THERMODYNAMIC PROPERTIES OF SOME ALKALI METAL PEROXIDES AND SUPEROXIDES

AND

THE DISSOCIATION ENERGY OF FLUORINE

by

John L. Margrave
B.S., University of Kansas, 1948

Submitted to the Department of Chemistry and the Faculty of the Graduate School of the University of Kansas in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Advisory Committee:

Redacted Signature

Redacted Signature

Redacted Signature

Redacted Signature

December, 1950

ACKNOWLEDGMENTS

Appreciation is to be expressed to Dr. Paul W. Gilles for suggesting these problems, and for his constant interest and help in the course of this work.

Dr. William H. Schechter of The Mine Safety Appliance Company and Dr. Edgar J. Seyb are to be thanked for supplying samples of Na_2O_2, NaO_2, and KO_2 which were used in the study of the superoxides. Mr. Virgil Haney is also to be thanked for his aid in preparing many of the samples for the gasometric and calorimetric experiments.

The author is particularly grateful for a University Fellowship, the E. E. Slosson Scholarship, and an Atomic Energy Commission grant which made this research possible.

PART I

THERMODYNAMIC PROPERTIES OF SOME ALKALI METAL PEROXIDES AND SUPEROXIDES

PART I

TABLE OF CONTENTS

INTRODUCTION

The action of oxygen on the alkali metals leads to the formation of three series of compounds: the normal or monoxides M_2O, the peroxides M_2O_2, and the superoxides MO_2. It has not been possible to prepare each of these oxides for all of the alkali metals in any form pure enough for analysis and study, but some of these compounds have been known for nearly fifty years. In spite of this, most of the thermodynamic properties of the alkali metal oxides have not been determined. It is the object of this thesis to present the results of a research project on which the superoxides of sodium and potassium and sodium peroxide were studied.

The direct action of oxygen at ordinary pressures on lithium produces the monoxide, Li_2O, and a trace of the peroxide, while sodium is oxidized directly to the peroxide, Na_2O_2, and potassium, rubidium, and cesium are oxidized to the superoxides KO_2, RbO_2, and CsO_2. It is only by special methods that one may form the other oxides. The monoxides may be produced by the action of a given alkali metal on the corresponding nitrate according to the equation

$$5\ M + MNO_3 = 3\ M_2O + \tfrac{1}{2}\ N_2$$

or by oxidation of the metal in the presence of a limited amount of oxygen. The peroxides are, of course, derivatives of hydrogen peroxide, but thus far only Li_2O_2 and Na_2O_2 are known definitely to exist. Lithium superoxide has never been prepared although experiments have indicated that this superoxide may be stable in liquid ammonia solutions at low temperatures (49). Sodium superoxide has been produced in high yield by methods developed at the University of Kansas by Schechter, Stephanou, Thompson, Seyb, Argersinger, Sisler, and Kleinberg (1, 34, 35) which involve either the oxidation of sodium metal while it is dissolved in liquid ammonia or the further oxidation of sodium peroxide under a high pressure of oxygen at elevated temperatures.

The Previous Work on Thermodynamic Properties of Alkali Metal Oxides

Since many of the alkali metal oxides were known fifty years ago, there have been several investigations of the thermochemistry of these compounds. Probably the most notable of the investigators was the French thermochemist, de Forcrand, (14, 15, 16, 17, 18, 19) who determined or estimated heats of formation for Li_2O, Li_2O_2, Na_2O_2, KO_2, Rb_2O_2, RbO_2, and CsO_2 using heats of solution in water or sulfuric acid. Another French worker who contributed to the knowledge of the alkali metal oxides was Rengade (43, 44) who studied Na_2O, K_2O, Rb_2O, Cs_2O and determined their heats of formation by heats of solution in water. This work was all done in the period 1898 - 1914, and it now seems that in some cases the compounds used were of uncertain composition. This makes it desirable to have new values for the heats of solution either to verify or to correct the presently available data on heats of formation since they may be used to compute equilibrium constants for the decomposition reactions and the electron affinity of oxygen when combined with other experimental and estimated data. Dissociation pressure studies have been carried out on KO_2 by Kraus and Whyte (36), Blumenthal (6), Kazarnovskii and Raikhshtein (32), and Todd (51). Blumenthal (5) has also studied the dissociation pressure of Na_2O_2. No experiments of this type have been performed with NaO_2.

The heats of solution as determined by these early twentieth century workers were accepted essentially without much question for many years, but, in 1946, Kaule and Roth (29) undertook a thorough investigation of the thermochemistry of sodium and re-determined the heats of solution of Na, NaOH, Na_2O, and Na_2O_2 in water. Their data differ from the old values by 2 - 5%. This deviation and the synthesis at the University of Kansas of the previously unknown NaO_2 have led to the work described in this thesis.

The Present Work on Thermodynamic Properties of Alkali Metal Oxides

A series of experiments has been carried out to determine:

(1) the heat of solution of Na_2O_2 in water. It was assumed

that the reaction taking place was

$$Na_2O_2(s) + H_2O \overset{MnO_2}{=} 2\ NaOH(sol'n) + \tfrac{1}{2}\ O_2(g)$$

(2) the heat of solution of Na_2O_2 in 0.0899 N. sulfuric acid. The reaction was assumed to be

$$Na_2O_2(s) + 2\ H_2SO_4(sol'n) = 2\ NaHSO_4(sol'n) + H_2O_2(sol'n)$$

(3) the heat of solution of NaO_2 in water. The reaction assumed was

$$2\ NaO_2(s) + H_2O \overset{MnO_2}{=} 2\ NaOH(sol'n) + 3/2\ O_2(g)$$

(4) the heat of solution of NaO_2 in 0.0899 N. sulfuric acid. The reaction assumed was

$$2\ NaO_2(s) + 2\ H_2SO_4(sol'n) = 2\ NaHSO_4(sol'n) + H_2O_2(sol'n) + O_2(g)$$

(5) the heat of solution of KO_2 in water. The reaction was assumed to be

$$2\ KO_2(s) + H_2O \overset{MnO_2}{=} 2\ KOH(sol'n) + 3/2\ O_2(g)$$

(6) the heat of solution of KO_2 in 0.1677 N. sulfuric acid. The reaction was assumed to be

$$2\ KO_2(s) + 2\ H_2SO_4(sol'n) = 2\ KHSO_4(sol'n) + H_2O_2(sol'n) + O_2(g)$$

(7) the heat of solution of KCl in water. The reaction was

$$KCl(s) + H_2O = KCl(sol'n)$$

(8) the heat of solution of Mg in 0.1084 N. HCl. The reaction was

$$Mg(s) + 2\ HCl(sol'n) = MgCl_2(sol'n) + H_2(g)$$

The data have been obtained with a Dewar flask calorimeter to a precision of about 0.5%.

The heats of solution have been used to calculate the heats of formation of the peroxides and superoxides involved by combination of the experimental data with data from the National Bureau of Standards Table "Selected Values of Chemical Thermodynamic Properties". The heats of formation of the superoxides have in turn been used to calculate the electron affinity of oxygen through a Born-Haber thermochemical cycle. The heats of the KCl and Mg reactions were measured for the purpose of calibrating the calorimeter.

A series of rough determinations was also undertaken to find values for the specific heats and melting points of sodium peroxide, sodium superoxide, and potassium superoxide.

The combination of the results of these experiments and the presently available thermochemical data allow some predictions to be made regarding the dissociation pressures of these compounds, their entropies of formation, and the various interconversion reactions. These topics are discussed in the final section of the superoxide portion of this thesis.

HEATS OF SOLUTION AND HEATS OF FORMATION

The heats of solution of sodium peroxide, sodium superoxide, and potassium superoxide in water were determined in a conventional calorimeter at 25 ± 1° C. The calorimeter consisted of a Dewar flask of two liters capacity fitted with a tight-fitting rubber stopper through which a stirring rod, gas escape tube, and a breaking mechanism were passed. The entire assembly was submerged in a constant temperature water bath at about 25° C. A ten-gallon crock served as the water bath and a 200 watt light bulb as the heat source which was turned on and off when necessary by a relay circuit in which the control device was a "Metastatic" mercury thermoregulator. The bath temperature was found to remain constant to ±0.02° C. as the column of mercury in the regulator moved from the high to the low position with variation in the temperature of the water bath. The circuit is illustrated in Figure 1.

Description of a Typical Calorimeter Run

In a normal run, the Dewar flask was filled with 950 grams of water or acid solution at 24° C. For the peroxides and superoxides reacting with water, it was necessary to add approximately two grams of MnO_2 to catalyze the decomposition of the intermediate peroxide to hydroxide. The sample

CONTROL CIRCUIT FOR CONSTANT TEMPERATURE WATER BATH

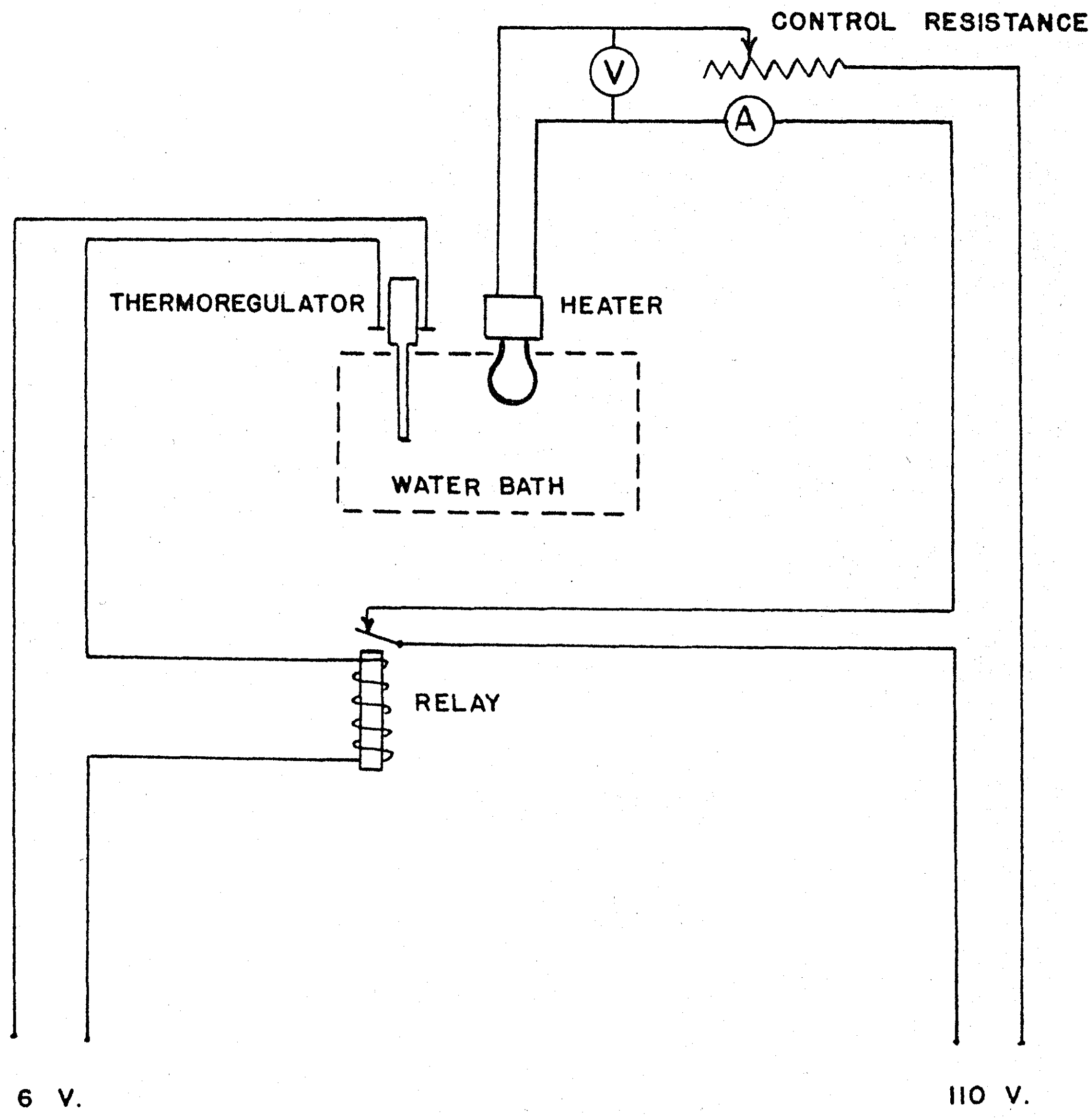


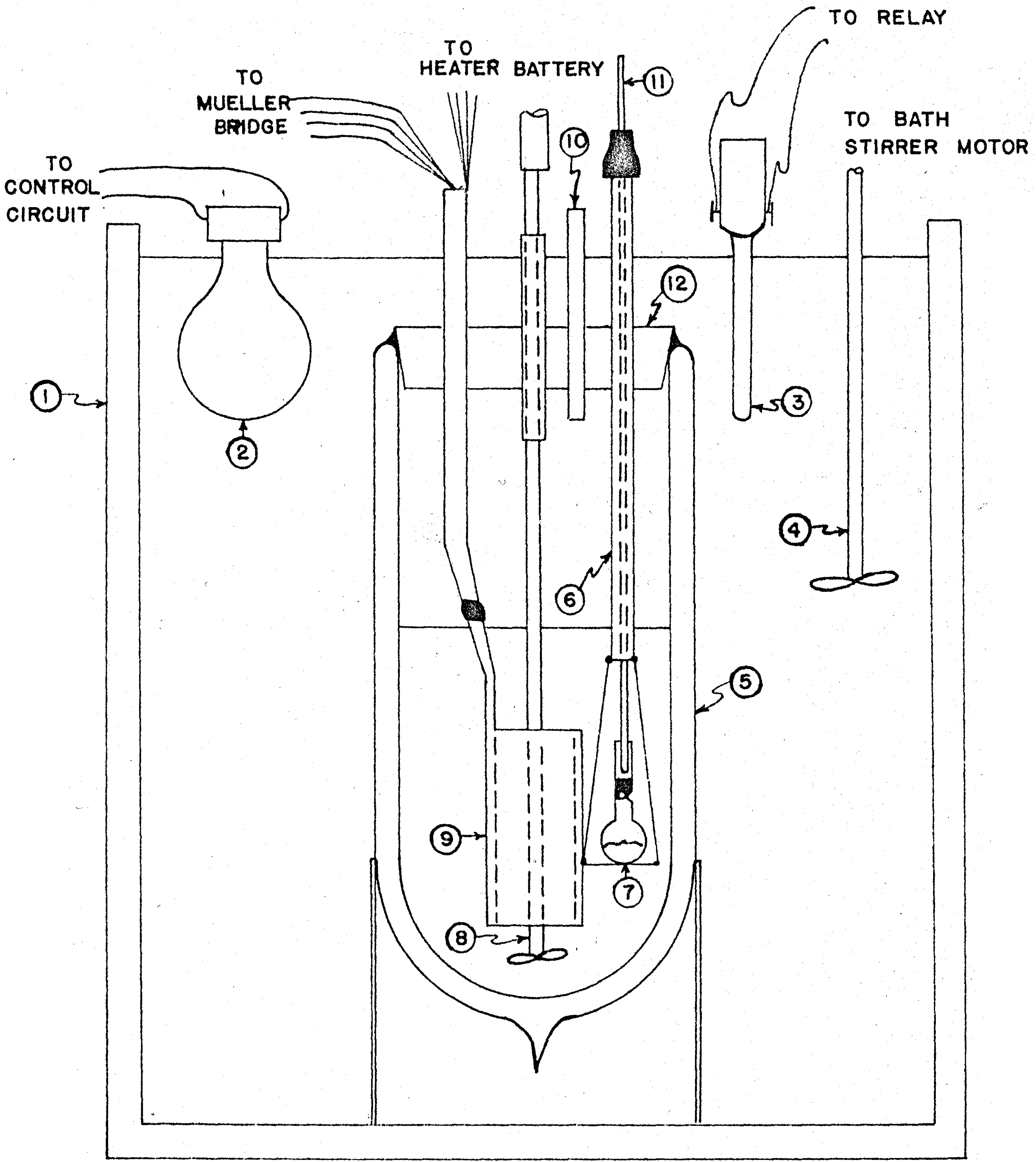
Figure 1

was placed in the breaking device and when the cork was fitted into the Dewar flask and sealed with Lubriseal grease, the entire flask was placed in the water bath as shown in Figure 2. The stirrer motor was connected to the stirrer and caused a constant stirring of the water in the Dewar ~~bath~~ at 375 ± 25 rpm.

The temperature of the liquid in the Dewar flask was brought to approximately 24° C. at the start of each run. After the flask was in place, the water level in the crock was raised to at least ½ inch above the top of the flask. The resistance of the resistance thermometer was read at three to ten minute intervals to determine the rate of temperature drift and thus, the rate of heat exchange between the water bath and the Dewar flask. When a constant rate of exchange, or drift, was obtained, heat was then added to the liquid in the Dewar flask by means of a current through the manganin heater coil enclosed in the same silver case as the resistance thermometer. Currents of the order of 0.15 amperes through the 77.72 ohm resistance were obtained from four storage batteries connected in a series-parallel arrangement such that the drain on each battery was approximately 0.075 amperes. The accurate measurement of current was made across a one ohm standard resistance with a K-2 type Leeds and Northrup potentiometer. This current value, together with the resistance of the heater coil which was measured when it was originally assembled, and re-measured

Figure 2

SCHEMATIC DIAGRAM OF CALORIMETER



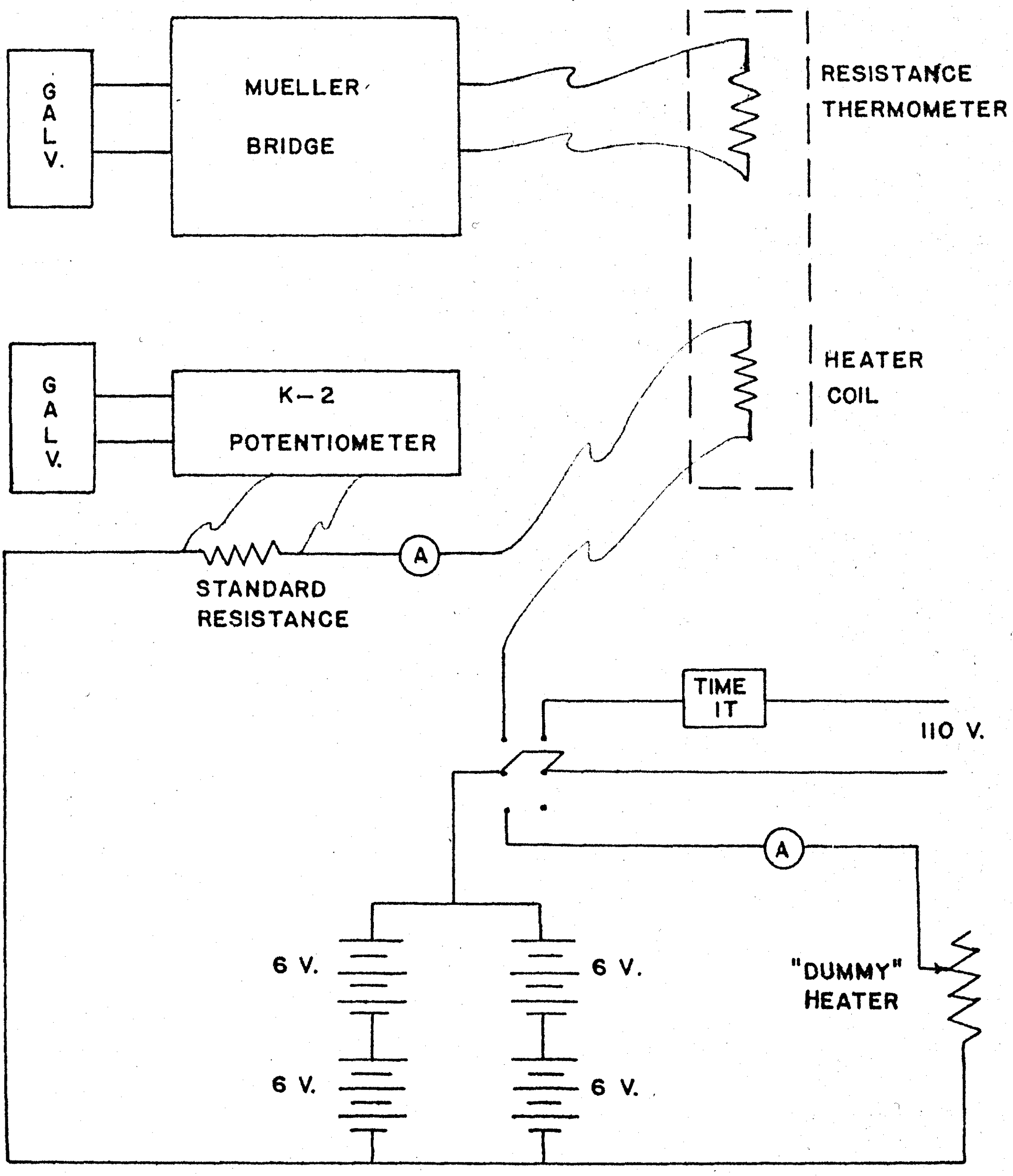
1. EARTHEN CROCK
2. 200 WATT LIGHT BULB
3. THERMOREGULATOR
4. WATER BATH STIRRER
5. DEWAR FLASK
6. BREAKING MECHANISM
7. SAMPLE BULB
8. DEWAR STIRRER
9. RESISTANCE THERMOMETER AND HEATER
10. GAS ESCAPE TUBE
11. GLASS ROD
12. RUBBER STOPPER

at frequent intervals, allowed the calculation of the energy put into the system as heat. The resistance thermometer was used to follow the temperature changes throughout this heating period of ten to twenty minutes and readings were taken until the drift or rate of heat exchange again became constant. The time of each heating was measured to the nearest 0.1 second with an electric Time-It manufactured by the Precision Scientific Company. The Time-It was turned on and off at the same instant the heating current was started or stopped since the two circuits were on different blades of the same knife switch. The heater and thermometer circuits are given in Figure 3.

As soon as the drift was once more constant, the bulb containing the sample to be studied was broken by depressing the glass rod of Figure 2 and crushing the bulb against the copper ring. Readings of the resistance thermometer were again made at intervals of one to five minutes to follow the solution of the sample and were continued until a constant drift was found. This, of course, provided all of the information actually required to determine a heat of solution; but, to assure a proper determination, a second electrical calibration was made. The results of such a run, interpreted graphically, were used along with the known weight of sample dissolved to calculate the heat of solution of the sample in calories per gram. In some of the runs performed after the characteristics of the calorimeter had been well established, two runs were made with just one calibration between the two serving for both runs.

Figure 3

CIRCUIT DIAGRAM FOR RESISTANCE THERMOMETER AND HEATER COIL



Description of Special Apparatus

Several parts of the calorimeter were necessarily built or chosen to fit the installation. These are described in the following section as to specifications and methods of assembly, as well as with some suggestions for improvements.

Water Bath

A ten-gallon earthen crock was used as a water bath and was filled with water to ½ inch from the top. This would cover the Dewar flask and rubber stopper with about ½ inch of water. The regulator circuit has been shown and a 200 watt light bulb was found to furnish a good source of heat for the bath which was in a constant temperature room regulated at 23° C. The mercury regulator in the bath was adjusted for 25° C. as nearly as possible, but it was found that over a period of time the regulator would show a definite drift such that the bath temperature once rose as high as 26.7° C. This change was slow and did not have any effect in the course of a normal run which required from two to four hours.

Heater Coil and Resistance Thermometer

The heater and resistance thermometer were both wound non-inductively on a core of five mil pure silver over a base of tissue paper lacquered with glyptal manufactured by General Electric. The heater coil was wound from No. 40 double silk covered manganin wire and had a resistance of

77.72 ohms, and the thermometer coil was of No. 40 black enameled copper wire of about 84.4 ohms resistance at 25° C. The heater and thermometer coils were separated about $\frac{1}{8}$ inch on the three inch core and were covered with a glyptal lacquered tissue paper layer when completely wound. The leads to the heater coil were of No. 24 copper wire about 12 inches long, while the thermometer had leads of No. 24 single silk covered manganin wire about 48 inches long.

Considerable difficulty was met in getting a heater assembly that did not leak. Any leakage would allow some electrolysis of water to occur in the heater between the positive and negative sides of the resistance, and this would make the calculated I^2R-heat wrong. The final heater was made with the inner cylinder flared outward about 1/16 inch on the ends so that after the wires were wound on the core, the outer shell fitted tightly. A soft-soldered joint around the periphery was necessary on each end. A silver tube was used to carry the leads from the coil to a glass tube that passed through the rubber stopper of the Dewar flask.

Apparatus for Measurement of Current

The current passing through the heater was measured by determining the voltage drop across a one ohm standard resistance in series with the heater. This resistance, Leeds and Northrup, Catalog No. 4210, Serial No. 661748, was calibrated at the National Bureau of Standards and was found to have a resistance of 0.999990 absolute ohms. Since the Leeds and Northrup type K-2 potentiometer, Serial No. 749003, could be read only to 0.00001 absolute volt, the standard resistance was for all practical purposes equal to one ohm; thus, the current through the resistance was assumed to be numerically equal to the voltage drop across it. The standard resistance was immersed in transformer oil and the temperature of the oil was observed during the course of several heatings with an accurate mercury thermometer, but no heating was noted. That the heater coil itself did not change resistance in the course of a heating period was shown by measuring the current and the voltage and calculating the heater resistance at various times during a run.

The K-2 potentiometer was checked with an Eppley Low Temperature Coefficient Standard Cell, Serial No. 425966, that had been calibrated at the Bureau of Standards and found to have a potential of 1.01920 absolute volts. The galvanometer that was used for balancing was a Leeds and Northrup, Catalog No. 24208, Serial No. 720212, with a sensitivity of 15 microvolts per millimeter and a period of 2.9 seconds.

Apparatus for Measurement of Resistance

All resistances were measured with a Mueller thermometer bridge, Leeds and Northrup, Catalog No. 8069, Serial No. 740547, to the nearest 0.0001 ohm. This bridge had been calibrated at the Bureau of Standards. The galvanometer used with the bridge was Leeds and Northrup, Catalog No. 2284-d, Serial No. 728926, which had a sensitivity of 0.1 microvolt per millimeter at one meter, and a period of 5.1 seconds. To increase the sensitivity of the system, a telescope and mirror arrangement was used to increase the length of the path of light from the galvanometer mirror to the scale. This corresponded very nearly to the addition of another significant figure to the measured resistance.

Calibration of the Calorimeter

The calorimeter was calibrated by (1) checking the known heats of certain chemical reactions, (2) calculating the total heat capacity of the calorimeter by considering its component parts, and (3) passing a known electric current through the heater resistance for a measured length of time and measuring the temperature change resulting.

