^2}$$

\*\* Equation (3)

+ Equation (4)

## APPENDIX E

## REVIEW OF LITERATURE ON DEFECTS IN CADMIUM OXIDE

Cadmium oxide is considered to be an n-type semiconductor with nearly metallic conductivity. Increased conductivity results upon decreasing oxygen pressure and increasing temperature during sample preparation indicating that the conductivity is related to an oxygen deficiency or to metal interstitials in the cadmium oxide lattice. Several different methods have been used to determine the concentration of the principal defect of nonstoichiometric cadmium oxide and the results have been interpreted in many ways. Cimino and Marezzio<sup>10</sup> concluded from lattice parameter measurements on pure and doped powder samples that the defect was of a cadmium interstitial type and was present in a concentration of  $1.5 \times 10^{19}/\text{cm}^3$ . Engell<sup>11</sup> used a direct chemical analysis method for measuring a cadmium excess of  $2 \times 10^{19}/\text{cm}^3$  in a sample sintered at  $650^\circ\text{C}$  in air. Oxygen tracer diffusion measurements were used by Haul and Just<sup>9</sup>, in material equilibrated at  $790^\circ\text{C}$  and 0.15 atm. oxygen, to determine an oxygen vacancy concentration of  $1.7 \times 10^{19}/\text{cm}^3$ . The reliability of the data from the aforementioned studies is open to question, either because of a lack of careful control of the experimental conditions or of the type of specimen used. Koffyberg<sup>8</sup> and Finkenrath and von Ortenberg<sup>12</sup> measured free carrier concentrations of  $10^{18} - 10^{20}/\text{cm}^3$  in quenched single

crystal<sup>8</sup> and polycrystalline<sup>12</sup> samples. They concluded that the carriers were produced by the ionization of atomic defects. This type of experiment cannot be used to separate the two types of defects.

It is evident from the literature review that the exact nature of the defect structure of cadmium oxide is yet to be established.

## APPENDIX F

## METTLER DATA AND INITIAL PRESSURE READINGS

TABLE IX

EFFECT OF ATMOSPHERE ON  $\frac{1}{Y}$  ASSUMING CONSTANT VOLUME OF  $\text{Cd}^{112.40}_0$  SAMPLE

Temp. (°C)	Atm. (atm)	$V_{S_3}$ ( $\text{cm}^3$ )	$P_1$	$P_1/P_2$ Exp.	$P_1/P_2$ Calc.	$\frac{1}{Y}$
25	Oxygen 0.724	0.628	205.2287	0.916102	0.915845	1.00028
500		0.628	205.9706	0.891934	0.916051	0.97367
600		0.628	205.5417	0.889102	0.916096	0.97053
700		0.628	205.5009	0.886487	0.916155	0.96762
800		0.628	205.6230	0.884777	0.916211	0.96569
25	Oxygen $10^{-1}$	0.628	211.4462	0.915964	0.915845	1.00013
500		0.628	205.3209	0.891653	0.916051	0.97337
600		0.628	205.6974	0.888795	0.916096	0.97020
700		0.628	205.9869	0.886384	0.916155	0.96750
800		0.628	205.8159	0.884050	0.916211	0.96490
25	Oxygen $10^{-2}$	0.628	199.5188	0.916147	0.915845	1.00033
500		0.628	205.4999	0.892153	0.916051	0.97391
600		0.628	205.5163	0.889066	0.916096	0.97049
700		0.628	205.7344	0.886457	0.916155	0.96758
800		0.628	205.6840	0.884066	0.916211	0.96492
25	Argon 0.724	0.628	203.7555	0.916031	0.915845	1.00020
500		0.628	205.2939	0.890939	0.916051	0.97259
600		0.628	205.0977	0.888632	0.916096	0.97002
700		0.628	205.8976	0.885693	0.916155	0.96675
800		0.628	205.6142	0.883444	0.916211	0.96424



TABLE X

EFFECT OF ATMOSPHERE ON  $\frac{1}{\gamma}$  ASSUMING CONSTANT VOLUME OF  $\text{Cd}^{112.74}_0$  SAMPLE

