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A STUDY OF METAL-OXYGEN AND METAL-NITROGEN SYSTEMS
FOR USE AS REDUCED-PRESSURE STANDARDS

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ABSTRACT

A series of metal-oxygen and metal-nitrogen binary systems were surveyed to determine their potential as sources for secondary reduced-pressure gas standards. The respective gases of interest were nitrogen and oxygen, which were studied independently. The technique employed was to measure the equilibrium reduced pressure of the gas in a static, closed system, otherwise evacuated of other gases, over a metal-gas alloy at each of a succession of temperature levels. Those systems found to demonstrate a first-order equation representing the \log_{10} of pressure versus reciprocal absolute temperature were studied extensively.

Ten metal-oxygen systems and thirteen metal-nitrogen systems were surveyed. None of the metal-oxygen systems was found to be applicable, whereas two metal-nitrogen systems demonstrated feasibility. These were the Ba-N and Zr-N systems. Statistical analyses of the fit of the respective data were conducted.

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SUMMARY

A Sievert's apparatus, specially designed to conduct the appropriate metal-gas studies for this program, was employed to survey a series of selected metal-oxygen and metal-nitrogen systems. The objective was to determine the potential of these systems as secondary, reduced-pressure gas standards. A total of ten metal-oxygen and thirteen metal-nitrogen systems were independently surveyed. Gas pressure as a function of temperature was measured accurately, after sufficient metal-gas equilibrium was established. These data were then statistically analyzed for a fit to the van't Hoff equation, which is an analytical representation of the logarithm of dissociation pressure as a function of the reciprocal of absolute temperature. A first order equation results which can then be treated as a straight line plot.

None of the metal-oxygen systems surveyed was sufficiently consistent or reproducible to be selected for further study. The principal difficulty was the extreme sluggishness in diffusion in the temperature range of study. Thus, none of the metal-oxygen systems selected was felt to have sufficiently rapid kinetics for a practical gas standard. On the other hand, two metal-nitrogen systems were studied which demonstrated potential as secondary reduced-pressure gas standards. These were the Ba-N and Zr-N systems, which were studied extensively. Dissociation pressure equations were obtained for both systems. They were as follows:

for the Ba-N system;

$$\log_{10} p \text{ (torr)} = - \frac{5480 \pm 70}{T} + 6.70 \pm 0.09$$

and for the Zr-N system;

$$\log_{10} p \text{ (torr)} = - \frac{5830 \pm 140}{T} + 4.03 \pm 0.13.$$

The number of data points taken for the Ba-N system was 39 and for the Zr-N system, 37. The error limits are included for the slope and intercepts and are standard deviations. The statistical analyses were least squares programs as computed on a Burroughs B5500 computer.

INTRODUCTION

The study reported herein is an extension of an earlier program⁽¹⁾ conducted by this author on the use of thermodynamic properties of metal-gas systems as reduced pressure standards employing metal-hydrides. The feasibility of the use of the thermodynamic approach to gas-pressure standardization with hydrogen gas was proven with the Er-H system. The objective of this study was the same, except that the gases of interest were not hydrogen, but oxygen and nitrogen.

The accurate measurement of reduced pressures of various gases is still very difficult at best in the range below 10^{-3} torr. This region of pressure has not evolved a practical gas standard against which one can calibrate a measuring system. This is particularly so in the case of primary standards. The standards generally available are comparison standards that are indirectly related to a primary source above 10^{-3} torr in pressure. Hot- or cold-filament ionization gauges are the principal means to measure reduced pressures in the lower ranges. These are usually calibrated at a remote source, and then used in practice with a calibration curve. The maintenance of the conditions that were present during calibration after the ionization gauge is in use is certainly a questionable assumption. Minor changes in gaseous environment and the electronics of the ionization gauge controls are expected to effect significant shifts in the calibration curve. Alternatively, the use of a thermodynamic system such as a metal-hydride as an in situ calibration device is practical and would avoid the uncertainties in the current calibration techniques. This is one of the main justifications for conducting this study. If one could develop a new and more foolproof secondary gas standard that has these features, it would certainly be a welcome contribution to high-vacuum technology. The application of thermodynamic properties of metal-gas systems has been demonstrated to provide a new and unique method of not only standardization, but accurate simulation of reduced-pressure gas atmospheres.

BACKGROUND

In the measurement of reduced pressures the gases that are considered the most vital to standardize are hydrogen, oxygen, and nitrogen. These are the common gases found between the atmosphere and hard space that NASA is most concerned with and also the usual contaminants in ultra-high vacuum practice. Thus, it was incumbent to study these gases first in an attempt to prove the feasibility of thermodynamic standardization. The program for the development of metal-oxygen and metal-nitrogen systems followed almost exactly the same pattern as with the Er-H system as well as employing the same equipment and techniques.

The concept of employing a metal-gas system as a secondary reduced pressure standard must follow several requirements. The gas-phase pressure must be consistent with a simple analytical relationship. Obviously, pressure has to be one variable in the relationship. At least one other variable which is

a function of pressure is a minimum requirement. Temperature is the most logical choice, since intuitively one knows that the two variables are closely coupled whether the system is entirely gas phase, or two states of matter are involved, such as the combinations of liquid-gas or solid-gas phases. The relationship must be reproducible, predictable, and accurate. The relationship can be established using a primary standard such as a manometer or a McLeod gauge to measure the gas-phase pressure and a standardized thermocouple to measure the temperature of the system. One is then in a position to calibrate other pressure-measuring devices. Thus, when determining the relationship, temperature is the independent variable and pressure is the dependent variable, and when one is, in turn, calibrating another pressure-measuring device, the reverse is true with the variables. A convenient and practical temperature range is another desirable requisite. This depends on selecting the right thermodynamic system, which leads one to the metallic system selection.

