MEASUREMENT OF DISSOCIATION PRESSURES OF HYDROUS MINERALS USING THERMISTORS

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Cooper Harry Wayman

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By

COOPER HARRY WAYMAN

AN ABSTRACT

Submitted to the School for Advanced Graduate Studies of
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Abstract

A high temperature cell has been designed for the measurement of dissociation pressures in hydrous minerals by a newly developed method of thermistors. The vapor pressure over Gypsum was determined with an accuracy of 7-17 per cent as compared to a manometer method. With the present experimental set-up, the thermistor method will not detect vapor pressures with any degree of confidence in substances that must be heated above 100°C.

A critical review of published thermodynamic data for Gibbsite and Boehmite was made. The dissociation pressure over Gibbsite measured experimentally does not agree with theoretically calculated curves as a result of complex surface reactions that occur during dehydration.

The application of certain concepts in physical chemistry and elementary thermodynamics to account for equilibrium assemblages of minerals in nature is discussed.

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Acknowledgements

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I am especially indebted to Dr. Gordon J.F. MacDonald, Institute of Geophysics, U.C.L.A., for originally suggesting the problem of measuring dissociation pressures of hydrous minerals with their possible implications to weathering processes in nature. I also would like to acknowledge Dr. Robert Garrels, Harvard University, for stimulating my interest in calculating equilibrium constants from free energy values.

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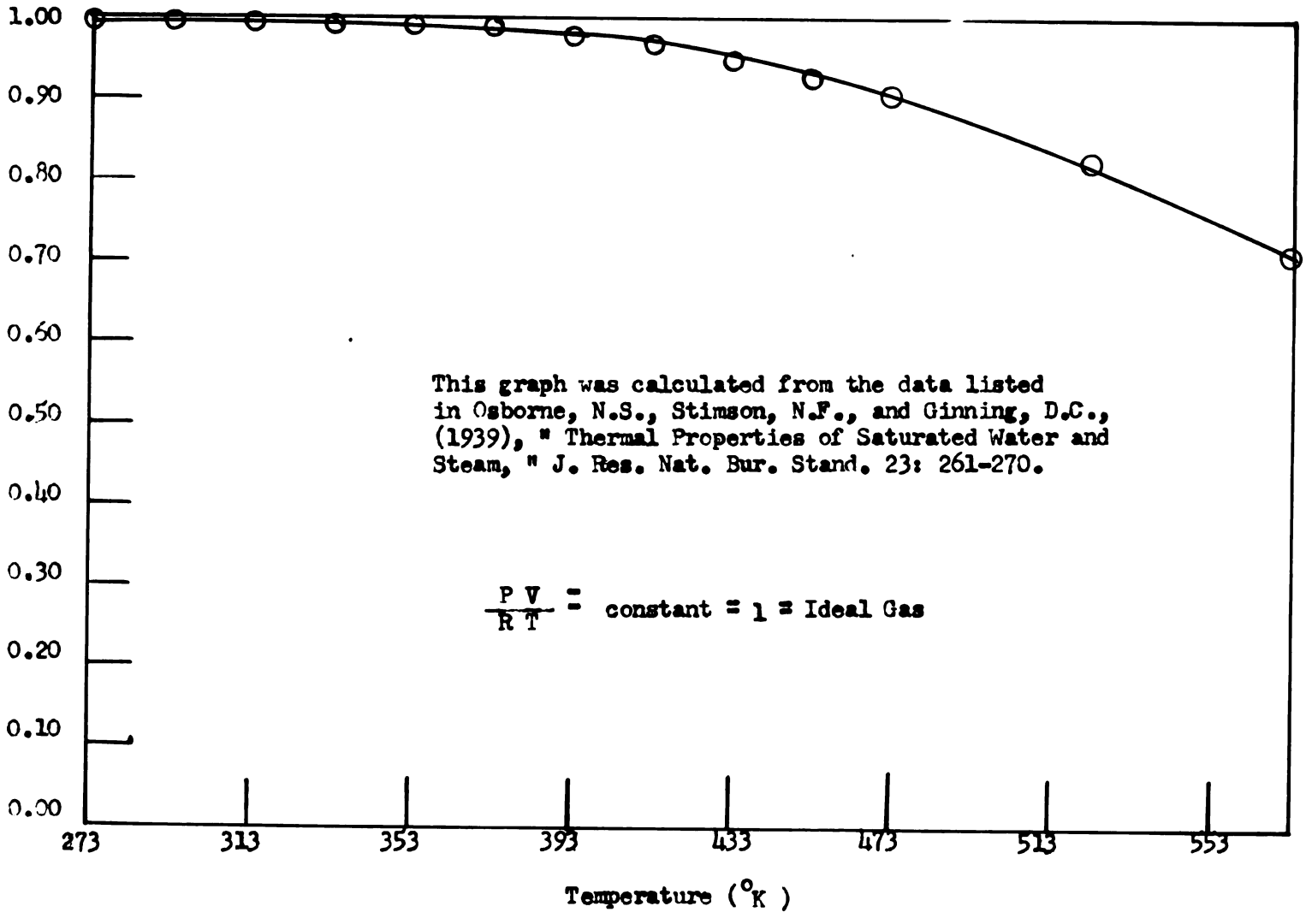
I. Introduction

In the past many geological problems have been investigated from a qualitative, or at best, a semi-quantitative point of view because some important thermodynamic values were lacking to permit quantitative considerations, but the interesting problems of weathering which occur at surface temperature and pressure can be considered on a quantitative basis. Schmalz (1959) has recently published significant data on the Fe_2O_3-H_2O system for the stability relationship of Goethite and Hematite under conditions of weathering. Other important weathering reactions that occur result in the formation of hydrous oxides of aluminum in "bauxite" deposits, hydrous borates in arid climates, and the hydrous copper carbonates and other oxysalts found in mining areas. In "bauxite" deposits, Gibbsite $Al(OH)_3$, Boehmite $AlO(OH)$, and Diaspore $AlO(OH)$ have been identified. On the basis of free energy relationships, Gibbsite should be the stable phase. The partial pressure of water at which Gibbsite dissociates into Boehmite plus water vapor can be determined from the simple reaction:

$$Al(OH)_3 \rightleftharpoons AlO(OH) + H_2O_{(v)}.$$

The equilibrium constant at surface temperature and pressure involves only the partial pressure of water or $K = P_{H_2O}$. In desert areas an interesting set of borates such as Inyoite ($Ca_2B_6O_{11} \cdot 13H_2O$), Meyerhofferite($Ca_2B_6O_{11} \cdot 7H_2O$), Colemanite ($Ca_2B_6O_{11} \cdot 5H_2O$) are found. The partial pressure of water as a function of temperature again would determine which of these hydrate-pairs could co-exist. In the case of hydrous copper carbonates both Malachite and Azurite are found intimately associated. It is difficult to determine whether Azurite alters to Malachite or vice-versa. No free energy values are available at the



2. $\frac{P\,V}{R\,T}$

Figure No. I.1 The deviation of water vapor from an ideal gas as a function of temperature.

present time for either of these species although Garrels (1957) has suggested a method for calculating the free energy of Malachite. This reaction can be written as

$$2Cu_3(CO_3)_2(OH)_2 + H_2O_{(v)} \longrightarrow 3Cu_2CO_3(OH)_2 + CO_{2(v)}$$

(Azurite) (Malachite)

If the reaction goes as written the equilibrium constant would be $K = \frac{P_{CO_2}}{P_{H_2O}}$. If Malachite alters to Azurite, then the equilibrium constant is $K = \frac{P_{H_2O}}{P_{CO_2}}$. It would thus be necessary to investigate these ratios to determine the direction of the reaction. On the basis of the equilibrium reaction, Malachite probably forms from Azurite under conditions of high relative humidities since P_{CO_2} is approximately constant in the atmosphere. It appears that some of the important weathering reactions involve some good, basic chemistry.

Any of the above problems studied experimentally from the viewpoint of vapor pressure measurements would reveal two things: (1) the partial pressure of gas or the partial pressure ratio of two gases as a function of temperature, at which the two solid phases can remain in equilibrium and (2) the heat of reaction (enthalpy) which can be calculated through the use of the Clausius-Clapeyron equation. It is tacitly assumed in the above that water vapor can be treated as an ideal gas for reactions at surface temperature and pressure; the validity of this statement can be demonstrated by plotting the ratio of $\frac{PV}{RT}$ against temperature (figure I.1) which shows little deviation from unity at temperatures up to 413°K (140°C).

A good summary of the various methods of measuring vapor pressures is given in Daniels, Mathews and Williams (1949). The most common types

listed are the dynamic method, static method, gas-saturation method (transpiration method), and the isopiestic method. Each of these methods has definite limitations with perhaps the isopiestic being the best. For example, the entire apparatus must be thermostated to permit vapor pressure measurements greater than those at the saturation pressure of water vapor at room temperature. If the unit were not thermostated, then water vapor would condense along the walls of the tubing and at joints whereby the only vapor pressure measured would be that at the point of lowest temperature in the system and not necessarily that over the sample. Other disadvantages are the elaborate glass blowing which is amenable to occasional leaks and requires a vacuum pump of high capacity due to the large volume of the system to be evacuated.

Recently much attention has been given to vapor pressure measurements from the adsorption of a gas on a solid by the use of the McBain balance. In this method a solid adsorbant is attached to a sensitive quartz spring. Knowing the adsorption isotherm of a specific adsorbant for various gases permits the determination of the vapor pressure by change in weight of the adsorbant in terms of units of spring deflection. The obvious disadvantages of this method are that the sensitive quartz spring is affected by small changes in temperature and that a series of selective adsorbants would be required to measure the presence of more than one gas.

An excellent method for measuring the concentrations, and therefore determining pressures, of multiple gases is infra-red spectroscopy. This method has the nearly unique property of being selective to any gas providing its spectrum is determined. In this method it is necessary to use a heated, calibrated sample cell with a heated attached absorption

cell to prevent condensation of vapor along the walls of the tubing and cell windows. The cell should be constructed of high quality pyrex glass and calcium fluoride windows must be used on the absorption tube to eliminate erosion from water vapor which would occur if sodium chloride windows were used. The entire spectrometer must be flushed with dry nitrogen to remove water vapor from all sources other than the sample apparatus during any run. The vapor pressure over distilled water and mixtures of distilled water and sulfuric acid can be used as standards for water vapor. The recent work of Tosh, Field, Benson and Haynes (1959) has established a possible standard for both water vapor and carbon dioxide by measuring the partial vapor pressures of these gases over solutions of potassium carbonate. Thus with this method one simply would compare the unknown vapor pressures to those obtained from standards in terms of percent transmission. Percent transmission can be expressed in terms of I_0, I_{100} and I_T where I_0 = the amount of stray energy reaching the detector when the beam is cut out, I_{100} = the 100% transmission = 0% absorption, I_T = quantity or point determined at the minimum of the absorbed band.

$$\%T = \frac{I_T - I_0}{I_{100} - I_0} \times 100$$

The writer investigated this method up to approximately 250mm. Hg. vapor pressure of water; pressures beyond this range could not be attained because of poor cell design . However, further exploration by this method should be undertaken since both water vapor and carbon dioxide are of geological interest and their presence can be simultaneously measured using this technique.

It was suggested that the measurement of dissociation pressures by thermistors might be fruitful and so this was investigated. The

dissociation pressure of water over Gypsum was measured and the accuracy compared to a manometer technique of Kelley, Southard, and Anderson (1941). An attempt was also made to measure the dissociation pressure of Gibbsite and thereby determine the free energy of formation.

This thesis is intended to have a three-fold purpose:

(1) To develop a new method for measuring vapor pressures

(2) To design a heated cell that can be used for making vapor pressure measurements on hydrous minerals

(3) (a) To use some of the fundamental concepts of physical chemistry and elementary thermodynamics to calculate theoretical curves for dissociation pressures of hydrate-pairs and

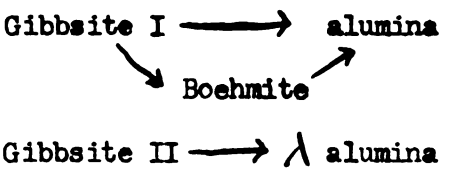
(b) To correlate the results of experiment and theory and their comparison with equilibrium processes in nature.

II. Historical Background

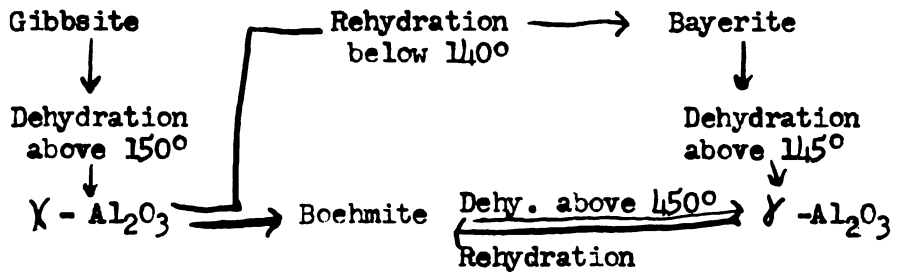
Much work has been done in the past on the dehydration of Gibbsite, but unfortunately at high temperatures. The emphasis was placed on the dehydration as applied to industrial preparations of alumina with little attention given to its geological possibilities. Hackspill and Stempfel (1929) found that Gibbsite could be irreversibly dehydrated at 220°C. They suggest that dehydration does not take place by progressive loss of water, but this is incorrect. Achenbach (1931) indicates that synthetic Gibbsite begins to lose water at 170°C and passes into orthorhombic boehmite at approximately 200°C. Schwiersch (1933) states that Gibbsite starts to lose water at 150°C and converts into boehmite. Borisevich (1948) has investigated the tensimetric dehydration of gibbsite and found three stages of water loss. Up to 175°C, ½ mole of water is released with a structural change to boehmite. At 200°C an additional 1½ moles of water is lost and a monohydrate is formed. The last stage of dehydration ends at 400°C. It is further pointed out that, within a rather narrow interval of temperature, two different reactions occur in the transition of the gibbsite lattice to that of boehmite which explains the complicated curves observed by some authors for thermal effects in dynamic experiments. Ginsberg and Köster (1952) investigated gibbsite by heating under pressure in the presence of alkali and indicate that gibbsite is completely converted to boehmite with yields of over 90% when heated at 180°C for two hours at alkali concentrations as low as 0.6g Na_2O/liter. These authors conclude that, if traces of Na_2O enter the gibbsite lattice, less stable compounds form, which are easily converted to boehmite. Tertian and Papee (1953) reveal that the slow heating of gibbsite under reduced pressure yields two phases, a smaller fraction of boehmite and a larger

one of poorly crystalline alumina. The results of these workers are in disagreement with most of the previous work. Tertian, Papee and Charrier (1954) studied the dehydration both in air and vacuo. In vacuo between 170° and 250°C, boehmite is the only well crystallized phase formed amounting to only about 25% of the sample. At 400°C the dehydration product, boehmite, decomposes to gamma alumina. In air between 200° and 400°C gibbsite completely converts to boehmite. Trambouze, The, Perrin and Mathieu (1954) investigated gibbsite by D.T.A., thermogravimetry and B.E.T. measurements and found that between 25 and 570°C gibbsite loses 2.94 moles of water. The surface area increases to a maximum of 235 sq. m./g. at 380°C when H_2O. Al_2O_3= 0.55. Alexanian (1955) used X-ray diffraction, dehydration and D.T.A. and found that gibbsite converts to boehmite at 220°C, while bayerite decomposes into gamma alumina up to 220°C. Courtial, Trambouze and Prettre (1956) suggest that the boehmite content of a gibbsite sample dehydrated rapidly at high temperatures is always much less than the boehmite content of a sample dehydrated to the same degree but more slowly and at lower temperatures. This work was done in air at temperatures that ranged from 134°-378°C with a maximum of 30% gibbsite found as a partial dehydration product. Since it was shown previously that gibbsite loses nearly two-thirds of its water at slightly over 200°C, this work is questionable. Theoretically, in an open system at temperatures greater than 200°C and given sufficient time, gibbsite should convert completely to boehmite. Ginsberg, Hüttig and Strunk-Lichtenberg (1957) have found that the phases present after dehydration depend upon the starting material. Technically prepared gibbsite with a grain size of 9.4 microns dehydrates at 105°C to gibbsite with a small amount of

boehmite. At 200°C both gibbsite and boehmite are present in large quantities. Gibbsite prepared from KOH with a grain size of 6.7 microns does not dehydrate to boehmite at 105°C. At 200°C the same material contains abundant gibbsite and boehmite after dehydration. Sato (1959) studied the dehydration of various preparations of gibbsite by thermobalance, D.T.A., and X-ray diffraction. It was determined that gibbsite has a lower decomposition temperature if bayerite is present as an impurity from preparation. Fine-grained gibbsite (88% less than 5 microns) does not give an endothermic peak at 220-230°C whereas coarse-grained gibbsite (17% less than 5 microns) shows a reaction at this temperature. This work would suggest that the stability of gibbsite is greater for fine-grained material. The dehydration mechanism given by Sato is



Day and Hill (1953) conclude that boehmite formed from the dehydration of gibbsite and bayerite is produced by secondary reactions between the original dehydration products, which are virtually anhydrous aluminas, and the water vapor released during dehydration. Their proposed mechanism of dehydration is



DeBoer, Steggerda and Zwietering (1954) have also studied the dehydration of gibbsite and indicate that the products formed depend on the method of preparation. Gibbsite (I) formed when 130g. $Al(OH)_3$ and

180g. NaOH in 1:1 H_2O were exposed to air for three months at room temperature and dehydrated to χ-alumina. Gibbsite (II) precipitates from a Na aluminate solution when carbon dioxide is bubbled through at 80°-90°C. Gibbsite (II) dehydrates to a mixture of -alumina and boehmite. In another portion of their work, these investigators found that normal water pressure and saturation water pressure give different reaction products on dehydration. The mechanism listed is

$$\text{Gibbsite} \xrightarrow[225^\circ]{\text{Normal Water Pressure}} \chi\text{-alumina}$$

$$\text{Gibbsite} \xrightarrow[200^\circ]{\text{Saturation Pressure}} \text{Boehmite}$$

All the above data, although somewhat controversial, suggest that $(OH)^-$ radicals in gibbsite are broken to form water, which is progressively lost after perhaps 150°C with boehmite forming most likely as a surface reaction. The obvious weakness of dehydration studies is that no information is given with respect to temperature-pressure relationships.

In addition to dehydration studies, some work has appeared recently on the rehydration of dehydrated gibbsite and a few accounts of the kinetics of these reactions. Imelik (1951) studied the rehydration of alumina that was a dehydrated $Al(OH)_3$ gel (boehmite structure). The gel was heated from 400-900°C. After dehydration this product was exposed to air saturated with water at 37°C (vapor pressure of 47mm. Hg). After one week the sample ignited at 400° showed evidence of rehydration to boehmite and gibbsite from X-ray studies. This information might suggest that gibbsite originally dehydrated to alumina would form boehmite if left in contact with water vapor in a closed system. Eyraud and Goton (1954) investigated the dissociation of gibbsite thermogravimetrically. The dissociation covered a temperature range of

206-243°C at pressures of 10^{-3}, 4.5, and 15mm. Hg. The dissociation was zero-order with activation energies of 31 kcal. at 10^{-3}mm. Hg
56 kcal. at 4.5mm. Hg
63 kcal. at 15mm. Hg

This data is interesting since it indicates that the reaction is independent of pressure. In general it obeys the Langmuir adsorption isotherm for strongly adsorbed, single reactants. This type of reaction can be expressed by the zero-order reaction as

$$\frac{dx}{dt} = k$$

dx = differential of products
dt = differential of time
k = reaction constant

which says that the reaction rate is constant and independent of pressure or in terms of the integrated form of the rate equation X=kt. A possible physical interpretation of this study is, that regardless of how small the pressure of water vapor over gibbsite, the gas is so strongly adsorbed at the surface and probably exerts a breaking effect or impedes the migration outward of $(OH)^-$ groups from within the crystal. Another important factor is suggested in that pressure influences the activation energy. Therefore, progressive increase of vapor pressure requires more energy for dehydration after water has been released from the crystal structure. The activation energy and heat of reaction would accordingly not be constant as pressure changed in the thermal system in the temperature range 206-243°C. It would be of interest to compare this observation to similar reactions under natural conditions. Eyraud, Goton and Prettre (1954) have found that gibbsite dehydrates in two steps. After making corrections for adsorption and diffusion interferences, the reaction is zero-order with an apparent activation energy of 31 kcal. between the temperature range 180°-245°C. Above 245°C, the reaction becomes slightly positive as pressure increases with an increase in

activation energy to 56-63 kcal. This result is explained in terms of the chemical adsorption of water on the surface of the solid without any transformation. Thibon and Calvet (1954) have studied the rehydration products of gibbsite which was dehydrated under vacuum at a temperature of 400°C. The reactions were given in terms of temperature-time curves of exothermic peaks which most likely suggest a recrystallization. The rehydration reaction apparently depends on temperature. A very strong exothermic reaction takes place after one hour at all temperatures. A second exothermic peak occurs in 3 hours at 35°, a very weak peak in 14 hours at 25° and no second peak after 24 hours at 10°. The X-rayed products were identified as amorphous material at 10° and a mixture of bayerite and anhydrous alumina at 25° and 35°. At best, one finds that dehydrated gibbsite can rehydrate to boehmite, amorphous material or alumina. It appears that the activation energy for gibbsite at temperatures below 245°C is about 31 kcal. and the reaction rate is of zero-order.

Similar to the kinetic investigations, little work has been done on the thermodynamic properties of gibbsite. The first thermodynamic approach to this problem was done by Hüttig and Wittgenstein (1928). The experimental method used was a manometer system whereby the volume and pressure of gas released could be measured. It was shown in this work that gibbsite loses about two-thirds of its water between 180° and 190°C and the remainder is lost continuously up to 448°C. The following equation is reported for the reaction:

$$\text{(Gibbsite) } Al_2O_3 \cdot 3H_2O \rightleftharpoons Al_2O_3 \cdot H_2O + 2H_2O_{(v)} - 43.14 \text{ kcal.}$$

or

$$Al(OH)_3 + 21.57 \text{ kcal.} \rightleftharpoons AlO(OH) + H_2O_{(v)}$$

giving ΔH° = 21.57 kcal. for the second reaction. Fricke and Severin (1932) used a manometer method to study the dehydration pressures of gibbsite isobarically at 100mm. Hg and found the dissociation temperature to be 165°C. Their results indicate that two thirds of the water is lost between 115° and 175°C. The following heat effects were calculated:

$$\text{(Bayerite) } Al(OH)_3 \rightleftharpoons AlO(OH) + H_2O_{(v)} \qquad \Delta H^{\circ} = 16.2 \text{ kcal.}$$

$$\text{(Gibbsite) } Al(OH)_3 \rightleftharpoons Al\,O(OH) + H_2O_{(v)} \qquad \Delta H^{\circ} = 18.15 \text{ kcal.}$$

Hüttig and Köebl (1933) investigated the isobaric decomposition of gibbsite and found that most of the water is released from 100° - 210°C and then more slowly up to 400° at which point the solid has a composition of 0.8 H_2O . Al_2O_3. They discuss the reaction $XY_{solid} \rightleftharpoons X_{solid} + Y_{gas}$ from classical thermodynamics, but no quantities were calculated from their data. Kugnetzov (1950) has listed the properties for gibbsite and boehmite as follows:

	ΔH° 298.16°K	ΔF° 298.16°K
Gibbsite	-307.7 kcal.	-274.82 kcal.
Boehmite	-234.9 kcal.	-217.10 kcal.

Using these data the heat effect for

$$Al(OH)_3 \rightleftharpoons Al\,O(OH) + H_2O_{(v)}$$

is 15.0 kcal. Funaki and Uchimura (1952) prepared pure bayerite and gibbsite and determined the dissociation pressure for a limited range of temperature by means of a spring manometer. The following thermodynamic relations were estimated from their results for the reactions:

Bayerite

$$Al_2O_3 \cdot 3H_2O \rightleftharpoons Al_2O_3 \cdot H_2O + 2H_2O_{(v)}$$

$$\Delta H^\circ = 32.7 \text{ kcal.}$$

$$\Delta F^\circ = 32.7 \times 10^3 - 68.5T$$

$$\log K_p = \frac{-7.18 \times 10^3}{T} + 14.9$$

Gibbsite

$$Al_2O_3 \cdot 3H_2O \rightleftharpoons Al_2O_3 \cdot H_2O + 2H_2O_{(v)}$$

$$\Delta H^\circ = 96.0 \text{ kcal.}$$

$$\Delta F^\circ = 96.0 \times 10^3 - 216T$$

$$\log K_p = \frac{-21.0 \times 10^3}{T} + 47.4$$

Latimer (1953) lists the following thermodynamic values for gibbsite and boehmite from the National Bureau of Standards as follows:

	$\Delta H^\circ_{298^\circ K}$	$\Delta F^\circ_{298^\circ K}$
Gibbsite	-613.7 kcal.	-435 kcal.
Boehmite	-471.0 kcal.	-547.9 kcal.

From these values the heat effect of

$$Al(OH)_3 \rightleftharpoons Al\,O(OH) + H_2O_{(v)}$$

is 13.55 kcal. Sabotier (1954) measured the heat of reaction of gibbsite by DTA and gives a value of 276 cal./g. which for the reaction

$$Al(OH)_3 \rightleftharpoons Al\,O(OH) + H_2O_{(v)}$$

can be recalculated as 21.5 kcal.

Eyraud, Goton, and Prettre (1955) found that gibbsite dehydrates in 3 steps:

(1) loss of 0.2 H_2O/Al_2O_3 requiring 3.5 kcal./g. water

(2) next step ends at a compn. of 0.5-0.6 H_2O/Al_2O_3 and requires 1.1 kcal./g. and

(3) last step consists of two rather ill-defined regions, one

requiring 1.0 -1.4 kcal./g. and the other 1.8 -2.0 kcal./ g.
A more intense study of step (1) showed that ΔH°_{298} is very close to that for the transformation into boehmite. Deltombe and Pourbaix (1956) determined electrochemically the standard free energies of formation of gibbsite and bayerite as -554.6 kcal./mole and -552.47 kcal./mole respectively. To say the least, the literature review on the thermodynamics of gibbsite shows a high degree of incompatible results. These discrepancies have contributed to an interest in part of this thesis, in which the thermodynamic properties for the reaction

$$Al(OH)_3 \rightleftharpoons Al\,O(OH) + H_2O_{(v)}$$

were reinvestigated.