Temp (°C)	Atm. (atm)	$V_{s_3}$ ( $\text{cm}^3$ )	$P_1$	$P_1/P_2$ Exp.	$P_1/P_2$ Calc.	$\frac{1}{\gamma}$
25	Oxygen 0.724	0.596	196.1401	0.916195	0.915935	1.00028
500		0.596	205.3930	0.891639	0.916141	0.97326
600		0.596	205.4616	0.889086	0.916186	0.97042
700		0.596	205.4270	0.886353	0.916245	0.96738
800		0.596	205.8685	0.883780	0.916301	0.96451
25	Oxygen $10^{-1}$	0.596	205.7340	0.916138	0.915935	1.00022
500		0.596	205.8422	0.891883	0.916141	0.97352
600		0.596	205.5261	0.889160	0.916186	0.97050
700		0.596	205.4132	0.886431	0.916245	0.96746
800		0.596	205.6044	0.884388	0.916301	0.96517
25	Oxygen $10^{-2}$	0.596	205.4933	0.916239	0.915935	1.00033
500		0.596	205.7103	0.891859	0.916141	0.97350
600		0.596	205.5935	0.888835	0.916186	0.97015
700		0.596	205.6759	0.886240	0.916245	0.96725
800		0.596	205.7741	0.884131	0.916301	0.96489
25	Argon 0.724	0.596	186.8627	0.916321	0.915935	1.00042
500		0.596	205.5092	0.891667	0.916141	0.97329
600		0.596	205.6742	0.889130	0.916186	0.97047
700		0.596	205.6262	0.886322	0.916245	0.96734
800		0.596	205.7241	0.884018	0.916301	0.96477

TABLE XI

## INITIAL PRESSURE READINGS OF CALIBRATION DATA

Temp. (°C)	Sample	Sample Height (in)	Net $V_s$ ( $\text{cm}^3$ )	$P_1$
25	None	0	0	194.5282
500			0	205.9106
600			0	205.5161
700			0	204.9921
800			0	205.4677
25	Alumina Powder	1	0.609	205.4267
500			0.618	202.1128
600			0.620	206.3339
700			0.622	205.3900
800			0.624	205.8709
25	Alumina Powder	3	1.441	207.8055
500			1.462	196.2568
600			1.466	202.2618
700			1.472	206.2572
800			1.476	206.5474
25	Alumina 60 Mesh	3	2.726	204.4774
500			2.766	205.6981
600			2.774	206.2195
700			2.784	206.1768
800			2.793	206.1983

TABLE XII

METTLER THERMOANALYZER RESULTS FOR  $\text{Cd}^{112.40}_0$ 

Temp (°C)	Atm. (atm)	Weight Loss* (%)	Weight (g)
25	Oxygen		5.1800
500	0.724	0.346	5.1621
600		0.347	5.1620
700		0.353	5.1617
800		0.357	5.1615
25	Oxygen	0.432	5.1576
500	$10^{-1}$	0.427	5.1579
600		0.427	5.1579
700		0.421	5.1582
800		0.427	5.1579
25	Oxygen	0.452	5.1566
500	$10^{-2}$	0.458	5.1563
600		0.461	5.1561
700		0.463	5.1560
800		0.467	5.1558
25	Argon	0.452	5.1566
500	0.724	0.461	5.1561
600		0.461	5.1561
700		0.469	5.1557
800		0.473	5.1555

\* Based on weight at 25°C (0.724 atm. oxygen). Time at temperature was 15 minutes.

TABLE XIII

METTLER THERMOANALYZER RESULTS FOR  $\text{Cd}^{112.74}_0$ 

Temp. (°C)	Atm. (atm)	Weight Loss* (%)	Weight (g)
25	Oxygen		4.9281
500	0.724	0.130	4.9217
600		0.132	4.9216
700		0.136	4.9214
800		0.138	4.9213
25	Oxygen	0.134	4.9215
500	$10^{-1}$	0.264	4.9151
600		0.266	4.9150
700		0.264	4.9151
800		0.266	4.9150
25	Oxygen	0.317	4.9125
500	$10^{-2}$	0.375	4.9096
600		0.381	4.9093
700		0.384	4.9092
800		0.388	4.9090
25	Argon	0.388	4.9090
500	0.724	0.461	4.9054
600		0.465	4.9052
700		0.471	4.9049
800		0.473	4.9048

\* Based on weight at 25°C (0.724 atm. oxygen). Time at temperature was 15 minutes.

## APPENDIX G

## FUTURE

The isotope exchange method of stoichiometry determination shows considerable promise. This method should prove to be a very important complementary tool in simultaneously establishing both stoichiometry and defect type. Materials where either cationic or anionic isotope substitution is feasible to a high degree of enrichment and those with a large range of stoichiometry should prove to benefit from use of this complementary tool.

Some modifications which will improve the precision of the high temperature gas pycnometer are to reduce the volume of the pycnometer not in the hot zone and increase the sample chamber volume.