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by A. W. Petrocelli and A. Capotosto, Jr.

Prepared under Contract No. NASw-559 *by*
GENERAL DYNAMICS/ELECTRIC BOAT
Groton, Conn.
for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • NOVEMBER 1964

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OBJECTIVE

The objective of this program was to conduct a research and development study for the synthesis and evaluation of the low molecular weight alkali metal ozonides for air revitalization purposes.

ABSTRACT

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The chemistry of alkali metal ozonides has been studied from the point of view of their use in non-regenerative air revitalization systems. Various methods have been explored for the synthesis of potassium, sodium, and lithium ozonides. The physical and chemical properties of potassium ozonide, which could be readily prepared in pure form (88-97%), have been characterized by studies of the compound's thermal stability, its reaction with water vapor, and its reaction with carbon dioxide. The handling and storage characteristics of potassium ozonide have also been determined. Theoretical discussions of chemical non-regenerative air revitalization systems in general, and of the synthesis and chemistry of alkali metal ozonides in particular, are presented in this report.

Author

I

INTRODUCTION

1.1 GENERAL

The complexity of the problems associated with the exploration of outer space by the use of manned vehicles is gradually and systematically being overcome to the extent that at the present time the goals set for this extensive exploration are in sight. One of the major objectives still to be achieved is the development of reliable and safe air revitalization systems. During the years of study devoted to such a development, there has appeared to evolve a subtle feeling on the part of many investigators that a search for a panacea; i.e., one system to meet the requirements of all space missions, should constitute our main effort in this area. In effect, such thinking spells out the requirements for the development of a reliable, completely regenerative, air revitalization system. Such a philosophy, on the part of those who espouse it, is valuable and should be encouraged.

The experience accumulated to date, however, dictates that this thinking must not predominate to the extent that the importance of fundamental research studies necessary to develop non-regenerative air revitalization systems be minimized. Also, such systems should not be simply viewed as stopgap measures taken to fill the void until all manned space missions can be met with a regenerative system.

In fact, it appears to be quite clearly established that non-regenerative air revitalization systems should, for many years to come, provide the most economical and reliable means of maintaining a habitable atmosphere for space missions which will last for at least one man-month. Among the missions adaptable to such systems are:

1. Shuttle trips to manned space stations.
2. Near-earth scientific space explorations.

3. Near-earth military reconnaissance missions.
4. Orbital space station excursion vehicles.
5. Extravehicular manned space equipment.
6. Emergency back-up systems for long-term space missions requiring a regenerative technique as the primary life support system.

The requirements of such missions emphasize the importance of continuing the search for efficient, safe, light-weight, small-volume air revitalization materials. An important phase of this search has been the work carried out on unfamiliar oxidation state inorganic chemicals such as peroxides, superoxides, and ozonides. The most spectacular results in this area have come from Russian researchers, due in great measure to their patient and extensive investigations of fundamental problems, the solution of which are so necessary if successful life support systems and engineering studies are to be obtained.

This report presents the results of the first Government-sponsored project devoted specifically to the investigation of the air revitalization potential of one of the most promising groups of unfamiliar oxidation state inorganic chemicals, the alkali metal ozonides.

1.2 THE THEORETICAL POTENTIAL OF ALKALI METAL OZONIDES AS AIR REVITALIZATION MATERIALS

A discussion of the history of the development of inorganic ozonides can be found in a recent review article by Petrocelli and Chiarenzelli.(1) The important chemistry of the ozonides with respect to their usefulness in air revitalization systems may be summarized as follows:

$$2\ MO_3 + HOH = 2\ MOH + 5/2\ O_2 \qquad (1)$$

$$2\ MOH + CO_2 = M_2CO_3 + H_2O \qquad (2)$$

Reactions (1) and (2) point out that the alkali metal ozonides function in a way analogous to the alkali metal superoxides (MO_2) in their manner of producing O_2 and scrubbing CO_2 from a closed system. The comparisons made in Table I emphasize the considerable potential which the ozonides have as air revitalization materials.

A comparison of the weight savings possible with the use of ozonides is given in Figure I. This is achieved by contrasting the total weight of solid chemical mixtures, based on ozonide and superoxide systems, required to remove all metabolic CO_2 produced by one man in one day with that required to replenish his required oxygen supply. The estimates shown in Figure I were calculated on the basis of moderate activity, resulting in an O_2 requirement of 1.87 lb/man-day and a CO_2 output of 2.11 lb/man-day. Estimates are presented for mixtures of the active O_2 source with both LiOH and Li_2O_2 as auxiliary CO_2 scrubbers. The use of LiOH in this manner is well established. As for Li_2O_2, it appears to offer an attractive method for CO_2 scrubbing via the reaction:

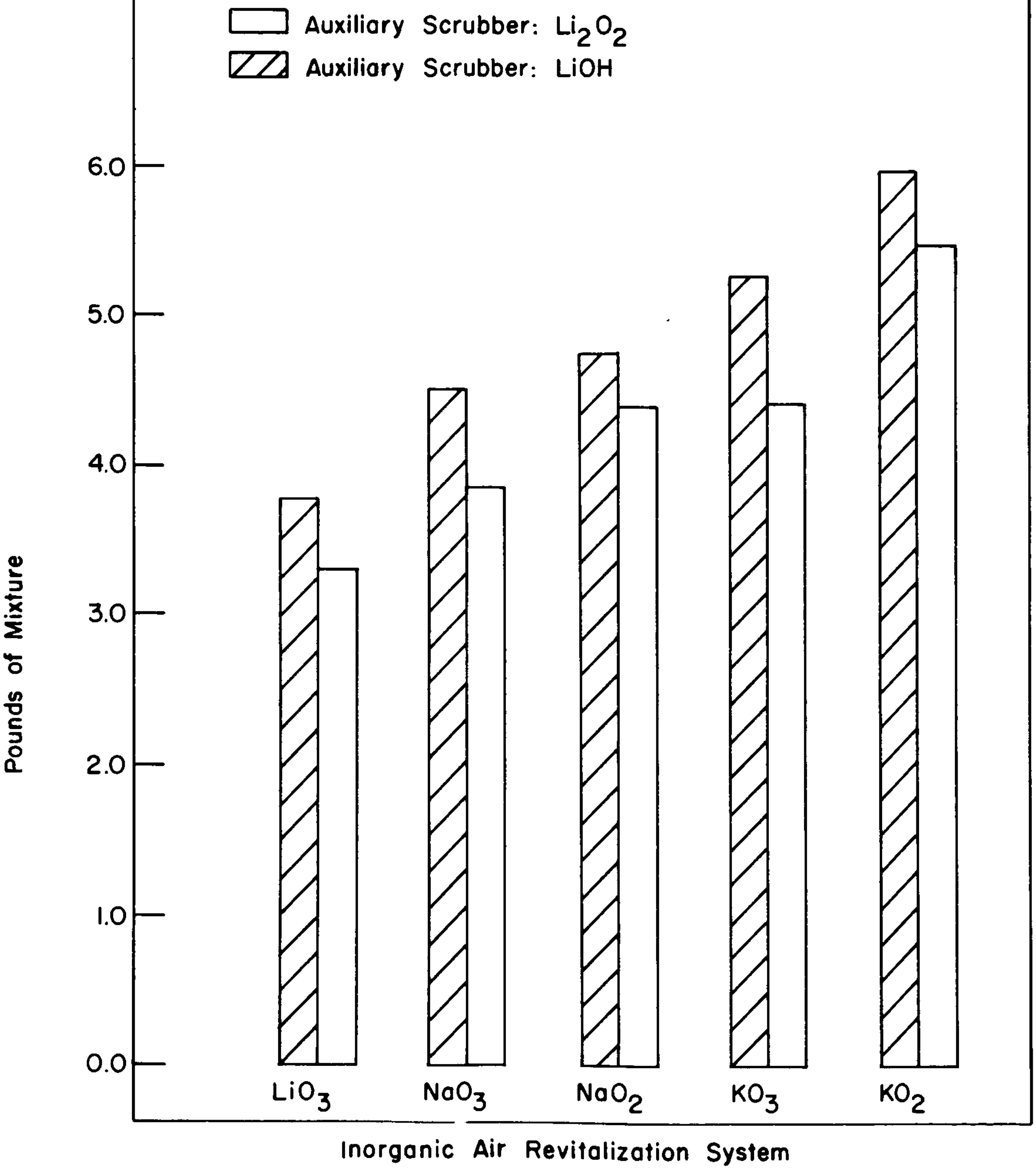
$$Li_2O_2 + CO_2 = Li_2CO_3 + 1/2\ O_2 \qquad (3)$$

Although much remains to be learned regarding the use of Li_2O_2 as a CO_2 scrubber, it is anticipated, on the basis of what is currently known about this system, that its future use has a very high probability of acceptance. Its use in conjunction with an ozonide would provide a most attractive basis for an air revitalization system. The comparisons made in Figure I point out that for the conditions stipulated, KO_3 - auxiliary CO_2 scrubber mixtures would offer an appreciable weight saving over similar KO_2 mixtures. Sodium ozonide mixtures would be superior to both KO_2 and the difficult to obtain NaO_2 mixtures, and LiO_3 would lead the field as a light-weight, air revitalization material.

On the basis of reactions (1) and (2) the use of an ozonide alone would not be sufficient to maintain a safe CO_2 level in a space cabin for an extended period of time. The rate of CO_2 build-up in a cabin assumed to have a volume of 200 cu ft and a two-man crew is shown in Figure II, along with the rate of build-up of CO_2 resulting if only KO_3 were used as a scrubber. Without scrubbing, the CO_2 concentration reaches the maximum allowable concentration of 3%, for short exposure times, in 3.4 hours, whereas with the use of KO_3, the danger point is not reached

FIGURE I

POUNDS OF MIXTURE OF INORGANIC AIR REVITALIZATION COMPOUND PLUS AUXILIARY CARBON DIOXIDE SCRUBBER NEEDED TO PROVIDE 1.87 POUNDS OF OXYGEN/MAN/DAY AND TO SCRUB 2.11 POUNDS OF CARBON DIOXIDE/MAN/DAY



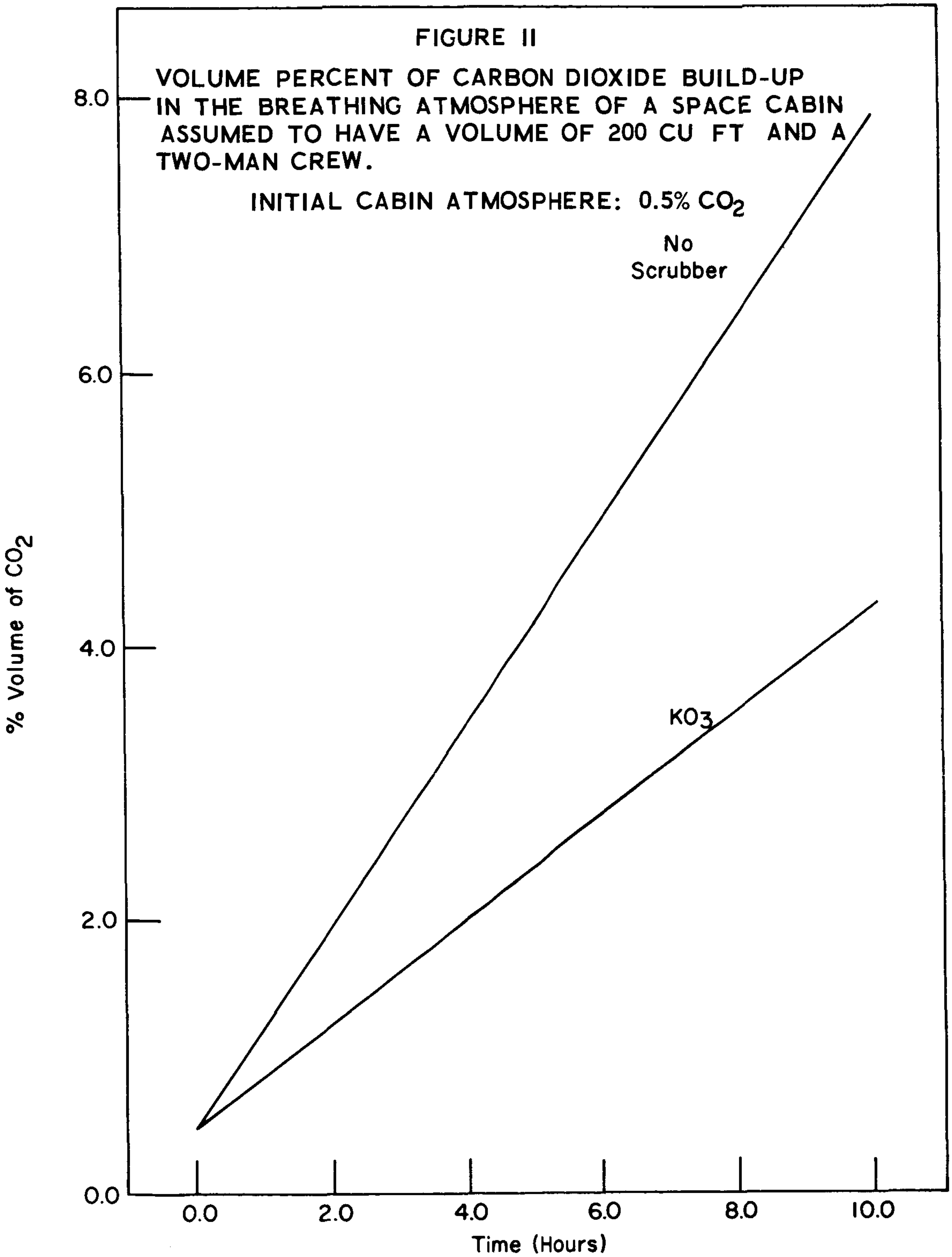


FIGURE II

VOLUME PERCENT OF CARBON DIOXIDE BUILD-UP IN THE BREATHING ATMOSPHERE OF A SPACE CABIN ASSUMED TO HAVE A VOLUME OF 200 CU FT AND A TWO-MAN CREW.