Two chemical reactions were used for calibration of the calorimeter:

$$M_g(s) \overset{2}{+} 2HCl(0.1\ N.) = M_gCl_2(\text{in } 0.1\ N.\ HCl) + H_2(g)$$

$$KCl(s) + 200\ H_2O = KCl(\text{in } 200\ H_2O)$$

The M_g reaction is very similar to the superoxide solution reaction. The heat of solution of M_g in 1.0 N. HCl has been determined by Shomate and Huffman (23) to be -111,322 ± 41 calories per mole at 25° C. The results of two runs of samples of Merck M_g ribbon, which was cleaned in HCl, washed, and dried before using, indicated a heat of solution of -111,650 calories per mole in 0.1 N. HCl at 22.6° C. This gives -111,400 calories per mole when corrected to correspond to the reaction studied by Shomate and Huffman.

Two runs were also made with samples of Baker's Analyzed KCl. The solution of KCl in water is an endothermic process and no gas is evolved contrary to the case for the superoxide solution reaction. The KCl was dried at 120° C. and had a heat of solution of 4,016 calories per mole at 24.8° C. in approximately 200 moles of water. By using values for heats of formation from the National Bureau of Standards Tables of Thermodynamic Properties, one finds that the heat of solution should be 4,201 calories per mole at 25° C. in 200 moles of water. Kaganovich and Mishchenko (24) give 4,194 ± 3 calories per mole as the heat of solution in 200 moles of water at 25° C. The deviations are of the order of four per cent, are not explainable on the basis of moisture or impurities in the sample, and as yet remain unexplained.

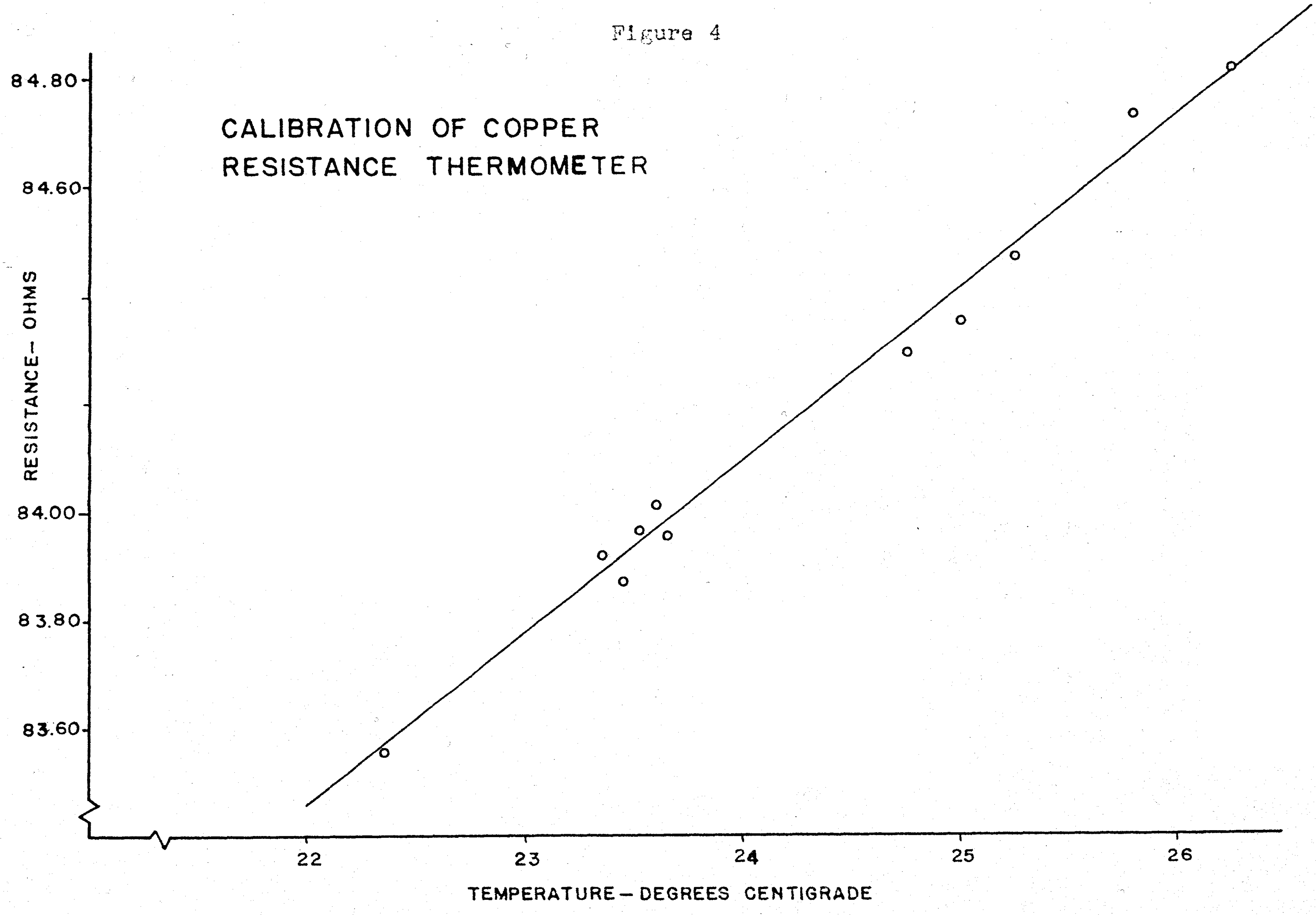
The total heat capacity of the calorimeter as used in a normal run has been calculated by considering the components of the system. These parts and their heat capacities were:

950 grams of H_2O at 25° C. - 948.10 calories/degree
2 grams of MnO_2 at 25° C. - 0.31 calories/degree
21 grams of silver at 25° C. - 1.13 calories/degree
5 grams of copper at 25° C. - 0.45 calories/degree
5 grams of glyptal at 25° C. - 1.00 calories/degree
240 grams of glass at 25° C. - 45.50 calories/degree
Total heat capacity - 996.49 calories/degree

The resistance thermometer was calibrated against a standard mercury thermometer which had been checked at the National Bureau of Standards. The sensitivity of the resistance thermometer was found to be 0.3229 ohms per degree by considering the plot of data in Figure 4. The value of the sensitivity as calculated from the temperature coefficient of resistance of copper, 0.00385, and the resistance of the resistance thermometer at 25° C., 84.4 ohms, was found to be 0.3249 ohms per degree. The agreement between the experimental and calculated values of the sensitivity is within the limits of accuracy of the calibration of the resistance thermometer. On the basis of the experimental value for the sensitivity and the calculated value for the heat capacity of the calorimeter and its contents, one finds that the amount of heat necessary to increase the resistance of the resistance thermometer 0.0001 ohms is 0.3086 calories. The mean of several experimental determinations of this quantity was 0.307 ± 0.002 calories.

The heat capacity of the calorimeter proper excluding the working liquids and samples has been computed by considering the values determined experimentally for the heating coefficient of the calorimeter in calories per 0.0001 ohm and the heat capacities of the individual liquids and solids present. For example, the average value of this coefficient for twelve runs with the calorimeter containing 950 grams of water, catalyst, and sample was 0.307. If one uses 0.998

Figure 4


CALIBRATION OF COPPER RESISTANCE THERMOMETER
RESISTANCE– OHMS
84.80
84.60
84.00
83.80
83.60
22
23
24
25
26
TEMPERATURE – DEGREES CENTIGRADE

calories per degree per gram as the specific heat of water, 0.152 calories per degree per gram as the specific heat of MnO_2, and 0.25 calories per degree per gram as the specific heat of the sample, he finds that the heat capacity of the calorimeter is 43.5 calories per degree. Similar calculations have been carried out on the basis of data taken on the calorimeter when filled with 0.1084 N. HCl, 0.1677 N. H_2SO_4, and CCl_4. The values computed for the heat capacity of the calorimeter were 39.6, 40.0, and 45.4 calories per degree respectively. The average of the experimental values for the heat capacity is 42.1 calories per degree as compared with the calculated value of 43.1 calories per degree.

The calorimeter was also studied with regard to its characteristics in exchanging energy with the water in the surrounding constant temperature water bath. The rate of change of the temperature of the liquid in the Dewar flask with time may be expressed by the equation

$$\frac{dT}{dt} = k(T_B - T) + w$$

where k is the leakage modulus of the system, T_B is the temperature of the water bath, T is the temperature of the liquid in the Dewar flask, and w is a constant term added to take into account the heat of stirring. Over the range of temperatures used in these experiments the resistance of the resistance thermometer was directly proportional to the temperature. The analytical expression describing the relation between R, the resistance of the resistance thermometer, and T, the temperature of the surrounding medium in degrees Centigrade, was found to be

$$T = \frac{R - 76.36}{0.3229}$$

Thus,

$$\frac{dT}{dt} = \left(\frac{dT}{dR}\right)\left(\frac{dR}{dt}\right) = k\left(\frac{R_B - 76.36}{0.3229} - \frac{R - 76.36}{0.3229}\right) + w$$

$$\frac{dR}{dt} = k(R_B - R) + w'$$

where $w' = 0.3229\ w$ and R_B is the resistance of the resistance thermometer at the temperature of the water bath. By considering the data obtained from several runs in the calorimeter containing water, computing the values for $\frac{dR}{dt}$, and plotting the average drift over a 0.1 ohm range of R versus ΔR, the difference between R_B and R when R_B is 84.96 ohms, one finds

$$k = 5.25 \times 10^{-4} \text{ per minute}$$

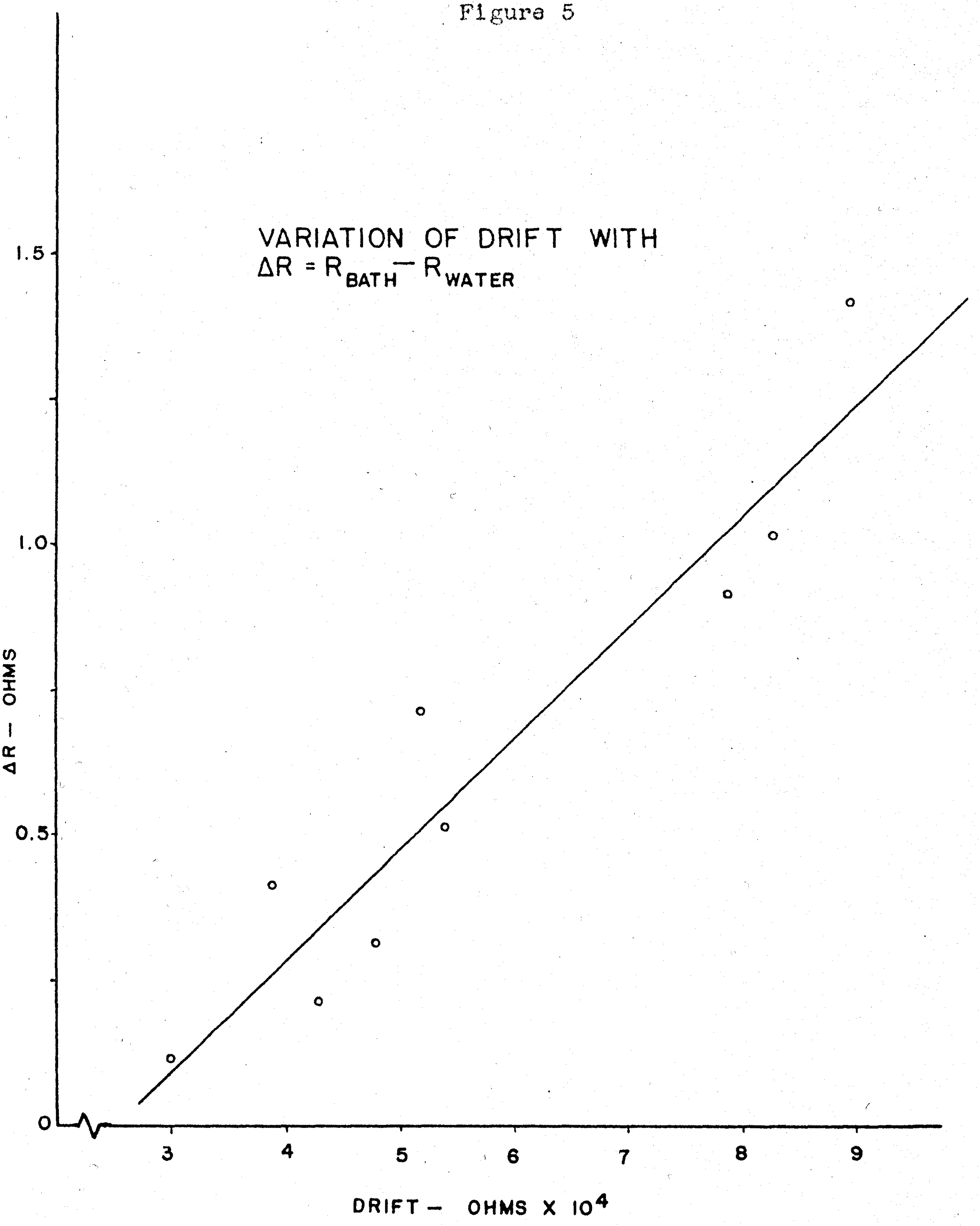
$$w' = 2.54 \times 10^{-4} \text{ ohms per minute}$$

from Figure 5. Converting to temperature units, the drift equation becomes

$$\frac{dT}{dt} = (5.25 \times 10^{-4})\ (T_B - T) + 7.7 \times 10^{-4}\ \frac{\text{degrees}}{\text{minute}}$$

These values, interpreted on the basis of the heat capacity data obtained experimentally, indicate a leakage from the

Figure 5


VARIATION OF DRIFT WITH
$\Delta R = R_{BATH} - R_{WATER}$
1.5
1.0
0.5
0
ΔR – OHMS
3
4
5
6
7
8
9
DRIFT – OHMS X 10^4

water bath into the Dewar flask of 0.52 calories per minute if the water in the Dewar flask is one degree cooler than the surrounding bath. The heat of stirring was found to be 0.78 calories per minute.

Preparation of Samples

The superoxides and peroxides used in these experiments were stored in a dry box or desiccator kept moisture free with P_2O_5 or $Mg(ClO_4)_2$. The bottles containing the tested materials were opened only for short periods in this dry atmosphere to remove samples for runs. The Na_2O_2 used was finely divided and showed rapid decomposition even with careful handling. The superoxides were supplied in small lumps and did not show such rapid reaction with the atmospheric water.

The lumps of NaO_2 and KO_2 were pulverized in an agate mortar, and the powdered sample was poured into a thin bulb blown from eight millimeter Pyrex tubing. The sample bulb had a constriction in the neck which served to hold a glass bead that was dropped in the neck after the bulb was filled. Several small pieces of Apiezon wax were melted over the bead with a nichrome heating coil connected to a 1 1/2 volt dry cell, sealing the sample in a dry atmosphere. This procedure is similar to one described by Robinson and Westrum (45) for preparing samples for calorimetric studies of various compounds of the transuranium elements.

Method of Calculation of Heats of Solution

The data obtained in the course of a normal run with a known weight of a given compound included a series of resistance measurements made before, during, and after two periods of electrical heating for measured times, and also a series of resistance measurements made at known times before, during, and after the given sample had been dissolved. The resistance measurements were plotted as ordinates versus time as abscissae and yielded graphs similar to those illustrated in Figure 6 for each run. The total resistance change from each heating or solution of sample was determined from these graphs by methods described by Weissberger (54).

The energy actually added to the calorimeter during an electric heating period could be determined from the relation

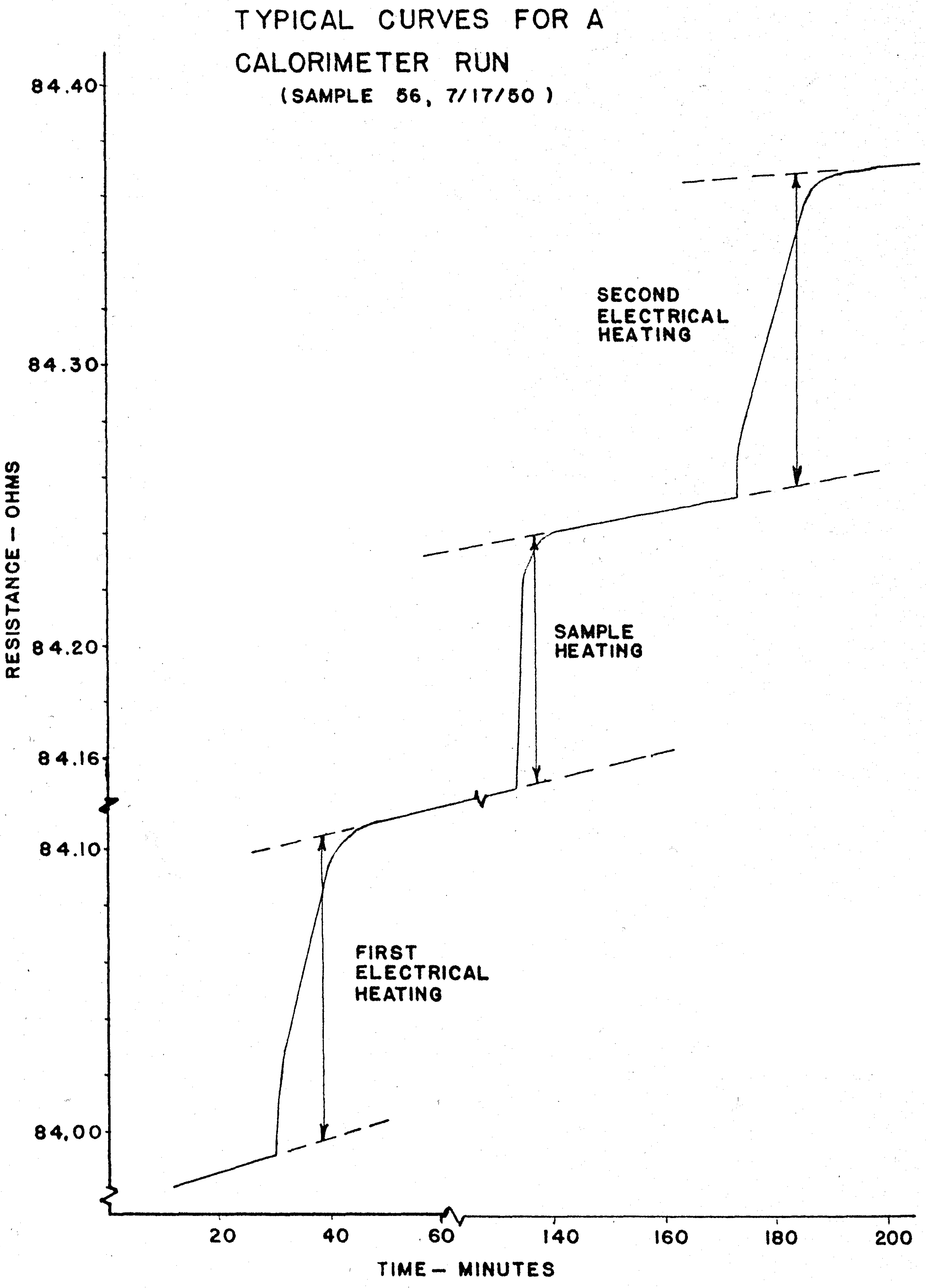
$$\text{calories} = \frac{I^2 \times R \times t}{4.1840}$$

where I is the average current in absolute amperes passing through the resistance of R ohms and t is the time in seconds for which the current flowed. The energy which was added to the calorimeter by the solution of a given sample was calculated by means of the ratio

$$\frac{\text{calories from sample}}{\text{res. change from sample}} = \frac{\text{calories from elec. heating}}{\text{res. change from elec. heating}}$$

The number of calories of heat liberated or absorbed per gram of sample was computed from this ratio. Such a ratio method

Figure 6


TYPICAL CURVES FOR A CALORIMETER RUN
(SAMPLE 56, 7/17/50)
84.40
84.30
84.20
84.16
84.10
84.00
RESISTANCE – OHMS
SECOND ELECTRICAL HEATING
SAMPLE HEATING
FIRST ELECTRICAL HEATING
20
40
60
140
160
180
200
TIME– MINUTES

implies that the change of resistance of the resistance thermometer is a linear function of the amount of heat added to the calorimeter. The plot of data in Figure 7 shows that this is really the case.

In order to calculate the heat of solution of the compound per mole, it was necessary to make corrections for any impurities present. Some of the samples of sodium superoxide used were 94.5% NaO_2 and, presumably, 5.5% Na_2O_2 (46). On this basis, for a sample of weight w,

$$w\left(\frac{\text{calories}}{\text{gram}}\right)_{\text{sample}} = 0.945\,w\left(\frac{\text{calories}}{\text{gram}}\right)_{NaO_2} + 0.055\,w\left(\frac{\text{calories}}{\text{gram}}\right)_{Na_2O_2}$$

whence

$$\left(\frac{\text{calories}}{\text{gram}}\right)_{NaO_2} = \frac{\left(\frac{\text{calories}}{\text{gram}}\right)_{\text{sample}} - 0.055\left(\frac{\text{calories}}{\text{gram}}\right)_{Na_2O_2}}{0.945}$$

and

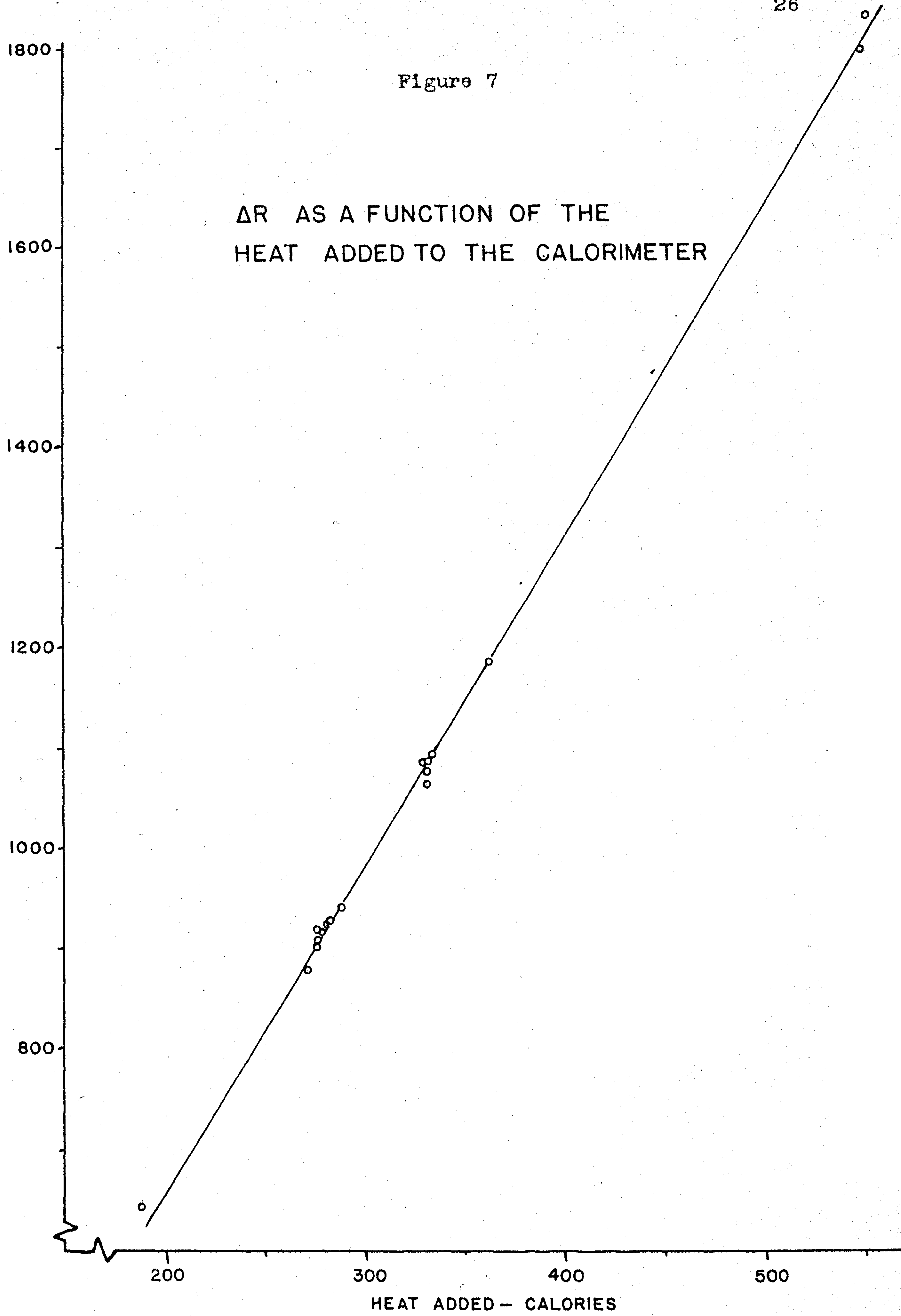
$$\Delta H_s \doteq -54.997\left(\frac{\text{calories}}{\text{gram}}\right)_{NaO_2}$$

For one sample of sodium peroxide of 96% purity, it was assumed that the other four per cent was sodium monoxide. The heat of solution of sodium peroxide was given by

$$\Delta H_s(Na_2O_2) = \frac{-77.994}{0.960}\left(\frac{\text{calories}}{\text{gram}}\right)_{\text{sample}} - 0.04\left(\frac{\text{calories}}{\text{gram}}\right)_{Na_2O}$$

The potassium superoxide used for most of the runs was 97.6% superoxide. The other 2.4% was assumed to be either KOH, KCl, K_2O, or K_2CO_3 and values for the heat of solution were

Figure 7


ΔR AS A FUNCTION OF THE
HEAT ADDED TO THE CALORIMETER
1800
1600
1400
1200
1000
800
ΔR – OHMS X 10⁴
200
300
400
500
HEAT ADDED – CALORIES

calculated on each of these bases.

It was necessary to add to the heats of solution as determined above a correction for vaporization of water that occurred during the solution and evolution of oxygen. It was assumed that the escaping gas was completely saturated with water vapor. Since at the temperature of the reaction, 25° C., the vapor pressure of water is 23.8 mm. of Hg and the total pressure was between 730 and 750 mm. of Hg, the number of moles of water vaporized per mole of oxygen liberated was approximately 0.032. It would require 336 calories of heat to vaporize this amount of water. Thus, the correction to be added to the measured heat of solution of sodium or potassium superoxide in water is 252 calories per mole, for sodium peroxide the correction is 168 calories per mole, and for the solution of Mg in HCl the corresponding figure is 336 calories per mole.

Results of Measurements of Heats of Solution

In the course of this research more than 65 samples were prepared and run in the calorimeter. The first 31 were done before any really consistent results were obtained, and the rest were done to get the better values presented in this thesis. Some of the runs were not satisfactory because of leaks in the heater-resistance thermometer or difficulties in breaking the sample bulb.

The best values for the heats of solution of the compounds and elements studied are presented in Tables 1, 2, 3, 4, 5, 6, 7, and 8.