III. Preparation of Materials and Mineralogy

A. Gibbsite

The gibbsite used in this investigation was supplied by Kaiser Aluminum and Chemical Corporation, Baton Rouge, Louisiana. The material was prepared by the Bayer method. The chemical analysis supplied with the sample was

	Per cent (weight
Loss on Ignition at 1000°C	34.70
SiO_2	0.02
Fe_2O_3	0.013
Na_2O	0.37
Free water (adsorbed)	0.06
Al_2O_3	64.90
	100.063

This analysis can be compared to the theoretical value of $Al_2O_3.3H_2O$ of Al_2O_3= 66.64% and H_2O = 33.36%. The size distribution of the grains was determined by dry screening a 25 gram sample on a Ro-Tap for 30 minutes. The results of this test are given in table III.1.

Table III.1

Mesh	Size (Microns)	% of Total
+100	+105	12.5
-100+270	53-105	73.7
-270 +325	44-53	10.0
-325	-44	3.8
		100.0

Table III.1 indicates that approximately 75 per cent of this material ranges from 53-105 microns which is fairly coarse-grained. The surface area of the material as described in Table III.1 was 1440cm.^{2}/gm. as

determined by the B.E.T. (Branauer, Emmett, and Teller) method. The details of this surface area adsorption method are given in Appendix I. Originally, it was intended to use samples with granularities of approximately 5 and 20 microns. Unfortunately, time did not permit any work on these size fractions. These fine size fractions were obtained by dry grinding the coarse gibbsite in a stainless steel ball mill for eight hours. The ball mill product was then sized by free-settling sedimentation techniques using Stokes' Law as the basis. Separations were made at 5 and 20 microns and the surface areas as determined by the B.E.T. method were respectively 60,400cm.^{2}/gm. and 52,500cm.^{2}/gm. The details of Stokes' Law calculation are given in Appendix II.

Examination of the unground material with the petrographic microscope revealed that gibbsite was the only phase present. Most of the fragments were coarse-grained, white aggregates. The indices of refraction obtained were

$$\alpha = 1.558 \pm 0.002$$

$$\beta = 1.558 \pm 0.002$$

$$\gamma = 1.579 \pm 0.002$$

and the optical sign was positive. Optical examination of the ground gibbsite showed that a dark, somewhat amorphous surface coating had formed as a result of grinding; this condition might be explained from the heat generated in the ball mill.

The unground gibbsite was also studied by X-ray diffraction using CuK_α radiation by recording the 2θ values. Gibbsite was the only phase detected at the characteristic 2θ values of 18.1, 20.1, and 36.1. X-ray examination of the ground gibbsite indicated that intense, but somewhat diffuse lines of gibbsite were present.

The crystal structure of gibbsite was first determined by Megaw (1934) from Weissenberg photos and ionization spectrometer measurements. The crystallographic constants of monoclinic gibbsite were

$$a = 8.6263 \pm 0.0007A^{\circ}$$

$$b = 5.0602 \pm 0.0006A^{\circ}$$

$$c = 9,699 \pm 0.004A^{\circ}$$

$$\beta = 85^{\circ}\ 26' \pm 5'$$

$$Z = 8$$

$$C^{5}_{2h} - P2,1n$$

The structure is a layer lattice and is pseudohexagonal. Each layer consists of two planes of nearly close-packed oxygens, enclosing a plane of Al, which occupy 2 out of 3 possible hexagonal close-packed positions.

Bayerite, the dimorph of gibbsite, is described by Montoro (1942) from Debye-Scherrer spectrograms. A sample with a composition of $Al_2O_3 .3.14H_2O$ had a hexagonal unit cell with parameters of

$$a = 5.01A^{\circ}$$

$$c = 4.76A^{\circ}$$

$$Z = 2$$

A specific gravity of 2.49 and molecular volume of 62.7 was calculated.

No solid-solution is known to exist between any phases of the hydrates (hydroxides) of aluminum. Beneslavskii (1957) claims that solid solution does occur such as an Al-containing goethite with the general formula $k\ Al_2O_3.mFe_2O_3.nH_2O$ with m greater than n. It is pointed out that a mineral of the type $Al_2O_3.2Fe_2O_3.5H_2O$ was isolated from insoluble residues from "bauxite" in the Enisei district. This

account is probably questionable, but no present work on phase equilibria is available to discredit it.

B. Boehmite

The synthetic Boehmite used as an X-ray standard was also supplied by Kaiser Aluminum and Chemical Corporation. The boehmite was prepared from the hydrothermal alteration of gibbsite. The chemical analysis given was

	Per cent
Loss on Ignition at 1000°C	14.60
Free water	0.08
Na_2O	0.41
Al_2O_3	85.00
	100.09

This analysis compared favorably to the theoretical amounts of water and alumina in boehmite which are respectively 15.02 per cent and 84.98 per cent.

Optical examination of this material revealed that the indices of refraction were

$$\alpha = 1.645 \pm 0.003$$
$$\beta = 1.655 \pm 0.002$$
$$\gamma = 1.663 \pm 0.002$$

The 2θ values obtained by X-ray diffraction indicated that boehmite was the only phase present. The characteristic peaks using CuK_α radiation appeared at 2θ values of 14.5, 28.2 and 38.2. Iberg (1956) has obtained the Infra-red absorption spectrum for boehmite. Two OH bands appear at wavelengths of 3.06 microns and 3.26 microns. It was considered unnecessary to identify boehmite with this new technique since positive results were obtained by other methods.

C. Gypsum

The gypsum used was supplied by K.K.Kelley, Minerals Experiment Station, Berkeley, California. This material was originally obtained from the Perkins Deposit, Alaska and is identical to that utilized by Kelley in his vapor pressure experiments. It was essentially free from impurities. The gypsum was ground gently in an agate mortar and separated into a -100 mesh fraction by hand sieving. This size fraction was also used by Kelley.

Optical and X-ray examination indicated that gypsum was the only phase present.

IV. Thermochemical Considerations

A. Thermodynamic Equilibrium Constant and the Phase Rule

In many types of experimental work, it is often possible to calculate theoretical curves for an assumed reaction to see how well theory and experiment agree. This statement is based on the fact that previous experimental values have been determined which can be applied to empirical equations for some process or chemical reaction.

The emphasis in this thesis has been to obtain additional data on the reaction

$$\text{Gibbsite} \rightleftharpoons \text{Boehmite} + \text{water vapor}$$

or

$$Al(OH)_3 \rightleftharpoons Al\,O(OH) + H_2O_{(v)}$$

(structural basis)

or

$$Al_2O_3 \cdot 3H_2O \rightleftharpoons Al_2O_3 \cdot H_2O + 2H_2O_{(v)}$$

(chemical Formula Basis)

The equilibrium constant for the reaction on a structural basis can be written as

$$K = \frac{a_{\text{boehmite}} \cdot a_{\text{water vapor}}}{a_{\text{gibbsite}}}$$ where a = activity

Since the activity of pure compounds can be considered unity at low temperatures, the expression reduces to $K = a_{\text{water vapor}}$. The activity is defined as

$$a = f/f_o \text{ where}$$

f = fugacity

f_o = fugacity is some standard state

For geological purposes at surface temperature and pressure the standard state can be chosen as one atmosphere pressure. Thus the activity

is $a = f/1 = f$. Figure I.1 shows that for surface conditions water vapor may be treated as an ideal gas. Since the fugacity of an ideal gas can be approximated very well by its partial vapor pressure, the equilibrium constant becomes

$$K = f = P_{H_2O} \text{ (partial pressure of water vapor)}$$

From the phase rule the number of degrees of freedom (F) equals C-P+2, where F = no. of degrees of freedom, P = no. of phases and C = no. of components. For the reaction under consideration three phases (gibbsite, boehmite, and water vapor) exist which can be described in terms of two components (water and aluminum). Hence F = 2-3+2=1. The experimental pressure, temperature or composition can therefore be varied and the condition under which the three phases, gibbsite, boehmite and water vapor are in equilibrium is determined. Since the equilibrium constant for this reaction involves only the pressure of water, it is convenient to use a system to obtain the equilibrium pressure as a function of temperature at fixed composition. In order to find this equilibrium pressure, it is necessary to know the change in the equilibrium constant with temperature. The following derivation should suffice to show how the equilibrium constant varies with temperature; the change in free energy in a system undergoing a chemical reaction, when all reactants and products are in their standard states is

(1) $\Delta F^\circ = -RT\ln K$

where R = gas const.

T = absolute temp.

K = equil. const.

ΔF° = change in standard free energy

The interpretation of ΔF° for a chemical reaction is

ΔF° = +(no spontaneous reaction)

ΔF° = 0(reaction is at equilibrium)

ΔF° = -(reaction is spontaneous)

If equation (1) is differentiated with respect to temperature at constant pressure we obtain

$$\left(\frac{\partial \Delta F^{\circ}}{\partial T}\right)_p = -RT\left(\frac{\partial \ln K}{\partial T}\right)_p - R\ln K$$

but from the Gibbs-Helmholtz equation

$$\left(\frac{\partial \Delta F^{\circ}}{\partial T}\right)_p = \frac{\Delta F^{\circ} - \Delta H^{\circ}}{T} = -RT\ln K - \Delta H^{\circ} = -R\ln K - \frac{\Delta H^{\circ}}{T}$$

Hence equating the expressions gives

$$-R\ln K - \frac{\Delta H^{\circ}}{T} = -RT\left(\frac{\partial \ln K}{\partial T}\right)_p - R\ln K \quad \text{or} \quad \left(\frac{\partial \ln K}{\partial T}\right)_p = \frac{\Delta H^{\circ}}{RT^2}$$

which in integral form is

$$\int_{K_1}^{K_2} d\ln K = \int_{T_1}^{T_2} \frac{\Delta H^{\circ}}{RT^2}\,dt = \frac{\Delta H^{\circ}}{R}\int_{T_1}^{T_2} \frac{dt}{T}$$

if ΔH° is independent of temperature thus

$$\ln K\Big]_{K_1}^{K_2} = \frac{\Delta H^{\circ}}{R}\left[-\frac{1}{T}\right]_{T_1}^{T_2}$$

$$= \frac{\Delta H^{\circ}}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\log \frac{K_2}{K_1} = \frac{\Delta H^{\circ}}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right] \qquad (2)$$

Equation (2) simply states that, if the equilibrium constant is known definitely at some temperature, in addition to knowing ΔH° as a function of temperature or if it is constant over the temperature range of interest, then the equilibrium constant at any other temperature can be determined.

B. Method I. Calculation of Equilibrium Constant From Free Energy Values

The data used for method I are listed in Table IV.1.

Table IV.1

Substance	$-\Delta F^\circ(298^\circ K)$	$-\Delta H^\circ(298^\circ K)$	Source
Gibbsite $Al(OH)_3$	274.82kcal./mole	307.7kcal./mole	Kuznetzov(1950)
Boehmite Al O(OH)	217.10kcal./mole	234.9kcal./mole	Kuznetzov(1950)
Water Vapor	54.635kcal./mole	57.798kcal./mole	Kelley (1949)
Gibbsite($Al_2O_3 3H_2O$)	547.9kcal./mole	613.7kcal./mole	Bureau of Standards (1952)
Boehmite($Al_2O_3 H_2O$)	435.0kcal./mole	471.0kcal.mole	Bureau of Standards (1952)
Gibbsite($Al_2O_3.3H_2O$)	554.60kcal./mole	-	Deltombe & Pourbaix (1956)

Using the data of Kuznetzov (1950) we can calculate the equilibrium constant at 25°C from the relation

$$\Delta F^\circ = -RT\ln K \quad \text{(at 1 atm. pressure)}$$

R = 1.987 cal./mole-deg.
T = 298° K

or converting to logarithms to the base ten

$$-\Delta F^\circ = 2.303 \cdot 1.987 \cdot 298 \log K$$

$$(\text{kcal.})-\Delta F^\circ = 1.364 \log K$$

Thus for

$$Al(OH)_3 \rightleftharpoons Al\,O(OH) + \text{water vapor}$$

$$\Delta F^\circ = \Delta F^\circ (\text{Products}) - \Delta F^\circ (\text{Reactants})$$

$$= 274.82 - 271.735$$

$$= 3.085 \text{ kcal./mole}$$

$$-\Delta F^\circ = RT \log K$$

$$= 1.364 \log K$$

$$\log K = \frac{-3.085}{1.364}$$

$$\log K = -2.26173$$

$$K = 10.00000-10$$
$$\underline{-2.26173}$$
$$7.73827-10$$

$$K(25^{\circ}C) = 0.0054735$$

$$= 5.47 \times 10^{-3} \text{ atmospheres}$$

$$= 4.16 \text{mm. Hg}$$

Next ΔH°, the standard heat of reaction, must be calculated before equation (2) can be used.

We first evaluate the heat of reaction at 25°C using Kuznetzov's data from the relation

$$\Delta H^{\circ}(25^{\circ}C) = \Delta H^{\circ}(\text{Boehmite}) + \Delta H^{\circ}(\text{water vapor}) - \Delta H^{\circ}_{(\text{Gibbsite})}$$

$$= (-234.9-57.798) + 307.7$$

$$= -292.698 + 307.7$$

$$= 15 \text{ kcal./mole}$$

We next assume that ΔH° as a function of temperature is not constant. Thus we calculate ΔH° at different temperatures. It is thus necessary to investigate this change by

$$\Delta H^{\circ} = \Delta H^{\circ}(\text{Products}) - \Delta H^{\circ}(\text{Reactants})$$

$$\left(\frac{\partial \Delta H^{\circ}}{\partial T}\right)_p = \left(\frac{\partial \Delta H^{\circ}\ \text{products}}{\partial T}\right)_p - \left(\frac{\partial \Delta H^{\circ}\ \text{Reactants}}{\partial T}\right)_p$$

The two terms on the right-hand side of the equation are simply the heat capacity terms C_p (products) and C_p (reactants). Hence

$$\left(\frac{\partial \Delta H^{\circ}}{\partial T}\right)_p = C_p(\text{PRODUCTS}) - C_p(\text{REACTANTS}) = \Delta C_p \quad (3)$$

Equation (3) is that of Kirchoff and upon integration

$$\Delta H^{\circ} = \int \Delta C_p dt + \Delta H^{\circ}_o \quad (4)$$

where ΔH_o^o is the integration constant. Equation (4) states that ΔH^o can be determined as a function of temperature if ΔH^o is known at some temperature and the heat capacities known as functions of temperature. The heat capacity, C_p, can be expressed as a power series in T of the type

$$C_p = a_0 + a_1 \times 10^{-3}T + a_2 \times 10^{5}T^{-2}$$

where a_0, a_1, and a_2 are empirical constants. Thus

$$\Delta C_p = C_p \text{ (boehmite)} + C_p \text{ (water vapor)} - C_p \text{(gibbsite)}$$

The constants listed below are for the reaction $Al(OH)_3 = Al\,O(OH) +$ water vapor. The values of the constants were obtained from Kelley (1949) and are listed in Table IV.2.

Table IV.2

Substance	a_0	a_1	a_2	Temp. Range
Gibbsite	8.65	45.6	—	298-425°K
Boehmite	14.43	4.2	—	298-500°K
Water Vapor	7.17	2.56	0.08	

Thus ΔC_p for the reaction is

a_0	+	a_1	+	a_2
21.60		6.76		0.08
-8.65		-45.60		
12.95		-38.84	+	0.08

or

$$\Delta C_p = 12.95 - 38.84 \times 10^{-3}T + 0.08 \times 10^{5}T^{-2}$$

from which

$$\Delta H^o = \int 12.95 - 38.84 \times 10^{-3}T + 0.08 \times 10^{5}T^{-2}dt + \Delta H_o^o$$

which upon integration yields

$$\Delta H^{\circ} = 12.95T - 19.42 \times 10^{-3}T^2 - \frac{0.08 \times 10^5}{T} + \Delta H^{\circ}_{o}$$

Since we know ΔH° at 298°K, we find that

$$15{,}000 = 12.95\ (298) - 19.42 \times 10^{-3}(298)^2 - \frac{0.08 \times 10^5}{298} + \Delta H^{\circ}_{o}$$

or $\Delta H^{\circ}_{o} = 12{,}893$

The final expression for determining ΔH° as a function of temperature becomes

$$\Delta H^{\circ}_{(T)} = 12.95T - 1942 \times 10^{-3}T^2 - \frac{0.08 \times 10^5}{T} + 12{,}893 \qquad (5)$$

which is equation (5). Equation (5) can now be used to calculate ΔH° at any temperature providing the heat capacity data are valid up to that temperature. Using equation (5), ΔH° has been calculated up to 180°C with the results shown in Table IV.3. It should be pointed out, however, that the heat capacity data for gibbsite are not accurate beyond 150°C, but the calculations were still made

Table IV.3

ΔH° (cal./mole)	T°C
15014	35
15025	50
15027	65
15025	75
15000	100
14995	103
14992	105
14963	120
14909	140
14878	150
14841	160
14779	175
14755	180

This certainly indicates that some error would be involved if ΔH° were assumed to be constant. It is also interesting to note that ΔH° drops off rapidly beyond 150°C, the upper limit for heat capacity data of gibbsite. However, it is important to remember that

the enthalpy values are only significant to three figures.

Equation (2) can now be used to calculate the equilibrium constant at various temperatures. As an example we will calculate K at 35°C.

$$\log \frac{K(35°C)}{K(25°C)} = \frac{\Delta H°}{4.57} \times \frac{308-298}{308 \times 298}$$

$$= \frac{15014}{4.57} \quad \frac{10}{91784}$$

$$= 3285 \times 0.000109$$

$$= 0.35807$$

$$\frac{K(35°C)}{K(25°C)} = 2.281$$

$$K(35°C) = 2.281 \times 5.47 \times 10^{-3}$$

$$= 12.5 \times 10^{-3}$$

$$K(35°C) = 0.0125 \text{ atm.} = 9.50 \text{mm. Hg}$$

Likewise, using Kuznetzov's $\Delta F°$ and calculating $\Delta H°$ in terms of heat capacity, the equilibrium constants were calculated up to 105°C. The results are given in Table IV.4.

Table IV.4

T°C	K(mm. Hg)
25	4.16
35	9.50
50	29.54
75	158.61
100	677.16
103	798.76
105	886.00

The equilibrium constant was also calculated for the reaction

$$Al_2O_3 \cdot 3H_2O = Al_2O_3 \cdot H_2O + 2H_2O_{(v)}$$

Using the free energy value of Deltombe and Pourbaix (1956) and assuming $\Delta H°$ constant and determing $\Delta H°$ as function of temperature using Kuznetzov's (1950) $\Delta H°$ values. The equilibrium constant at 25°C was $2.64 \times 10^{-8}(atm)^2$ since $K = (P_{H_2O})^2$ and $(K)^{\frac{1}{2}} = 1.6 \times 10^{-4}$ atm.

= 0.12mm. Hg. The results are listed in Table IV.5.

Table IV.5

$T^{\circ}C$	(ΔH°const.) Kmm. Hg	$\Delta H^{\circ} = f(T)$ Kmm. Hg
25	0.12	0.12
35	0.28	0.28
50	0.84	0.84
75	4.63	4.71
100	19.76	19.76
120	56.24	56.24
140	136.80	136.80
150	220.40	205.20
160	336.68	310.08
175	598.12	524.40
180	722.00	628.52

Examination of Table IV.5 indicates that discrepancies appear between the two values after 150°C. It is difficult to draw any conclusions here because the heat capacity data for gibbsite is not necessarily valid beyond this temperature. Thus, the differences may not be real, but may be caused by extrapolating the data (heat capacity) beyond its measurement.

The values of free energy and ΔH° taken from the National Bureau of Standards (1952) and also given in Latimer (1953) were used to calculate the equilibrium constant for the reaction $Al_2O_3 \cdot 3H_2O = Al_2O_3 \cdot H_2O + 2H_2O_{(v)}$. At 25°C, $(K)^{\frac{1}{2}}$ = pressure of water, was 0.046 atmospheres or 34.96mm. Hg. The results of this calculation with ΔH° constant are given in Table IV.6.

Table IV.6

$T^{\circ}C$	K(mm. Hg)
25	34.96
35	73.72
50	205.20
60	402.80
65	528.20
70	706.80

Torkar and Worel (1957) have obtained the same results as given in Table IV.6 by using the relation

$$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} + \frac{\Delta \bar{C}_p \cdot f(t)}{R}$$

and the same thermodynamic constants.

After making these calculations, the validity of published thermodynamic data on this system is questionable. The most enlightening thing about the equilibrium constant is that a small change in the free energy value has a large effect on the vapor pressure since this is a logarithmic relationship. It is also of interest at this point to anticipate which of the values best agree with the experimental values and also to those obtained from calculating the equilibrium constant by another method.

C. Method II. Calculation of the Equilibrium Constant from Calorimetric and Spectroscopic Data

As a result of the discrepancies cited above, it appeared desirable to look into an independent method for calculating the dissociation pressure (equilibrium constant) for the reaction Gibbsite = Boehmite + water vapor. Credit for this type of calculation is due to Guggenheim and Prue (1955). These authors developed a method for the theoretical calculation of the dissociation pressure for the reaction

$$Mg(OH)_2 = MgO + H_2O_{(v)}$$

This reaction was measured experimentally by Giaque and Archibald (1937). At 190°C the dissociation pressure was determined as 20mm. Hg both experimentally and by theoretical calculation. Their method is used in its entirety to estimate the dissociation pressure for the reaction

Gibbsite = Boehmite + water vapor.

(1) Object

Estimate the dissociation pressure for Gibbsite = Boehmite + water vapor from calorimetric and spectroscopic, data and compare to experimental values and to those obtained by Method I.

(2) Data

Shomate and Cook (1946) measured the molar heat capacities of gibbsite and boehmite from 52°K to 298.16°K. The results of their measurements are listed in Table IV.7.

Table IV.7

Gibbsite ($Al_2O_3 \cdot 3H_2O$)		Boehmite ($Al_2O_3 \cdot H_2O$)	
T°K	C_p(cal./deg. mole)	T°K	C_p(cal./deg. mole)
52.8	3.213	52.7	2.179
104.7	11.54	104.5	7.865
155.3	21.39	155.4	14.62
196.0	28.97	195.8	20.00
246.2	37.19	246.2	25.99
298.16	44.49	298.16	31.37

The authors indicate that the structure of the trihydrate was that of gibbsite and that the monohydrate gave a bayerite structure instead of boehmite so that the data should be used cautiously. The monohydrate was prepared by heating the trihydrate for three days at 220°C. Enough water was added to stabilize the structure. The addition of water probably rehydrated some of the boehmite to bayerite which accounts for the observed structure. More likely their monohydrate might represent the properties of a mixture of boehmite and bayerite. This information should be kept in mind when the final result is interpreted. The same authors measured the entropies at 298.16°K (entropy units/mole) as given in Table IV.8.

Table IV.8

	Gibbsite($Al_2O_3.3H_2O$)	Boehmite($Al_2O_3.H_2O$)
0-52.00°K (extrapolated)	1.40	0.94
52.00-298.16°K (measured)	32.11	22.21
	33.51(±0.1E.U.)	23.15 ± 0.1 E.U.

The data in Table IV.7 were plotted and the differences in the heat capacities appear in Table IV.9.

Table IV.9

T°K	C(Gibbsite) $Al_2O_3.3H_2O$	-C(Boehmite) $Al_2O_3.H_2O$ cal./deg. -mole
200		9.05
250		11.20
300 (extrapolated)		12.82

The heat of dissolution for the reaction Gibbsite = Boehmite + liquid water is

$$\Delta H^\circ = (234.9 - 68.317 + 307.7 = 4.483 \text{ kcal./mole})$$

using ΔH° values of Kuznetzov for gibbsite and boehmite and ΔH° of liquid water from the Bureau of Standards. The heat of vaporization $\Delta_f H^\circ$ of water was measured by Giaque and Stout (1936)

$$\Delta_f H^\circ = 10.50 \text{ kcal./mole}$$

The vibrational wave numbers ω of water vapor are listed in Herzberg (1945) from which the characteristic vibrational temperature can be calculated by the formula

$$\Theta_v = \frac{h c \omega}{k}$$

C = velocity of light
h = planck's const.
k = Boltzmann's const.

ω/cm^{-1}	1595	3652	3756
$\Theta_v/10^3$deg.	2.30	5.20	5.40

The rotational characteristic temperature Θ_r of water is 22.2 degrees. It is defined by Guggenheim (1949) as equation 4.32.2

$$\Theta_r = \frac{h^2}{8\pi^2(I_1I_2I_3)^{1/3}k}$$

where I_1, I_2 and I_3 are the principle moments of inertia.

(3) Introduction

The calculation is begun by determining the conventional entropy of gaseous water at 298.16°K and 1 atmosphere pressure. Equation 4.63.2 in Guggenheim (1949) is used

$$S/R = 4 + 3/2 \ln \frac{T}{4.331\,deg.} + 3/2 \ln M + \ln \frac{\pi^{1/2} T^{3/2}}{\Theta_r^{3/2} \sigma}$$
$$- \sum_{\Theta_v} \ln \left\{1 - \exp\left(-\frac{\Theta_v}{T}\right)\right\} + \sum_{\Theta_v} \frac{\Theta_v/T}{\exp(\Theta_v/T) - 1} - \ln P(atm.)$$

M = molecular weight

σ = symmetry number

Then, by adding the entropy values for boehmite and water vapor from which the value for gibbsite is subtracted, the value of ΔS° for the process Gibbsite = Boehmite + water vapor $\left(\begin{matrix}1\text{ atm.}\\ 298.16^\circ K\end{matrix}\right)$ is determined.

