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A DETERMINATION OF VAPOR PRESSURE OF BARIUM IN THE THERMAL PRODUCTION OF BARIUM METAL

By

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A

THESIS

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ABSTRACT

The Knudsen effusion method was used to find the equilibrium reaction pressure of barium for the following reactions:

$$4BaO + 2Al = 3Ba + BaO\cdot Al_2O_3 \qquad (1)$$

$$4BaO + Si = 2Ba + 2BaO\cdot SiO_2 \qquad (2).$$

The resulting barium pressure for reaction (1) ranged from 0.27 mm. Hg to 1.77 mm. Hg in a temperature range of 940°C to 1086°C. The barium pressures for reaction (2) varied from 0.38 mm. Hg to 1.94 mm. Hg in a temperature range of 1000°C to 1086°C. The free energies of formation of $BaO\cdot Al_2O_3$ and $2BaO\cdot SiO_2$ at 1087°C were calculated from the pressure data and found to be -360,800 calories and -376,900 calories, respectively.

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CHAPTER I

INTRODUCTION

Vapor pressure measurements of a gaseous metal constituent above a reaction mixture are of great importance in the thermochemical study of metallurgical processes, such as the thermal reduction of alkaline earth metal oxides with aluminum or silicon in vacuo. The measurement of the reaction pressure of barium vapor in the reduction of barium oxide with aluminum and silicon in the temperature range of 900°to 1100°C and the application of these measurements in the thermochemical analysis of this process are the principal purposes of this investigation.

In the past much work has been done in perfecting the process for the thermal reduction of magnesium oxide with silicon in vacuo. This particular process has been very successful commercially since its conception during World War II. Several processes have been developed which apply the same principles to the thermal production of other alkaline earth metals such as calcium, strontium, and barium. With regard to magnesium, calcium, and strontium, the interest in a thermal process for producing these metals originates from the fact that the direct heating method is more economical than the electrolytic method usually employed in alkaline earth metal production.

In the case of barium, the interest in a thermal reduction process arises from the fact that electrolytic production of barium is very difficult. Kroll tried unsuccessfully to produce barium metal by the electrolysis of a molten barium chloride-barium fluoride mixture.[1] However, alloys containing barium are made by electrolytic methods as well as by thermal methods. Probably the best known of the barium alloys is Frary metal which is a lead base alloy used as a bearing metal. K. W. Ray has shown that this alloy can be produced commercially by electrolysis of a fused mixture of calcium and barium chlorides using molten lead as the cathode.[2] Other alloys of barium which have been produced electrolytically include aluminum, magnesium, tin, antimony, copper, zinc and bismuth alloys.[3]

Barium metal has found limited use except in alloyed form such as is mentioned above. This is due largely to the high activity of barium. That is, barium metal reacts with almost all of the common gases, such as nitrogen, oxygen, hydrogen, carbon dioxide, water vapor, and others. However, this property has lead to the utilization of barium as a "getter" material in electronic high-vacuum tubes. It was found that the vacuum obtainable by ordinary vacuum pumps was not sufficient to ensure the long life desired of these electronic tubes. It was then discovered that by introducing a highly reactive substance, such as barium, to clean-up the residual gases in the vacuum tubes, a very low pressure could be maintained and long life and more efficient performance could be obtained. Dushman states that barium metal is one of the most efficient "getters" known.[4] Barium-aluminum alloys are also used as "getters".

The reasons for this investigation are: (1) the increasing interest in the thermal production of barium on a commercial scale, (2) the fact that Missouri is one of the leading producers of barite which is barium sulfate, and (3) the continuing interest in applying high temperature vacuum techniques to metallurgical processes.

The chemical equations involved in the thermal production of barium using aluminum and silicon as the reducing agents are as follows:

$$4BaO + 2Al = 3Ba + BaO \cdot Al_2O_3$$

$$4BaO + Si = 2Ba + 2BaO \cdot SiO_2.$$

Since these reactions involve barium in the vapor phase, it is logical that any study of these reactions should involve the measurement of the reaction pressure of barium vapor. To do this the Knudsen method of vapor pressure measurement was used.

This thesis is arranged as follows: after a review of the literature, theoretical considerations are presented.

Then the apparatus employed in the experimentation is described after which the procedure used in obtaining the data is outlined. Next follows the tabulation of the data and its thermochemical treatment. Finally the overall results and the experimental errors are discussed, and some recommendations for the improvement of the apparatus are presented.

CHAPTER II

REVIEW OF THE LITERATURE

Many articles have been written pertaining to the production of the alkaline earth metals by the thermal reduction of their oxides and the distillation and condensation of the metal vapor in a vacuum. Several of the important articles are reviewed here.

Thermal Processes for the Production of Barium

It is well known that barium oxide can be reduced by several reducing agents, the most common of which are aluminum and silicon. W. J. Kroll has reviewed the literature and found that Mallet reduced alkaline earth metal oxides with aluminum in 1877.[5] He states also that Guntz worked out a process, using aluminum as a reducing agent, in which the barium vapor was distilled and condensed in vacuo, and that Matignon suggested using silicon or a 90% ferrosilicon to reduce barium oxide. Other reducing agents mentioned by Kroll include Mg, Ti, Zr, Th, Ta, Cb, V, Ni, and $CaSi_2$. Kroll found that Guntz suggested the use of $CaSi_2$. He further found that Guntz mentioned that the barium produced would be contaminated with calcium.

In a patent by G. N. Kirsebom[6] there is described a method in which lump barium oxide is placed into a closed vessel along with metallic magnesium, and the mixture is heated to a temperature above the melting point of magnesium. No vacuum is employed in this process, and metallic barium is produced. The barium metal sinks to the bottom of the closed vessel while the lighter magnesium oxide floats on top. After cooling, pure barium is removed from the cylinder. He states that one could obtain pure barium or a barium-magnesium alloy, depending upon the relative amounts of magnesium and barium oxide added at the start.

M. Pruvot outlined a process by which barium could be recovered from caustic barite or barium aluminate by using magnesium metal or alloys of magnesium.[7] In this process barium oxide is first reduced by aluminum in vacuo to obtain about 40% recovery of the barium originally contained in the barium oxide. The residue, presumably barium aluminate, is then treated with magnesium metal or an alloy of magnesium at atmospheric pressure and at a temperature above the melting point of the magnesium or the alloy of magnesium. The product of this second stage is an alloy of barium, magnesium, and any other metal originally present with the magnesium, and an oxide slag. By treating the slag several times it was possible to recover over 90% of the barium originally contained in the barium oxide.

Other reducing agents mentioned in the literature are methane,[8] carbon, and calcium carbide,[9] the latter producing barium, calcium oxide, and carbon upon reaction with barium oxide. Carbides of the alkaline earth metals themselves have been decomposed at high temperatures to yield alkaline earth metal vapor and carbon monoxide. B. J. Wilson[10] has patented a process whereby the impure carbide of either calcium, barium, strontium, or lithium is decomposed to produce a gaseous mixture of metal vapor and carbon monoxide. Subsequently the gaseous mixture is passed into a purifying zone containing a refractory metal heated to above the condensation temperature of the particular metal vapor so as to remove the carbon monoxide from the gaseous mixture by the reaction of carbon monoxide with the refractory metal to form refractory metal oxides and carbides. The purified metal vapor is then passed into a condenser. For calcium, the reaction temperature is about 1600°C, and the purifying zone temperature is about 1000°C.

Aluminum and silicon are the most popular reducing agents for barium oxide. They generally are more favorable from an economic and chemical standpoint than most of the other reducing agents proposed. For instance, carbon would be ideal if it were not for the danger of the barium metal produced reacting with the carbon monoxide also produced in the reduction.

The Effect of Additions to the Charge

Certain additions to the charge have been proposed in order to increase the efficiency of the process. For instance, Kroll[11] suggests that the addition of calcium fluoride or barium fluoride to the charge may speed up the rate of diffusion and thus reduce the reaction time and promote a greater yield at any given temperature. Certain British patents state that the reaction is accelerated by adding barium fluoride in the amount of 2% of the weight of the charge.[12]

It would be advantageous to add calcium oxide in order to tie up some of the alumina or silica as calcium aluminate or calcium silicate. This would prevent the loss of barium oxide as barium monoaluminate or barium orthosilicate. However, even though calcium oxide is more difficult to reduce with silicon or aluminum than is barium oxide, there would be some contamination of the resulting barium by calcium. That is, some calcium metal would also be produced.

In regard to the use of barium peroxide in the reaction mixture, Kroll[13] says that its use increases the efficiency of the reaction because of the higher temperature obtained. But, since a mixture of barium peroxide and aluminum is explosive at high temperatures, the addition of BaO_2 is of doubtful value due to the danger of overheating, sintering, and dusting resulting from such an explosive mixture. The use of Fe_3O_4 is open to the same criticism. However, a French patent designates BaO_2 as the only barium containing raw material in the aluminothermic production of barium metal.[14] In this patent, the idea is to add certain catalysts such as Cu_2O, MnO_2, SiO_2, or CuO which will lower the temperature of dissociation of the reaction, $BaO_2 = BaO + (O)$. The procedure is to mix BaO_2, the catalyst, and fine aluminum grains. This mixture is heated to a temperature which is high enough to dissociate the BaO_2 in vacuo in a reasonable time but below the ignition point of $(BaO_2 + Al)$. After the pressure in the system indicates that one oxygen has been released from the BaO_2, the temperature is raised to about 1350°C to complete the reaction between barium oxide and aluminum and produce barium metal. An alternative is to use a reducing agent such as Cu powder, Cu_2O, or Mn powder to absorb one half of the oxygen in the BaO_2. The heating procedure used when employing such a reducing agent is similar to that used when employing a catalyst. The main purpose in using BaO_2 in such a fashion is to get away from the adverse effects of the hydration and carbonization of BaO in air.

Frank R. Kemmer proposes the use of a certain moderating agent in the production of alkaline earth metals by the aluminothermic process.[15] This moderating agent is composed of aluminum nitride, aluminum carbide, and aluminum oxide. The advantages he claims by its use are that the reaction is made to proceed at a fairly uniform rate as well as at a rapid rate, the temperature of the reaction is lowered resulting in extended retort life, and that these compounds of aluminum provide an additional reducing effect. Additional advantages are realized in the use of an aluminum dross containing these compounds of aluminum. One advantage is that the constituents in such a dross are intimately mixed. Another advantage is that the amount of fluoride, often used as a catalyzer in commercial processes, can be reduced or completely eliminated when using a dross containing the moderating agents.

Thus it is seen that there are several types of additions that can be mixed with the charge in order to facilitate the reaction. One of the greatest advantages obtained from such additions is the lowering of the temperature of reaction. This saves on fuel costs and retort maintenance costs.

Vapor Pressure Measurements

Shortly after the advent of the high temperature vacuum process developed by Pidgeon for the ferrosilicon reduction of dolomite, there was considerable interest in studying similar processes applied to the production of calcium, strontium, and barium. One of the first investigations of this kind was made by Pidgeon and Atkinson.[16] They studied the aluminothermic reduction of calcium oxide. To do this, they measured the reaction pressure of calcium vapor by the Knudsen effusion method. They considered the following reaction:

$$4CaO + 2Al = 3Ca + CaO \cdot Al_2O_3.$$

The vapor pressures obtained varied from 1.0 to 1.3 millimeters of mercury from 1150°C to 1200°C. From the experimental vapor pressures, the heat and entropy of formation of calcium aluminate were calculated and then compared with the corresponding heat and entropy of formation estimated from the literature. Their value of 680,000 calories for the heat of formation of calcium aluminate compared somewhat favorably with that from the literature, but their value for the entropy of formation (50 cal./deg.) of calcium aluminate appeared to have been high compared with the estimated value. From their calculations they suggested that the reaction proceeded by the reduction of lime with aluminum in the vapor phase rather than in the liquid phase. It is interesting to note that Dr. P. Gross, in his discussion of this investigation,[17] opposed the view held by the authors that the reaction preceeded by way of aluminum vapor. He based his opposition upon the results gathered from an investigation of the same reaction with magnesia. By this analogy, he stated

> "At the temperature at which magnesium evaporates with reasonable speed, the aluminum vapour pressure is still so small that the assumption of reaction via aluminum vapour would appear very improbable."[18]

He also made further calculations from the literature of the free energy of the calcium oxide reduction reaction and derived an equation for log p. From this equation he calculated the calcium pressures at the temperatures used by Atkinson and Pidgeon. He showed that satisfactory agreement with the experimental values was obtained both for the free energy of reaction and for the calcium pressures.

Only recently has any reaction pressure data for the vacuum reduction of barium oxide been obtained, and even these data are not extensive. V. V. Zhukovetskii has determined the reaction pressure of barium vapor from 1165°C to 1214°C. for the reaction,

$$4BaO + 2Al = 3Ba + BaO \cdot Al_2O_3.$$[19]

His values ranged from 10.91 to 17.02 mm. Hg. Also considered was a similar reaction for the reduction of strontium oxide with aluminum in the same temperature range. He obtained, for strontium, reaction pressures varying from 7.06 to 11.17 mm. Hg. His reaction pressures for calcium in the reaction,

$$6CaO + 2Al = 3Ca + 3CaO \cdot Al_2O_3$$

were low compared to those of Atkinson and Pidgeon. However, he used different reaction stoichiometry from that used by Atkinson and Pidgeon. Vedula and Gavrilyuk give the reaction pressure for $2BaO + Si = SiO_2 + 2Ba$ as $2.5 \cdot 10^{-5}$ mm. Hg at 1273°K and $4 \cdot 10^{-4}$ mm. Hg at 1600°K.[20] The Knudsen effusion method has been applied by Hoch, Lamantia, and Johnston[21] to the following reactions:

$$BaO + C = Ba + CO \qquad (1)$$

$$4BaO + Si = Ba_2SiO_4 + 2Ba \qquad (2).$$

Their data were not published, but it was stated that in reaction (1) the partial pressure of CO was in agreement with the calculated value, but the barium pressure was much lower than that calculated. In reaction (2) the barium pressure agreed with the calculated value.

Brown[22] studied the reaction,

$$BaO + C = Ba + CO,$$

by using a static method for determining the partial pressure of CO. The pressure of the barium vapor in contact with the reaction mixture was maintained at a constant value by heating a reservoir of solid barium at a known temperature. A capillary connection to the pressure measuring device limited the escape of barium vapor and thus prevented a difference in pressure between the reaction zone and the reservoir zone. The known partial pressures of barium and carbon monoxide were used to calculate the equilibrium constant and then the free energy change associated with the reaction. His value for the free energy of formation of barium oxide at 1223°K compares satisfactorily with the value from the literature.

CHAPTER III

THEORETICAL CONSIDERATIONS

Reaction Mechanism

The reduction of barium oxide by aluminum or silicon takes place at low pressures ($\sim 10^{-3}$ mm. Hg) and high temperatures (900-1200°C). The barium produced is condensed at the cool end of the furnace.

Various experimental parameters have been studied. There is general disagreement as to the temperature of reduction which would give the highest yield. The effect of molar ratio of barium oxide to reducing agent has been investigated also. These will be discussed later.