Calculation of Heats of Formation

The heats of formation of the compounds studied have been calculated using the analyses of the samples and heats of formation of other compounds as presented in the National Bureau of Standards Table of Thermodynamic Properties. A summary of the values used is presented in Table 9.

The Heat of Formation of Na_2O_2

Two different samples of sodium peroxide were studied in this research. The first was used in Run 41 and consisted of 96% Na_2O_2 and 4% Na_2O. On this basis, the heat of solution in water of 466.00 calories per gram, when corrected to consider only the Na_2O_2 present, was 447.67 calories per gram. The second sample was furnished by The Mine Safety Appliance Company and was 99.2% Na_2O_2. The first runs made with this sample gave values of the heat of solution averaging 440 calories per gram, which were in agreement with the results of Kaule and Roth (29); but after the sample bottle was opened several times in the dry box, the heat of the solution decreased until a run on this sample made seven months after its receipt gave only 251.20 calories per gram. Using the values for the heat of solution obtained in the first runs on the 99.2% Na_2O_2, and assuming that the other 0.8% of the sample was Na_2O, the heat of formation of Na_2O_2

Table 1

Heat of Solution of Na_2O_2 in Water

Date	Run Number	Weight Sample	ΔR Sample	$\frac{\Delta R}{\text{gram}}$	$\left(\frac{\text{calories}}{\Delta R}\right)_{\text{avg.}}$	$\left(\frac{\text{calories}}{\text{gram}}\right)_{\text{obs.}}$	Temp. °C.
5-2-50	41	0.66275	611	921.9	0.50548	466.00	25.5
7-10-50	54	0.49745	726	1459.4	0.30694	447.95	24.8
7-11-50	55	0.52190	723	1385.3	0.30829	427.07	23.8
7-17-50	56	0.61755	875	1416.9	0.30952	438.56	24.2
12-1-50	83	0.61825	493	797.2	0.31510	251.20	26.5

Table 2

Heat of Solution of Na_2O_2 in H_2SO_4

Date	Run Number	Weight Sample	ΔR Sample	$\frac{\Delta R}{\text{gram}}$	$\left(\frac{\text{calories}}{\Delta R}\right)_{\text{avg.}}$	$\left(\frac{\text{calories}}{\text{gram}}\right)_{\text{obs.}}$	Temp. °C.
12-4-50	91	0.83300	1360	1637.65	0.3181	519.35	25.4
12-5-50	90	1.33205	1761	1321.58	0.3181	420.39	25.1

Table 3

Heat of Solution of NaO_2 in Water

Date	Run Number	Weight Sample	ΔR Sample	$\frac{\Delta R}{\text{gram}}$	$\left(\frac{\text{calories}}{\Delta R}\right)_{\text{avg.}}$	$\left(\frac{\text{calories}}{\text{gram}}\right)_{\text{obs.}}$	Temp. °C.
3-29-50	32	0.73520	423	575.4	0.52242	300.60	24.4
3-31-50	33	1.01535	526	518.0	0.57318	296.91	25.1
4-5-50	36	0.70845	401	566.0	0.53807	304.55	25.0
4-6-50	37	0.86330	458	530.5	0.56844	301.56	25.3
4-12-50	39	0.88650	493	556.1	0.54026	300.44	25.3
11-29-50	89	0.88060	807	916.42	0.31510	288.76	24.2
11-30-50	85	0.48035	439	913.92	0.31510	287.98	23.2
12-2-50	93	2.01060	1841	915.65	0.31510	288.52	24.5

Table 4

Heat of Solution of NaO_2 in H_2SO_4

Date	Run Number	Weight Sample	ΔR Sample	$\frac{\Delta R}{\text{gram}}$	$\left(\frac{\text{calories}}{\Delta R}\right)_{\text{avg.}}$	$\left(\frac{\text{calories}}{\text{gram}}\right)_{\text{obs.}}$	Temp. °C.
11-22-50	88	0.73360	880	1199.56	0.28382	340.46	23.6
11-24-50	84	0.54775	693	1265.17	0.28382	359.08	23.9
12-4-50	92	1.42370	1684	1175.40	0.3181	373.89	24.4
12-5-50	94	0.93345	1102	1180.57	0.3181	375.54	26.3

Table 5

Heat of Solution of KO_2 in Water

Date	Run Number	Weight Sample	ΔR Sample	$\frac{\Delta R}{\text{gram}}$	$\left(\frac{\text{calories}}{\Delta R}\right)_{\text{avg.}}$	$\left(\frac{\text{calories}}{\text{gram}}\right)_{\text{obs.}}$	Temp. °C.
7-19-50	57	0.89495	485	541.9	0.33375	180.86	24.7
7-21-50	58	0.54875	335	610.5	0.30338	185.21	23.1
8-7-50	64	1.39775	830	593.8	0.30944	183.75	25.2
10-17-50	68a	0.67040	420	626.5	0.3075	192.50	27.2
10-18-50	69	0.46425	273	588.0	0.3307	194.46	26.0

Table 6

Heat of Solution of KO_2 in H_2SO_4

Date	Run Number	Weight Sample	ΔR Sample	$\frac{\Delta R}{\text{gram}}$	$\left(\frac{\text{calories}}{\Delta R}\right)_{\text{avg.}}$	$\left(\frac{\text{calories}}{\text{gram}}\right)_{\text{obs.}}$	Temp. °C.
6-26-50	52	0.26860	219	815.3	0.30562	249.17	23.6
8-25-50	68	0.64375	552	857.5	0.30131	258.37	23.2
8-28-50	65	0.65390	539	824.3	0.30131	248.37	23.4
10-16-50	66a	0.60035	502	836.2	0.2770	232.32	22.2
10-17-50	70	0.40050	337	841.4	0.2770	233.06	23.7

Table 7

Heat of Solution of Mg in 0.1084 N. HCl

Date	Run Number	Weight Sample	ΔR Sample	$\frac{\Delta R}{\text{gram}}$	$\left(\frac{\text{calories}}{\Delta R}\right)_{\text{avg.}}$	$\left(\frac{\text{calories}}{\text{gram}}\right)_{\text{obs.}}$	Temp. °C.
6-1-50	47	0.10070	1524	15,134	0.30163	4564.9	22.4
6-8-50	53	0.10895	1652	15,163	0.30263	4588.8	23.2

Table 8

Heat of Solution of KCl in Water

Date	Run Number	Weight Sample	ΔR Sample	$\frac{\Delta R}{\text{gram}}$	$\left(\frac{\text{calories}}{\Delta R}\right)_{\text{avg.}}$	$\left(\frac{\text{calories}}{\text{gram}}\right)_{\text{obs.}}$	Temp. °C.
3-23-50	31	1.9911	196	98.4	0.54765	53.89	24.4
4-12-50	34	1.50770	149	98.8	0.54478	53.82	25.0

Table 9

Heats of Formation of Some Alkali Metal Compounds at 298° K. *

Compound	Heat of Formation Kilocalories per Mole	Compound	Heat of Formation Kilocalories per Mole
$H_2O(l)$	-68.317	$K(g)$	21.51
$H_2O(g)$	-57.7979	$K_2O(s)$	-86.4
$H_2O_2(aq)$	-45.68	$K_2O_2(s)$	-118.
$H_2SO_4(l)$	-193.91	$KO_2(s)$	-67.
$H_2SO_4(500\ H_2O)$	-212.25	$KOH(s)$	-101.78
$(800\ H_2O)$	-212.54	$KOH(aq)$	-115.00
$(1000\ H_2O)$	-212.69	$KHSO_4(s)$	-276.8
$(2000\ H_2O)$	-213.24	$KHSO_4(800\ H_2O)$	-274.3
$Li(g)$	37.07	$K_2CO_3(s)$	-273.93
$Li_2O(s)$	-142.4	$K_2CO_3(1000\ H_2O)$	-281.56
$Li_2O_2(s)$	-151.7	$Rb(g)$	20.51
$LiOH(s)$	-116.45	$Rb_2O(s)$	-78.9
$LiOH(aq)$	-121.511	$Rb_2O_2(s)$	-101.7
$Na(g)$	25.98	$RbO_2(s)$	-63.1
$Na_2O(s)$	-99.4	$RbOH(s)$	-98.9
$Na_2O_2(s)$	-120.6	$RbOH(aq)$	-113.9
$NaO_2(s)$	-61.9	$Cs(g)$	18.83
$NaOH(s)$	-101.99	$Cs_2O(s)$	-75.9
$NaOH(aq)$	-112.236	$Cs_2O_2(s)$	-96.2
$NaHSO_4(s)$	-269.2	$CsO_2(s)$	-62.1
$NaHSO_4(200\ H_2O)$	-270.6	$CsOH(s)$	-97.2
$Na_2CO_3(s)$	-270.3	$CsOH(aq)$	-114.2
$Na_2CO_3(200\ H_2O)$	-276.17		

* From "Selected Values of Chemical Thermodynamic Properties", National Bureau of Standards.

has been calculated as -121.5 ± 0.5 kilocalories per mole.

In an effort to explain the low value for the heat of solution of the Na_2O_2 sample after long standing, gasometric analyses and base titrations were performed. The results of these indicated that 112 cc. of oxygen at standard conditions were evolved, and that 19.5 milliequivalents of base were formed per gram of sample dissolved. The possible molecular species present are listed below along with the number of milliequivalents of base per gram formed on solution in water:

Molecular Species	Milliequivalents per Gram
NaO_2	18.2
$NaO_2 \cdot H_2O$	13.7
$NaO_2 \cdot 2\ H_2O$	11.0
Na_2O_2	25.6
$Na_2O_2 \cdot H_2O$	20.8
$Na_2O_2 \cdot 2\ H_2O$	17.5
Na_2O	32.3
NaOH	25.0
$NaOH \cdot H_2O$	17.2
$NaOH \cdot 2\ H_2O$	13.1

One gram of pure sodium peroxide would evolve 143.6 cc. of oxygen at standard conditions, and thus, the 112 cc. of oxygen measured is indication of considerable peroxide still present in the sample. To decide more definitely on the composition of this material, one must make some assumptions or have knowledge of the species present, and much doubt as to the decomposition products of these compounds exists. Because of this uncertainty, the last value for the heat of solution of sodium peroxide in water in Table 1 and the two values for the heat of solution of sodium peroxide in 0.0899 N. sulfuric acid in Table 2 are not useful for computation of the heat of formation of the compound.

The Heat of Formation of KO_2

Samples of KO_2 were furnished for this study by The Mine Safety Appliance Company. One of these samples was received as a fine powder, while the other was in lumps.

The finely powdered sample was analyzed by the Kansas City Testing Laboratory as follows:

% K = 55.37
% Na = 0.84
% CaO, MgO, and R_2O_3 = 0.2
Milliequivalents of base formed per gram of KO_2 dissolved in water = 14.02

By dissolving the superoxide in water in the presence of MnO_2, measuring the volume of oxygen evolved and converting this volume to standard conditions, it was found that 220 cc. of oxygen gas at standard conditions were evolved per gram of powdered sample. If the sodium detected above is assumed to be present as Na_2O_2, then the oxygen which is evolved from KO_2 only (K_2O_2 has never been shown to exist under these conditions) is 218 cc. per gram of sample which must have resulted from the solution of 0.9237 grams of KO_2. Combining this result with the number of milliequivalents of base resulting from solution in water, 14.02, and assuming that the remaining base resulted from the solution of K_2O, one then finds that the K_2O present is 0.0316 grams per gram of sample. Thus, 97.15% of the sample is accounted for, but, of the 14.16 milliequivalents of potassium present per gram of sample, only 13.66 milliequivalents have been identified. If the remaining 2.85% of the sample were K_2CO_3, a very likely contaminant, back calculation of the per cent of potassium present in the total sample gives 55.12%. This is well within the experimental error which results mainly from uncertainty in the gasometric analysis for superoxide oxygen. Potassium chloride was also believed to be a possible contaminant, but tests failed to show its presence.

The KO_2 which was received in lumps was found to yield 218 cc. of oxygen gas at standard conditions, and to form 13.77 milliequivalents of base per gram of sample on solution in water with an MnO_2 catalyst present. This sample was also studied spectroscopically by volatilizing it between carbon electrodes; traces of Ca and Na were observed to be present here in about the same amounts as in the powder. On this basis, the KO_2 present is 0.9153 grams, the Na_2O_2 present is 0.0142 grams, and, if the remaining base results from solution of K_2O, the K_2O present is 0.0254 grams. This accounts for 95.69% of the sample. This material gave a positive chloride test and, if the remaining 4.31% is KCl, one may interpret the calorimetric data from Table 5 as follows:

	KO_2(powder)	KO_2(lump)
$\left(\frac{\text{calories}}{\text{gram}}\right)^{\text{avg.}}_{\text{obs.}}$	193.48	183.27
$\left(\frac{\text{calories}}{\text{gram}}\right)_{KO_2}$	173.51	173.76
$-\Delta H_s$(kilocalories per mole)	12.59	12.61
$-\Delta H_f$(kilocalories per mole)	68.19	68.17

The data from Table 6 give the heats of reaction of KO_2 in various sulfuric acid solutions approximately 0.1 normal. Interpreting these data on the basis of the analyses given in the preceding paragraphs, one finds:

	KO_2 (powder) in 0.0899 N. H_2SO_4	KO_2 (lump) in 0.1677 N. H_2SO_4
$\left(\frac{\text{calories}}{\text{gram}}\right)^{\text{avg.}}_{\text{obs.}}$	233.19	251.97
$\left(\frac{\text{calories}}{\text{gram}}\right)^{\text{avg.}}_{KO_2}$	203.66	238.98
$-\Delta H_s$ (kilocalories per mole)	14.65	17.16
$-\Delta H_f$ (kilocalories per mole)	69.80	66.82

If, on the other hand, K_2CO_3 and not KCl were the main constituent of the 4.31% of the KO_2 sample which did not lead to base on solution in water, then the heat of solution in water would be -12.23 kilocalories per mole and the heat of solution in 0.1677 N. H_2SO_4 would be -16.79 kilocalories per mole. These values lead to heats of formation for KO_2 of -68.55 and -67.69 kilocalories per mole respectively.

The heat of solution in sulfuric acid is not as reliable as the heat of solution in water since (1) some of the H_2O_2 formed during the solution reaction in H_2SO_4 may be decomposed due to local heating of the sample and (2) the heats of formation of H_2O_2 and $KHSO_4$ in solution are not very well known at the concentrations used in these experiments. It would be of interest to study this reaction in a medium like diethyl phthalate with acetic acid as a decomposant after the method of Seyb (46) for specific superoxide analysis.

The heat of formation of KO_2 is believed to be -68.2±0.3 kilocalories per mole.

The Heat of Formation of NaO_2

Samples of NaO_2 of reasonably high purity were obtained from Seyb (46) who prepared them by oxidation of Na_2O_2 at elevated temperatures and pressures, and from The Mine Safety Appliance Company. Seyb's material was analyzed and the percentage of NaO_2 was found to be 93.5% using a newly developed method of analysis specifically for superoxide oxygen. For the same sample, on the basis of a total decomposition with an $HCl-FeCl_3$ decomposant, 94.5% NaO_2 was indicated.

The sample from The Mine Safety Appliance Company was found to have this analysis by the Kansas City Testing Laboratory:

% Na = 42.89

% K = 0.00

% CaO, MgO, and R_2O_3 = less than 0.05

milliequivalents of base formed
per gram of NaO_2 dissolved in water = 18.64

The sample was found to evolve 292 cc. of oxygen under standard conditions per gram of sample dissolved in water with MnO_2 present. If only NaO_2 and Na_2O_2 are assumed to be present, as is the case for both of these samples, one may determine the percentage composition on the basis of either a gasometric analysis or a base titration. From the gasometric analysis, since pure NaO_2 evolves 305 cc. of oxygen per gram at standard conditions, and pure Na_2O_2 evolves 144 cc. of oxygen per gram under these same conditions, one may calculate the percentage of superoxide present as 91.92%, and the remaining 8.08% is peroxide. The data from the base titration indicate 93.83% NaO_2 and 6.17% Na_2O_2. The gasometric analysis thus indicates 43.19% Na while the base titration indicates 42.87% Na. The latter analysis was taken as correct for the NaO_2 and the observed heats of solution were corrected for Na_2O_2 impurity on this basis.

The average of five runs with the material prepared by Seyb indicated that 300.81 calories per gram of sample were evolved, while the samples from The Mine Safety Appliance Company evolved 288.42 calories per gram. Treatment of these data as outlined in the previous section shows that the heat of solution of NaO_2 in water is -15.6 ± 0.5 kilocalories per mole.

Then, on the assumption that the reaction occurring on solution in water is

$$2\ NaO_2 + H_2O \overset{MnO_2}{=} 2\ NaOH + 3/2\ O_2\ ,$$

the heat of formation is -62.4 kilocalories per mole.

Studies were also made on NaO_2 by dissolving it in approximately 0.1 N. H_2SO_4 and measuring the heat of the reaction calorimetrically. The results obtained with samples furnished by The Mine Safety Appliance Company did not show the consistency from run to run as was exhibited by all of the water solution results; the average of four runs tabulated in Table 4 was 362.24 calories per gram. The heat of solution then has the value -19.6 kilocalories per mole, and the heat of formation calculated from this value is -61.2 ± 1.0 kilocalories per mole.

Because the reaction of the superoxides with water is simple and does not present the problem of accounting for partial decomposition of H_2O_2 as is the case for the sulfuric acid reaction, the data thus obtained are believed most dependable. Thus, the best value for the heat of formation of NaO_2 is believed to be -62.4 ± 0.5 kilocalories per mole.

A summary of the heats of formation as determined for Na_2O_2, NaO_2, and KO_2 and an estimated value for LiO_2 are presented in Table 10, along with the calorimeter calibration data. In Figure 8, the heats of formation of a number of alkali metal oxides are plotted versus the logarithm of the atomic number of the metal.

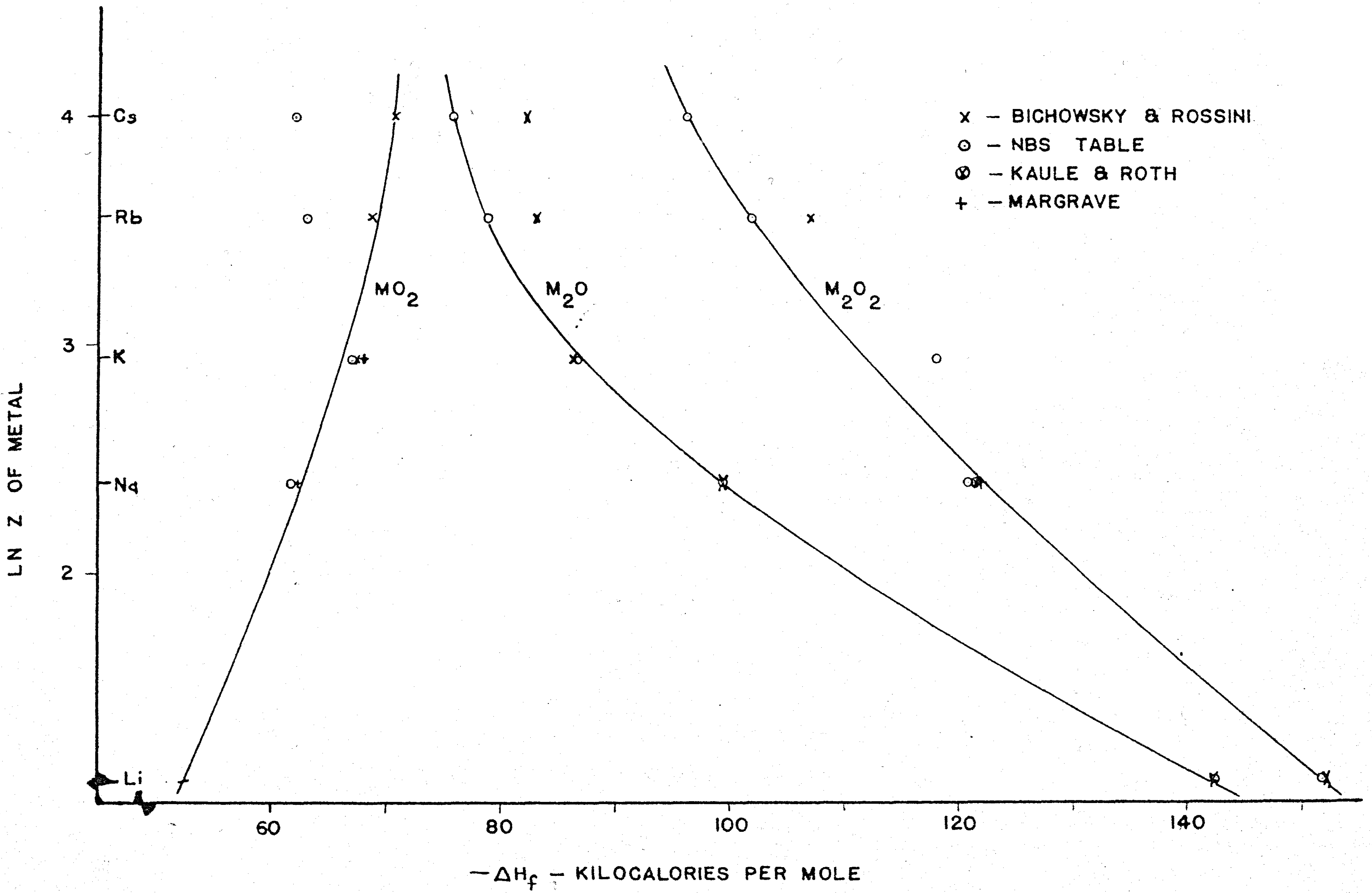
Table 10

Summary of Experimentally Determined Heats of Reaction

Substance	Reaction Type	Heat of Reaction kcal/mole	Remarks
Mg	Solution in 0.1084 N. HCl	-111.4	Calibration Reaction
KCl	Solution in H_2O	4.016	Calibration Reaction
Na_2O_2	Solution in H_2O MnO_2 catalyst	-34.5 ± 0.5	$\Delta H_f(Na_2O_2) = -121.5 \pm 0.5$ kcal/mole
Na_2O_2	Solution in 0.0899 N. H_2SO_4	not consistent	no calculation made
KO_2	Solution in H_2O MnO_2 catalyst	-12.6 ± 0.3	$\Delta H_f(KO_2) = -68.2 \pm 0.3$ kcal/mole
KO_2	Solution in 0.1677 and 0.0899 N. H_2SO_4	-15.0 ± 1.0	$\Delta H_f(KO_2) = -68.0 \pm 1.0$ kcal/mole
NaO_2	Solution in H_2O MnO catalyst	-15.6 ± 0.5	$\Delta H_f(NaO_2) = -62.4 \pm 0.5$ kcal/mole
NaO_2	Solution in 0.0899 N. H_2SO_4	-19.6 ± 1.0	$\Delta H_f(NaO_2) = -61.2 \pm 1.0$ kcal/mole
LiO_2	________	________	$\Delta H_f(LiO_2) = -53 \pm 5$ kcal/mole (estimated)

Figure 8

HEATS OF FORMATION OF ALKALI METAL OXIDES



CRYSTAL ENERGIES AND THE ELECTRON AFFINITY OF OXYGEN

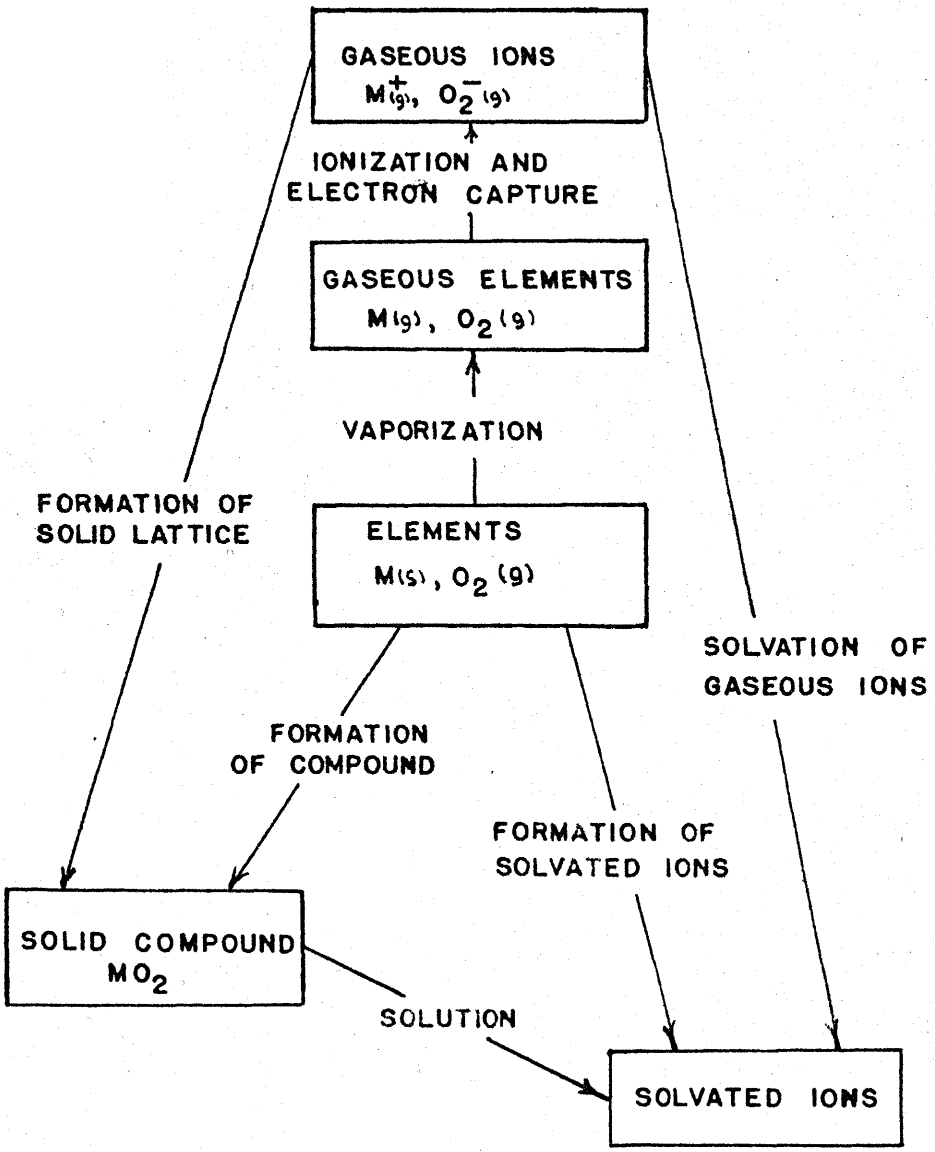
The crystal energies of ionic compounds may be calculated for most crystal structures by several methods. The alkali metal superoxides show either a NaCl or a CaC_2 type of crystal structure and their crystal energies have been computed four ways. This crystal energy, i.e., the energy necessary to separate the gaseous ions from their normal lattice positions to infinity, has its greatest significance when used as a connecting link in the various thermochemical cycles illustrated in Figure 9.