ΔH° for the same process is found by adding the molar heat of vaporization of water to the experimental value of the heat of dissociation to liquid water. Next the values of ΔS and ΔH must be corrected from T' = 298.16°K to T" which is the temperature for which the calculation is made by means of the formula

$$H(T") - H(T') = \int_{T'}^{T"} \Delta C\, dt$$

$$S(T") - S(T') = \int_{T'}^{T"} \Delta C\, d\ln T$$

where ΔC represents the increase in heat capacity for the dissociation to water vapor or

$$\Delta C = C\text{ (Boehmite)} + C\text{ (water vapor)} - C\text{ (gibbsite)}$$

C (water vapor) can be calculated at temperatures of 200°K, 250°K, and 300°K from $C/R = 4 + \sum_{\Theta_v} \left\{ \frac{\Theta_v/2T}{\sinh(\Theta_v/2T)} \right\}^2$

Thus combining this result with the measured values for gibbsite and boehmite Δ C is obtained at the three temperatures. An extrapolation must be made from 300°K to the temperature of interest to obtain Δ C. The whole correction due to Δ C is not too great so that a high degree of accuracy in extrapolation is not too critical. Then, after Δ H and Δ S are obtained at T", the dissociation pressure is obtained by

$$\ln P\,(\text{atm})_{T''} = \frac{\Delta S_{T''}}{R} - \frac{\Delta H_{T''}}{RT''}$$

$$\text{where } \Delta H_{T''} = \Delta H^\circ_{298} + \underbrace{\Delta H_{T''} - \Delta H^\circ_{298}}_{\Delta\Delta H}$$

$$\Delta S_{T''} = \Delta S^\circ_{298} + \underbrace{\Delta S_{T''} - \Delta S^\circ_{298}}_{\Delta\Delta S}$$

The above equation is derived from

$$\Delta F^\circ = \Delta H^\circ - T\Delta S^\circ = -RT \ln K$$

$$K = P \text{ (water pressure)}$$

$$-T\Delta S^\circ + \Delta H^\circ = -RT \ln (P)$$

$$\frac{-T\Delta S^\circ + \Delta H^\circ}{-RT} = \ln (P)$$

$$\ln (P) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

$$\ln (P_{H_2O})_{T''} = \frac{\Delta S^\circ_{298} + \Delta\Delta S}{R} - \frac{\Delta H^\circ_{298} - \Delta\Delta H}{RT''}$$

(4) The Calculation

The molecular weight of water is 18.02 and the symmetry no. (σ) is 2. For the entropy of gaseous water at 298.16°K and a hypothetical pressure of one atmosphere ($\ln 1 = 0$)

$$S/R = 4 + 5/2 \ln \frac{298.16}{4.331} + 3/2 \ln 18.02 + \frac{1}{2} \ln \frac{\pi (298)^3}{4(22.2)^3} - \ln \left\{ 1-\exp(- 2.30/0.298) \right\} + \frac{2.30/0.298}{\exp \frac{2.30}{0.298} - 1}$$

$$S/R = 4 + 10.58 + 4.34 + 3.78 + 0 + 0 = 22.70$$

$$S = 22.70 \times 1.987 \text{ cal./deg. mole} = 45.10 \text{ cal./ deg.-mole}$$

The contributions from the other two stretching modes are $\Theta_v \simeq 5 \times 10^3$ degrees which is very much higher than the temperature of the calculation so they add nothing to the entropy and are neglected. Thus ΔS° for Gibbsite = Boehmite + water vapor (1 atm, 298°K) is

$$\Delta S^\circ = \left[11.575 + (45.10)\right] - 16.755$$

$$= 39.92 \text{ cal./ deg.- mole}$$

The enthalpy increase of the same process is $\Delta H^\circ = (4.483 + 10.5) = 14.983$ kcal./mole. We next calculate the heat capacity (C) of gaseous water at 300°K, 250°K and 200°K.

At 300°K, $\Theta_v = 2.30 \times 10^3$ degrees

$$\frac{\Theta_v}{2T} = 3.83 \; ; \quad C/R = 4 + \left(\frac{\Theta_v/2T}{\sinh \Theta_v/2T} \right)^2 = \left(\frac{3.83}{23.0} \right)^2 = .028$$

$$C/R = 4.028 \times 1.987 = 8.00 \text{ cal./ deg.-mole}$$

The contributions from the other two stretching modes can be neglected as previously indicated

$$\frac{C(250^\circ K)}{R} = 4 + \frac{4.60}{49.7} = 4.009$$

$$C(250^\circ K) = 7.97 \text{ cal./deg.-mole}$$

$$\frac{C(200^\circ K)}{R} = 4 + \left(\frac{5.75}{157} \right)^2 = 4.001$$

$$C(200^\circ K) = 7.95 \text{ cal./ deg.- mole}$$

Thus the values of ΔC are

$200^{\circ}K$ (ΔC in cal./deg.-mole) = 7.95 -4.53 = 3.42

$250^{\circ}K$ (ΔC in cal./deg.-mole) = 7.97 -5.60 = 2.37

$300^{\circ}K$ (ΔC in cal./deg.-mole) = 8.00-6.41 = 1.59

A plot of the ΔC values against absolute temperature and the extrapolation of the curve to the temperature of the calculation for $\Delta H(T)$ follows. Likewise a plot of ΔC against the natural logarithm of absolute temperature enables $\Delta S(T)$ to be determined. Using the results a calculation of the dissociation pressure at T" can be made. The dissociation pressure is calculated for the data of Kuznetzov's (1950) ΔH° values of the entropy values of Shomate and Cook (1946). The detailed calculation at $100^{\circ}C$ ($373^{\circ}K$) is

$$\Delta H\,(373) - \Delta H\,(298) = \int_{298}^{373} \Delta C\, dt$$

$$= .95 \left[T\right]_{298}^{373}$$

$$= .95 \times 75$$

$$= 71 \text{ cal.}$$

$$\Delta S\,(373) - \Delta S(298) = \int_{298}^{373} \Delta C\, d \ln t$$

$$= .65 \ln \frac{373}{298}$$

$$= .65 \times .223$$

$$= .14 \text{ cal./deg. mole}$$

$$\ln(P_{H_2O})_{373} = 39.92 - \frac{14,983}{373} + .14 - \frac{71}{373}$$

$$= 40.06 - 40.17 - .19$$

$$= -.30$$

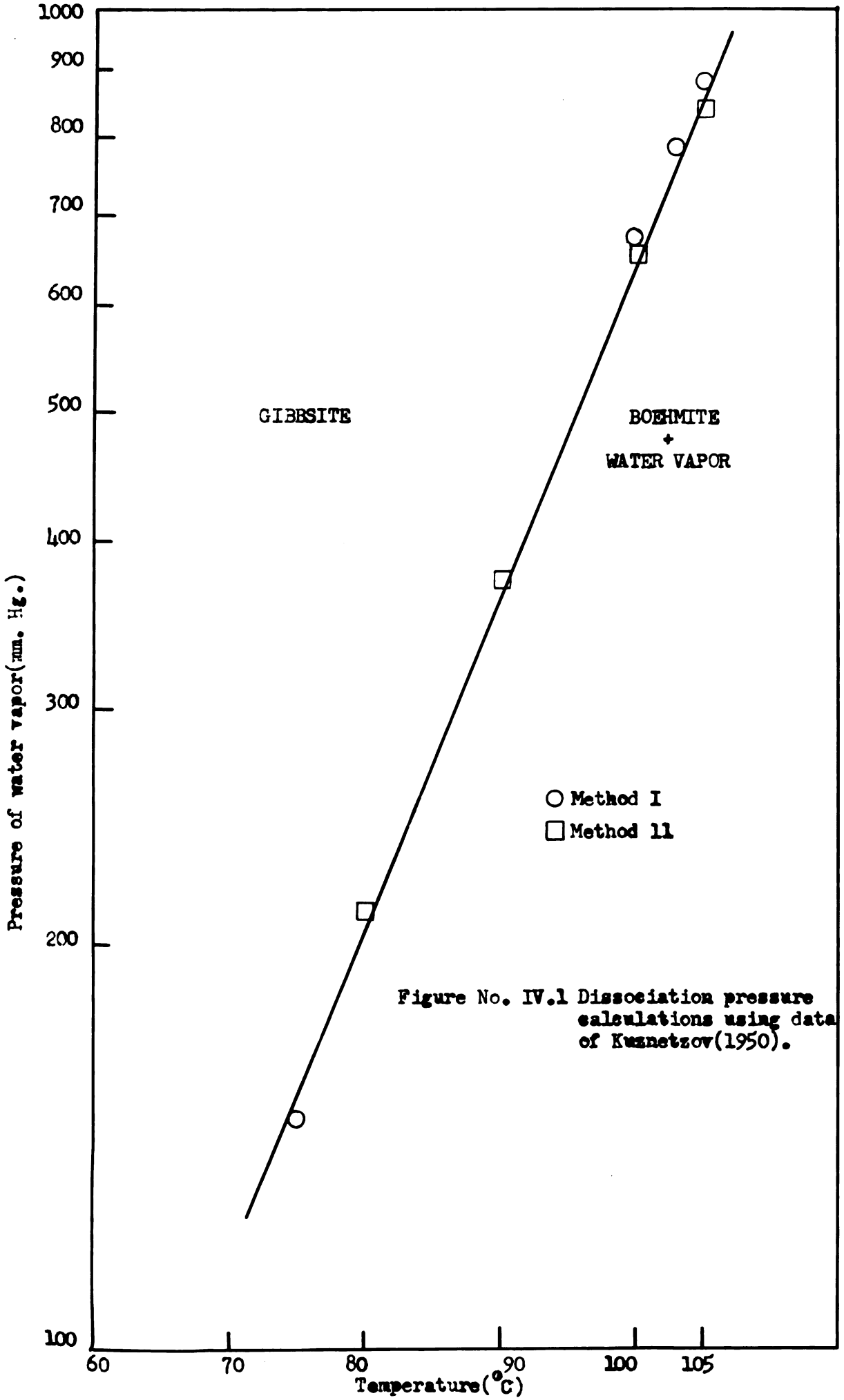


Figure No. IV.1 Dissociation pressure calculations using data of Kuznetzov(1950).

$$\ln P \text{ (atm.)} = \frac{-.30}{1.987} = -.15$$

$$P_{H_2O} = e^{-.15} = .861 \text{ atm.} = 654 \text{mm. Hg.}$$

The same method was used to calculate the pressure at other temperatures. The results are plotted in Figure IV.1 and given in Table IV.10 in which they are compared to Method I. calculations.

Table IV.10

T°C	P(mm.Hg) Method I	P(mm.Hg) Method II
25	4.16	--
35	9.50	--
50	29.54	--
75	158.61	--
80	--	211.00
90	--	378.00
100	677.16	654.00
103	798.76	--
105	886.00	845.00

The data plotted in Figure IV.1 show that there is good agreement of the calculated dissociation pressures. This fact suggests that the thermodynamic data of Kugnetzov (1950) is accurate.

The same approach was used to calculate the dissociation pressure using the Bureau of Standards (1952) values and the entropy values of Shomate and Cook (1946). Thus $\Delta H^{\circ}(298)$ for Gibbsite = Boehmite + liquid water is

$$\Delta H^{\circ} = (-235.5 - 68.317) + 306.85$$

$$= -303.82 + 306.85$$

$$= 3.03 \text{ kcal./ mole}$$

$\Delta H^{\circ}(298)$ for Gibbsite = Boehmite + water vapor is

$$\Delta H^{\circ} = 3.03 + 10.5 = 13{,}530 \text{ cal./mole}$$

The detailed calculation is made at 70°C (343°K).

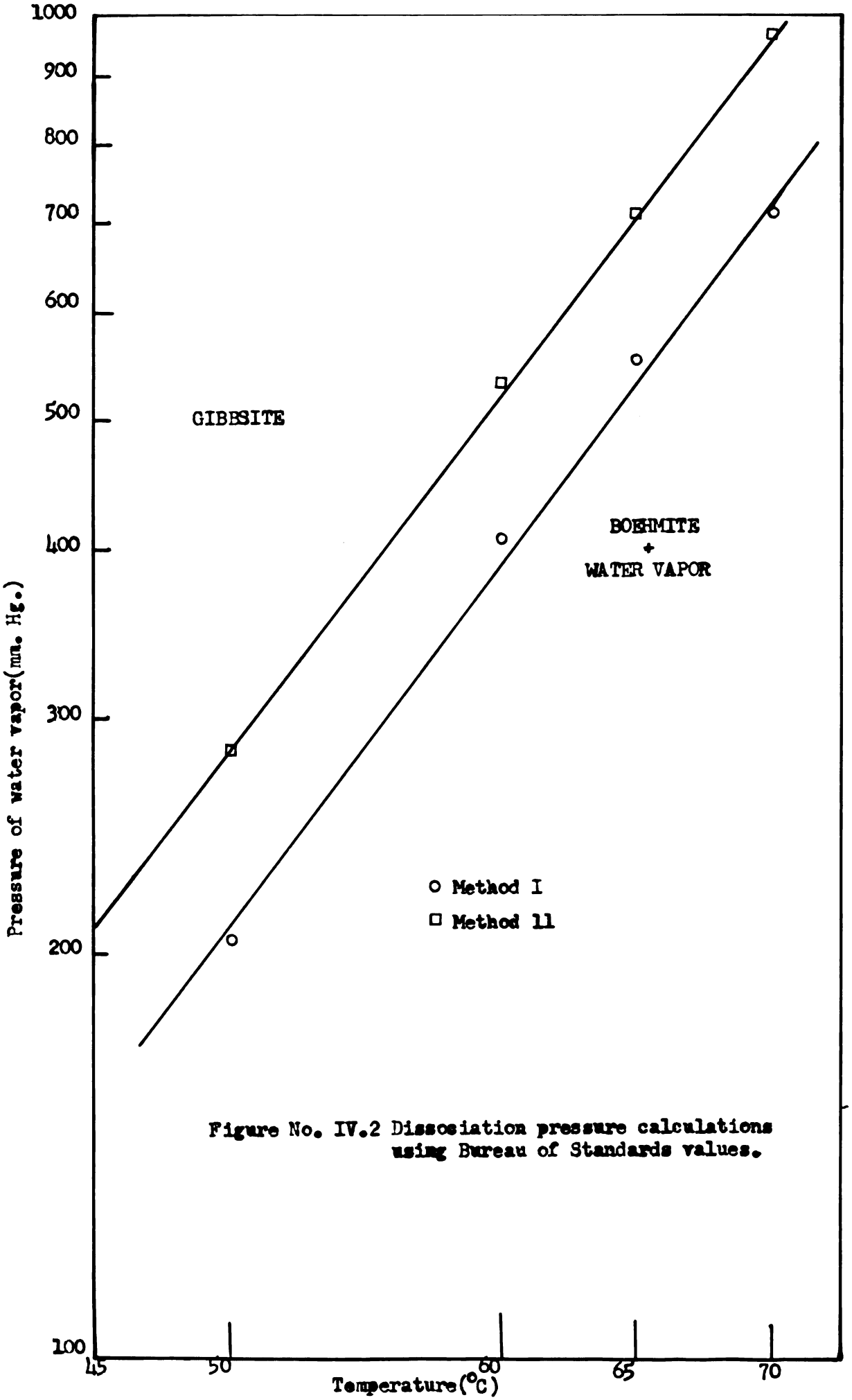


Figure No. IV.2 Dissociation pressure calculations using Bureau of Standards values.

$$\Delta H\ (343) - \Delta H(298) = \int_{298}^{343} \Delta C\ dt$$

$$= 1.18 \times \left[T\right]_{298}^{343}$$

$$= 1.18 \times 45$$

$$= 53 \text{ cal.}$$

$$\Delta S\ (343) - \Delta S\ (298) = \int_{298}^{343} \Delta C\ d \ln t$$

$$= 1.02 \times \ln 1.15$$

$$= 1.02 \times .139$$

$$= .14$$

$$\ln (P_{H_2O})_{343} = 39.92 - \frac{13.530}{343} + .14 - \frac{53}{343}$$

$$= 40.06 - 39.45 - .15$$

$$= 40.06 - 39.60$$

$$= .46$$

$$\ln P(atm)_{343} = \frac{.46}{1.987} = .232$$

$$P_{H_2O} = e^{.232} = 1.262 \text{ atm.} = 959 \text{mm. Hg}$$

The dissociation pressures were calculated at other temperatures and the results are plotted in Figure IV.2 and listed in Table IV.11 which also compares these values to Method I.

Table IV.11

$T^{\circ}C$	Pmm. Hg (Method I)	Pmm. Hg (Method II)
25	34.96	--
35	73.72	--
50	205.20	282.00
60	402.80	534.00
65	528.20	715.00
70	706.80	959.00

Examination of Figure IV.2 shows that the pressures calculated by method II are much higher than those calculated by Method I. These results suggest that the thermodynamic constants for gibbsite and boehmite listed in the Bureau of Standards (1952) are not consistent.

It appears that these type of calculations can detect inconsistencies in published data. The independent work of Kuznetzov (1950) agrees well with the experimental work of Shomate and Cook (1946). The results of the calculations for the Bureau of Standards (1952) values suggest certain inconsistencies, but the method of their calculated values may be more accurate even though this cannot be evaluated. The values that the Bureau of Standards report for Boehmite were calculated by the methods of Bichowsky and Rossini (1936). The work of Deltombe and Pourbaix appears to be deficient, but it may be that the material used accounts for such a wide variety of free energy values.

A Ball and Socket Joint
B Stopcock
C Ground Glass Joint
D8 Thermocouple
E7 Thermocouple
F11 Thermocouple and Thermistor
G10 Thermistor
H9 Thermocouple
I Calcium Fluoride Window

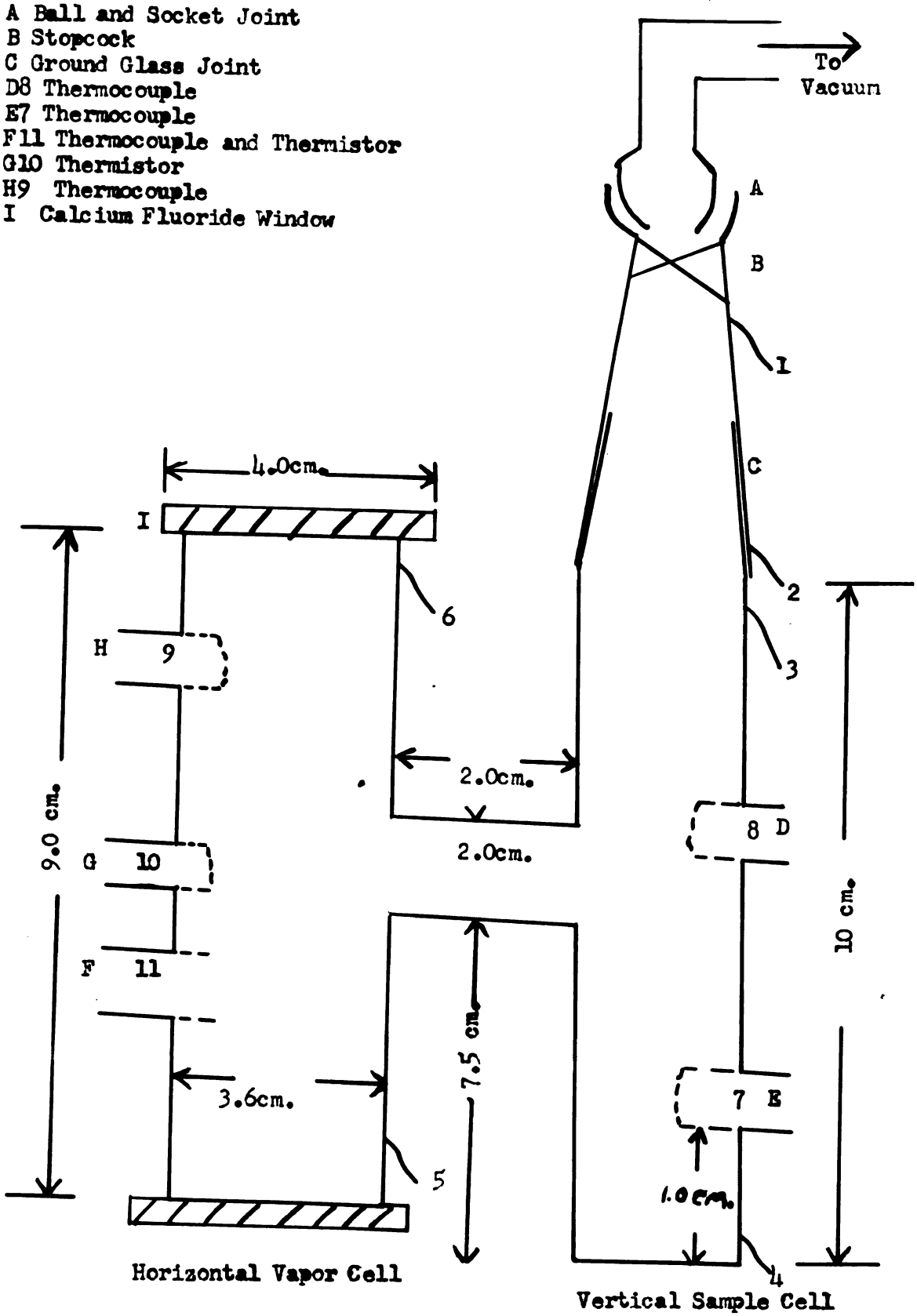


Figure No. V.1 Schematic diagram of high temperature cell for vapor pressure measurements.

V. Description and Design of Experimental Apparatus

A. High Temperature Cell

When the research was in its preliminary stages, it was originally planned to use both infra-red spectroscopy and thermistors for determining vapor pressure. Hence, a cell was designed that had a sample tube which was connected to an absorption tube by pyrex glass. Although infra-red spectroscopy was investigated in a preliminary manner only, this design was well suited for vapor pressure measurements by thermistors. A schematic diagram of this cell is shown in Figure V.1; all parts of the heated cell were constructed of high quality pyrex glass tubing. Both portions of the cell are drawn vertically for convenience, but the vapor cell is mounted perpendicular to the sample cell and attached to it by a 2 cm. diameter pyrex tube, 2 cm. in length. The apparatus could be evacuated through the ball and socket joint (A) via the stop-cock (B). The sample tube could be loaded or the cell cleaned through the ground glass joint (C).

Calcium fluoride windows* were attached to the ends of the vapor cell by clear glyptal. Each window was ground perfectly flat and polished. The windows were 4 centimeters in diameter and 0.3 centimeters in thickness. It is vitally necessary that the ends of the vapor cell have flat surfaces before the glyptal is applied. After the windows have been cemented by glyptal the apparatus is placed under an infra-red lamp for at least 20 hours. Lord, McDonald and Miller (1952) have indicated

*These windows were purchased from the Frank Cooke Corporation, North Brookfield, Mass. at a price of $26 each. The delivery date after ordering was four weeks.

Figure No. V.2. Photograph of high temperature cell.

that clear glyptal resin holds well up to 250°C providing heating and cooling are not too rapid to crack the seals. Calcium fluoride windows are extremely useful in this type of work since they are not eroded by water vapor which might be conducive to leaks and in addition their transparent character allows observation of any water vapor which may have condensed on the cell walls or windows during the preliminary calibration work.

The three different parts of the cell were heated independently; this was necessary since the sample cell was heated to temperatures beyond which thermistors would have disintegrated. The sample cell was maintained at a temperature above or below that of the vapor cell depending on the test measurement. The temperature was varied by three "Variacs" which were connected to three "Sola" constant voltage sources. The vapor cell was heated by a chromel 'A' heating wire (leads 5and 6, figure V.1) that had a total resistance of 110 ohms. The sample cell was heated by a chromel 'A' heating wire (leads 3 and 4) that had a total resistance of 150 ohms and the vacuum attachment piece (leads 1 and 2) heated by a wire with 125 ohms resistance. The wire was separated from contact with the glass tubing by small strips of asbestos paper. Radiation was kept to a minimum by placing several wrappings of asbestos paper over this wire. Power was supplied by the line voltage which was fed to the "Sola" constant voltage sources. Although the sample tube was not operated above 180°C, it could easily be used to temperatures up to 250°-300°C. A photograph of the high temperature cell is shown in Figure V.2.

Temperature was measured by copper constantin thermocouples that were calibrated in the Heat Measurements Laboratory of the MIT Mechanical

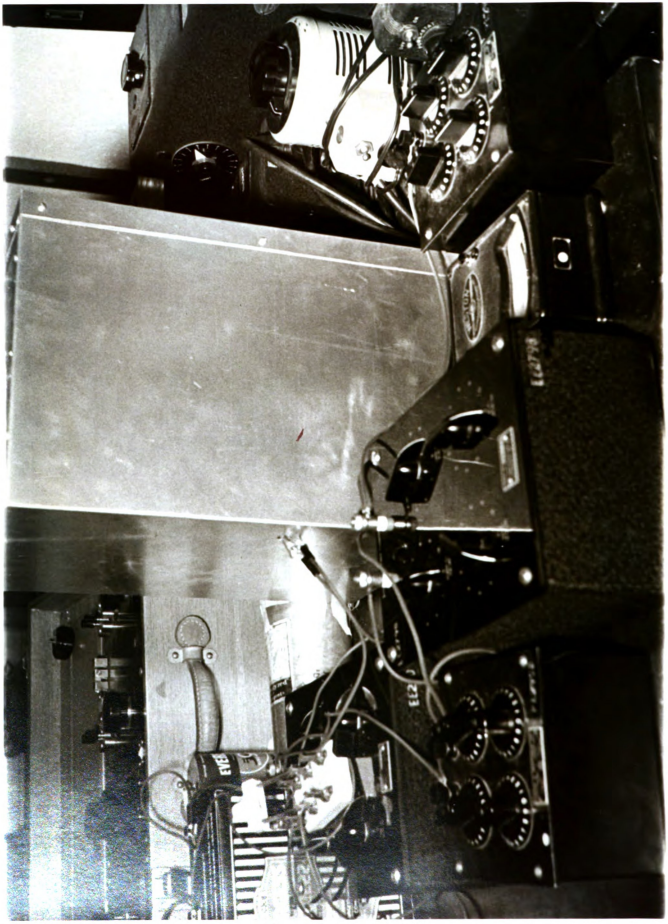


Figure No. V.3. Photograph of hood used to help control temperature.