The simplest analytical relationship for the purpose of this program, a straight line, is available from the van't Hoff equation. This equation fits the necessary criteria in that its variables are pressure and temperature, and it conveniently is a measure of the equilibrium dissociation pressure of a gas from a solid metal-gas alloy. The appropriate form of the van't Hoff equation is as follows:

$$\log_{10} p = \frac{A}{T} + B$$

where p is the reduced pressure in torr and T is the absolute temperature. A straight line of $\log_{10} p$ versus the reciprocal of absolute temperature is thus produced. There are certain limitations under which this equation is valid in a metal-gas system. The phase equilibria of the solid system must be such as to have a wide two-phase field present for the van't Hoff relationship to be valid for the intended standards application. The two-phase region is unique for this purpose because, on either heating or cooling the alloy, gas is desorbed or absorbed without the composition of either of the two individual phases changing. This allows the van't Hoff relationship to be maintained throughout. Another way of expressing this important factor is that within a two-phase region, pressure is constant. Minor overall compositional shifts in a metal-gas alloy that are naturally associated with the absorption or desorption as temperature falls or rises do not cause deviations from the van't Hoff relationship that is characteristic for the respective two-phase region. A specific example of these effects was demonstrated in the study of the erbium-hydrogen system⁽¹⁾ as a secondary reduced-pressure standard. An earlier program⁽²⁾ evolved the thermodynamic properties of the system. The following equilibrium-dissociation-pressure equation was obtained:

$$\log_{10} p \text{ (torr)} = - \frac{11,490 \pm 18}{T} + 10.668 \pm 0.019$$

The standard deviations to both the slope and the intercept of the straight line are given from the least squares analysis. The minimal standard deviations of the slope and intercept demonstrate the success of the use of a

metal-gas system for a secondary reduced-pressure standard. The coefficient of determination for the data presented was computed to be 0.999.

A thermodynamic treatment of the data will give the enthalpy and entropy of the reaction occurring in the plateau region. These values for the erbium-hydrogen system are $\Delta H = -52.6 + 0.3$ kcal/mole of H_2 , $\Delta S = -35.2 + 0.3$ cal/deg. mole of H_2 .

EXPERIMENTAL

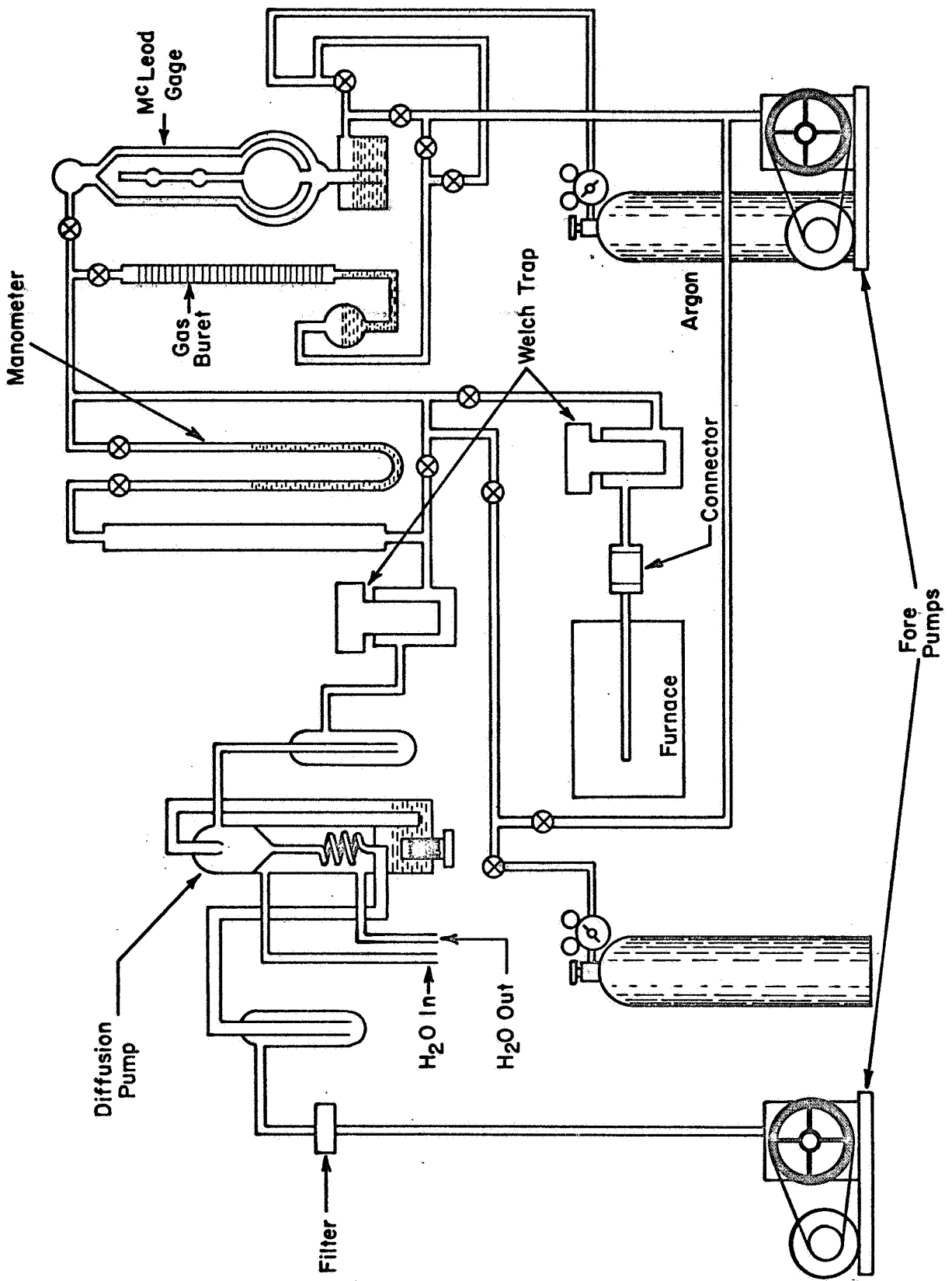
Materials. - The metals employed in this study were obtained from commercial sources in the form of solid ingot, wire, powder, or sponge. The metals and their nominal purities are listed below:

Ba	99.9%	Pd	99.9
Cu	99.99	Ge	99.99
Fe	99.8	Cr	99.9
Pt	99.9	Si	99.99
W	99.6	V	99.8
Mo	99.8	Sn	99.9
B	95+	Ti	99.9
Yb	99+	Zr	99.8
Ag	99.999		

Specimen preparation. - Although in some cases solid pieces of metal were used, the ultimate form in all cases was powder. This allowed more surface to be exposed so that diffusion was accelerated as much as possible. Equilibrium kinetics were considerably speeded by this approach. The powder size varied from -10 mesh for barium to -325 mesh for some of the other metals. However, the nominal size most used was -200 mesh. The powders that were prepared from ingot, wire, or sponge were done so by either crushing if the metal was brittle, such as in the case of silicon, germanium, and boron, or by filing. The comminution was always done in a glove box provided with an inert atmosphere to prevent contamination. Prior to loading, the sample was weighed on an analytical balance to the nearest 0.1 mg. To prevent contact with the quartz reaction chamber, the sample was placed in a 1-mil-tungsten-foil capsule. There is practically no reaction at the temperatures employed in this study with tungsten. There would be a reaction with the quartz if this protection were not accorded. The capsule and specimen were then placed in the quartz tube at the bottom of the closed-end section.

Sievert's apparatus. - The modified Sievert's apparatus that was employed to obtain the pressure-temperature data for the metal-oxygen and metal-nitrogen systems was constructed for the earlier study on the Er-H system. The principal components of the apparatus consist of a heated reaction chamber, a manometer, a McLeod gauge, a precision gas buret, and a vacuum source. Figure 1 is a schematic drawing of the modified Sievert's apparatus. The design was very carefully considered to allow the utmost in temperature and pressure accuracy. Much attention was given to maintaining cleanliness and to the

Figure 1. Schematic Drawing of the
Modified Sievert's Apparatus



measurement of temperature and pressure. Since the basis for this study was to develop a new approach to reduced-pressure secondary standards, the variables in the process had to be accurately established.

The temperature-control system for the furnace was selected after a study of the available systems from the various manufacturers. The unit felt to be the best for this application was a Set-Point Control System. It provided precision temperature control with range flexibility and fast response. It had an adjustable zero suppression and excellent reproducibility of control and control-point setting. The system consisted of 1) a Set Point Unit, 2) a DC null detector, 3) a current-adjusting-type control unit, and 4) a final-control device. The Set Point Unit was a DC potentiometer in the range of 0 to 55 millivolts. Each setting was reproducible to 0.05%. Reference-junction compensation was automatic for chromel-alumel thermocouples which were to be employed. The signal from the thermocouple was bucked against the potentiometer, and the deviation, plus or minus, was fed to the DC null detector. The sensitivity was continuously adjustable to a maximum of 1.0 microvolt per scale division. Since the response of chromel-alumel was 40 microvolts per degree centigrade, this unit detected deviations as small as 1/40 degree centigrade. The signal from the DC null detector was fed to the current-adjusting-type control unit. Its output was fed to the final control device. This component consisted of a silicon-controlled rectifier. The degree of furnace control to be expected was ± 0.1 degree centigrade. The chromel-alumel control thermocouple was calibrated and traceable to Bureau of Standards calibration at 50°C intervals between 550 and 900°C. In addition to this control thermocouple, another independently calibrated thermocouple was employed to measure the exact temperature of the specimen with a Precision Potentiometer. A mock run was initiated at midrange of the temperature to be employed in the study. According to the null-point detector reading and its specified sensitivity, the degree of control was $\pm 0.01^\circ\text{C}$. However, another potentiometer was used with the independent thermocouple designed to represent the specimen temperature which is limited to $\pm 0.25^\circ\text{C}$.

The pressure measurements were made in the range of 1×10^{-3} to 10 torr with a McLeod gauge, Model No. GM-100A. THE GM-100A covered the 1×10^{-5} to 10 torr range on three scales. On the 0 - 10 torr scale the measuring errors were no larger than $\pm 1.1\%$ of indicated pressure, on the 0 - 1 torr scale, $\pm 1.2\%$ of indicated pressure, and on the quadratic scale, $\pm 1.5\%$ of indicated pressure.

For added precaution, a foreline trap was incorporated to prevent oil backstreaming. The mercury diffusion pump was a three-stage pump capable of an ultimate vacuum of 5×10^{-8} torr. The addition of the cold traps reduced this considerably. Convoil 20 was used in the forepump as added insurance for low oil-vapor pressure in this region of the system.