<u>Calculation of Crystal Energies</u>

The calculation of the energy of an orderly arrangement of charges was first considered by Madelung in 1918, but the Born-Mayer crystal model, along with a modification suggested by Kazarnovskii, offers the most practical basis for calculations of crystal energies. (7, 20, 31, 33, 38, 40, 42, and 47)

In this approach one considers separately the potential energy of a given lattice of charges arising from (1) electrostatic long-range interactions, (2) short-range repulsive forces, (3) short-range attractive forces (van der Waals or London forces), (4) quadrupole-charge interactions, (5) dipole-quadrupole interactions, and (6) quadrupole-quadrupole

Figure 9



THERMOCHEMICAL CYCLES

interactions. The combination of these interactions appears to represent fairly accurately the potential energy of most crystal structures and is usually written

$$U = N\left[-\frac{Ae^2}{r_o} + B(r) - \frac{C}{r_o^6} - \frac{D}{r_o^3} - \frac{E}{r_o^8} - \frac{F}{r_o^{10}}\right]$$

where U = total crystal energy per mole
A = Madelung constant
N = Avogadro's number
r_o = equilibrium interionic distance
$-\frac{Ae^2}{r_o}$ = electrostatic attractive energy
$B(r)$ = short-range repulsive energy
$-\frac{C}{r_o^6}$ = van der Waals attractive energy
$-\frac{D}{r_o^3}$ = quadrupole-charge attractive energy
$-\frac{E}{r_o^8}$ = dipole-quadrupole interaction energy
$-\frac{F}{r_o^{10}}$ = quadrupole-quadrupole interaction energy.

Electrostatic Energy

The higher superoxides of the alkali metals crystallize in a distorted NaCl type lattice which is elongated in one direction but NaO_2 has an undistorted cubic crystal structure. These higher superoxides have a structure like CaC_2 (21) with the superoxide ion oriented along the elongated axis and are different from NaO_2, a compound in which the superoxide ion apparently has a random orientation with respect to the crystal axes (12). The calculation of the electrostatic energy of the crystal lattices has been carried out with Madelung constants determined by the method of Madelung (38) and interionic distances given by Dauben and Templeton (12). The results are presented in Table 11.

van der Waals Energy

The van der Waals' energy of a crystal lattice is given by

$$E_{vdw} = - \frac{N}{r_o^{\,6}} \left[S_V \, C_{+-} + S_V{}' \left(\frac{C_{++} + C_{--}}{2} \right) \right.$$

where C_{++}, C_{--}, and C_{+-} are the coefficients of $\frac{1}{r_o^{\,6}}$ in the equation of Slater and Kirkwood (33) for interactions between the respective ion pair types, and S_V and $S_V{}'$ are geometrical factors dependent upon the crystal arrangement.

The Slater-Kirkwood treatment of van der Waals forces is a quantum mechanical perturbation method which assumes that such attractive forces have their origins in mutual polarization of molecules. It is shown that the energy of interaction between two ions, $\mathcal{E}$, is given by:

$$\mathcal{E}_{12} = \frac{-13 \nu_1 \nu_2 e^2 a_0^5}{27 r_0^6} \left\{ \frac{\left[n_1^4 (n_1+1)^2 (n_1 + \frac{1}{2})^2 \right] \left[n_2^4 (n_2+1)^2 (n_2 + \frac{1}{2})^2 \right]}{(Z_1 - S_1)^2 (Z_2 - S_2)^2 [(Z_2 - S_2)^2 n_1^2 (n_1+1)(n_1+\frac{1}{2}) + (Z_1 - S_1)^2 n_2^2 (n_2+1)(n_2+\frac{1}{2})} \right\}.$$

Table 11

Electrostatic Energies of Superoxides

Compound	A	r Å	$\frac{Ae^2}{r}$ ergs/molecule	$\frac{Ae^2}{r}$ kcal/mole
NaO_2	1.748	5.49	14.67×10^{-12}	211.2
KO_2	1.693	5.71	13.67×10^{-12}	196.3
RbO_2	1.697	6.01	13.00×10^{-12}	187.0
CsO_2	1.708	6.29	12.49×10^{-12}	179.2

and the polarizabilities are given by

$$\alpha_1 = \frac{\nu_1 a_0^3 \, n_1^4 (n_1+1)^2 (n_1+\frac{1}{2})^2}{2(Z_1-S_1)^4}$$

$$\alpha_2 = \frac{\nu_2 a_0^3 \, n_2^4 (n_2+1)^2 (n_2+\frac{1}{2})^2}{2(Z_2-S_2)^4}$$

where n = the effective quantum number of the outermost electrons

ν = the number of electrons in the outermost shell of the atom

Z = the atomic number of the atom

S = the screening constant of the outermost electrons

a_0 = the radius of the first Bohr orbit in the hydrogen atom.

Then, if one sets

$$A_1 = n_1^4 (n_1+1)^2 (n_1+\tfrac{1}{2})^2 = \frac{2\alpha_1 (Z_1-S_1)^4}{\nu_1 a_0^3}$$

$$A_2 = n_2^4 (n_2+1)^2 (n_2+\tfrac{1}{2})^2 = \frac{2\alpha_2 (Z_2-S_2)^4}{\nu_2 a_0^3}$$

$$D_1 = (Z_1-S_1)^2$$

$$D_2 = (Z_2-S_2)^2$$

one finds that

$$\mathcal{E}_{12} = -\frac{13 \nu_1 \nu_2 a_0^5 e^2}{27 r_0^6} \left[\frac{A_1 A_2}{D_1 D_2 \left(D_2 A_1^{1/2} + D_1 A_2^{1/2} \right)} \right]$$

The values of the van der Waals interaction constants to be used in the crystal energy calculation were computed from the equation

$$C_{12} = \frac{13\,\nu_1 \nu_2 e^2 a_o^5}{27}\left[\frac{A_1 A_2}{D_1 D_2 \left(D_2 A_1^{1/2} + D_1 A_1^{1/2}\right)}\right]$$

The A's were evaluated from the expression below involving the polarizabilities and the screening constants because the values of n, the effective quantum number, are difficult to derive

$$A_i = \frac{2\alpha_i \left(Z_i - S_i\right)^4}{\nu_1 a_o^3}$$

The values of S_V and S_V' for the calculations on KO_2, RbO_2, and CsO_2 were taken from Kazarnovskii (31) who summed the convergent series

$$S_V = \sum_i \left(\frac{1}{R_i^6}\right)$$

where R_i = the distance between a given ion and the i-th ion of the opposite sign relative to $r_o = 1$

and

$$S_V' = \sum_i \left(\frac{1}{R_i^6}\right)$$

where R_i = the distance between a given ion and the i-th ion of the same sign relative to $r_o = 1$.

The values for NaO_2 were taken from Born and Mayer (7).

The results of these calculations are tabulated in Table 12.

Table 12

van der Waals' Energies of Superoxides

Compound	r_o A^o	α_+ cm^3	α_- cm^3	S_v	S_v'	C $erg\text{-}cm^6$	$\frac{C}{r_o^6}$ $\frac{ergs}{molecule}$	$\frac{C}{r_o^6}$ $\frac{kcal}{mole}$
NaO_2	2.745	0.21×10^{-24}	2.56×10^{-24}	6.595	1.807	288×10^{-60}	0.674×10^{-12}	9.7
KO_2	2.855	0.88×10^{-24}	2.56×10^{-24}	5.107	1.262	462×10^{-60}	0.854×10^{-12}	12.3
RbO_2	3.005	1.41×10^{-24}	2.56×10^{-24}	5.148	1.274	632×10^{-60}	0.859×10^{-12}	12.4
CsO_2	3.145	2.45×10^{-24}	2.56×10^{-24}	5.242	1.314	940×10^{-60}	0.972×10^{-12}	14.0

Quadrupole Energy

The superoxide ion in KO_2, RbO_2, and CsO_2 is usually regarded as a prolate ellipsoid of charge with a = 2.05 A° and b = 1.53 A°. Because of this deviation from spherical symmetry, it does possess a positive quadrupole moment. No calculations have been carried out on the superoxide ion, but Kazarnovskii (31) concluded that 3×10^{-26} esu is a reasonable estimate for the quadrupole moment of O_2^- by considering the calculated quadrupole moments of O_2 and H_2. The interaction energy of a point charge $\pm e$ with a quadrupole moment Q is given by

$$\mathcal{E} = \pm \frac{eQ(3 \cos^2 \theta - 1)}{2r_o^3}$$

where r = the distance from the charge to the center of the ellipsoid of charge, and

θ = the angle of the vector r with the axis of the ellipsoid.

Thus, for several charges, the total energy of interaction is

$$E_q = \frac{NeQ_{O_2^-}}{2r_o^3} \sum_i \frac{(3 \cos^2 \theta - 1)}{R_i^3} = \frac{NeQ_{O_2^-} S_q}{2r_o^3}$$

where S_q = a geometrical factor characteristic of the crystal lattice.

The results of such calculations carried out for KO_2, RbO_2, and CsO_2 are tabulated in Table 13.

Table 13

Quadrupole Energies of Superoxides*

Compound	$Q_{O_2^-}$ esu	S_q	r_o A°	E_Q $\frac{\text{ergs}}{\text{molecule}}$	E_Q $\frac{\text{kcal}}{\text{mole}}$
NaO_2	0		2.745		
KO_2	3×10^{-26}	-1.454	2.855	0.45×10^{-12}	6.5
RbO_2	3×10^{-26}	-1.423	3.005	0.38×10^{-12}	5.5
CsO_2	3×10^{-26}	-1.312	3.145	0.32×10^{-12}	4.4

* By the method of Kazarnovskii (31)

In NaO_2 the superoxide ion is apparently spherically symmetrical; thus, it has no quadrupole moment.

Repulsive Energy

The repulsive interaction energy between two ions is assumed to be given by the expression

$$\varphi(r) = c_{12}\,be^{\frac{r_1 + r_2 - r}{\rho}}$$

where r = the distance between the centers of the two ions,

r_1 = the ionic radius of ion 1,

r_2 = the ionic radius of ion 2,

b = the repulsive coefficient,

c_{12} = a coefficient showing the dependence of repulsion on the signs of the ionic charges, and

ρ = a constant characteristic of the crystal structure.

Born (7) has shown that for two ions 1 and 2

$$c_{12} = 1 + \frac{Z_1}{N_1} + \frac{Z_2}{N_2}$$

where Z_1 and Z_2 = the ionic charges of the ions, and

N_1 and N_2 = the number of outer electrons of the ions.

Thus, for the ions Na^+, K^+, Rb^+, Cs^+,

$$Z_1 = 1 \text{ and } N_1 = 8$$

and for O_2^-,

$$Z_2 = -1 \text{ and } N_2 = 13 \quad .$$

Consequently, for the various ion combinations found in superoxide crystals,

$$c_{12} = C_0 = 1 + 1/8 - 1/13 = 1.048$$

$$c_{11} = C_1 = 1 + 1/8 + 1/8 = 1.250$$

$$c_{22} = C_2 = 1 - 1/13 - 1/13 = 0.846$$

Now, one finds from thermodynamics that in a mechanically stable crystal at absolute zero,

$$\left(\frac{\partial U}{\partial V}\right)_{V = V_o} = 0 \qquad \text{and} \quad \left(\frac{\partial^2 U}{\partial V^2}\right)_{V = V_o} = \frac{1}{\beta V}$$

where β is the compressibility of the crystal, U is the potential energy of the crystal, and V is the molecular volume. Then, since $U = N\varphi(r)$ and $V = kr^3$, one finds that

$$\left(\frac{\partial U}{\partial V}\right) = N\left(\frac{\partial \varphi}{\partial r}\right)\left(\frac{\partial r}{\partial V}\right)$$

$$\left(\frac{\partial U}{\partial V}\right)_{V = V_o} = \frac{Nr}{3V_o}\left(\frac{\partial \varphi}{\partial r}\right) = 0$$

and $r\left(\frac{\partial \varphi}{\partial r}\right) = 0$. Also,

$$\left(\frac{\partial^2 U}{\partial V^2}\right) = \frac{\partial}{\partial V}\left[\frac{N}{3kr^2}\left(\frac{\partial \varphi}{\partial r}\right)\right]$$

$$= \frac{\partial}{\partial r}\left[\frac{N}{3kr^2}\left(\frac{\partial \varphi}{\partial r}\right)\right]\frac{\partial r}{\partial V}$$

$$= N\left[-\frac{1}{6kr^2}\left(\frac{\partial \varphi}{\partial r}\right) + \frac{1}{3kr^2}\left(\frac{\partial^2 \varphi}{\partial r^2}\right)\right]\frac{1}{3kr^2}$$

$$\left(\frac{\partial^2 U}{\partial V^2}\right)_{V = V_o} = N\left[0 + \frac{r^2}{9V_o^2}\left(\frac{\partial^2 \varphi}{\partial r^2}\right)\right] = \frac{1}{\beta V}$$

whence $$r^2\left(\frac{\partial^2 \varphi}{\partial r^2}\right) = \frac{9V_o}{N\beta}$$

where φ is the lattice energy per molecule and N is Avogadro's number. The values of β have not been experimentally determined but were calculated from the equation

$$\beta = 8.6 \times 10^{-14}\left(\frac{\text{molecular weight}}{\text{density}}\right)^{\frac{4}{3}}$$

taken from Bridgman (11). These calculated values are given in Table 14.

The crystal energy may be represented as the sum of several attractive and repulsive energy terms as shown by

$$\varphi\,(r) = -\frac{Ae^2}{r_o} - \frac{C}{r_o^6} - \frac{D}{r_o^3} + B(r) \quad .$$

Then,

$$r\left(\frac{\partial \varphi}{\partial r}\right)_{r = r_o} = \frac{Ae^2}{r_o} + \frac{6C}{r_o^6} + \frac{3D}{r_o^3} + r_o\left(\frac{\partial B}{\partial r}\right)_{r = r_o} = 0$$

$$r_o^2\left(\frac{\partial^2 \varphi}{\partial r^2}\right)_{r = r_o} = -\frac{2Ae^2}{r_o} - \frac{42C}{r_o^6} - \frac{12D}{r_o^3} + r_o^2\left(\frac{\partial^2 B}{\partial r^2}\right)_{r = r_o} = \frac{9V_o}{N\beta}$$

and one may define the expressions

Table 14

Compressibilities of Superoxides

Compound	Molecular Weight	Density	V	β
NaO_2	54.997	2.21	24.9	6.2×10^{-12}
KO_2	71.096	2.14	33.2	9.1×10^{-12}
RbO_2	117.48	3.07	38.3	11×10^{-12}
CsO_2	164.91	3.81	43.3	13×10^{-12}

$$\tau = -r_0\left(\frac{\partial B}{\partial r}\right)_{r = r_0} = \frac{Ae^2}{r_0} + \frac{6C}{r_0^6} + \frac{3D}{r_0^3}$$

$$\sigma = r_0^2\left(\frac{\partial^2 B}{\partial r^2}\right)_{r = r_0} = \frac{9V_0}{N\beta} + \frac{2Ae^2}{r_0} + \frac{42C}{r_0^6} + \frac{12D}{r_0^3}$$

which enable one to determine the repulsive energy of a given crystal arrangement. Let C_0, C_1, and C_2 be the ion interaction constants for mixed ion pairs, positive ion pairs, and negative ion pairs, respectively. Then, assuming that the first equation in this section on repulsive energies holds, one finds that the repulsive energy for NaO_2 is given by

$$B(r) = 6C_0 b e^{\frac{r_1 + r_2 - r}{\rho}} + 6C_1 b e^{\frac{2r_1 - 2r}{\rho}} + 6C_2 b e^{\frac{2r_2 - 2r}{\rho}}$$

assuming that like ion repulsions are, on the average, half negative and half positive. Rearranging the expression, one finds

$$B(r) = b e^{\frac{r_1 + r_2}{\rho}}\left[6C_0 e^{-\frac{r}{\rho}} + 6C_2\left(e^{\frac{r_2 - r_1 - 2r}{\rho}} + \frac{C_1}{C_2} e^{\frac{-r_1 - r_2 - 2r}{\rho}}\right)\right]$$

or

$$B(r) = b e^{\frac{r_1 + r_2}{\rho}}\left[6C_0 e^{-\frac{r}{\rho}} + 6C_2\left(e^{\frac{\delta - ar}{\rho}} + \frac{C_1}{C_2} e^{\frac{-\delta - ar}{\rho}}\right)\right]$$

where $\delta = r_2 - r_1$ and $a = \sqrt{2}$.

Thus,

$$B(r) = be^{\frac{r_1+r_2}{\rho}}\left[6C_0e^{-\frac{r}{\rho}} + 6C_2\left(1 + \frac{C_1}{C_2}e^{-\frac{2\delta}{\rho}}\right)e^{\frac{\delta - ar}{\rho}}\right]$$

and

$$\tau = -r_0\left(\frac{\partial B}{\partial r}\right)_{r=r_0} = \left(\frac{r_0}{\rho}\right)be^{\frac{r_1+r_2}{\rho}}\left[6C_0e^{-\frac{r_0}{\rho}} + 6aC_2\left(1+\frac{C_1}{C_2}e^{-\frac{2\delta}{\rho}}\right)e^{\frac{\delta - ar_0}{\rho}}\right]$$

$$\sigma = r_0^2\left(\frac{\partial^2 B}{\partial r^2}\right)_{r=r_0} = \left(\frac{r_0^2}{\rho^2}\right)be^{\frac{r_1+r_2}{\rho}}\left[6C_0e^{-\frac{r_0}{\rho}} + 12C_2\left(1+\frac{C_1}{C_2}e^{-\frac{2\delta}{\rho}}\right)e^{\frac{\delta - ar_0}{\rho}}\right]$$

Dividing and rearranging,

$$\left(\frac{r_0}{\rho}\right)\left(\frac{\tau}{\sigma}\right) = \frac{6C_0e^{-\frac{r_0}{\rho}} + 6aC_2(1+\frac{C_1}{C_2}e^{-\frac{2\delta}{\rho}})e^{\frac{\delta - ar}{\rho}}}{6C_0e^{-\frac{r_0}{\rho}} + 12C_2(1+\frac{C_1}{C_2}e^{-\frac{2\delta}{\rho}})e^{\frac{\delta - ar}{\rho}}}$$

$$= \frac{1 + a\left(\frac{C_2}{C_0}\right)\left(1 + \frac{C_1}{C_2}e^{-\frac{2\delta}{\rho}}\right)e^{\frac{\delta - ar + r}{\rho}}}{1 + 2\left(\frac{C_2}{C_0}\right)\left(1 + \frac{C_1}{C_2}e^{-\frac{2\delta}{\rho}}\right)e^{\frac{\delta - ar + r}{\rho}}}$$

If one sets $X = \left(\frac{r}{\rho}\right)\left(\frac{\tau}{\sigma}\right)$ and $\ell = \frac{\delta}{r} + 1 - a$ and uses these values for N_aO_2,

$\ell = -0.108 \qquad r_1 = 0.95\ \text{A}^{\circ}$

$a = 1.414 \qquad r_2 = 1.79\ \text{A}^{\circ}$

$C_0 = 1.048 \qquad r = 2.745\ \text{A}^{\circ}$

$C_1 = 1.250 \qquad \delta = 0.84\ \text{A}^{\circ}$

$C_2 = 0.846 \qquad \sigma = 117.72$ ergs/molecule

$\tau = 18.71$ ergs/molecule

one finds that

$$X = \frac{1 + 1.414 \times 0.8072\left(1 + 1.4776\, e^{-\frac{2X\sigma\delta}{r\tau}}\right) e^{\frac{\sigma X\ell}{\tau}}}{1 + 2 \times 0.8072\left(1 + 4.776\, e^{-\frac{2X\sigma\ell}{r\tau}}\right) e^{\frac{\sigma X\ell}{\tau}}}$$

$$= \frac{1 + 1.1414\, e^{\frac{\sigma X\ell}{\tau}} + 1.6866\, e^{\frac{X\sigma}{\tau}\left(\ell - \frac{2\delta}{r}\right)}}{1 + 1.6144\, e^{\frac{\sigma X\ell}{\tau}} + 2.3854\, e^{\frac{X\sigma}{\tau}\left(\ell - \frac{2\delta}{r}\right)}}$$

This equation may be solved graphically for X by setting

$$Y = X$$

and

$$Y = \frac{1 + 1.1414\, e^{-0.6782X} + 1.6866\, e^{-4.52X}}{1 + 1.6144\, e^{-0.6782X} + 2.3854\, e^{-4.52X}}$$

and graphing the two equations on the same scale. The intersection of the two curves gives the value of X characteristic of the crystal.

A similar calculation carried out for the other superoxides with their distorted cubic lattices shows that

$$B(r) = 4C_0 be^{\frac{r_1 + r_2 - r}{\rho}} + 2C_0 be^{\frac{r_1 + r_2 - \gamma r}{\rho}} + 2C_1 be^{\frac{2r_1 - ar}{\rho}}$$

$$+ 2C_2 be^{\frac{2r_2 - ar}{\rho}} + 4C_1 be^{\frac{2r_1 - dr}{\rho}} + 4C_2 be^{\frac{2r_2 - dr}{\rho}}$$

where γ = the ratio of the long and short sides of the unit cell,

$a = \sqrt{2}$, and

$d = \sqrt{r^2 + \gamma^2 r^2} = r\sqrt{1 + \gamma^2}$

Thus,

$$B(r) = be^{\frac{r_1 + r_2}{\rho}} \left[4C_0 e^{-\frac{r}{\rho}} + 2C_0 e^{-\frac{\gamma r}{\rho}} + 2C_1 e^{\frac{r_1 - r_2 - ar}{\rho}} \right.$$
$$\left. + 2C_2 e^{\frac{r_2 - r_1 - ar}{\rho}} + 4C_1 e^{\frac{r_1 - r_2 - dr}{\rho}} + 4C_2 e^{\frac{r_2 - r_1 - dr}{\rho}} \right]$$

$$= be^{\frac{r_1 + r_2}{\rho}} \left[4C_0 e^{-\frac{r}{\rho}} + 2C_0 e^{-\frac{\gamma r}{\rho}} + 2C_2 \left(1 + \frac{C_1}{C_2} e^{-\frac{2\delta}{\rho}}\right) e^{\frac{\delta - ar}{\rho}} \right.$$
$$\left. + 4C_2 \left(1 + \frac{C_1}{C_2} e^{-\frac{2\delta}{\rho}}\right) e^{\frac{\delta - dr}{\rho}} \right]$$

where $\delta = r_2 - r_1$. Then,

$$\tau = -r\left(\frac{\partial B}{\partial r}\right)_{r = r_0} = \left(\frac{r}{\rho}\right) be^{\frac{r_1 + r_2}{\rho}} \left[4C_0 e^{-\frac{r}{\rho}} + 2\gamma C_0 e^{-\frac{\gamma r}{\rho}} + 2aC_2 \left(1 + \frac{C_1}{C_2} e^{-\frac{2\delta}{\rho}}\right) e^{\frac{\delta - ar}{\rho}} \right.$$
$$\left. + 4dC_2 \left(1 + \frac{C_1}{C_2} e^{-\frac{2\delta}{\rho}}\right) e^{\frac{\delta - dr}{\rho}} \right]$$

$$\sigma = r^2\left(\frac{\partial^2\beta}{\partial r^2}\right)_{r=r_0} = \left(\frac{r^2}{\rho^2}\right) b\, e^{\frac{r_1+r_2}{\rho}} \left[\begin{array}{l} 4C_0 e^{-\frac{r}{\rho}} + 2\gamma^2 C_0 e^{-\frac{\gamma r}{\rho}} \\ + 2a^2 C_2\left(1+\frac{C_1}{C_2} e^{-\frac{2\delta}{\rho}}\right) e^{\frac{\delta - ar}{\rho}} \\ + 4d^2 C_2\left(1+\frac{C_1}{C_2} e^{-\frac{2\delta}{\rho}}\right) e^{\frac{\delta - dr}{\rho}} \end{array}\right]$$

and

$$\left(\frac{r}{\rho}\right)\left(\frac{\tau}{\sigma}\right) = \frac{4C_0 e^{-\frac{r}{\rho}} + 2\gamma C_0 e^{-\frac{\gamma r}{\rho}} + 2aC_2\left(1+\frac{C_1}{C_2}e^{-\frac{2\delta}{r}}\right)e^{\frac{\delta-ar}{\rho}} + 4dC_2\left(1+\frac{C_1}{C_2}e^{-\frac{2\delta}{\rho}}\right)e^{\frac{\delta-dr}{\rho}}}{4C_0 e^{-\frac{r}{\rho}} + 2\gamma^2 C_0 e^{-\frac{\gamma r}{\rho}} + 2a^2C_2\left(1+\frac{C_1}{C_2}e^{-\frac{2\delta}{\rho}}\right)e^{\frac{\delta-ar}{\rho}} + 4d^2C_2\left(1+\frac{C_1}{C_2}e^{-\frac{2\delta}{\rho}}\right)e^{\frac{\delta-dr}{\rho}}}$$

$$= \frac{1+0.5\gamma e^{\frac{r-\gamma r}{\rho}} + 0.5a\left(\frac{C_2}{C_0}\right)\left(1+\frac{C_1}{C_2}e^{-\frac{2\delta}{\rho}}\right)e^{\frac{\delta+r-ar}{\rho}} + d\left(\frac{C_2}{C_0}\right)\left(1+\frac{C_1}{C_2}e^{-\frac{2\delta}{\rho}}\right)e^{\frac{\delta+r-dr}{\rho}}}{1+0.5\gamma^2 e^{\frac{r-\gamma r}{\rho}} + 0.5a^2\left(\frac{C_2}{C_0}\right)\left(1+\frac{C_1}{C_2}e^{-\frac{2\delta}{\rho}}\right)e^{\frac{\delta+r-ar}{\rho}} + d^2\left(\frac{C_2}{C_0}\right)\left(1+\frac{C_1}{C_2}e^{-\frac{2\delta}{\rho}}\right)e^{\frac{\delta+r-dr}{\rho}}}$$

If one sets

$X = \left(\frac{r}{\rho}\right)\left(\frac{\tau}{\sigma}\right)$

$m = (1-\gamma)\left(\frac{\sigma}{\tau}\right)$

$a = 1.414$

$\ell_1 = \frac{\delta}{r} + 1 - a$

$\ell_2 = \frac{\delta}{r} + 1 - d$

$C_0 = 1.048$

$C_1 = 1.250$

$C_2 = 0.846$

the equation becomes

$$X = \frac{1+0.5\gamma e^{-mx} + 0.707\left(\frac{C_2}{C_0}\right)\left(1+\frac{C_1}{C_2}e^{-\frac{2x\sigma\delta_1}{r\tau}}\right)e^{\frac{\sigma x \ell_1}{\tau}} + d\left(\frac{C_2}{C_0}\right)\left(1+\frac{C_1}{C_2}e^{-\frac{2x\sigma\delta_2}{r\tau}}\right)e^{\frac{\sigma x\ell_2}{\tau}}}{1+0.5\gamma^2 e^{-mx} + \left(\frac{C_2}{C_0}\right)\left(1+\frac{C_1}{C_2}e^{-\frac{2x\sigma\delta_1}{r\tau}}\right)e^{\frac{\sigma x\ell_1}{\tau}} + d^2\left(\frac{C_2}{C_0}\right)\left(1+\frac{C_1}{C_2}e^{-\frac{2x\sigma\delta_2}{r\tau}}\right)e^{\frac{\sigma x\ell_2}{\tau}}}$$

and, using the values

	KO_2	RbO_2	CsO_2
r	2.855	3.005	3.145
r_1	1.33	1.47	1.74
r_2 (minor)	1.53	1.53	1.53
r_2 (major)	2.05	2.05	2.05
δ_1	0.20	0.06	-0.21
δ_2	0.72	0.58	0.31
γ	1.184	1.171	1.157
m	-1.124	-1.052	-0.973
d	1.55	1.54	1.53
ℓ_1	-0.347	-0.397	-0.484
ℓ_2	-0.30	-0.35	-0.43
$\frac{\sigma}{\tau}$	6.11	6.15	6.20

the equations for X are:

$$X_{KO_2} = \frac{1 + 0.592\, e^{-1.124X} + 0.5707\, e^{-2.12X} + 0.8432\, e^{-2.98X} + 1.251\, e^{-1.83X} + 1.847\, e^{-4.89X}}{1 + 0.701\, e^{-1.124X} + 1.193\, e^{-2.98X} + 0.8072\, e^{-2.12X} + 1.939\, e^{-1.83X} + 2.864\, e^{-4.89X}}$$

$$X_{RbO_2} = \frac{1 + 0.585\, e^{-1.052X} + 0.5707\, e^{-2.44X} + 0.8432\, e^{-2.68X} + 1.243\, e^{-2.152X} + 1.836\, e^{-4.55X}}{1 + 0.685\, e^{-1.052X} + 0.8072\, e^{-2.44X} + 1.193\, e^{-2.68X} + 1.914\, e^{-2.152X} + 2.827\, e^{-4.55X}}$$

$$X_{CsO_2} = \frac{1 + 0.578\, e^{-0.973X} + 0.5707\, e^{-2.85X} + 0.8432\, e^{-2.19X} + 1.235\, e^{-2.67X} + 1.825\, e^{-3.91X}}{1 + 0.669\, e^{-0.973X} + 0.8072\, e^{-2.85X} + 1.193\, e^{-2.19X} + 1.889\, e^{-2.67X} + 2.792\, e^{-3.91X}}$$

which may be solved for X graphically as described for NaO_2.