Engineering Department. Two thermocouples were attached externally at positions 7 and 8 of Figure V.1 on the sample cell. Thermocouples were attached externally to the vapor cell at position 9 (Figure V.1) and another was sealed in hermetically by glyptal along with a thermistor at position 11 on the vapor cell (Figure V.1). The E.M.F. of the thermocouples was measured by a Leeds and Northrup Model 8662 Potentiometer. The E.M.F. (m.v.) could be read to the nearest 0.01 m.v. and estimated to the nearest 0.001 m.v. Hence the temperature could be calculated from standard tables to the nearest 0.01 degrees centigrade. This type of potentiometer had a room temperature compensating dial which could be used for the cold junction. Unfortunately, the ambient change was as great as 2°C depending on conditions, and this compensator could not be used. The cold junction was accordingly placed in a mixture of cracked ice and distilled water in equilibrium at 0°C. To calculate the temperature the potentiometer is read (E observed) and the correction term ($-\Delta E$) determined from the calibration chart. By adding $-\Delta E$ to E (observed), the standard E.M.F. is obtained. The standard E.M.F. can be used to determine the temperature by reference to standard tables. With these particular thermocouples ΔE was negative or E(Standard) = E (Observed) - ΔE. All measurements were made in a constant temperature room, the temperature of which fluctuated between 1.5 and 2.0°C. In order to reduce the change in ambient temperature to practical limits, an aluminum hood lined with glass wool as insulation was placed over the apparatus, controlling the temperature to a maximum variation of $\pm$0.6 degrees with $\pm$0.3°C being about the average. A photograph of the hood is shown in Figure V.3. The control of temperature depended on how well the airconditioner was functioning, the diurnal variation and other technical factors.

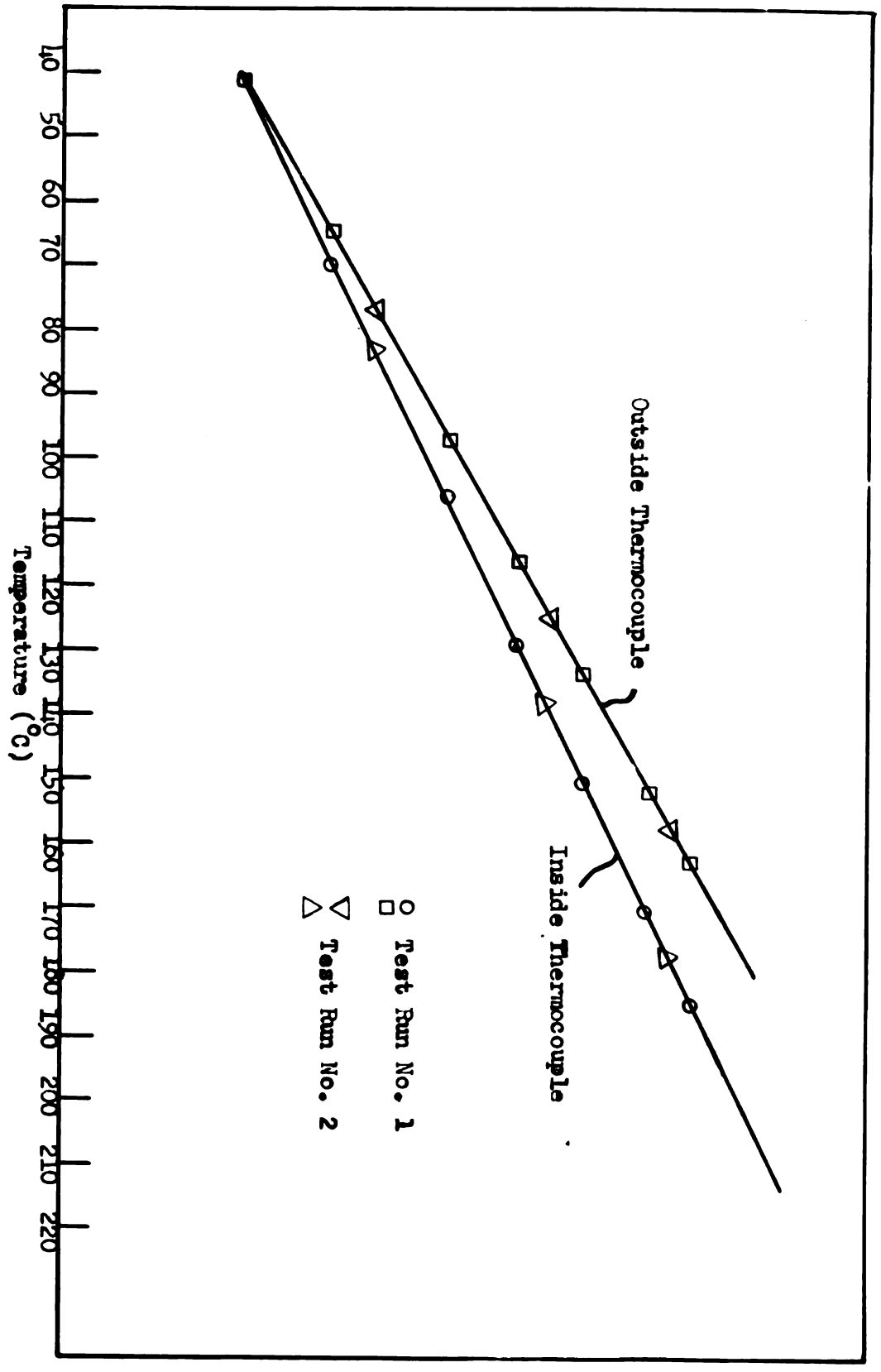


Figure No. V.4 Temperature correction chart for inside and outside thermocouples.

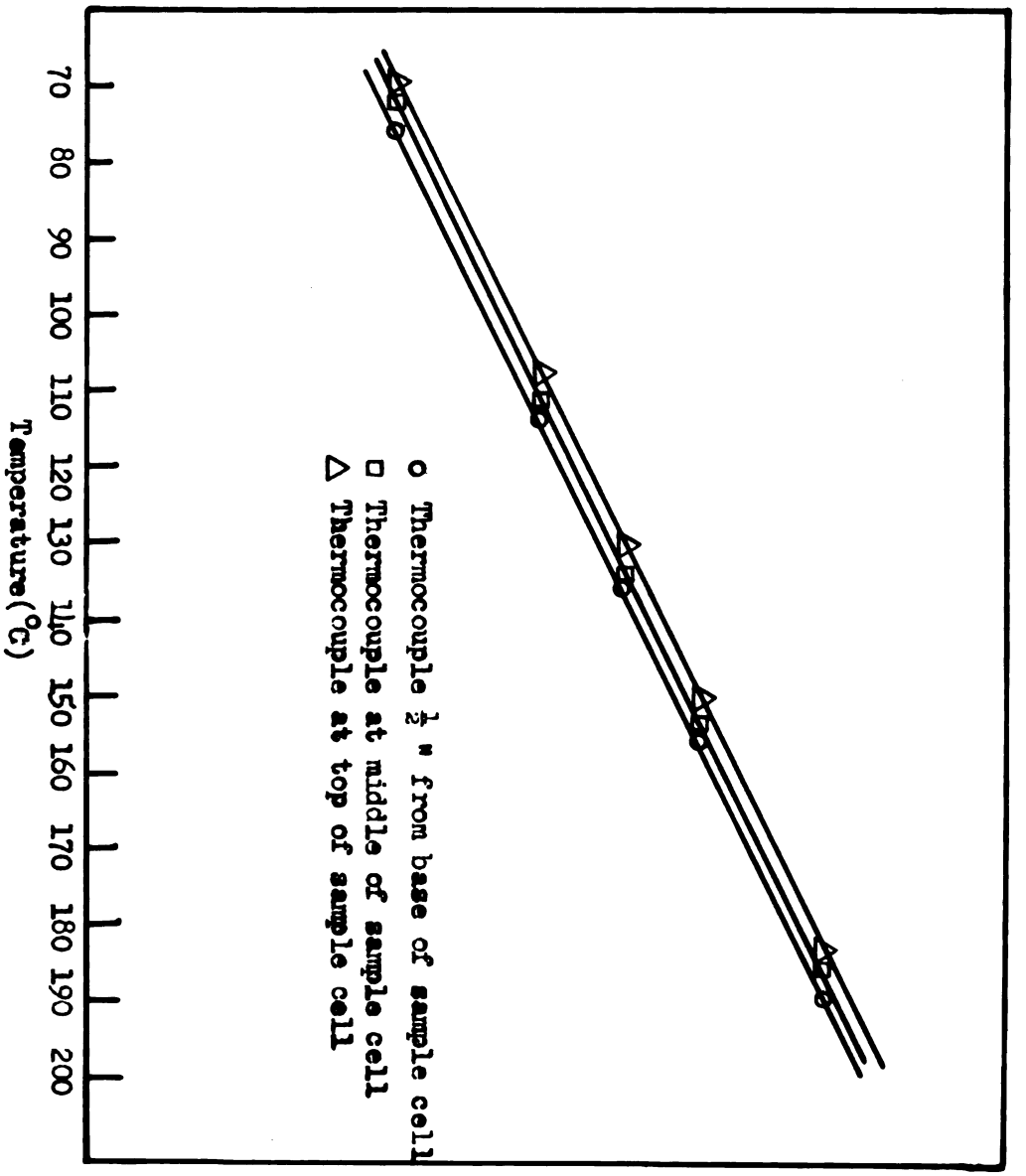


Figure No. V.5 Graph of temperature variation from top to bottom of sample cell.

After calibration work it was decided to record only the temperature of the sample cell at position 7 (figure V.1) and use the other thermocouples merely for control work. Since the thermocouple at position 7 (figure V.1) was mounted externally by a rigid packing of asbestos, it was necessary to run a calibration by inserting a thermocouple inside the cell opposite the thermocouple tap and compare the temperatures measured. The results of this calibration are given in Figure V.4. It is obvious that corrections are necessary between temperatures determined on the inside sample by an external thermocouple, partly due to the weak heat conductivity through the thick glass which houses the external thermocouple. Another calibration was made to determine what thermal gradients might exist within the sample cell. This test consisted of inserting a thermocouple inside the sample cell at three positions, $\frac{1}{2}$" from the bottom, at the midpoint and at the top. The results shown in Figure V.5 indicate that there is a general increase in temperature from the bottom to the top of the sample cell. This fact is reasonable since there is an additional source of heat at the top of the cell from the heated vacuum attachment piece over the sample cell. No correction is necessary for the gradient, since all samples were within $\frac{1}{2}$" of the thermocouple at position 7 (figure V.1).

B. Thermistor Characteristics

Thermistors can be defined as delicate electronic devices that have negative temperature coefficients so that their resistance decreases with an increase in temperature. Thermistors have been used as detectors in gas chromatography as indicated by Davis and Howard (1958). Musgrave (1959) has also used thermistors for gas chromato-

graphic detectors. In Musgrave's work the thermistors were sealed in the test unit by "cold-curing" silicone rubber. Pairs of thermistors with 1000,2000 and 500,000 ohms resistance respectively, had comparatively little tendency to disintegrate when used for the detection and separation of quinones, phenols and phenolic ethers at 180°-220°. Miller (1958) has shown that thermistors can be used in "Thermistor Bridges" as very sensitive temperature detectors. Miller (1957) has published some data on considerations in testing thermistors. Some of the important points listed are the negative temperature coefficient, the approach to equilibrium resistance with respect to time, and the power that thermistors can dissipate. These three points were investigated during the process of thesis research.

The thermistors used in this work were purchased from Victory Engineering Corporation, Union, New Jersey. A matched pair of Catalog No. A-59 thermistors with a resistance of 100,000 ohms each at 25°C was used. At 25°C, the R_o(resistance at room temperature) of the lower resistance unit is greater than 90% of the R_o of the other unit in terms of tolerance. The dissipation constant is 1.0 milliwatt/deg. C. The time constant is 25 seconds and the temperature coefficient-4.6% deg. C. All values quoted at 25°C. Miller (1957) lists the thermistor equation as

$$R_1 = R_2 e^{\beta\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

where R_1 = thermistor resistance at temperature T_1

R_2 = thermistor resistance at temperature T_2

e = Napierian base 2.713

β = Material constant (°K)

T_1 = Reference temperature (°K) of thermistor

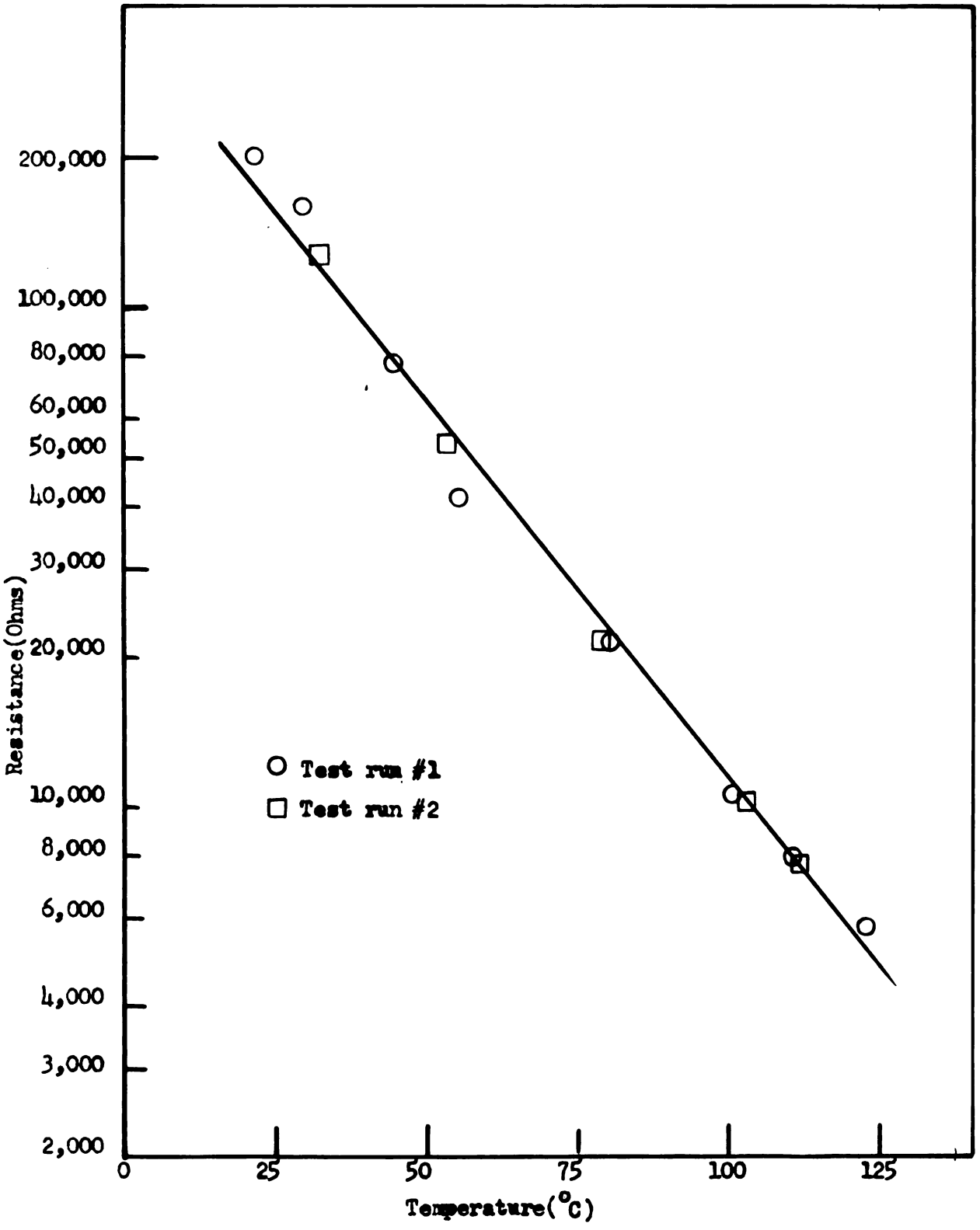


Figure No. V.6 Variation of resistance of thermistors as a function of temperature using a 1.5 volt battery.

T_2 = Another thermistor temperature (^oK)

In this work the two thermistors were connected in series, one inside the vapor cell under vacuum and the other outside the vapor cell. The resistance of this series pair was measured by a Leeds and Northrup Wheatstone Bridge. No. 4760 with 1.5 volts put into the circuit. The temperature (^oC) at the thermistor bead was measured and plotted against the resistance in ohms. The data are plotted in Figure V.6. This plot shows a reasonable linear logarithmic change in resistance with temperature or

$$\log R(T) = A - BT$$

where $\log R(T)$ = resistance at temperature T

A = intercept on ordinate

$-B$ = negative slope

The approach to a steady state equilibrium for the thermistors was obtained by measuring the resistance over a time period for three different resistances. The results of this test are given in Figure V.7. At 8850 ohms steady state is approached within one minute, but an ambient variation of $\pm$ 15 ohms is present. At 10,180 ohms the airconditioner cut on and reduced the resistance 50 ohms; after the air conditioner shut off the resistance increased back to about 10,190 ohms so the ambient variation is 50 ohms. At 18,500 ohms, the airconditioner was on for the entire 10 minutes. A steady state was obtained in about 7 minutes. Accordingly, using this information the current was turned on for each run an appropriate amount of time depending on the resistance before making a measurement.

The other important point considered in testing these thermistors was the amount of power that could be dissipated at the lowest possible

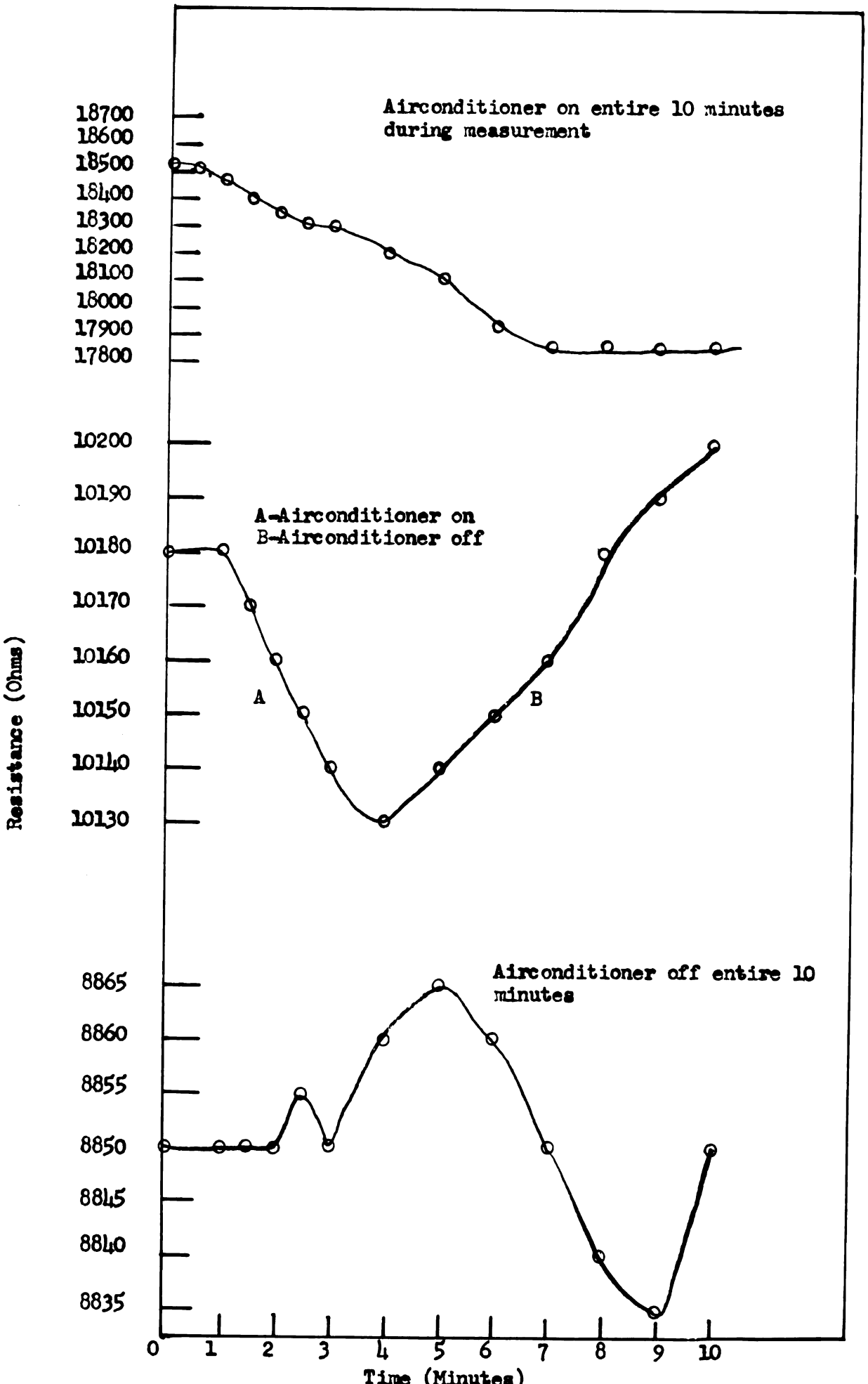


Figure No. V.7 Approach to steady state equilibrium for thermistors.

resistance. By mounting the thermistors in series, a safety factor of two was gained in power dissipated. The maximum temperature for the vapor cell was 125°C. The dissipation constant was 1.0 milliwatts/deg.C which for two thermistors is 2.0 milliwatts/deg.C. Since the temperature at the thermistor junction ranged from 25°-125°C, Δ T was 100°C. The total power that this series combination could dissipate is 2.0 milliwatts/deg.C x 100°C = 200 milliwatts.

Power = $\frac{(\text{Voltage})^2}{\text{Resistance}}$ = 200 m.w. = 0.2 watts. The battery finally selected was 22.5 volts and the lowest resistance encountered was 8000 ohms. Hence

$$0.2 = \frac{(22.5)^2}{8000} = \frac{506.25}{8000} = 0.063 \text{ watts}$$

Thus a 22.5 volt battery would only create 0.063 watts through the thermistors and a safe operation was permitted. However, if a 45 volt battery had been used 0.25 watts would have been created and the thermistors probably would have burned out. The importance of these tests on thermistors is thus demonstrated.

In mounting the thermistors in series, opposite ends of the thermistor leads were joined together with silver solder. One thermistor was maintained at a much lower temperature than the other by being mounted externally at position 10 on the vapor cell (figure V.1) After positioning the cold thermistor, asbestos was forced around it to make it firm and the end of the lip was sealed off with clear glyptal. The other thermistor was hermetically sealed inside the vapor cell with a thermocouple at position 11 (figure V.1) by placing a thick film of glyptal around it. The apparatus was then heated slowly to 50°C in a vacuum oven. After doing this several times the seal was firm and non-porous. A thick film of glyptal was next placed at the back of the

inside film and heated to 50°C. Asbestos was used to give firmness to the seal and more glyptal was applied at the end of slit 11 for protection.

C. The Wheatstone Bridge Circuit

The principle involved in measuring the vapor pressure in terms of resistance drop of the thermistors necessitated the design of a "Wheatstone bridge" circuit. The simple principle for vapor pressure detection was that a calibration curve would be run in vacuum without water vapor at fixed temperatures on the vapor cell and varying temperatures on the sample cell. Then the resistance of the thermistors would be plotted as a function of temperature of sample tube. This would be repeated with a liquid of known vapor pressure, such as water in the sample tube. The change in resistance called Δ R resulting from the water vapor is a measure of the vapor pressure at the temperature on the sample tube.

This uses the thermal conductivity properties of gases (water vapor). Thermal conductivity is a measure of quantity of heat conducted in unit time between two unit surfaces in the gas when they are unit distance apart and the temperature difference is 1°C; this condition pertains to single gases, binary mixtures and ternary mixtures. In the determination, a fine wire, which is heated by a current, is surrounded by a gas that conducts heat from the wire to the walls of the chamber. A thermocouple in contact with the hot wire measures its temperature above that of the wall of the chamber, which difference is inversely proportional to the thermal conductivity of the gas for a given power imput to the wire. In practice, two similar current-heated filaments in two similar cells with two similar inert resistances are used, the

four elements being connected to form a wheatstone bridge. If one cell contains air and the other cell contains a gas of different thermal conductivity, the two hot wires will not have the same resistance and the bridge will become unbalanced to an extent depending on the thermal conductivity of the gas relative to the standard or reference gas (Minter 1946).

Minter and Burdy (1951) have evaluated the effect of cell diameter by a so-called two bridge circuit. In their work a two bridge circuit was employed. Bridge 1, in which cells have a diameter of 3/16" is conventional, whereas bridge 2 is of unconventional design, having cells with a diameter of 3/4". All the filaments used in the bridges (1 and 2) are as nearly as possible alike, but the difference in cell diameter has an appreciable effect on the heat loss from the filament when both types of cells contain air, so that when both bridges carry the same current, bridge 2 with large cells will have the higher resistance. The difference between the rate of loss of heat in the large cell and that in the small cell becomes greater as the thermal conductivity of the gas decreases. This gaseous "convection" increases with the molecular weight of the gas and cell diameter. From the foregoing, it would appear appropriate to use a cell with a large diameter for gases like water vapor with a medium thermal conductivity value.

Minter (1947) has suggested that heat loss by natural convection is a function of gas pressure and that the magnitude of effects of pressure on convection depends uniquely on the nature of the gas. An equation proposed without experimental support indicates that the loss of heat by natural convection can be expressed by

$$H \propto X P^{n}$$

where H =heat loss

P = absolute pressure

X = convection factor depending on the gas

The effect of pressure on convection is so negligibly small for hydrogen that there can be no heat transfer by convection and X in the above equation would then be zero. For all other gases X has a positive value which in general increases with the molecular weight of the gas. The relationship between convection and other physical properties of gases has not been investigated. A tentative approximate relationship between conductivity and convection in a gas might be written as

$$X \propto \ln \frac{K_{H_2}}{K_X}$$

where K_{H_2} = absolute conductivity of hydrogen

K_X = absolute conductivity of gas

The relative deflections of various gases is given by Gow-Mac with their commercial unit; their values are listed below in Table V.1.

