LBL-1498
Preprint c.1

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April 1973

Prepared for the U. S. Atomic Energy Commission
under Contract W-7405-ENG-48

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THE ANOMALOUS VAPORIZATION BEHAVIOR OF MAGNESIUM NITRIDE

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ABSTRACT

Previous measurements of the vapor pressure of magnesium nitride by effusion methods when treated by a usually successful extrapolation to zero orifice area yield apparent equilibrium pressures that seriously disagree with vapor pressures determined by the transpiration method or by calculation from thermochemical data. Additional effusion measurements have been made over a wider range of sample to orifice area ratios and as a function of time. Mass spectrometer measurements show that a time dependence of the measured pressures that in earlier work was interpreted as due to degassing is, in fact, primarily a consequence of variation in pressures of the principal species of the vaporization reaction, Mg and N_2. Motzfeldt-Whitman extrapolations made at constant weight losses with constant sample loadings yield a family of curves for which the extrapolated apparent equilibrium pressures are weight loss dependent. The low weight loss extrapolations approach the equilibrium pressures calculated by other means. A magnesium oxide coating that forms as a more effective effusion barrier in cells with near equilibrium pressures than in cells of lower pressures appears to be responsible for the observed behavior. The total vapor pressure of magnesium nitride by the dissociation reaction to Mg and N_2 is given by

$$-4 \log P(\text{atm}) + 0.978 = \frac{210,300}{4.75T} - \frac{124.9}{4.57}$$

I. Introduction

Several workers (1-3) have measured the vapor pressure for the reaction

$$Mg_3N_2(s) \rightarrow 3Mg(g) + N_2(g) \qquad (1)$$

by effusion methods. Analysis of the data by a method that was expected to yield equilibrium pressures (2,3) gave pressures markedly lower than those calculated from independent thermochemical data (see Fig. 1). An examination of the data on which the calculated pressures are based and a review of the vapor pressure measurements will be helpful in fully appreciating this discrepancy.

The calculated vapor pressure is obtained from the enthalpy and entropy of formation at 298K and from high temperature heat capacity data for the reactant and products in Eq. (1). The enthalpy of formation of magnesium nitride measured by Lebedev and Nefedova (4) and by Mitchell (5) are in good agreement at -110.7 kcal/mole and -110.2 kcal/mole, respectively, and the values by Neuman, et al. (6), Brunner (7), and Neuman, et al. (8), show good support for these ranging from -109 kcal/mole to -116 kcal/mole. A value of -110.2 kcal/mole can be accepted as a weighted average that is probably in error by no more than 1 kcal/mole.

Mitchell (5) reported heat capacity data for the nitride in the range 462K to 1273K, and Satoh (9) reported data in the range 273K to 691K; however, the low temperature measurements needed for establishing the entropy at 298K have not been made. Mitchell (5) estimated this

entropy to be 22.4 eu by using a modified form of Latimer's rule for estimating the entropy of oxides; the reliability of this value is almost certainly better than ±5 eu. Thermochemical data for elemental magnesium (10) and N_2 (11) gas are well established.

Figure 1 shows the vapor pressure above magnesium nitride that is calculated from these data. The dashed lines shown in the figure allow ±5 eu for the uncertainty in the entropy of formation of the nitride.

The results of several vapor pressure studies on magnesium nitride are also shown in Fig. 1. Soulen, Sthapitanonda, and Margrave (1) measured vapor pressures by the Knudsen effusion method and also by the transpiration method--shown in Fig. 1 as an extrapolation from the 1330K to 1600K range where the measurements were made. They also spectroscopically examined the vapors over the compound in the temperature range 1570K to 1670K and detected $Mg_2(g)$. Their data indicated a very low $Mg_2(g)/Mg(g)$ ratio (0.001) above the nitride at 1600K with the ratio decreasing at lower temperatures, thus showing that the dimer is of little importance in the products of vaporization in the temperature range of effusion studies. They attributed their high transpiration results to the reaction of small amounts of oxygen in the nitrogen flow gas with Mg(g) and explained the low Knudsen values by suggesting that the evaporation coefficient* is low.

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*The evaporation coefficient in vacuo is the ratio of the measured flux in Langmuir vaporization (12-14) to the flux that would strike the surface in the equilibrium vapor and is calculated by using the Hertz-Langmuir-Knudsen equation (12-17). It is usually assumed that the evaporation coefficient is independent of the vapor pressure above the vaporizing material (18) and that it is equal to the condensation coefficient.

Hildenbrand and Theard (2) employed the torsion effusion technique with three different orifice sizes to measure vapor pressures; they used magnesium nitride that they reported to be better than 99% pure. Their results show a marked dependency on orifice area, which led them to use the Motzfeldt-Whitman equation (19,20)

$$\frac{1}{P_K} = \frac{1}{P_E} + \frac{W_B B}{P_E \alpha A'} \qquad (2)$$

to obtain equilibrium pressures by extrapolation from their data, where P_E is the equilibrium pressure, P_K is the measured pressure, W_B is the orifice Clausing factor (21-23), B is the effusion cell orifice area, α is the evaporation coefficient, and A' is the effective sample surface area (18).

Hildenbrand and Theard calculated apparent equilibrium pressures in rough agreement with the large orifice data of Sthapitanonda, et al. (1) and calculated an upper limit to the evaporation coefficient of 5×10^{-3}. The equilibrium pressures obtained in this way are lower by more than a factor of ten than pressures calculated from the thermochemical data discussed above and show a markedly different temperature dependence.

Hildenbrand and Theard concluded that either the heat of formation of $Mg_3N_2(s)$ is in error, or the rate of vaporization is limited by a secondary process which leads to false apparent equilibrium pressures when Eq. (1) is applied. They favored the second explanation, largely because the heat of formation seemed to be well established. They noted

that Eq. (2) when used with effusion data for the reaction $Mg(OH)_2(s) = MgO(s) + H_2O(g)$ was found by Kay and Gregory (24) also to yield apparent equilibrium pressures far lower than the known equilibrium pressure.

Blank and Searcy (3) made a torsion-effusion and a torsion-Langmuir (15-17, 28) study of magnesium nitride using two orifice sizes; they observed no significant orifice area dependence, but their measured pressures were in good agreement with the extrapolated pressures of Hildenbrand and Theard. The range of evaporation coefficients, 2×10^{-2}, at 1000K to 3×10^{-3} at 1250K, calculated by Blank and Searcy from the ratio of their Langmuir (free surface) pressures to their Knudsen pressures has an average near the value which Hildenbrand and Theard calculated by means of Eq. (2). Blank and Searcy expressed doubt, however, on the basis of the independent thermochemical data, that equilibrium pressures and valid evaporation coefficients had been measured in their work, placing particular stress on the observation that the apparent entropy calculated for the reaction (Eq. (1)) from the effusion data differs by 54 eu from the expected value.

Another unusual aspect of the behavior of magnesium nitride is that for the effusion data there is a large difference between second law (26,27) and third law (27) values of the enthalpy of sublimation. For equilibrium data, these two values usually differ by no more than 5 to 10%; however, for magnesium nitride, deviations ranging from 21 to 39% were found in the effusion studies. The difference was only 9% for the transpiration study which also had a second law heat only 4% greater than the equilibrium value. Thus the evidence strongly indicates that

previous measurements of the vapor pressure of magnesium nitride--except perhaps the transpiration results--have not been done at equilibrium and that application of the usually successful orifice dependency equation (19,20) to obtain equilibrium data does not work in this case.

Effusion methods for vapor pressure determination, which appear to have failed when applied to magnesium nitride, are our most important sources of quantitative data for high temperature condensed phase-vapor equilibria. It is vital to understand why the method apparently failed when applied to magnesium nitride and how the method can be used to obtain equilibrium data for that substance so that the reliability of the method as an experimental tool will be clearly known. This paper reports an effort to achieve these objectives by means of a further study of the magnesium nitride vaporization reaction by the torsion effusion technique, supplemented by X-ray diffraction, and by mass spectrometry.