It is advantageous to assume the molar ratio of 4 BaO to 2 Al and 4 BaO to 1 Si when discussing the chemistry of this reduction. The following equations and discussion come from Dr. Kroll's article.[23]

The chemical reactions of the aluminum reduction and silicon reduction of barium oxide are represented by the following equations:

Reduction by Si:

(1) $4BaO + Si = SiO_2 \cdot 2BaO + 2Ba$

(2) $4BaO + 7Si = SiO_2 \cdot 2BaO + 2BaSi_3$

(3) $Ba + 3Si = BaSi_3$

(4) $12\ BaO + BaSi_3 = 3(SiO_2 \cdot 2BaO) + 7Ba$

Reduction by Al:

(1) $4BaO + 2Al = BaO\cdot Al_2O_3 + 3Ba$

(2) $4BaO + 14Al = BaO\cdot Al_2O_3 + 3BaAl_4$

(3) $Ba + 4Al = BaAl_4$

(4) $8BaO + BaAl_4 = 2(BaO\cdot Al_2O_3) + 7Ba$.

As can be seen from the above reactions, an orthosilicate is formed in the reduction by silicon, and a monoaluminate is formed in the reduction by aluminum. Several investigators have proven that such is the case in mixtures of BaO and Al_2O_3 and BaO and SiO_2 at elevated temperatures.

Formation of the orthosilicate instead of the metasilicate is attributed to the higher speed of crystallization of the former and to the higher rate of diffusion of barium oxide through the ortho variety.

The starting point in the proposed mechanism is the reaction of a silicon particle with BaO which is present in excess at the beginning. This reaction results in the formation of a metasilicate at the interface between the BaO and the Si particle. The metasilicate forms orthosilicate with more BaO. Through the orthosilicate more BaO diffuses and the orthosilicate layer grows, silicon being supplied by diffusion through the metasilicate layer. The orthosilicate is reducible to metasilicate and metal, but the metasilicate is stable against Si. This means that the metasilicate is continually growing into orthosilicate with diffusing BaO and then is broken back down into metasilicate and metal by silicon. This occurs only at the interface, and the orthosilicate grows in a direction opposite to the flow of the diffusing BaO. This diffusion of barium oxide through the orthosilicate layer is the main factor that affects the speed of the reaction.

It is also seen in equation (2) above that barium oxide and silicon react to form orthosilicate and the silicide. Equation (3) states that the barium liberated reacts with silicon to form the silicide. Thus a thin layer of $BaSi_3$ coats the Si particles. This compound may be melted at the high operating temperatures used and thus speed up the reaction by wetting the mixture. The $BaSi_3$ reacts with the BaO to liberate barium as seen in equation (4).

The aluminum reduction of barium oxide proceeds only a little differently due to the formation of the monoaluminate instead of an ortho variety.

The mechanism is essentially the same for aluminum reduction, and it is known that the aluminide melts at the temperature of operation whereas there is some doubt about the melting of $BaSi_3$.

According to Fujita and Yokomizo[24] a film of barium aluminate is formed at the boundary between the BaO and the melted aluminum. At this boundary of aluminate, the reaction proceeds by a diffusion process whereby either aluminum or BaO diffuses through the barium aluminate. In this case, the aluminum becomes ionic at this boundary. The aluminum ion has a smaller radius than does the BaO and, therefore, is more mobile. So the reaction proceeds by the penetration of the aluminum through the aluminate layer by what they call a lattice diffusion method. The aluminum then reacts with the BaO at the interface between the BaO and the aluminate.

The Effect of Temperature

The effect of temperature upon the yield of barium metal in the aluminothermic reduction of barium oxide at reduced pressures has been studied by Fujita and Yokomizo.[25] They used a balance which consisted of a quartz spring from which the crucible was suspended. By knowing the sensitivity of the quartz spring and measuring the change in length of the quartz spring, as the reaction proceeded, they were able to follow the reaction closely.

In one of their experiments the reaction initiation temperature was studied. They noticed a sharp increase in weight loss with respect to time at a temperature of about 1040°C, and, thus, they deduced that this was the reaction initiation temperature. Also, they noticed that increased moisture content of the barium oxide decreased the initiation temperature of the reaction. They claim that this phenomena was caused by the rise in local temperature resulting from the oxidation of aluminum by the dissociation gases given off from the reaction mixture at about 800-900°C.

They performed experiments to determine the effect of moisture adsorption in the barium oxide and found that, at constant temperature, increased moisture content of barium oxide caused a decrease in the yield of barium metal. They concluded that the reaction began before the dehydration of the barium oxide was complete, causing some of the metallic barium produced to react with the dissociation gases. They also admit the possibility that there could be a change in the composition of the barium aluminate produced if a considerable amount of moisture was originally adsorbed in the barium oxide.

They also studied the production rates of metallic barium at various temperatures, using a constant BaO:Al molar ratio, by the thermal balance method. In this case, they measured the total weight loss at various time intervals for four different temperatures. The production rate was calculated by expressing the weight loss as a percentage of the total weight of the barium oxide present before the reaction started. For 160 minutes of reaction time the temperature (°C) and corresponding production rate (%) respectively are as follows: 1085°C, 17.1%; 1130°C, 32.3%;

1150°C, 37.3%; 1200°C, 45.7%. It can be seen that increasing the temperature increases the production rate. Orman and Zembala give the temperature (°C) and the corresponding yield (%) as follows: 925°C, 27.4%; 1025°C, 28.2%; 1075°C, 32.3%; 1125°C, 34.0%.[26]

In general, there is some disagreement among the various authors as to the best temperature at which to carry out the reaction. The temperatures mentioned by these authors are in the range of 1040°C to 1400°C.

Reactant Molar Ratio

Another variable in the reduction of barium oxide with aluminum or silicon is the molar ratio of barium oxide to reducing agent. The ideal ratio for the reaction using aluminum would be 3BaO:2Al in accordance with the following reaction stoichiometry:

$$3BaO + 2Al = 3Ba + Al_2O_3.$$

However, several workers have proven that the conditions for the formation of double oxides or, in this case, barium aluminates, exist. An analogous condition occurs when magnesium is produced from dolomite. But, in this case, the calcium oxide in the dolomite ties up the aluminum oxide formed, and no magnesium is lost in combination with the aluminum oxide. We have seen that in the case of barium oxide reduction, the presence of calcium oxide would mean contamination of the barium metal with calcium metal. Thus, some of the barium oxide is sacrificed in order to tie up the aluminum oxide.

Most authors agree that the monoaluminate is formed in preference to the formation of a double or triple aluminate. Kroll says that this has been proven by others.[27] He also states that the dialuminate can definitely be reduced by aluminum but that the monoaluminate may not be reduced by aluminum. Also Gvelisiani and Pazukhim have established that the barium monoaluminate is formed in the reduction of barium oxide by aluminum.[28] They also found that by increasing the ratio of barium oxide to aluminum the per cent of aluminum consumed increases and the yield of barium metal goes through a maximum. Grube and Heintz studied the barium aluminates between 900°C and 1050°C, and they stated that the monoaluminate is formed in this temperature range.[29]

Therefore, the reaction is better represented by the following equation:

$$4BaO + 2Al = 3Ba + BaO \cdot Al_2O_3,$$

and the ideal molar ratio of barium oxide to aluminum is 4:2.

Fujita and Yokomizo have studied the effect of reactant molar ratio upon the production rate of barium.[30] They used molar ratios of 1:1, 1.5:1, and 2:1 and found that, at reaction times of two and three hours, the production rate was approximately the same for all three ratios. They concluded that when aluminum is present in an excess amount over the correct ratio, the barium produced forms an alloy with the aluminum and that the reaction rate at the beginning of the reaction is excessive.

For the reduction of barium oxide, using silicon, the ideal ratio would be two moles of barium oxide to one mole of silicon for the reaction:

$$2BaO + Si = 2Ba + SiO_2.$$

Again, the conditions for the formation of double oxides have been proven to exist. In this case, many investigators have found that the orthosilicate is preferentially formed. According to Kroll,

> "The preferential formation of orthosilicate has been explained by the greater speed of crystallization of this compound, which produces more nuclei than the metasilicate. It is also said that the alkaline-earth oxide diffuses faster through ortho than through metasilicate."[31]

Therefore, it is agreed that the following reaction for the reduction of barium oxide by silicon is the most correct one:

$$4BaO + Si = 2Ba + 2BaO \cdot SiO_2.$$

It can be seen that the ideal molar ratio of barium oxide to silicon is 4:1. This is the ratio most commonly described in patents for this process.

Vapor Pressure Methods

Several techniques have been developed for the measurement of the vapor pressure in heterogeneous equilibria involving a single gaseous component. According to Kubaschewski and Evans there are three principal methods.[32]

The static method involves placing the material to be investigated into an evacuated container which is connected to a suitable manometer. After equilibrium is achieved the vapor pressure is determined from the manometer.

The dynamic method or transportation method utilizes a steady, measured stream of inert gas which is passed over the material to be investigated. The vapor from the material is removed by the stream of inert gas at a rate which is dependent upon the rate of flow of the inert gas and the relative partial pressures of the two gases. The vapor is transported to the cool end of the apparatus where it is removed from the inert gas by condensation or chemical combination. Different rates of flow of inert gas are used to obtain different rates of removal of the vapor. In theory, saturation of the inert gas with the vapor should occur at zero rate of flow. By extrapolation, the actual vapor pressure can be determined. The calculation of the vapor pressure of the substance being investigated depends upon the measurement of the volumes of the vapor and of the transportating gas at standard temperature and pressure.

The effusion method or the Knudsen method of measuring vapor pressures is based upon the rate of effusion, in vacuo, of the vapor of the substance being investigated through a small orifice. Due to the characteristics of the apparatus employed in this investigation the effusion or Knudsen method was chosen. It was believed that more accurate data could be obtained by this method than by the other methods. The Knudsen method consists of placing the material into a container equipped with an orifice of known area. The experiment is carried out at a constant temperature and for a known length of time. The amount of vapor effused through the orifice is determined by weighing the container and its contents before and after the heating or by chemical or weight analysis of the condensate obtained from the experiment. By knowing the orifice area, the temperature, the time, the amount of material effused through the orifice, and its molecular weight, the vapor pressure can be calculated from the following equation:

$$p = \frac{G}{t \cdot A}\sqrt{\frac{2\pi RT}{M}}$$

where $p =$ vapor pressure of the material

$G =$ amount of material

$A =$ area of the orifice

$t =$ time of experiment

$R =$ gas constant

T = absolute temperature

M = molecular weight of the material effusing through the orifice.

The above equation can be derived from the kinetic theory of gases. From the Maxwell-Boltzman laws governing the distribution of molecular velocities, it has been proven that the arithmetical average velocity, $\bar{v}$, is given by the following equation:

$$\bar{v} = \sqrt{\frac{8RT}{\pi M}}$$

where R is the gas constant, T is the absolute temperature and M is the molecular weight.

From the kinetic theory of gases it has been found that the total number of collisions of molecules with the walls of a container per unit area per unit time, from all directions and with all speeds, is $1/4\ n\ \bar{v}$ where n is the number of molecules per unit volume and $\bar{v}$ is the average speed of the molecules. This expression can be written as $1/4(N/V)\bar{v}$ where N is the number of molecules and V is the volume. Then the total mass, m_1, striking the walls per unit area per unit time is $1/4(mN/V)\bar{v}$ where m is the mass of a single molecule. Written in terms of density, this expression becomes $1/4\ \rho\ \bar{v}$ where ρ is the density. So,

$m_1 = 1/4\rho\bar{v}$.

The equation of state of a perfect gas can be manipulated to obtain an expression for the density of a gas. This is done in the following way:

$$pV = \frac{N}{N_o}RT$$

where p is the pressure, V is the volume, N is the number of molecules, N_o is Avogadro's number, R is the gas constant, and T is the absolute temperature. Dividing both sides of the equation by V,

$$p = \frac{N}{VN_o}RT.$$

Then multiplying both sides of the equation by M, the molecular weight, and setting N/N_o equal to n_1, the number of moles of gas, one obtains

$$pM = \frac{n_1M}{V}RT.$$

Now, n_1M/V equals the density of the gas. So, $pM = \rho RT$ and

$$\rho = \frac{pM}{RT}.$$

Combining this equation with the expression derived for the total mass striking the walls of the container per unit area per unit time and the expression for the arithmetical average velocity, one obtains:

$$m_1 = \frac{1}{4}\rho\bar{v} = \frac{1}{4}\frac{pM}{RT}\cdot\sqrt{\frac{8RT}{\pi M}}\,.$$

Squaring this expression results in the following equation:

$$m_1^2 = \frac{1}{16} \cdot \frac{p^2 M^2}{R^2 T^2} \cdot \frac{8RT}{\pi M} .$$

Cancelling the terms and solving for the pressure, the following expression results:

$$p^2 = m_1^2 \frac{2\pi RT}{M} .$$

The square root of this expression gives the pressure in terms of total mass striking the walls of the container per unit area per unit time, the absolute temperature and the molecular weight of the gas. Thus,

$$p = m_1 \sqrt{\frac{2\pi RT}{M}} .$$

Since the quantity actually measured in the experiments is the total amount, G, of gas effusing through an orifice for a period of time, the total mass, m_1, striking the walls per unit area per unit time is,

$$m_1 = \frac{G}{A \cdot t}$$

where A is the orifice area and t is the total time of heating. Thus the expression for the pressure becomes

$$p = \frac{G}{A \cdot t} \sqrt{\frac{2\pi RT}{M}} .$$

By using the cgs system of units and equating the gas constant to 8.31×10^7 ergs per degree, this equation expresses the pressure in terms of dynes per cm^2. To express the pressure in terms of atmospheres or millimeters of mercury, it is necessary to apply the appropriate physical constants.

There are several ideal conditions under which the Knudsen method gives accurate vapor pressure measurements. According to Dushman,

> ". . . let us consider the case in which molecules evaporating from a hot surface pass through a small orifice into another chamber in which they are condensed. If the pressure of residual gas in this 'cool' compartment is extremely low and the radius of the opening is less than L, the mean free path of the evaporating molecules in the 'hot' compartment, then the rate at which molecules pass through the hole is equal to the rate at which they strike this opening."[33]

The general rule is that the mean free path of the evaporating molecules at the pressure of effusion should be ten times greater than the diameter of the orifice.

Another condition is that the thickness of the wall of the orifice must be very small compared to the radius of the orifice. In other words, a knife-edged orifice would be ideal. However, such ideality is not always possible and often the orifice may be in the form of a very short cylindrical tube with a wall thickness, to radius of orifice ratio varying from zero to 1.5. An orifice in the form of a tube offers more resistance to the flow of gas through it than does a knife-edged orifice. Dushman shows that Clausing and Kennard have derived correction factors for non-ideal orifices.[34] Kennard's factor, K, is the one used in this investigation and it is given by the following equation:

$$K = \frac{1}{1 + 0.5(\ell/a)}$$

where ℓ is the wall thickness and a is the radius of the orifice. Dushman states that such a correction factor represents ". . . the ratio between the rate at which gas leaves the outlet of the tube and that at which gas strikes the inlet."[35]

Other conditions which must be followed are that the effective sample area must be very much larger than the orifice area, the temperature must be kept constant and the temperature of the orifice must not be less than that of the sample, and the time necessary to heat and to cool the sample must be negligibly short compared to the total time that the sample is held at constant temperature. Also, the molecular weight of the gas effusing through the orifice must be known. This necessitates knowledge of the composition of the gas.