Table V.1

Gas	Relative Deflection per 1% Gas in Air	Approx. Bridge Output in MV without Load
Acetone	-0.180	-5.39
Argon	-0.133	-3.99
Benzene	-0.190	-5.70
Carbon Dioxide	-0.143	-4.30
Carbon Monoxide	-0.014	-0.42
Ethyl Alcohol	-0.080	-2.40
Ethyl ether	-0.136	-3.90
Helium	+0.640	+19.18
Hydrogen	+1.000	+30.00
Methyl alcohol	-0.079	-2.36
Nitrogen	-0.001	-0.03
Oxygen	+0.006	+0.18
Water Vapor	+0.068	+2.04

It is shown that many important gases, chemically and geochemically speaking, can be determined by thermal conductivity.

By consideration of many of the points listed above, it seemed reasonable to set up a bridge circuit and evaluate the effects of water vapor in conducting heat away from a thermistor, consequently lowering the temperature and increasing the resistance. It is also possible that the change in resistance of the thermistors can be attributed to a competitive heat effect. The amount of heat reaching the thermistor (detector) is proportional to that not absorbed by the water vapor. It is obvious in this type of approach that two measurements must be made to detect an absolute difference in vapor pressure. This condition is disadvantageous as compared to conventional thermal conductivity methods, but the apparatus is much less cumbersome. The real advantage of measuring vapor pressure by thermistors is that the absolute pressure can be detected whereas in the normal thermal conductivity method only relative changes in per cent of gases can be obtained by comparison with those of the reference gas.

In the preliminary design of the Wheatstone bridge, first 1.5 volts were used as the EMF source and then 6.0 volts. Both of these sources were insufficient to heat the thermistors hot enough to enable the pressure of water to conduct heat away. Hence, no pressure effect was noted on the resistance measured in vacuum or under pressure of water vapor. The next step was the use of a 22.5 volt source of E.M.F. This change in source permitted the determination of the effect of pressure on resistance change and was used throughout the course of the investigation. A schematic diagram of the wheatstone bridge (D.C.) circuit is shown in Figure V.8. A photograph of the laboratory apparatus which includes the D.C. bridge circuit and high temperature cell is shown in Figure V.9.

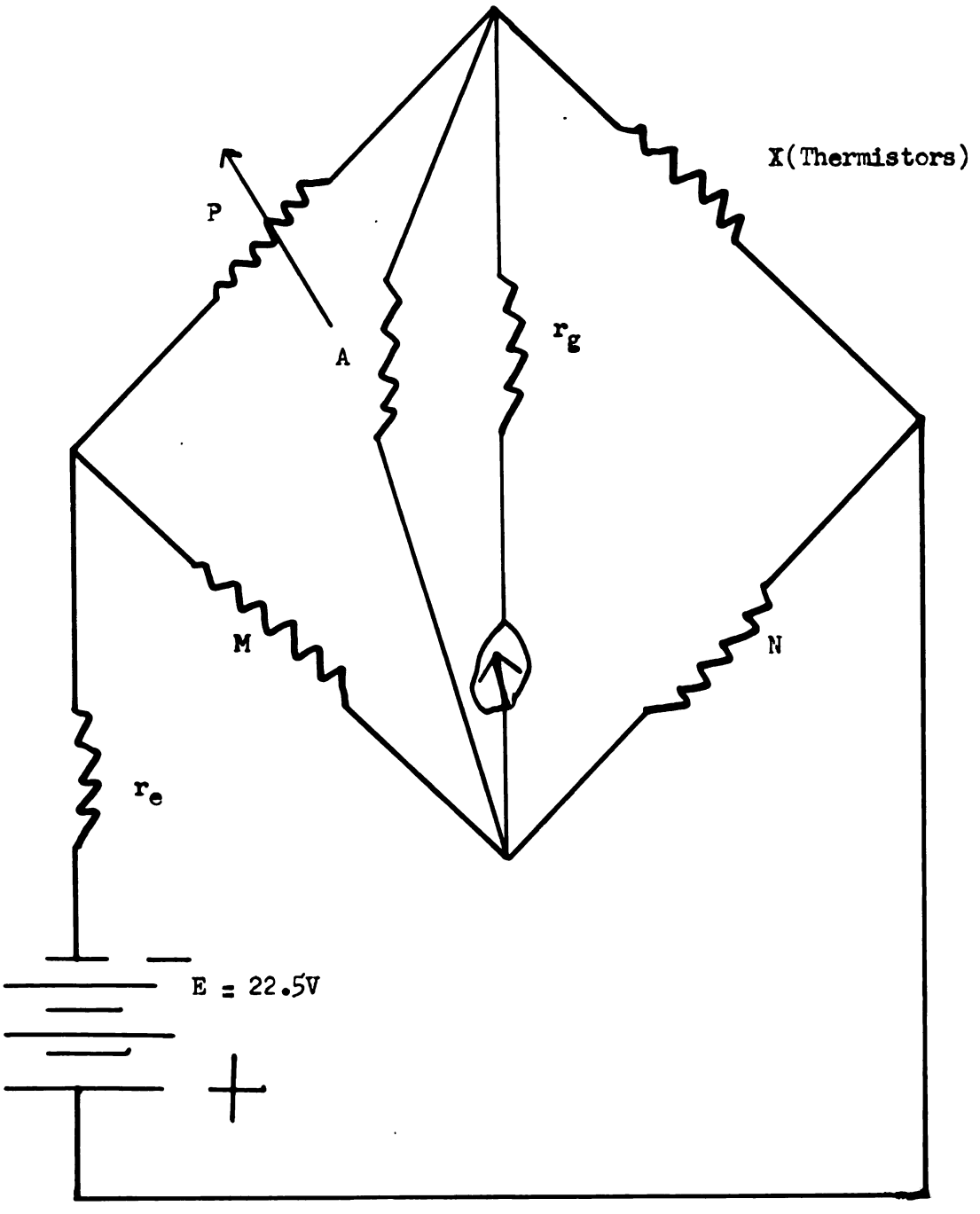


Figure No. V.8 Schematic diagram of (D.C.) wheatstone bridge circuit.

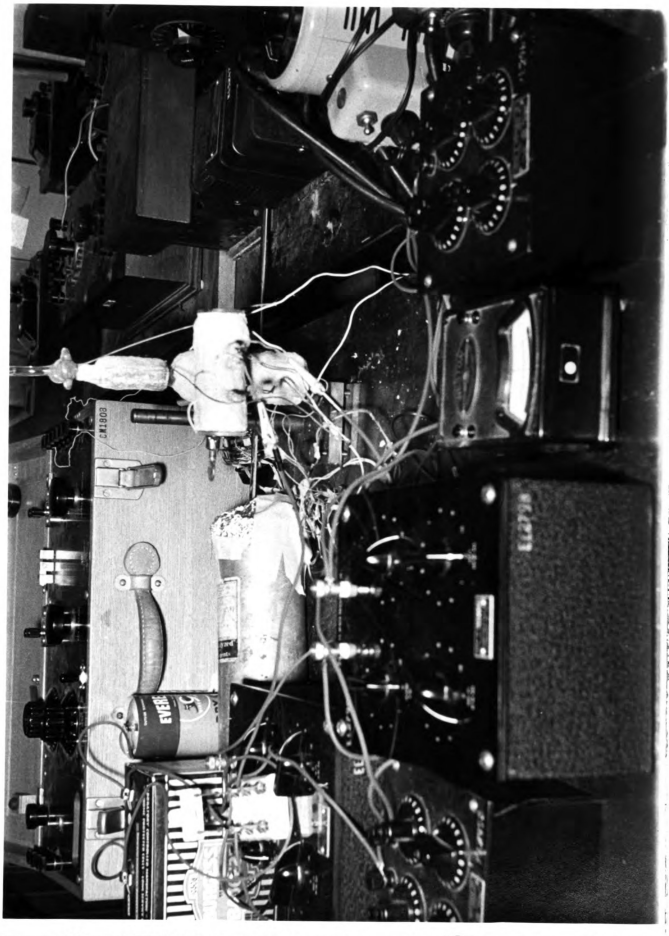


Figure No. V.9 Photograph of laboratory apparatus.

In Figure V.8, the letters have the following significance

P = 100 K resistance box (variable resistor)

M = 100 K resistance box = 9990 ohms

N = 10 K resistance box = 9990 ohms

X = Thermistor resistance

r_e = internal battery resistance

r_g = galvanometer resistance = 51 ohms

E = source of E.M.F. = 22.5 volts

A = shunt resistance = 9000 ohms

The condition of balance for this bridge, that is, when no current goes through the galvanometer or there is zero deflection, is given by the voltage splitting rule as

$$\frac{N}{N+M}(E) = \frac{X}{X+P}(E)$$

$$NX + NP = NX + MX$$

$$MP = MX \text{ (at balance)}$$

Hence, by reading the three resistances N, P, and M, the unknown thermistor resistance (X) can be determined by

$$\frac{NP}{M} = X \text{ (ohms)}$$

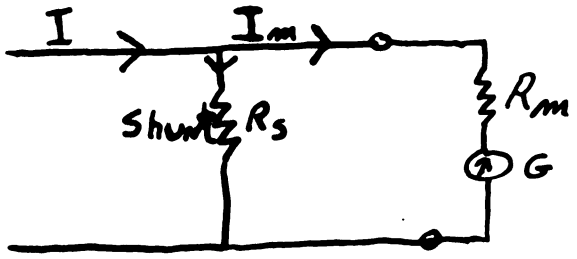
Two important points about balanced wheatstone bridges are

(1) The balance condition is independent of the battery source and

(2) The galvanometer and battery can be interchanged without affecting balance.

After taking some preliminary readings, it was found that the galvanometer was too sensitive. Hence, it was necessary to desensitize or protect the galvanometer from the high incoming current by a shunt resistance (A). There are several methods of protecting galvanometers,

but the one selected was that of a "simple" shunt as suggested in Frank (1959). The galvanometer used was a Weston Model 440 that had an internal resistance of 51 ohms and required an external resistance of 190 ohms for critical damping. Thus the shunt designed served a two-fold purpose of desensitizing the galvanometer in addition to providing the critical external damping resistance of 190 ohms. The "simple" shunt consists of a resistance across the terminals of the galvanometer. In diagrammatical form it has the appearance



I = incoming current

R_s = shunt resistance

G = galvanometer

R_m = galv. resistance

I_m = galv. current

The decrease in current, I_m, delivered to the galvanometer can be determined from the current splitting rule:

$$I_m = \frac{R_s \times R_m}{R_s + R_m} \quad I = FI$$

where F is the current desensitizing factor

Experimentally it was found that 9000 ohms was convenient to use as the shunt resistance.

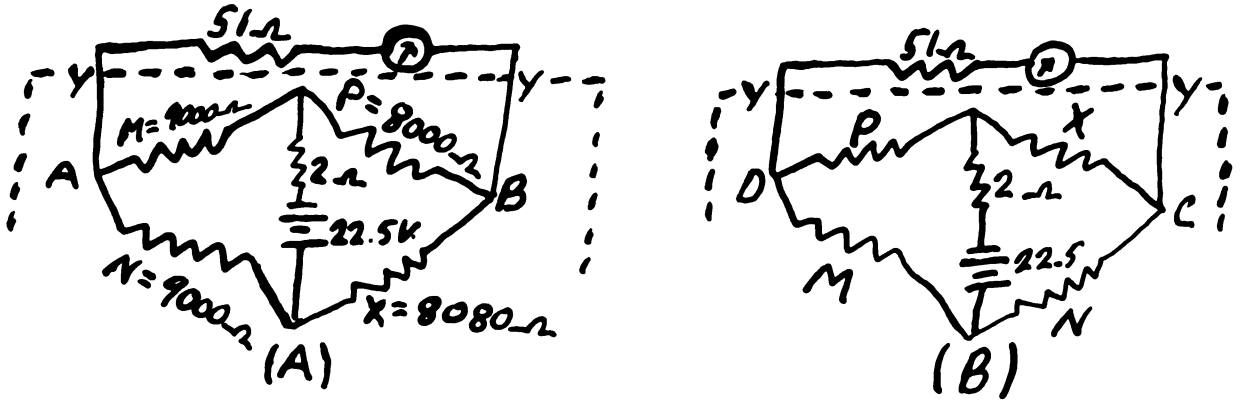
Comparing the F factors by using $R_s = 1$ and $R_s = 9000$ ohms:

$$I_m = \frac{1 \times 51}{1 + 51} I = 51/52 I = 0.98 I \quad (R_s = 1)$$

$$I_m = \frac{9000 \times 51}{9000 + 51} I = \frac{459000}{9051} I = 50.71 I \quad (R_s = 9000)$$

Thus the 9000 ohm shunt protects the galvanometer $\frac{50.71}{.98} = 51.74$ times greater than a one ohm resistor would.

Another important feature was bridge sensitivity which can be demonstrated by using a slightly unbalanced wheatstone bridge and interchanging the resistances in the battery and galvanometer branches. The two set-ups (A and B) used were as follows:



The most sensitive bridge circuit will be the one which has the largest galvanometer current, I_g. The unbalance is made by letting X = 8080 ohms as compared to 8000 ohms for P. A constant of 2 ohms was used for comparative purposes for the internal battery resistance. In calculating I_g it is best to use Thevenin equivalent circuits instead of mesh equations. The circuit can be set up by letting everything below the Y—Y on both diagrams equal the Thevenin internal circuit. Hence the R_i (Thevenin internal resistance) can be calculated by letting the battery resistance go to infinity or

$$\text{Case (A): } R_i = \frac{(M+P)\ (N+X)}{M+P+N+X} = \frac{(9000+8000)\ (9000+8080)}{18000 + 16{,}080}$$

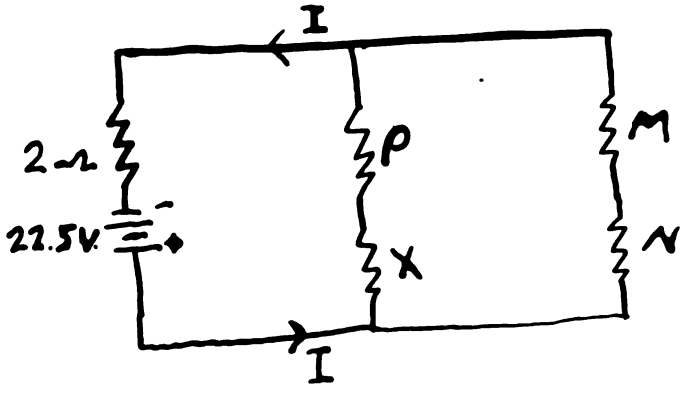
$$= \frac{290{,}360{,}000}{34{,}080} = 8520 \text{ ohms}$$

$$\text{Case (B): } R_i = \frac{(P+X)\ (M+N)}{P+X+M+N} = \frac{(8000+8080)\ (9000+9000)}{34080}$$

$$= \frac{289{,}440{,}000}{34080} = 8493 \text{ ohms}$$

Next the Thevenin open circuit voltage (E_o) is calculated.

For Case (A):



$$R_i = 8493 \text{ ohms}$$

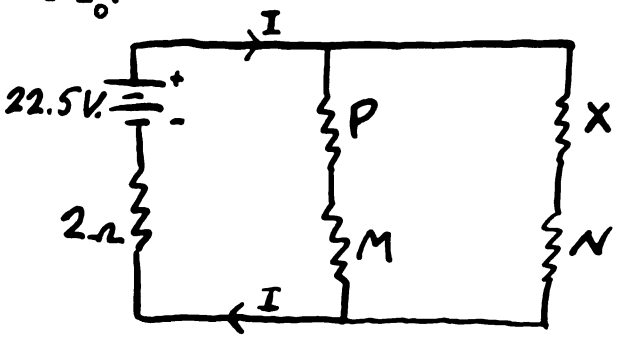
$$I = \frac{22.5}{8493 + 2} = \frac{22.5}{8495} = .0026\text{a}$$

$$V_A = \frac{22.49 \times 9000}{18000} = \frac{202{,}410}{18000} = 11.25\text{V}$$

$$V_B = \frac{22.49 \times 8080}{16080} = \frac{181719}{16080} = 11.30\text{V}$$

$$E_o(A) = V_B - V_A = 0.05\text{V}.$$

Case (B) for E_o:



$$R_i = 8520 \text{ ohms}$$

$$I = \frac{22.5}{8520+2} = \frac{22.5}{8522} = 0.0026a$$

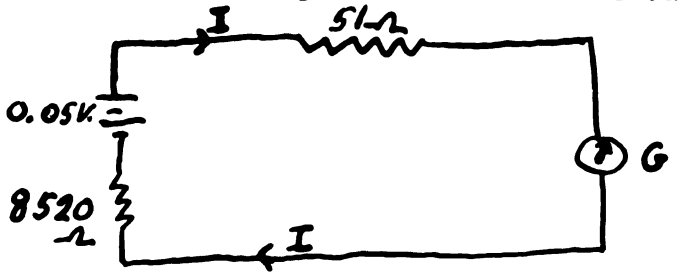
Terminal Voltage $E_T = 22.5 - 2X.0026 = 22.49V$

$$V_C = \frac{22.49 \times 9000}{17080} = \frac{202410}{17080} = 11.85V$$

$$V_D = \frac{22.49 \times 9000}{17000} = \frac{202,410}{17000} = 11.91V$$

$$E_o \text{ (B)} = V_D - V_C = 0.06V$$

Thus using the Thevenin equivalent circuit for Case A: I_g



$$I_g = \frac{.05}{8520 + 51} = 5.83 \text{ microamps}$$

Case B: I_g

$$I_g = \frac{.06}{8493 + 51} = 7.11 \text{ microamps}$$

Therefore the ratio of sensitivities for this circuit is $\frac{7.11}{5.83} = 1.23$ or set-up B is 1.2 times more sensitive than A. Thus by having the fixed resistances on the same arms of the bridge, optimum sensitivity is achieved; this consideration was applied to the bridge designed. The results of experiments with this bridge are discussed in the following section.

VI. Experimental Method and Results

A. Basis for Determining Vapor Pressure

The basis of the experimental method for measuring vapor pressure was to heat the vapor cell to a constant temperature and then vary the temperature on the sample cell. The thermistor resistance was determined, first in a vacuum, at various temperatures and the logarithm of this quantity was plotted as a function of temperature of the sample cell. Next a liquid was introduced into the sample cell and the apparatus again evacuated. The liquid, whose vapor pressure is known as a function of temperature was heated and again the resistance of the thermistor determined. The heat conducted away from the thermistor will decrease its temperature or increase its resistance. A curve of the logarithm of the resistance against temperature is drawn and the increase in the log of the resistance at a specified temperature is a measure of the vapor pressure in terms of the quantity log Δ R where

$$\log \Delta R = \log R(\text{Water vapor},T) - \log R(\text{Vacuum},T)$$

Thus by determining the log Δ R values the vapor pressure as a function of temperature can be plotted. A solid hydrate or hydroxide can be placed in the sample cell and heated under identical conditions. Again the log Δ R values are determined and compared to those of the standard in terms of a ratio method. If the vapor pressure over the dissociating hydrate is identical to that of the liquid as observed by the log Δ R values, then the liquid may be used as a calibration curve for the solid. Practically this is rarely the case, so that the ratio method must be used.

Assuming that a log Δ R value of 3.5 ohms has been determined which corresponds to a vapor pressure over the liquid of 300mm. Hg and

a value of log Δ R for the solid at the same temperature is 3.3, the vapor pressure of the solid is

$$\frac{\log \Delta R \text{ (Solid)}}{\log \Delta R \text{ (liquid)}} \times \text{Vapor Pressure(liquid)}$$

or

$$\frac{3.3}{3.5} \times 300 = 0.94 \times 300$$
$$= 282 \text{mm. Hg}$$

It can be readily seen that this approach is best when the vapor pressure of the liquid and that of the solid are not too dissimilar.

B. Dehydration of Gypsum ($CaSO_4 \cdot 2H_2O$)

Gypsum is an interesting substance to study for several reasons. The structure as determined by Wooster (1936) is of the layer lattice type. Sheets of Ca^{2+} and SO_4^{2-} ions are so arranged that each cation is surrounded by six O^{2-} ions and by two water molecules. Each water molecule is linked to one Ca^{2+} ion, to one O^{2-} ion in a neighboring sheet, and these last-mentioned bonds are the only ones holding the sheets together. The perfect cleavage arises from the rupture of these weak bonds, and this weakness is also further revealed by the much higher coefficient of thermal expansion normal to the sheets than in any other direction. Hence, this weak water bond should be easy to remove when gypsum is heated. The loosely bound structural water in gypsum is like many other hydrates of geological interest such as the hydrous borates. Gypsum is additionally interesting because its vapor pressure was measured by Kelley, Southard and Anderson (1941) using a manometer method. Thus, the accuracy of the thermistor method can be determined by direct comparison to manometer results. The measured vapor pressure of gypsum follows quite closely the vapor pressure of liquid water.

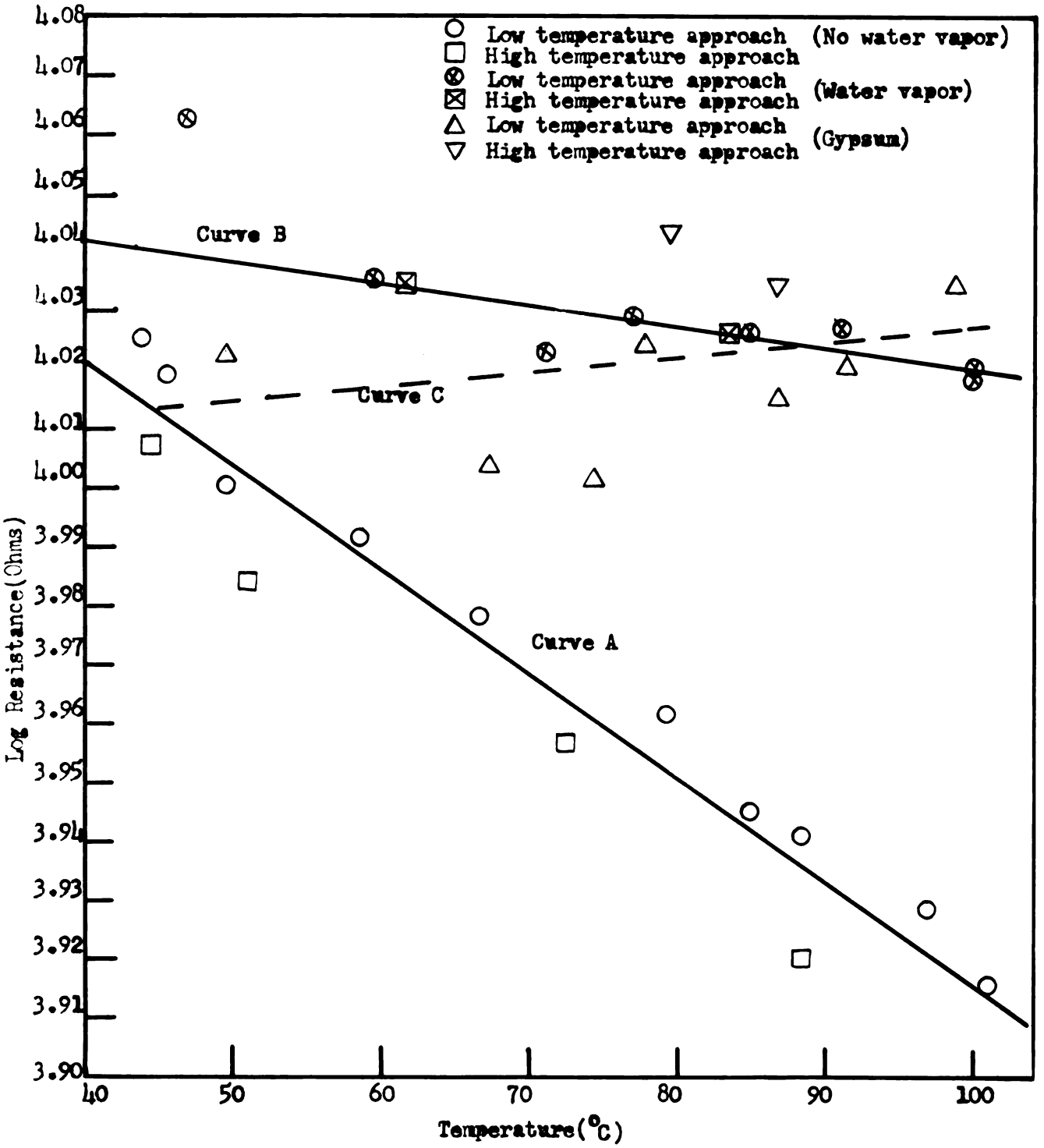


Figure No. VI.1 Experimental curves for determining vapor pressure of Gypsum by thermistors.

Therefore, liquid water can be used as a calibration tool for the ratio method previously described. After evacuating the vapor cell for one hour to $< 1 \times 10^{-1}$ mm. Hg, it was heated to a constant temperature of 94.25°C. Then the temperature of the sample cell was varied and the change in the resistance of the thermistors recorded. In general, thermal equilibrium was obtained within one hour, but additional time was allowed to check on the equilibrium value with respect to time before the sample temperature was again changed. In this particular test, the sample temperature was varied from 43.89°C to 100.60°C, and the corresponding resistances varied from 10,637 ohms to 8243 ohms. Resistance observations were approached from both a high temperature and a low temperature side, with the former being lower than the latter. This difference is most likely explained by failure to dissipate heat fast enough under the aluminum hood to enable the same values to be obtained from both the high side and low side approached. The results are tabulated below in Table VI.1 which also shows a standard deviation of the resistance and temperature of each point and plotted (curve A) in Figure VI.1. In general, a low standard deviation in temperature coincides with a low standard deviation in resistance, but there are exceptions. The method used for calculating standard deviation is from Youden (1955).