II. Experimental

A. Vapor Pressure Measurements

A detailed description of the torsion effusion technique has been given by Freeman (28) and several papers (29-31) have described its use in this laboratory. Four different effusion cells--three made of graphite, types "A", "B", and "C", and one made of nickel, type "D"--were used in this work. The temperature of the effusion cell was measured with a platinum/platinum-10% rhodium thermocouple (the probe thermocouple) placed 6 mm below the effusion cell. Difference in cell and probe temperatures as a function of temperature was measured by comparing probe readings with readings of a thermocouple placed in the

effusion cells in calibration runs. The thermocouples were calibrated by measuring the melting point of copper in a graphite crucible.

Since magnesium nitride readily reacts with water vapor, the nitride was loaded into the effusion cell inside a dry box that contained a phosphorous pentoxide desiccator. The sample was then transferred to the torsion effusion furnace in a closed weighing dish and was mounted in the furnace through a glove box assembly over the furnace opening (the furnace was purged with dry nitrogen before and during this operation). Despite these precautions, there was significant degassing of water vapor in the early stages of heating.

Pressures were calculated on the assumption that the deflections were due entirely to effusion of vapor from the orifices; to insure that extraneous deflections were not significant, the graphite cell "B" and the nickel cell--the ones with the smallest orifice areas--were heated with full magnesium nitride charges but with no orifice. For the "B" cell, deflections measured with no orifices amounted to 4% of the deflections measured when the smallest orifices, 0.10 mm, were present. For the nickel cell, deflections with no orifices were 0.5% of the deflections with 0.25 mm orifices, the smallest used.

For Eq. (2) where the total weight loss due to effusion was important, an effective pore area was measured to account for vapor effusing through pores in the cell or through interfaces between cell parts. It was 1.4×10^{-4} cm^2 and was added to the orifice area to obtain the effective orifice area.

To determine the accuracy of the vapor pressure measurements, the vapor pressure of silver was measured over the temperature range 1100K to 1400K. Most datum points were within 10% of the accepted values (10) and the enthalpy of vaporization calculated from the slope was 63.8 kcal/mole compared to the accepted values (10) of 63.5 kcal/mole at 1234K.

B. Gas Analysis

A quadrapole mass filter and an ionization gauge were used to determine the partial pressures of the residual gases in the vacuum system and the quadrapole was used to identify the vapors streaming out of the effusion cell. To measure the transmission probability of a molecule in the mass filter, n-butane at 3.3×10^{-5} torr was introduced and the resulting fragmentation pattern, for 70 eV, was compared with a standard fragmentation pattern (32). Ionization cross sections from Otvos and Stevenson (33) were used for all molecules except that values determined by Reed (34) were used for water vapor. The ionization gauge was calibrated by comparing it to a McLeod gauge at various pressures of nitrogen.

C. Sample Preparation

X-ray diffraction patterns of the magnesium nitride from various suppliers* showed that magnesium nitride was the major phase (35), but magnesium oxide peaks were also produced by some samples. These materials were analyzed for magnesium oxide by completely evaporating the magnesium nitride in a graphite crucible at 1250K and then weighing the residual material which was found by X-ray diffraction to be

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*Ventron, Metal Hydrides, Semi-Elements, Hall Labs.

magnesium oxide; the amount of oxide ranged from 4 to 25%. Magnesium nitride with 1% magnesium oxide was prepared in this laboratory by sublimation of the nitride in a 304 stainless steel tube in a temperature gradient of 90K at 1370K. This reaction was carried out in a 3 psig atmosphere of nitrogen.

D. Lattice Parameter Measurements

Magnesium nitride samples were placed in a 12 mil diameter tubing made of Lindemann glass; this operation was done in a dry box. Measurements of the lattice parameter were made by the Debye-Scherrer X-ray diffraction technique (36,37). The K_α radiation of copper was used with a nickel filter.

III. Results and Discussion

A. Investigation of the Evaporation Reaction

To confirm that the vaporization of magnesium nitride proceeds according to reaction (1), vapor species were studied by means of a quadrapole mass filter and lattice parameter measurements were made of the solid phase. One effusion experiment was done with silver and two with magnesium nitride. On heating to 900K the partial pressures of H_2, H_2O, and N_2 plus CO (N_2 and CO gases cannot be distinguished) increased for both the silver and the magnesium nitride experiments. The increases must reflect desorption of these gases from the vacuum chamber and reaction of $H_2O(g)$ with the graphite effusion cell to give $H_2(g)$ and $CO(g)$. $NH_3(g)$ was observed to increase then decrease at 900K in the magnesium nitride experiments. The $NH_3(g)$ was probably produced by the reaction of $H_2O(g)$ (from $Mg(OH)_2$ in the nitride sample) with the nitride.

At 800K a shutterable Mg^+ peak that decayed with time was observed. At that temperature the nitrogen peak was not shutterable. The nitride sample must have contained some unreacted magnesium metal.

Above 1100K, in the expected range of magnesium nitride vaporization, $N_2(g)$ and $Mg(g)$ effused as evidenced by the shutterability of these molecules. A check of mass 38 for $MgN(g)$ gave no shutter effect; thus the vapor phase in equilibrium with the nitride is $Mg(g)$ and $N_2(g)$, which is consistent with (1).

To insure that the magnesium nitride was not changed in composition as a result of selective vaporization or change in oxygen content, the lattice parameter was measured. The parameter for the cubic lattice was measured to be 9.9654 ± 0.0005Å where the reproducibility of the experiments was 0.0005Å. Lattice constants were measured for nitride that had been annealed at pressures of 1.2 atm of nitrogen and pressures of 10^{-5} atm of nitrogen, nitride that was unvaporized and nitride vaporized for 100 hours at 1180K, and nitride with magnesium oxide contents that ranged from less than 1.2% to 30%; all gave lattice parameters within the reproducibility of measurement. Thus, the principal solid phase was magnesium nitride with a composition that was not measurably changed under the experimental conditions in this work, and reaction (1) was confirmed as the vaporization reaction.

B. Pressure Versus Temperature Experiments

Measurements of the vapor pressure as a function of the temperature were made to see if the anomalous results obtained by earlier workers (1-3) (Fig. 1) could be duplicated and to provide additional data for understanding the vaporization of the nitride. Experiments were made

with charge ratios, the ratio of the sample weight in grams to the effective orifice area in cm^2, ranging from 15 gm/cm^2 in the A2.0* cell to 28,000 gm/cm^2 in the B0.10 cell. The second law enthalpy of vaporization was calculated by using pressures for which λ/D** was greater than one--Blair and Munir (40) found a change from molecular flow to transition flow (38) at this value in their effusion study of calcium nitride.

The results of experiments conducted in the D0.25 cell are shown in Fig. 2, together with the results of experiments in a C0.5 cell and an A2.0 cell. In the D0.25 cell Metal Hydrides and Ventron magnesium nitride were used after outgassing to remove Mg(g) and H_2O(g); the charge ratio was 12,000 for both. Each datum point is numbered in the order that it was taken. The first and last series of points in the Metal Hydrides experiment are presented to show how the magnesium nitride vaporization changed during this type of experiment.

The first points were measured about 10 min after the samples reached the temperatures of appreciable vaporization. It is seen by following points one to six in the Metal Hydrides experiment that the pressure approached the calculated equilibrium line in the middle of the temperature range while at the ends of the temperature range the pressure bent away from equilibrium; similar behavior is shown by points 1 through 10 of the run with the Ventron materials. After many intervening

*The letter refers to the type of effusion cell and the number to the nominal orifice diameter in mm; there are two orifices per cell.
**λ/D is the ratio of the mean free path of the vapor to the orifice diameter; it is calculated by using the hard sphere approximation (38) and the molecular diameter of nitrogen (39).

measurements, points 55 through 63 were taken; it is seen that they had a steeper slope and that at higher temperatures the pressure approached the calculated equilibrium.

The intervening pressure measurements are omitted in Fig 2; however, it was observed that at the highest temperatures the ratio of the highest to the lowest pressures was about 1.4, while at the lowest temperatures the ratio was 3.5. It was also observed that the enthalpy of vaporization calculated from each successive series of points has an increased value with the exception that heating at a temperature above 1180K prior to determining the slope resulted in a near equilibrium slope--the enthalpy of vaporization at 1100K is 210 kcal/mole. Thus for the Metal Hydrides material the first series of points had a near equilibrium slope of 211 kcal/mole and the last series had a slope of 321 kcal/mole; the Ventron material behaved similarly. Such large changes are completely atypical of experience with effusion studies of congruent systems.