Thermodynamics

The change in free energy associated with a reaction is related to certain other functions also associated with the reaction. For instance, one such relationship is that between the standard free energy change and the equilibrium constant. Thus,

$$\Delta F^{\circ} = -RT \ln K_a \quad (1)$$

where K_a is the equilibrium constant and ΔF° is the standard free energy change. In reactions involving a single gaseous component as a product of the reaction, such as is under consideration here, the equilibrium constant becomes equal to the reaction pressure of that gaseous component. The exponent of the pressure term is dependent upon the reaction stoichiometry. In the following equation:

$$4BaO(s) + 2Al(l) = 3Ba(g) + BaO \cdot Al_2O_3(s)$$

where barium is a product and forms an ideal vapor phase, the equilibrium constant becomes,

$$K_a = p_{Ba}^3,$$

and the corresponding standard free energy change is,

$$\Delta F^\circ = -RT \ln p_{Ba}^3.$$

Similarly for the reaction,

$$4BaO(s) + Si(s) = 2Ba(g) + 2BaO \cdot SiO_2(s),$$

the standard free energy change is,

$$\Delta F^\circ = -RT \ln p_{Ba}^2.$$

Combining equation (1) above with the following Gibbs-Helmholtz equation:

$$\Delta F^\circ = \Delta H^\circ - T \Delta S^\circ \qquad (2)$$

one obtains

$$-RT \ln K_a = \Delta H^\circ - T \Delta S^\circ.$$

Changing to common logarithms and rearranging the terms, the following equation is derived:

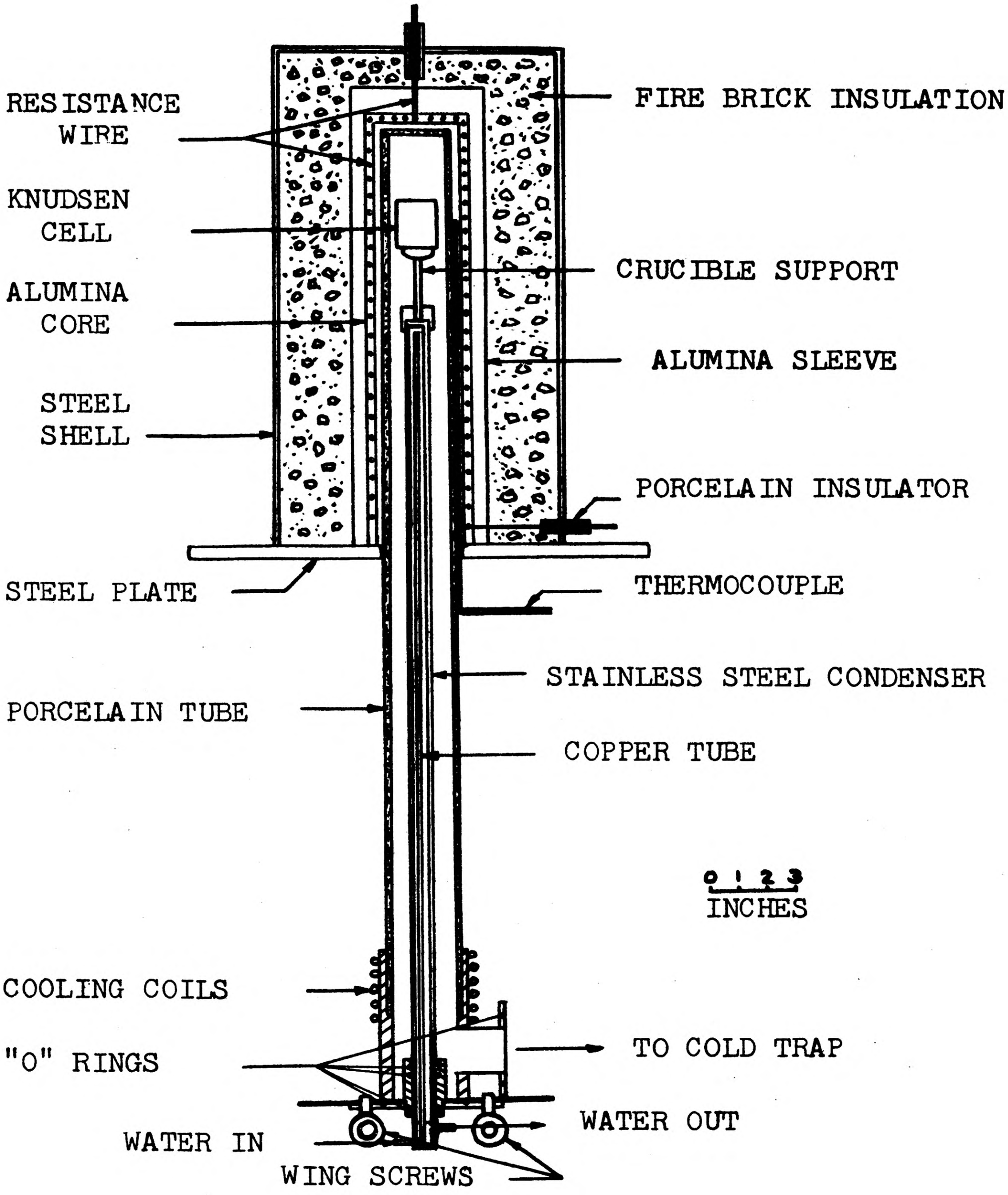
$$\log K_a = \frac{-\Delta H^\circ}{4.574 \cdot T} + \frac{\Delta S^\circ}{4.574} .$$

This is an equation of a straight line in the form of

$$\log K_a = \frac{A}{T} + B$$

where A is equal to $\frac{-\Delta H^\circ}{4.574}$ and is the slope of the line and B is equal to $\Delta S^\circ/4.574$ and is the intercept of the line with the ordinate. Thus, the change in the enthalpy and the change in the entropy of the reaction can be found by plotting log K_a values against corresponding values of the reciprocal of the absolute temperature and then finding the slope and the intercept of the line.

These values of the change in the enthalpy and the change in the entropy of the reaction can be used to calculate the standard free energy change of the reaction in the temperature range considered. From this free energy of reaction, the standard free energy of formation of barium monoaluminate and barium orthosilicate can be determined by using known free energy data for barium oxide.



FURNACE CONSTRUCTION *

Figure 1.

*Norbert F. Neumann, "Preparation and Separation of Metallic Chlorides" (unpublished Doctor's thesis, The University of Missouri, Rolla, 1955), p. 50.

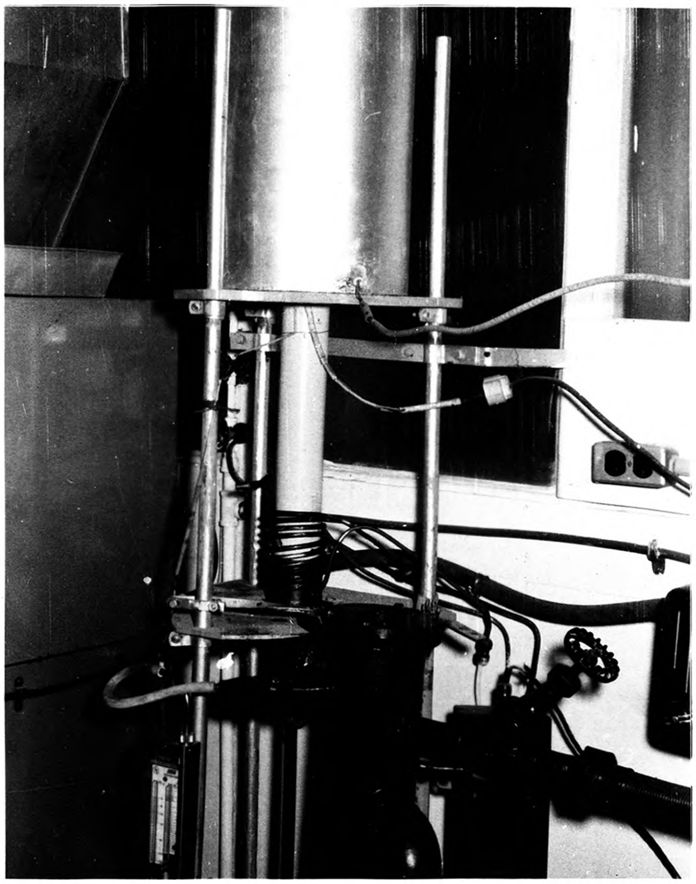


Figure 2. The Arrangement of the Furnace.

core. This heating assembly was insulated by fire bricks. The fire bricks were contained in a steel shell and a five-eighths inch thick steel plate was welded to the bottom of the steel shell. The steel plate also supported the heating assembly.

The water-cooled condenser assembly consisted of a hollow stainless steel tube which was thirty inches long and five-eighths of an inch in diameter. The upper end of the tube was closed with a stainless steel cap. The lower end was closed with a brass cap. Into the brass cap was soldered a copper tube which extended to three-eights of an inch from the top of the condenser. Another short copper tube was also soldered into the brass cap to complete the cooling water circuit.

The cooling water entered the condenser through the long copper tube. The water flowed up this tube and was sprayed against the cap at the top of the condenser after which it flowed down between the long copper tube and the inside wall of the condenser. The water left the condenser through the outlet copper tube as shown in Figure 1.

A stainless steel cap was placed on the top of the condenser. Into a hole in this cap was inserted a porcelain heat reflector which served as the Knudsen cell support.

The condenser was supported by a hollow steel cylinder which was soldered onto a steel plate. The steel plate was attached to the base of the furnace by two wing screws. The condenser fitted tightly into the inside of the hollow steel cylinder. "O" rings were employed between the condenser and the steel cylinder in order to ensure a vacuum tight seal. The condenser could be raised or lowered without breaking the vacuum.

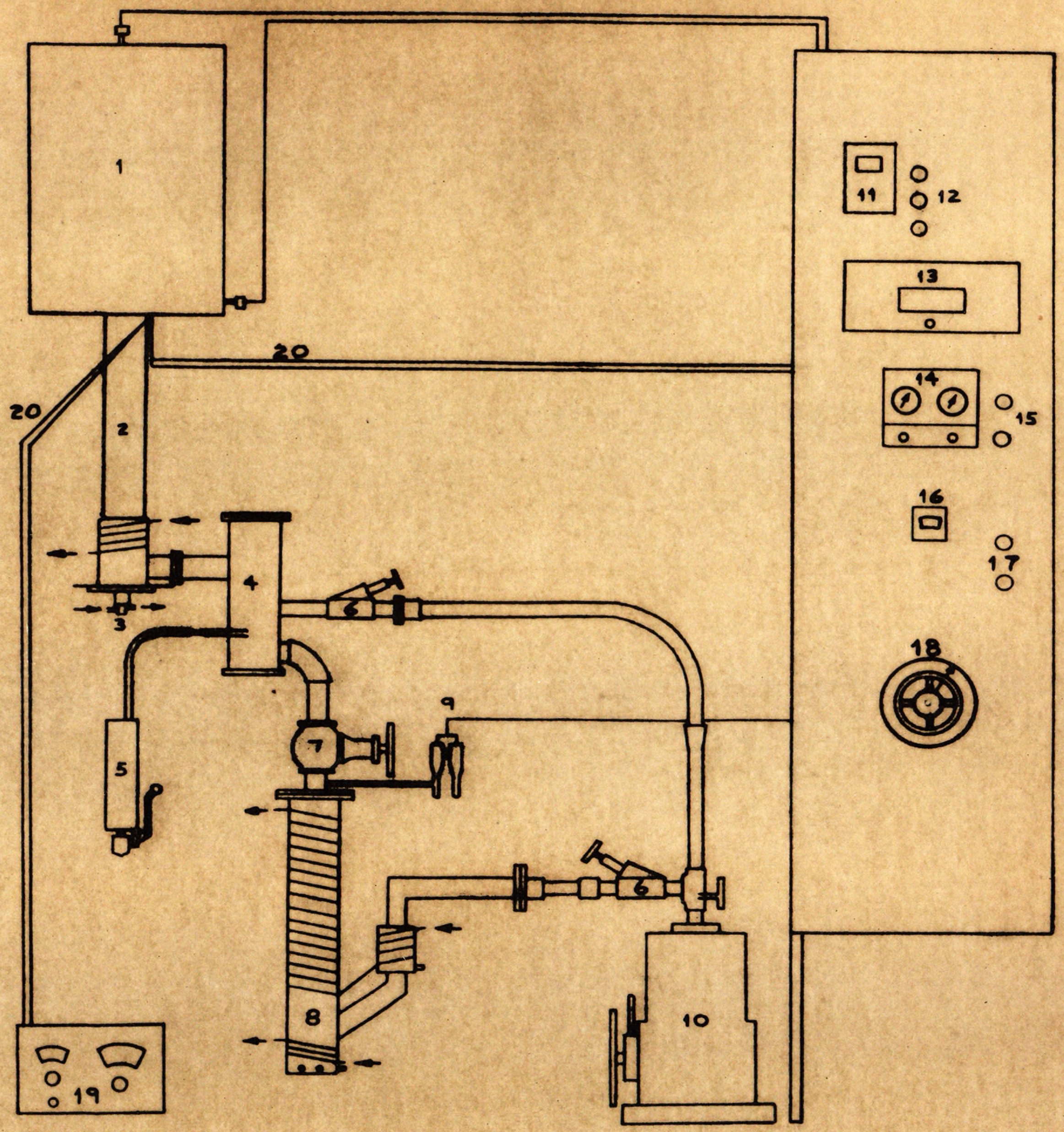
The temperature of the furnace was measured by an Alumel-Chromel thermocouple which was placed on the outside of the procelain furnace tube. This thermocouple was connected to a Wheelco Controller which controlled the temperature within ±5°C. Since this controller did not give the correct temperature reading, it was necessary to use a calibrated platinum - 90% platinum, 10% rhodium thermocouple, connected to a potentiometer. By reading the millivoltage during the experiment and then finding the corresponding temperature from a standard conversion table, the correct temperature on the outside of the furnace could be determined. Both thermocouples were placed at the same height as that of the Knudsen cell during the actual experiments.

The temperature on the outside of the furnace tube was compared to that inside the furnace tube by placing a calibrated Chromel-Alumel thermocouple in the same position as that of the Knudsen cell during the operation of the furnace. This internal thermocouple was sealed into the furnace tube so that the comparison could be made using a vacuum. Several comparisons were made in the temperature range of 800°C to 1100°C. It was found that the internal temperature was, on the average, sixteen degrees lower than the temperature recorded on the outside of the porcelain furnace tube in this range. A plot was made of the temperature on the outside of the furnace tube versus the temperature inside of the furnace tube. This calibration plot was used to obtain the correct temperature.