INITIAL CABIN ATMOSPHERE: 0.5% CO_2

TABLE I

SUMMARY OF IMPORTANT PROPERTIES OF VARIOUS INORGANIC AIR REVITALIZATION MATERIALS

	Formula	Lb O_2 Produced/ Lb Compound	Lb CO_2 Scrubbed/ Lb Compound	Remarks
Lithium ozonide	LiO_3	0.73	0.39	1
Sodium ozonide	NaO_3	0.56	0.31	2
Potassium ozonide	KO_3	0.46	0.25	3
Lithium superoxide	LiO_2	0.61	0.56	4
Sodium superoxide	NaO_2	0.43	0.40	5
Potassium superoxide	KO_2	0.34	0.31	6
Calcium superoxide	$Ca(O_2)_2$	0.46	0.42	7
Sodium chlorate (Candles)	$NaClO_3$	0.40	None	8
Hydrogen peroxide	H_2O_2	0.47	None	9
Hydrogen superoxide	H_2O_4	0.73	None	10
Lithium peroxide	Li_2O_2	0.35	0.96	11

REMARKS

1. As yet unprepared; evidence is far from conclusive that it cannot be prepared. Outstanding O_2 source.
2. Prepared. Conflicting reports concerning its stability.
3. Prepared. Conflicting reports concerning its stability.
4. Unsubstantiated Russian claims for its preparation and stabilization at room temperature.
5. Commercial route for its preparation available. Expensive.
6. Commercial route for its preparation available. Widely used.
7. Produced in low purity. Highly desirable due to high melting point of $Ca(OH)_2$.
8. Widely used as emergency O_2 source.
9. Liquid solutions. Requires auxiliary chemical for CO_2 removal.
10. Essentially unsubstantiated Russian claims. Highly attractive as high energy oxidizer.
11. High interest in this compound for use in air revitalization systems; necessary basic work in progress.

until 6.7 hours. These times would, of course, change proportionately with the free volume of the space cabin. In any event, these numbers probably represent the minimum effectiveness to be expected of the ozonides as CO_2 scrubbers. Keating(2), in a series of extremely well planned experiments demonstrated that KO_2, if properly used, can by itself supply metabolic oxygen and remove CO_2, water vapor, gaseous contaminants, and odors from a sealed environment. Such engineering considerations are important, since at the present time there is no reason to believe that the same can not be accomplished with stable ozonides with the added attraction attending the weight saving advantages of the ozonides. Those studies which have led to the conclusion that it is not feasible, with the use of KO_2 alone, to match man's Respiratory Quotient must be carefully analyzed within the framework of the engineering design used in the employment of the superoxide, especially with respect to canister design. However, any consideration to the use of superoxides or ozonides alone, without providing for additional CO_2 scrubbing, should be approached with guarded optimism. Thus, in making comparisons, as in Table I and Figure I, it is best to consider the use of supplementary chemical CO_2 scrubbers with the awareness that improved engineering practice may further optimize the system to our greater advantage.

Keating(2) has pointed out that a sealed atmosphere conditioning system based on a "passive atmosphere-chemical reaction" use of solid chemicals is feasible and is advantageous for the following reasons:

1. it does not use electrical power,
2. it is light in weight,
3. it occupies a small volume,
4. it need have no moving parts,
5. it should require little maintenance.

Such feasibility has been adequately demonstrated for KO_2.

What of the ozonides? It is expected that the availability of stable ozonides would make use of all the engineering know-how built up for superoxide systems, without major modifications, and bring to such systems definite improvements in weight and volume characteristics.

With respect to the oxygen storage capabilities of ozonides, an important point which must be kept in mind in the course of research on these compounds is the fact that for alkali metal ozonides to be competitive with the available metal superoxides as air revitalization materials, it may not be necessary to prepare ozonides in absolutely pure form. In the course of the work carried out under NASA Contract NASw-559, we have verified that ozonides can be synthesized witn relative ease by at least two routes; e.g., the ozonization of solid KOH and the ozonization of solid, dry KO_2. Thus, a stable solid mixture containing as little as 74% KO_3 and 26% KOH, prepared from a potassium hydroxide-ozone reaction, would provide as much O_2 per pound of mixture as is obtained from a pound of pure KO_2. Solid hydroxide-ozonide mixtures containing an amount of ozonide greater than 74% would provide a clear advantage over pure KO_2 as an oxygen storage media. Figure III illustrates the relationship between the pounds of oxygen available per pound of alkali metal ozonide-alkali metal hydroxide mixtures. Mixtures prepared "in situ" via the reaction between alakli metal hydroxide and ozone whose O_2 yield falls below the yield for pure KO_2 or NaO_2, shown on the figure by horizontal lines, would not be competitive with the superoxides. However, the importance of this discussion lies in the possibility of carrying out relatively straightforward ozonization reactions with the hydroxides and superoxides so as to produce, without the need for purification or separation procedures, mixtures of ozonide and hydroxide or superoxide whose compositions are greater than the critical compositions shown in Figure III. Thus, the concern of various investigators over the difficulties that may be encountered in preparing pure alkali metal ozonides, may not be as serious as first supposed, when the intended end use of these materials in air revitalization systems is considered.

The optimum situation, of course, calls for the synthesis of these materials in as pure a form as possible, but the considerations outlined

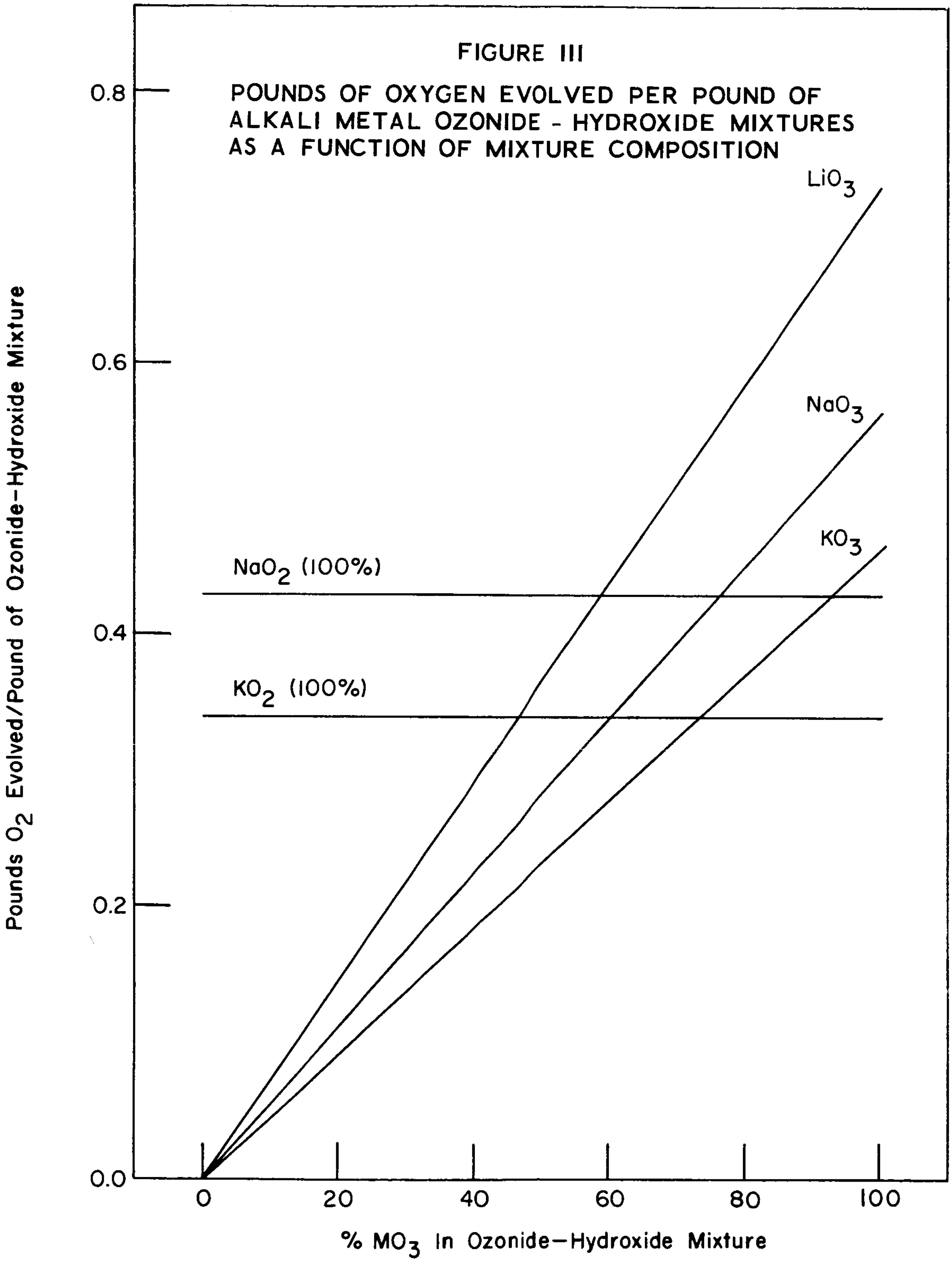


FIGURE III

POUNDS OF OXYGEN EVOLVED PER POUND OF ALKALI METAL OZONIDE - HYDROXIDE MIXTURES AS A FUNCTION OF MIXTURE COMPOSITION above allow us a region of "trade off" between processing difficulties, cost, and oxygen yields of which we must be aware.

1.3 BRIEF SUMMARY OF SOVIET ACTIVITY IN THE AREA OF UNFAMILIAR OXIDATION STATE CHEMISTRY

The Russian successes in the use of unfamiliar oxidation state compounds as air revitalization materials in space vehicles have been dramatic, particularly in the life support systems of the Vostoks I and II.(3) Instead of using a reduced-pressure all-oxygen system, as in the case of our Mercury vehicles, all indications are that the Vostok flights, as well as some of their animal flights, employed a slightly oxygen-rich air at normal pressures, and regenerated the air by means of a superoxide.(3)

It must be pointed out that as far as can be discovered, nowhere in the Russian literature describing Russian manned space flights is the source of breathing oxygen employed specifically identified as a superoxide. However, careful analysis of their published works(4,5,6) very clearly points to the use of unfamiliar oxidation state compounds of the alkali or alkaline metal peroxide, superoxide, or alkali metal ozonide type. As an example, Volynkin, et al,(6) points out that "at the present time, highly efficient regeneration substances are able not only to give off oxygen in exchange for that used in breathing, but also to absorb, simultaneously, great quantities of carbon dioxide and moisture. In addition, these substances, as research has shown, have the ability to oxidize and absorb certain harmful gaseous products formed in the course of human vital activity."

Among the important advantages ascribed to the air revitalization systems of the Vostoks are the following:(6)

1. Efficiency of operation at a temperature of 20 ± 10°C, a relative humidity of 30 to 70%, and a barometric pressure of 760 ± 50 mm Hg.
2. Absorption of gaseous products liberated in the course of human vital activity.
3. Resistance to the influence of vibration and high overloads; heat and explosion resistance.

4. Simplicity of construction.
5. Minimum power consumption.
6. High operational reliability.
7. Complete automation of processes for maintaining the required microclimatic conditions.

In addition to the "active chemical" described above, the Vostoks required an additional chemical for control of the cabin's relative humidity. This fact serves as more evidence that the "active chemical" is an unfamiliar oxidation state compound since peroxides, superoxides, or ozonides would not be efficient enough to maintain the conditions of Respiratory Quotient specified above.

The Russian literature clearly indicates that the great attention they have given to the use of high active chemical compounds for air regeneration has payed off handsomely. In the words of Volynkin, et al,(6) the problems associated with their use was "in principle and in practice, solved in preparing and conducting the biological experiments in the two earth satellites."

Seryapin(7) writes that "the application of chemical substances (underlining ours), capable of simultaneous absorption of moisture and carbon dioxide and liberation of oxygen, is quite economical in comparison with other systems." These chemical systems were developed "to regenerate the air in sealed capsules occupied by animals during space flights" and "the air was brought in contact with the regenerator by electric fans." He goes on to offer that "systems employing chemical lime absorbers and silica gel along with liquid oxygen or gaseous oxygen would be 3.5 and 8 times as heavy, respectively, as a system based on the use of these so-called 'active chemical substances'." This chemical system "was subsequently used in the second space flight with the dog, Layka."

The Russian capability in the field of superoxides can be directly traced to the many years of work in this field by their inorganic and physical chemists, led principally by Kazarnovskii.

In an article entitled "Toward New Achievements in Soviet Chemistry," which appeared in Pravda,(8) June 25, 1962, Kazarnovskii is described as a major inorganic chemist. His work on superoxides is noted, and he is credited with being responsible for the current industrial-scale production of NaO_2 in Russia.

All of these considerations, coupled with other numerous evidence offered by the Soviet scientific literature, lends strong support to the contention that a superoxide has been successfully employed for air revitalization purposes in the Russian manned space flights.(9)

It is noted that the same school of Russian chemists responsible for the superoxide successes have, in recent years, been concentrating on the chemistry of the alkali metal ozonides in an effort to develop an even more efficient chemical for such purposes. Kazarnovskii has also been the leader in inorganic ozonide chemistry and much of what is known of ozonides emanates from the Russian scientific literature(10,11).