Table VI.1

Resistance (ohms)	Log Resistance	Temp. °C
10,637 ± 70	4.02680	43.89 ± 0.13
10,452 ± 108	4.01920	45.30 ± 0.02
10,020 ± 105	4.00087	51.20 ± 0.03
9822 ± 66	3.99220	58.41 ± 0.19
9537 ± 91	3.97941	68.70 ± 0.38
9166 ± 54	3.96218	77.30 ± 0.08
8825 ± 64	3.94571	84.78 ± 0.10
8741 ± 51	3.94156	88.25 ± 0.02
8509 ± 55	3.92988	94.84 ± 0.08
8243 ± 39	3.91609	100.60 ± 0.25
* 8325 ± 10.8	3.92038	88.12 ± 0.09
* 9076 ± 41	3.95789	72.42 ± 0.11
* 9646 ± 47	3.98435	50.95 ± 0.12
*10170 ± 25	4.00732	44.29 ± 0.07

*These points correspond to measurements made from the high temperature side while the others represent the low temperature side.

The next test was to determine the effect that the vapor pressure of water would have on the thermistor resistance. The total volume of the high temperature cell was 934 cubic centimeters. Hence, using the ideal gas law, it was possible to calculate the minimum amount of water necessary to fill the cell at a given temperature. From the ideal gas law PV = NRT where

P = pressure of gas in atmospheres = 760mm. Hg

V = volume of cell = 934 ml.(neglecting the volume occupied by the liquid)

$$N = \text{no. of moles of gas} = \frac{\text{wt. of gas in grams}}{\text{M.W.}}$$

where wt. of gas = wt. of water in condensed state

R = gas constant = 82.07 ml.-atm./mol°C

T = temperature in °K.

As an example the amount of liquid water necessary to fill the cell at a pressure of one atmosphere when the temperature is 100°C is

$$\frac{760}{760} \times 934 = 82.07 \times 373$$

$$X = \frac{934}{30612} = 0.031 \text{ gms.}$$

Thus, the minimum amount of liquid water required to fill the cell with one atmosphere pressure was 0.031 grams. In consideration of the evacuation of the cell, thirty milliliters of distilled water were actually used. After the distilled water was placed in the cell, the apparatus was evacuated for fifteen minutes and heated to 94.18°C. The equilibrium was permitted to develop for two hours, when the temperature on the sample was 46.80°C. Another evacuation was made and then the temperature of the sample increased. A constant reading in resistance after evacuation was considered to be the true equilibrium value and thus was approached from both the high temperature and low temperature side. One of the major difficulties encountered experimentally was that the removal of the hot cell to the vacuum line caused the windows on the vapor cell to crack and also developed leaks in the form of cracks on the glyptal seals. This problem was solved before any of these tests by forcing a gentle stream of heated nitrogen, passed through hot copper tubing, on the vapor cell and no additional leaks were observed. The ability to develop a tight vacuum and the constancy of resistance was considered evidence that no leaks were in

the system. The previous experience with a cracked cell window never permitted a tight vacuum to be developed.

The precision or reproducibility of the method was tested by taking ten consecutive readings at two minute intervals at resistances of 11,575 ohms, 10,647 ohms and 10,554 ohms where the respective vapor pressure of water was 78,546, and 760mm. Hg. The reproducibility in terms of standard deviation is given below in Table VI.2.

Table VI.2

Resistance (ohms)	Pressure(mm. Hg)
11575 ± 33	78
10647 ± 13	546
10454 ± 8	760

This data suggests that an increase in water pressure gives a better reproducible reading. During the actual conditions of the experiment, only two readings were taken at any one time. The results of the test on water vapor are listed in Table VI.3 and plotted as curve B in Figure VI.1.

Table VI.3

Resistance (ohms)	log Resistance	Temp. °C
11,580 ± 31	4.06371	46.80 ± 0.11
10,880 ± 87	4.03663	57.53 ± 0.27
10,555 ± 24	4.02345	71.05 ± 0.18
10,710 ± 10	4.02979	76.75 ± 0.16
10,638 ± 10	4.02680	84.63 ± 0.16
10,647 ± 13	4.02715	91.08 ± 0.17
10,445 ± 23	4.01892	99.91 ± 0.22
10,454 ± 8	4.01925	100.04 ± 0.09
* 10,630 ± 17	4.02653	83.47 ± 0.06
* 10,840 ± 27	4.03503	61.32 ± 0.15

* The last two points in Table VI.3 represent approach from the high temperature side while the others are from the low temperature side.

An example of the calculation of the standard deviation is given in Appendix III which is the method given in Youden (1955). The point calculated in Appendix III is (57.53, 10,880) in Table VI.3. Since the experimental method gave points somewhat spread out on the curve, the human error in drawing a line then was removed by calculating the best fit of the line by the method of least squares. In addition, the least squares method gives the minimum deviation that any point will have from the calculated line. The detailed calculation of the method of least squares was taken from Thomas (1956). The calculation is shown in Appendix IV for Curve A, Figure VI.1. The equation of the line for curve A, Figure VI.1 is $Y = -0.00174X + 4.09$ and that of curve B is $Y = -0.00036X + 4.056$. There is good agreement between the points determined from the high temperature side and those from low temperature side. The experimental measurement at 46.80°C on curve B is not consistent with the line equation. This fact would suggest that the thermistors are not sensitive or give reproducible results to vapor pressures less than 100mm. Hg or slightly higher since the measurement at 57.53°C compares well with the others and the vapor pressure is about 133mm. Hg.

After the work on liquid water was completed, dehydration tests on gypsum were begun; 27.4 gms. of gypsum were placed in the cell and the system was evacuated for one hour. Then the vapor cell was heated to 94.49°C. It seemed of interest to see how effective the vacuum system was in removing water adsorbed on the walls of the apparatus and also on the surface of the solid during the initial evacuation.

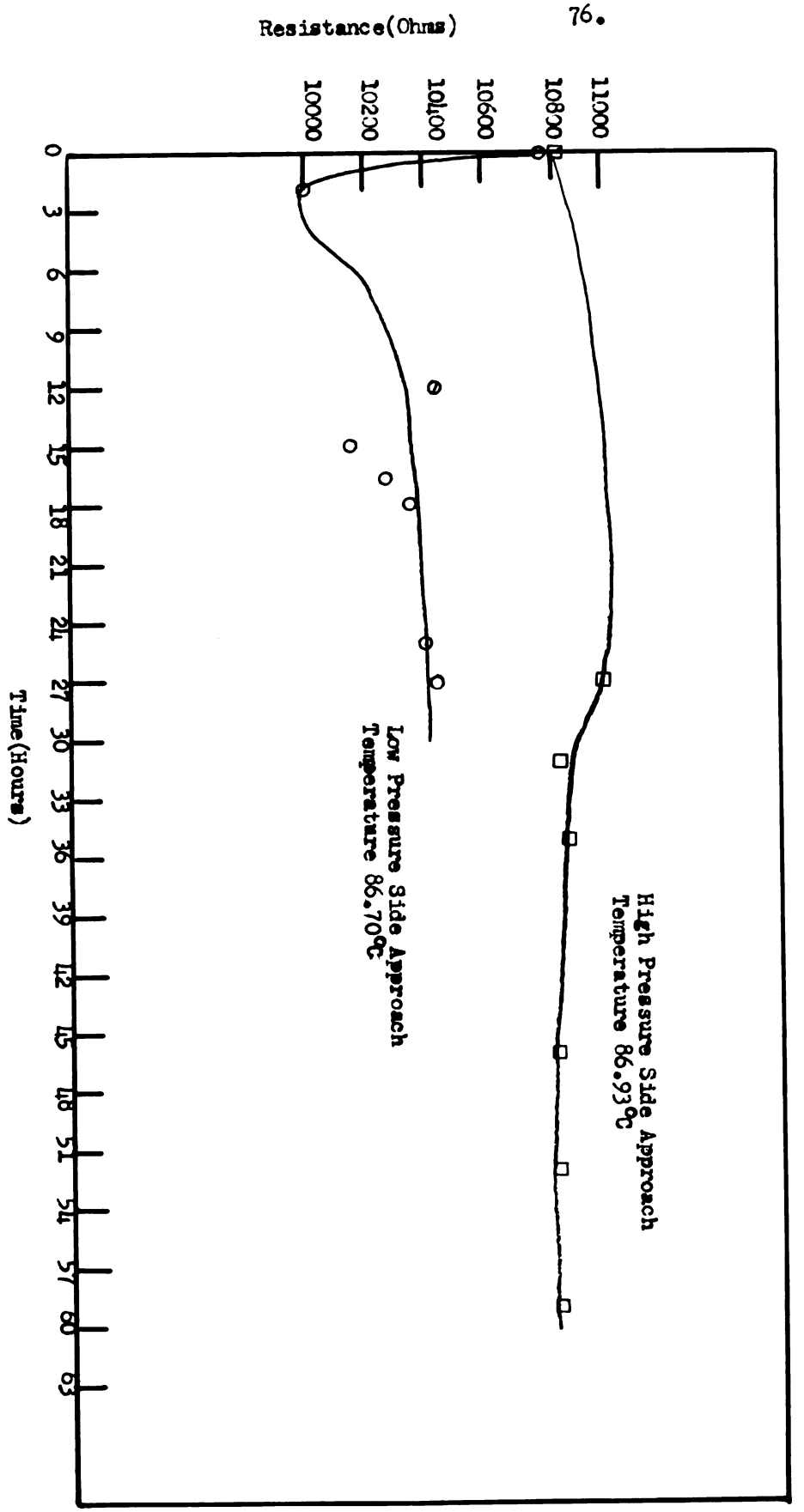


Figure No. VI.2 Approach to equilibrium from high and low pressure sides for Gypsum.

Consequently three measurements were made at temperatures of 51.43°C, 67.17°C and 74.21°C before the system was evacuated. Then the system was evacuated and the subsequent points were measured. The equilibrium was approached from both the high temperature side and the low temperature side at temperatures of 77°C and 86°C. The two directional approach to equilibrium at 86°C is shown in Figure IV.2. The high side approach at 86°C gives a higher pressure than the low side approach. This might suggest that equilibrium takes a much longer time to establish from a high temperature approach as a result of the inability of water vapor to be readsorbed on the surface or to diffuse back into the broken down structure of the solid. The same effect was noted at 77°C for the high side approach. The results of the measurements on gypsum are listed in Table IV.4 and plotted as curve C, Figure VI.1.

Table VI.4

Resistance (Ohms)	Log Resistance	Temp.°C
10553 ± 52	4.02335	51.43 ± 0.18
10094 ± 51	4.00405	67.17 ± 0.41
10061 ± 89	4.00270	74.21 ± 0.35
10605 ± 124	4.02550	77.81 ± 0.21
10361 ± 114	4.01540	86.70 ± 0.23
11050 ± 64	4.04336	77.50 ± 0.18
10504 ± 26	4.02140	91.10 ± 0.33
10854 ± 18	4.03558	98.54 ± 0.17
10854 ± 14	4.03558	86.93 ± 0.08

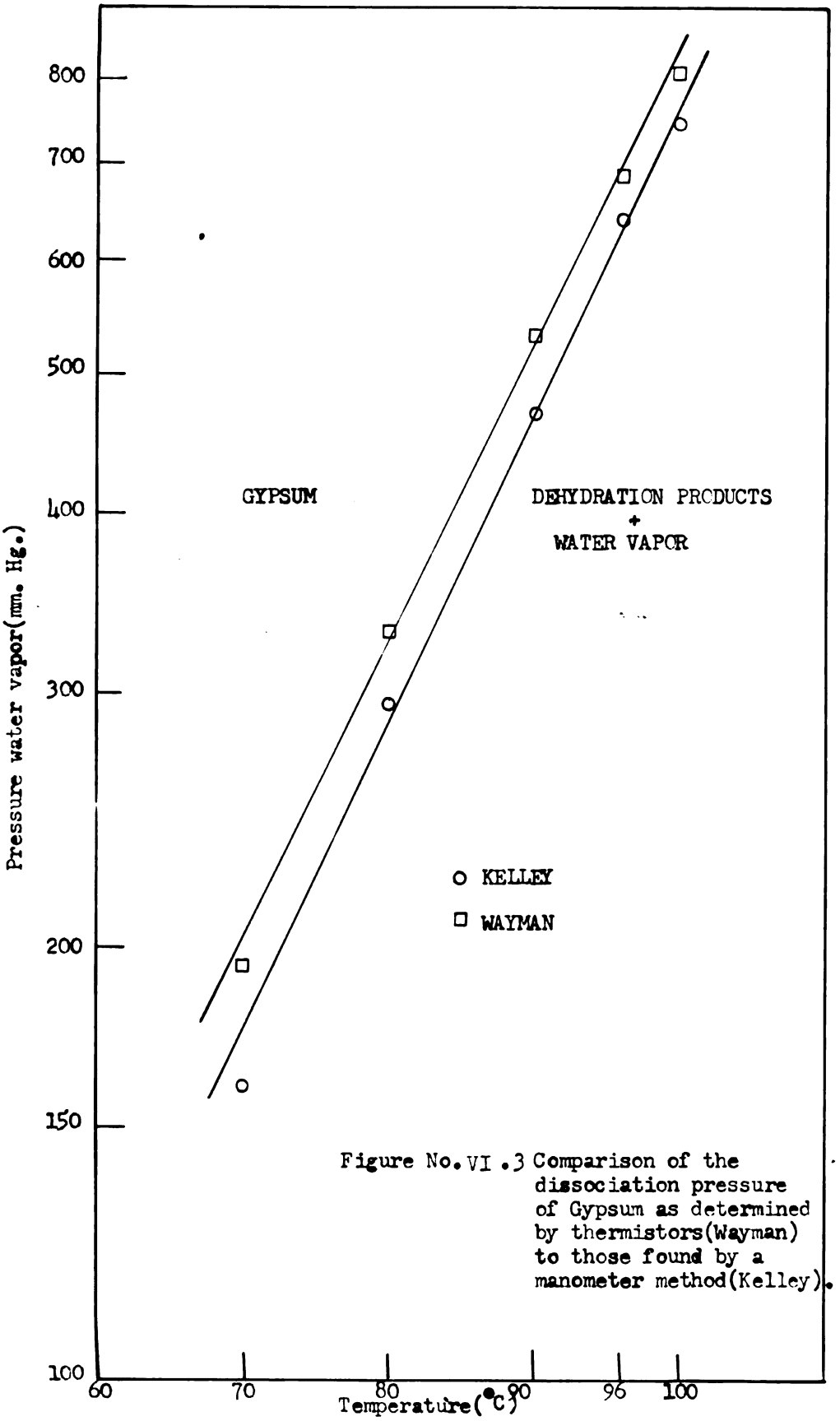


Figure No. VI .3 Comparison of the dissociation pressure of Gypsum as determined by thermistors(Wayman) to those found by a manometer method(Kelley).

The equation of the line for curve C, Figure VI.1 by the least squares method is $Y = 0.000256X + 4.002$. It appears that the original vacuum on the sample does not remove all the water vapor along the walls of the apparatus and that adsorbed on the surface of the solid. This is demonstrated by the fact that the pressures at 67.17°C and 74.21°C are much higher than those compared to Kelley's measurements. Also part of this error at 67.17°C may be attributed to poor temperature control (±0.41°C). One criticism of curves B and C, Figure VI.1 is the difference in slope. Curve B (liquid water) is negative and curve C (gypsum) is positive. The difference might be explained by the fact that the vapor pressure of gypsum increases much faster than water, partly from the error introduced by using the method of least squares, and somewhat due to the overall error in the method itself of measuring the vapor pressure.

In order to calculate the vapor pressure of gypsum, it is necessary to use the ratio method described in VI.A. In using this method, we find that the vapor pressure of gypsum is

$$\text{V.P. (Gypsum)} = \frac{\log \Delta R \text{ (Gypsum)}}{\log \Delta R \text{ (liquid Water)}} \times \text{V.P.(liq.Water)}$$

Hence, using the curves B and C, we calculate the pressure at 70° by

$$\frac{\text{Log } \Delta R(G)}{\text{Log } \Delta R(W)} \times \text{V.P.(W)} = \frac{.052}{.063} \times 235 = 194\text{mm. Hg}$$

Thus the vapor pressure as determined by the thermistors method is 194mm. Hg at 70°C. Using the same method the vapor pressures are calculated at other temperatures. The values for the vapor pressure of water were taken from the International Critical Tables (1928). The vapor pressures are compared to those of Kelley, Southard and Anderson (1941) in Table VI.5 and plotted as the pressure against temperature (°C) in Figure VI.3.

Table VI.5

Temperature °C	V.P. (Kelley)	V.P. (Wayman)	% Error
70	160mm. Hg	194mm. Hg	+17.53
80	295mm. Hg	331mm. Hg	+10.88
90	470mm. Hg	531mm. Hg	+11.49
96	640mm. Hg	686mm. Hg	+ 6.71
100	745mm. Hg	810mm. Hg	+8.02

The per cent error was based on comparing the measurement by thermistors to that of Kelley by a manometer. Thus at 70°C the error is

$$\frac{160}{194} \times 100 = 17.53\%$$

It is shown in Table VI.5 that the accuracy of the thermistor method for measuring vapor pressure in substances that contain (H_2O) structural water increases as the vapor pressure curves of liquid water and the unknown become more alike. Thus the overall accuracy for vapor pressures in the range 300-760mm. Hg. ranges from 7-10 per cent.

The overall mechanism of this new method might be viewed as a tool by which the gas conducts heat away from the thermistor just as a gas conducts heat away from a wire in the thermal conductivity method for a gas. The equation to represent best the mechanism is

Pressure of Water Vapor = log Δ R = log R (water)-log R(vac.)

where log Δ R = log change in resistance

log R (water) = log resistance due to water vapor

log R (vac.) = log resistance measured under vacuum

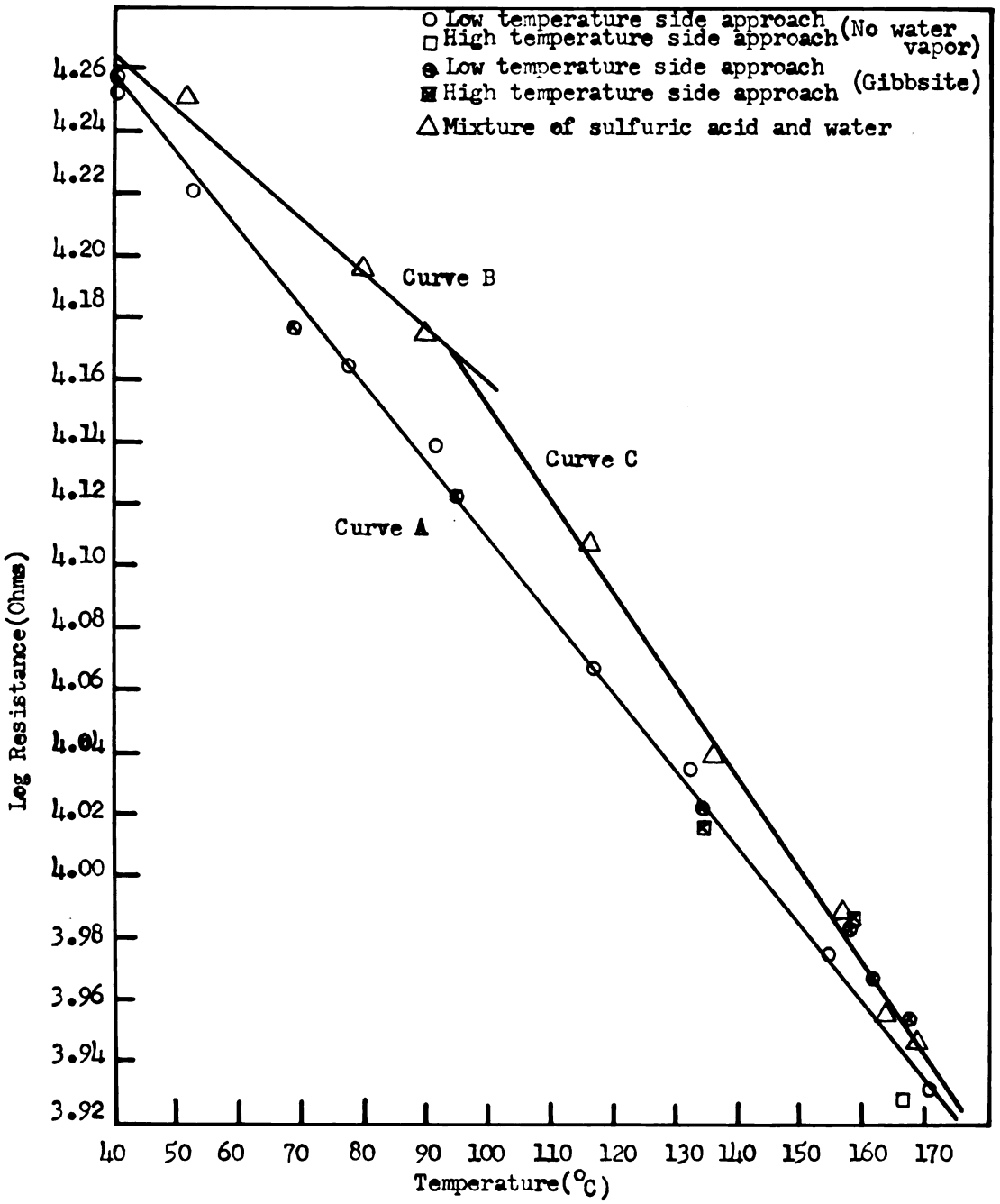


Figure No. VI.4 Experimental curves for determining vapor pressure of Gibbsite by thermistors.

C. Dehydration of Gibbsite [$Al(OH)_3$]

As previously indicated gibbsite is interesting geologically because it is the main constituent of "bauxite" deposits. It also is one of the important minerals which contains OH type water and should therefore be called a hydroxide as compared to the true hydrates with H_2O structural water. In addition, the thermodynamic properties of gibbsite are still not accurately known on the basis of dehydration studies. All of the above factors make gibbsite an interesting mineral to investigate.

The work on gibbsite was begun with the same pattern as used for gypsum. However, from the previously published data of Funaki and Uchimura (1952) it was reasoned that the vapor pressure of gibbsite should be nil below 100°C. This permitted the heating of the vapor cell to a much lower temperature before starting measurements since water vapor would not condense on the cell walls. In addition, these tests had to be run at a lower temperature on the vapor cell, otherwise the high heat convected from the sample cell to the vapor cell would have burned out the thermistors. The first test was run with no water vapor in the cell. After evacuating, the vapor cell was heated to 82.15°C and later the temperature on the sample cell was varied. The resistance was then measured as a function of temperature. The results of this test are given in Table VI.6, and plotted as Curve A in terms of log resistance against temperature in °C in Figure VI.4. The equation of the line (by method of least squares) is $Y = -0.00249X + 4.357$.

Table VI.6

Resistance (ohms)	log Resistance	Temp. °C
17912 ± 48	4.25318	40.40 ± 0.07
16643 ± 305	4.22128	52.41 ± 0.38
14651 ± 24	4.16588	77.01 ± 0.08
13795 ± 280	4.13975	91.51 ± 0.80
11678 ± 59	4.06732	116.84 ± 0.15
10850 ± 28	4.03543	132.22 ± 0.06
9473 ± 119	3.97649	154.69 ± 0.31
8555 ± 45	3.93222	170.85 ± 0.13
*8475 ± 109	3.92814	166.51 ± 0.40

*The last point in Table VI.6 was the only one approached from the high temperature side.

Finding a good standard for this part of the work was a problem. A liquid whose concentration would not change with respect to time was the appropriate thing to use since equilibrium is much faster with liquids than solids. The liquid chosen was a 70.78% by volume mixture of distilled water and sulfuric acid. Burt (1904) measured the vapor pressure of water of this 70.78% solution by a dynamical method. It is realized that the concentration of this solution probably changed during Burt's work as a result of evacuation and consequently errors are involved by this method, but it was the only reasonable standard available . Thomas and Ramsay (1923) have shown that sulfuric acid has no appreciable dissociation below 200°C so no effect of SO_3 need be considered. The results of Burt's measurements are given in Table VI.7.

Table VI.7

Temp. °C	Vapor Pressure H_2O (70.78% H_2SO_4 - H_2O) mm.Hg
120	140.4
125	171.3
130	205.2
135	246.3
140	291.2
145	355.4
150	426.9
155	501.5
160	589.0
166.47	740.05

It will be shown later that the vapor pressures of water over gibbsite as measured by Funaki and Uchimira (1952) have an approximate relationship to these values. Accordingly the sulfuric acid-distilled water mixture (30 milliliters) was placed in the cell and evacuated for ten minutes. Then the vapor cell was heated to 81.90°C and measurements commenced. Only one evacuation (at 116.34°C) was made after the test was begun to prevent a change in the concentration of the mixture on which the vapor pressure is based. The results of this test are given in Table VI.8 and plotted in Figure VI.4 as curve B and curve C which had to be resolved into two parts.

Table VI.8

Resistance (ohms)	log Resistance	Temp. °C
18268 ± 82	4.26165	39.67 ± 0.09
17886 ± 169	4.25254	51.45 ± 0.21
15722 ± 147	4.19659	79.66 ± 0.33
14981 ± 48	4.17555	89.46 ± 0.16
12836 ± 118	4.10843	116.34 ± 0.45
10954 ± 147	4.03968	135.92 ± 0.32
9768 ± 49	3.98981	156.99 ± 0.15
9045 ± 50	3.95641	163.65 ± 0.10
8868 ± 62	3.94783	168.73 ± 0.18

The equations of lines for Curve B and Curve C, Figure VI.4 are respectively Y = -0.00175X + 4.335 and Y = -0.00296X + 4.446. An analysis of Curve C strongly suggests that this method of measuring vapor pressures is invalid at higher temperatures. It appears that the effect of temperature becomes very important at approximately 100°C and destroys the effect of pressure. The most reasonable explanation for this fact probably is that the heat is so great in the vicinity of the thermistor that pressure has little or no effect on the resistance. The same result has been observed for gibbsite.

After the unfortunate results with the sulfuric acid-water mixture, gibbsite was investigated. Thirty grams of gibbsite that had a surface area of 1440cm^2/gm. was placed in the cell. After evacuating for one hour, the vapor cell was heated to 82.38°C and the measurements were begun. The results of the measurements on gibbsite are given in Table VI.9 and the points are plotted in Figure VI.4 along curve A and curve C.