The Vacuum System

The vacuum system employed was an all metal system. Connected to the furnace tube by means of an "O" ring connection was a short flexible metal tube which lead directly to the cold trap. The cold trap was made of four inch diameter steel pipe which was ten inches long. A steel plate was welded to the bottom of the steel pipe. A place for the refrigerant was provided by a two inch diameter, eight inch long copper tube which was vacuum sealed to the top of the cold trap by an "O" ring.

The cold trap was connected to the vacuum pumps through two openings. One opening led directly to the mechanical vacuum pump through a flexible metal tube. A valve was placed in this line which was used as a rough-down line. A steel pipe welded to the second opening led through



1. RESISTANCE FURNACE
2. PORCELAIN TUBE
3. CONDENSER
4. COLD TRAP
5. KINNEY GAUGE
6. ONE INCH VALVES
7. TWO INCH VALVE
8. DIFFUSION PUMP
9. PIRANI GAUGE TUBE
10. N.R.C. PUMP
11. TORK CLOCK
12. FURNACE SWITCH
13. WHEELCO CONTROLLER
14. PIRANI GAUGE
15. MECHANICAL PUMP SWITCH
16. AMMETER
17. DIFFUSION PUMP SWITCH
18. POWERSTAT
19. POTENTIOMETER
20. THERMOCOUPLES

Figure 3. The Arrangement of the Apparatus.

a valve to the top of the oil diffusion pump. The oil diffusion pump was connected to the mechanical pump by a metal tube. A valve was also placed in this line.

The valves in the system served to control the direction of flow of the gases into the pumps and to isolate various parts of the system when desired. Flanged joints sealed by "O" rings were employed at various locations in the system so that the system could be taken apart easily for repair. The entire system is illustrated in Figure 3.

The pressure in the system was measured at two different locations. A Kinney mercury gauge was connected to the cold trap. This connection also served as the vacuum connection to the small vacuum bottle used to transfer the samples to the dry atmosphere box. A Pirani gauge tube was connected to the top of the oil diffusion pump.

A Distillation Products, Inc. oil diffusion pump, type MC 275, was used in this investigation. This pump was backed by a National Research Corp. rotary gas ballast mechanical pump.

The instrument panel contained the Pirani gauge, the powerstat, the ammeter, the Wheelco temperature controller, and a Tork clock used for turning the furnace on and off. The instrument panel is shown in Figure 5.

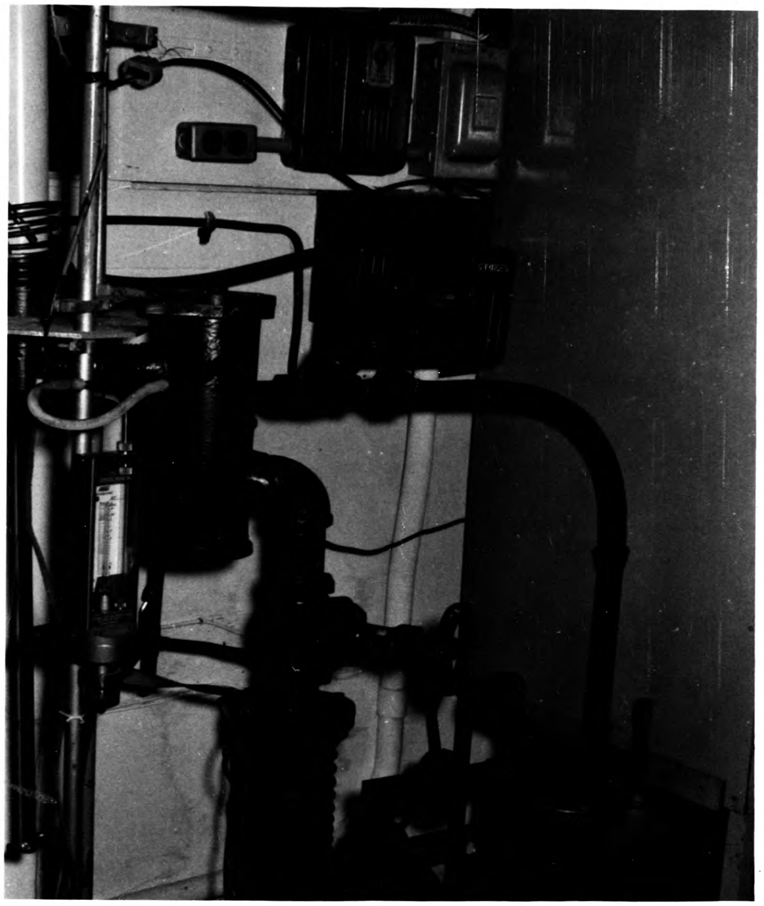


Figure 4. The Vacuum System.

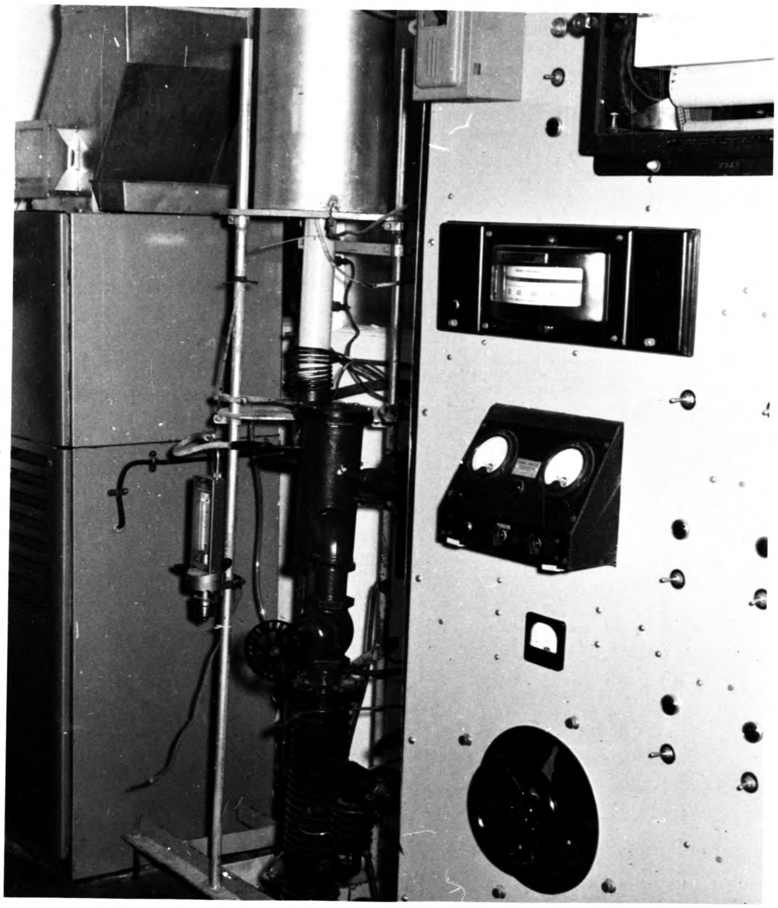


Figure 5. The Instrument Panel.

The Dry Atmosphere Box

The dry atmosphere box, as shown in Figure 6, was made of five-eighths inch thick plywood. A window was installed in the front of the dry box. This window extended almost the entire length of the dry box and allowed vision of the entire interior of the box. There was also a window in one side of the dry box. All joints were sealed with beeswax to ensure air tightness.

To the front of the dry box was fastened a one-quarter inch thick rectangular piece of plywood. Four holes were cut out of this piece, and wooden rings were mounted on these holes. Two pairs of eighteen inch long obstetrical gloves were glued to the wooden rings. The gloves extended to the inside of the dry box. Thus, the operator could reach any part of the inside of the box.

A door through which large equipment could be moved was situated on top of the box. Small items were introduced into the box and removed from it through a small sliding door in the front of the box. This door led to a lock chamber. Another sliding door led from the lock chamber to the inside of the box.

The air inside of the box was dried by six trays of anhydrous phosphorus pentoxide and two large boxes of barium oxide. One tray of phosphorus pentoxide was located

Figure 6. The Dry Atmosphere Box.

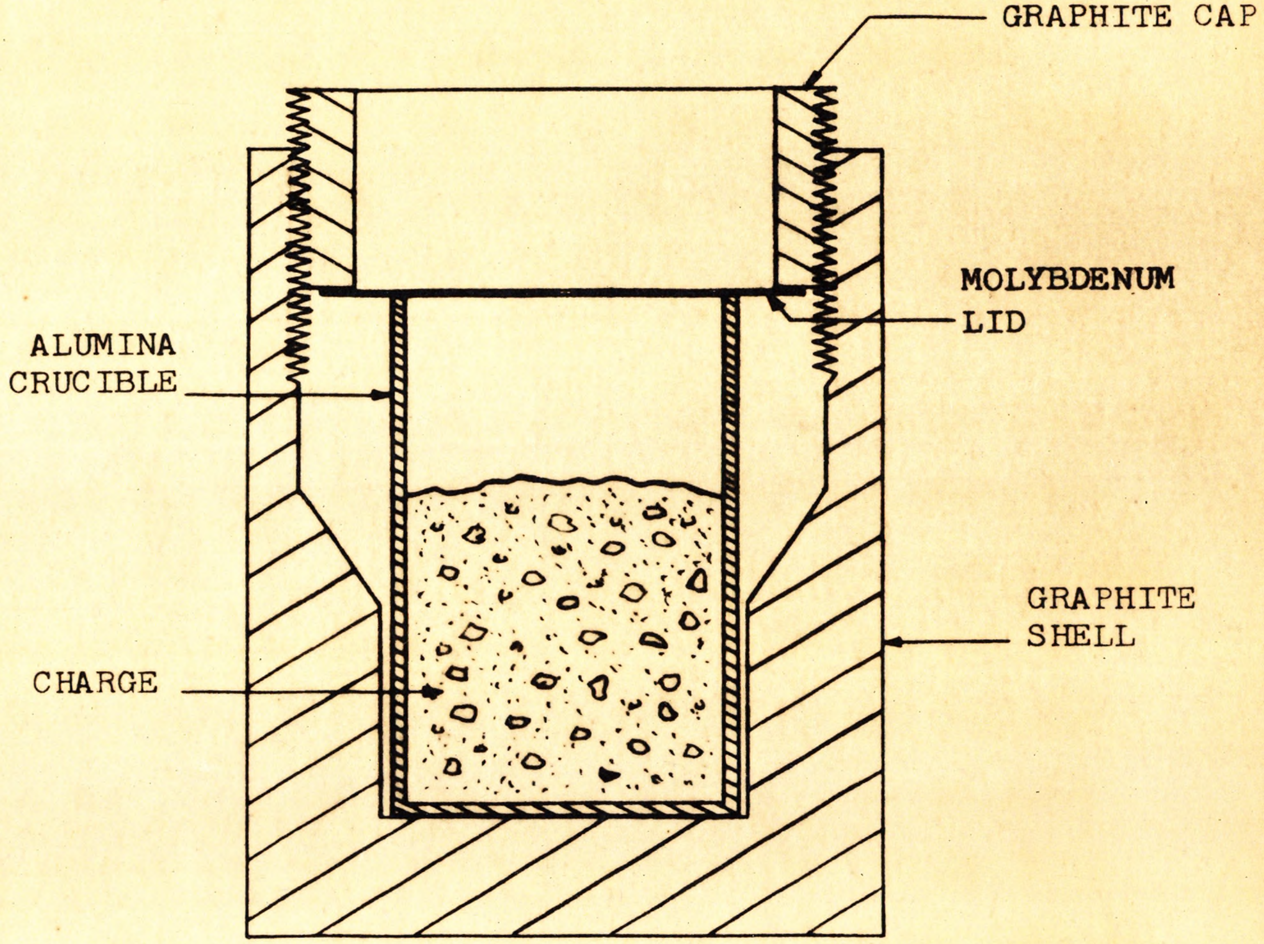
inside of the balance. When the phosphorus pentoxide became liquid it was replaced with dry pentoxide. A small blower was used to circulate the air over the drying agents.

An analytical balance was placed directly in front of one pair of gloves. The weights used in this balance were calibrated on a sensitive chainomatic balance. Reagents, mortar and pestle, tongs, crucibles, and various other equipment used in the preparation of the charge were placed inside of the dry box. Lighting was provided by a fluorescent lamp placed at the top of the back wall of the box.

The Knudsen Cell

A cut-away view of the Knudsen cell is shown in Figure 7. The outside shell and the cap were machined from high purity graphite rod. The shell had an outside diameter of one and one-half inches and was two inches long. The inside depth of the shell was one and eleven-sixteenths inches. The cap which screwed down inside of the shell was one-half inch long and had an inside diameter of one inch.

The crucible which fitted into the shell was made of recrystallized alumina and had a capacity of ten cubic centimeters. Its outside diameter was thirteen-sixteenths of an inch, and its length was one and five-sixteenths



KNUDSEN CELL CONSTRUCTION

Figure 7.

inches. Before being weighed, the crucible was fired and allowed to cool to room temperature in a desiccator. Then the top of the crucible was sanded in order to ensure as tight a fit as possible with the molybdenum lid.

The lid was cut from five-thousandths inch thick molybdenum sheet. The diameter of the lid was made slightly smaller than the inside diameter of the graphite shell. Thus, when the graphite cap was screwed down upon the lid, the lid was pressed down tightly upon the top of the crucible.

The orifice was made by drilling a hole in the center of the lid. Two different orifice sizes were used for each temperature. Drill bits whose diameters were 0.0625 inches and 0.041 inches were used to drill the respective orifices. After drilling the orifice was examined under a microscope. Metal burrs were then removed from the edge of the orifice by using the drill bit manually and by sanding. The diameter of the orifice was measured under a microscope with a filar eyepiece.

After the charge was prepared the alumina crucible was placed into the graphite shell. The lid was then placed on top of the crucible after which the graphite cap was screwed down tightly upon the lid.

CHAPTER V

PROCEDURE

The following procedure was used for the measurement of the barium vapor pressure above the reaction mixture in the reduction of barium oxide in vacuo using aluminum or silicon as the reducing agent. The three basic reactions involved in this determination are:

(1) $BaO_2 = BaO + (O)$

(2) $4BaO + 2Al = 3Ba + BaO \cdot Al_2O_3$

(3) $4BaO + Si = 2Ba + 2BaO \cdot SiO_2$.

Preparation of BaO

Barium oxide has a tendency to hydrate and carbonize upon exposure to air. This behavior makes it difficult to obtain a correct weight balance and causes some difficulty in the actual process itself during the course of the rapid heating of the charge required in the measurement of vapor pressures. That is, water vapor and carbon dioxide would be driven off so fast at the high temperatures required that the charge would blow out of the crucible.

Therefore, it was necessary to prepare fresh barium oxide for each run and to prevent any prolonged exposure of it to the air and particularly to moist air. In this way, the difficulties mentioned above could be minimized.