II

RESULTS OF EXPERIMENTAL STUDIES

2.1 THE SYNTHESIS OF ALKALI METAL OZONIDES

2.1.1 Gas-Solid Reactions

2.1.1.1 Theoretical Considerations

The passage of a gaseous ozone-oxygen mixture over a solid alkali metal hydroxide represents the most common method of producing alkali metal ozonides. The yields of ozonide via this method have been characteristically small, 5-10%. Intuitively, one could predict such poor conversion rates since the synthesis reaction is between a gas and a solid. A plausible mechanism has been offered for the ozonide synthesis reaction by Kazarnovskii, et al.(12) This proposal is illustrated below using potassium as the alkali metal:

$$KOH + O_3 = KOH \cdot O_3 \qquad (3)$$

$$KOH \cdot O_3 + O_3 = KO_3 + HO_2 + O_2 \qquad (4)$$

$$HO_2 + O_3 = HO + 2O_2 \qquad (5)$$

$$HO + O_3 = HO_2 + O_2 \text{ (chain)} \qquad (6)$$

The overall synthesis reaction may thus be written as:

$$6KOH + 4O_3 = 4KO_3 + 2KOH \cdot H_2O + O_2 \qquad (7)$$

Nikol'skii, et al,(13)have also determined the heat of formation of potassium ozonide to be -62.1 Kcal/mole.

As a result, it is possible to estimate the enthalpy and entropy changes associated with reaction (7). The thermodynamic quantities necessary to make these estimates are listed in Table II. They have been carefully selected and represent the best values available to date. In some cases,

TABLE II

SELECTED THERMODYNAMIC QUANTITIES FOR PERTINENT MOLECULAR SPECIES AT 298.16°K

	Thermodynamic Function	
Species	ΔH_f^o Kcal/mole	S^o Cal/deg/mole
OH (g)	9.37 ± 0.3 (15)	43.888 (15)
O_2H (g)	ca. 6 (14)	52*
O_3 (g)	33.93 ± 0.5 (16)	56.8 (15)
O_2 (g)	------	49.003 (15)
KOH (c)	-101.78 (15)	18.958 (16)
$KOH \cdot H_2O$ (c)	-179.6 (15)	28**
$KOH \cdot 2H_2O$ (c)	-251.2 (15)	37**
$KOH \cdot O_3$ (c)	------	ca. 19***
KO_2 (c)	-67.9 (13)	25 (13)
KO_3 (c)	-62.1 (13)	33 (13)
H_2O (g)	-57.7979 (15)	45.106 (15)

---

*In estimating this value the assumption was made that the entropy difference between $OH(g)$ and $O_2H(g)$ is equal to the entropy difference between $O_2(g)$ and $O_3(g)$.

**These values have been estimated by adding the entropy of ice (9 cal/deg/mole) to the entropy value for the anhydrous crystalline KOH.

***See text for a discussion of this value.

the values used in this treatment differ from those originally used by the Russian investigators in 1950. The values of ΔH^o, ΔS^o, ΔF^o and K_{eq}. 298^oK calculated for reaction (7) are given in Table III.

The mechanism represented by equations (3-6) depends on the formation of a complex, $KOH \cdot O_3$. Postulation for the formation of such an intermediate is reasonable, based on the very high value of the electron affinity of the ozone molecule. The entropy change for reaction (3) has been calculated by us to be -56.8 cal/deg. For this calculation, an assumption is necessary relative to the entropy of the molecular species $KOH \cdot O_3$. The assumption was made that the entropy of this species would differ from the entropy of crystalline anhydrous potassium hydroxide by the entropy value of solid ozone. This calculation is analogous to the situation found in crystalline hydrates where the entropy of various hydrates of the same crystalline compound differ by the entropy of ice; i.e., 9 cal/deg per hydrated water molecule. In the case of $KOH \cdot O_3$, it is thus assumed that the entropy of solid ozone is essentially zero. An alternate reaction path involving the following reaction:

$$KOH + O_3 = KO_3 + OH \qquad (8)$$

cannot be supported by the thermodynamic data which yields a positive ΔF^o value of approximately 17 calories.

It is possible that the reaction mechanism for the formation of alkali metal ozonides postulated by Kazarnovskii, et al,(12) overlooks a key role played by the HO_2 radical in the direct formation of alkali metal ozonides. Thus a mechanism involving the following processes can also be postulated:

$$KOH + O_3 = KOH \cdot O_3 \qquad (9)$$

$$KOH \cdot O_3 + O_3 = KO_3 + HO_2 + O_2 \qquad (10)$$

$$KOH + HO_2 = KO_2 + H_2O \qquad (11)$$

TABLE III

SUMMARY OF THERMODYNAMIC FUNCTIONS OF PERTINENT CHEMICAL REACTIONS AT 298.16°K

Reaction	Text Number	Thermodynamic Function			
		ΔH^o Kcal	ΔS^o cal/deg	ΔF^o Kcal	log K_{eq}
$KOH + O_3 = KOH \cdot O_3$	3	---	-56.8	---	---
$KOH \cdot O_3 + O_3 = KO_3 + HO_2 + O_2$	4	---	+58.2	---	---
$HO_2 + O_3 = HO + 2O_2$	5	-30.5	+33.1	-40.4	+29.4
$HO + O_3 = HO_2 + O_2$ (Chain)	6	-37.3	+0.3	-37.4	+27.2
$6KOH + 4O_3 = 4KO_3 + 2KOH \cdot H_2O + O_2$	7	-132.6	-104.2	-101.5	+74.0
$KOH + HO_2 = KO_2 + H_2O$	11	-29.9	-0.9	-29.6	+21.6
$KOH + H_2O = KOH \cdot H_2O$	12	-20.0	-36.1	-9.2	+6.7
$KO_2 + O_3 = KO_3 + O_2$	13	-28.1	+0.2	-28.2	+20.5
$3KOH + 3O_3 = 2KO_3 + KOH \cdot H_2O + 2O_2$	14	-100.2	-35.4	-89.6	+65.4
$2KO_3 + H_2O = 2KOH + 5/2\ O_2$	15	-21.6	+49.4	-36.3	+26.5
$KO_3 = KO_2 + 1/2\ O_2$	19	-5.8	+16.5	-10.7	+7.8

$$KOH + H_2O = KOH{\cdot}H_2O \qquad (12)$$

$$KO_2 + O_3 = KO_3 + O_2 \qquad (13)$$

The overall formation reaction would then be:

$$3KOH + 3O_3 = 2KO_3 + KOH{\cdot}H_2O + 2O_2 \qquad (14)$$

The thermodynamic properties for the above reactions are given in Table III. A comparison of the thermodynamic data calculated in support of the mechanism offered above with the data calculated for the Russian mechanism point out that no clear-cut choice can be made between the mechanisms. Our mechanism differs from that of the Russian investigators mainly via reactions (11) and (13), i.e., the superoxide is considered an intermediate in the formation of the ozonide. The fact that reaction (13) proceeds with great ease has been demonstrated in these laboratories and elsewhere.(17,18) The assumption that reaction (11) occurs is supported by the thermodynamic data offered in Table III.

As complete a thermodynamic analysis for sodium and lithium ozonides is not possible, since the heats of formation of these compounds have not as yet been determined. However, it is felt that the mechanisms outlined above for the formation of potassium ozonide will also account for the formation of sodium and lithium ozonides.

From our observations on the rapidity with which the surface of a potassium hydroxide bed changes color in the presence of ozone, it can be said that kinetically the reaction is quite rapid. However, in spite of the favorable thermodynamics and kinetics associated with the conversion of solid potassium hydroxide to solid potassium ozonide, the conversion yields are low. Some insight as to the reason for the low conversion rates may be obtained from a consideration of gas-solid reaction phenomena.

Basically, a reaction between a solid and a gas can be expected to involve three major steps:

1. Adsorption of the gas molecules on the solid surface.
2. Diffusion of the gas molecules to a reaction site.
3. Diffusion of the reaction products away from the reaction site.

In such reactions, the diffusion process is often found to be rate determining. Thus, the almost instantaneous conversion of the surface layers of potassium hydroxide to potassium ozonide can be accounted for by a nearly simultaneous adsorption and reaction on the potassium hydroxide surface via reaction (7) or (14). It is doubtful that such reactions occur to a depth greater than one or two molecular thicknesses. For wholesale conversion of potassium hydroxide to potassium ozonide it then becomes necessary for the ozone to diffuse, without dissociation, into the bulk of the bed. Since water is a product of the formation reaction, it must, in turn, diffuse away from the reaction site to the surface layers of anhydrous potassium hydroxide. This process must occur rapidly enough so as to prevent the reaction between water and potassium ozonide; i.e.,

$$2KO_3 + H_2O = 2KOH + 5/2\ O_2 \qquad (15)$$

2.1.1.2 Synthesis of Potassium Ozonide

As pointed out in the previous sections, it has been clearly established (11,12,19,20,21) that the passage of gaseous ozone over solid alkali metal hydroxides results in the formation of solid alkali metal ozonides. For example, Kazarnovskii, et al,(12) have reported the formation of potassium ozonide by exposing dry powdered potassium hydroxide to a dilute gaseous ozone stream (6-8% in oxygen) at -10 to -15°C. The recovery of essentially pure ozonide from hydroxide mixtures was then accomplished by taking advantage of the solubility of the ozonide in liquid ammonia.(11) A red solution was obtained which yielded reddish-brown crystals of potassium ozonide upon evaporation of the ammonia.

The above method of alkali metal ozonide synthesis remains today as the principal means of preparing potassium ozonide and has been followed, with minor modifications, by many investigators.(11,19.21)

Due to the limited work that has been done in this field, it was considered doubtful that the optimum conditions, with respect to yield, stability, and purity of potassium ozonide, had been achieved for the reaction of gaseous ozone with dry solid potassium hydroxide. Accordingly, under this contract a study of this reaction path was carried out.

Two ozone sources were available for these studies. A laboratory ozonator was constructed and used for preliminary studies. A diagram of this ozonator is shown in Figure IV. Ozone production in an oxygen stream from this ozone generator was less than one percent, as determined by the iodometric method.(22) The low ozone output is due to the fact that pyrex glass was used in the construction of this ozonator. Somewhat higher output would be expected if "soft" glass had been used.

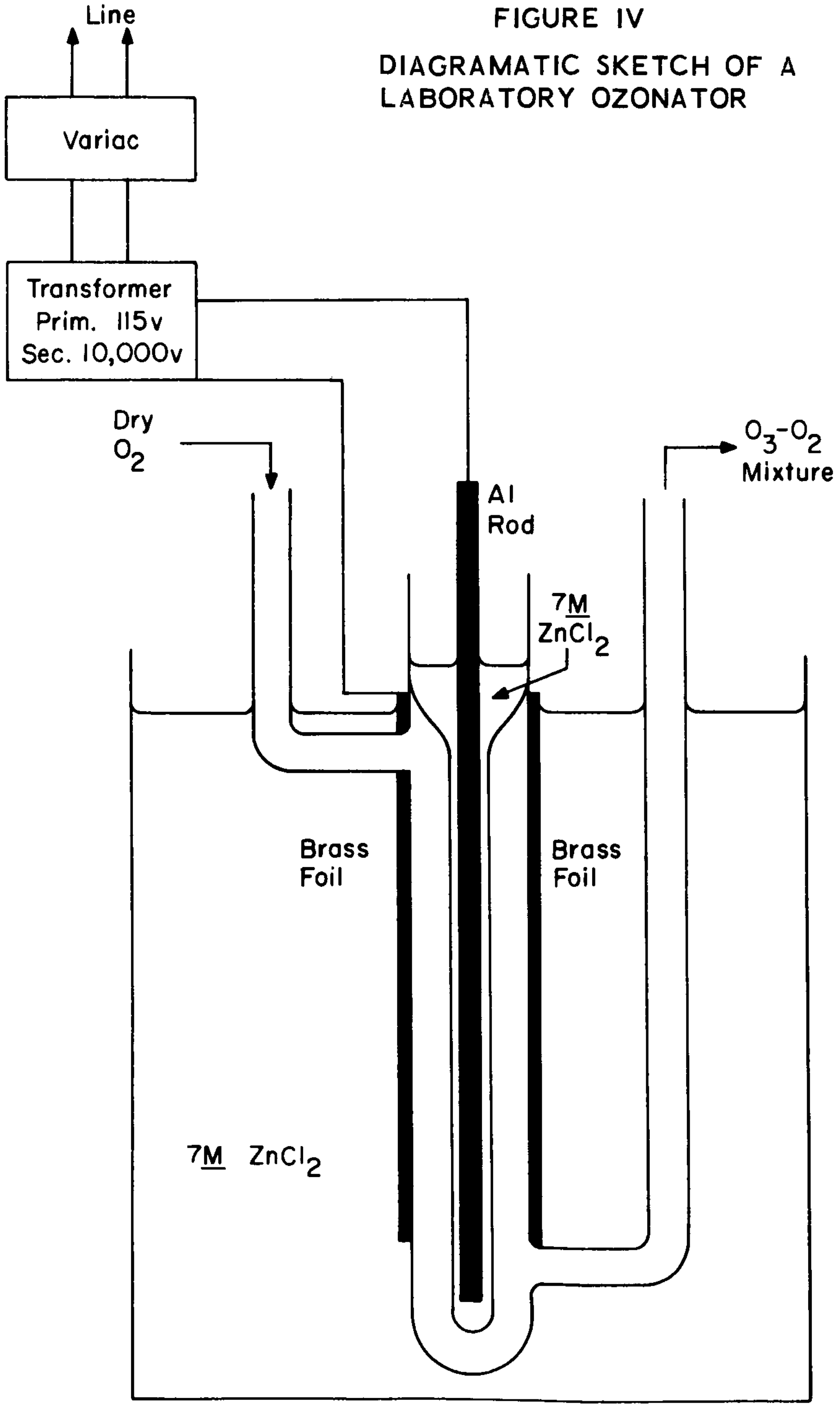
Under the terms of this contract, a Welsbach Model T-408 laboratory ozonator was purchased. This instrument is capable of delivering concentrations of ozone in an oxygen stream up to eight percent by weight. This instrument was used daily to prepare potassium ozonide samples for detailed kinetic studies. A Welsbach Model H-80 ozone meter was also purchased for this program and was used to monitor the ozone-oxygen stream from the generator. The meter was calibrated periodically according to the manufacturer's specifications.