The nitrogen employed for these studies was prepurified grade at 99.997% of purity, and the oxygen was extra-dry grade at 99.6% purity. The gas buret is normally operated with air on the other side of the system as is the McLeod

gauge. Instead, purified argon was used to operate both of these devices. This eliminated any possibility of air or dust getting into the mercury and diffusing through to the Sievert's system.

The quartz reaction chamber consisted of a closed-end tube about 9 mm. in diameter. It was inserted in a hole through a Lavite plug and into an Inconel heat sink. In turn these were both contained within the 1-in. diameter hole in a tube furnace. The Inconel heat sink was employed to even out thermal gradients and to eliminate temperature cycling from the control system. This assured an extremely even temperature control. A chromel-alumel thermocouple fit into the opposite end of the furnace through another Lavite plug. The Lavite plugs at either end of the furnace served as insulators to keep the longitudinal heat loss down. The thermocouple tip was placed against the closed end of the quartz reaction chamber which was intended to accommodate the thermocouple. Immediately inside the quartz chamber, the specimen was placed. The temperature of the specimen was very accurately read with this arrangement.

The Nichrome-wound tube furnace was provided with a means of sliding the furnace back and forth. The quartz tube, being stationary, would either be in or out of the furnace as the furnace was moved from one position to the other. This feature facilitated loading and unloading specimens in the quartz reaction chamber. The furnace mounting unit consisted of a heavy-duty framework with two roller systems and a track on which the furnace was bolted. The travel of the furnace was restricted by metal stops at either end so that the furnace could be brought back to the same position.

Equilibration procedure. - As standard procedure the Sievert's apparatus was intermittently leak-checked with a helium leak detector and always found to be helium-leak tight. Prior to the run itself, the Sievert's apparatus was evacuated to its ultimate vacuum and the tube furnace heated to the required temperature, but not yet moved onto the reaction chamber. Thus, the specimen was at room temperature at this stage. The system nominally pumped to a vacuum in the low 10^{-7} torr region. The reaction tube was independently baked by moving the tube furnace onto the quartz tube for about 30 sec. at 973°K . The specimen did not have an opportunity to heat for this period of time, so it could not be contaminated by the out-gassing from the tube, albeit small. The system was then alternately purged with high-purity gas and evacuated to clear the system of any minor remaining contaminating gases. The gas absorption was initiated at this stage. From the weight of the specimen, the amount of gas required to bring the appropriate composition was calculated. An amount of gas was then admitted into the precision gas buret, and its volume and pressure were measured to determine the quantity. By admitting or removing small amounts of gas, the correct quantity to bring the metal to composition was obtained. At this point, the furnace was moved onto the quartz reaction tube containing the specimen. Evacuation of the system was continued for about 5 min. while the specimen was coming to temperature. The stopcock to the vacuum source was then closed and the gas in the buret admitted. The only components of the system involved in the equilibria measurements from this point on were the manometer, the McLeod gauge, the quartz reaction tube and interconnecting tubing. The temperature-pressure equilibria study was initiated at this stage. The equilibrium point was taken and the temperature adjusted to the next level,

usually about an increment of 50°K above. Equilibrium was allowed at this temperature, the pressure measured, and the next level was set. This procedure was continued up to the upper temperature limit, and then the cycle reversed downward in similar temperature increments to the lower temperature limit. Before the run was completed, several thermal cycles between these limits were conducted to obtain the temperature-pressure equilibria data. There was no indication of hysteresis observed in the data obtained in the downward temperature cycles as compared with the upward cycles for the two nitrogen systems that were finally selected for study, the Ba-N and Zr-N, systems. The Ba-O system showed some hysteresis effect. An average run was conducted for a week before the specimen was removed and replaced with another. However, this was only a precautionary measure to be assured that excessively long periods of time at temperature did not contaminate the specimen. Several runs were carried out for as long as two weeks without any problems. Each run was cycled up and down several times. Again, the equilibria did not shift as a result.

RESULTS AND DISCUSSION

In the first phase of this study, the metal-oxygen systems were surveyed in an attempt to select an optimum single system on which to conduct a more intense study. The following systems were briefly analyzed to determine 1) whether the kinetics were sufficiently rapid, 2) whether the data were reproducible, and 3) whether the pressure and temperature ranges were practical. Also included are the temperature ranges studied and the nominal compositions and related two-phase fields which were selected from the available phase diagram information.

<u>System</u>	<u>Temperature Range, °K</u>	<u>Oxygen, Nominal Composition, %</u>	<u>Two-Phase Fields</u>
Cu-O	873-1173	16	(Cu + CuO)
Fe-O	833-1183	25	(Fe + Wustite)
W-O	973-1223	64.5	(WO ₂ + WO ₃)
Mo-O	973-1173	40	Complex
B-O	973-1173	40	(B ₆ O + B ₂ O ₃)
Ba-O	673-823	25	(Ba + BaO)
Yb-O	773-973	25	(Yb + Yb ₂ O ₃)
Ag-O	773-1073	25	(Ag + AgO)
Pd-O	873-1073	25	(Pd + PdO)
Ge-O	773-973	35	(Ge + GeO ₂)

The survey of these ten systems demonstrated that oxygen would be a difficult gas to use as a standard by the thermodynamic technique. The major problem was the extremely slow diffusion rate even with powder metal samples. Absorption would take place in many instances, but it was the uptake of the

remaining 5 or 10% of gas that became exceedingly more difficult. Saturation to the intended composition became slower the closer the approach to equilibrium. The concentration gradient at this stage was very small, so the activation energy for diffusion was not high enough to provide reasonable energetics. The slow rate of diffusion is understandable because of the large ionic size of oxygen in the lattice. Thus, the times to attain equilibrium for those systems that did absorb oxygen were impractical for the intended use. The Ba-O system appeared to come nearest to practicality of all the systems studied. The absorption of oxygen occurred reasonably fast. The pressure sensitivity as a function of temperature appeared to be good. In the 150°K range from 673 to 823°K studied, the pressure varied from 0.013 to 0.380 torr. There was some hysteresis on reversal of the temperature cycle. Reproducibility between different samples was not too good. However, should sufficient time be allowed for more study, these difficulties might diminish. A rough estimate of the required times to each equilibrium point would involve tens of days, which, in the interest of completing the study of the nitrogen systems, could not be tolerated.