Preparation of the barium oxide is illustrated in equation (1). Ten grams of barium peroxide were weighed in a previously weighed alundum crucible. All weighings were carried out in a dry box. The crucible containing the barium peroxide was transferred to a desiccator and was then taken to the furnace. The condenser and the crucible support were removed from the furnace. The crucible was taken out of the desiccator and was placed upon the crucible support, and the entire assembly was put into the furnace. A small quantity of vacuum grease was applied to the condenser tube to facilitate its movement through the "O" rings. The charge was then raised into the cold furnace. The cooling water was turned on after which the vacuum pumps were started. When the pressure in the system was reduced to $2\text{-}5 \cdot 10^{-3}$ mm. Hg, the furnace was turned on, and the sample was heated slowly. The sample was then allowed to react at a constant temperature of 840°C for three hours. At the end of this time the sample was withdrawn from the heated zone of the furnace and allowed to cool to room temperature under vacuum. After cooling the vacuum was released, and the condenser assembly was removed from the furnace. The crucible and its contents were quickly placed into a small bottle whole lid was equipped with a vacuum hose connection. The condenser assembly was replaced into the cold end of the furnace. The vacuum bottle was then connected to the vacuum system, and the furnace and the small bottle were evacuated. After evacuation, the bottle was isolated from the vacuum system by means of a hose clamp and then disconnected from the system.

At this point the vacuum pumps were stopped, and the furnace temperature controller was set at the temperature desired for the reduction step.

The bottle and its contents were then taken to the dry box and placed inside of the dry box. The vacuum in the bottle was released, and the crucible and its contents were removed and immediately weighed. Stoichiometrically, the weight of oxygen given off from a ten gram sample of barium peroxide is 0.95 grams. If the loss of weight from the crucible and its contents was 0.95 grams or greater, then it was assumed that enough oxygen had been given off and that the residue was barium oxide.

Preparation of the Reaction Mixture

The barium oxide produced in the first step was removed from the alundum crucible and crushed in a mortar and pestle. Several grams of this barium oxide were then weighed in a previously weighed crucible. To this was added a stoichiometric amount of reducing agent. For reaction (2) granular aluminum grains of particle size 20 mesh or finer were used.

For reaction (3) hand crushed fused silicon of particle size 20 mesh or finer was used. The reducing agent and the barium oxide were thoroughly mixed in the crucible.

The crucible containing the charge and the previously weighed molybdenum lid were then placed into the shell, and the cap was screwed down upon the lid. The shell was transferred to a desiccator and taken to the furnace.

The Reduction Process

The shell and its contents were placed into the cool end of the furnace in the same manner as is described in the preparation of barium oxide. The vacuum pumps were turned on, and when a pressure of $2\text{-}3 \cdot 10^{-3}$ mm. Hg was obtained, the charge was raised into the heated portion of the furnace. The temperature and the exact starting time of the trial were noted.

The reaction was allowed to proceed for two or three hours at a constant temperature. After this time had elapsed, the condensate and the shell containing the crucible were lowered into the cool end of the furnace and were allowed to cool to room temperature under reduced pressure. The exact finish time was noted.

After cooling, the vacuum was released, and the condenser assembly and the shell containing the crucible and residue were removed from the furnace. The shell and its contents were immediately placed into the small bottle, put under a vacuum, and taken to the dry box. After the shell was removed from the vacuum bottle, inside of the dry box, it was taken apart, and the small crucible containing the residue plus the molybdenum lid were removed and then weighed. The combined weight of the crucible, the residue, and the molybdenum lid was subtracted from the original combined weight of the crucible, the charge, and the molybdenum lid. The weight difference constituted the weight loss, and this weight loss was assumed to be the weight of the barium metal effusing through the small orifice in the lid.

The condensate was discarded. A small amount of the residue was retained for qualitative X-ray analysis.

After each trial run the furnace was evacuated and left under reduced pressure until the next trial run. The valves between the furnace and the pumps were closed, and the pumps were turned off.

CHAPTER VI

CALCULATIONS AND RESULTS

There were two correction factors for the measured barium pressure. The first was Kennard's factor, K, for a tube-like orifice. This factor is given by the relationship

$$K = \frac{1}{1 + 0.5(\ell/a)}$$

where ℓ is the length of the orifice and a is its radius. The experimental barium pressures were all divided by this factor. For the particular orifice sizes used, K varied from 0.93 for the large orifice to 0.89 for the small orifice.

An overall correction factor was determined by substituting pure metallic silver for the normal reaction mixture. The vapor pressure of silver in the temperature range used is considerably below the experimental barium pressures. However, it was assumed that the correction factor derived was a function of the method and the characteristics of the orifice and was independent of the magnitude of the pressure. The vapor pressure of silver was determined in the same manner as were the barium pressures. Only the highest temperature attainable in the furnace was used in order to obtain the largest weight loss from the crucible as was possible. At lower temperatures the data were not reliable. In this way, the error was reduced. It was found that the silver vapor pressures determined in two trials using the small orifice were higher and agreed more closely to the values given in the literature than the pressures determined in two trials using the large orifice. Therefore, a correction factor for each orifice size was calculated. The results and the calculated correction factors are given in Table I. The silver vapor pressures calculated from the literature are those from an equation given by Kubaschewski and Evans.[36] Atkinson and Pidgeon[37] determined an orifice calibration factor of 1.46 by finding the vapor pressure of silver using the Knudsen method and then comparing their results to the values from the literature. They applied this factor to the experimental calcium pressures obtained in an investigation of the aluminothermal reduction of calcium oxide.

Since the overall correction factor was determined at only one temperature, the subsequent calculations from the data were done in both the uncorrected form and in the corrected form. Another reason for doing this was that the barium pressure calculated from the use of the small orifice at the highest temperature was greater in each case than that calculated from the use of the large orifice at the same temperature. This trend was reversed at the lower temperatures, and, therefore, the correction factors calculated at

TABLE I

Calculation of Correction Factor Based on Measurement of Silver Vapor Pressures

Time of each trial, 2 hours

Orifice Area	Temp.	Wt. Ag Effused	Experimental Vapor Pressure	Calculated Vapor Pressure	Correction Factor
$cm^2 \cdot 10^{+4}$	^oK	grams	$mm.Hg \cdot 10^{+2}$	$mm.Hg \cdot 10^{+2}$	
222.1	1358	0.041	1.68	2.69	
215.9	1355	0.042	1.77	2.63	
			Ave. = 1.725	Ave. = 2.66	1.54
95.0	1362	0.025	2.49	2.88	
95.0	1362	0.023	2.28	2.88	
			Ave. = 2.385	Ave. = 2.88	1.21

the highest temperature may not have applied at the lower temperatures.

The uncorrected barium pressures were calculated from the following equation,

$$p = \frac{G}{A \cdot t \cdot K} \sqrt{\frac{2\pi RT}{M}}$$

where K is Kennard's factor for a tube-like orifice, G is the amount of metal vapor of molecular weight, M, effusing through the orifice of area, A, in time, t, R is the gas constant, and T is the temperature in degrees Kelvin. By using the cgs system of units, the equation gave the pressure in dynes/cm^2. The pressure was then multiplied by $760/1.013 \cdot 10^6$ in order to express it in millimeters of mercury for the purpose of comparison. Table II contains the measurements of the variables and the uncorrected barium pressures for the aluminum reduction of barium oxide. The last column contains the values of log K_a calculated from the uncorrected pressures expressed in atmospheres. Table IV contains the same data for the silicon reduction of barium oxide.

The corrected pressure was calculated by multiplying the uncorrected value by the appropriate correction factor. The corrected barium pressures and the corresponding log K_a values for the aluminum and silicon reduction of barium oxide are given in Tables III and V, respectively.

TABLE II

Calculation of the Uncorrected Barium Pressure
and the Corresponding Log K_a
for the Reaction,
$4BaO + 2Al = 3Ba + BaO \cdot Al_2O_3$

Orifice Area	Temp.	$1/T \cdot 10^{+4}$	Time of Trial	Weight Barium Effused	Barium Pressure (uncorrected)	Log K_a
$cm^2 \cdot 10^{+4}$	^oK	$1/^oK$	hours	grams	mm. Hg	p_{Ba} in atm.
226.0	1213	8.24	3	1.515	0.34	-10.052
99.0	1213	8.24	3	0.595	0.32	-10.146
210.1	1222	8.17	2	0.852	0.31	-10.168
94.1	1213	8.24	2	0.270	0.23	-10.577
214.7	1273	7.85	2	2.263	0.82	- 8.912
93.7	1273	7.85	2	0.887	0.77	- 8.987
225.0	1359	7.36	2	3.224	1.15	- 8.454
94.0	1359	7.36	2	1.583	1.40	- 8.206
208.8	1346	7.44	2	2.781	1.07	- 8.562
95.4	1358	7.37	2	1.666	1.46	- 8.150

TABLE III

Calculation of the Corrected Barium Pressure and the Corresponding Log K_a for the Reaction,

$$4BaO + 2Al = 3Ba + BaO \cdot Al_2O_3$$

Correction factor for large orifice, 1.54

Correction factor for small orifice, 1.21

Orifice Area	Temp.	Barium Pressure (Uncorrected)	Barium Pressure (Corrected)	Log K_a
$cm^2 \cdot 10^{+4}$	^oK	mm. Hg	mm. Hg	p_{Ba} in atm.
226.0	1213	0.34	0.52	- 9.487
99.0	1213	0.32	0.38	- 9.900
210.1	1222	0.31	0.48	- 9.608
94.1	1213	0.23	0.27	-10.327
214.7	1273	0.82	1.26	- 8.340
93.7	1273	0.77	0.93	- 8.741
225.0	1359	1.15	1.77	- 7.898
94.0	1359	1.40	1.69	- 7.961
208.8	1346	1.07	1.64	- 7.997
95.4	1358	1.46	1.76	- 7.904

TABLE IV

Calculation of the Uncorrected Barium Pressure
and the Corresponding Log K_a
for the Reaction,
$4BaO + Si = 2Ba + 2BaO \cdot SiO_2$

Orifice Area	Temp.	$1/T \cdot 10^{+4}$	Time of Trial	Weight Barium Effused	Barium Pressure (Uncorrected)	Log K_a
$cm^2 \cdot 10^{+4}$	^{o}K	$1/^{o}K$	hours	grams	mm. Hg	p_{Ba} in atm.
210.8	1270	7.87	2	1.454	0.54	-6.302
93.7	1270	7.87	2	0.365	0.31	-6.772
91.1	1268	7.90	2	0.445	0.40	-6.568
217.4	1331	7.51	2	2.112	0.77	-5.983
98.1	1327	7.55	2	0.988	0.83	-5.925
213.4	1358	7.37	2	3.096	1.17	-5.625
92.4	1349	7.42	2	1.766	1.60	-5.351
224.1	1358	7.37	2	3.052	1.10	-5.683

TABLE V

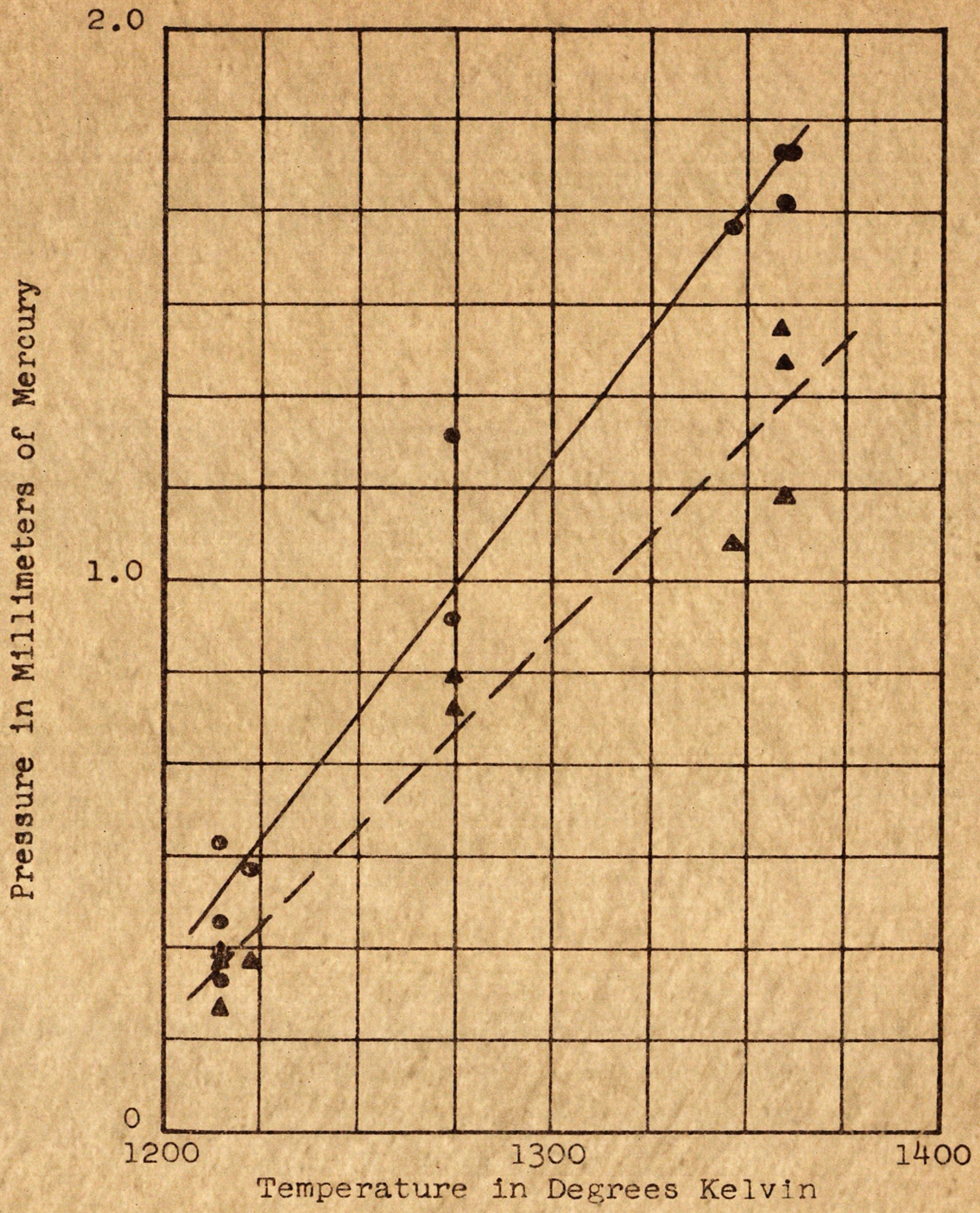
Calculation of the Corrected Barium Pressure
and the Corresponding Log K_a
for the Reaction,
$4BaO + Si = 2Ba + 2BaO \cdot SiO_2$