The technique and apparatus employed in these studies have evolved from the initial studies modeled after those of Whaley and Kleinberg.(21)

Since the alkali metal ozonides are extremely hydroscopic, it is essential that all handling or transferral operations be carried out in a dry atmosphere. Two dry boxes were used on this project. One was a

FIGURE IV

DIAGRAMATIC SKETCH OF A LABORATORY OZONATOR



Fischer model Isolator/Lab box which was desiccated with phosphorous pentoxide in flat open dishes. The second dry box was one specially-designed and successfully used in our laboratories during the past three years for work on superoxide systems. This dry box is constructed of lucite and has a volume of approximately 12 cu ft. The desiccants, phosphorous pentoxide and magnesium perchlorate, were placed in open dishes on the floor of the dry box. A tray of lithium hydroxide was also placed in each dry box to scrub the atmosphere of carbon dioxide. Manipulations could also be carried out under an atmosphere of a dry inert gas. A small fan was used to circulate the air in the dry boxes.

The reaction flask, a commercial glassware item with a fritted disc (shown in Figure V) was charged in a dry box with a weighed sample of dry, powdered, potassium hydroxide. The apparatus was assembled in a hood as shown in Figure VI. The apparatus containing the hydroxide sample was then flushed with oxygen for 20 minutes prior to starting the ozone generator. The gaseous ozone-oxygen stream was then passed over the sample above the frit and the hydroxide sample began immediately to take on an orange color. For reasons noted below, the sample was agitated by gently tapping the reaction flask with a rubber hammer during the course of the ozonization. This ozonization process was normally continued for at least four hours. The sample was then flushed again with dry oxygen for five minutes and finally flushed with gaseous ammonia. A dry ice-acetone bath was then placed around the reaction flask and the ammonia condensed above the frit. (Note: Extreme caution is suggested when using the acetone bath since potassium ozonide will react violently with the acetone if the reaction flask should break and contact is made between the ozonide and acetone.) The orange potassium ozonide immediately dissolved in the liquid ammonia, yielding a dark, blood-red solution. Pressure from the ammonia gas above the solution and from the ammonia tank then forced the red liquid ammonia solution through the frit and over into the collection flask (Figure V). The extraction process was continued until the liquid ammonia solution was almost colorless. The collection flask was maintained at the same temperature as the bath used during the extraction process. The liquid

FIGURE V

REACTION CELL FOR GAS-SOLID REACTIONS AND COLLECTION VESSEL FOR SOLVENT EXTRACTIONS

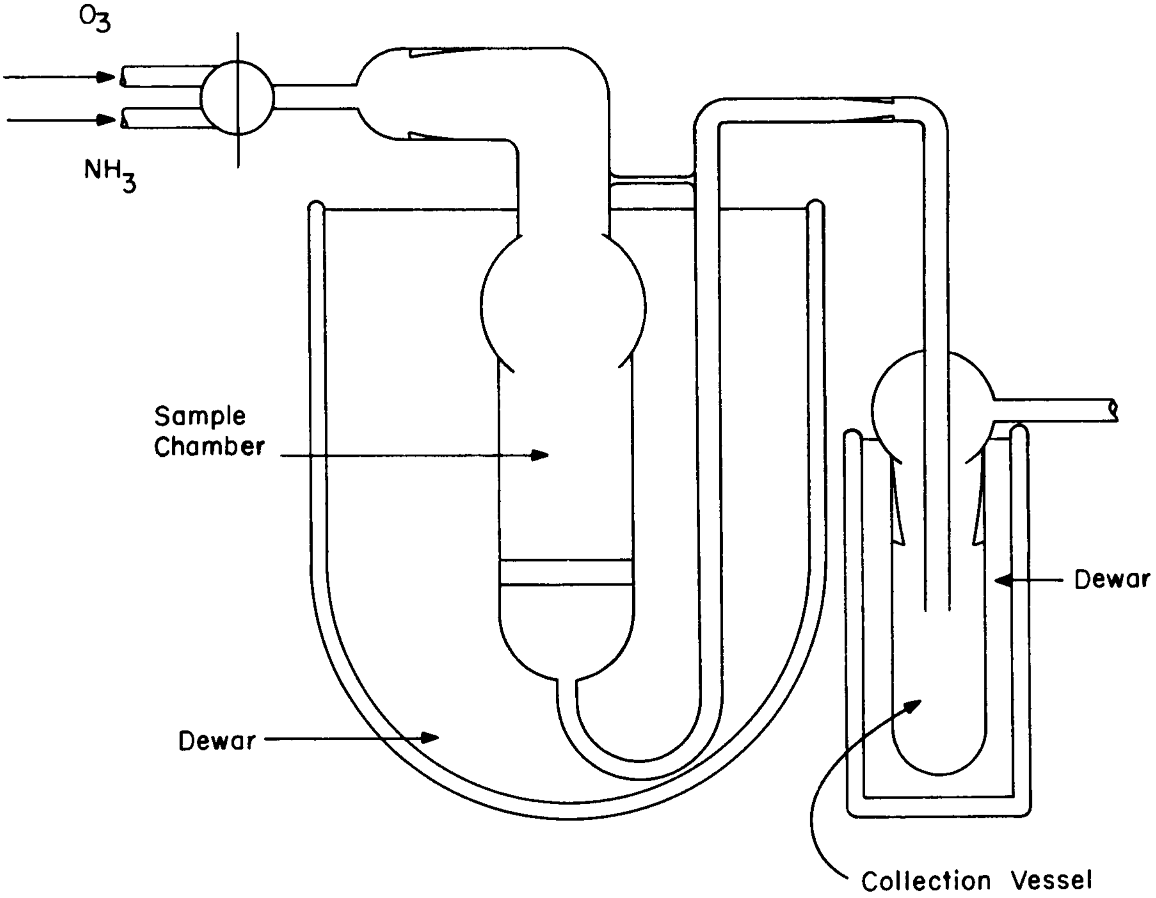
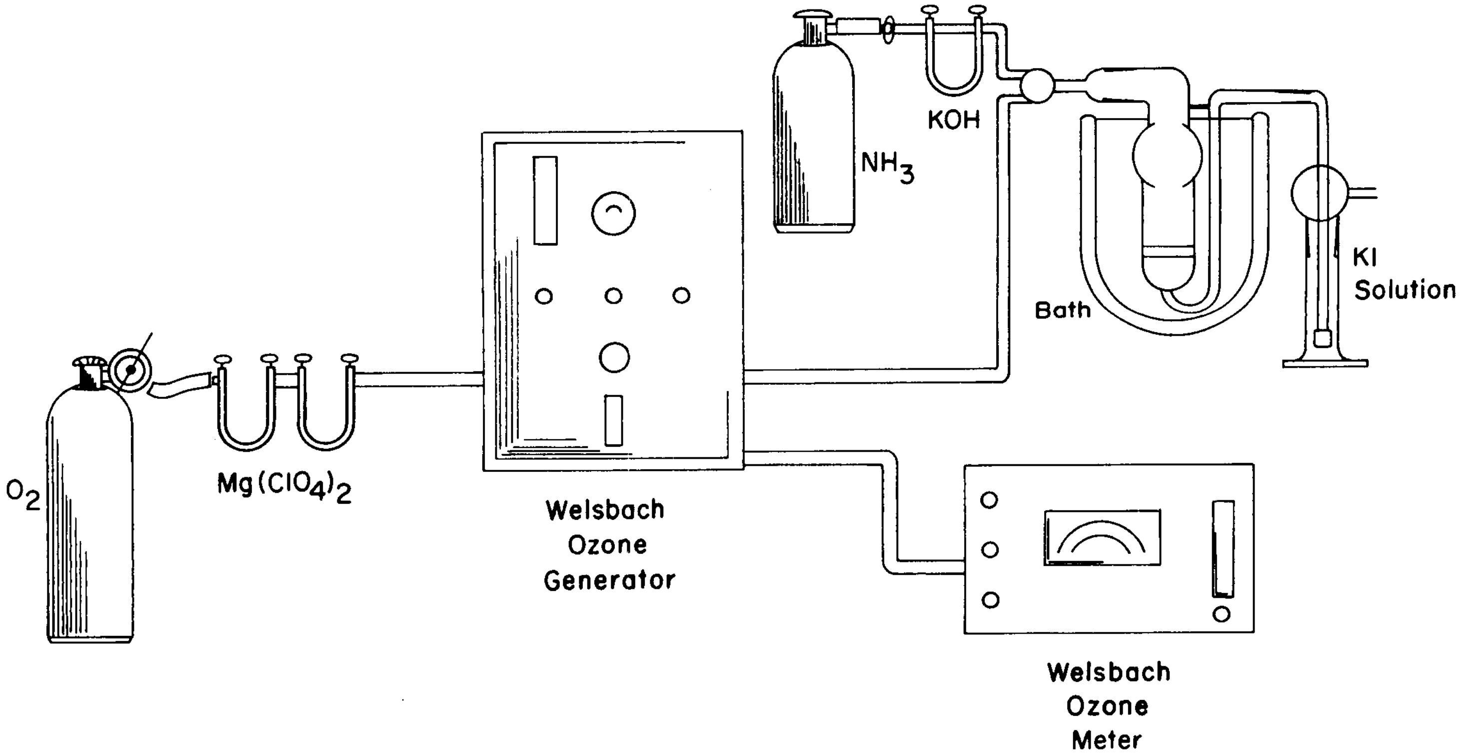


FIGURE VI

EXPERIMENTAL SET-UP FOR THE OZONIZATION OF SOLID ALKALI METAL HYDROXIDES OR OXIDES



ammonia solution was allowed to evaporate slowly, after which the solid potassium ozonide was vacuum pumped to completely remove the ammonia. The collection flask was removed, placed in a dry box, and the sample scraped put into a tared vial. The vial with the reddish-orange ozonide sample was kept in a polyethylene bag with a suitable desiccant and stored at -35°C until ready for use. Storage times normally did not exceed five days.

Using the procedure outlined above, samples of potassium ozonide up to 0.5 gram have been obtained in yields of the order of 7% for a single ozonization process. By flushing the potassium hydroxide that remains after extraction with dry oxygen to remove the residual ammonia, repeating the ozonization and extraction processes, and combining the liquid ammonia extractions, samples of potassium ozonide greater than one gram have consistently been obtained from a given batch of potassium hydroxide. The purity of the prepared potassium ozonide samples ranged from 88 to 97%. The analysis of alkali metal ozonides is discussed below.

The control studies carried out on the gaseous ozone-solid potassium hydroxide have emphasized certain points in the synthesis procedure that was followed. An excess of anhydrous potassium hydroxide was used to insure that the water formed in the synthesis reaction will be tied up by the formation of hydrated potassium hydroxide. As pointed out above, an accumulation of unbound water in the reaction system would prove extremely detrimental to the synthesis of alkali metal ozonides. The presence of excess moisture has not been observed in these synthesis reactions. In order that a fresh potassium hydroxide surface would be exposed to the ozone-oxygen gas stream, the reaction chamber was frequently agitated and the potassium hydroxide-ozonide bed mixed.

Our best yields (ca. 7%) for a single ozonization were obtained when the following procedures were observed:

1. An excess of anhydrous potassium hydroxide was used to tie up the water formed by the synthesis reaction, thus preventing the reaction between water and potassium ozonide.

2. The reaction chamber was agitated frequently to insure continual exposure of a fresh surface area of potassium hydroxide.

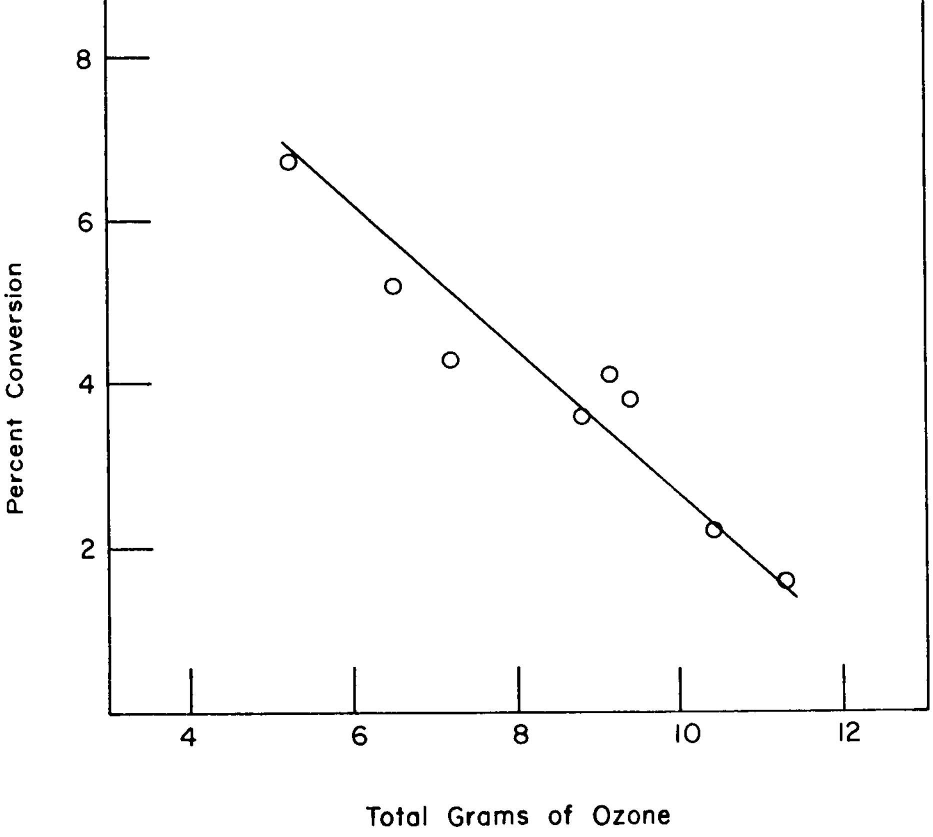
3. Low concentrations of ozone at high flow rates were found to produce the higher yields. High ozone concentrations were not necessary for efficient conversion of potassium hydroxide to potassium ozonide, and, apparently, were detrimental to higher yields. Figure VII illustrates the effect of the total amount of ozone passed through the reaction chamber in 225 minutes on the yields obtained. The size of the potassium hydroxide sample varied between 5.5 and 8 grams.