The second phase of study was then undertaken. The metal-nitrogen systems were surveyed in the same manner as the metal-oxygen systems. The following metal-nitrogen systems, the temperature range of study, their nominal compositions, and the related two-phase regions are indicated below:

<u>System</u>	<u>Temperature Range, °K</u>	<u>Nitrogen Nominal Composition, %</u>	<u>Two-Phase Fields</u>
Ba-N	610-825	20	(Ba + Ba ₂ N)
B-N	873	20	(B + BN)
Cr-N	673-873	20	(Cr + CrN)
Si-N	973	20	(Si + SiN)
Cu-N	973	15	(Cu + CuN)
V-N	673-1173	20	(V + VN)
Mo-N	773-1173	20	(Mo + MoN)
Ge-N	773-1073	20	(Ge + GeN)
Sn-N	423-473	20	(Sn + SnN)
Pd-N	973-1173	20	Unknown
Pt-N	973-1173	20	Unknown
Ti-N	673-1173	20	(Ti + Ti ₃ N)
Zr-N	873-1273	35	(Zr + ZrN)

The survey of these systems resulted in two systems being selected for further investigation. These were the Ba-N and Zr-N systems. Both demonstrated potential in the survey as secondary reduced-pressure standards. A third system, the Ti-N system, also showed potential, but further studies indicated that the pressure-temperature data in the higher temperature region deviated from a van't Hoff straight line rather distinctly. On examining the phase

diagram, it was found that the metal solid solution solubility boundary in this region changed drastically, to which the aberration was attributed. Therefore, this system was abandoned.

The kinetics of approach to equilibrium were noticeably improved in the metal-nitrogen systems compared to the metal-oxygen systems. This phenomenon can be rationalized on the basis of the ionic size of nitrogen, which is between that of oxygen and hydrogen.

The Ba-N system was analyzed by obtaining a total of 38 equilibrium values of pressure and temperature. The data are presented in Table I. The temperature was cycled up and down eight times over the range of temperature from 610 to 825°K. Very little, if any, hysteresis was noted. The specimen was nitrified to 20 atomic percent prior to the thermal cycling, which is in the two-phase region, Ba + Ba₂N. Nothing else is known about the phase diagram other than it has one intermediate phase of Ba₂N. The average time to equilibrium was about 24 hours for each pressure-temperature couple.

A statistical treatment of these data was carried out to fit the values to the van't Hoff relationship. This was accomplished on a Burroughs Datatron B 5500. The following equilibrium dissociation pressure equation was obtained with standard deviations on the slope and intercept as follows:

$$\log_{10} p \text{ (torr)} = - \frac{5480 \pm 70}{T} + 6.70 \pm 0.09$$

where p = equilibrium nitrogen pressure, torr
 T = absolute temperature, Kelvin

Figure 2 is a plot of the data of \log_{10} pressure versus reciprocal of absolute temperature. The standard deviations are considered to be quite good, since a relatively small number of points are included compared to those taken for the Er-H system. The standard error of estimate was 0.055. The Ba-N system studies are felt to prove that the thermodynamic approach is valid in the application of the system as a secondary reduced-pressure nitrogen standard.

The enthalpy of reaction of BaN from Ba was determined from the slope of the van't Hoff equation as described in the Background section. The value obtained was $\Delta H = -25.1 \pm 0.3$ kcal/mole of N₂. The entropy of reaction as calculated from the intercept was $\Delta S = -17.5 \pm 0.4$ cal/deg. mole of N₂.

The Zr-N system was analyzed by obtaining a total of 37 equilibrium values of pressure and temperature. Table II contains the data. The temperature was cycled up and down six times over the range of temperature from 873 to 1273°K. No obvious hysteresis effects were noted in the thermal cycling. The average time to attain equilibrium was approximately 24 hours. The specimen was nitrified to 35 atomic percent prior to the thermal cycling. This places the specimen composition in the two-phase region, Zr + ZrN. The phase diagram is referenced in Hansen⁽³⁾ and is presented in Figure 3.

TABLE I

Equilibrium Pressure-Temperature Data
for the Barium-Nitrogen System

<u>Temperature, °K</u>	<u>Pressure, Torr</u>
724	0.150
675	0.036
623	0.0080
624	0.0076
674	0.035
724	0.160
773	0.402
737	0.207
697	0.069
648	0.015
610	0.0053
634	0.011
660	0.023
686	0.0525
712	0.118
736	0.211
749	0.273
761	0.345
720	0.180
700	0.077
692	0.063
673	0.045
667	0.030
652	0.0185
640	0.0135
628	0.0097
618	0.007
614	0.0069
638	0.0127
656	0.021
662	0.026
710	0.0925
825	0.98
754	0.345
793	0.696
783	0.590
779	0.550
770	0.460

Figure 2. Plot of Equilibrium Dissociation Pressure
Relationship for the Ba-N System