Correction factor for large orifice, 1.54

Correction factor for small orifice, 1.21

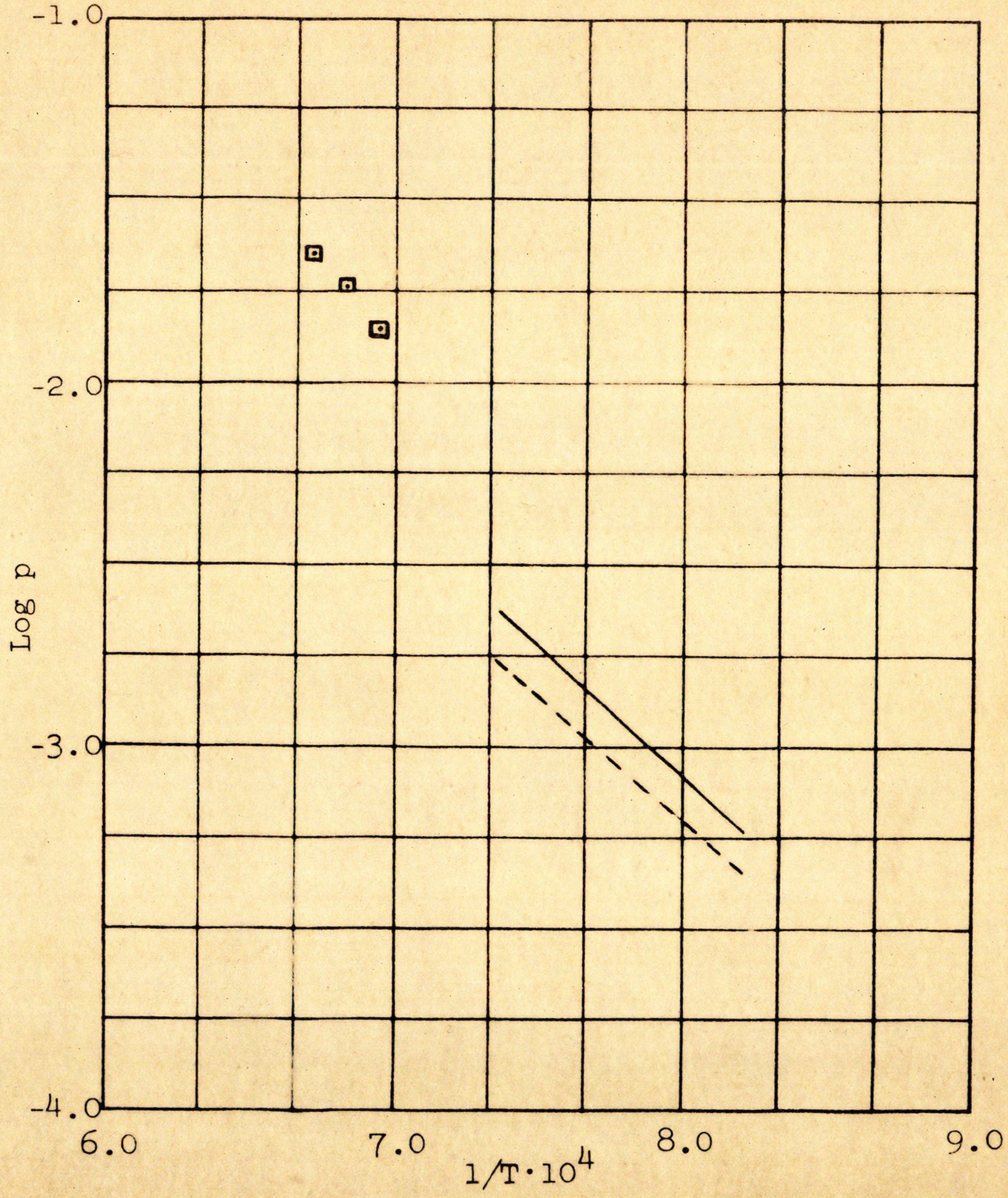
Orifice Area	Temp.	Barium Pressure (Uncorrected)	Barium Pressure (Corrected)	Log K_a
$cm^2 \cdot 10^{+4}$	$^{\circ}K$	mm. Hg	mm. Hg	p_{Ba} in atm.
210.8	1270	0.54	0.83	-5.925
93.7	1270	0.31	0.38	-6.604
91.1	1268	0.40	0.48	-6.403
217.4	1331	0.77	1.19	-5.608
08.1	1327	0.83	1.00	-5.759
213.4	1358	1.17	1.79	-5.254
92.4	1349	1.60	1.94	-5.187
224.1	1358	1.10	1.68	-5.311

Figures 8 and 9 show the barium pressures at various temperatures for the aluminum and silicon trials, respectively. The method of least squares was used in order to construct a line to fit the data. The least squares lines for both the corrected and the uncorrected pressures are shown in each figure. The greater slope of the line for the corrected pressures in each case is attributed to the greater amount of correction at higher pressures. In comparing the two figures, the barium pressures for the aluminum trials were greater than those for the silicon trials at a temperature of about 1270°K. This is in agreement with the accepted advantage of aluminum over silicon as a reducing agent. However, in the temperature range of 1350° to 1360°K, the difference in the pressures obtained by the use of aluminum and silicon is considerably decreased, and it would seem that the experimental pressures from the aluminum trials were too low at this temperature. Zhukovetskii determined the vapor pressure of barium above the reaction, $4BaO + 2Al = 3Ba + BaO \cdot Al_2O_3$.[38] His data were extrapolated to the temperature range used in this study for the purpose of comparison. The temperature (°K) and the corresponding barium pressures (mm. Hg) were as follows: 1173°K, 0.049 mm. Hg; 1273°K, 1.84 mm. Hg; 1373°K, 5.68 mm. Hg. His barium pressures at 1273°K and 1373°K are substantially higher than the experimental barium pressures we obtained in



Legend
O Corrected pressure
Δ Uncorrected pressure
____ Least squares line for corrected pressures
--- Least squares line for uncorrected pressures

Figure 8. Vapor pressures above the reaction, $4BaO + 2Al = 3Ba + BaO \cdot Al_2O_3$



Legend

□ Log p values from data given by Zhukovetskii*
—— Least squares line for corrected pressures
--- Least squares line for uncorrected pressures

Figure 8a. Comparison of log p vs. $1/T \cdot 10^4$ curves with that from the data given by Zhukovetskii for the reaction, $4BaO + 2Al = 3Ba + BaO \cdot Al_2O_3$

*Zhukovetskii, loc. cit.

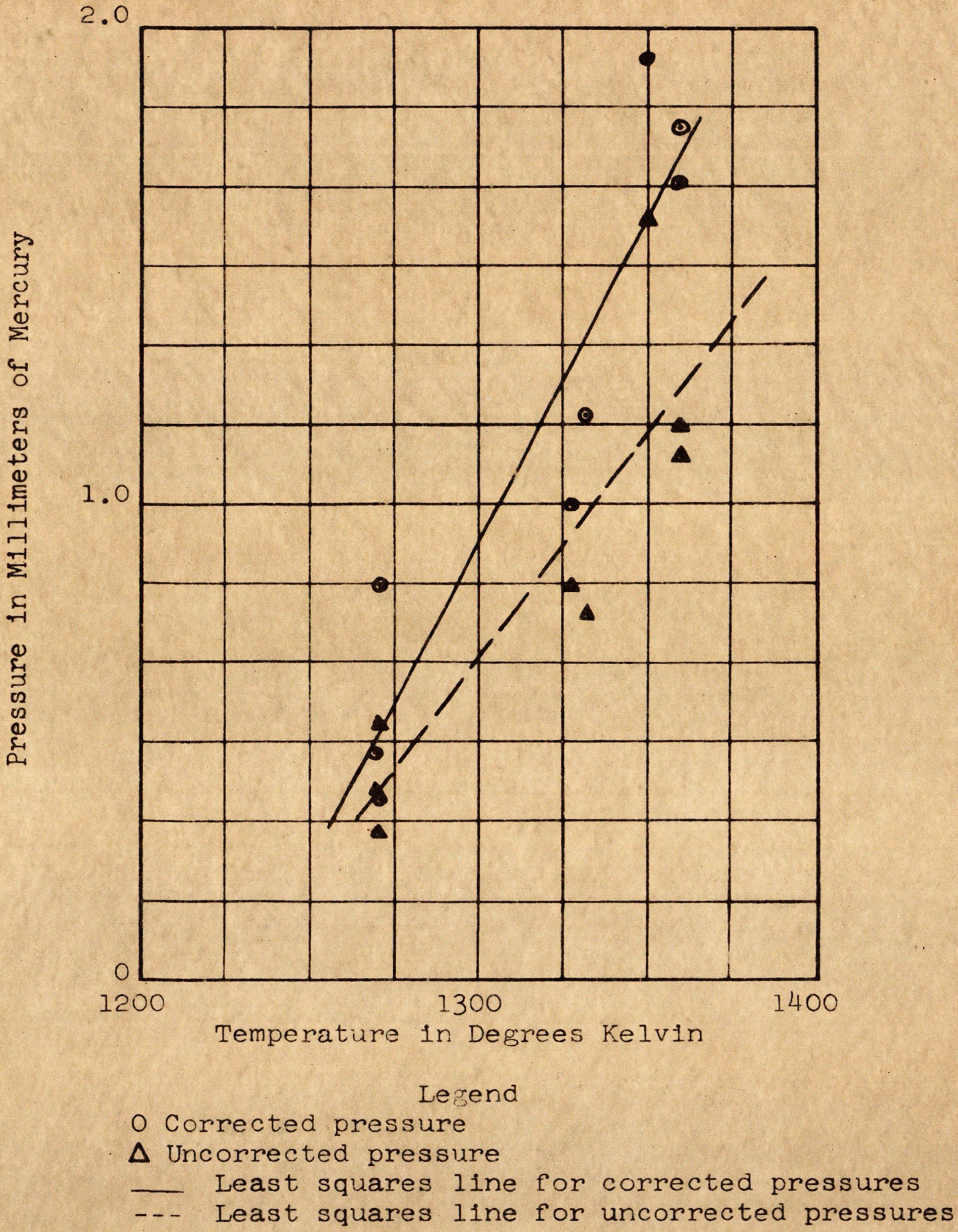


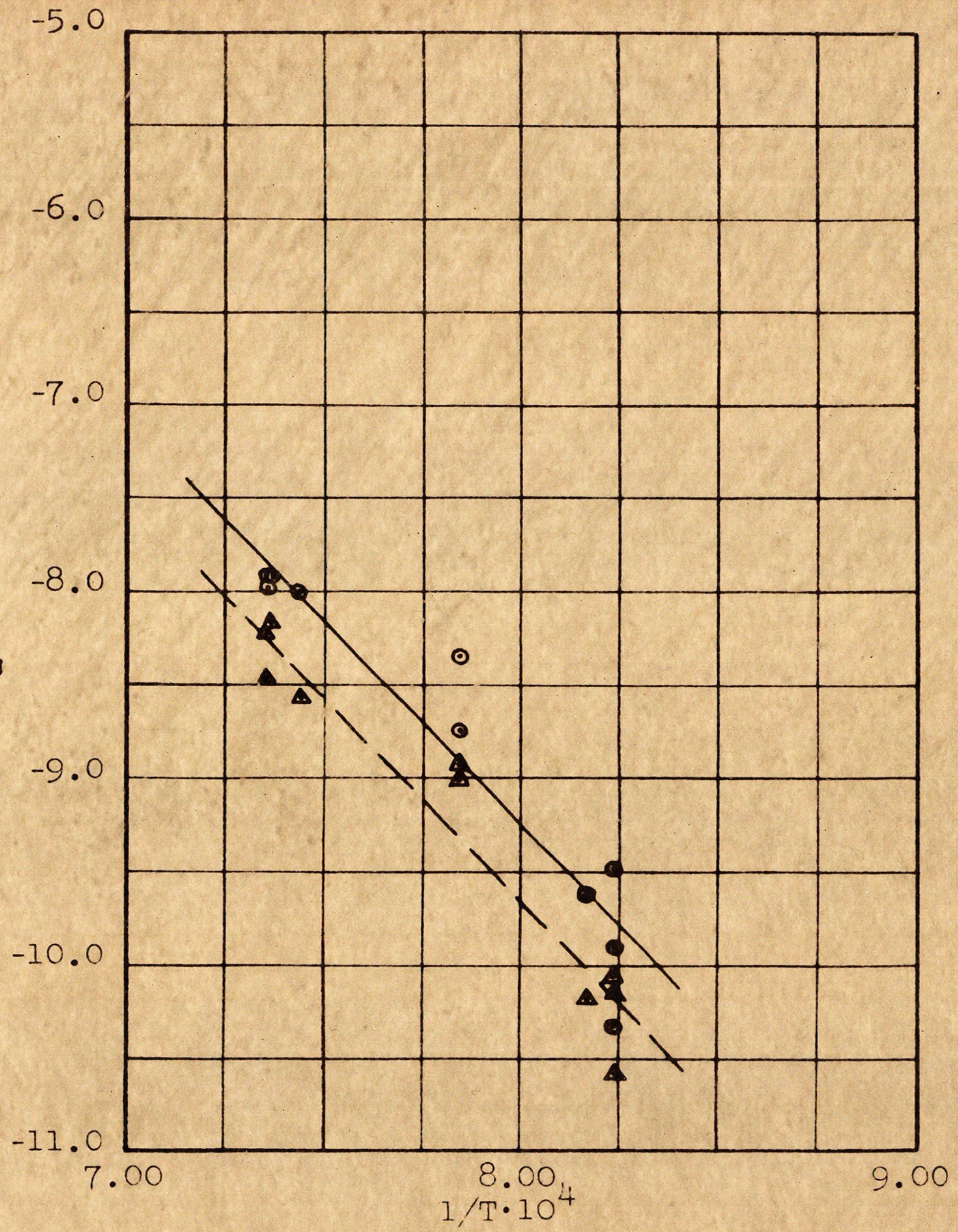
Figure 9. Vapor pressures above the reaction, $4BaO + Si = 2Ba + 2BaO \cdot SiO_2$.

this temperature range. This is further support of the belief that the pressures determined in the aluminum trials may be too low.

Figure 8a shows the comparison of the data from this investigation with that given by Zhukovetskii using the log p versus $1/T \cdot 10^4$ relationship.

Figures 10 and 11 show the relationship between log K_a and $1/T \cdot 10^4$ for the aluminum and the silicon trials, respectively. Again, the method of least squares was used to fit a line to each set of data and to determine the slope and the intercept of each line. The general equation of each line is, $y = mx + b$ where y is equal to log K_a, m is the slope of the line and is equal to $(-\Delta H^\circ/4{,}574) \cdot 10^{-4}$, x is equal to 1/T, and b is the intercept of the line with the ordinate and is equal to $\Delta S^\circ/4.576$. Thus the heat and entropy of the reaction can be calculated from the slope and the intercept of the line.