4. The length of time that the ozonization reaction was allowed to run was kept within 2.5 to 4.5 hours. Our observations are in agreement with Kazarnovskii, et al,(12) who carried out their synthesis reaction for 2.5 to 3 hours. Qualitative observations indicate that extended ozonization does not improve the yield of potassium ozonide. In fact, the yields were low, and, in most cases, the ozonide sample was destroyed when the synthesis reaction was extended for long periods of time. For example, several studies were carried out in which potassium hydroxide was ozonated for 20 hours. In all of these cases, the orange-colored potassium ozonide that formed within the first three hours was found to revert gradually to the white color of the starting material. Similar observations were made when potassium superoxide was allowed to ozonate overnight. The orange ozonide gradually reverted to white hydroxide and yellow superoxide.

To obtain information regarding the synthesis reaction itself, the ozone concentration exiting from the reaction chamber was monitored while potassium hydroxide was ozonated in the "static" state, i.e., shaking of the sample was avoided. When the ozone-oxygen gas stream was diverted into the reaction chamber, it was expected that the ozone concentration

FIGURE VII

PERCENT CONVERSION OF POTASSIUM HYDROXIDE TO POTASSIUM OZONIDE AT 0°C AS A FUNCTION OF THE TOTAL AMOUNT OF OZONE PASSED THROUGH THE REACTION SYSTEM IN 225 MIN.



would decrease as the synthesis reaction occurred. The ozone concentration was then expected to level off and increase as the hydroxide surface layers became fully ozonated. As shown in Figure VIII, this expected phenomenon was not observed. The ozone concentration did decrease, exponentially, but did not exhibit an increase after six hours. In less than 20 minutes from the start of the synthesis reaction, an approximately 4-mm layer of potassium ozonide formed at the top of an approximately 5-cm column of potassium hydroxide. During the experiment, the white potassium hydroxide below the ozonated layer did not change color. Shaking the sample chamber to obtain mixing of the ozonide and hydroxide did increase the scattering of the experimental data obtained, but did not change the shape of the curve.

Thus, after three to four hours, the ozone is apparently consumed without a significant increase in ozonide formation. It is possible that the surfaces of potassium ozonide and/or hydrated potassium hydroxide are catalytic for the decomposition of ozone.

We believe that these studies have served to establish the optimum conditions for the preparation of potassium ozonide via the gaseous ozone-solid potassium hydroxide reaction path. Although the yields are relatively low, extremely pure samples are obtainable. As a result, this method was used throughout the course of this program to obtain potassium ozonide samples for evaluation as air revitalization material.

The preparation of potassium ozonide by the passage of gaseous ozone over solid potassium superoxide has been observed in the Electric Boat laboratories. This independent observation has confirmed recent reports of the preparation of cesium and potassium ozonides by this method.(17,18,23) Apparently purer ozonides are obtained; however, investigations in our laboratories do not readily indicate any significant increase in the yield of potassium ozonide obtained via the gaseous ozone-solid potassium hydroxide method.

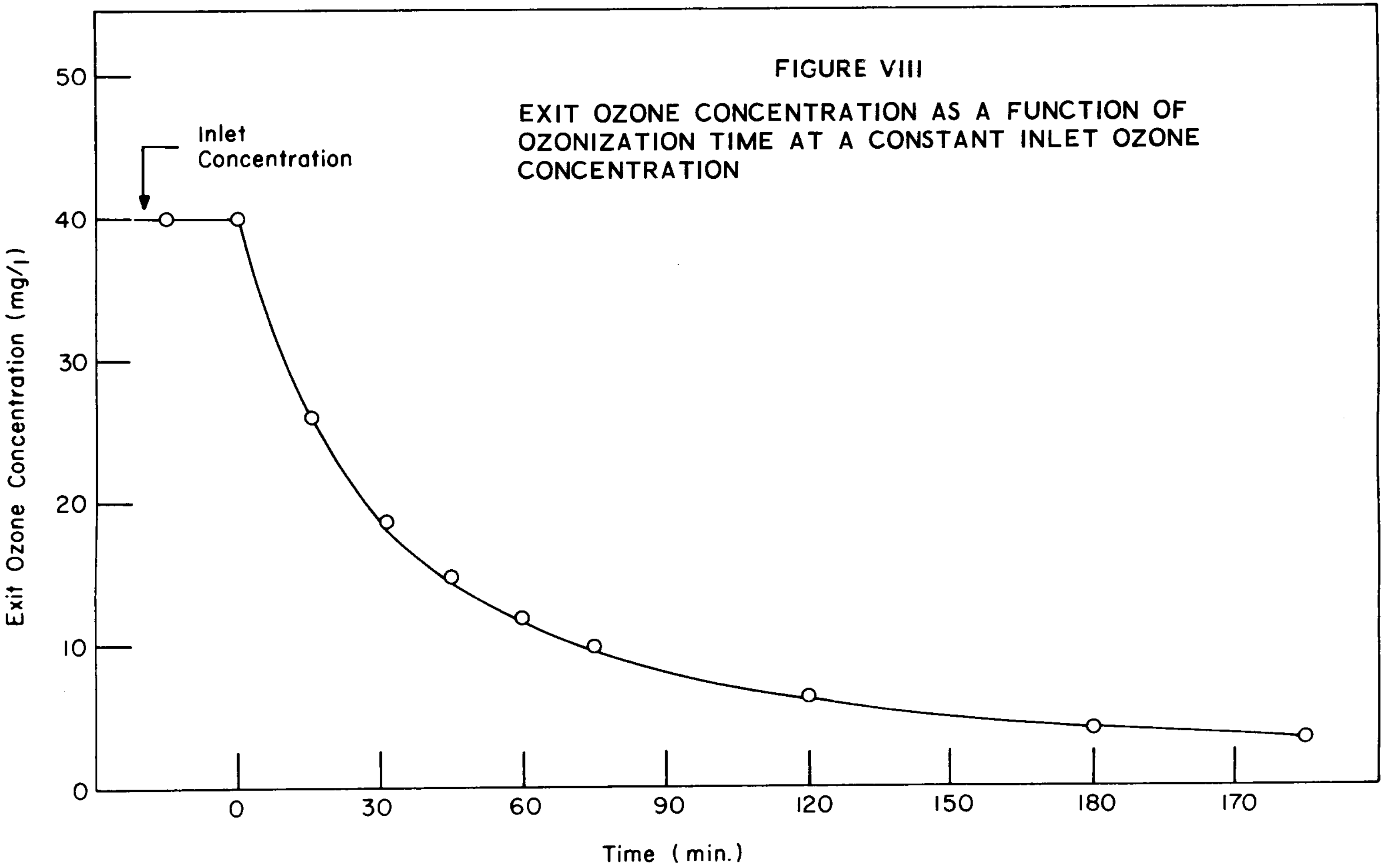


FIGURE VIII

EXIT OZONE CONCENTRATION AS A FUNCTION OF OZONIZATION TIME AT A CONSTANT INLET OZONE CONCENTRATION

2.1.1.3 Synthesis of Sodium and Lithium Ozonides

Nikolskii, et al,(24) have claimed the synthesis of sodium ozonide by exposing anhydrous sodium hydroxide to a gaseous ozone stream at -55°C. The ozonide was extracted at -50°C with liquid ammonia. Upon evaporation of the ammonia solution, red crystals were obtained which were analyzed to be 90% sodium ozonide. Kuznetsov(25) has prepared sodium ozonide at -80°C in a similar manner, followed by extraction with liquid ammonia which was removed in a vacuum at -50°C. Red crystals were obtained containing 90-92% sodium ozonide. The Russian investigators point out the solubility of sodium ozonide in liquid ammonia and report that the ozonide is unstable at room temperature. The decomposition of sodium ozonide to sodium superoxide and molecular oxygen is reported to be complete in 53 hours.(24)

Whaley and Kleinberg(21) have prepared sodium ozonide by passing ozone through powdered sodium hydroxide at room temperature. Their observations are in direct conflict with the Russian results. Whaley and Kleinberg report their product to be insoluble in liquid ammonia and stable at room temperature, noting no decomposition in sodium ozonide samples which had stood for 18 months. The observations of Whaley and Kleinberg have been confirmed by McLachlan, et al.(26)

The apparent discrepancies concerning the solubility and stability of sodium ozonide have been investigated by Kacmarek(17) and Solomon.(20) These investigators have concluded that the discrepancies resulted from the probable existence of two crystalline forms of sodium ozonide; one soluble in liquid ammonia and unstable at room temperature, the other insoluble in liquid ammonia but stable at room temperature.

Attempts in our laboratories to synthesize and isolate sodium ozonide by the methods described above have been only partially successful. When gaseous ozone was passed through dry powdered sodium hydroxide at room temperature, a pale yellow color developed in the hydroxide bed. This yellow product, presumably sodium ozonide, was insoluble in liquid ammonia and could be stored under anhydrous conditions for at least one week without any noticeable loss of color. These observations tend to confirm the reports of Whaley and Kleinberg(21) that sodium ozonide prepared at room temperature is stable but insoluble in liquid ammonia.

Attempted synthesis at -80°C by the same method produced the same yellow color in the sodium hydroxide bed. When extracted, the yellow product dissolved in liquid ammonia, resulting in a pale, orange-red solution that was similar in appearance to dilute liquid ammonia solutions of potassium ozonide. Upon evaporation of this solution under vacuum, a white solid, predominantly sodium hydroxide, was obtained instead of the expected red crystals of sodium ozonide. In no cases were we able to isolate sodium ozonide via this procedure. Indications are that the observations of previous investigators are confirmed that sodium ozonide prepared at temperatures between -80 and -60°C is soluble in liquid ammonia and unstable at room temperature.

Thus, it would appear that a stable form of sodium ozonide can be prepared by the ozonization of sodium hydroxide at room temperature. Once again we are faced with a gas-solid reaction which gives low conversion yields. In addition, the stable crystal form of sodium ozonide is insoluble in liquid ammonia and can not be extracted from the unreacted starting material to yield highly pure samples.

It is evident, therefore, that if advantage is to be taken of sodium ozonide as an air revitalization material, a novel reaction procedure will have to be developed which will produce high yields of pure sodium ozonide in its stable form.

Russian investigators(24) have failed to synthesize lithium ozonide by the action of gaseous ozone on solid lithium hydroxide and have postulated that the formation of lithium ozonide is thermodynamically unfavorable. However, the validity of their thermodynamic values has been questioned.(26,27)

Kacmarek, et al,(28) have reported the formation of a thermally unstable tetraammoniate of lithium ozonide from the reaction of gaseous ozone with anhydrous powdered lithium hydroxide which had ammonia absorbed on its surface. The compound assayed as $Li(NH_3)_4O_3$ and was characterized by its visible spectrum in a liquid ammonia solution.

Since the formation of lithium ozonide was still questionable, attempts were made to synthesize lithium ozonide by passing gaseous ozone through pure, anhydrous lithium hydroxide at temperatures between 25°C and -80°C. A pale yellow color developed briefly in the lithium hydroxide bed but disappeared quickly. The transitory yellow color was very similar to that developed during the attempted synthesis of sodium ozonide via the same method. This yellow product may indeed have been lithium ozonide. Attempts were not made to extract the yellow product with liquid ammonia because it quickly disappeared when the ozone flow was stopped.

2.1.2 The Study of Novel Reaction Paths for the Synthesis of Alkali Metal Ozonides

The theoretical and experimental work presented in this report clearly establishes the potential of alkali metal ozonides as air revitalization materials. The major obstacle preventing an engineering evaluation of these materials on a large-scale basis is the inability to produce batch-size quantities of the material via the preparative methods thus far developed. Thus the following promising ideas were pursued in an effort to establish a method of synthesizing potassium ozonide in batch-size quantities. Batch-size quantities are defined here as one or more pounds of product per preparative run.

2.1.2.1 Reactions in Liquid Ammonia

The fact that potassium ozonide is soluble in liquid ammonia,(11) whereas the hydroxide is not, suggested the possibility of a more efficient conversion of the base to the ozonide by the passage of an ozone-oxygen stream through a dispersion of the solid hydroxide in liquid ammonia or through a solution of potassium metal in liquid ammonia.

The formation of ammonium ozonide has been reported,(29) resulting from the passage of ozone through pure liquid ammonia. Evidence for the formation of this compound was based on the similarity of the visible absorption spectrum of the ozonated liquid ammonia to the spectra of alkali metal ozonide solutions in liquid ammonia.(20) It was further reported that ammonium ozonide is thermally unstable above -126°C, but its formation has been observed at -80°C, followed by immediate decomposition when the ozone flow is removed.(29)

If an ozone-oxygen stream were to be passed through a dispersion of potassium hydroxide in liquid ammonia, the temperature at which the study was to be made must be greater than at least -80°C so as to prevent the formation of ammonium ozonide. It was expected that as the ozonide was formed on the surface layers of the hydroxide particles, it would dissolve in the liquid ammonia, thereby renewing fresh surface for further reaction with ozone.