Another feature of interest was that the pressures could be raised by 50% at low temperature as a result of heating at high temperatures. An isothermal experiment after such a rise in pressure showed that 1000 min were required for the pressures to fall to their former level when the temperature was 1050K.

The various results indicate that initially the Knudsen pressures increase with time but subsequently decrease. After many hours of vaporization, the pressures have fallen considerably--more so at lower temperatures than at high temperatures. This time dependency of the data suggests that a barrier to the vaporization process is being built up as the vaporization progresses.

This observation is the key to the failure of the Motzfeldt-Whitman plot to yield equilibrium pressures in Hildenbrand and Theard's study of magnesium nitride. That plot requires a series of experiments in which all of the factors in Eq. (2) are held constant save the orifice area. That time dependency in magnesium nitride vaporization was observed made the use of Eq. (2) questionable. That the decrease was not caused by clogging of the orifices was verified by examination after vaporization; some other condition that affected the pressure inside the cell, α and/or A' from Eq. (2), changed with time of heating.

The pressures in the D0.25 effusion cell averaged a factor of 5 greater than the pressures of Blank and Searcy; however, when the charge ratio was decreased by one order of magnitude to charge ratios similar to theirs, and the Ventron material was heated for 2000 min at 1210K prior to making the measurements, a procedure comparable with their procedure of heating at 1280K for 1200 min, close agreement with their data was obtained, as shown in Fig. 2. As with the previous experiment, it was observed here that heating at a high temperature (on the order of 1250K) followed by a pressure measurement at around 1100K gave rise to a datum point that was much higher in pressure than points not taken in this way--datum point 15 was a result of this procedure.

When the charge ratio was reduced again by almost two orders of magnitude by using an A2.0 effusion cell, the measured pressures fell considerably below the pressures of Blank and Searcy. These samples were degassed at low temperatures to drive off $H_2O(g)$ and $Mg(g)$. Here it is again noted that the apparent enthalpy of vaporization increased as vaporization progressed and the effusion pressures decreased.

Figure 3 shows the results of experiments in a B0.10 effusion cell and a B0.25 effusion cell for which the charge ratios were 28,000 gm/cm^2 and 22,000 gm/cm^2, about twice that used in the D0.25 experiments described above. The Metal Hydrides material was heated for 40 min at 1200K and the Ventron material was heated for 20 min at 1200K prior to making vapor pressure measurements. The main feature of interest in this figure was that pressures above the calculated equilibrium line were obtained.

With $\lambda/D < 1$ the measured pressures were a factor of four greater than the calculated equilibrium pressures at $T^{-1} = 7.25 \times 10^{-4}\ K^{-1}$; however, Carlson (41-42) has shown that for the effusion of mercury, the change from molecular flow to hydrodynamical flow (38) caused an increase in the apparent vapor pressure by a factor of two. Using this factor to correct the vapor pressure at $T^{-1} = 7.25 \times 10^{-4}\ K^{-1}$ gave an estimate of the equilibrium pressure of 7×10^{-2} atm; this was near the upper error limit of the calculated vapor pressure. Several measurements with $\lambda/D > 1$--point 1 for the Ventron run and points 4, 10, and 15 for the Metal Hydride run--also yielded pressures near the upper limit suggesting that the equilibrium vapor pressure is near the upper limit.

C. Inflection Point Experiment and Equilibrium Vapor Pressure

It was observed in most of the experiments that the temperature dependency of the measured vapor pressures was greater than the equilibrium value. It was also remarked in the Introduction that the transpiration studies of Sthapitanonda, et al. in the higher temperature range, 1330K to 1600K, yielded pressures near the calculated equilibrium pressures.

An experiment to measure the equilibrium pressure at 1110K was conducted by rapidly cooling the effusion cell from 1390K, where an equilibrium condition may prevail, to 1110K and monitoring the pressure. The results are shown in Fig. 4; cooling was complete in 20 min and the inflection point in the curve was at 27 min. This experiment indicated that the equilibrium pressure was about 5.2×10^{-4} atm at 1110K.

In Fig. 5 the value for the equilibrium pressure derived from the inflection point experiment is presented with the values from the experiment in the B0.10 effusion cell described above and from the lower limits provided by the maximum in Fig. 6 and by the Motzfeldt-Whitman treatment in Figs. 7 and 8. It is seen that they all fall near the upper error limit that was calculated for the vapor pressure from the thermochemical data. This taken with transpiration results of Sthapitanonda, et al. which were high because of oxygen contamination of the flow gas--it is doubted that these pressures are high by more than a factor of three--give strong evidence that the true vapor pressure is near the upper error limit of the calculations from the thermochemical data.

As mentioned in the Introduction, the uncertainty in the vapor pressures calculated from the thermochemical data arose because of uncertainty in the estimate of the entropy of magnesium nitride at 298K. The above results allow the entropy to be calculated from the measured vapor pressures and the other thermochemical data. The result is a value of 20.2 eu for the entropy of magnesium nitride at 298K compared to the values that were previously accepted of 22.4 eu by Mitchell (5) and Schick (43) and a value of 21 eu that was used in the JANAF tables (44).

The essential agreement between the vapor pressures calculated from thermochemical data and the estimated values obtained by the several methods in Fig. 5 provide strong evidence that the vapor pressure for magnesium nitride vaporization can be given by

$$-4 \log P \text{ (atm)} + 0.978 = \frac{210,300}{4.57T} - \frac{124.9}{4.57} \qquad (3)$$

to an accuracy of ± 50%, in the temperature range 1100K to 1400K where P is the total pressure in the effusion cell. The vapor pressures calculated from Eq. (3) are presented in Fig. 5.

D. Modified Motzfeldt-Whitman Plot

A more important objective than that of improving on the thermochemical data for magnesium nitride vaporization is that of explaining why the Motzfeldt-Whitman extrapolation failed in the earlier investigations of magnesium nitride. The extrapolation normally appears to yield reliable values for the equilibrium vapor pressures of congruently vaporizing systems with low vaporization coefficients.

Blank and Searcy observed a time dependency of the effusion pressures at 1130K over a period of 600 min in the early stages of a heating of magnesium nitride and assumed degassing of the sample was responsible. Accordingly, they waited to initiate pressure measurements until the rate of effusion became insensitive to time. Probably Hildenbrand and Theard followed a similar procedure. However, the quadrapole mass filter measurements establish that decreases in pressures with time at a constant temperature (above 1100K) do not reflect

degassing, but are measures of a time-dependent escape of magnesium and nitrogen; the degassing is complete in a few minutes at these temperatures. Microscopic studies (to be described in a separate communication) indicate that the changing rate is correlated with development of a thickening layer of magnesium oxide on the surface of magnesium nitride.

The time dependency of the effusion pressures observed in this work is shown in Fig. 6 where each sample was completely degassed at 950K and then heated to 1110K. Modified Motzfeldt-Whitman extrapolations were made from these data by using pressures measured after samples had lost identical weights of magnesium nitride. The initial properties of all samples were the same--each cell was charged with the same amount of magnesium nitride and each charge was prepared from the same batch of nitride with a sample splitter, and thus had the same distribution of particles. If equal weight losses produced equal oxide diffusion barriers, as would be expected if the oxide were all initially present in the nitride samples, one would expect from Eq. (2) a series of lines possibly curved,[17,18] but each line should extrapolate to the same value of P_E^{-1} since neither solid state diffusion nor a slow surface step should limit the rate for sufficiently small orifices. Figures 7 and 8 show that the intercepts vary with the weight loss. The extrapolation for 5mg losses provides a lower limit to the vapor pressure at 1110K of 2.1×10^{-4} atm and at 1180K of 1.2×10^{-3} atm.