The calculated thermodynamic functions for the two reactions are given in Tables VI and VII. The standard free energy of reaction was calculated from both the uncorrected and the corrected data for each reaction. These values are given in the fifth column of both Table VI and Table VII. The calculation of the standard free energy of reaction for $4BaO + 2Al = 3Ba + BaO \cdot Al_2O_3$ from the data given by



Legend

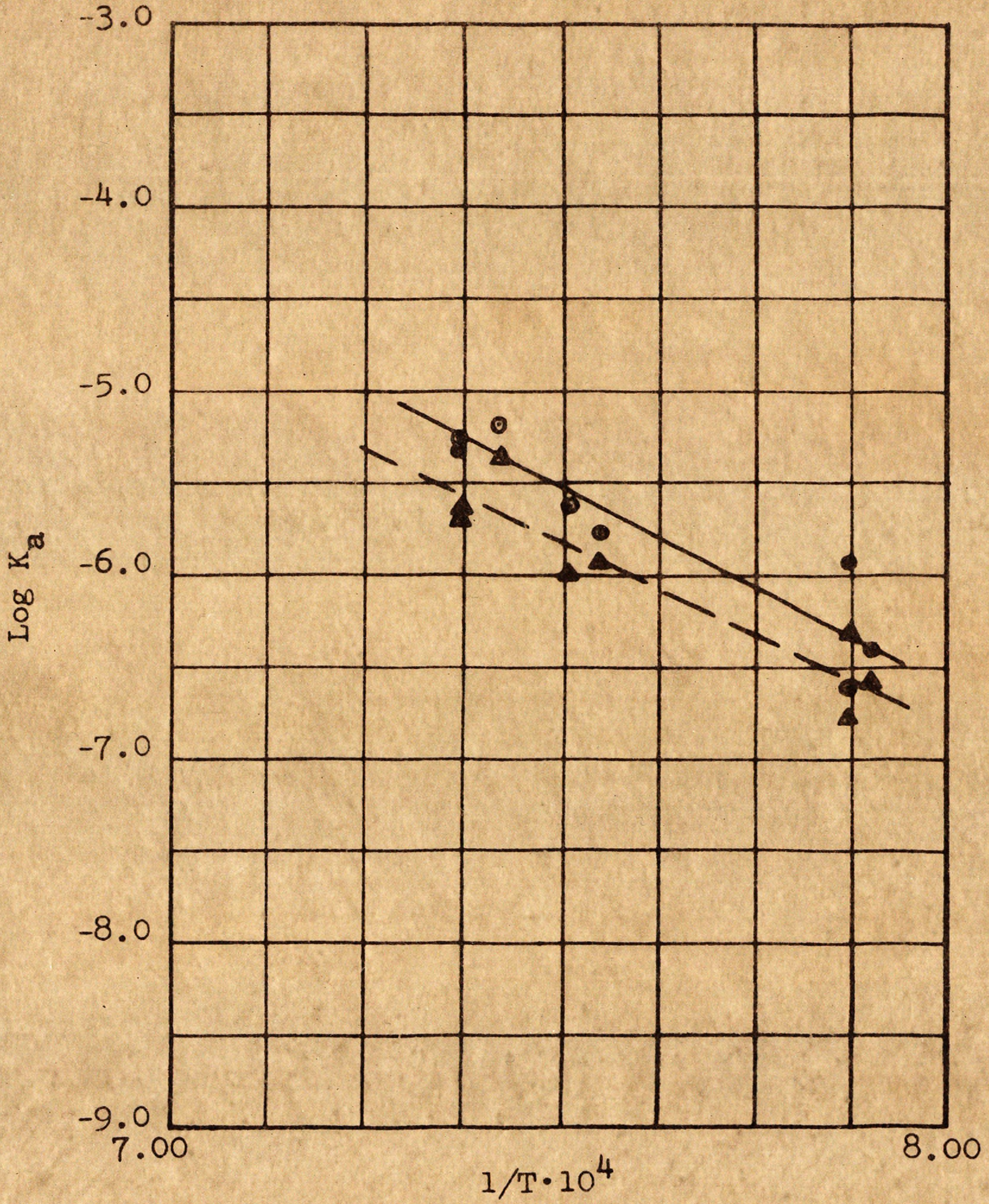
○ Corrected pressure

△ Uncorrected pressure

____ Least squares line for corrected pressures

\- - - Least squares line for uncorrected pressures

Figure 10. Relationship between log K_a and $1/T \cdot 10^4$ for the reaction, $4BaO + 2Al = 3Ba + BaO \cdot Al_2O_3$.



Legend

O Corrected pressure

Δ Uncorrected pressure

___ Least squares line for corrected pressures

--- Least squares line for uncorrected pressures

Figure 11. Relationship between log K_a and $1/T\cdot 10^4$ for the reaction, $4BaO + Si = 2Ba + 2BaO\cdot SiO_2$.

TABLE VI

Calculation of the Thermodynamic Functions for the Reaction, $4BaO + 2Al = 3Ba + BaO \cdot Al_2O_3$, in the Temperature Range of 1200°K to 1360°K

$\log K_a = A/T + B$

A (slope)	ΔH^o_{Rx}	B (intercept)	ΔS^o_{Rx}	ΔF^o_{Rx} (1360°K)	ΔF^o_f of $BaO \cdot Al_2O_3$ (1360°K)
	cal.		cal./deg.	cal.	cal.
		Uncorrected Data			
-2.224	101,800	8.152	37.3	51,100	-358,100
		Corrected Data			
-2.221	101,600	8.534	39.1	48,000	-360,800

TABLE VII

Calculation of the Thermodynamic Functions for the Reaction, $4BaO + Si = 2Ba + 2BaO \cdot SiO_2$, in the Temperature Range of 1270°K to 1360°K

$\log K_a = A/T + B$

A (slope)	ΔH°_{Rx}	B (intercept)	ΔS°_{Rx}	ΔF°_{Rx} (1360°K)	ΔF°_f of $2BaO \cdot SiO_2$ (1360°K)
	cal.		cal./deg.	cal.	cal.
		Uncorrected Data			
-2.023	92,600	9.364	42.9	34,300	-374,900
		Corrected Data			
-2.201	100,700	10.988	50.3	32,300	-376,900

Zhukovetskii yields a value of 40,800 calories at 1360°K. The experimental value obtained from the corrected data for the same reaction was 48,400 calories at the same temperature. This agreement is better than what was expected considering the experimental difficulties.

The standard free energy of reaction for the reduction with silicon was found to be more negative than that for the reduction with aluminum. Such a result indicates that reduction by silicon is more spontaneous than reduction by aluminum. Despite this indication, this study revealed that the use of aluminum as the reducing agent resulted in higher barium pressures than did the use of silicon. Therefore, aluminum has the advantage over silicon as a reducing agent. The stoichiometry of the reactions shows that reduction by aluminum yields more barium metal than does reduction by silicon for an equal weight of barium oxide. The advantage of aluminum over silicon has been proven in a study of the production of magnesium by this process.[40]

From the calculated free energy of reaction and the known free energy of formation of barium oxide (102,300 cal.),[41] the standard free energies of formation of barium monoaluminate and barium orthosilicate at 1360°K were calculated and are given in the last column of Tables VI and VII, respectively. The standard free energy of formation of $BaO \cdot Al_2O_3$, calculated from the corrected data, was found to be -360,800 calories at 1360°K. The value calculated from the data given by Zhukovetskii was -368,400 calories. No free energy data at this temperature were available from the literature for $2BaO \cdot SiO_2$.

CHAPTER VII

DISCUSSION OF ERRORS

There were three general types of errors encountered in this study of the reaction pressure of barium vapor.

Experimental Error

Since the equation for the pressure involved measurement of four variables there were several experimental errors to be considered. The amount of metal vapor effusing through the orifice was measured by the weight loss of the crucible and its contents. The condenser temperature was not controllable and its temperature was too cool to obtain a good deposit of barium metal. Instead, the deposit of metallic barium was in a finely divided state. When the condenser was removed from the furnace, the finely divided deposit immediately oxidized in the air and peeled off the condenser in the form of flakes. This made it impossible to analyze the condensate in any way. Consequently, dependence on the weight loss of the crucible and its contents as the sole criterion of the amount of metal vapor effusing through the orifice was necessary. An error was encountered here because some weight loss from the crucible and charge was to be expected from the outgassing of water vapor, carbon dioxide, and other common gases at the temperature of reaction. This was indicated by a temporary increase in the pressure in the system to about 0.1 mm. Hg at the beginning of each reduction experiment. Actually, the weight of the condensate should have been used, and this weight should have been compared to the weight loss from the crucible and charge. The accuracy of the weighings of the components of the charge and of the residues was affected by the fact that barium oxide, barium aluminates, and barium silicates all have a strong tendency to adsorb the common gases. These weighings were also affected by the fact that the barium metal condensed on the underside of the molybdenum lid and on the walls of the crucible oxidized upon exposure to the atmosphere. Despite the precautions taken, some error was caused by this behavior. The weights used were calibrated and, in the case of the heavier weights, were found to actually weigh somewhat more than their listed weights. The 0.1 gram weight and all of the lighter weights were found to weigh slightly less than their listed weight. Since the quantity measured was the weight loss, some of this error was cancelled. Also, the weight losses of barium metal were relatively large (smallest was 0.270 grams) so that the percentage error was small. However, the weight losses associated with the determination of the silver vapor pressure were considerably smaller than those for the determination of the barium vapor pressure. These weight losses varied from

0.023 grams to 0.042 grams depending on the size of the orifice. Therefore, the error due to the inaccuracy of the weights increased in this case and varied from 2% to 5% of the weight loss of silver. Due to the characteristics of the balance and the weights used, weighings were done only to the nearest milligram.

By the method explained in the description of the apparatus, the temperature variation was found to be ±5°C at the exact location of the Knudsen cell inside of the furnace. Thus, a constant temperature was not maintained due to the turning on and turning off of the furnace by the controller. Only an average temperature was used. It was noticed that at the beginning of each reduction experiment the temperature decreased considerably for a short time. This was due to the absorption of heat by the cold Knudsen cell and the cold charge upon being raised into the hot part of the furnace. This also introduced an error in the temperature readings. One of the necessary conditions of the Knudsen method regarding temperature is that the temperature at the orifice must not be less than that in other parts of the cell. Although there was no way of checking this, there was no reason to believe that this condition was not present.

It was difficult to determine the exact length of time during which the barium vapor was allowed to effuse through the orifice at a constant temperature. Ideally, the heating and cooling periods should be very short compared to the total time that the cell is held at the temperature of the reaction. The starting time was taken to be the moment that the sample was raised into the hot furnace, and the finish time was the moment it was withdrawn from the hot furnace. It was hoped that heating and cooling would be sufficiently rapid so that this error could be minimized. However, this condition did not prevail, and the resulting error in the time variable can not be neglected.

The fourth variable in the pressure equation is the area of the orifice. The diameter of the orifice was measured with a filar eyepiece at a magnification of 5x. The hole drilled for each orifice was not perfectly round, and, therefore, six to eight diameter readings were taken. The average reading was then used to determine the diameter and then the area. There was some error involved in this method of measuring the area.

Small burrs of metal left on the edge of the orifice would account for added error due to their hindrance of the effusion of the metal vapor near the edge of the orifice. A factor for the expansion of the orifice at high temperature was included in the calculation of the orifice area. The non-ideality of the orifice was the reason for including the correction factor, K, for a tube-like orifice in the calculations of the reaction pressures. It was also the principal reason for obtaining an overall correction factor for the experimental barium pressures by determining the vapor pressure of silver by this method and comparing the experimental silver pressures with known data from the literature.

The pressure in the system, which was approximately $2 \cdot 10^{-3}$ to $5 \cdot 10^{-3}$ mm. Hg, was not considered low enough. Some oxidation of the barium in the vapor phase was to be expected with a pressure as high as 10^{-2} to 10^{-3} mm. Hg. More reliable data could have been obtained if a system pressure between 10^{-4} and 10^{-5} mm. Hg could have been maintained.

It is known that briquetting the charge in this type of thermal production of the alkaline earth metals is advantageous and increases the yield of metal with a corresponding increase in the reaction pressure. This work was done without briquetting the mixture since such an operation would have involved the additional steps of briquetting and weighing with the resulting increase in H_2O and CO_2 pickup of the charge. Therefore, the charge was in powdered form, and the presence of fines would be expected to decrease the efficiency of the reducing agent and to decrease the reaction pressure.

Error in the Chemistry of the Reactions

Several assumptions were made regarding the chemistry of the reactions considered in the experiments.

For instance, it was assumed that each of the reactants was in its standard state of unit activity. This assumption must be questioned for three reasons. First, an X-ray analysis of a sample of the barium oxide, produced by the dissociation of barium peroxide, revealed that a small quantity of barium peroxide still remained in the sample. It was estimated that the sample contained 5% barium peroxide. In addition to the effect on the unit activity of the barium oxide, the presence of barium peroxide would tend to accelerate the reduction because of the explosive nature of mixtures of barium peroxide and aluminum or silicon. This would cause an increase in the temperature in the reaction zone.

Secondly, the possibility that the aluminum and the silicon were slightly oxidized cannot be overlooked since both of these reducing agents were in the form of a powder and were exposed to the air.

The third reason is that there was undoubtedly an effect on the assumed unit activity of the reactants by the accumulation of reaction end-products at the interface between barium oxide and reducing agent.

There are several possible side reactions that would affect the results. For example, the formation of the intermediate $BaAl_4$ or $BaSi_3$, as has been suggested,[42] would decrease the yield of metal. Also, the side reaction of barium vapor with water vapor given off from the charge could cause another reaction to occur within the cell, producing barium hydroxide. This would decrease the pressure of barium vapor in the cell to below the equilibrium value for the reaction being studied. However, since water vapor and other adsorbed gases were given off only temporarily at the beginning of the reaction and since a dry atmosphere was used in the preparation of the charge, this side reaction would not be expected to seriously affect the results.

The formation of double oxides in the reduction of alkaline earth metal oxides by aluminum or by silicon has been generally agreed upon by most authors. In the particular case of the reduction of barium oxide, the formation of the monoaluminate and the orthosilicate, respectively, has been agreed upon. This was discussed in a previous section, and further reference is made in similar reactions for the reduction of magnesium oxide with aluminum where the formation of magnesium monoaluminate has been proven by X-ray analysis.[43] Therefore, it was assumed that the aluminate formed was the monoaluminate only, and the silicate was the orthosilicate only. Proof of the validity of this assumption was sought in the qualitative X-ray analysis of the residues.

A great deal of dependence could not be placed on the results of the X-ray analysis due to the strong tendency of the residues to adsorb gases from the air. It was noticed that each sample of the residues expanded considerably during the course of its X-ray analysis. This phenomena could have altered the X-ray patterns and made positive identification of the residues impossible. Nevertheless, the patterns were compared to the patterns of the barium aluminates and silicates whose ASTM cards were available. The only conclusion drawn from this comparison was that the residues were mixtures of various forms of barium aluminates and silicates and reducing agent. Specifically, for the aluminum reduction residues the mixture was one of $BaO \cdot Al_2O_3$, $2BaO \cdot Al_2O_3 \cdot 4\text{-}5H_2O$ and Al at each temperature. For the silicon reduction residues a mixture of Ba_2SiO_4, $Ba_2Si_3O_8$ and Si was found at each temperature.

Whether the aluminates and silicates, which were different from the forms assumed as end-products of the reactions, were intermediate forms or actual end-products is unknown, but the lack of direct proof that only the monoaluminate and the orthosilicate are formed should be kept in mind with regard to reaction stoichiometry.

Errors in Theoretical Assumptions

Since barium metal vapor was continuously being removed from the reaction zone by effusion through the orifice, the rates of the reactions had to be sufficiently rapid in order to maintain equilibrium within the cell. This rapid rate is necessary where a method such as this is employed to determine the equilibrium constant. Since the rate of the reaction was most rapid at the highest temperature, more dependence was placed on the results obtained at this temperature.