Table VI.9

Resistance (Ohms)	log Resistance	Temp.°C
18163 ± 79	4.25920	40.11 ± 0.13
15055 ± 150	4.17770	68.33 ± 0.60
13296 ± 13	4.12371	94.17 ± 0.10
10525 ± 69	4.02225	134.20 ± 0.16
9625 ± 38	3.98340	157.77 ± 0.16
* 10380 ± 15	4.01620	134.43 ± 0.09
8992 ± 48	3.95386	167.24 ± 0.24
* 9699 ± 30	3.98673	158.36 ± 0.33
9293 ± 40	3.96816	161.69 ± 0.30

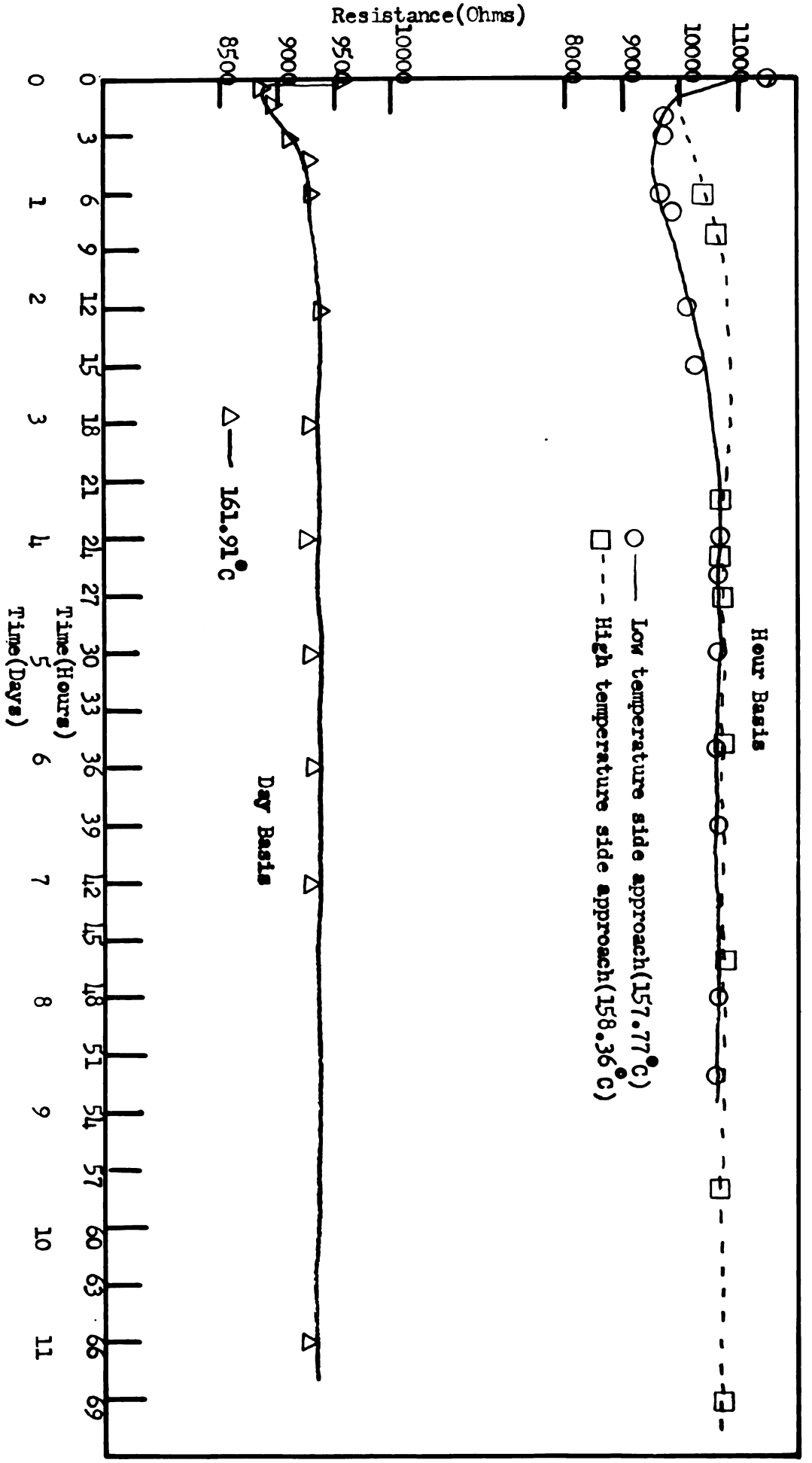


Figure VI.5 Approach to equilibrium at approximately 158°C for gibbsite along the high and low temperature sides.

*The equilibrium was approached from both a low pressure side and a high pressure side at temperatures of 158°C and 134°C.

To insure that equilibrium was established within 48 hours, a test was run for ten days at 161.91°C. The results of the approach to equilibrium from two directions and the test run for ten days are given in Figure VI.5. Only the resistance against time is plotted since the pressures could not be determined. The positive result from the gibbsite test is that no water is lost before 135°C. The experimental points measured above 150°C appear to follow the curve C quite well. However, as will be shown, no confidence can be placed on the measurements in this range. Since the experimental measurements on gibbsite coincided with those for liquid water-sulfuric acid solutions, it was assumed that these points represented the vapor pressure of the acid solution mixture at that temperature. The three points on the curve C that correspond to gibbsite are at temperatures of 157.77°C, 161.69°C and 167.24°C with respective vapor pressures of 530, 615, and 775mm. Hg. The proof that the method is negative at high temperatures is assured when the heat of reaction was calculated by the Clausius-Clapeyron equation. A derivation of this equation for the hydrate (or hydroxide) reaction is given in Appendix V. The calculation of the heat of reaction for Gibbsite = Boehmite + water vapor was based on the data given in Table VI.10.

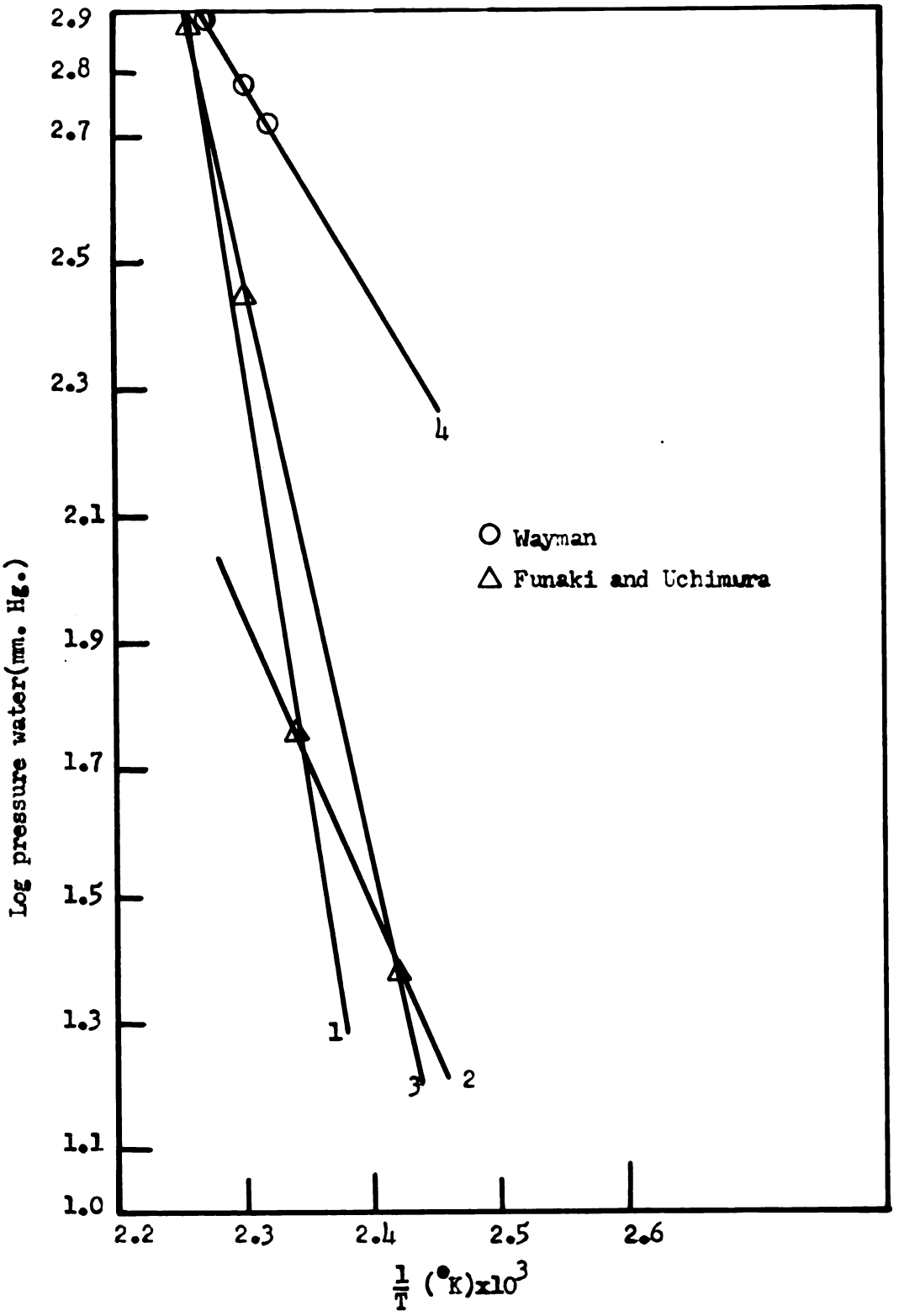


Figure VI.6 Plot used to calculate the heat of reaction of dehydrated gibbsite from the Clausius-Clapeyron equation.

Table VI.10

	T°C	T°K	$\frac{1}{T} \times 10^3$ (°K)	P(mm.Hg)	log P
(Wayman)	157.77	430.77	2.32	530	2.724
	161.69	434.69	2.30	615	2.788
	167.24	440.24	2.27	775	2.889
(Funaki and Uchimura)	140	413	2.42	24	1.380
	154	427	2.34	58	1.763
	162	435	2.30	282	2.450
	170	443	2.26	760	2.880

The measurements of Funaki and Uchimura (1952) are also given in Table VI.10. The above data are plotted in Figure VI.6 in terms of log P(mm.Hg) against $\frac{1}{T}$ (°K) x 10^3. The heat of reaction was calculated for four curves, in one for Wayman's measurements (curve 4) and three for Funaki and Uchimura's work (curves 1, 2 and 3). The calculation of the heat of reaction for (curve 4) is as follows:

$$-\frac{\Delta H}{2.303R} = \text{slope}$$

$$= \frac{2.889 - 2.724}{2.27 - 2.32}$$

$$= \frac{.165}{-.05} = -3.3$$

$$\Delta H = 3.3 \times 4.57 = 15.08 \text{ kcal./mole}$$

Although this value agrees quite well with the work of Kuznetzov (1950) it disagrees with the dehydration work of Funaki and Uchimura and no confidence can be attached to it since there is no way to check the accuracy and it may be merely fortuitous based on the assumption that the gibbsite vapor pressures agree with those of sulfuric acid-water at the corresponding temperature. The heat of reaction was also calculated for the curves of the Japanese workers. The results for curves 1, 2, and 3 are respectively 63.80 kcal., 21.89 kcal., and 42.87 kcal. It appeared reasonable that one could get three possible Δ H values

from their results. It may be that their first two points at 140°C and 154°C are accurate since this Δ H value is reasonable. At higher temperatures their values are most likely in error. The temperature in their work could only be controlled to ±1°C. It is quite reasonable to suspect that small errors in temperature measurement would lead to large errors in vapor pressure determinations.

A critical analysis of both methods (Wayman) and (Uchimura and Funaki) would thus suggest that our knowledge of the thermodynamic constants for dehydrated gibbsite are questionable and the system should still be studied. It is clear, however, at this point that the properties of gibbsite determined through heat of solution measurements and those from dehydration studies are at variance. The reason for this observation is discussed in a later section.

VII. Microscopic and X-ray Diffraction Examination of Dehydration Products

In order to justify the assumption that gibbsite dehydrates to boehmite plus water vapor, the dehydrated products were examined by the petrographic microscope and X-ray diffraction techniques.

It is believed that this is the first time that vapor pressure studies have been correlated with microscopic and X-ray examination. Fricke and Severin (1932) measured the isobaric dehydration of gibbsite at a pressure of 100mm. Hg and identified the product as boehmite but did this only at one temperature and no microscopic identification.

For this examination samples of gibbsite were dehydrated under identical conditions to those used in the vapor pressure measurements. Twenty milligram samples were dehydrated for 48 hours at 150°C and 166°C. In addition twenty milligram samples were dehydrated in air at 200°C and 225°C in a laboratory oven.

A. Microscopic Examination

The original gibbsite, before dehydration, was transparent, white and occurred in aggregate-like fragments. The samples dehydrated at 150°C and 166°C were somewhat amorphous-like and pitted on the surface. Examination of the same samples with a magnification of 500X indicated that the sample at 166°C was highly fractured while the aggregates of the one at 150°C were somewhat intact. The samples dehydrated in air at 200°C and 225°C appeared amorphous-like and the surface was so obliterated that no significant detail was distinguished.

B. X-ray Diffraction Examination

Samples were prepared for X-ray investigation by hand crushing in a cast iron mortar. Approximately one milligram of the crushed sample (-200 mesh) was then mixed with Duco cement and rolled between

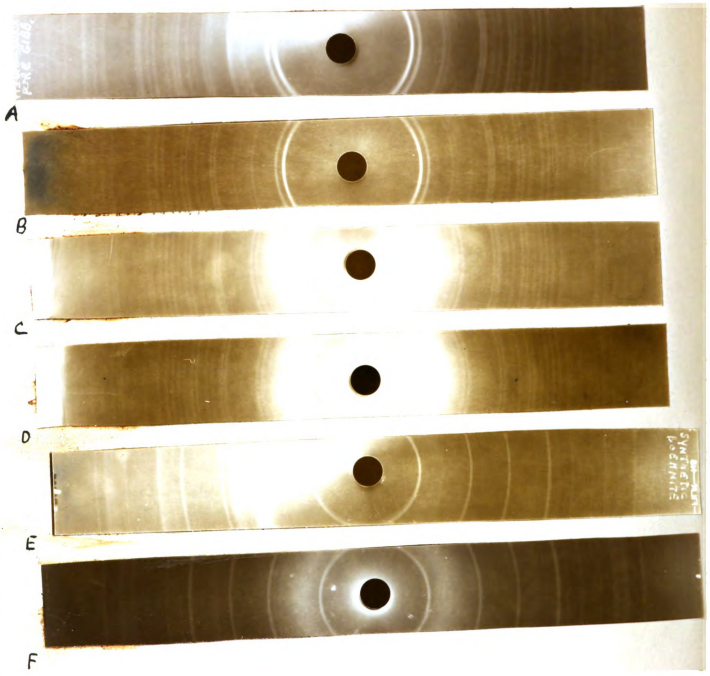


Figure No. VII.1 X-ray diffraction patterns of dehydrated gibbsite.

two glass slides in the form of a small rod 0.5mm. in diameter and 1 cm. in length. The formed rods were glued to a pedestal in a Debye-Scherrer camera and X-rayed by CuK_{α} radiation using a nickel filter.

Standard X-ray patterns were prepared from synthetic gibbsite (same as used in the dehydration studies) and synthetic boehmite. The lines used to identify gibbsite correspond to d spacings (A°) of 4.82, 4.33, 2.44, and 2.37. Those used for boehmite identification had d values (A°) of 6.15, 3.15, 2.33 and 1.85.

The gibbsite samples X-rayed from the dehydration at 150°C and 166°C for five hours revealed that gibbsite was the only phase present. After extending the X-ray test to ten hours, the 166°C sample showed faint boehmite lines while the 150°C sample was unchanged. This data supports well the original premise that gibbsite = boehmite + water vapor. In addition, the structure of gibbsite is not altered up to 150°C.

The sample dehydrated at 200°C in air gave a good indication of boehmite; the sample heated to 225°C was completely converted to boehmite. These latter two tests might suggest that the amount of gibbsite converted to boehmite is dependent on temperature and it would seem probably that dehydration time is also an important factor, but this was not investigated.

The importance of using the X-ray technique and petrographic microscope is demonstrated. Both of these tools have their peculiar limitations but used together they complement one another. The results of the X-ray work appear in Figure VII.1 and are listed below in Table VII.1.

Table VII.1

X-ray Sample	Temp. °C	Phases Identified
(A) Synthetic gibbsite	--	Gibbsite
(B) Gibbsite Dehydrated (in vacuum) at 150°C	150°	Gibbsite
(C) Gibbsite Dehydrated (in vacuum) at 166°C	166°	Gibbsite, boehmite
(D) Gibbsite Dehydrated in air at 200°C	200°	Gibbsite, boehmite
(E) Synthetic boehmite	--	Boehmite
(F) Gibbsite Dehydrated in air at 225°C	225°	Boehmite

C. Discussion of Results

Achenbach (1931), Schwiersch (1933), Borisevich (1948), Alexanian (1955) and Courtial, Trambouze, and Prettre (1956) have found that boehmite is the only well crystallized phase resulting from the dehydration of gibbsite up to 225°C. The detailed work in vacuo of Tertian, Papee, and Charrier (1954) indicates that boehmite is the only phase formed. The results of this study are in accord with those enumerated above, but apparently no one has been concerned with the amorpheus-like surface which was previously described. A good petrographic microscope and electron microscope study of these surfaces might be rewarding. Contrary to this theory of boehmite formation only as a dehydration product, Tertian and Papee (1953) suggest that gibbsite dehydrates into boehmite plus a poorly crystalline variety of alumina. In the present work, no lines of any form of alumina were detected on the X-ray film. However, the work of Tertian and Papee is interesting and the amorpheus-like phase observed microscopically could very well be their poorly crystalline alumina, but the amount insufficient to be detected by X-rays. The microscope might well throw some light on the theory that gibbsite first dehydrates to alumina plus water vapor and

later the water vapor rehydrates the surface to form boehmite.

With regard to the mechanism of dehydration Garner (1955) has perhaps the most extended treatment. It is pointed out that during dehydration of a hydrate crystal in hard vacuum, water molecules or OH groups evaporate from the surface giving a dehydrated ionic network which is only stable to some extent in the case of some zeolites. In most other hydrate systems, the structure is unstable and undergoes rearrangement to give a phase which possesses no clearly defined structure. This partly amorphous phase may consist of extremely small crystallites which are so separated in space that they cannot readily grow to larger units. The transformation is accompanied by only small changes in bulk volume and the absence of visible cracks. A further rearrangement then occurs in this disorganized material giving crystalline nuclei of a new phase, which process is accelerated in the presence of water vapor. The process of crystallization is accompanied by considerable shrinkage of the products, allowing cracks to form usually at right angles to the interface. This excellent description has been observed on many of the hydrate equilibria that Garner has investigated. It will be recalled that Tertian and Papee (1953) suggested that gibbsite dehydrates into boehmite plus a poorly crystalline variety of alumina. Also the microscopic examination in the present study indicated a somewhat amorphous surface product. The dehydration mechanism of Garner appears to have some of the characteristics of gibbsite dehydration built into it.

Garner further indicates that two factors determine the rate of dehydration namely (1) the rate of loss of water from the interface between the hydrate and its products and (2) the rate of diffusion of

water molecules through the solid. In addition to these two factors, it seems that another point to consider is the net rate of loss of water, i.e. outward diffusion minus inward diffusion rates. As a result of the small temperature coefficient of diffusion, the impedance to release of water vaper is less at lower temperatures than higher temperatures. This point is demonstrated quite nicely with gibbsite since Courtial, Trambouze and Prettre (1956) found that the boehmite content of a gibbsite sample dehydrated rapidly at high temperatures is much less than the boehmite content of a sample dehydrated to the same degree but more slowly and at lower temperatures. The impedance offered to the escape of water from within the crystal depends apparently somewhat on the micro-structure of the surface layer and its thickness. The impedance is greatest when the layer is amorpheus or microcrystalline and less so when the interface layer is coarsely crystalline and full of cracks.

These few notes on the mechanism reassure us that the dehydration of hydrous substances is complex. A future investigation on reaction rates accompanied by detailed examination of the surfaces could lead to some valuable information with respect to the mechanism of gibbsite dehydration.

To form a molecule of water either from a surface evaporation or removal of OH^- groups from the crystal lattice, the recombination reaction probably involves

$$OH^- + OH^- = H_2O_{(g)} + O^=$$

Other possible methods of forming the water molecule are

(1) A—O ∠ H; in which the H-O bond breaks to reunite
A—O — H; with the OH bond severed from A or

(2) A $\frac{/}{/}$ O $\frac{/}{/}$ H in which the H and O atoms are severed
A $\frac{/}{/}$ O $\frac{/}{/}$ H from bonds and recombine to form water.

It certainly must be recognized that much more energy is necessary to eliminate hydroxyl-type water (Brucite and Gibbsite) than the H_2O type water (Gypsum and hydrous borates).

VIII. Discussion

A. Importance of Dissociation Pressure Measurements

Much of the work on thermodynamic systems in the past has been done by heat of solution measurements, from concentration cells and by other means. Many natural geologic and mineralogic changes take place under atmospheric conditions and from relatively simple experiments it is possible to calculate the three important quantities, heat of reaction (ΔH°), change in standard free energy (ΔF°), and the entropy change (ΔS°) from studies of vapor pressure measurements over hydrate and hydroxide dissociations. The heat of reaction can be determined through the use of the Clausius-Clapeyron equation. The change in free energy can be determined from the relationship

$$\Delta F^\circ = -RT\ln K_p = -4.57T \log P_{H_2O}$$

The change in entropy is given by $\Delta S^\circ = \frac{\Delta H^\circ - \Delta F^\circ}{T}$ and the equilibrium vapor pressure can be represented by $\log P = -\frac{\Delta H^\circ}{4.57}\frac{1}{T}$ + constant. Hence some very important thermodynamic constants can be determined from these dehydration studies providing the gas can be represented under ideal conditions. The most direct application for this information is at surface temperature and pressure where the processes of weathering and sedimentation occur.

B. Surface Reactions on Solids

One of the important contributions from this study has been the recognition of the difference in heat effects for the system gibbsite = boehmite + water vapor when determined from heat of solution measurements as opposed to dehydration investigations. This effect has not been emphasized before for this particular system. The best ΔH° value determined thus far for this reaction by heat of solution investigations have been that of Kuznetzov (1950) which is 15.0 kcal./mole. The most reliable values of ΔH from dehydration work are those of Sabetier (1954) and Funaki and Uchimura (1952) and are respectively 21.5 kcal./mole and 21.89 kcal./mole for a limited range. The difference in the values is probably a surface effect. In heat of solution measurements, the solid usually is completely dissolved and a true equilibrium is measured. With dehydration work, there is apparently an interplay at the surface between the originally formed dehydrated product and water vapor and the subsequent reactions that follow. It is also important to note that the effect of pressure on the system is contributory to the ease of escape of water molecules from within the crystal. Consequently, the reaction investigated by dehydration is complex and a true equilibrium between the crystal and the environment is never attained; that is, the vapor pressure which is measured may represent an equilibrium between the original crystal, the complex surface products, and the vapor itself. These complexities could account for the difference in heat effects as determined by two different methods. Giaque (1949) has considered the same problem for the Brucite = Periclase + $H_2O_{(g)}$ reaction. One of the important points raised by Giaque is how often have experimenters recorded equilibrium

data which did not correspond to the macro-crystalline properties of the phases present. Giaque has calculated the free energy difference between

MgO (crystals) - MgO (fine powder) as 800 cal/mole. It is concluded from his work that the dehydration of crystalline brucite should produce particles of MgO which become detached before they reach macroscopic dimensions, and it is believed that this is a fairly commonplace occurrence in other cases. It is thus easy to appreciate why the higher free energies of substances in a finely divided form give lower decomposition pressures than do macroscopic phases. For this particular system $Mg(OH)_2 = MgO + H_2O_{(v)}$ the true dissociation pressure, as determined from the third law of thermodynamics, is 130% higher than the measured values of Giaque on this system which had a reproducibility of 0.1%. This mechanism no doubt accounts for the higher vapor pressures from heat of solution measurements than for the low values obtained by dehydration studies.

MacDonald (1955) has also calculated theoretical curves for the brucite-periclase reaction and interprets the differences in his curves in terms of the method of preparation of material. These observations on dehydration certainly show the complexity of surface reactions and should suggest that much caution be taken when making interpretations from such results.

C. Effect of Total Pressure on Dehydration

An important point to consider in applying results from dehydration studies in vacuum to those at natural conditions (1 atmosphere pressure) is what effect does an inert gas at one atmosphere pressure have on the vapor pressure (ideal gas). This point can be examined

in terms of a problem given in Glasstone (1958). The problem cited is that the true vapor pressure of water is 23.76 mm. at 25°C. Calculate the vaper pressure when water vaperizes into a space already containing an insoluble gas at 1 atmosphere pressure, assuming ideal behavior. In a vacuum the vaper pressure of water is the total pressure whereas under a total pressure of 1 atmosphere at 25°C it is only a fraction of the total pressure. The effect of external (total) pressure on the vaper pressure of a liquid or solid can be calculated by the Poynting equation

$$\frac{dp}{dP} = \frac{pV_\ell}{RT}$$

but since the change in small $\frac{dp}{dP}$ can be replaced by $\frac{\Delta p}{P}$ where

Δp is the change in vapor pressure

p is the partial vapor pressure

ΔP is the Total Pressure change

V_ℓ is the specific volume

R = gas constant

T = absolute temperature

or

$$\frac{\Delta p}{p} = \frac{V_\ell}{RT} \Delta P$$

At 25°C we have

$$\frac{\Delta p}{23.76} = \frac{0.018 \times 1.0}{0.082 \times 298}$$

$$\Delta p = \frac{0.018 \times 23.76}{0.082 \times 298} = 0.0175\text{mm.}$$

Hence the vapor increases by only a small fraction since p = 23.79. Perhaps the same results can be used for solids but at temperatures not higher than 50°C without involving too much error. Thus the change in total pressure on a solid in the range of one atmosphere at low temperatures can be neglected as affecting the vapor pressure developed over the solid. In terms of kinetics, the effect of total pressure becomes important. Between the temperature range 206-243°C, Eyraud and Geten (1954) have shown that small changes in pressure lead to large differences between activation energies. This observation might suggest that total pressure is quite important as to the extent at which the rate of equilibrium is attained.