The observed effect of the orifice area on barrier effectiveness is unexpected. The observed dependence of apparent pressures on weight loss indicate[5] that for small orifices the barrier was more effective than

expected. An assumption that background oxygen enters the cell to form a diffusion barrier does not resolve the discrepancy.

Since the B1.0 cell of Fig. 11 had orifices 36 times the area of the B0.15 cells but effusion pressures in the latter cell were four times as great, the time to lose a given amount of nitride is about nine times as great for the B0.15 cell as for the B1.0 cell. If the barrier were formed from reaction of oxygen that enters the orifice from outside the cell, the available oxygen supply at the nitride surface would be increased in proportion to the size of the orifice area. Thus, for the assumed reaction with oxygen, the oxide layer in the cell with the larger orifice should be thicker for any given weight loss than in the other cell if oxygen arrival rate governed the oxide build up or should be the same thickness if magnesium diffusion through the oxide governed oxide build up. In neither case is the direction of shift in measured pressures found in Figs. 7 and 8 expected.

It is known that gaseous products of dissociation reactions sometimes catalyze crystallization of the solid reaction product.[45] The unexpected variation of pressures with orifice area in these effusion studies may result because the higher pressure in the small orifice cell catalyzes the formation of a coating of decreased permeability, perhaps by promoting grain growth with consequent reduction in grain boundary diffusion.

ACKNOWLEDGEMENTS

Discussions with David Meschi and assistance with the design and building of the apparatus by Emery Kozak were of great help. The research was supported by the United States Atomic Energy Commission.

References

1. P. Sthapitanonda, Ph.D. thesis, University of Wisconsin (1955). J. R. Soulen, P. Sthapitanonda, and J. L. Margrave, J. Phys. Chem. 59, 132 (1955).

2. D. L. Hildenbrand and L. P. Theard, ASTIA Unclassified Report 258410 Aeroneutronic Report U-1274 (1961).

3. B. Blank and A. W. Searcy, J. Phys. Chem. 72, 2241 (1968) and B. Blank, UCRL 16018 (1965).

4. Lebedev and Nefedova, Zhur. Fiz. Khim. 32, 819 (1958).

5. D. W. Mitchell, Ind. Engr. Chem. 41, 2027 (1949).

6. B. Neuman, C. Kroger, H. Kunz, Z. Anorg. Chem. 207, 133 (1932).

7. Brunner, Z. Elektrochem. 38, 67 (1932).

8. B. Neuman, C. Kroger, and H. Haebler, Z. Anorg, Chem. 304, 90 (1932).

9. Shun-ichi Satoh, Sci. Papers Inst. Phys. Chem. Research (Tokyo) 34, No. 1, 3992 (1938).

10. R. Hultgren, R. L. Orr, P. D. Anderson and K. K. Kelley, Selected Values of Thermodynamic Properties of Metals and Alloys (John Wiley & Sons, Inc., New York, 1963) (Supplement for Mg Oct. 1966).

11. D. R. Stull and G. C. Sinke, Thermodynamic Properties of the Elements (American Chemical Society, Washington, D.C., 1956).

12. I. Langmuir, Phys. Rev. 2, 329 (1913).

13. O. Knacke and I. N. Stranski, Prog. Met. Phys. 6, 181 (1956).

14. R. C. Paule and J. L. Margrave in J. L. Margrave (Ed.), The Characterization of High Temperature Vapors, (Wiley, New York, 1967) Ch. 6.

15. H. Hertz, Ann. Phys. (Leipzig) 17, 177 (1882).

16. M. Knudsen, Ann. Phys. (Leipzig) 47, 697 (1915).

17. A. W. Searcy in A. W. Searcy, D. V. Ragone, and U. Colombo (Eds.) Chemical and Mechanical Behavior of Inorganic Materials, (Wiley-Interscience, New York, 1970) Chap. 6.

18. G. M. Rosenblatt, J. Electrochem. Soc. 110, 563 (1963).

19. K. Motzfeldt, J. Phys. Chem. 59, 139 (1955).

20. C. I. Whitman, J. Chem. Phys. 20, 161 (1952).

21. D. Clausing, Ann. Physik, 12 (5), 961 (1932).

22. D. A. Schulz and A. W. Searcy, J. Chem. Phys. 36, 3099 (1962).

23. D. A. Schulz, Ph.D. Thesis, University of California, Berkeley, 1962.

24. E. Kay and N. W. Gregory, J. Phys. Chem. 62, 1079 (1958).

25. Z. A. Munir and A. W. Searcy, J. Chem. Phys. 42, 4223 (1965).

26. J. R. McCreary and R. J. Thorn, J. Chem. Phys. 50, 3725 (1969).

27. G. N. Lewis, M. Randall, K. S. Pitzer and L. Brewer Thermodynamics, 2nd Edition (McGraw-Hill Book Company, New York, 1961).

28. R. D. Freeman, J. L. Margrave (Ed.), The Characterization of High Temperature Vapors, (Wiley, New York, 1967) Ch. 7.

29. M. J. Lim and A. W. Searcy, J. Phys. Chem. 70, 1762 (1966).

30. R. W. Mar and A. W. Searcy, J. Phys. Chem. 71, 888 (1967).

31. H. B. Skinner and A. W. Searcy, J. Phys. Chem. 72, 3375 (1968).

32. American Petroleum Institute Research Project Number 44.

33. J. W. Otvos and D. P. Stevenson, J. Am. Chem. Soc. 78, 574 (1956).

34. R. I. Reed, Ion Production by Electron Impact, (Academic Press, New York, 1962).

0 0 0 0 3 9 0 4 7 5 2

35. J. V. Smith, (Ed.) X-ray Powder Data File (Inorganic), (American Society for Testing Materials, Philadelphia, 1960).

36. C. W. Bunn, Chemical Crystallography, 2nd Edition, (Oxford Press, London, 1961).

37. P. Debye and P. Scherrer, Phys. Z. 17, 227 (1916).

38. S. Dushman and J. M. Lafferty, Scientific Foundations of Vacuum Technique, 2nd Edition, (John Wiley & Sons, Inc., New York, 1962).

39. R. W. Weast, Editor in Chief, Handbook of Chemistry and Physics, 46th Ed., (Chemical Ruber Co., Cleveland, 1965).

40. R. C. Blair and Z. A. Munir, J. Phys. Chem. 72, 2434 (1968).

41. K. D. Carlson, J. L. Margrave (Ed.), The Characterization of High Temperature Vapors, (Wiley, New York, 1967), Ch. 5.

42. K. D. Carlson, P. W. Gilles, and R. J. Thorn, J. Chem. Phys. 38, 2725 (1963).

43. H. Schick, Thermodynamic Properties of Certain Refractory Compounds, Vol. II (Academic Press, New York, 1966).

44. JANAF Thermochemical Tables, Dow Chemical Company, USAF Contract No. AF33(616-6148) 1969.

45. D. A. Young, Decomposition of Solids (Pergamon, Oxford, 1966).

Figure Captions

Fig. 1. Knudsen effusion vapor pressures measured for magnesium nitride.

Fig. 2. Vapor pressure of magnesium nitride: (a) in a D0.25 effusion cell using 7 gm charges, open symbols; (b) in a C0.5 cell with 1.3 gm charge, half open symbols, (c) in a A2.0 effusion cell with 0.7 gm charge, closed symbol. Circles are for Metal Hydrides material and squares for Ventron material.

Fig. 3. Vapor pressure of magnesium nitride in a B0.10 effusion cell with a 5.5 gm charge of Ventron magnesium nitride and in a B0.25 effusion cell with a 7.4 gm charge of Metal Hydrides magnesium nitride.

Fig. 4. Inflection in vapor pressure vs time curve for B0.15 effusion cell cooled from 1390K, inflection gives equilibrium at 1110K.

Fig. 5. Data points giving an indication that the equilibrium vapor pressure is near the upper error limit of the calculated value.

Fig. 6. Vapor pressure of Metal Hydrides magnesium nitride at 1110K for three different orifice areas in a B cell.

Fig. 7. Motzfeldt-Whitman extrapolation at 1110K for magnesium nitride vapor pressure at constant weight losses.

Fig. 8. Motzfeldt-Whitman extrapolation at constant weight loss for runs T11, T12, T13 and T14 at 1180K.