In considering the effect of orifice size on the reaction pressure, it must naturally be assumed that the orifice area is small enough so that equilibrium will be maintained. At the highest temperatures used in this study it was noticed that the use of the small orifice yielded the highest reaction pressures in all determinations. This discrepancy might be explained by the fact that, at this constant rate of reaction, equilibrium was more nearly approached by using the small orifice than by using the large orifice. The trend was reversed at lower temperatures. That is, use of the large orifice yielded higher reaction pressures. It is thought that the decreased rate of reaction at these lower temperatures decreased the effect of these particular orifice sizes on the reaction pressures due to a greater departure from equilibrium. The assumption that equilibrium conditions existed must be questioned since an open system was employed.

As was stated previously, the mean free path of the molecules of barium vapor ideally should have been ten times greater than the diameter of the orifice. In this case, the mean free path and the orifice diameter were of the same order of magnitude. This would affect the equality of the rate at which molecules pass through the orifice and the rate at which they strike the orifice, and such a departure from ideality must be taken into consideration.

According to Atkinson and Pidgeon, another assumption regarding studies of this kind must be questioned. It is that the diffusion process which occurs in the solid state has no effect on the reactions considered here.[44] This is important since both Kroll[45] and Fujita and Yokomizo[46] postulate a diffusion process in explaining the mechanism of the reactions.

CHAPTER VIII

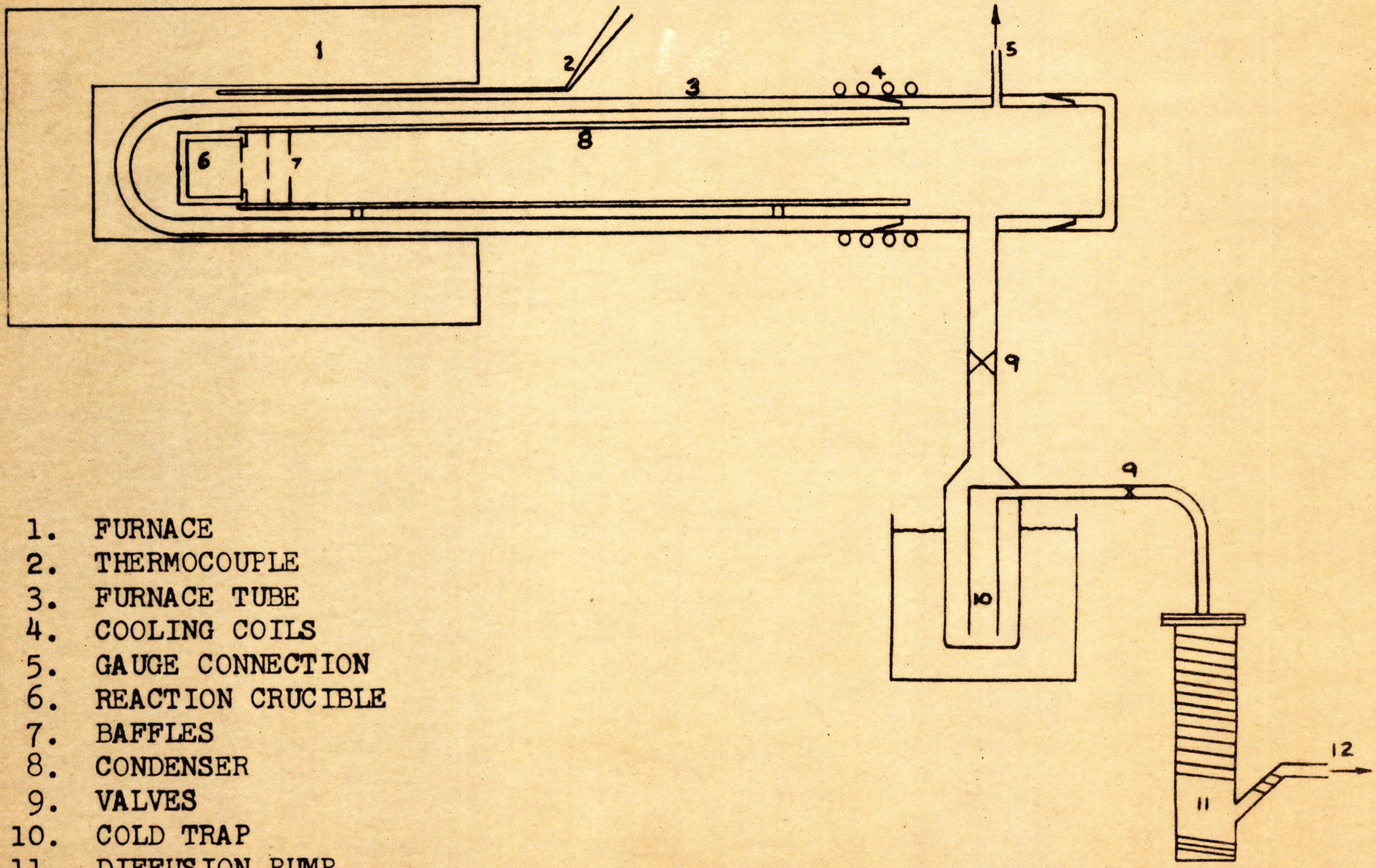
RECOMMENDATIONS FOR THE IMPROVEMENT OF THE APPARATUS

Several problems were encountered with the apparatus employed in this research. For the purpose of solving some of these problems and obtaining more reliable data in the measurement of the reaction pressure of a gaseous metal product, an improved apparatus has been designed.

The furnace is designed so that it can be used in either a horizontal position or a vertical position with upward condensation. Figure 12 shows the furnace in the horizontal position.

The furnace tube is made of porcelain and is open at only one end. A short glass tube is fitted to the open end of the porcelain tube. A ground glass joint serves to connect the two tubes so that the connection is vacuum tight. This joint is water-cooled. There are two openings in the short glass tube. One is the vacuum connection and leads directly to the cold trap. The other leads to a vacuum gauge. The furnace tube is vacuum sealed at its open end by a glass cap attached to the short glass tube by a ground glass joint. This cap is removable for access to the inside of the furnace tube.

An assembly consisting of the condenser and the reaction crucible is inserted into the furnace. The condenser



1. FURNACE
2. THERMOCOUPLE
3. FURNACE TUBE
4. COOLING COILS
5. GAUGE CONNECTION
6. REACTION CRUCIBLE
7. BAFFLES
8. CONDENSER
9. VALVES
10. COLD TRAP
11. DIFFUSION PUMP
12. TO MECHANICAL PUMP

Figure 12. The Arrangement of the Apparatus

is tubular in shape and is made of steel or some other suitable material. A short section of the condenser tube is slipped on to the cap of the reaction crucible as shown in Figure 13. The inside of the condenser tube and the outside of the cap should be machined accurately for a close fit. Two baffles are welded inside of this short section of the condenser. These baffles serve to maintain the temperature of the zone adjacent to the reaction zone at the same temperature as that in the reaction zone and to direct the vapor to the cooler portion of the condenser. The baffled section is attached to the rest of the condenser by means of a slip-on joint. The condenser extends to the end of the porcelain furnace tube. The condenser is in two parts to facilitate the removal of the condensate.

The steel reaction crucible which is illustrated in Figure 13 is cylindrical in shape. The open end of the crucible is threaded on the outside and the rim is machined accurately so that there is a tight fit between the rim and the lid. The cap screws on the crucible and presses the edge of the lid to the rim of the crucible. The machining of the cap is critical since there must be a close fit with the lid and the condenser tube. The lid with the orifice can be made of any suitable metal such as molybdenum or tantalum. It must also be carefully prepared to insure

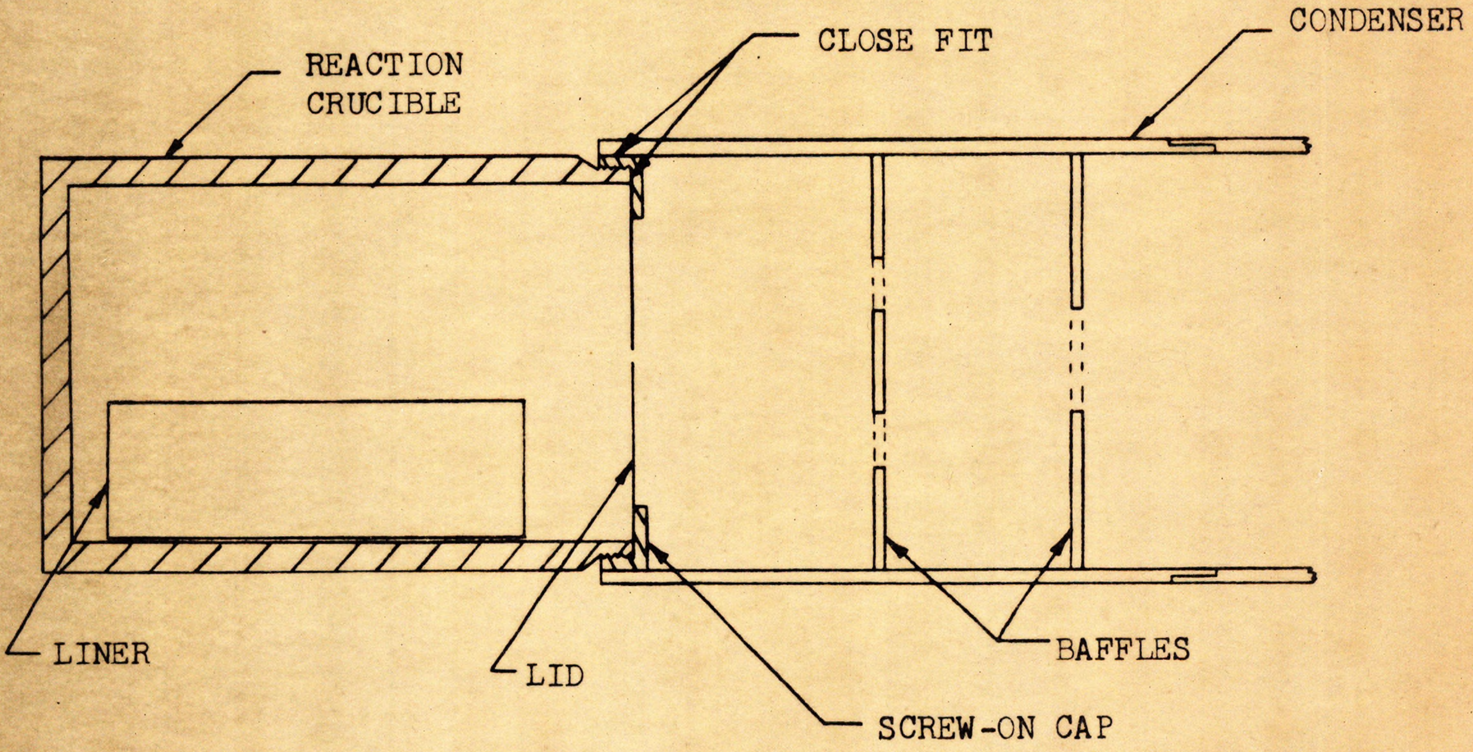


Figure 13. Reaction Crucible Construction

a tight fit with the crucible and the cap. The charge may be placed directly into the steel crucible, or a lightweight liner may be used to contain the charge. The lightweight liner has advantages when determining the weight loss of the charge. However, some metal may deposit on the inside wall of the reaction crucible during the cooling period, in which case the liner would serve no purpose, and the entire reaction crucible would have to be weighed.

In either the horizontal position or the vertical position the entire assembly must be supported inside of the furnace tube. In the horizontal position shown in Figure 12, the supports can be placed at regular intervals along the condenser tube.

Heat can be supplied by either resistance or induction. With resistance heating the time during which the metal is allowed to effuse at constant temperature could be measured by making two separate trials for each pressure determination and finding the difference in time and weight lost from the charge between these two trials. In this way, the error due to the effusion of metal vapor during the heating and cooling periods could be eliminated. However, such a procedure is rather long since two trials must be made and slow cooling is involved. Some arrangement may be made whereby the furnace tube could be inserted and withdrawn from the furnace so that the heating and cooling periods would be of negligibly short duration. The advantage of induction heating lies in the fact that heating and cooling are rapid.

The present design shows a resistance heated furnace. The temperature is measured by means of a thermocouple placed on the outside of the furnace tube at the exact location of the reaction crucible. The outside temperature readings may be correlated to the corresponding temperatures inside of the reaction crucible by making a trial run using no charge and inserting a thermocouple inside of the crucible. With induction heating, the controlling thermocouple would have to be vacuum sealed into the end of the furnace tube in such a way as to measure the temperature of the reaction crucible directly. Considering all factors, it seems preferable to use resistance heating and to make two trial runs for each pressure determination.

The vacuum system, as shown in Figure 12, consists of a cold trap, a diffusion pump, and a mechanical pump. The cold trap is of all glass construction and employs a refrigerant such as dry ice and acetone or liquid nitrogen. The diffusion pump should be one which uses a silicon based fluid and not a hydrocarbon oil and has cooling coils around the heater for rapid cooling of the fluid. All connections between the vacuum equipment are made with rubber vacuum hose and suitable clamps. The valves shown in Figure 12 are of the ground glass variety.

The advantages of this design over that of the apparatus employed in this research are that there is less chance of a leak in the reaction crucible, the condensate can be collected quantitatively and analyzed, temperature control is better in the zone adjacent to the reaction zone, and a lower pressure in the system can be attained by using a glass and rubber hose system and eliminating the sliding vacuum joint.

CHAPTER IX

CONCLUSIONS

The vapor pressure of barium over the reaction,

$$4BaO + 2Al = 3Ba + 3BaO \cdot Al_2O_3,$$

was found to vary from 0.27 to 1.77 mm. Hg in a temperature range of 940° to 1086°C. For the reaction,

$$4BaO + Si = 2Ba + 2BaO \cdot SiO_2,$$

the barium vapor pressure was found to vary from 0.38 to 1.94 mm. Hg in a temperature range of 1000°C to 1086°C. At a higher temperature of about 1200°C, the barium pressure above both reactions would be great enough for commercial production, and any further work on this specific system should be done at a higher temperature than was used here.

The standard free energy of reaction for both reactions was calculated from the experimental barium pressures. In the case of reduction with aluminum, the free energy of reaction was found to be 48,400 calories at 1087°C. For reduction with silicon, the value was 32,300 calories at the same temperature.

The standard free energy of formation of $BaO \cdot Al_2O_3$ at 1087°C was calculated and found to be -360,800 calories. That of $2BaO \cdot SiO_2$ was found to be -376,900 calories at 1087°C.

The measurement of the vapor pressure of silver at 1090°C showed that, for this particular method and for this type of Knudsen cell, more reliable pressure data could be obtained if the orifice diameter was 0.041 inches or smaller. This is attributed to the fact that the reactions are not rapid enough in this temperature range to maintain a close proximity to equilibrium in the system if the orifice size is too large.

An improved apparatus, capable of a lower pressure in the system and of collecting the condensate quantitatively, could probably be used to obtain more reliable data. Also, a two trial procedure is recommended for determining the time of effusion at constant temperature when resistance heating is employed.

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