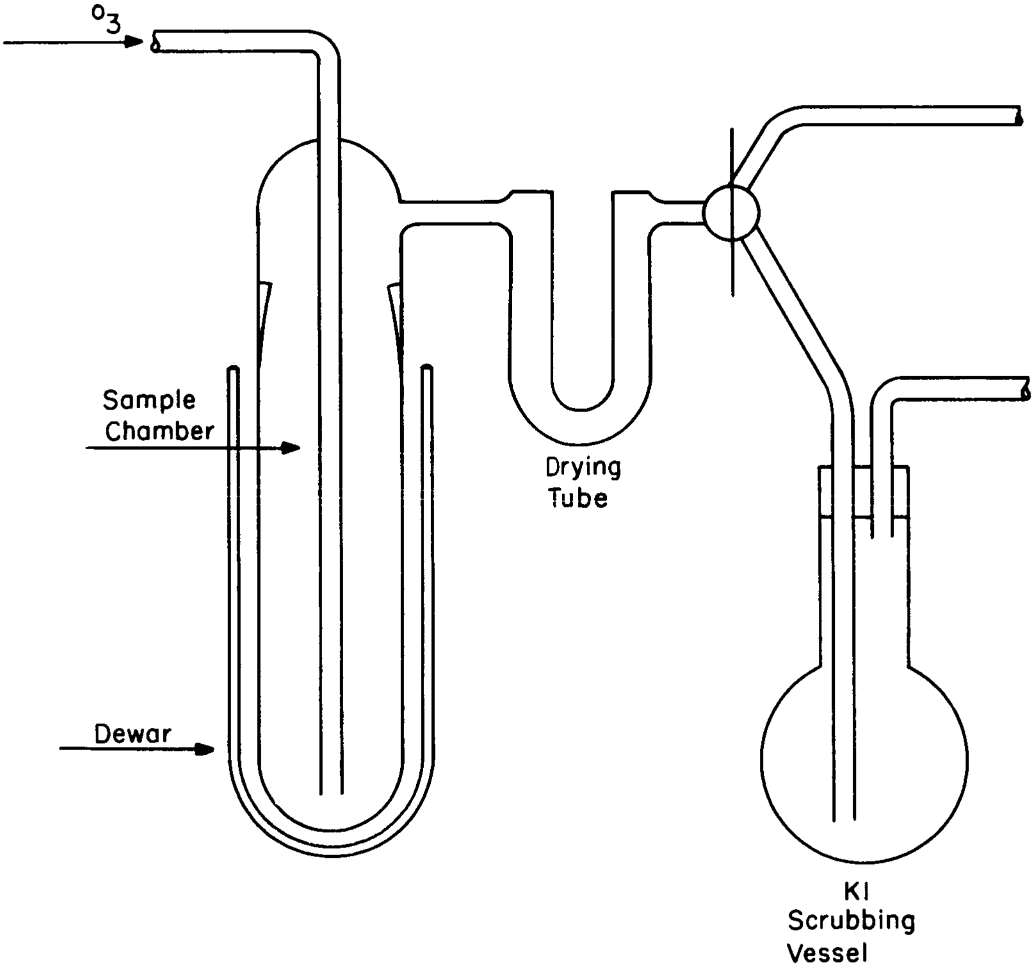
Studies were carried out in the temperature range from -80 to -60°C to investigate this reaction path with potassium hydroxide as the starting material. The apparatus used for studies in non-aqueous solvents is shown in Figure IX. After the reaction chamber had been charged with potassium hydroxide in the dry box, the apparatus was assembled, and the ammonia condensed over the hydroxide sample. The ozone flow was started and the liquid ammonia immediately turned a pale red color, characteristic of ozonide solutions in liquid ammonia. The ozonization process was continued for a short period, the ozone flow stopped, and the liquid ammonia evaporated. In no cases were we able to obtain pure potassium ozonide via this procedure. Instead, yellow-green crystals were obtained which qualitatively were shown to be nitrates. This indicated that significant amounts of ammonium ozonide were formed which decomposed to nitrates in the following manner:(29)

$$2NH_4O_3 = NH_4NO_3 + 1/2O_2 + 2H_2O \qquad (16)$$

The results of these studies, however, are far from discouraging. The tendency to form ammonium ozonide at the reaction temperatures employed appears to be a mitigating factor against the formation of the alkali metal ozonide. The evidence indicates that at higher temperatures this mitigating factor may be overcome. It seems that the study of this reaction path should be continued using a specially-designed pressure vessel which would allow the ozonization reaction to take place in

FIGURE IX

APPARATUS USED FOR THE STUDIES OF NOVEL REACTION PATHS IN NON-AQUEOUS SOLVENTS FOR THE SYNTHESES OF ALKALI METAL OZONIDES



suspensions of alkali metal hydroxides in liquid ammonia or in liquid ammonia solutions of alkali metals at room temperature.

2.1.2.2 Potassium Hydroxide Dispersions in Freon

An interesting and promising approach investigated during the time period covered by this contract concerned the ozonization of potassium hydroxide dispersed in Freon. Freon is inert to ozone and does not dissolve the hydroxides. It has been established in our laboratories that the ozonides and superoxides are likewise insoluble and non-reactive. Therefore, it was expected that Freon would act solely as a dispersing medium. It has been reported that Freon, in addition to being resistant to the oxidizing action of ozone, also has preferentially high specific solubility for ozone in comparison to oxygen,(30) which fact should allow a means of separating and further concentrating ozone from an oxygen-ozone mixture as produced by a standard ozonator. By this technique it has been demonstrated that high concentrations of ozone can be stored for periods of time at low temperatures without marked decomposition.

Studies were initiated to employ the Freon technique to provide higher concentrations of ozone for reaction with dry, powdered potassium hydroxide using the apparatus illustrated in Figure IX. Freshly distilled Freon TF, CCl_2FCClF_2, was used as the dispersing medium.

The possibility also existed that the violent turbulence resulting from the gaseous ozone bubbling through the dispersion would renew, at least in part, the surface of the hydroxide, enhancing the hydroxide to ozonide conversion rate. Subsequent extraction of the solid products with liquid ammonia or some other suitable solvent was expected to produce a high yield of potassium ozonide.

The reactions studied were carried out at $0^{\circ}C$. The changes that occurred upon the passage of an ozone-oxygen gas mixture through the potassium hydroxide-Freon suspension were very dramatic. The suspended solid almost immediately took on an orange to red color. Detectable color changes characteristically occurred within the first 10 minutes after the start of ozonization. The ozonization was then allowed to continue for one to three hours. At the end of this time, the reaction chamber was transferred to a dry box, and the reddish solid powder separated from the Freon by vacuum filtration through a sintered glass filter. The powder was transferred to a vacuum desiccator charged with magnesium perchlorate, and pumped to dryness. The best analyses obtained to date on samples obtained via this method were 7%, indicating once again a very low conversion of potassium hydroxide to potassium ozonide.

In several runs, attempts were made to extract a pure sample of potassium ozonide from the solid mixtures of potassium hydroxide and potassium ozonide. Accordingly, liquid ammonia extractions were dark red and characteristic of potassium ozonide. However, a remarkable phenomenon occurred when these samples were scraped with a spatula against the glass walls of the collection flask. Such scraping caused the samples to explode. In all such occurrences the product was a fine white residue. Significant amounts of the residue could not be collected for adequate analysis. At this time, we are unable to account for this behavior. This phenomenon is not at all characteristic of alkali metal ozonide samples collected via the reaction of the hydroxide with ozone in other media. This problem will have to be solved before this promising reaction path can be exploited.

2.1.2.3 Ozonization of an Alkali Metal t-Butoxide

Milas and Djokic(31) have shown that it is possible to obtain potassium ozonide via the reaction of ozone and solid potassium t-butoxide at $-78^{\circ}C$. The procedure for producing potassium t-butoxide involves refluxing a mixture of t-butyl alcohol and potassium metal in an atmosphere of dry nitrogen until all of the potassium has reacted forming a solution of $(CH_3)_3COK$. The excess alcohol is removed by means of a rotating evaporator under high vacuum and the potassium t-butoxide is recovered as a white powder. Upon ozonization of the white powder, the following reactions are assumed to occur:

$$2(CH_3)_3COK + 2O_3 = 2KO_3 + 2(CH_3)_3CO\cdot \qquad (17)$$

$$2(CH_3)_3CO\cdot = (CH_3)_3COOC(CH_3)_3 \qquad (18)$$

By modifying the above procedure, it was hoped that potassium ozonide could be obtained in good yield. The modification involved the ozonization of the potassium t-butoxide while still in the alcohol solution using the apparatus shown in Figure X, with the expectation that the reaction could be caused to go to completion on the basis that as the ozonide is formed it would precipitate out of solution. Preliminary investigations in our laboratories have determined that pure potassium ozonide is essentially insoluble and non-reactive in absolutely dry t-butyl alcohol, thereby removing doubt that the ozonide could not be recovered via the proposed method. The best samples obtained via this procedure contained 4.6% potassium ozonide. These studies have indicated the formation of impure potassium ozonide but were successful enough to enhance our enthusiasm for this synthetic route. A great deal of fundamental work and specially-designed equipment will be required to optimize this method of ozonide production with respect to quantity and purity.

2.2 ANALYSIS OF ALKALI METAL OZONIDES

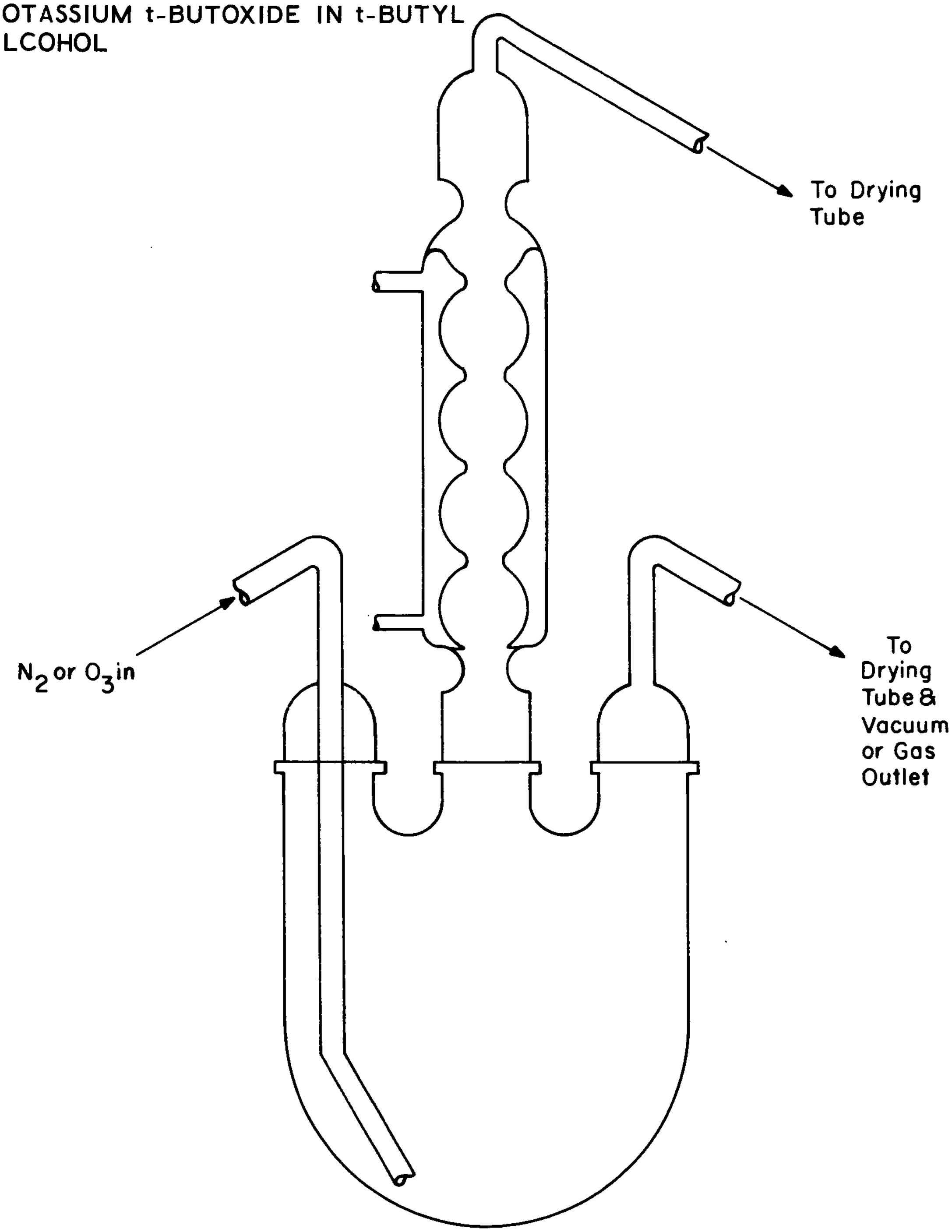
If the kinetic and thermodynamic data to be obtained during this program were to be of value, it was most important that a reliable procedure be developed for the analysis of alkali metal ozonides in the presence of lower oxides.