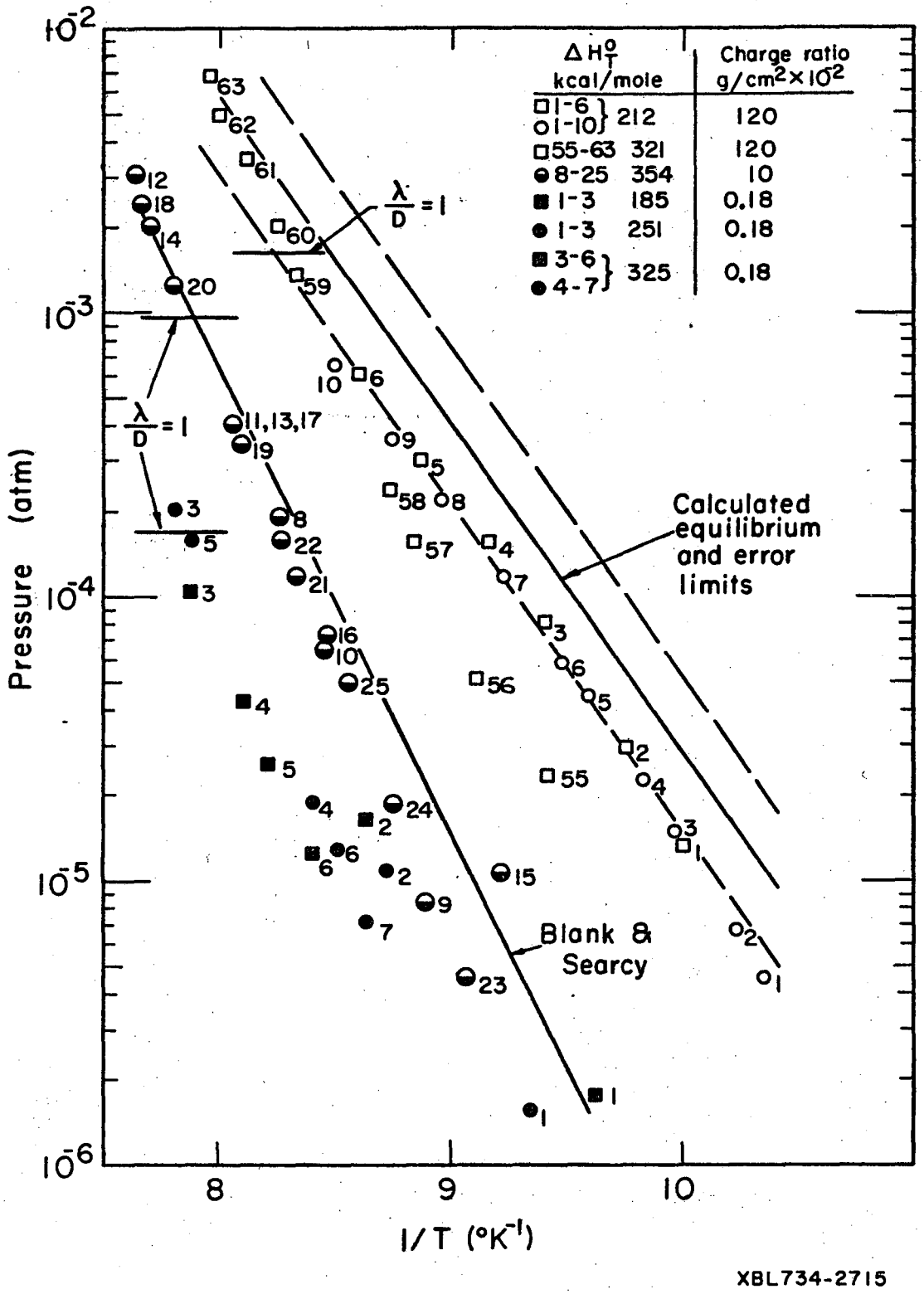
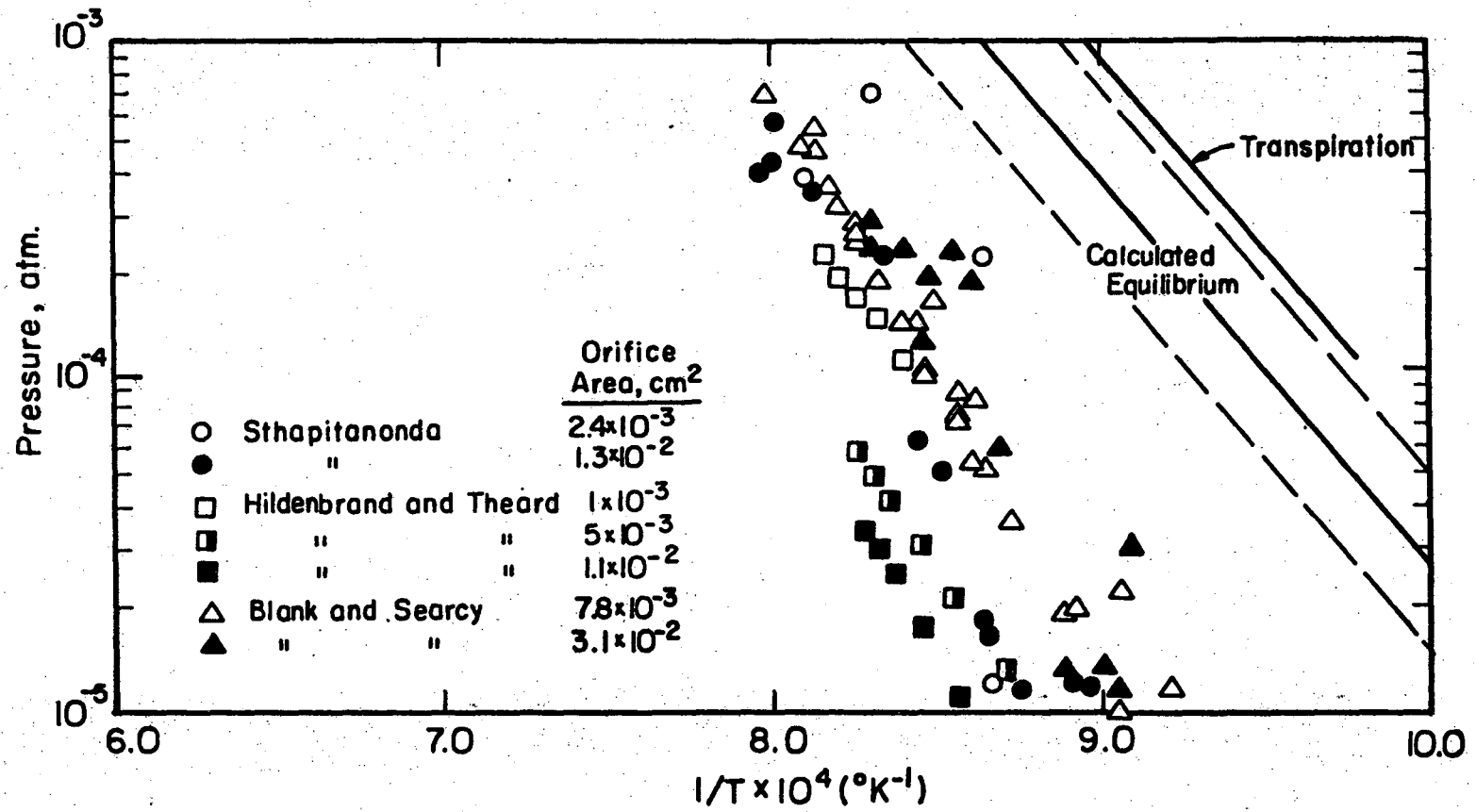

ΔH_T^o kcal/mole
Charge ratio g/cm^2 × 10^{-2}
□1-6 ○1-10 212 120
□55-63 321 120
8-25 354 10
■1-3 185 0.18
●1-3 251 0.18
■3-6 ●4-7 325 0.18
$\frac{\lambda}{D}$ = 1
Calculated equilibrium and error limits
Blank & Searcy
Pressure (atm)
1/T (°K^{-1})
XBL734-2715