The values for X obtained graphically are

$$X_{NaO_2} = 0.8570$$
$$X_{KO_2} = 0.8636$$
$$X_{RbO_2} = 0.8789$$
$$X_{CsO_2} = 0.8886$$

which lead to

$$\rho_{NaO_2} = 0.5100 \text{ A}^\circ$$
$$\rho_{KO_2} = 0.5411 \text{ A}^\circ$$
$$\rho_{RbO_2} = 0.5559 \text{ A}^\circ$$
$$\rho_{CsO_2} = 0.5708 \text{ A}^\circ \; .$$

Then, since $$\varphi(r) = A(r) + B(r)$$

and $$B(r) = b e^{\frac{r_1 + r_2}{\rho}} \quad k_1$$

where k_1 = a factor characteristic of the crystal arrangement,

$$-r\left(\frac{\partial B}{\partial r}\right)_{r = r_o} = \tau = \left(\frac{r}{\rho}\right) b e^{\frac{r_1 + r_2}{\rho}} \quad k_1'$$

$$r^2\left(\frac{\partial^2 B}{\partial r^2}\right)_{r = r_o} = \sigma = \left(\frac{r^2}{\rho^2}\right) b e^{\frac{r_1 + r_2}{\rho}} \quad k_1'' \quad .$$

One may solve for b:

$$b = \frac{\rho\tau}{rk'} = \frac{\rho^2\sigma}{r^2k''}$$

$$= \frac{\rho}{rk'}\left[\frac{Ae^2}{r} + \frac{6C}{r^6} + \frac{3D}{r^3}\right]$$

For NaO_2 one finds

$$B(r) = \frac{\rho}{r}\left(\frac{Ae^2}{r} + \frac{6C}{r^6} + \frac{3D}{r^3}\right)\frac{k}{k'}$$

$$= \frac{\rho}{r}\left(\frac{Ae^2}{r} + \frac{6C}{r^6} + \frac{3D}{r^3}\right)\left[\frac{6C_0 e^{-\frac{r}{\rho}} + 6C_2\left(1 + \frac{C_1}{C_2} e^{-\frac{2\delta}{\rho}}\right) e^{\frac{\delta - ar}{\rho}}}{6C_0 e^{-\frac{r}{\rho}} + 6aC_2\left(1 + \frac{C_1}{C_2} e^{-\frac{2\delta}{\rho}}\right) e^{\frac{\delta - ar}{\rho}}}\right]$$

$$B(r) = \frac{\rho}{r}\left(\frac{Ae^2}{r} + \frac{6C}{r^6} + \frac{3D}{r^3}\right)\left[1 - \frac{(a-1)6C_2\left(1 + \frac{C_1}{C_2}e^{-\frac{2\delta}{\rho}}\right)e^{\frac{\delta - ar}{\rho}}}{6C_0e^{-\frac{r}{\rho}} + 6aC_2\left(1 + \frac{C_1}{C_2}e^{-\frac{2\delta}{\rho}}\right)e^{\frac{\delta - ar}{\rho}}}\right]$$

$$= \frac{\rho}{r}\left(\frac{Ae^2}{r} + \frac{6C}{r^6} + \frac{3D}{r^3}\right)\left[1 - \frac{(a-1)6C_2\left(1 + \frac{C_1}{C_2}e^{-\frac{2\delta}{\rho}}\right)e^{\frac{r}{\rho}\left(\frac{\delta}{r} + 1 - a\right)}}{6C_0 + 6aC_2\left(1 + \frac{C_1}{C_2}e^{-\frac{2\delta}{\rho}}\right)e^{\frac{r}{\rho}\left(\frac{\delta}{r} + 1 - a\right)}}\right]$$

$$= \frac{\rho}{r}\,(1 - k)\left(\frac{Ae^2}{r} + \frac{6C}{r^6} + \frac{3D}{r^3}\right)$$

where

$$(1 - k) = 1 - \frac{6(a-1)C_2\left(1 + \frac{C_1}{C_2}e^{-\frac{2\delta}{\rho}}\right)e^{\frac{r}{\rho}\left(\frac{\delta}{r} + 1 - a\right)}}{6C_0 + 6aC_2\left(1 + \frac{C_1}{C_2}e^{-\frac{2\delta}{\rho}}\right)e^{\frac{r}{\rho}\left(\frac{\delta}{r} + 1 - a\right)}}$$

and, for the other superoxides,

$$B(r) = \left(\frac{\rho}{r}\right)\left(\frac{Ae^2}{r} + \frac{6C}{r^6} + \frac{3D}{r^3}\right)\left[\frac{4C_0e^{-\frac{r}{\rho}} + 2C_0e^{-\frac{\gamma r}{\rho}} + 2C_2\left(1 + \frac{C_1}{C_2}e^{-\frac{2\delta}{\rho}}\right)e^{\frac{\delta - ar}{\rho}} \quad 4C_2\left(1 + \frac{C_1}{C_2}e^{-\frac{2\delta}{\rho}}\right)e^{\frac{\delta - dr}{\rho}}}{4C_0e^{-r/\rho} + 2\gamma C_0e^{-\frac{\gamma r}{\rho}} + 2aC_2\left(1 + \frac{C_1}{C_2}e^{-\frac{2\delta}{\rho}}\right)e^{\frac{\delta - ar}{\rho}} + 4dC_2\left(1 + \frac{C_1}{C_2}e^{-\frac{2\delta}{\rho}}\right)e^{\frac{\delta - dr}{\rho}}}\right]$$

$$B(r) = \left(\frac{\rho}{r}\right)\left(\frac{Ae^2}{r} + \frac{6C}{r^6} + \frac{3D}{r^3}\right)\left[1 - \frac{2C_0(\gamma-1)e^{-\frac{\gamma r}{\rho}} + 2C_2(a-1)\left(1+\frac{C_1}{C_2}e^{-\frac{2\delta}{\rho}}\right)e^{\frac{\delta-ar}{\rho}} + 4C_2(d-1)\left(1+\frac{C_1}{C_2}e^{-\frac{2\delta}{\rho}}\right)e^{\frac{\delta-dr}{\rho}}}{4C_0e^{-r/\rho} + 2\gamma C_0e^{-\frac{\gamma r}{\rho}} + 2aC_2\left(1+\frac{C_1}{C_2}e^{-\frac{2\delta}{\rho}}\right)e^{\frac{\delta-ar}{\rho}} + 4dC_2\left(1+\frac{C_1}{C_2}e^{-\frac{2\delta}{\rho}}\right)e^{\frac{\delta-dr}{\rho}}}\right]$$

$$= \left(\frac{\rho}{r}\right)\left(\frac{Ae^2}{r} + \frac{6C}{r^6} + \frac{3D}{r^3}\right)\left[1 - \frac{C_0(\gamma-1)e^{-\frac{(\gamma-1)r}{\rho}} + C_2(a-1)\left(1+\frac{C_1}{C_2}e^{-\frac{2\delta}{\rho}}\right)e^{\left(\frac{\delta}{r}+1-a\right)\left(\frac{r}{\rho}\right)} + 2C_2(d-1)\left(1+\frac{C_1}{C_2}e^{-\frac{2\delta}{\rho}}\right)e^{\left(\frac{\delta}{r}+1-d\right)\left(\frac{r}{\rho}\right)}}{2C_0 + \gamma C_0e^{-\frac{(\gamma-1)r}{\rho}} + aC_2\left(1+\frac{C_1}{C_2}e^{-\frac{2\delta}{\rho}}\right)e^{\left(\frac{\delta}{r}+1-a\right)\left(\frac{r}{\rho}\right)} + 2dC_2\left(1+\frac{C_1}{C_2}e^{-\frac{2\delta}{\rho}}\right)e^{\left(\frac{\delta}{r}+1-d\right)\left(\frac{r}{\rho}\right)}}\right]$$

$$= \left(\frac{\rho}{r}\right)\left(\frac{Ae^2}{r} + \frac{6C}{r^6} + \frac{3D}{r^3}\right)\ (1 - k)$$

where

$$(1 - k) = \left[1 - \frac{C_0(\gamma-1)e^{-\frac{(\gamma-1)r}{\rho}} + 2C_2(d-1)\left(1+\frac{C_1}{C_2}e^{-\frac{2\delta}{\rho}}\right)e^{\left(\frac{\delta}{r}+1-d\right)\frac{r}{\rho}} + C_2(a_i-1)\left(1+\frac{C_1}{C_2}e^{-\frac{2\delta}{\rho}}\right)e^{\left(\frac{\delta}{r}+1-a\right)\frac{r}{\rho}}}{2C_0 + \gamma C_0e^{-\frac{(\gamma-1)r}{\rho}} + aC_2\left(1+\frac{C_1}{C_2}e^{-\frac{2\delta}{\rho}}\right)e^{\left(\frac{\delta}{r}+1-a\right)\frac{r}{\rho}} + 2dC_2\left(1+\frac{C_1}{C_2}e^{-\frac{2\delta}{\rho}}\right)e^{\left(\frac{\delta}{r}+1-d\right)\frac{r}{\rho}}}\right]$$

One may thus use the values of ρ as determined previously to calculate k and, with this, the value of B(r), the repulsive energy of the crystal lattice. The final results of such a calculation as well as many intermediate results are given in Tables 15 and 16.

Higher Energy Terms

The terms in the expression for the crystal energy in which r_o^8 and r_o^{10} appeared were not calculated since they are not believed to be as large as the terms involving the quadrupole-charge interaction which made up only 2% of the total crystal energy themselves.

Total Crystal Energy

The summation of these various energy contributions gives the total energy of the crystal lattice and the results of these calculations for the superoxides indicate

$$U_{NaO_2} = 176.9 \text{ kilocalories/mole}$$
$$U_{KO_2} = 166.1 \text{ kilocalories/mole}$$
$$U_{RbO_2} = 158.7 \text{ kilocalories/mole}$$
$$U_{CsO_2} = 150.7 \text{ kilocalories/mole}$$

There is, of course, considerable uncertainty in the crystal energy of any compound as calculated from the equations just discussed. These crystal energies are calculated on the basis of Born's assumption that crystal energies are functions only of interatomic distances, and the consistency of many results calculated from such crystal energies lends validity to this assumption. Outstanding in this regard are the alkali metal halides which have been studied quite thoroughly. Independent experimental determinations of the electron affinity of I and Br have yielded results which agree well with the values calculated from thermochemical data and crystal energies through the Born-Haber cycle.

Table 15

Values of $\frac{\sigma}{\tau}$ for Superoxides

Compound	τ $\frac{\text{ergs}}{\text{molecule}}$	σ $\frac{\text{ergs}}{\text{molecule}}$	$\frac{\sigma}{\tau}$
NaO_2	18.71×10^{-12}	117.72×10^{-12}	6.28
KO_2	20.15×10^{-12}	123.15×10^{-12}	6.11
RbO_2	19.29×10^{-12}	118.71×10^{-12}	6.15
CsO_2	19.28×10^{-12}	119.43×10^{-12}	6.20

Table 16

Repulsive Energies of Superoxides

Compound	σ $\frac{\text{ergs}}{\text{molecule}}$	τ $\frac{\text{ergs}}{\text{molecule}}$	X	ρ A°	1 - k	$\left(\frac{Ae^2}{r_o}+\frac{6C}{r_o^6}+\frac{3D}{r_o^3}\right)$ $\frac{\text{ergs}}{\text{molecule}}$	B(r) $\frac{\text{ergs}}{\text{molecule}}$	B(r) $\frac{\text{kcal}}{\text{mole}}$
NaO_2	117.72×10^{-12}	18.71×10^{-12}	0.8886	0.5100	0.88	18.71×10^{-12}	3.06×10^{-12}	44.0
KO_2	123.15×10^{-12}	20.15×10^{-12}	0.8789	0.5411	0.89	20.15×10^{-12}	3.40×10^{-12}	49.0
RbO_2	118.71×10^{-12}	19.29×10^{-12}	0.8636	0.5559	0.90	19.29×10^{-12}	3.21×10^{-12}	46.2
CsO_2	119.43×10^{-12}	19.28×10^{-12}	0.8570	0.5708	0.93	19.28×10^{-12}	3.26×10^{-12}	46.9

Since the superoxide ion is more complex than the ordinary halide ion, certain approximations must be made in order to adapt the original Born-Mayer method to the superoxide problem. These major approximations and an estimate of the uncertainties they create are:

(1) The crystal of superoxide is assumed to be ideal, i.e., with no broken edges or holes in the crystal lattice, showing the regular, repeating NaCl or CaC_2 type structure. It seems reasonable to say that this approximation cannot lead to an error of greater than one per cent.

(2) The quadrupole moment of O_2^- has been estimated as 3×10^{-26} esu from calculations previously carried out on O_2 and H_2. Although this is only an estimated value for the quadrupole moment, the small contribution of the quadrupole energy to the total crystal energy makes any error due to this approximation quite small.

(3) The repulsive energy has been computed using both the $\frac{1}{r^n}$ and $e^{-\frac{r}{\rho}}$ type repulsive potentials. The exponential type, although leading into a very involved calculation, appears to approximate more closely the form of the repulsive potential, and thus, it has been used in this work. However, values for U, the crystal energy calculated by other simpler methods, shows only small variations from the value calculated by the exponential

method. The uncertainty in the repulsive energy contribution to U probably amounts to about five per cent of the total crystal energy.

If these are the only uncertainties in the crystal energy as calculated, then it seems reasonable to suppose that the total probable error in the crystal energies of the alkali metal superoxides as presented in the preceding sections of this thesis amounts to ± 10 kilocalories per mole.

Although the method of Born and Mayer is extremely complex and apparently considers most of the possible crystal interactions, the results still may be uncertain by as much as ten per cent because of uncertainty in the value of the repulsive energy. If one considers this inherent uncertainty, then in many cases it seems reasonable to use one of the approximate formulas derived by Kapustinskii in 1934 and 1949 which give the energy of most crystal lattices simply and in terms of convenient parameters.

In 1934, Kapustinskii (25) showed that the Madelung constant of a given crystal and the number of ions in the crystal are approximately related by

$$A = K\left(\frac{\Sigma n}{2}\right)$$

where A is the Madelung constant, Σn is the number of ions in a molecule, and k is a constant equal to 1.748 using NaCl as a standard. Then, with this relation and assuming that the crystal energy is given by

$$U = \frac{ANe^2 \eta_1 \eta_2}{r} + \frac{B}{r^n}$$

where n is 9 for most crystals, Kapustinskii showed that

$$U = 256.1 \left[\frac{(\Sigma n) \quad \eta_1 \eta_2}{r_1 + r_2} \right]$$

where η_1 and η_2 = the valences of ions 1 and 2,

r_1 and r_2 = the ionic radii of ions 1 and 2, and

(Σn) = the number of ions in a molecule of the compound.

Also, in 1949, using a different idea and introducing the concept of crystallochemical electronegativities, Kapustinskii (28) has derived the equation

$$U = \Sigma (\chi_C - \chi_{A^-})^2$$

where Σ = the number of bonds formed in the molecule,

χ_C = the crystallochemical electronegativity of the cation, and

χ_A = the crystallochemical electronegativity of the anion.

The values for the χ's have been computed relative to $\chi_{F^-} = 1.0$. Values for other ions have been computed using known crystal energies from Born-Mayer calculations or those derived through thermochemical cycles. These values may then be used to calculate energies for compounds that have not been previously studied.

Both of these methods, as well as the more involved Born-Mayer computation, have been applied to the superoxides of the alkali metals. Figure 10 shows the variation of crystal energy from one superoxide to another as calculated by these methods.

The ionic radii used in these calculations are those listed in Table 17 and are taken from Brewer (10). In Table 18 are listed the χ's for various anions and cations as given by Kapustinskii (28) as well as two newly computed values for $\chi_{Hg^{++}}$ and $\chi_{O_2^-}$. The crystal energies presented in Table 19 have been calculated from the formulae discussed above.

Figure 10

LATTICE ENERGIES OF ALKALI METAL SUPEROXIDES

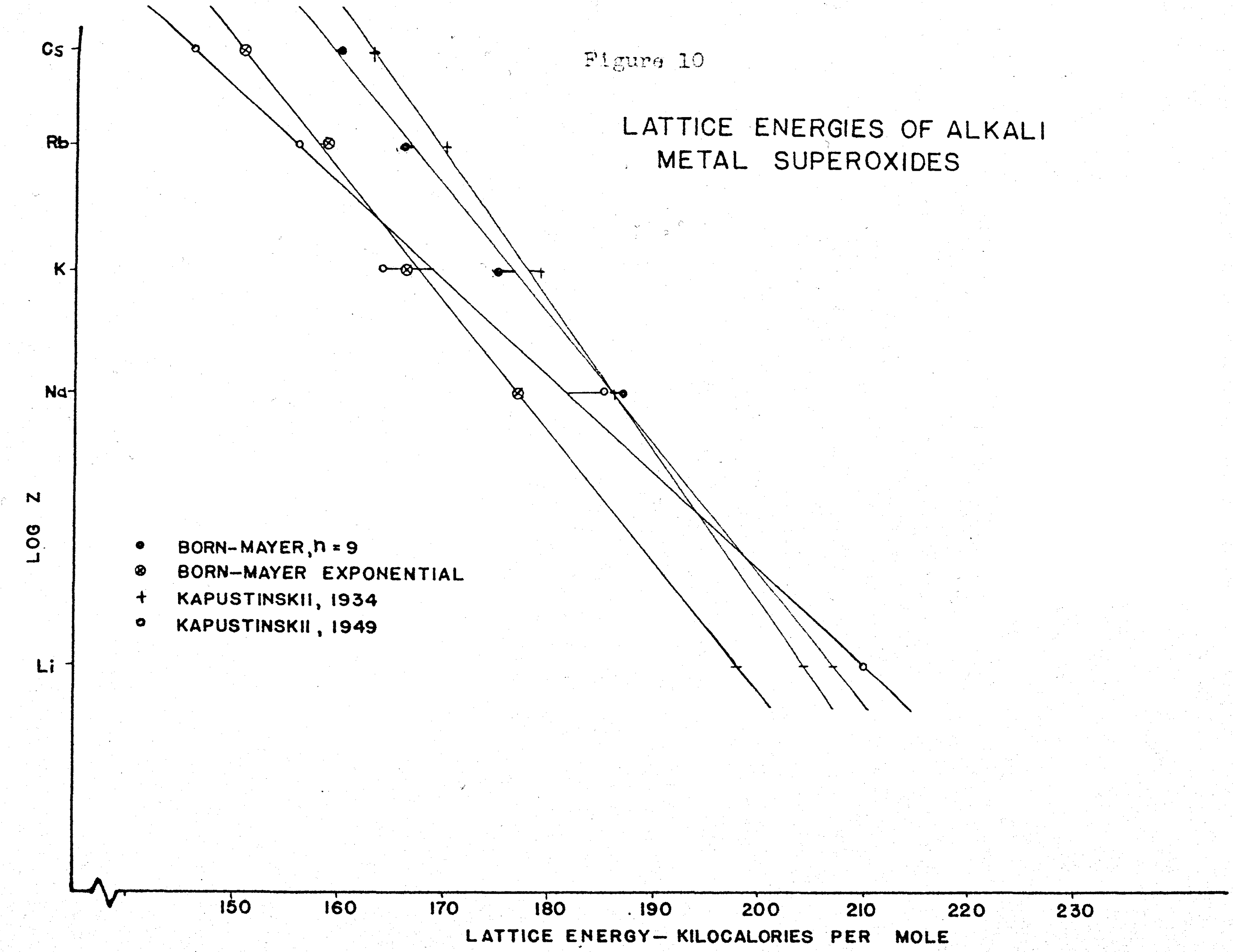


Table 17

Ionic Radii

Cation	Ionic Radius A^{o}
Li^+	0.71
Na^+	0.95
K^+	1.33
Rb^+	1.47
Cs^+	1.74
Tl^+	1.59
Ag^+	1.21
Be^{++}	0.38
Mg^{++}	0.66
Ca^{++}	0.99
Sr^{++}	1.15
Ba^{++}	1.37
Zn^{++}	0.72
Cd^{++}	0.96
Hg^{++}	1.10
Cu^{++}	0.72
Pb^{++}	1.27

Anion	Ionic Radius A^{o}
F^-	1.34
Cl^-	1.80
Br^-	1.90
I^-	2.23
$O^{=}$	1.35
$S^{=}$	1.84
O_2^-	1.52 * 1.79 **

* KO_2, RbO_2, CsO_2

** NaO_2

Table 18

Crystallochemical Electronegativities *

Cation	$\varkappa_C$	Anion	$\varkappa_A$
Li^{+}	16.5	F^{-}	1.0
Na^{+}	15.6	Cl^{-}	2.1
K^{+}	14.8	Br^{-}	2.3
Rb^{+}	14.5	I^{-}	2.7
Cs^{+}	14.1	$O^{=}$	-1.8
Tl^{+}	15.2	$S^{=}$	-0.4
Ag^{+}	16.8	$O_2^{=}$	2.0
Be^{++}	21.2		
Mg^{++}	19.7		
Ca^{++}	18.6		
Sr^{++}	18.1		
Ba^{++}	17.6		
Zn^{++}	20.0		
Cd^{++}	19.0		
Hg^{++}	18.5		
Pb^{++}	18.0		

---

* Kapustinskii (28)

Table 19

Crystal Energies of Various Compounds in Kilocalories per Mole

Compound	Kapustinskii (25) U	Kapustinskii (28) U	Born-Mayer n	Born-Mayer U	Born-Mayer exponential U'
LiF	249	240	6	240	
NaF	223	213	7	213	
KF	191	190	8	190	
RbF	182	182	8.5	182	
CsF	166	172	9.5	172	
TlF	175	202	9.5		
AgF	201	250	8.5	208	219
NaCl	186	182	8.0	180	183
TlCl	151	171	10.5	159	167
AgCl	170	216	9.5	187	203
NaBr	179	177	8.5	175	
TlBr	147	166	11	154	164
AgBr	165	210	10	181	197
NaI	161	166	9.5	164	
TlI	134	156	12	146	159
AgI	149	199	11	176	190
LiO_2	(202)	(210)	(9)	(204)	
NaO_2	186	185	9	187	176.9
KO_2	179	164	9	175	166.1
RbO_2	170	156	9	166	158.7
CsO_2	163	146	9	160	150.7
BeO	1,182	1,058	6	1,215	
MgO	1,018	925	7	941	
CaO	875	833	8	845	
SrO	819	794	8.5	794	
BaO	752	753	9.5	750	
ZnO	987	950	8	976	
CdO	885	866	8.5	870	
HgO	835	824			
PbO	781	784			
Na_2O	667	605	7	595	
K_2O	573	551	8	525	
BeS	922	933	7	885	
MgS	819	809	8	780	
CaS	723	722	9	723	
SrS	685	684	9.5	704	
BaS	638	648	10.5	658	
ZnS	800	832	9	816	
CdS	730	753	9.5	744	
HgS	696	717	10.5	717	
CuS	800	800			
PbS	658	677		634	
Na_2S	550	512	8	517	
K_2S	485	462	9	464	

( ) indicate estimated values.

The Electron Affinity of Oxygen

The electron affinity of oxygen has been computed from the data previously discussed through this Born-Haber cycle:

$$\begin{tikzcd}
MO_2(s) \arrow[r, "U"] & M^+(g),\ O_2^-(g) \\
M(s),\ O_2(g) \arrow[u, "\Delta H_f^{MO_2}"] \arrow[r, "\Delta H_{sub}^{M}"'] & M(g),\ O_2(g) \arrow[u, "I-E"']
\end{tikzcd}$$

Here, $E_{O_2} = I + \Delta H_{sub.}^{M} - U - \Delta H_f^{MO_2}$ and thus, one may easily determine E_{O_2}. The data for this calculation are given in Table 20, and E_{O_2} is found to be 27± 2 kilocalories per mole, a value somewhat in disagreement with those determined by other methods.