Alkali metal ozonides are known to decompose thermally with an appreciable rate in the temperature range of 60-100°C to the superoxide and oxygen:

$$MO_3 = MO_2 + 1/2\ O_2 \qquad (19)$$

FIGURE X

APPARATUS USED FOR THE PREPARATION AND OZONIZATION OF POTASSIUM t-BUTOXIDE IN t-BUTYL ALCOHOL



At these temperatures the superoxide is quite thermally stable.(32,33) The approaches suggested by reaction (19) as a quantitative method of analysis for the purity of alkali metal ozonides include thermogravimetry and gas analysis. However, for a complete analysis of the ozonide in which the major impurities would be the corresponding superoxide, hydroxide, and/or hydrated hydroxide, additional techniques would be required. A literature survey emphasized the fact that the methods of analysis that were in use were varied, often quite vague, and of questionable precision and accuracy. In all cases, an adequate analysis of the ozonide sample could not be obtained by any one single procedure.(12,17,21,34)

The following scheme was developed in our laboratories for the analysis of alkali metal ozonides in the presence of lower oxides:

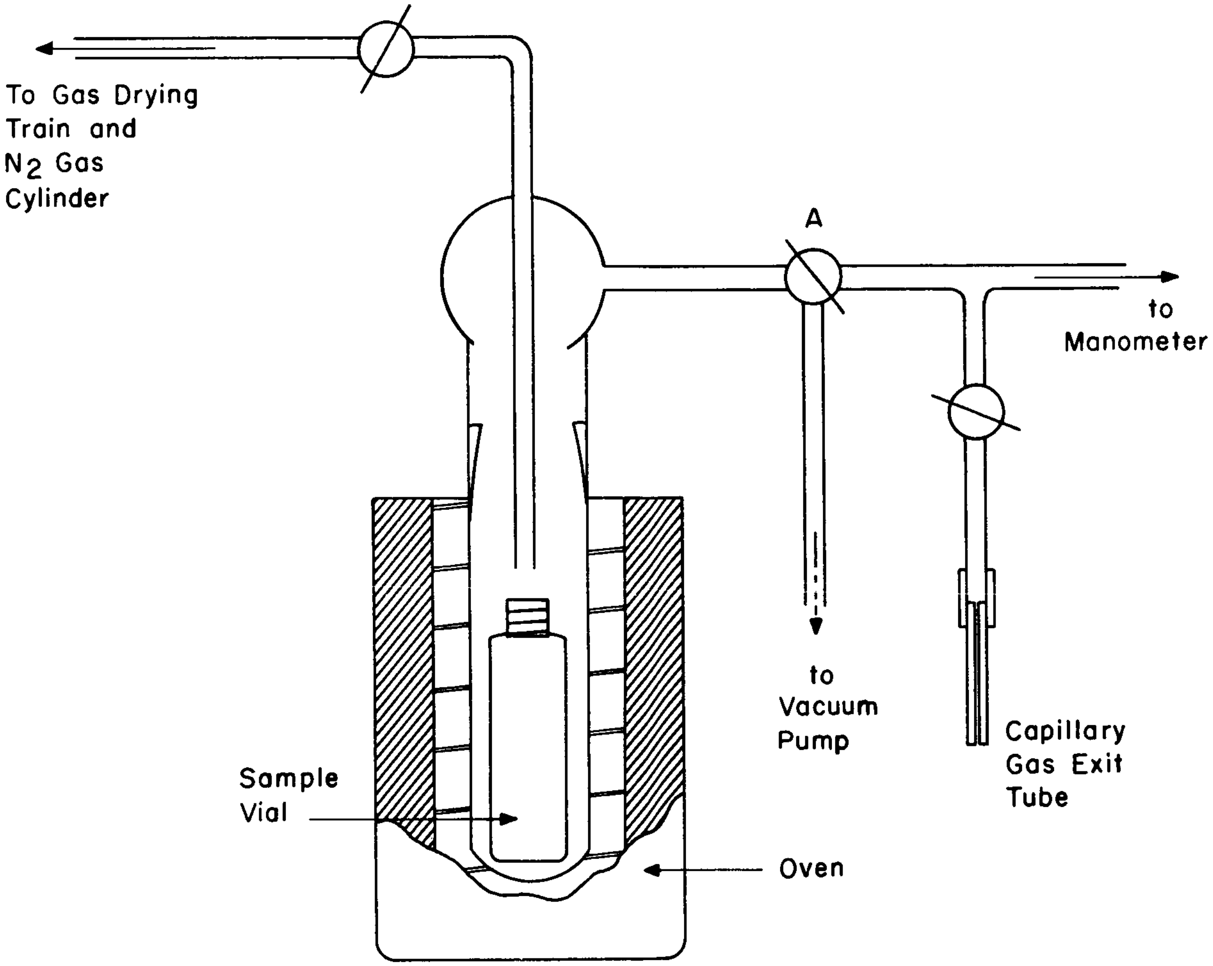
1. Determination of Ozonide Content

A thermogravimetric method was developed in which the ozonide sample was decomposed thermally under an inert atmosphere to the superoxide and oxygen via reaction (19). The apparatus designed for this analysis is shown in Figure XI. The ozonide sample, powder or pellet, was placed in a vial in the dry box. Under a flow of nitrogen, the tared vial was quickly transferred to the sample chamber, the nitrogen flow stopped, and the system evacuated to 10^{-3} mm Hg. Dry nitrogen was then bled into the system and the flow rate adjusted so as to maintain a positive pressure of 10mm Hg over the sample. The sample was heated to $70^{\circ} \pm 5^{\circ}$C, held at that temperature for at least one hour, cooled, quickly removed from the reaction chamber, and reweighed.

The ozonide content was then calculated on the basis of the weight loss observed according to the stoichiometry of reaction (19). The reproducibility of this analytical procedure has been excellent. For example, three analyses of a given batch of potassium ozonide yielded values of 92.0, 92.1, and 92.2%.

FIGURE XI

APPARATUS USED FOR THERMOGRAVIMETRIC ANALYSIS OF ALKALI METAL OZONIDES



2. Determination of Superoxide Content

The sample obtained after the analysis for ozonide content consisted of the superoxide and hydroxide present initially, and the superoxide produced by the thermal decomposition of the ozonide. The superoxide content of the initial sample was calculated from a knowledge of the amount of ozonide in the original sample and the total superoxide content of the decomposed sample. The method of Seyb and Kleinberg(33,35,36) has proven quite satisfactory for the analysis of alkali metal superoxides and was used for such in these laboratories.

3. Determination of Hydroxide Content

The major disadvantage in using the Seyb-Kleinberg method for superoxide is the prevention of a simultaneous determination of the hydroxide content. Therefore, in nearly all of our analyses, the unaccountable material was assumed to be potassium hydroxide or its hydrated form.(12)

2.3 THE CHEMISTRY OF POTASSIUM OZONIDE

2.3.1 Thermal Stability

The thermodynamic data reported in Table III points out that potassium ozonide tends to decompose spontaneously at room temperature to potassium superoxide and molecular oxygen according to reaction (19). Therefore, the important questions that must be answered regarding the stability of potassium ozonide concern the rate at which the decomposition takes place in the temperature ranges of interest in a space cabin, and the temperature(s) at which the rate is slow enough to allow long-term storage of the material without fear of significant amounts of decomposition.

A literature survey of this problem disclosed certain discrepancies between Soviet and American investigators with regard to the stability characteristics of potassium ozonide. Table IV summarizes typical kinetic data obtained in these laboratories along with the results reported in the literature by other investigators.

TABLE IV

SUMMARY OF KINETIC DATA FOR THE THERMAL DECOMPOSITION OF POTASSIUM OZONIDE

Sample	Temperature (°C)	Rate of Decomposition (%/hr)		Time	
		Induction Period	Active Period	Induction Period	Total Decomposition
I. KO_3 Powder (N_2 dry)	40 ± 1	---	20.2	None	3.5h
	30 ± 1	---	7.0	None	10h
	22 ± 1	---	4.5	None	15.5h
	0 ± 1	---	0.5	None	139h
II. KO_3 Pellet (N_2 dry)	40 ± 1	11.8	54.2	4h	11h
	30 ± 1	5.1	17.5	9h	30h
	23 ± 1	1.8	7.5	24h	60-80h
	0 ± 1	0.6	---	---	---
III. KO_3 Pellet (P_2O_5 dry)	30 ± 1	1.2	35.4	12h	25h
	23 ± 1	0.8	16.7	28h	50h
IV. KO_3 Pellet Russian data(34)	50	---	---	---	---
	19	0.23	2.3	40h	240h
		0.28*	3.2*	---	---
	0	---	---	20d	101d
	-9	0.03	1.5	54d	230d
	-18	---	---	205d	---
V. KO_3 Data of Kacmarek(17)	25	---	4.9-50	None	---

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*Computed in our laboratories by a least-squares treatment of the available Russian data.(34)

The Russian investigators have reported that the decomposition reaction is complete in approximately 10 days at room temperature,(12) while at 50-60°C, the decomposition is over in 30 minutes.(12,34) The Russian data also discloses the existence of a so-called "induction period," i.e., a time period during which the decomposition rate is very much slower than the rate of active decomposition of the sample. An example of the Russian data illustrating this induction period is shown in Figure XII. Kazarnovskii, et al,(12,34) have reported that the thermal decomposition of potassium ozonide at 19°C, in pellet form, has an induction period of 40 hours (Figure XII), a half-life period of 90 hours, and complete decomposition time of about 10 days. The average rate of decomposition at this temperature for the induction period was only 0.23%/hr, and for the active period, 2.3%/hr. Analyses by a least-squares treatment in these laboratories of the available Russian data(34) yielded 0.28 and 3.2%/hr as the decomposition rates of the induction and active period, respectively.

To illustrate the dramatic effect on stability obtained by a decrease in temperature, the Russian investigators(34) report that at -18°C the induction period was 205 days and a decomposition of less than 1% of potassium ozonide took place during this entire period. This corresponded to a loss of only 0.2% of the active oxygen. Russian data at other temperatures are also listed in Table IV.

Kacmarek(17) has expressed disagreement with the Russian data with regard to the presence of an induction period. Induction periods were not observed by Kacmarek for kinetic studies of the thermal decomposition of potassium ozonide at 20 and 25°C. He does not, however, report whether the ozonide was in the form of a powder or a pellet. In addition, in contrast to the excellent reproducibility of the Russian data, Kacmarek's results, at a given temperature, showed very wide differences in the rate of decomposition. For example, for eight runs at 25°C, the rate of active decomposition ranged from 4.9 to 50%/hr.

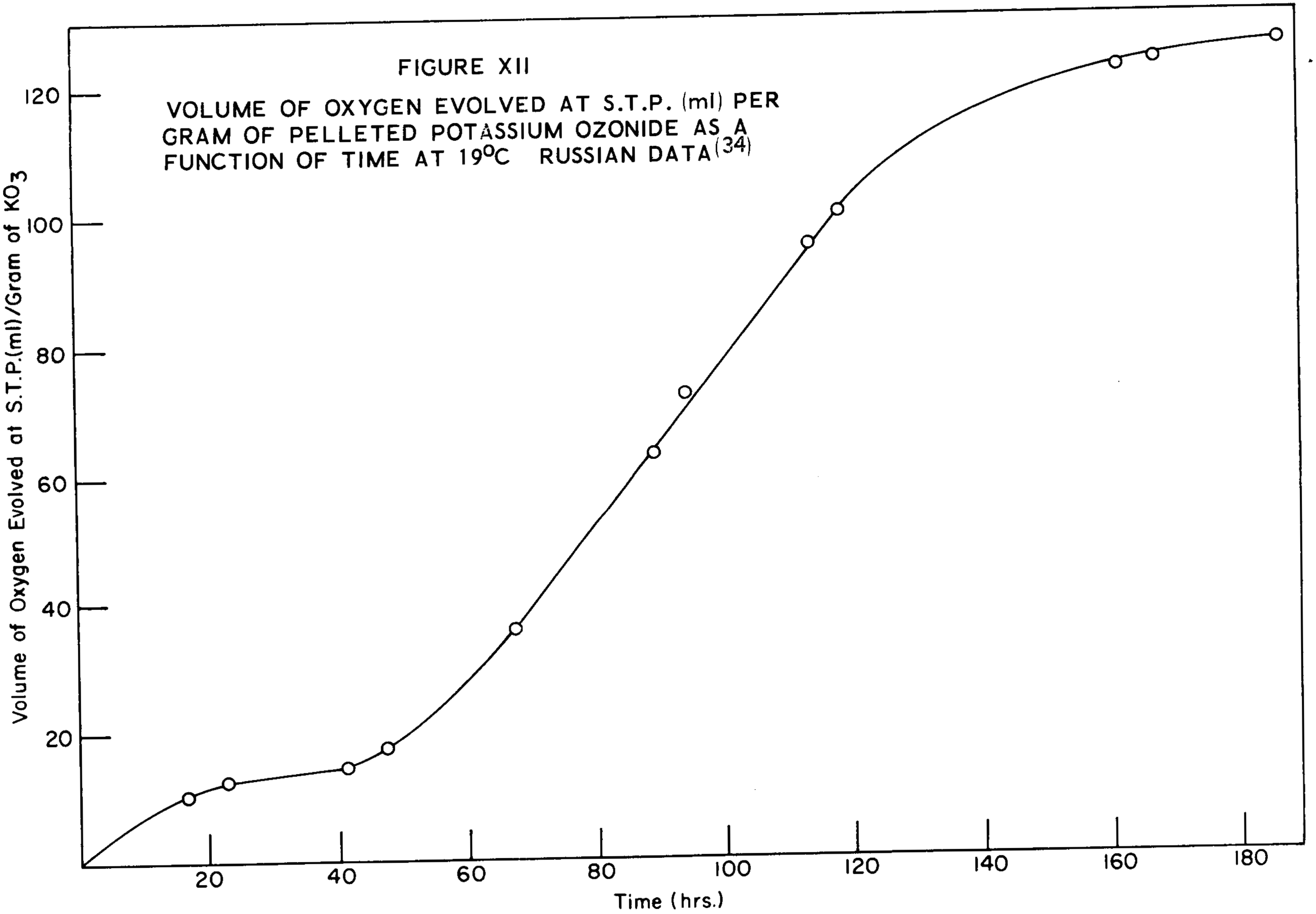


FIGURE XII

VOLUME OF OXYGEN EVOLVED AT S.T.P. (ml) PER GRAM OF PELLETED POTASSIUM OZONIDE AS A FUNCTION OF TIME AT 19°C RUSSIAN DATA(34)

Accordingly, a kinetic study of the thermal decomposition of potassium ozonide was carried out to resolve the apparent discrepancies concerning the stability characteristics of potassium ozonide. The apparatus used for these studies is shown in Figure XIII and was designed to follow the rate of oxygen evolution gasometrically as the sample decomposed via reaction (19) in a thermostated bath. The potassium ozonide sample was loaded into a vial in the dry box, quickly transferred to the sample chamber, the gas burette equilibrated, and the volume of oxygen evolved recorded as a function of time. Our results, Table IV, fell into three classes, depending upon the state of the potassium ozonide sample and the drying procedure followed.