Fig. 2



XBL 719-7250

Fig. 1

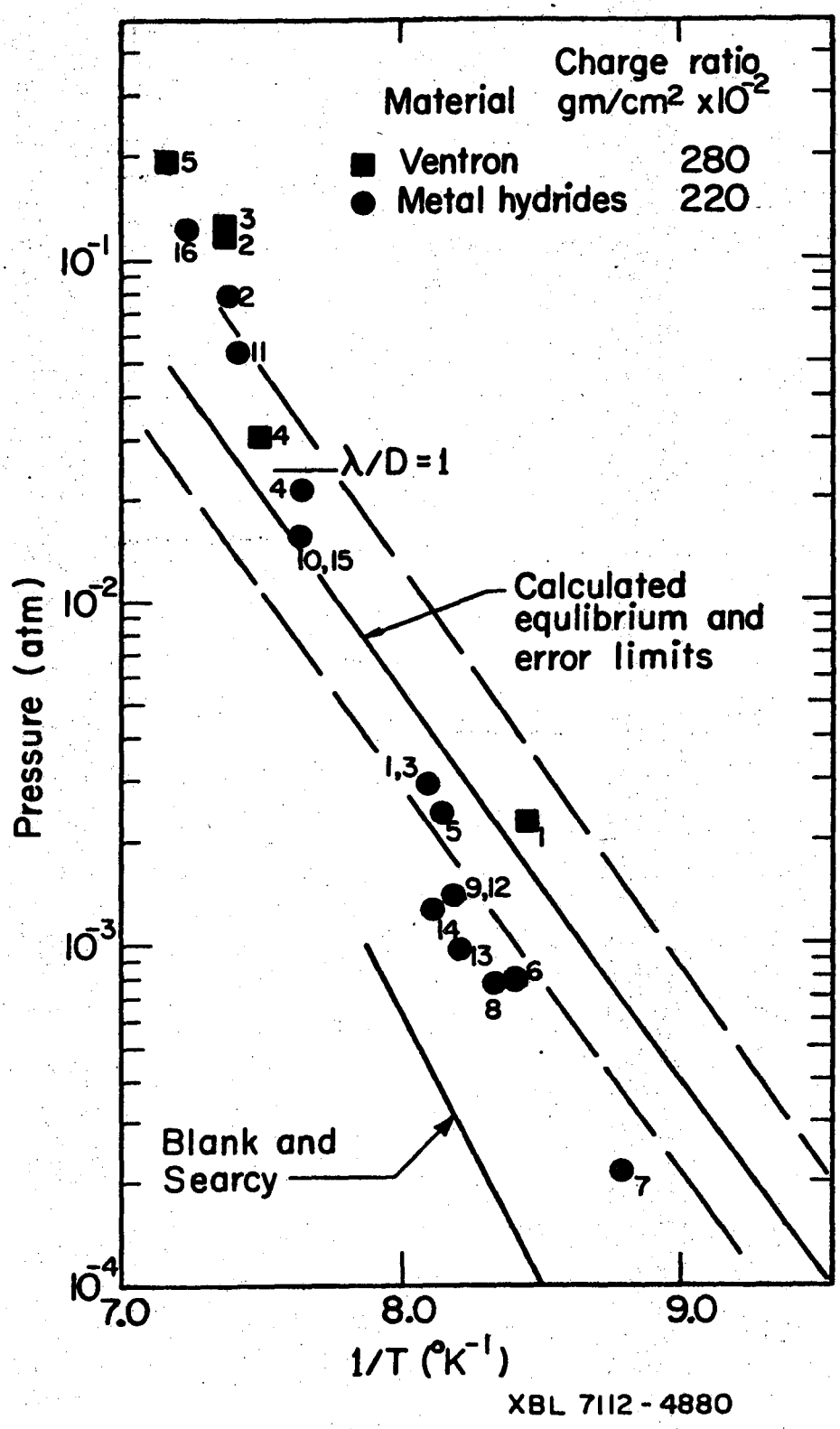

Charge ratio
Material gm/cm2 x10-2
Ventron 280
Metal hydrides 220
λ/D = 1
Calculated equlibrium and error limits
Blank and Searcy
Pressure (atm)
1/T (°K-1)
10-1
10-2
10-3
10-4
7.0
8.0
9.0
XBL 7112-4880

Fig. 3

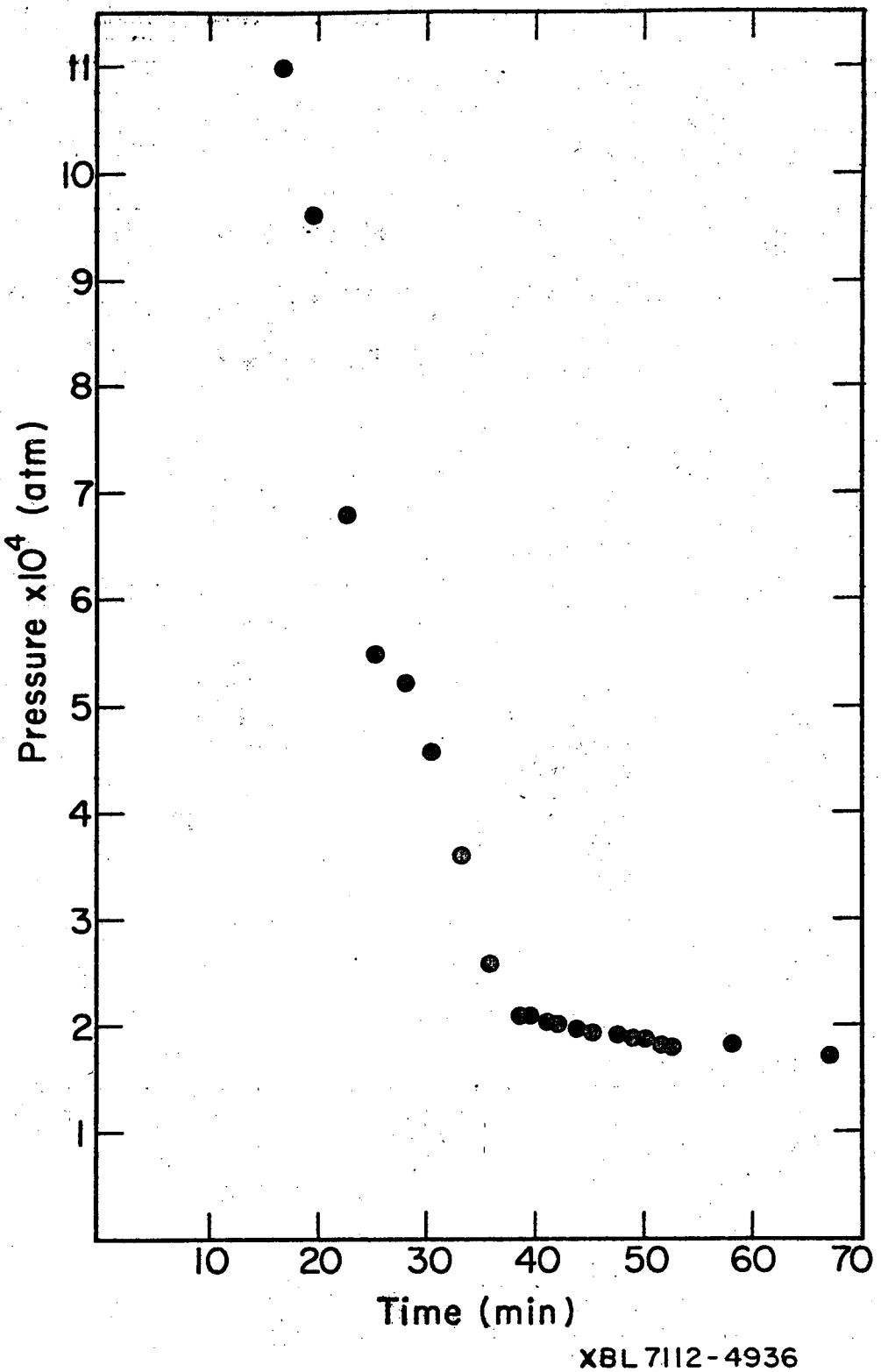

Pressure x10^4 (atm)
11
10
9
8
7
6
5
4
3
2
1
10
20
30
40
50
60
70
Time (min)
XBL 7112-4936