A value for E_{O_2} may be estimated by considering the reactions:

$$\begin{array}{rcl@{\qquad}rcl}
X_2 + e & = & X_2^- & \Delta H_1 & = & -E_{X_2} \\
X^- & = & X + e & \Delta H_2 & = & E_X \\
X_2^- & = & X + X^- & \Delta H_3 & = & D(X_2^-) \\
\hline
X_2 & = & 2\,X & \Delta H_4 & = & D(X_2)
\end{array}$$

Table 20

The Electron Affinity of Oxygen

Compound	$\Delta H^{M}_{sub.}$ $\frac{kcal}{mole}$	I_M $\frac{kcal}{mole}$	U $\frac{kcal}{mole}$	ΔH_f $\frac{kcal}{mole}$	E_{O_2} $\frac{kcal}{mole}$
NaO_2	25.9	118.5	176.9	-62.4	29.9
KO_2	21.5	100.0	166.1	-68.2	23.6
RbO_2	20.5	96.3	158.7	-68.5	26.6
CsO_2	18.8	89.8	150.7	-70.0	27.9

Thus, $$D(X_2) = -E_{X_2} + E_X + D(X_2^-)$$

or $$E_{X_2} = E_X - (D_{X_2} - D_{X_2^-})$$

Now, $D(O_2)$ is 117.2 kilocalories per mole and E_O is either 70.8 kilocalories per mole (9), or 53.8 kilocalories per mole as determined by Metlay and Kimball (reference 32, Part II of this thesis). Then, if one assumes that $D(O_2^-)$ is 3/4 $D(O_2)$, E_{O_2} is either 41.5 or 24.5 kilocalories per mole. A study of the effects of slow electrons on oxygen gas by Bredbury (8) indicates E_{O_2} is about 3-8 kilocalories per mole, while Weiss (52, 53) has suggested a value of 69 kilocalories per mole on the basis of studies involving the HO_2 radical. Since these values are only approximate, and involve large uncertainties, they are not in complete disagreement with the value obtained in this research. Kazarnovskii (31) has suggested that Weiss' value is so high because of an incorrect value for the hydration energy of the superoxide ion, and, when modified properly, should lead to a value of about 16 kilocalories per mole. Recently, Evans and Uri (13) have studied the dissociation of H_2O_2 and have also made crystal energy calculations using the Born-Mayer $1/r^n$ approximation for the higher superoxides. Their results are essentially in agreement with the data of Table 20 except where values of the heat of formation have been changed on the basis of the present calorimetric data.

The best value for the electron affinity of O_2 is 27±2 kilocalories per mole, and $D(O_2^-)$ is predicted to be 90 kilocalories per mole. One may also use this value for the electron affinity of oxygen along with an estimated crystal energy for LiO_2 to estimate a heat of formation for this compound which has not thus far been isolated. The data indicate $\Delta H_f(LiO_2) = -65$ kilocalories per mole, a value considerably more negative than the -53 kilocalories per mole predicted from Figure 8.

MELTING POINTS AND SPECIFIC HEATS OF NaO_2, KO_2, AND Na_2O_2

Melting Points

An attempt was made to determine the melting points of Na_2O_2, NaO_2, and KO_2. The melting point of sodium peroxide is given by Brewer (9) as 500° C. while Kazarnovskii (31) and Brewer (9) give 380° C. as the melting point of KO_2. Todd (51) gives 530° C. as the melting point of KO_2. No observations have been made on NaO_2. In the experiments performed an ordinary porcelain crucible of about 25 cc. capacity was used as a container for the compound which was melted by means of a Bunsen burner. A chromel-alumel thermocouple connected to a Brown Electronik recorder was used to measure temperature. The compound was heated until it melted completely, and then, the burner was removed, the crucible was allowed to cool, and the cooling curve was carefully observed to determine whether or not a cooling flat occurred. Preliminary tests were made with NaOH which did show a definite cooling flat at about 10° C. below the melting point recorded in the literature. In each experiment the melt was allowed to cool slowly without stirring.

Na_2O_2

Two samples of sodium peroxide were studied and they appeared to melt at about 700° C. They melted to form a black liquid which solidified on cooling, but no flat occurred in the cooling curve.

NaO_2

Four samples of sodium superoxide were studied. They were originally yellow, but became successively whitish-orange, greenish-yellow, and brownish-black at temperatures of 200 - 400° C., 400 - 500° C., and 500 - 600° C., respectively. The apparent melting point was about 550° C. The liquid present when melted was black and it still gave a positive test for peroxide when tested with an acid vanadate solution. A very slight discontinuity in the cooling curve was noted several times at $275\pm10^{\circ}$ C., possibly due to some NaOH present as a decomposition product. A gray solid which was very hygroscopic and had a melting point of about $115\pm5^{\circ}$ C. was formed as the product after extensive heating.

KO_2

Four samples of potassium superoxide were studied and they behaved essentially like the sodium superoxide except that no discontinuity was observed in the cooling curve. The melt became completely liquid at 450 - 500° C. and gave a positive peroxide test even after strong heating.

It was concluded that sharp melting points for these oxides could not be determined by such methods and that dissociation pressures should be measured for these compounds in order to get more information about their nature at temperatures much above 25° C.

Specific Heats

The specific heats of Na_2O_2, NaO_2, and KO_2 were measured by the method of mixtures using a Dewar flask of 500 ml capacity, a hand stirrer, and a Beckmann thermometer. Carbon tetrachloride which had been previously dried over NaO_2 was used as the liquid medium and the heat equivalent of the system was determined by an electric calibration. The results of the measurements are recorded in Table 21.

Table 21

Specific Heats of Peroxides and Superoxides

Compound	$\frac{\left(\frac{\text{calories}}{\text{degree}}\right)}{\text{gram}}$	$\frac{\left(\frac{\text{calories}}{\text{degree}}\right)}{\text{mole}}$	Literature Values
NaO_2	0.26 ± 0.03	14	
Na_2O_2	0.27 ± 0.03	21	20.7 calories per degree per mole (29)
KO_2	0.27 ± 0.03	19	19.6 calories per degree per mole (31)

ENTROPIES OF FORMATION AND DISSOCIATION PRESSURES

No low temperature heat capacities have been measured for sodium peroxide, sodium superoxide, or potassium superoxide, and thus, the entropies of formation of these compounds may only be estimated. Brewer (9) has suggested values of -32 e.u. for the oxides, -54 e.u. for the peroxides, and the author has estimated -44 entropy units for the alkali metal superoxides. Thus, for the general reaction

$$M_2O(s) + \tfrac{1}{2}\ O_2(g) \quad = \quad M_2O_2(s)$$

the entropy change for the reaction is -22 e.u. and for the reaction

$$\tfrac{1}{2}\ M_2O_2(s) + \tfrac{1}{2}\ O_2(g) \quad = \quad MO_2(s)$$

the entropy of reaction is -17 e.u.

The entropies for the reactions written above may be used along with the heats of formation of the compounds involved to compute the free energy of reaction, the equilibrium constant, and the dissociation pressure of oxygen. Such calculations have been carried out for Na_2O_2 and KO_2. The dissociation pressures as calculated from these data are plotted in Figures 11 and 12 along with experimental data of Blumenthal (5) on Na_2O_2 and Kazarnovskii and Raikhshtein (32), Blumenthal (6), Todd (51), and Kraus and White (36) on KO_2. No experimental work has been carried out on NaO_2 with the idea in mind of determining its dissociation pressure, but

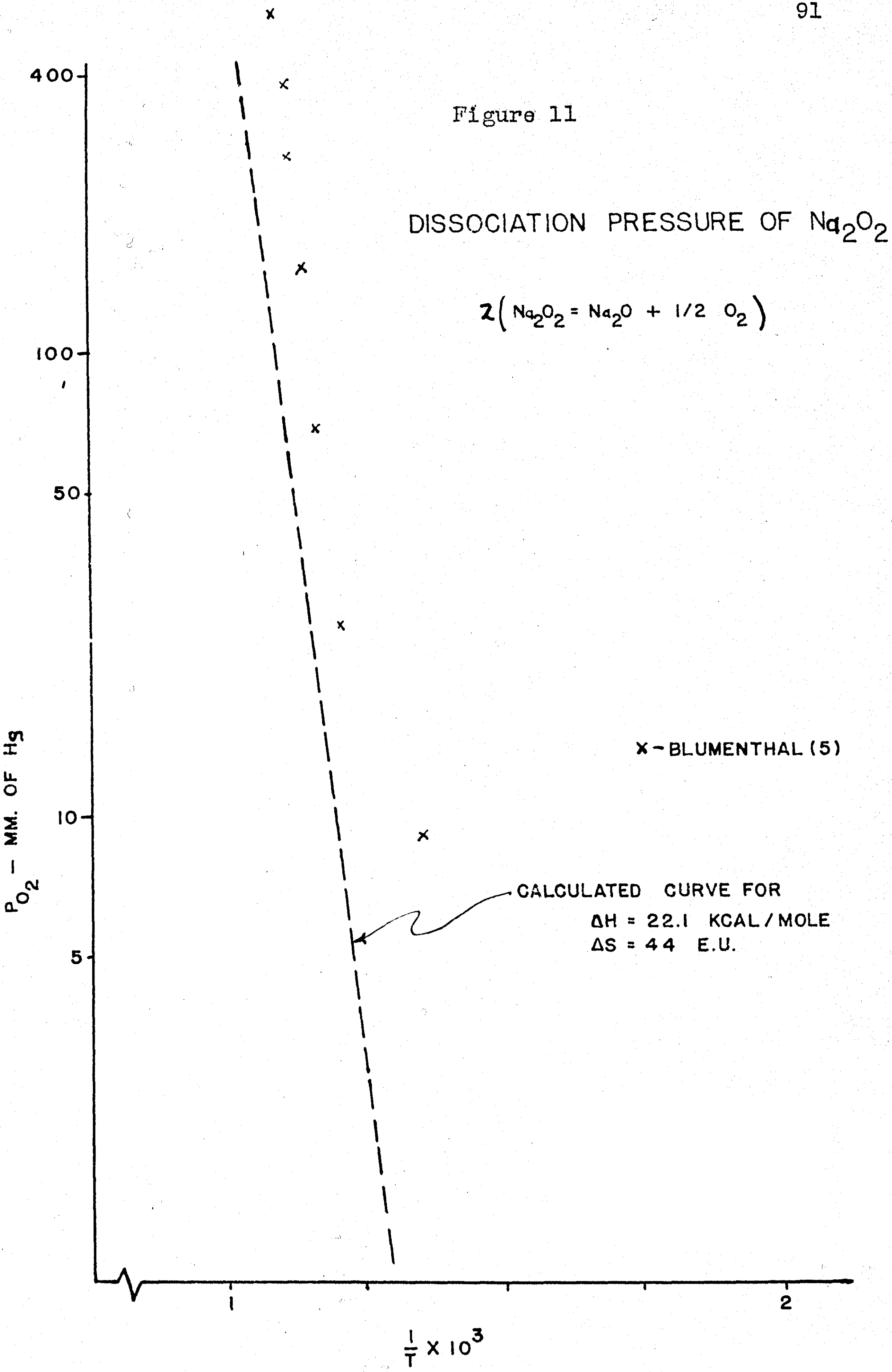
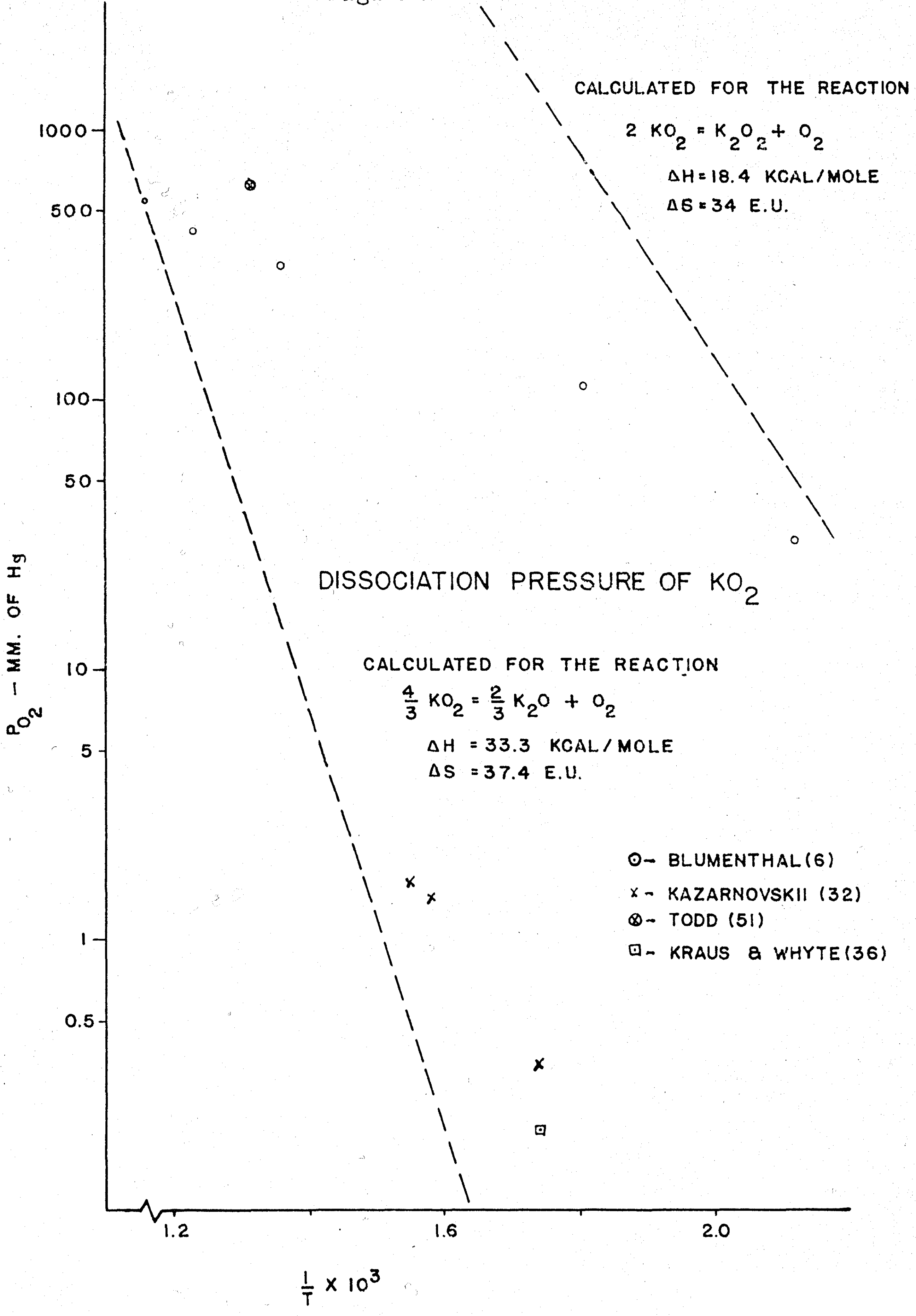


Figure 11

DISSOCIATION PRESSURE OF Na_2O_2

$2(Na_2O_2 = Na_2O + 1/2\ O_2)$

Figure 12


CALCULATED FOR THE REACTION
$2\ KO_2 = K_2O_2 + O_2$
$\Delta H = 18.4$ KCAL/MOLE
$\Delta S = 34$ E.U.
DISSOCIATION PRESSURE OF KO_2
CALCULATED FOR THE REACTION
$\frac{4}{3} KO_2 = \frac{2}{3} K_2O + O_2$
$\Delta H = 33.3$ KCAL/MOLE
$\Delta S = 37.4$ E.U.
○ - BLUMENTHAL (6)
x - KAZARNOVSKII (32)
⊗ - TODD (51)
⊡ - KRAUS & WHYTE (36)
P_{O_2} - MM. OF Hg
1000
500
100
50
10
5
1
0.5
1.2
1.6
2.0
$\frac{1}{T} \times 10^3$

estimates may be made on these data from Stephanou(48) : a compound which evolved 92% of the theoretical superoxide oxygen was prepared by heating Na_2O_2 to 763° K. under an oxygen pressure of 298 atmospheres. By using this pressure as the dissociation pressure at this temperature and the entropies previously estimated, one calculates that the heat evolved in the conversion reaction from sodium peroxide to sodium superoxide should amount to approximately 17 kilocalories per mole whereas the value obtained from calorimetrically determined heats of formation is only about 3 kilocalories per mole. On the basis of the calorimetric heats of formation, the dissociation pressure at 763° K. is calculated to be 3.9×10^6 atmospheres, indicating that Stephanou should not have been able to convert the peroxide to superoxide. The fact that the reaction did occur indicates clearly that either the calorimetric data are incorrect as they have been interpreted or that the entropy of formation estimated for the compounds involved is incorrect. Since the other heats of formation of alkali metal peroxides and superoxides measured in the identical apparatus were in good agreement with values obtained by other workers and led to fair agreement with measured dissociation pressures, it seems reasonable that the calorimetric data are dependable at least to the nearest kilocalorie. To decide definitely which factor causes the disagreement noted above, one should study some of the other reactions of the superoxides, determine the decomposition products, and measure the low temperature heat capacities.

SUGGESTED FUTURE RESEARCH

The results of the research reported in this thesis raise several questions about the alkali metal oxides, peroxides, and superoxides. The general subjects which would seem to be of most value for future investigations are:

(1) a calorimetric study of the higher superoxides, CsO_2 and RbO_2, to determine their heats of solution in water and allow recalculation of their heats of formation.

(2) a study of the reaction of the peroxides and superoxides with small amounts of water and CO_2 with the idea of deciding whether or not intermediate hydrates are formed in the slow decomposition process, what these hydrates are, and how the complete analysis of any sample of peroxide or superoxide can be accomplished.

(3) a measurement of the low temperature heat capacities of the peroxides and superoxides in order to allow determination of the entropies and calculation of dissociation pressures by combination with measured heats of formation.

(4) a study of the dissociation pressures of the superoxides to complete the validation of the results calculated from thermodynamic data.

(5) a new attempt to prepare LiO_2, which is indicated to be fairly stable on the basis of extrapolated data on the other superoxides, taking into account the fact that the formation reaction is considerably exothermic and using pressures of oxygen higher than those used by Seyb (46).

BIBLIOGRAPHY

1. Argersinger, W., Kleinberg, J., Schechter, W., and Stephanou, S., J. Am. Chem. Soc. 71: 1819-1821, (1949).
2. Beketoff, Bull. Acad. Science Russia 32: 186-194, (1888).
3. Beketoff, ibid. 33: 173-175, (1890).
4. Beketoff, ibid. 35: 541-544, (1894).
5. Blumenthal, M., Roczniki Chem. 11: 865, (1931).
6. Blumenthal, M., ibid. 12: 119, (1932).
7. Born, M., and Mayer, J. E., Z. Physik 75: 1-18, (1932).
8. Bradbury, N., Phys. Rev. 44: 883-890, (1933).
9. Brewer, L., "The Thermodynamic Properties of the Oxides", UCRL - 104, (1948).
10. Brewer, L., "The Thermodynamic and Physical Properties of the Elements" and "The Thermodynamic Properties of the Halides", The Transuranium Elements, McGraw-Hill, pp. 13-39, 165-168, (1949)
11. Bridgman, P., The Physics of High Pressure, Macmillan, p. 167, (1931)
12. Dauben, C., and Templeton, D., J. Am. Chem. Soc. 72: 2251-2254, (1950).
13. Evans, M. G., and Uri, N., Trans. Faraday Soc. 45: 224-230, (1949).
14. de Forcrand, R., Comptes Rendus 127: 514-516, (1898).
15. de Forcrand, R., ibid. 130: 1465-1468, (1900).
16. de Forcrand, R., ibid. 143: 98-99, (1906).

17. de Forcrand, R., _ibid._ 146: 802-806, (1908).

18. de Forcrand, R., _ibid._ 150: 1399-1402, (1910).

19. de Forcrand, R., _ibid._ 158: 991-994, (1914).

20. Helmholtz, L., and Mayer, J. E., _Z. Physik_ 75: 19-29, (1932).

21. Helms, A., and Klemm, W., _Z. anorg. u. allg. Chemie_ 242: 201, (1939).

22. Hildebrand, J., and Latimer, W., _Reference Book of Inorganic Chemistry_, Macmillan, pp. 14 and 44, (1940).

23. Huffman, E. H., and Shomate, C. H., _J. Am. Chem. Soc._ 65: 1625-1629, (1943).

24. Kaganovich, K. P., and Mishchenko, Yu. Ya., _J. Appl. Chem._ (USSR) 22: 1078, (1949).

25. Kapustinskii, A. F., _J. Chem. Phys._ (USSR) 5: 59-63, (1934).

26. Kapustinskii, A. F., _Acta. Physicochem._ (USSR) 18: 370-377, (1943).

27. Kapustinskii, A. F., _Izvest. Akad. Nauk. SSSR Otdel. Klim. Nauk._, 568-580, 581-589, (1948).

28. Kapustinskii, A. F., _Doklady Akad. Nauk._ (USSR) 67: 467-470, (1949).

29. Kaule, H. L., and Roth, W. A., _Z. anorg. Chem._ 253: 352-356, (1947); 255: 324, (1948).

30. Kazarnovskii, I. A., _J. Chem. Phys._ (USSR) 13: 320, (1940).

31. Kazarnovskii, I. A., _Doklady Akad. Nauk._ (USSR) 59: 67-70, (1948).

32. Kazarnovskii, I. A., and Raikhshtein, S. I., J. Chem. Phys. (USSR) 21: 245-255, (1947).

33. Kirkwood, J., and Slater, J., Phys. Rev. 37: 682-697, (1931).

34. Kleinberg, J., Schechter, W., and Sisler, H., J. Am. Chem. Soc. 70: 267-269, (1948).

35. Kleinberg, J., Schechter, W., and Thompson, J., J. Am. Chem. Soc. 71: 1816-1818, (1949).

36. Kraus, C. A., and Whyte, E. F., J. Am. Chem. Soc. 48: 1781-1790, (1926).

37. Loeb, L. B., Phys. Rev. 48: 684, (1935).

38. Madelung, W., Phys. Z. 19: 524-532, (1918).

39. Matsui and Nakata, J. Soc. Chem. Ind. Japan 28: 740, (1925).

40. Mayer, J., J. Chem. Phys. 1: 270-279, (1933).

41. Pauling, L., Proc. Roy. Soc. A 114: 181-211, (1927).

42. Pauling, L., The Nature of the Chemical Bond, Cornell University Press, (1948).

43. Rengade, E., Comptes Rendus 145: 236-238, (1907).

44. Rengade, E., Ann. Chim. Phys. (8) 14: 540-553, (1908).

45. Robinson, H., and Westrum, E., "A Semi-microcalorimeter for Precise Thermochemical Measurements", The Transuranium Elements, McGraw-Hill, pp. 889-907, (1949).

46. Seyb, E., Ph. D. Thesis, University of Kansas, (1950).

47. Sherman, J., Chem. Rev. 11: 93-170, (1932).

48. Stephanou, S., Ph. D. Thesis, University of Kansas, (1949).

49. Thompson, J., Ph. D. Thesis, University of Kansas, (1950).

50. Thomson, M., "The Total and Free Energies of Oxides of Thirty Two Metals", The Electrochemical Society, (1942).

51. Todd, B., Naval Research Laboratory, Unpublished Work.

52. Weiss, J., _Trans. Faraday Soc._ 31: 966, (1935).

53. Weiss, J., _ibid._ 42: 133, (1946).

54. Weissberger, A., _Physical Methods of Organic Chemistry,_ Interscience, pp. 311-434, (1945).

55. Wyckoff, R., _Crystal Structures,_ Interscience, (1948).

PART II

THE DISSOCIATION ENERGY OF FLUORINE

PART II

TABLE OF CONTENTS

INTRODUCTION

Fluorine, the most powerful oxidizing agent of the elements, occupies a place of particular interest among the halogens since it is the most simple and should be the easiest to consider from a theoretical basis. Although many successful studies of the other halogens have been made during the last twenty years, only a few determinations of the dissociation energy of the fluorine molecule have been carried out by methods which are dependable, and the interpretation of the results of some of these studies is still in doubt.

The dissociation energies of iodine, bromine, and chlorine have been determined by locating the convergence limits of their band spectra, by measurements of the thermal conductivity of the gases as a function of temperature, by vapor density studies, and by studies of compounds which contain the respective halogens. The application of such methods to the study of fluorine, however, has failed to lead to a reliable value of the dissociation energy. It is the attempt of this thesis to present some new experimental data and to calculate a value of the dissociation energy consistent with the presently available thermochemical data.

PREVIOUS ATTEMPTS TO DETERMINE D(F_2)

The attempts to obtain a value for the dissociation energy of fluorine will be considered in two categories. The first to be discussed are those that involve a study of the element, while those involving studies of fluorine compounds are to be considered second.

Studies of the Spectrum of Fluorine

The early efforts to determine the dissociation energy of the F_2 molecule were concerned with studies of the spectrum of the gas. Gale and Monk (20) studied the absorption spectrum of fluorine gas contained in a glass tube with CaF_2 windows. They worked with tubes varying in length from 7 cm. to 3 m. filled with fluorine at atmospheric pressure. In their studies they found no discrete absorption bands, but only a continuous absorption beginning at 4100 A^o and extending to shorter vave lengths. By studying the emission spectrum produced by fluorine in a discharge tube, Gale and Monk (19, 20, 21) were able to find and analyze several emission bands believed to be produced by excited F_2 molecules. Aars (1) also carried out some work on these emission bands of fluorine and analyzed one of the bands described incompletely by Gale and Monk. On the basis of these studies, it was impossible to make any prediction at all regarding the dissociation energy.

It was suggested by Franck (16) that the location of the maximum in the continuous absorption spectrum was characteristic of the halogen and related to the dissociation energy. This was the basis for the work of Sprenger, Taylor, and von Wartenberg (59) who compared the absorption spectrum of F_2 with that of the other halogens. In their studies to locate this maximum in the region of continuous absorption, these workers used a glass tube with quartz windows sealed on the ends with a litharge and glycerine paste. The maximum was located at 2900 A^o for F_2 while the maxima for Cl_2, Br_2, and I_2 occur at 3390 A^o, 4200 A^o, and 4600 A^o, respectively. These three latter halogens also show banded absorption spectra and have well-defined convergence limits which allow accurate determination of their dissociation energies. By obtaining the differences between the wave length of the maximum of continuous absorption and the convergence limit for each halogen, plotting this difference as a function of atomic number, and by extrapolating to get a convergence limit for F_2, these early investigators concluded that the dissociation energy of fluorine was 63.3 kilocalories per mole. A later study along the same line by Bodenstein, Jockusch, and Shing Hou Chong (9) indicated that the maximum absorption occurred at 2820 A^o. By considering the dissociation energies of the other halogens and hydrogen, and graphing these values versus atomic number, these workers chose a value of 70.1 kilocalories per mole for $D(F_2)$.

Quite recently, Nathans (46) has studied the infra-red absorption spectrum of fluorine in the photographic infra-red (7000-9600 A^{o}) but detected no absorption. The fluorine was contained in a Pyrex tube 185 cm. long at a pressure of one atmosphere and a tungsten ribbon lamp was used as the light source.