D. Relationship Between Natural Mineral Phases, Thermodynamics and Kinetics

In nature all three of the hydrous oxides of aluminum have been observed. The following Table VIII.1 lists the various phases that have been identified with geographical location in a few of the representative deposits around the world.

Table VIII.1

PHASES PRESENT	LOCATION	REFERENCE
	UNITED STATES	
G, D	Arkansas	Wysor (1916)
G	Oregon	Allen (1948)
G	Georgia	Alexander, Hendricks and Faust (1941)
G	No. Carolina	Alexander, Hendricks and Faust (1941)
G	So. Carolina	Alexander, Hendricks and Faust (1941)
G, D	Missouri	Wysor (1923)
	CARRIBEAN AREA	
G, B	Jamaica, B.W.I.	Hill (1955)
G, B	Jamaica, B.W.I.	Hase (1950)
G	Grenada, B.W.I.	Hardy-Redrigues (1939)
G, B	Dominican Republic	Goldich-Bergquist (1947)
G	British Guiana	Bishopp (1955)
G, B	Surinam	van Kersen (1956)
G	Brazil	de Ravel (1953)
	EUROPE	
B, G	Spain	Miralles (1952)
B, D, G	Spain	Tullet (1951)
G	Ireland	Eyles (1952)
D, B	Greece	Vachtl (1956)
G	Poland	Spangenberg (1949)
G, B	Croatia-Bosnia	Miholic (1956)
Bayerite	Hungary	Gedeon (1956)
G	Hungary	Nemerz (1954)
G, D	Hungary	Kiss (1952)
G, B, D	Hungary	de Weisse (1948)
G	Russia	Chirvinskii (1940)
	AFRICA	
G, D	Portugese Guiana	de Weisse (1954)
	ASIA	
B, D	Turkey	Ekrem (1954)
G, B, D	India	Oda (1955)
	PACIFIC	
G	Australia	Rogatt (1945)
G	Hawaii	Sherman (1957)

G = Gibbsite B = Boehmite D = Diaspore

The first letter of each series represents the predominant form.

There is no doubt that gibbsite predominates in these weathering profiles on a world-wide basis. Even when associated with boehmite or diaspore, it is dominant except in a few instances. This data suggests that gibbsite is the stable phase at surface temperature and pressure. The instances where gibbsite and boehmite occur together could represent a dehydration equilibrium. It is interesting to note that in the areas with high relative humidity (U.S., Hawaii, Jamaica, Brazil, and British Guiana), gibbsite is most stable; high relative humidities would probably be conducive to the rehydration of boehmite to gibbsite. In rain forest areas, the excellent cover of high trees prevents extreme heat from penetrating the soil and dehydration of gibbsite is probably eliminated. In areas like Jamaica, however, boehmite has been identified and might be the result of intense heat from the sun permitting surface dehydration of the gibbsite.

In order to establish whether gibbsite or boehmite is the stable phase in nature, it is necessary to consider the relative humidity and temperature. At first glance, it would appear that a three coordinate system is required, the coordinates being temperature, partial pressure of water vapor, and relative humidity. However, relative humidity is given as

$$R.H.(T) = \frac{\text{partial pressure water in air (T)}}{\text{partial pressure water at saturation(T)}}$$

Since the saturation vapor pressure is fixed at a given temperature, it is necessary to know only the relative humidity and temperature from which the partial pressure of water in air can be calculated. It would be extremely interesting to gather data on relative humidity and temperature, both areally and on a world-wide basis. By statistically plotting the relative humidity (ordinate) against temperature (abscissa)

and superimposing the curve for dissociating pressure of water vapor for gibbsite (ordinate) against temperature (abscissa) and noticing where these curves intersect, it would be possible to establish the conditions of stability of gibbsite and boehmite in terms of relative humidity and temperature. Schmalz (1959) has expressed an equilibrium for the reaction hematite + water = goethite in terms of a ratio η which represents the relative humidity in a system calculated at any temperature. He lists an expression for calculating η as follows:

$$-RT \ln \eta = (T'-T).\left[\Delta V' (dp/dt)' - \Delta C_p\right] + \Delta C_p T \ln (T'/T)$$

where the volume $\Delta V'$ = expansion due to water or water vapor, $dp/dt = \Delta S'/\Delta V'$ and where $T' \neq T$. Thus a knowledge of all the above quantities would give a specific value for the relative humidity for a reaction in some definite system. Then it would be possible to construct a two-dimensional plot for a dehydration reaction in terms of relative humidity and temperature. Having this plot, only a knowledge of relative humidity and temperature would be necessary to predict whether gibbsite or boehmite would be stable.

Even though we might be able to predict the stability of one phase or the other in weathering profiles, this information places no limit on the time factor since thermodynamics is independent of time. A thermodynamically stable situtation may exist in nature, but kinetically may be impossible. Thus if boehmite is found in an environment which is unstable to its existence, it may be rehydrating to gibbsite, but on a kinetic basis the reaction rates may be so complex and slow that it remains in nature in a metastable state. In the future a thorough study of both the kinetics and thermodynamics may shed light on this stability problem. There are many limitations in the use of quantitative chemistry for solving geological problems, but an understanding of the real mechanisms that prevail in nature can only be understood in this manner.

IX. Conclusions

1. A quantitative approach to contribute more data on the understanding of the problem of weathering in geology has been done. To correlate measurements of vapor pressure on dissociation reactions, relative humidity, and temperature, at least a two - coordinate plot is necessary. Through the use of an equation by Schmalz (1959), it is possible to calculate the relative humidity of a reaction as a function of temperature. Then a knowledge of relative humidity and temperature dictates the stability of mineral phases which can be applied to nature. Probably effects of rate studies might explain disequilibrium mineral assemblages observed in bauxite deposits.

2. A high temperature cell has been designed for use in either infra-red spectroscopic studies or for measuring the vapor pressure of geologically important hydrous minerals by thermistors.

3. A new method was developed for measuring dissociation pressures for substances that contain H_2O type structural water. The accuracy of the method varies from 7-10 per cent for measuring vapor pressures in the range 300-760mm. Hg. The technique appears to be unreliable for minerals that contain OH^- type of water since the temperature effect sensed by the thermistor exceeds that of pressure.

4. Equilibrium constants for the reaction Gibbsite = Boehmite + water vapor have been calculated by two methods. A method is suggested for evaluating the inconsistencies of thermodynamic constants by the use of these calculations. When discrepancies are found between the two methods, the thermodynamic values should be questioned.

5. The best values currently for the heat of reaction for gibbsite = boehmite + water vapor are

$$\Delta H^{\circ} = 15.0 \text{ kcal./mole (Heat of Solution)}$$

$$\Delta H = 21.5 \text{ kcal./mole (Dehydration studies)}$$

6. The variance between thermodynamic values by heat of solution measurements and dehydration studies can be explained on the basis of complex reactions that occur on the surface of dehydration.

7. The most reasonable products formed from the dehydration of gibbsite are boehmite and an amorphous, poorly crystallized phase.

X. Suggestions for Future Research

1. The accuracy of the thermistor method for measuring vapor pressure could be improved by using a system where the temperature is controlled to $\pm$ 0.01°C. In order to study systems where the heat effects are high, a wheatstone bridge circuit of the Kelvin type should be investigated. An extremely sensitive galvanometer like the Leeds and Northrup Model 2430 could be used. This galvanometer is 1000 times more sensitive than the ordinary Weston 440.

2. Theoretical curves for relative humidity as a function of temperature should be made with the use of Schmalz's (1959) equation.

3. A theoretical phase diagram for the system Al-Water would be interesting to calculate through the use of heat of solution and dehydration ΔH° values.

4. The effect of grain size on dehydration should be investigated at a single temperature in order to evaluate reaction rates and equilibrium dissociation pressures.

5. A comprehensive study of reaction rates on gibbsite might lead to results that account for more than one mineral phase as observed in nature.

6. The thermister method should be used, after improvement, to investigate other substances like the hydrous borates.

7. The possibility of using thermistors to measure the partial vapor pressure of CO_2 and H_2O simultaneously should be studied. If these results are positive, then complex equilibria investigations like the Azurite-Malachite reaction could be undertaken.

Appendix I

Brief Description of B.E.T. Method

The B.E.T. method enables one to determine the volume of gas necessary to form an adsorbed monolayer on the substance whose surface area is in question. Usually krypton gas is used. Known amounts (volume) of krypton are added to a sample container and the amount not adsorbed on the surface of the sample is measured. The difference between the amount not adsorbed and the amount added is a measure of the amount adsorbed on the sample. This data, in addition to the pressure of the gas in the container and the vapor pressure of the gas at the experimental temperature, can be used in the B.E.T. equation which states that

$$\frac{P}{V(P_o-P)} = \frac{1}{V_mC} + \frac{C-1}{V_mC}\,\frac{P}{P_o} \quad \text{where}$$

V = volume of gas adsorbed (STP)

P = pressure in sample container when Vcc. are adsorbed

P_o = vapor pressure of the gas at the experimental temperature

V_m = volume of gas required to form a monomolecular layer

C = a constant related to the heat of adsorption

Hence a plot of $\frac{P}{V(P_o-P)}$ as ordinate against P/P_o gives terms of the form $y = mx + B$ where b is equal to $\frac{1}{V_mC}$ and m is equal to $\frac{C-1}{V_mC}$. The above relationship by rearranging terms can be written as $V_m = \frac{1}{\text{slope} + \text{intercept}}$. If the weight of sample used is known along with V_m, the surface area is

$$\text{S.A.} = \frac{V_m \times 5.243 \times 10^4}{\text{gm. wt. of sample}} = \text{sq. cm./ gm.}$$

The value of 5.243×10^4 is found by the following:

(1) one cc. of gas at (STP) has

$$\frac{6.02 \times 10^{23} \text{ molecules/mol. wt.}}{22.400 \text{ cc. gas per mol. wt.}} = 2.688 \times 10^{19} \text{ molecules}$$

(2) although Livingston (1949) has suggested a cross-sectional area for the krypton molecule as 18.5 sq. A., most people assume a value of 19.5 sq. A.

Thus the area covered by 1 cc. of gas for V_m is

$$\frac{2.688 \times 10^{19} \times 19.5\text{A}}{10^{16} \text{ sq. A./ sq. cm.}} = 5.243 \times 10^4 \quad \frac{\text{sq. cm. area}}{\text{cc. gas}}$$

Using the above reasoning, the surface area was calculated for the gibbsite samples as follows: (coarse gibbsite)

(1) 5.61 gms. was placed in the sample container

(2) V_m was calculated as 0.169

Hence

$$\text{S.A.} = \frac{0.169 \times 5.234 \times 10^4}{5.61}$$

$$= 1440 \text{ cm.}^2\text{/gm.}$$

Appendix II

Description of Sedimentation Method

The sedimentation container was made of glass and had the shape of a cylinder with an inside diameter of 6" and a length of 20". Approximately 1% of solids by weight was used in these experiments. For any predetermined grain size, 20 grams of gibbsite was placed into two liters of water to which 10cc. of a 10% solution of Calgon, as dispersant, was added. The mixture was then violently agitated with the use of a glass rod, first in a clockwise direction and then slowly in a counter-clockwise motion until the liquid was at rest. The stopwatch was then started and the experiment was run for a length of time necessary for a calculated particle size to settle a definite distance. After the particle has settled to the calculated distance, the portion above this liquid plane is siphoned off and the container is again refilled to volume. The same process is repeated until the liquid above the settling plane becomes clear which is the end point for particles finer than the calculated size to be present. The siphoned material is then allowed to dry slowly at 50°C.

For all wet-sedimentation methods, the following conditions must be met:

(1) Reynolds number is less than 0.6.

(2) the solid is completely dispersed

(3) the suspension is no greater than 1% solids by weight

(4) the minimum diameter of the sedimentation tube is 10 cm.

(5) experiments be run at constant temperature

(6) no mechanical disturbance of the liquid

(7) particles are larger than imhomogeneities in the liquid (greater than intermolecular distances in liquid)

According to Stokes' law, the terminal settling velocity of a single spherical particle falling at low velocity in a quiescent, homogeneous fluid of infinite extent is given by:

$$v = \frac{g(\rho - \rho_F)d^2}{18u}$$

where v = terminal velocity in cm./sec.

g = acceleration of gravity in centimeters per second per second

ρ = density of particle in gms./cc

ρ_F = density of fluid in gms./cc.

d = diameter of particle in cm.

u = viscosity of fluid in poises

Calculation of the settling velocity of a 20 micron particle of gibbsite would be

$$v = \frac{980(2.4-1.0)\ (.002)^2}{18(.01)}$$

$$= \frac{0.005488}{.18} = 0.031 \text{ cm./sec}$$

$$v = .031 \text{ cm./sec. x } 60 \text{ sec./min.}$$

$$= 1.86 \text{ cm./min}$$

Thus a 20 micron particle would settle through 25 cm. in

$$\frac{25 \text{ cm.}}{1.86 \text{ cm./min.}} = 13.41 \text{ minutes}$$

In the particular case at hand, the experiment would run for 13.41 minutes for settling a 20 micron particle through a distance of 25 cm. The liquid above the 25 cm. would then be siphoned off and theoretically should contain only particles less than 20 microns. It is realized that in practice only an approximation to Stokes' law calculations can be made which necessitates almost an infinite number of sedimentations to effect a pure separation.

A portion of the 20 micron sample is still available for future work should the occasion arise.

Appendix III

Calculation of Standard Deviation

Measurement (X)	$X-\bar{X}$	$(X-\bar{X})^2$
57.81	+.28	.0784
57.81	+.28	.0784
57.97	+.44	.1936
57.22	-.31	.0961
57.54	+.01	.0001
57.54	+.01	.0001
57.21	-.32	.1024
57.88	+.05	.0025
57.19	-.34	.1156
57.46	-.07	.0049
57,533		.6721

$$\bar{X} = \frac{\Sigma X}{n}$$

$\bar{X}$ = average of measurements

X = a single measurement

n = no. of measurements

$$\text{Standard Dev.} = \left(\Sigma \frac{(X-\bar{X})^2}{n-1}\right)^{\frac{1}{2}}$$

$$\bar{X} = 57.53$$

$$\text{S.D.} = \left(\frac{.6721}{9}\right)^{\frac{1}{2}} = 0.27$$

Thus in the table the temperature is recorded as 57.53 ± 0.27. This simply means that the temperature determined for all these points can be expressed 68% of the time or one standard deviation as $57.53^{\circ}C \pm 0.27^{\circ}C$.

For the resistance we have

(See following page for table)

X	$X-\bar{X}$	$(X-\bar{X})^2$
11010	+130	16900
10970	+ 90	8100
10970	+ 90	8100
10820	- 60	3600
10760	-120	14400
10730	-150	22500
10870	- 10	100
10810	- 60	3600
10940	+ 60	3600
10920	+ 40	1600
108,800		65,600

$$\bar{X} = 10,880$$

$$S.D. = \left(\frac{65,600}{9}\right)^{1/2} = 87$$

The resistance is 10880 $\pm$ 87 ohms 68% of the time. Thus by the methed of standard deviation the points have been determined as

$$57.53 \pm 0.27^{\circ}C$$

$$10880 \pm 87 \text{ ohms}$$

Appendix IV

Method of Least Squares

This method is an important application of minimizing a function of two variables and is important to the fitting of a straight line to experimental points. The line is of the form

$$y = mx + b \text{ (positive slope)}$$

$$y = -mx + b \text{ (negative slope)}$$

Let the observed experimental points be (X_1, Y_1), (X_2, Y_2).....(X_n, Y_n). Corresponding to each of the observed values of X we consider two values of y, namely, the observed value Y_{OBS} and the value predicted by the straight line $mX_{OBS}+b$. The difference is $Y_{OBS} - (mX_{OBS}+b)$ called a deviation. Each deviation measures the amount by which the predicted value of y falls short of the observed value. The set of all deviations

$$d_1 = y_1-(mX_1+b),.....dn = y_n-(mX_n+b)$$

which gives the description of how well the line fits the observed data. The line is perfect, if and only if, all of these deviations are zero. In general, no straight line will give a perfect fit. The problem thus established is to find the line which best fits the data. This is the method of least squares. For a straight line which comes close to fitting all of the observed points, some of the deviations will be positive and some negative. Their squares, however, will all be positive and the expression

$$f(m,b) = (Y_1-mX_1-b)^2 + (Y_2 -mX_2 -b)^2+.....+(Y_n-mX_n-b)^2$$

counts a positive deviation d and a negative deviation -d equally. This sum of squares of deviations depends upon the choice of m and b. It is never negative and it can be zero only if m and b have values which produce a perfectly fitting straight line. Thus the method of

least squares seeks to determine the line of best fit for which the sum of squares of the deviations

$$f(m,b) = d_1^2 + d_2^2 + \ldots\ldots d_n^2$$

is a minimum. Hence, it is necessary to solve for m and b where the surface expression $w = f(m,b)$ in mbw-space has a minimum. Thus we must solve simultaneously the equations

$$\frac{\partial f}{\partial m} = 0 \; ; \quad \frac{\partial f}{\partial b} = 0$$

This is done by having

$$f(m,b) = \Sigma (Y_{OBS} - mX_{OBS} - b)^2$$

where Y_{OBS}, X_{OBS} are the observed or given coordinates of the points to be fitted to the line. The data for curve A, Figure VI.1 are tabulated as follows:

X_{OBS}	Y_{OBS}	Dev. = $Y_{obs}-mX_{obs}-b$	$(Dev.)^2$
43.89	4.026	$4.026-43.89m-b$	$16.21-8.052b+b^2-353.4m+87.78mb+1926m^2$
45.30	4.019	$4.019-45.30m-b$	$16.15-8.038b+b^2-364.2m+90.60mb+2052m^2$
51.20	4.000	$4.000-51.20m-b$	$16.00-8.000b+b^2-409.6m+102.40mb+2621m^2$
58.41	3.992	$3.992-58.41m-b$	$15.94-7.984b+b^2-466.4m+116.82mb+3411m^2$
68.70	3.979	$3.979-68.70m-b$	$15.83-7.958b+b^2-546.8m+137.40mb+4720m^2$
77.30	3.962	$3.962-77.30m-b$	$15.70-7.924b+b^2-612.5m+154.60mb+5975m^2$
84.78	3.945	$3.945-84.78m-b$	$15.56-7.890b+b^2-669.0m+169.56mb+7188m^2$
88.25	3.941	$3.941-88.25m-b$	$15.53-7.882b+b^2+695.6m+176.50mb+7788m^2$
94.84	3.929	$3.929-94.84m-b$	$15.44-7.858b+b^2-745.2m+189.68mb+8995m^2$
100.60	3.916	$3.916-100.60m-b$	$15.34-7.832b+b^2-787.8m+201.20mb+10120m^2$
88.12	3.920	$3.920-88.12m-b$	$15.37-7.840b+b^2-690.8m+176.24mb+7765m^2$
72.42	3.957	$3.957-72.42m-b$	$15.66-7.914b+b^2-573.2m+144.84mb+5245m^2$
50.95	3.984	$3.984-50.95m-b$	$15.87-7.968b+b^2-405.8m+101.90mb+2596m^2$
44.29	4.007	$4.007-44.29m-b$	$16.06-8.014b+b^2-355.0m+88.58mb+1962m^2$

$$\Sigma (dev)^2 = 220.66 - 111.154b + 14b^2 - 7675.3m + 1938.10mb + 72364m^2$$

$$\frac{\partial f}{\partial m} = 0 = -7675.3 + 1938.1b + 144728m$$

$$\frac{\partial f}{\partial b} = 0 = -111.154 + 28b + 1938.1\,m$$

or we have the two equations

$$7675.3 = 1938.1\,b + 144728\,m \qquad (1)$$

$$111.154 = 28\,b + 1938.1\,m \qquad (2)$$

Multiplying (1) by +1 and (2) by -69.217 we get

$$7675.3 = 1938.1\,b + 144728\,m \qquad (1)$$

$$-7693.7 = -1938.1\,b - 134149\,m \qquad (2)$$

$$(1)+(2) \quad -18.4 = 0 + 10579\,m$$

$$m = \frac{-18.4}{10579}$$

$$m = -0.00174$$

Then substituting m into (2) gives $111.154 = 28\,b + 1938.1(-0.00174)$

$$28\,b = 111.154 + 3.37$$

$$b = 4.09$$

$$y = -0.00174X + 4.09$$

X	Y
40	4.021
50	4.003
60	3.986
70	3.968
80	3.951
90	3.933
100	3.916

Thus the equation of the line for curve A, Figure VI.1 is

$$Y = -0.00174X + 4.09$$

and the plotted points are those given above for X and Y.

Appendix V

Derivation of the Calusius-Clapeyron Equation for Calculating Heat of Reaction

For a system of the type

(1) $AB_{solid} \rightleftharpoons A_{solid} + B_{gas}$ at a given P_1T_1

$\Delta F_R = 0$ at equilibrium. Now if the system is changed so that

(2) $AB_{solid} \rightleftharpoons A_{solid} + B_{gas}$ at $P + dP$ and $T + dT$

$d\Delta F = 0$ at equilibrium.

We can write

(3) $dF_{AB} = -S_{AB}dt + V_{AB}dP$ and

(4) $dF_{A+B} = -S_{A+B}dt + V_{A+B}dP$

$$dF = (3)-(4) = -(S_{AB} - S_{A+B})dt + (V_{AB} - V_{A+B})dP = 0$$

$$dP = \frac{(S_{AB} - S_{A+B})\,dt}{(V_{AB} - V_{A+B})}$$

$$\frac{dp}{dt} = \frac{S_{AB} - S_{A+B}}{V_{AB} - V_{A+B}} = \frac{\Delta S}{\Delta V}$$

From the relationship

$\Delta F = \Delta H - T\Delta S$ at equilibrium where $\Delta F = 0$

$\Delta S = \frac{\Delta H}{T}$ which gives

$$\frac{dp}{dt} = \frac{\Delta H}{T\Delta V}$$

If the stated reaction takes place at temperatures where the change in volume of AB and A can be neglected, we can write $V = V_B$ = volume of the gas. If the gas behaves as an ideal substance at the temperature range of interest,

$V_B = \frac{RT}{P}$ from the relationship

$PV = RT$ which now yields

$$\frac{dp}{dt} = \frac{P \Delta H}{RT^2}$$ or separating variables

gives

$$\frac{dp}{P} = \frac{\Delta H\, dt}{RT^2}$$ which is written

in the form

$$\frac{d\ln P}{dt} = \frac{\Delta H}{RT^2} \qquad (5)$$

This is the form of the Calusius-Clapeyron equation.

Now the Clausius-Clapeyron equation can be applied to calculate ΔH for hydrate or hydroxide dissociation pressures. The equilibrium constant at moderate temperatures for these reactions involves only the partial vapor pressure of water. The equilibrium constant can be written as

$$K_R = P^M$$ where P = partial pressure of water vapor

M = no. of moles of water vapor

Hence $$\frac{d\ln P^M}{dt} = \frac{\Delta H}{RT^2}$$ which becomes

$$\frac{d\ln P}{dt} = \frac{\Delta H}{MRT^2}$$

This expression can be integrated by assuming ΔH constant and converting to logarithms to the base 10 to give

$$\log_{10} P = \frac{(-\Delta H)}{(2.303MR)} \frac{1}{T} + \text{constant}$$

If the $\log_{10} P$ vs. $\frac{1}{T}$ is plotted, the slope of the line is $(-\Delta H/2.303MR)$. Hence ΔH can be calculated from the expression $\Delta H = -2.303MR\ (\text{slope})$.

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Biographical Sketch

Cooper Harry Wayman was born at Trenton, New Jersey on January 29, 1927. He is the son of Cooper O. and Helen U. Wayman, Trenton, New Jersey. He received his pre-college education in the public school system of Hamilton Township, Trenton, New Jersey.

He entered the U.S. Navy on February 20, 1945 and was honorably discharged as a radarman third class on July 23, 1946.

He has attended the following educational institutions:

Trenton State Teachers College, Trenton, New Jersey	1947-1949
Rutgers University, New Brunswick, New Jersey	1949-1951
University of Pittsburgh, Pittsburgh, Pa.	1953-1954
Carnegie Institute of Technology, Pittsburgh, Pa.	1953-1954
Massachusetts Institute of Technology, Cambridge, Mass.	1954-1958
Michigan State University, E. Lansing, Michigan	1958-1959

He received a B.S. in Geology from Rutgers University, 1951, an M.S. in Geology from the University of Pittsburgh, 1954, and a Ph.D. in Geology with a minor in physical chemistry from Michigan State University in September 1959.

He is a member of the following honorary societies:

Sigma Xi(MIT)
Sigma Gamma Epsilon (Michigan State)

and holds professional membership in the American Institute of Mining, Metallurgical, and Petroleum Engineers and the American Geophysical Union.

His professional experience consists of the following:

Geologist	American Agricultural Chem. Co. Pierce, Florida	1951-1952
Geologist	Lone Star Steel Co. Lone Star, Texas	1952-1953
Research Technologist	U.S.Steel Corporation Pittsburgh, Pa.	1953-1954

(Professional experience con't):

Research Assistant	Department of Metallurgy MIT, Cambridge, Mass.	1954-1956
Consultant	U.S. Steel Corporation Pittsburgh, Pa.	1955
Consultant	Union Carbide Ore Co. New York, New York	1956
Consultant	Kaiser Aluminum and Chem. Corp. Oakland, Calif.	1957-1958
Teaching Assistant	Department of Geology & Geophysics MIT, Cambridge, Mass.	1956-1957
Teaching Assistant	Department of Geology Michigan State University East Lansing, Michigan	1958-1959
Senior Technologist	Applied Research Lab. U.S. Steel Corp. Monroeville, Pa.	September 1959

He is co-author of a paper entitled "The Effect of Chemical Reagents on the Size, Shape and Terminal Velocity of Single Air Bubbles in Solution" with D.W. Fuerstenau, Mining Engineering, June 1958.

He married Ruth Treier on June 16, 1951, and they have two children, Carol Beth ($2\frac{1}{2}$ years) and Andrea Lee (8 months) of age.