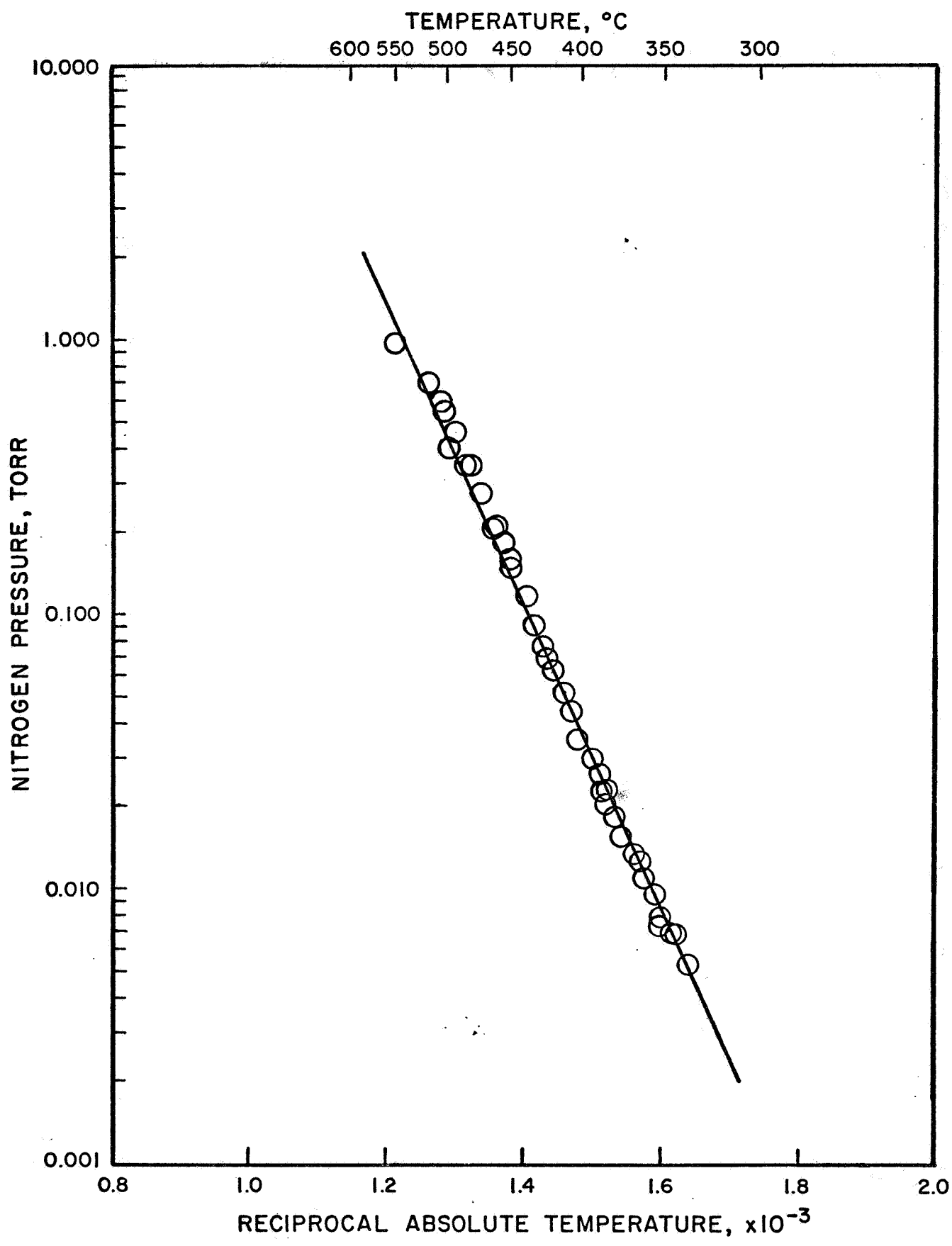
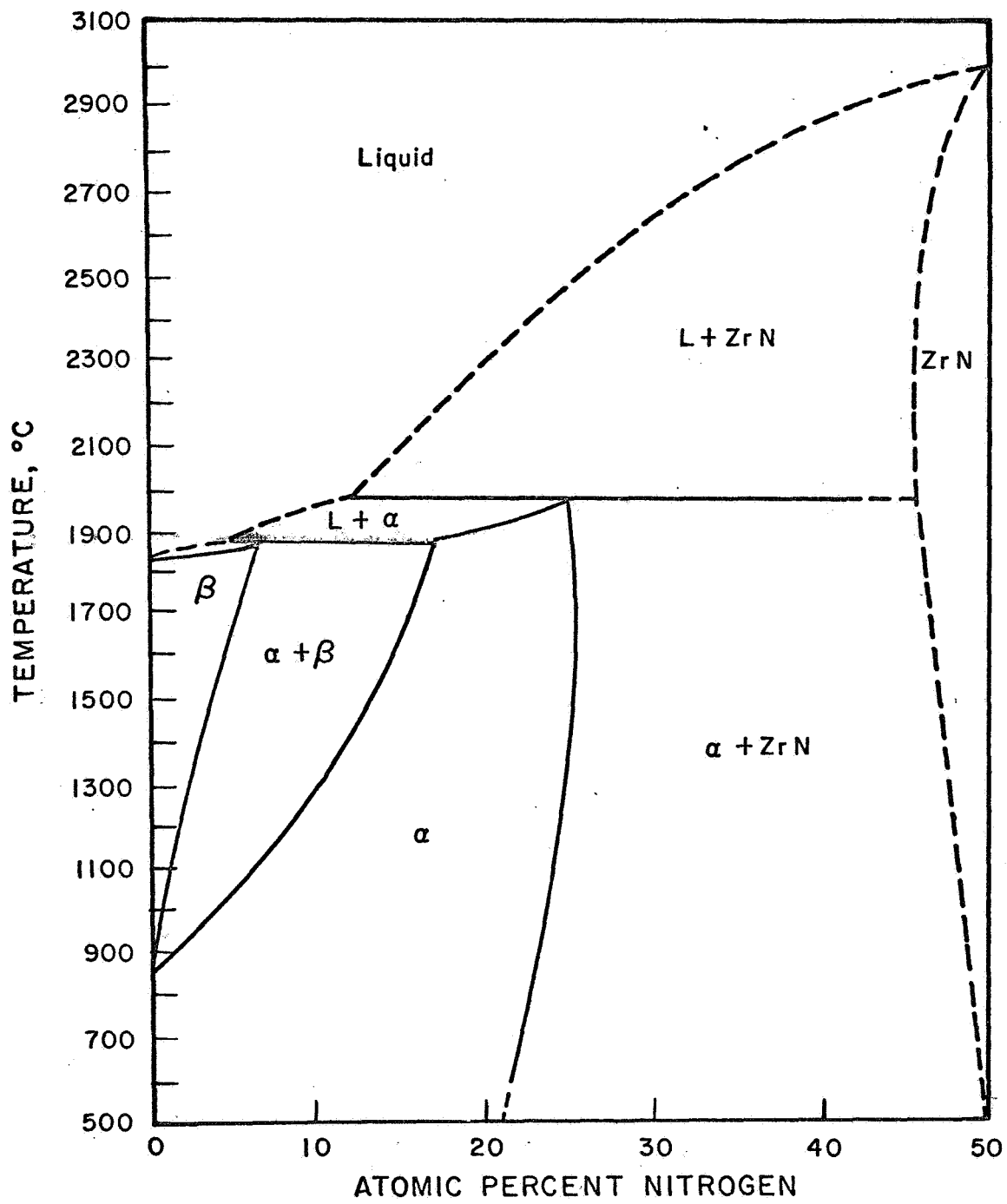