The Raman spectrum of F_2 has now been observed by Andrychuk (2) after an unsuccessful attempt by Garner and Yost (23). Andrychuk used a powerful light source which enabled him to overcome the problem of Garner and Yost, that of getting a sufficient exposure of the plate in the time before the fluorine reacted with the windows of its container. The detected Raman displacement, $\Delta\nu$, was found to be 892 cm^{-1}, slightly higher than that predicted by Badger's rule, 856 cm^{-1} (3).

The probable explanation of the lack of useful spectroscopic data for a determination of the dissociation energy on fluorine is that the diatomic molecule either does not have a low lying stable excited state, or that a stable state exists with its potential minimum shifted to considerably larger distances than that of the ground state. Either of these cases could give rise to the type of continuous absorption observed for the molecule. It is believed that no one has previously attempted to study the variation of the characteristics of the absorption spectrum with temperature for fluorine, although such studies have been carried out with chlorine by Bayliss and Gibson (6) and with bromine and iodine by Koenigsberger and Vogt (35). The theoretical behavior has been derived by Bayliss, Gibson, and Rice (7) for Cl_2. The problem of containers for fluorine at high temperatures is one not yet satisfactorily solved, but experiments to be described in subsequent sections of this thesis have been carried out in which the absorption spectrum has been studied at temperatures up to 350° C.

Studies of the Thermal Conductivity of F_2

Wicke (61) has measured the thermal conductivity of fluorine up to 1000° C. in an experiment similar to the hot wire experiment on hydrogen performed by Langmuir (36). The apparatus used consisted of two nickel wires 0.016 mm. in diameter stretched inside a glass tube 60 cm. long and 38 mm. inside diameter kept in a water bath at room temperature. The current and voltage drops across the wires were measured and used to calculate the total heat flow from the tube by radiation and conduction. The amount of heat flow due to radiation was determined by measurements with the tube evacuated, and for conduction measurements, N_2 gas was used as the standard. To the limits of accuracy of the experiment, the heat conductivity of F_2 and N_2 were identical over the entire temperature range, and thus Wicke has presented this as evidence in favor of a value for $D(F_2)$ greater than 60 kilocalories per mole. More recently, U. Franck (17) has repeated Wicke's experiments and Wicke has now modified his interpretation of the experimental results to state that at temperatures up to 400° C. no detectable dissociation of fluorine is believed to occur (15). This interpretation is compatible with a value for $D(F_2)$ of 40 kilocalories per mole as calculated from data on ClF to be discussed later. Nathans (46) has objected to Wicke's conclusions on the basis that in his calculation of the theoretical heat conductivity of F_2, λ (T), from the equation

$$\lambda(T) = 2.73 \times 10^{-5} \left[\frac{1}{\sigma_\infty \sqrt{M}} \left(\frac{T^{\frac{3}{2}}}{C + T} \right) \left\{ 9.43 + 1.3\, c\left(\frac{\theta}{T}\right) \right\} \right]$$

where σ_∞ = the effective molecular diameter in A°,

C = the Sutherland constant,

$\theta = \frac{hf}{k}$ where f is the molecular vibrational frequency, h is Planck's constant, and k is the Boltzman constant,

M = the molecular weight of the gas, and

T = the absolute temperature

Wicke has used values for σ_∞ that are too small (3.2 A° for N_2 and 3.1 A° for F_2) and Nathans suggests using Pauling's values for the van der Waals radii of these gases (4.10 A° for N_2 and 4.18 A° for F_2). Use of these values for σ_∞ as well as use of the value 892 cm^{-1} for the vibrational frequency makes Wicke's data more nearly compatible with a value for $D(F_2)$ of 40-50 kilocalories per mole.

The Electron Affinity of Fluorine

The only available data on the electron affinity of fluorine are those of Mayer and Helmholtz (37) who calculated E_F = 95.3 kilocalories per mole from calculations using the Born-Haber thermochemical cycle and other thermodynamic data available in 1932 at the time of their work, of Ionov (30) who determined E_F = 94.7 kilocalories per mole from studies of the dissociation products of alkali fluorides on tungsten, and of Metlay and Kimball (33) who have studied the adsorption of fluorine on a tungsten surface.

The results of Mayer and Helmholtz have inherent within them not only the uncertainties of the crystal energy calculations (see discussion in Part I of this thesis), but also since the electron affinity as calculated from the Born-Haber cycle depends directly on the value used for the dissociation energy of the halogen, have the uncertainties present in the dissociation energy. Their electron affinity was calculated on the basis that $D(F_2)$ = 63 kilocalories per mole, and thus this result is subject to the same doubt as is the dissociation energy.

Ionov has studied a group of alkali halides and determined values for the electron affinities of I, Br, Cl, and F which are in reasonable agreement with values determined through calculations of the type of Mayer and Helmholtz and also through direct experiments by Mayer and Sutton (38), Glockler and Calvin (12), and Blewett (8).

The method used by Metlay and Kimball consisted of passing fluorine gas at a given pressure over a hot tungsten filament and measuring the relative currents of negative ions and electrons emitted from the filament. Such a method was successfully used with oxygen by these same authors (32), and a value of the electron affinity of oxygen was obtained that agreed well with other data and also exhibited a small probable error. The paper presenting the results of the experiments with fluorine treated the electron affinity as if it were known to be 95 kilocalories per mole, and then tried to justify the results that were obtained when they did not agree with this value. The results of 27 runs have almost a normal distribution about the value 81.8 kilocalories per mole, and the probable error of one observation is calculated as 3.1 kilocalories per mole. If one uses this value of the electron affinity along with other thermochemical data from the National Bureau of Standards Tables of Thermochemical Properties and the crystal energies of the alkali metal fluorides as presented in Table 19, Part I of this thesis, he obtains 31±4 kilocalories per mole as the dissociation energy of fluorine. This set of experiments is apparently the first to have been performed which indicates a low value for the dissociation energy of fluorine based on studies of properties of the element, i.e., a value less than the 63.3 kilocalories per mole obtained by Sprenger, Taylor, and von Wartenberg (59).

Studies of the Spectra of Fluorine-containing Molecules

As is expected on the basis of its powerful attraction for electrons, fluorine forms compounds with most of the other elements, and through a study of these compounds, their spectra, and thermodynamic properties, it is often possible to arrive at a value for the heat of dissociation of fluorine. The metal fluorides, MF, HF, and the interhalogen fluorides have been the most useful in such studies.

The alkali metal fluorides were studied spectroscopically by Desai (13) and by Caunt and Barrow (4, 5). The gaseous molecules show a banded spectrum with a well-defined convergence limit which allows accurate estimation of the dissociation energy. The dissociation products may be ions and not atoms, and if so, correction must be made for the ionization potential of the metal atom and the electron affinity of the halide atom. Since the electron affinity of fluorine is in as much doubt as is the dissociation energy itself, this correction is impossible to make with present data.

Several other metal fluorides have also been studied in the gaseous state: CuF, AgF, AuF, HgF, and TlF. In general, there is not sufficient experimental data to allow the calculation of the dissociation energy of fluorine, but estimates of this quantity are possible. The results of extensive calculations along these lines involving one of the thermochemical cycles shown in Figure 9, Part I of this thesis, are presented in Table 1. It is apparent that,

Table 1

Dissociation Energies of the Halogens

Compound	$\Delta H_f(g)$ (Bichowsky and Rossini)	D(MX) (Herzberg)	ΔH^M_{sub} (Brewer)	$\frac{1}{2}$ D(X_2)
LiI	23.	82.3	37.0	22.3
NaI	18.9	72.7	26.0	27.8
KI	30.0	76.5	21.5	25.0
RbI	31.2	75.7	20.5	24.0
CsI	37.5	77.5	18.8	21.2
LiBr	39.0	104.2	37.0	28.2
NaBr	32.9	88.5	26.0	29.6
KBr	44.0	91.1	21.5	25.6
RbBr	45.0	90.4	20.5	24.9
CsBr	47.8	92.9	18.8	23.1
LiCl	51.	117.3	37.0	29.0
NaCl	41.2	97.7	26.0	30.3
KCl	52.4	101.7	21.5	27.8
RbCl	53.6	91.1	20.5	17.0
CsCl	55.4	103.	18.8	28.8
LiF	82	132 (Desai)	37.0	13
NaF	64	120 (Desai)	26.0	30
KF	84.3	127 (Desai)	21.5	22.2
RbF	79.8		20.5	
CsF	81		18.8	

although such calculations are informative, there is still much lacking in the way of consistent data.

Hydrogen fluoride has been studied rather extensively in the effort to determine its dissociation energy which would, in turn, allow calculation of the dissociation energy of fluorine. The absorption spectrum of HF was studied by Plumley (52), Plumley and Sige (51), Kirkpatrick and Salent (34), and Kaylor, Nielson, and Talley (31). Plumley and Sige studied the ultra-violet absorption while the other experimenters investigated the infra-red spectrum of the molecule. No absorption due to HF at atmospheric pressure was found above 2000 A^o in the ultra-violet. Four vibrational bands have been detected in the infra-red: $1 \leftarrow 0$, $2 \leftarrow 0$, $3 \leftarrow 0$, $4 \leftarrow 0$. Two of these, the $1 \leftarrow 0$ and $2 \leftarrow 0$ bands, have also been studied for DF. Since the spacing of successive vibrational levels in real diatomic molecules becomes smaller, and eventually becomes zero on dissociation, one may graph the vibrational level spacing versus the vibrational level quantum number and estimate the level at which dissociation would occur. The area under such a plot gives the dissociation energy of the molecule involved. Using the spacings of the energy levels as determined by the investigators named above, and making such a plot, one finds that an extremely long extrapolation to zero spacing is necessary. It is believed to be the case that in non-ionic molecules such a Birge-Sponer extrapolation should be a straight line, but HF is far from non-ionic. Depending on the manner of extrapolation, one may obtain values for D(HF) varying from 120-150 kilocalories per mole, and thus, values for D(F_2) which vary from 10-70 kilocalories per mole.

Fluorine forms compounds with each of the other halogens, but only ClF and BrF are particularly useful from the viewpoint of determining a value of D(F_2). The existence of these compounds is well established, but their heats of formation appear to be somewhat in doubt. The heat of formation of ClF has been measured by Schmitz and Schumacher (57) as -15 ± 0.5 kilocalories per mole and by Wicke (61) as -11.6 ± 0.4 kilocalories per mole. No known measurements have been made for BrF, although Brodersen and Schumacher (11) say that the formation reaction is considerably exothermic.

Both ClF and BrF show banded spectra which have been studied extensively. Wahrhaftig (60) first studied the spectrum of ClF and concluded that, on the basis of the dissociation energy of ClF determined by a medium-length Birge-Sponer extrapolation, the dissociation energy was 60 kilocalories per mole if the dissociation products were an unexcited ($^2P_{3/2}$) Cl atom and an excited ($^2P_{\frac{1}{2}}$) F atom. Although dissociation into atoms both of which are in the ground state is impossible, the chlorine atom could be the excited one and the fluorine unexcited. If this were the case, the dissociation energy of ClF would be smaller by about 1.1 kilocalories per mole. Schmitz and Schumacher (56) confirmed this result. This value may be combined with one of the heats of formation and the dissociation energy of chlorine, 57.22 kilocalories per mole, to give either 40.0 or 33.2 kilocalories per mole as the dissociation energy of fluorine if the dissociation products are assumed to be a Cl atom ($^2P_{3/2}$) and a F atom ($^2P_{\frac{1}{2}}$).

The band spectrum of BrF has been studied and the dissociation energy is either 59.9 kilocalories per mole or 50.3 kilocalories per mole, depending on whether the F atom or the Br atom is the excited one (11). Unfortunately, the lack of a value for the heat of formation of BrF makes any computation of a value for $D(F_2)$ impossible.

Although fluorine forms many thousand other compounds than those discussed above, they are either triatomic or even more complicated, and determination of their dissociation products is extremely difficult. Some of the less simple molecules which might be used for studies leading to the dissociation energy of fluorine are OF_2, the higher metallic fluorides MF_2 and MF_3, and CF_4 and SiF_4. Analysis of the spectra of complex molecules is very difficult, and it seems very unlikely that the dissociation energy of fluorine will be finally determined in this manner when so many diatomic molecules are available for study. Experimental studies of the absorption spectrum of OF_2 have been carried out by Glissman and Schumacher (26) in the ultra-violet, and by Hettner, Pohlman, and Schumacher (29) in the infra-red, while

Sutherland and Penney (48) and Potter (53) have calculated the thermodynamic properties of the compound from these data.

Methods for Calculation of $D(F_2)$

There have been many attempts to find some general relationship which will describe the variation of the dissociation energies of diatomic molecules as a function of some easily determinable parameter. Most of the relationships thus far derived or suggested are not universally applicable, and most lead to the high value (63 kilocalories per mole) for the dissociation energy of fluorine.

Glockler (27) has suggested that if one plots the bond force constants of diatomic molecules and their heats of dissociation, he obtains similar curves. In this manner he arrived at $D(F_2)$ = 64 kilocalories per mole in a study which included N_2, O_2, CN, C_2, CO, OF, and HCN.

Wicke and Eucken (15) have considered the relationship between ν, the fundamental vibrational frequency of the diatomic molecule, D, the dissociation energy, and μ, the reduced mass. Thus,

$$\nu = C\sqrt{\frac{D}{\mu}}$$

where C is a constant. They have calculated values of this constant for several diatomic molecules and then estimated what the value for F_2 should be. On this basis they estimate $D(F_2)$ is between 40 and 50 kilocalories per mole, a range consistent with the value obtained by interpretation of the band spectrum of ClF.

Some calculations on the hydrogen halides have been made using the idea just discussed and are tabulated in Table 2. The value for D(HF) of 140 kilocalories per mole would indicate that the dissociation energy of fluorine was about 50 kilocalories per mole, while D(HF) = 130 kilocalories per mole indicates that $D(F_2)$ = 30 kilocalories per mole. The intermediate value of 40 kilocalories per mole for $D(F_2)$ would lead to a value of C consistent with the values for the other hydrogen halides.

An empirical formula for the estimation of dissociation energies of diatomic molecules has been given by Portner (54). According to this formula, the bond energy, E_{A-B}, is given by

$$E_{A-B} = \frac{C'}{d}(1.5 + \log Z_B)$$

where C' = a constant characteristic of the bond type,

d = the sum of the covalent radii of atoms A and B, and

Z_B = the atomic number of element B.

Some calculated values of the constant, C', for a number of compounds are presented in Table 3 along with some tentative values for the constants for HF and F_2. The rather large variations in the results indicate that this formula is not particularly useful in this situation.

Table 2

Calculation of C in the Equation of Eucken and Wicke (15)

Compound	ν	D	μ	$C \times 10^2$
HCl	2989.7	102	0.973	296
HBr	2649.7	86.4	0.987	303
HI	2309.5	70.2	0.993	326
HF	4138.5	140	0.950	281
		130	0.950	302
		120	0.950	327
		110	0.950	357

Table 3

Calculation of C' in the Equation of Portner (54)

Compound	r_A	r_B	log Z_B	E_{A-B}	d	C'
HCl	0.30	0.99	1.232	102	1.29	48.1
HBr	0.30	1.14	1.544	86.3	1.44	40.8
HI	0.30	1.33	1.725	70.3	1.63	35.5
ClF	0.99	0.72	1.232	60.3	1.71	37.7
BrF	0.72	1.14	1.544	50.4 59.8	1.86	30.8 36.6
Cl_2	0.99	0.99	1.232	56.9	1.98	41.2
Br_2	1.14	1.14	1.544	45.4	2.28	34.0
I_2	1.33	1.33	1.725	36.5	2.66	31.0
F_2	0.72	0.72	0.954	60 40	1.44	35.2 23.4
HF	0.30	0.72	0.954	140 130 120	1.02	58.3 54.1 50.0

Recently, a new theoretical concept for evaluating bond energies in terms of the overlap of the wave functions of the atoms bonded together has been suggested by Pitzer (50). He has suggested that in a single bond between the first row elements, the attractive force of the bond is balanced against the repulsion of the other valence shell electrons, while in bonds between heavier elements, the repulsion between the bonding orbital and the inner shells of electrons becomes very important. By evaluating the atomic orbitals and considering the overlap, Pitzer has estimated $D(F_2)$ to be about 50 kilocalories per mole.

Mulliken, Riecke, D. Orloff, and H. Orloff (43) have evaluated tables of overlap integrals using Slater atomic orbitals, and Mulliken (42) presented the results of calculations made by using these tables for the dissociation energies of Li_2, N_2, and F_2. The computed values were 26.2 kilocalories per mole, 166 kilocalories per mole, and 32.0 kilocalories per mole, respectively.

THEORETICAL BASIS FOR THE PRESENT ATTEMPTS TO DETERMINE D(F_2)

The work undertaken in this study was of two types: first, a study of the behavior of $F_2(g)$ at various temperatures by measurement of the pressure exerted by a constant mass of gas enclosed in a heated volume; and second, a study of the light absorption characteristics of $F_2(g)$ at various temperatures and at various wave lengths.

For the first of these studies a copper tube, twenty centimeters long and five centimeters outside diameter, was used as the pressure cell, and the fluorine was brought to this tube in smaller copper tubing. A bronze tube, Bourdon type Dura gauge with a range of 0-30" Hg vacuum was used to measure the pressure of gas in the system as the gas was held tight in an easily measureable volume by a Hoke #413 monel valve. The arrangement of the apparatus was such that the large copper tube,which made up most of the volume of the system being observed, could be heated electrically and the temperature determined by measuring the emf's of four chromel-alumel thermocouples placed around the tube. The variation of pressure with temperature was determined by measuring the pressure with the Dura gauge after the system had been heated to constant temperature for approximately one hour.

The behavior of an ideal gas either with or without dissociation in a system like the one used for these experiments may be easily derived if some relationship is assumed between the temperature of the heated volume and the temperature of that volume external to the heater. Doerner (14) has used a tube with a small capillary projection in an apparatus for the determination of vapor pressures of chromium chlorides, and Perlman and Rollefson (49) used a system somewhat like this for studies of iodine gas a elevated temperatures.

For the purposes of calculation it was assumed that the system containing the fluorine could be represented as three separate volumes: V_h, the volume of the heated zone; V_m, the volume of an intermediate zone; and V_c, the volume of the cold zone (at room temperature). The temperatures of the gas in these zones were taken as T_h, T_m, and T_c respectively. If there are X moles of fluorine gas present in the heated zone initially, and the fraction of dissociation is α, then,

$$\text{moles of } F_2 = X(1-\alpha) = n_h''$$

$$\text{moles of } F = 2\alpha X = n_h'$$

and,

$$n_h' = \frac{2\alpha n_h''}{1-\alpha} .$$

Thus,

$$n_h' + n_h'' = n_h''\left(1 + \frac{2\alpha}{1-\alpha}\right) = n_h''\left(\frac{1+\alpha}{1-\alpha}\right) .$$

Since the pressure is the same in each zone of the system,

$$P = \frac{n_c R T_c}{V_c} = \frac{n_m R T_m}{V_m} = \frac{(n_h' + n_h'') R T_h}{V_h}$$

and

$$n_c = (n_h' + n_h'')\left(\frac{T_h V_c}{T_c V_h}\right)$$

$$n_m = (n_h' + n_h'')\left(\frac{T_h V_m}{T_m V_h}\right) .$$

The total number of moles which were initially present before any dissociation occurred, n_o, is given by

$$n_o = \frac{n_h'}{2} + n_h'' + n_m + n_c$$

which becomes

$$n_o = \frac{n_h''}{1 - \alpha}\left[1 + (1+\alpha)\left(\frac{T_h V_c}{T_c V_h} + \frac{T_h V_m}{T_m V_h}\right)\right]$$

Also, n_h = total moles in the hot zone = $n_h' + n_h''$

$$= \frac{n_o(1+\alpha)}{1 + (1+\alpha)\left(\frac{T_h}{V_h}\right)\left(\frac{V_c}{T_c} + \frac{V_m}{T_m}\right)}$$

and

$$P = \frac{n_h R T_h}{V_h} = \frac{T_h}{V_h}\left[\frac{P_o(V_c + V_m + V_h)/T_c}{1 + (1+\alpha)\left(\frac{T_h}{V_h}\right)\left(\frac{V_c}{T_c} + \frac{V_m}{T_m}\right)}\right]$$

Thus,

$$\frac{P}{P_o} = \left(\frac{V_t}{V_h}\right)\left(\frac{T_h}{T_c}\right)\left[\frac{1}{\left(\frac{1}{1+\alpha}\right) + \left(\frac{T_h}{V_h}\right)\left(\frac{V_c}{T_c} + \frac{V_m}{T_m}\right)}\right]$$

and

$$\alpha = \frac{V_h}{T_h\left[\frac{V_t}{T_c}\left(\frac{P_o}{P}\right) - \left(\frac{V_c}{T_c} + \frac{V_m}{T_m}\right)\right]} - 1$$

For a gas with no dissociation, $\alpha = 0$, and

$$P = \frac{P_o V_t}{T_c \left(\frac{V_h}{T_h} + \frac{V_m}{T_m} + \frac{V_c}{T_c} \right)} = \frac{P_o V_t}{T_c \Sigma \frac{V_i}{T_i}}$$

as would be expected.

From these equations, it is easily seen that, for a system of this type, one would be able to calculate the fraction α of molecules dissociated in the hot zone by merely measuring the pressure in the system, the various temperatures, and the volumes involved.

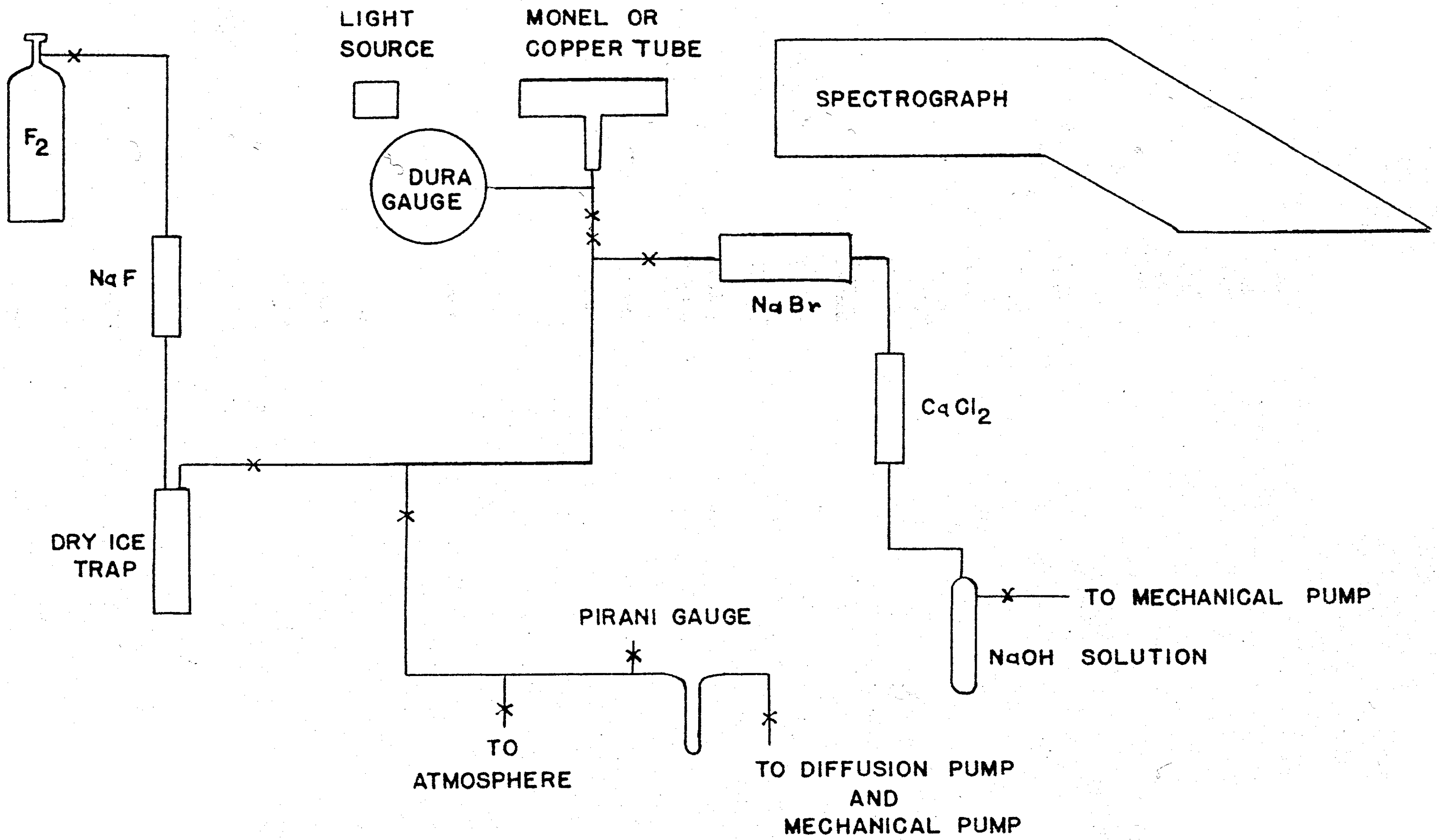
The attempted determination of $D(F_2)$ by studying the absorption spectrum at various temperatures was based on the fact that fluorine molecules are known to show continuous light absorption to the ultra-violet of 4100 A° (9, 20, 59), while fluorine atoms show no absorption of light over this range. The fluorine molecule energy levels are not at all well understood while the fluorine atom has two low-lying states, ${}^2P_{3/2}$ and ${}^2P_{\frac{1}{2}}$, separated by 404 cm^{-1} and the next higher energy level is 102,000 cm^{-1} above these. On this basis, it was decided that if one could observe the absorption characteristics of F_2 at various temperatures, it might be possible to use any change in these characteristics to determine the dissociation energy of F_2, or, in the event that the absorption coefficient of F_2 changed too rapidly itself with temperature to allow use of absorption measurements as an indication of the concentration of F_2 present, one might, by determining this change, be able to get the slope of the potential energy curve of the excited state of F_2, and thus be able to understand more about the molecular structure.

Studies of the absorption characteristics of F_2 have been made at room temperature and indicate a maximum in the absorption coefficient at either 2820 or 2900 A° (9, 59). It was the object of this research to confirm these results and to study variations in the absorption characteristics with temperature. Each run could ideally do both of these things, as well as confirm the fact that Beer's Law was valid for the system. A hydrogen arc lamp was used as a source of ultraviolet continuum, and the lines of the iron arc were placed on each plate for calibration purposes. The absorption tube for the system was a monel tube, 17.5 cm. long, with brass fittings screwing in each end of the tube and holding CaF_2 windows tightly between Teflon gaskets. Kodak Panchromatic plates were used to record the absorption spectra which were taken through a Bausch and Lomb one-prism quartz spectrograph. The exposures on each plate included (1) five calibration marks of varying known intensities, (2) five exposures for the same time through the absorption tube containing F_2 at different pressures, and (3) several exposures taken through the absorption tube containing a known pressure of fluorine at different temperatures. These plates were then read with an Applied Research Laboratory photoelectric microdensitometer and the absorption coefficients calculated.