Fig. 4

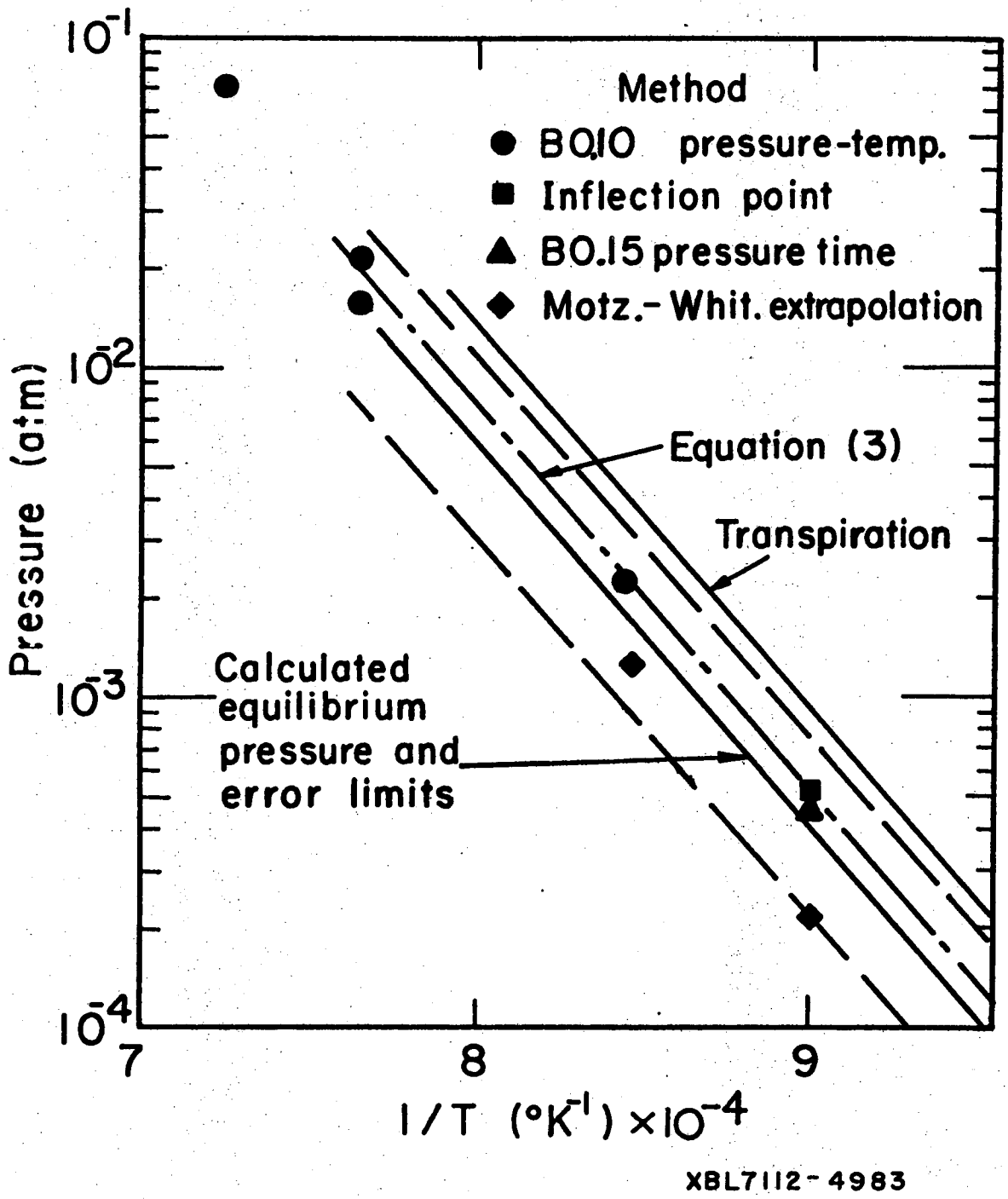
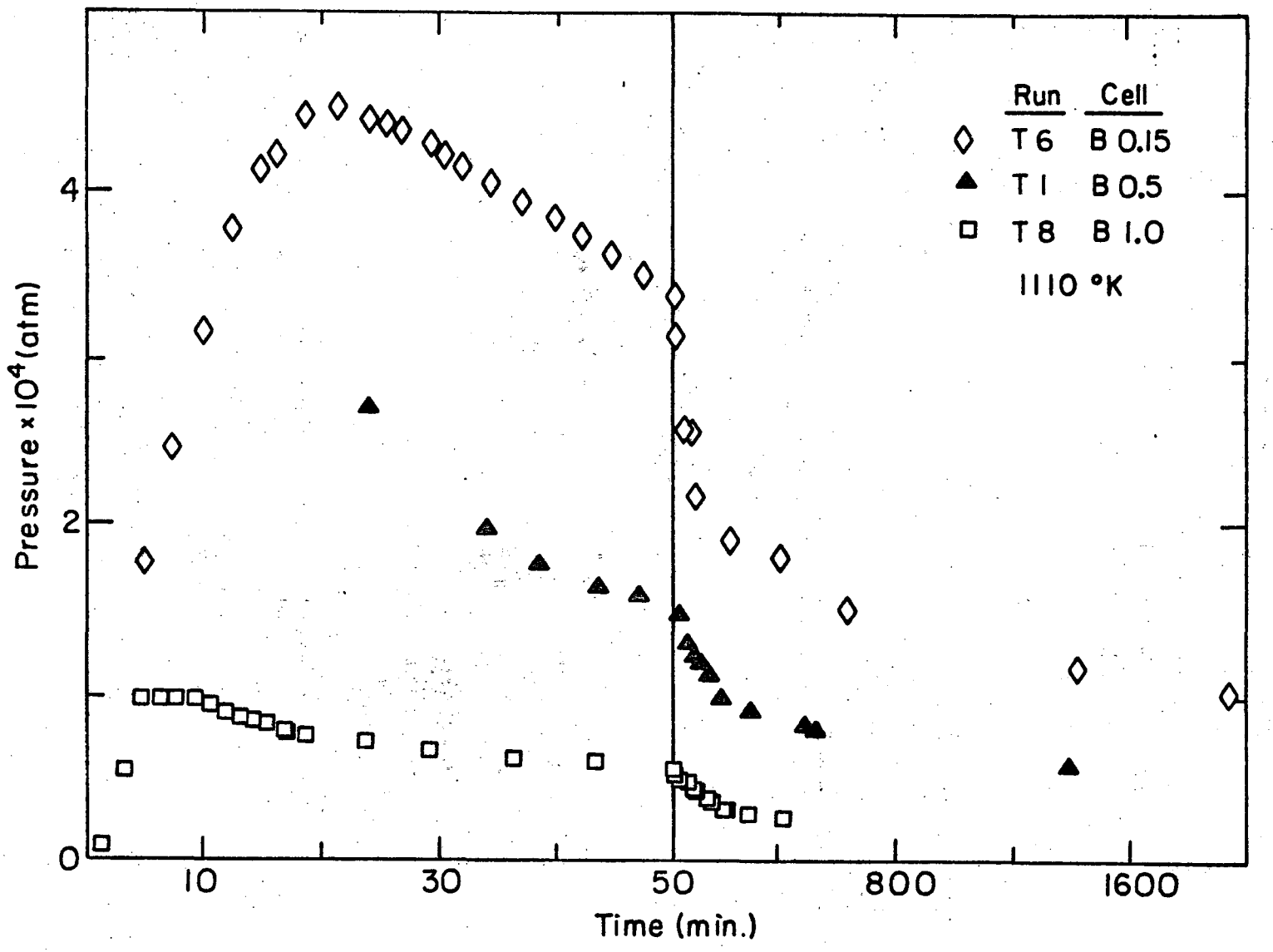
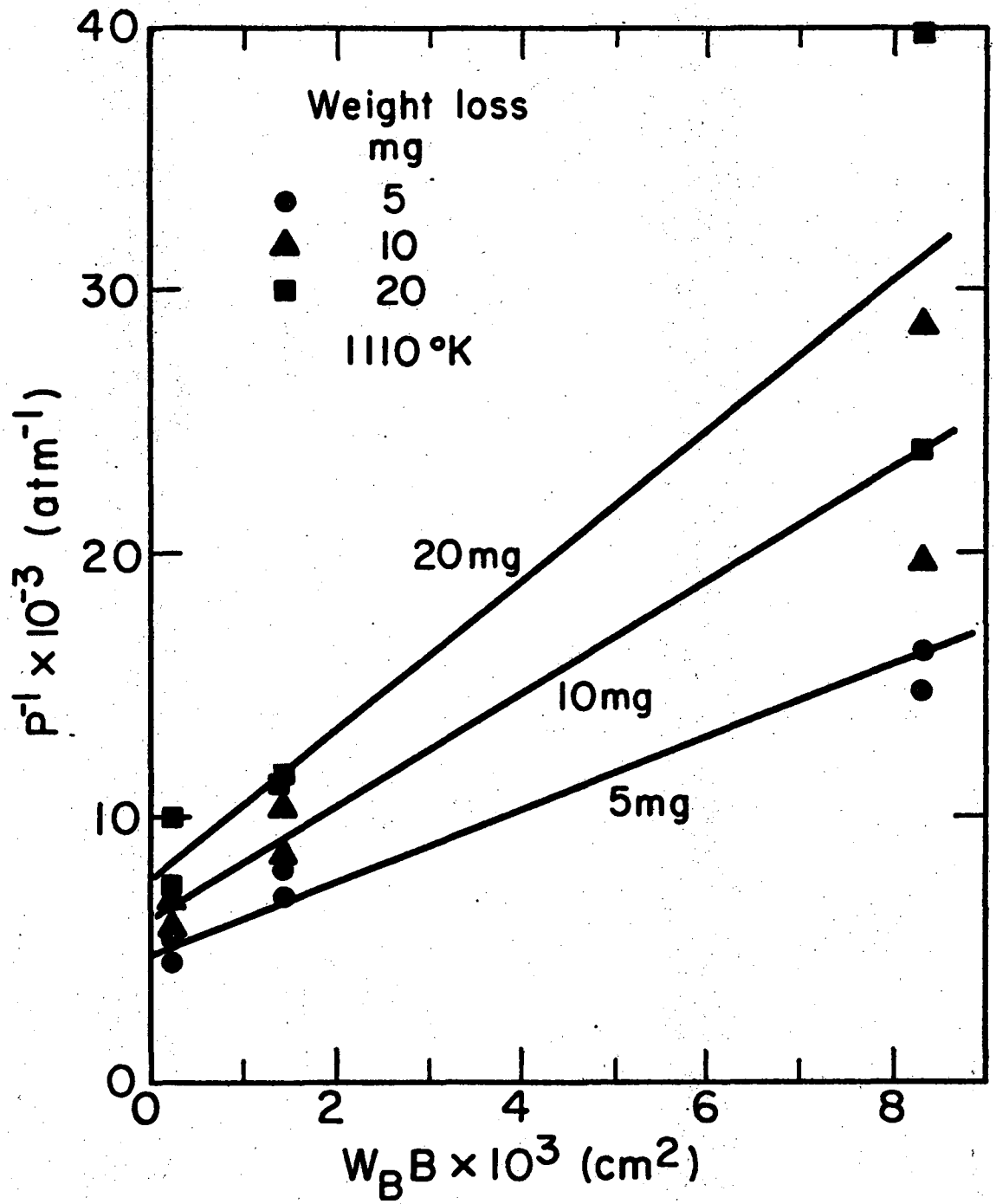