TABLE II

Equilibrium Pressure-Temperature Datafor the Zirconium-Nitrogen System

<u>Temperature, °K</u>	<u>Pressure, Torr</u>
931.0	0.0035
973.0	0.0085
1026.0	0.018
1074.0	0.034
1125.0	0.064
1174.0	0.120
1226.0	0.159
1175.0	0.120
1126.0	0.159
1075.0	0.045
1026.5	0.0235
975.0	0.0101
928.0	0.006
874.5	0.0029
927.5	0.0064
975.0	0.0126
1025.0	0.0275
1073.5	0.050
1125.0	0.096
1175.0	0.157
1227.0	0.216
1277.0	0.275
1226.5	0.237
1075.0	0.029
1025.0	0.0165
955.0	0.0073
923.0	0.0052
872.5	0.0028
924.5	0.0065
973.5	0.013
1024.5	0.025
0174.0	0.040
1126.0	0.075
1176.0	0.116
1213.0	0.137
1223.0	0.168
1183.0	0.155

Figure 3. Phase Diagram of the Zr-N System



The data were treated statistically to a van't Hoff plot, which is a straight line representation of \log_{10} pressure versus the reciprocal of absolute temperature. Again the analysis was accomplished on a Burroughs Datatron B 5500. The equilibrium dissociation pressure equation obtained from this analysis was as follows:

$$\log_{10} p \text{ (torr)} = - \frac{5830 \pm 140}{T} + 4.03 \pm 0.13$$

where p = equilibrium nitrogen pressure, torr
 T = absolute temperature, Kelvin

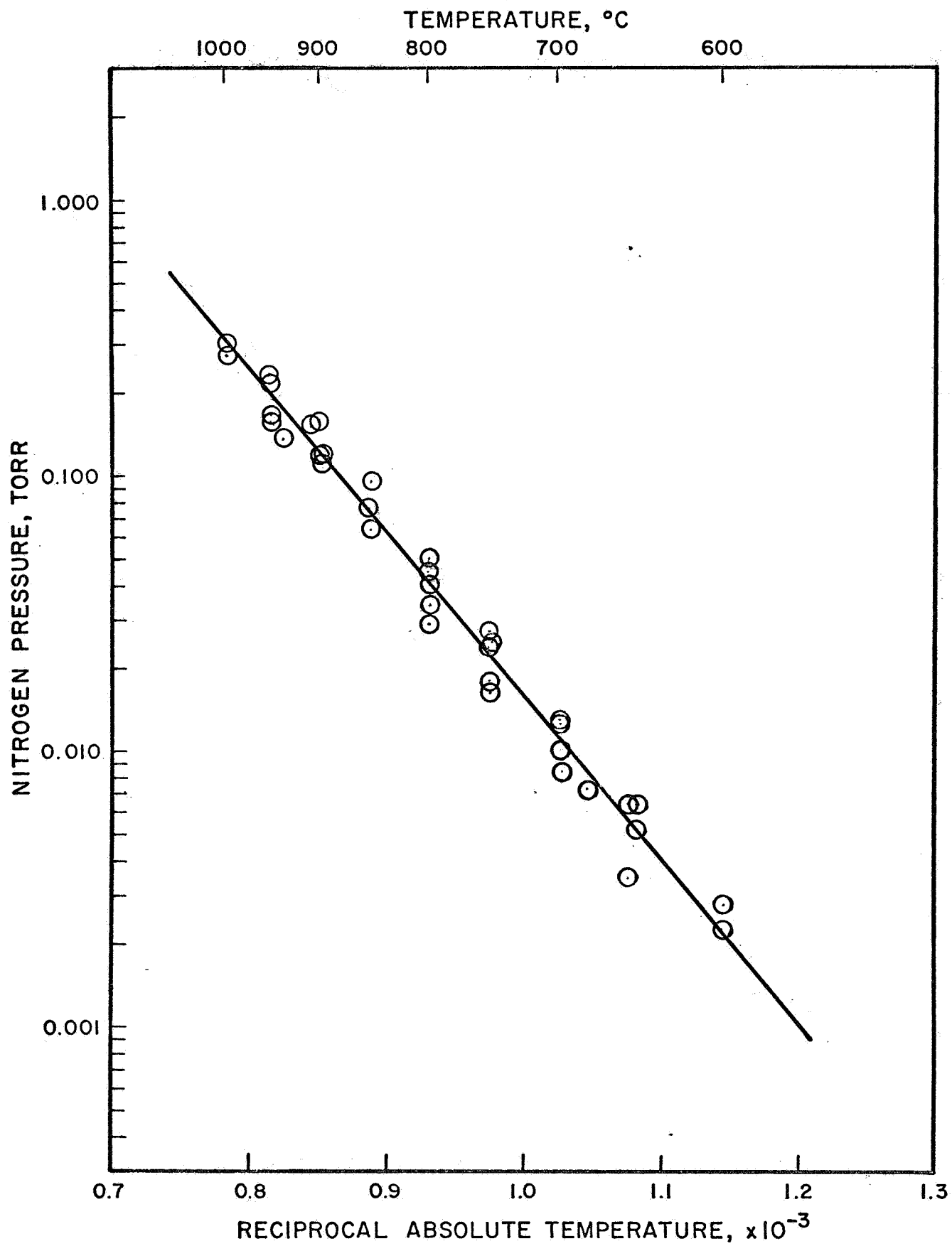
The standard deviations are included for the slope and intercept. The standard error of estimate was 0.085. Figure 4 is a plot of the equilibrium data in the Zr-N system.

The enthalpy of reaction of ZrN from the zirconium metal solid solution was determined from the slope to be $\Delta H = -26.7 \pm 0.6$ kcal/mole of N_2 . The entropy of reaction was calculated from the intercept to be $\Delta S = -5.26 \pm 0.60$ cal/deg. mole of N_2 .

Although the metal-oxygen systems studied did not demonstrate standards potential, this does not signify there is no system which will qualify. It is recommended that the search should continue to find such a metal-oxygen system. The metal-nitrogen systems studied provided two examples that fit the criteria for secondary reduced-pressure standards. The advantages of the Ba-N and Zr-N systems for secondary reduced-pressure standard application are as follows:

1. Once the dissociation pressure equation is established and standardized, one can calculate the corresponding temperature setting for any desired pressure. Then, by adjusting the temperature to the appropriate value, the pressure is attained.
2. There is no apparent hysteresis in the nitrogen pressure. The system was cycled several times, and the pressure returned to the value as prescribed by that specific temperature.
3. In the appropriate temperature range, pressure equilibrium is reasonably rapid.
4. The equilibrium pressure for each respective temperature is independent and unaffected by the volume or geometry of the system. There is an exception to this when the composition is shifted off the plateau by having a small specimen and a large system.
5. The partial-pressure plateau in the two-phase region is extensive, and shifts in overall composition do not affect the pressure at any specific temperature.

Figure 4. Plot of Equilibrium Dissociation Pressure Relationship for the Zr-N System



6. Contamination from outgassing or inleakage does not seriously affect the equilibria established according to the dissociation equation.
7. A metal-gas system will establish accurate reduced pressures which bracket the manometer, the McLeod gauge, and the ionization gauge in a continuous manner.
8. There is no reason to believe that a standardized dissociation equation for such a system prepared in the higher pressure range where good primary standards exist could not be extrapolated to lower pressures with a high degree of confidence in accuracy. This is so because of the immutability of the thermodynamic properties. It is known that in the lower temperature regions, where the lower equilibrium pressures obtain, no phase changes occur in either the metal solid solution or the nitride. Furthermore, the solubility boundaries change slowly with temperature. Therefore, the enthalpy and entropy values for the reaction across the two-phase region are not expected to change over quite a range of temperature. This means the dissociation equation can be confidently extrapolated. This feature is probably one of the most important advantages to be gained using this type of system.
9. One distinct advantage of this technique is that an in situ calibration can easily be devised for any ultrahigh vacuum apparatus, where an immediate calibration of the measuring apparatus can be available.
10. The system is inexpensive to build and relatively simple in design and use. The temperature range can be easily attained and measured with commercially available thermocouples. The components for the apparatus to contain the system are commercially available. There are no electronics involved, which considerably lessens the chance for error. The metal is not expensive for the amount required.
11. The specimen can be reacted to the appropriate composition, removed to air, and transported to another system without affecting its dissociation relationships.
12. Other metal-gas systems exist which give somewhat different equilibria. This would give flexibility in selecting the appropriate temperature and partial pressures for the specific application.
13. The range of temperatures over which the wide spread of pressures exists are easily measured. A chromel-alumel thermocouple can be employed which has a high EMF per unit temperature increase. Also, standard materials of construction for the furnace chamber can be employed because the highest temperatures required are not at all severe.
14. The simulation of a reduced pressure atmosphere is feasible in any type of chamber or system by simply placing a small heating source and a prereacted specimen in the chamber with a means for measuring the temperature of the specimen.

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