APPARATUS AND EXPERIMENTAL TECHNIQUES

The handling of F_2 at very low pressures was found to be not so difficult as one might first believe. Copper tubing and pipe, red brass fittings, monel pipe, and silver solder were exposed to F_2 in this system. A diagram of the entire arrangement including the disposal system is shown in Figure 1. Before the fluorine was admitted to the tube for either study, it was passed over NaF and also through a dry ice trap to remove any HF which might be present. No great attack of the copper was noted on any occasion, although a red-brown scale, probably cuprous fluoride, was observed to form inside the tube after use. Teflon gaskets which were used between the windows in experiments at temperatures greater than 400° C. did not appear to be greatly attacked, although their thickness changed after being heated and the tube usually leaked. With new gaskets and a clean system, it was possible to reach pressures of about 5 microns, a fair vacuum for such a system of long, narrow tubing which cuts down the pumping speeds tremendously.

The pressures of F_2 were measured with a Dura gauge having a bronze Bourdon tube silver soldered to the inlet, a threaded brass fitting. This gauge was calibrated to read inches of vacuum and could be read to the nearest 0.1". An H_2SO_4 manometer was also used for pressure measurements in some preliminary runs, but the Dura gauge was simpler to use, and also minimized the effects of small leaks in the system.



SYSTEM FOR HANDLING FLUORINE

Figure 1

This manometer gave a more sensitive measure of the pressure changes in the system.

For a run, fluorine gas was admitted from a ½-pound cylinder at about 400 psi tank pressure into the short section of copper tubing before the first valve and then the tank valve was closed. The first valve was opened and the gas allowed to fill the next volume and then the next valve opened to bring F_2 up to the entrance of the pressure or absorption tube. Two Hoke valves were used to make certain that this tube did not leak back through the valves. The tube was filled with fluorine at a pressure of 1 - 5 " Hg, the two valves were closed, and everything was ready for a run. During or after the run, the disposal of the fluorine was begun in the external system by opening the valve leading to the NaBr trap and pumping the F_2 gas over the NaBr, through the $CaCl_2$, and bubbling the Br_2 or Cl_2 formed through a concentrated NaOH solution. Short sections of the system were opened at a time so that the amount of F_2 passing through the trap at any given time was small. The entire system was eventually opened to the disposal mechanical pump, a Cenco Pressovac, and exhausted overnight before the valves leading to the diffusion pump and Duo-Seal mechanical pump were opened and the system re-evacuated for another run.

A split tubular electric heater unit which could be fitted around the pressure or absorption tube was used to raise the temperature of the gas samples. Fillers of asbestos were placed around the tube to reduce circulation and give a more constant temperature. After the system was heated for about an hour, it attained a temperature not varying more than 10° C. over the tube length, as determined by four thermocouples placed around the tube.

The Kodak Panchromatic plates used for the absorption studies were 4" x 10" and were usually developed for three minutes with Ansco MQ developer, fixed fifteen minutes with Kodak Acid Fixer solution, and washed for thirty minutes in cold, running water. In general, the background fog was low, and in order to help assure even development, the tray was hand rocked during development. For equal exposure times, it was found that the per cent transmission of the plate at a particular wave length was reproducible in different exposures to about 1%. The time of exposure was measured with an electric Time-It to the nearest 0.01 minute, and the exposure times used ranged from 0.50 - 5.00 minutes.

EXPERIMENTAL RESULTS AND CONCLUSIONS

The behavior of F_2 gas at higher temperatures was studied by observing the pressure in a system like that described previously. From each observed pressure, the temperature of the heated zone, room temperature, and the various volumes of the system, one may calculate a value for $D(F_2)$. The results of such calculations are presented in Table 4. In Figure 2 are plotted the curve for an ideal gas in the system studied and the experimental points observed for some of the runs. On the basis of the values calculated, one would conclude that $D(F_2)$ is about 36 kilocalories per mole using the data from Figure 3 and Figure 4. The several points for which no calculation is possible (observed pressure less than the calculated ideal pressure) tend to indicate no detectable dissociation at these temperatures, and thus, an even higher value for $D(F_2)$. In most of these cases where a $D(F_2)$ calculation is not possible, the possible error in reading the Dura gauge is enough to allow for this occurrence.

The fluorine used for study was obtained from the Pennsylvania Salt Manufacturing Company and had these specifications:

F_2 - 96.6% (by weight)
O_2 and inerts - 2.8% (by weight)
HF - 0.6%(by weight)

The absorption spectrum at room temperature was found to agree

Table 4

Computation of $D(F_2)$ from Pressure Measurements

P_o = 0.58" Hg

T_o = 298° K.

V_t = 255.28 cc.

V_h = 238.64 cc.

V_m = 5.55 cc.

V_c = 10.09 cc.

P	T_h	T_m		-log K	$D(F_2)$
0.55	301	300			
0.59	314	305			
0.72	395	325			
0.85	413	330	0.09	1.545	ca 20
0.85	502	355			
0.95	501	355	0.01	3.192	27
1.10	628	390			
1.12	608	385			
1.23	723	415			
1.26	713	412			
1.35	708	410	0.05	2.34	34
1.35	716	413	0.04	2.42	36
1.48	815	440	0.01	3.00	44
1.60	810	438	0.12	1.86	37
1.80	860	450	0.21	1.59	36
	P_o = 0.30" Hg				
0.95	828	443	0.37	1.69	35
1.00	828	443	0.46	1.46	33

Figure 2

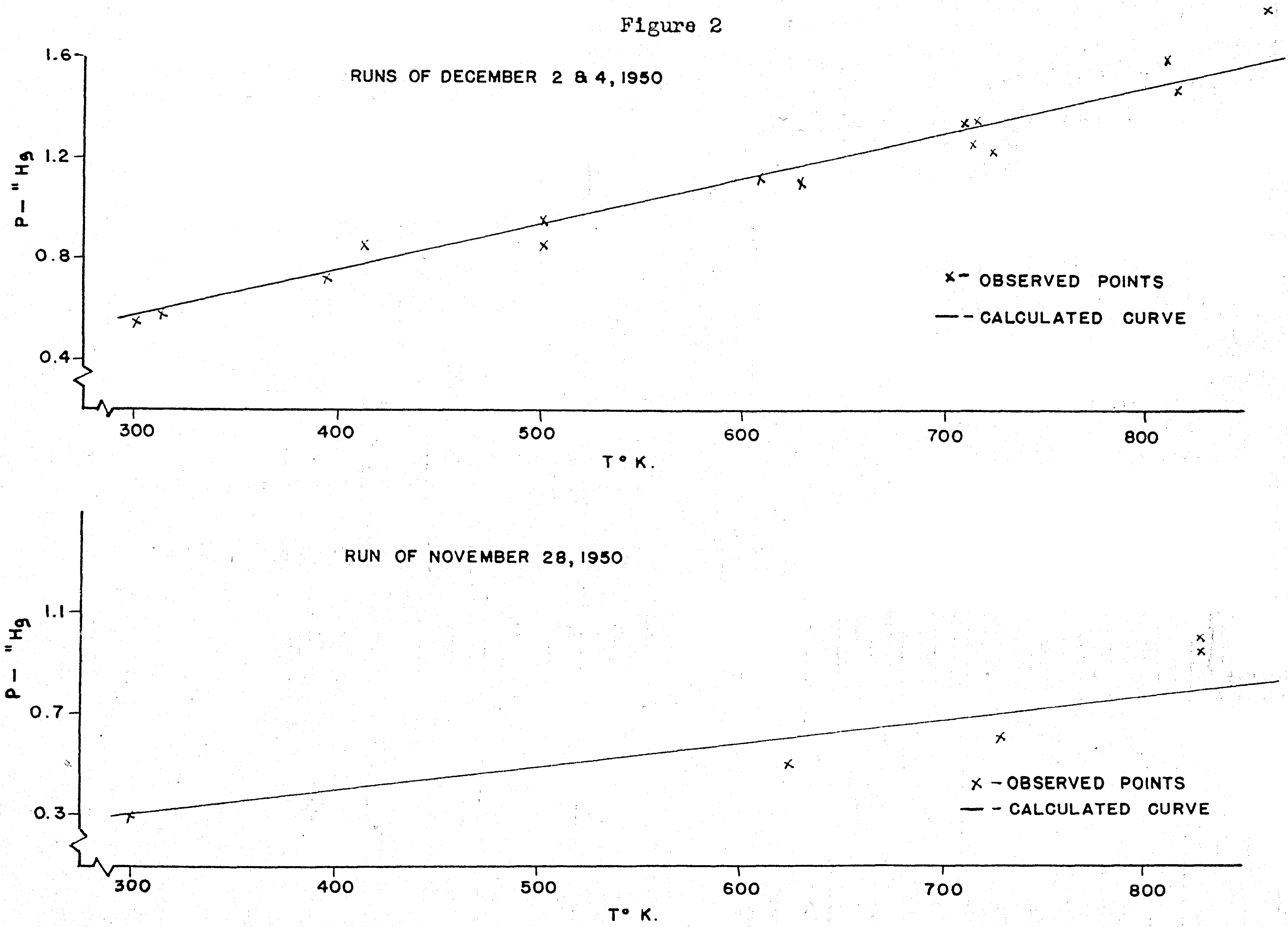
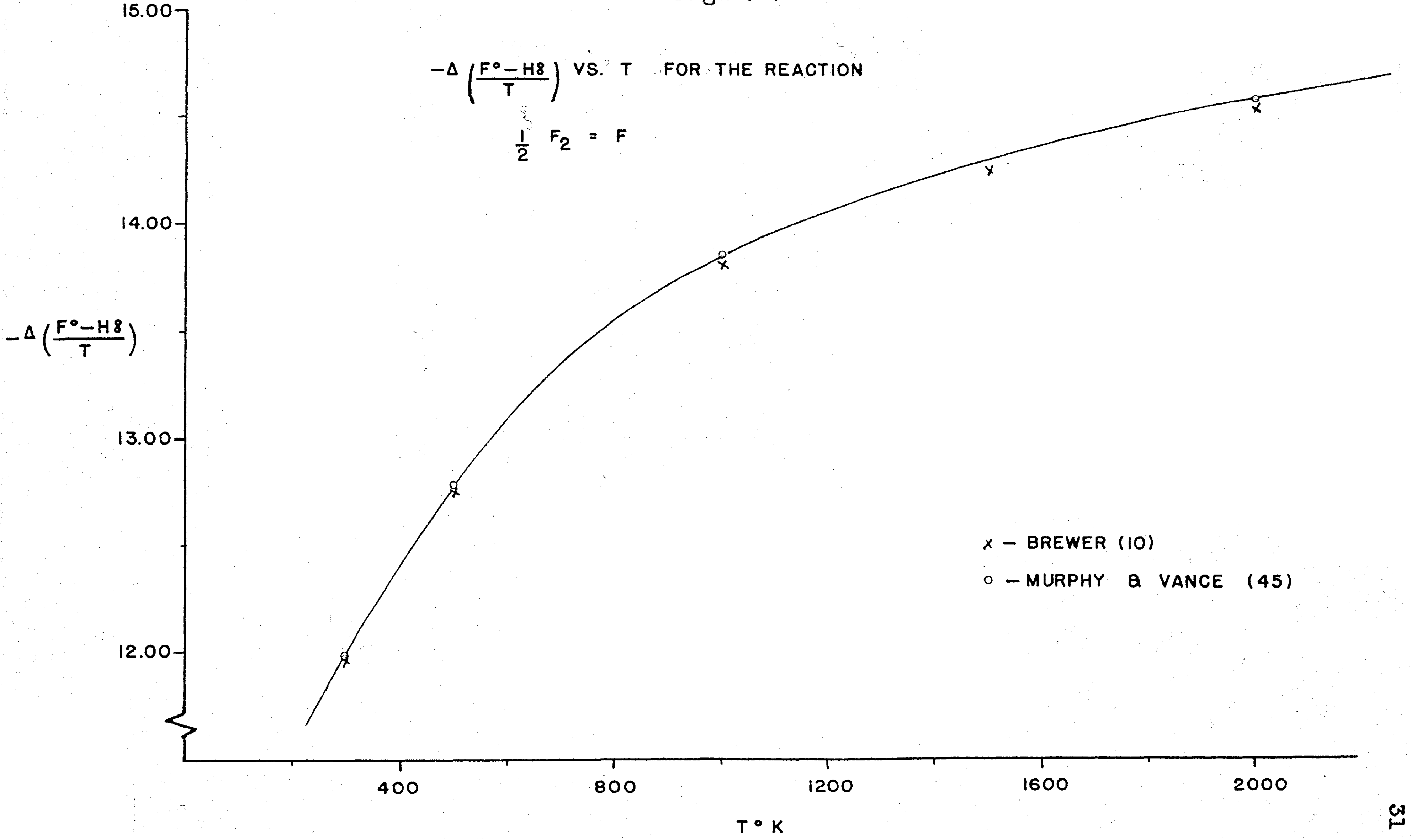

RUNS OF DECEMBER 2 & 4, 1950
P — "Hg
1.6
1.2
0.8
0.4
300
400
500
600
700
800
T° K.
X — OBSERVED POINTS
—— CALCULATED CURVE
RUN OF NOVEMBER 28, 1950
P — "Hg
1.1
0.7
0.3
300
400
500
600
700
800
T° K.
X — OBSERVED POINTS
—— CALCULATED CURVE

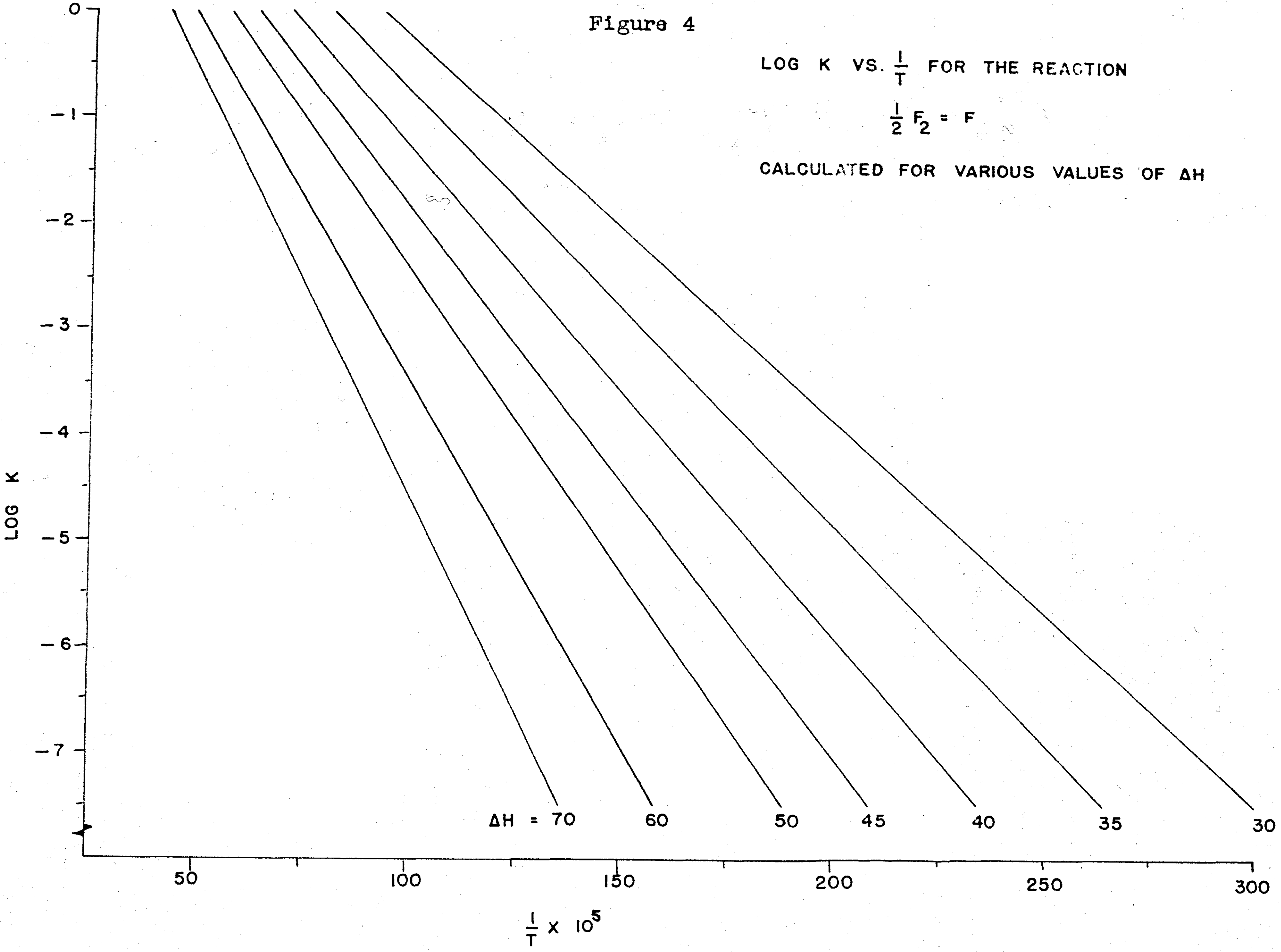
Figure 3



$-\Delta\left(\frac{F^\circ - H_0^\circ}{T}\right)$ VS. T FOR THE REACTION

$\frac{1}{2}F_2 = F$

Figure 4



LOG K VS. $\frac{1}{T}$ FOR THE REACTION

$\frac{1}{2} F_2 = F$

CALCULATED FOR VARIOUS VALUES OF ΔH

with that found by Sprenger, Taylor, and von Wartenberg (59) and Bodenstein, Chong, and Jockusch (9), and the maximum absorption was located at 2850 ± 20 A°. No indication of other impurities was found.

The absorption at higher temperatures was not very well characterized since the Teflon gaskets reacted slightly with the F_2 and the pressure as read on the Dura gauge could not be taken as indicative of the fluorine present. However, for runs in which the temperature became as high as 300° C., no appreciable difference in the amount of absorption was noted at the different temperatures as measured on the photographic plate. Thus, no conclusions regarding the dissociation energy of F_2 were possible from this experiment.

In both of the experiments performed, one of the major problems was to prevent the reaction of F_2 with the container. When a tube was filled with new F_2, a decrease in pressure was observed as the tube reacted, but eventually a constant pressure was obtained and heating and cooling led to the same fluorine pressure in the closed copper cylinder. The absorption cell with CaF_2 windows and Teflon gaskets appeared to react with the fluorine, and, after being heated, usually developed a slight leak. In some of the absorption pictures, bands believed to be due to ozone were observed after the tube leaked and oxygen and water vapor had entered the system.

On the basis of the experiments performed, it is believed that $D(F_2) = 36 \pm 5$ kilocalories per mole. The spectroscopic data on ClF indicate either 33.6 or 40.2 kilocalories per mole and the hot wire studies of U. Franck (17) tend to confirm the higher value. In the opinion of the author, the best value for $D(F_2)$ is 40 ± 2 kilocalories per mole.

SUGGESTED FUTURE RESEARCH

The experiments performed in this research indicate two methods of attacking the problem of determination of D(F_2) but neither method has been developed to the extent of giving results which are as accurate as those obtained from good spectroscopic and thermochemical data. The major problem arising in any study of either F_2 or HF is that of finding a suitable container for the gas. Copper or monel appear to be satisfactory metals for use with these gases but the best gasket material, Teflon, is not very satisfactory at elevated temperatures in the presence of F_2. CaF_2 is believed to be completely satisfactory as a material for windows in absorption cells.

For future research, the methods of attack for determining D(F_2) which seem to be most promising to the author are:

(1) measurement of the pressure-temperature relationship for fluorine gas as done in this research but with an apparatus having a larger heated volume and with more sensitive pressure measuring devices. If possible, the measurements should be made on a system containing F_2 which could be heated all over, thus eliminating the corrections for different zones at different temperatures. A monel sylphon bellows which would move in and out with pressure variations is suggested as a container for such a study.

(2) determination of the heat of formation of BrF so

that it could be used in combination with the spectroscopic data of Brodersen and Schumacher (11) for computing D(F_2).

(3) further study of the absorption spectrum of F_2 using different containers and gasket materials in the attempt to determine how this absorption varies with temperature and to use this information in an interpretation of the changes actually taking place within the fluorine molecule with rising temperature.

BIBLIOGRAPHY

1. Aars, J., Z. Physik 79: 122-138, (1932).
2. Andrychuk, D., J. Chem. Phys. 18: 233, (1950).
3. Badger, R., J. Chem. Phys. 2: 128-131, (1934).
4. Barrow, R., and Caunt, A., Nature 164: 753-754, (1949).
5. Barrow, R., and Caunt, A., Trans. Faraday Soc. 46: 154-156, (1950).
6. Bayliss, N., and Gibson, G., Phys. Rev. 44: 188-192, (1933).
7. Bayliss, N., Gibson, G., and Rice, O., Phys. Rev. 44: 193-200, (1933).
8. Blewett, J., Phys. Rev. 49: 900, (1936).
9. Bodenstein, M., Jockusch, H., and Sing Hou Chong, Z. anorg. Chem. 231: 24-33, (1937).
10. Brewer, L., "Thermodynamic and Physical Properties of the Elements", "Thermodynamic Properties of the Halides", The Transuranium Elements, McGraw-Hill, pp. 13-39, 76-192, (1949).
11. Brodersen, P., and Schumacher, H., Z. Naturforsch. 2a: 358-359, (1947).
12. Calvin, M., and Glockler, G., J. Chem. Phys. 3: 771, (1935); 4: 492, (1936).
13. Desai, M., Proc. Roy. Soc. 136 A: 76-82, (1932).
14. Doerner, H., "Chemistry of the Anhydrous Chlorides of Chromium", Bureau of Mines Technical Paper 577, (1937).

15. Eucken, A., and Wicke, E., <u>Naturwissenschaften</u> 37: 233-234, (1950).

16. Franck, J., <u>Trans. Faraday Soc.</u> 21: 536, (1926).

17. Franck, U., Dissertation, Goettingen, (1950).

18. Fredenhagen, K., and Krefft, O., <u>Z. Phys. Chem.</u> 141 A: 221-222, (1929).

19. Gale, H., and Monk, G., <u>Astrophys. J.</u> 59: 125-132, (1924).

20. Gale, H., and Monk, G., <u>Phys. Rev.</u> 29: 211, (1927).

21. Gale, H., and Monk, G., <u>Astrophys. J.</u> 69: 77-102, (1929).

22. Garman, R., and Moquin, H., <u>Ind. Eng. Chem.</u> (<u>Anal. Ed.</u>) 9: 287, (1937).

23. Garner, C., and Yost, D., <u>J. Am. Chem. Soc.</u> 59: 2738-2739, (1937).

24. Gaydon, A., <u>Dissociation Energies and Spectra of Diatomic Molecules</u>, Wiley and Sons, (1947).

25. Germer, E., and Senftleben, H., <u>Ann. Physik</u> 2: 847-864, (1929).

26. Glissman, A., and Schumacher, H., <u>Z. Phys. Chem.</u> 24B: 328-334, (1934).

27. Glockler, G., <u>J. Chim. Phys.</u> 46: 103-105, (1949).

28. Herzberg, G., <u>Spectra of Diatomic Molecules</u>, D. Van Nostrand, (1950).

29. Hettner, G., Pohlman, R., and Schumacher, H., <u>Z. Physik</u> 96: 203-209, (1935).

30. Ionov, N., and Dukelskii, V., <u>J. Exp. Theoret. Chem. (USSR)</u> 10: 1248-1256, (1940).

31. Kaylor, M., Nielsen, A., and Talley, R., Phys. Rev. 77: 529-534, (1950).

32. Kimball, G., and Metlay, M., J. Chem. Phys. 16: 774-778, (1948).

33. Kimball, G., and Metlay, M., J. Chem. Phys. 16: 779-781, (1948).

34. Kirkpatrick, D., and Salant, E., Phys. Rev. 48: 945-948, (1935).

35. Koenigsberger, J., and Vogt, K., Z. Physik 13: 292-311, (1923).

36. Langmuir, I., J. Am. Chem. Soc. 37: 417, (1915).

37. Mayer, J., and Helmholtz, L., Z. Physik 75: 19-29, (1932).

38. Mayer, J., and Sutton, P., J. Chem. Phys. 3:20-28, (1935).

39. Menzel, W., and Ruff, O., Z. anorg. Chem. 198: 375-382, (1931).

40. Moissan, H., Comptes Rendus 138: 728, (1904).

41. Mulliken, R., J. Chem. Phys. 2: 782-793, (1934).

42. Mulliken, R., Abstracts, 117th Meeting A.C.S., 31-0, (1950).

43. Mulliken, R., Orloff, D., Orloff, H., and Rieke, C., J. Chem. Phys. 17: 1248-1267, (1949).

44. Murphy, G., and Vance, J., J. Chem. Phys. 7: 806-810, (1939).

45. Murphy, G., and Vance, J., J. Chem. Phys. 18: 1514, (1950).

46. Nathans, M., J. Chem. Phys. 18: 1122, (1950).

47. Pauling, L., *The Nature of the Chemical Bond*, Cornell University Press, (1948).

48. Penney, W., and Sutherland, G., *Proc. Roy. Soc.* 156 A: 654-686, (1936).

49. Perlman, M., and Rollefson, G., *J. Chem. Phys.* 9: 362-369, (1941).

50. Pitzer, K., *J. Am. Chem. Soc.* 70: 2140-2145, (1948).

51. Plumley, H., and Sige, K., *Phys. Rev.* 48: 105, (1935).

52. Plumley, H., *Phys. Rev.* 49: 405, (1936).

53. Potter, R., *J. Chem. Phys.* 17: 957-959, (1949).

54. Portner, *Helv. Chem. Acta.* 32: 1438-1441, (1949).

55. Rabinowitch, E., and Wood, W., *J. Chem. Phys.* 4: 358-362, (1936).

56. Schmitz, H., and Schumacher, H., *Z. Naturforsch.* 2a: 359-362, (1947).

57. Schmitz, H., and Schumacher, H., *Z. Naturforsch,* 2a: 362, (1947).

58. Sherman, J., *Chem. Rev.* 11: 93-170, (1932).

59. Sprenger, G., Taylor, J., and von Wartenberg, H., *Z. Phys. Chem.*, Bodenstein Festband, 61, (1931).

60. Wahrhaftig, A., *J. Chem. Phys.* 10: 248, (1942).

61. Wicke, E., *Nachrichten Akad. Wiss. Goettingen, Math-Physik Klasse*, 89-90, (1946).

62. Wicke, E., *Z. Elektrochem.* 53: 212-216, (1949).