Method
BO.10 pressure-temp.
Inflection point
BO.15 pressure time
Motz.- Whit. extrapolation
Equation (3)
Transpiration
Calculated equilibrium pressure and error limits
Pressure (atm)
10^{-1}
10^{-2}
10^{-3}
10^{-4}
7
8
9
$1/T\ (°K^{-1}) \times 10^{-4}$
XBL7112-4983

Fig. 5



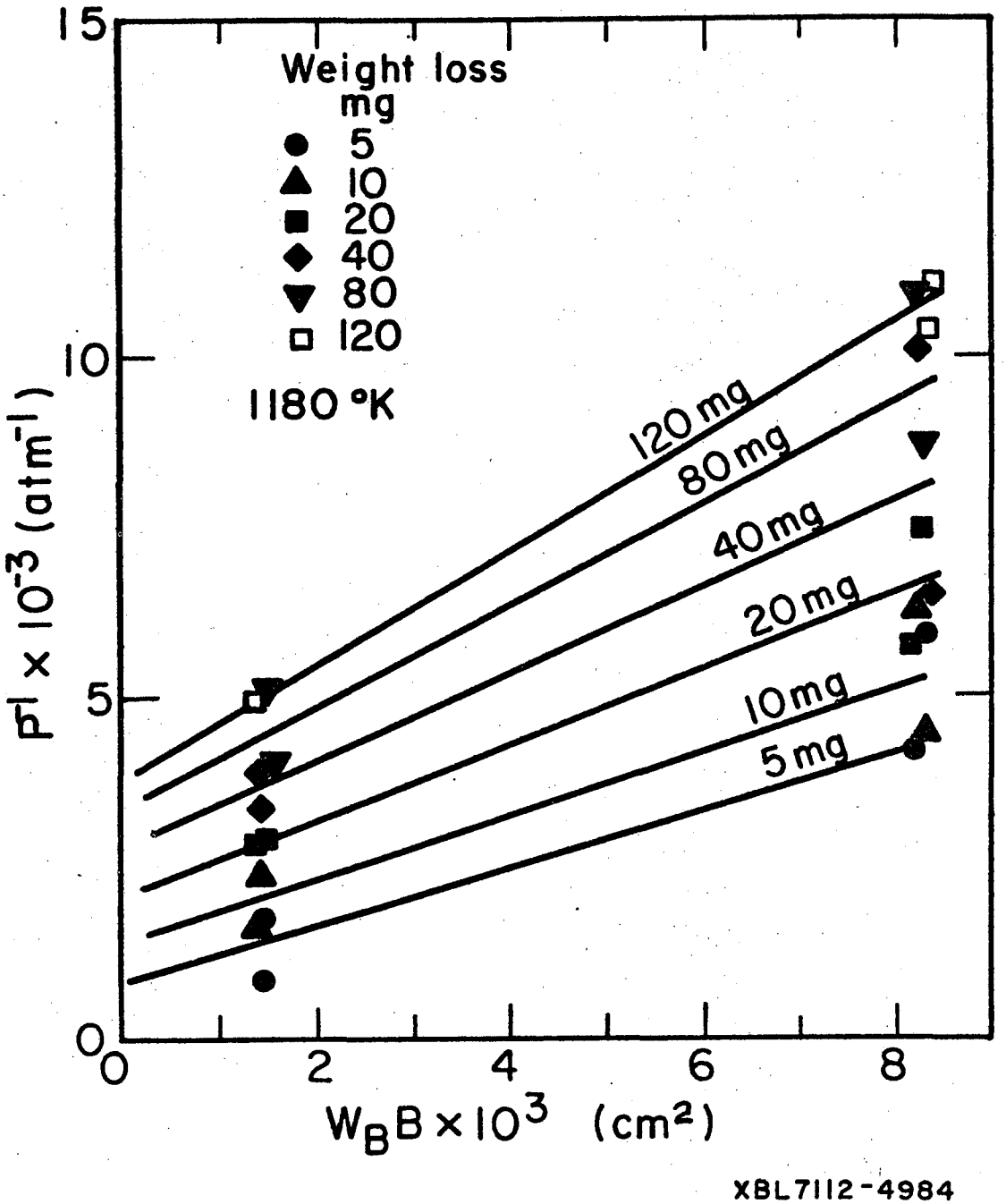
XBL 7110-7464

Fig. 6



XBL7112-4982

Fig. 7



XBL7112-4984

Fig. 8

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