1. Class I

The first kinetic runs during this study were made using powdered potassium ozonide samples. The reaction chamber was flushed with dry nitrogen prior to introduction of the tared sample vial in an attempt to exclude water vapor from the system. Figure XIV illustrates typical kinetic curves obtained during these studies. In all cases, an induction period, as reported by the Russian investigators, was not observed. Some data reported by Kacmarek does, however, resemble these results, but only with respect to the shape of the curve. The rates of decomposition of powdered potassium ozonide reported in Table IV for various temperatures were determined from the first-order reaction rate plots illustrated in Figure XV.

2. Class II

Following the kinetic studies using powdered potassium ozonide samples, runs were made with the ozonide in pellet form at the same temperatures. A hand pellet press (Parr Instrument Co.) was used and attempts were made to insure the uniformity of pellet dimensions by having only one technician prepare the pellets from nearly equal weights of potassium ozonide samples. The reaction chamber was flushed with dry nitrogen prior to introduction of the sample as in the previous set of runs. The results obtained

FIGURE XIII

APPARATUS USED FOR KINETIC STUDIES OF THE THERMAL DECOMPOSITION OF ALKALI METAL OZONIDES

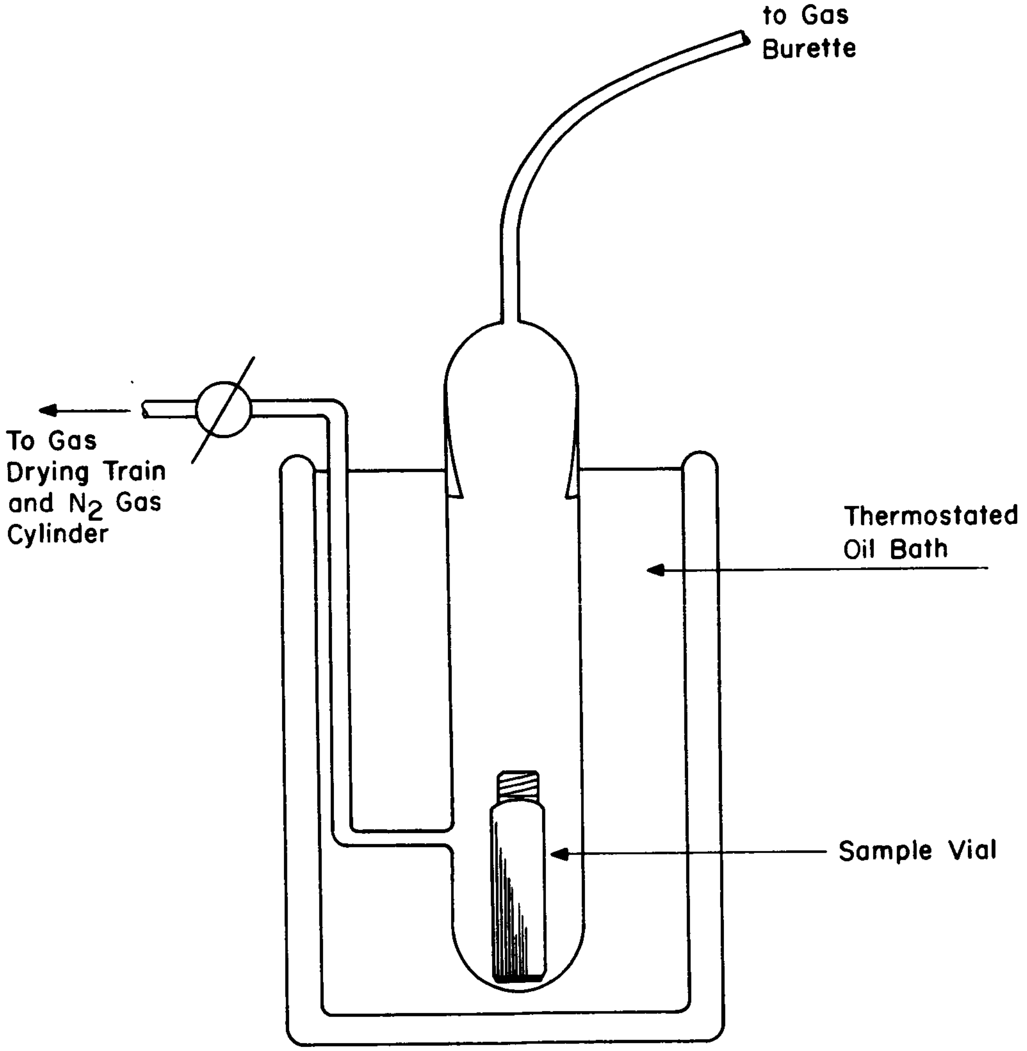
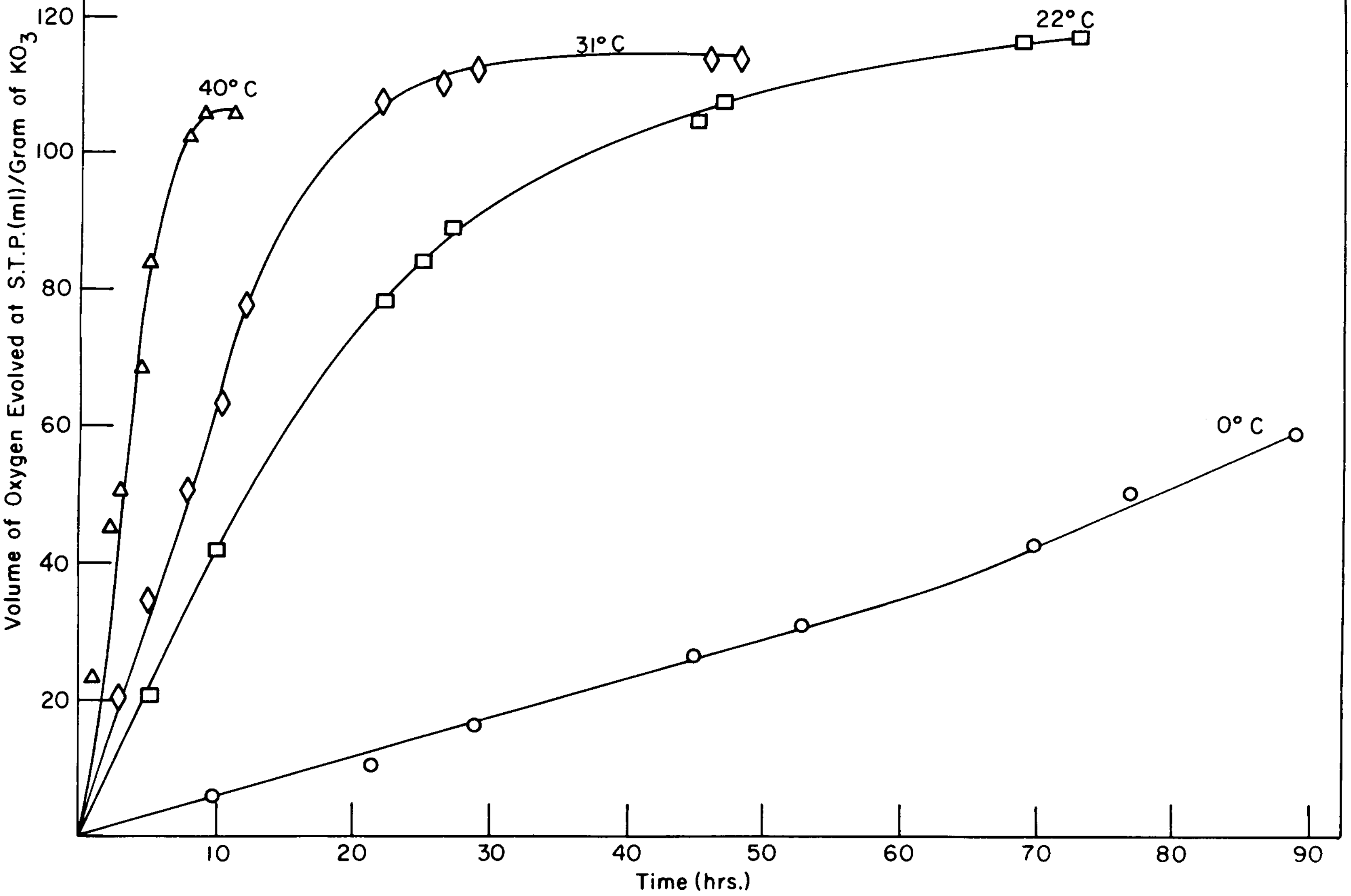


FIGURE XIV

VOLUME OF OXYGEN EVOLVED AT S.T.P. PER GRAM OF POWDERED POTASSIUM OZONIDE AS A FUNCTION OF TIME AT VARIOUS TEMPERATURES



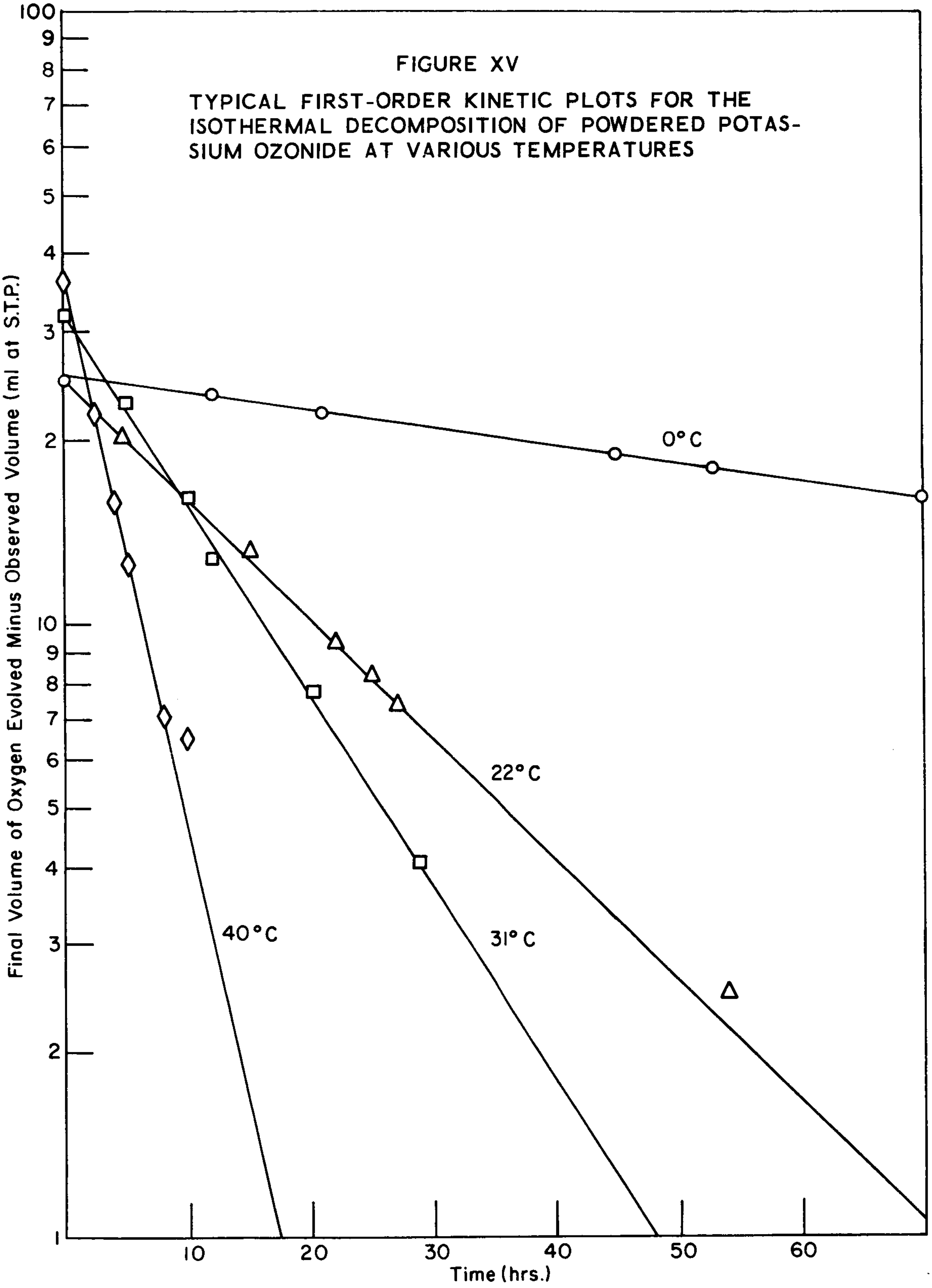


FIGURE XV

TYPICAL FIRST-ORDER KINETIC PLOTS FOR THE ISOTHERMAL DECOMPOSITION OF POWDERED POTASSIUM OZONIDE AT VARIOUS TEMPERATURES for these studies are also listed in Table IV. In approximately 50% of the cases, an "induction period" was observed (see Figure XVI), similar to that reported by Kazarnovskii, et al.(34)

Certain observations were made during these runs which suggested that the nitrogen flushing procedure was not sufficiently effective for removing moisture.

The slightest amount of water is apparently capable of catalyzing the decomposition reaction, thus obscuring or destroying the induction period. Examination of the pellets at the end of the kinetic runs confirmed the presence of moisture in the system. The pellet in most cases had a thin white coating, indicative of potassium hydroxide formed by the reaction of the ozonide with water. Further confirmation resulted when the total volume of oxygen evolved during the decomposition was slightly greater than that calculated for the particular weight of ozonide sample of known purity.

In those cases where an induction period was not actually evident when the raw kinetic data was plotted, two slopes could still be drawn for the first order reaction rate plot; the length of the first rate corresponded to the length of the apparent or visible induction period. These observations are amply demonstrated in Figures XVI and XVII. Figure XVI shows the typical kinetic curves obtained for the thermal decompositions of potassium ozonide in pellet form at 30°C; curve A illustrates the induction period observed. Figure XVII is the first-order reaction rate plot of the same data, both curves showing two slopes, the first of which corresponds to the induction period.

These data also showed significant variance among the runs at a given temperature, possibly due to the non-uniformity of the pellets with respect to thickness, porosity, and density, and/or due to the moisture phenomenon described above.

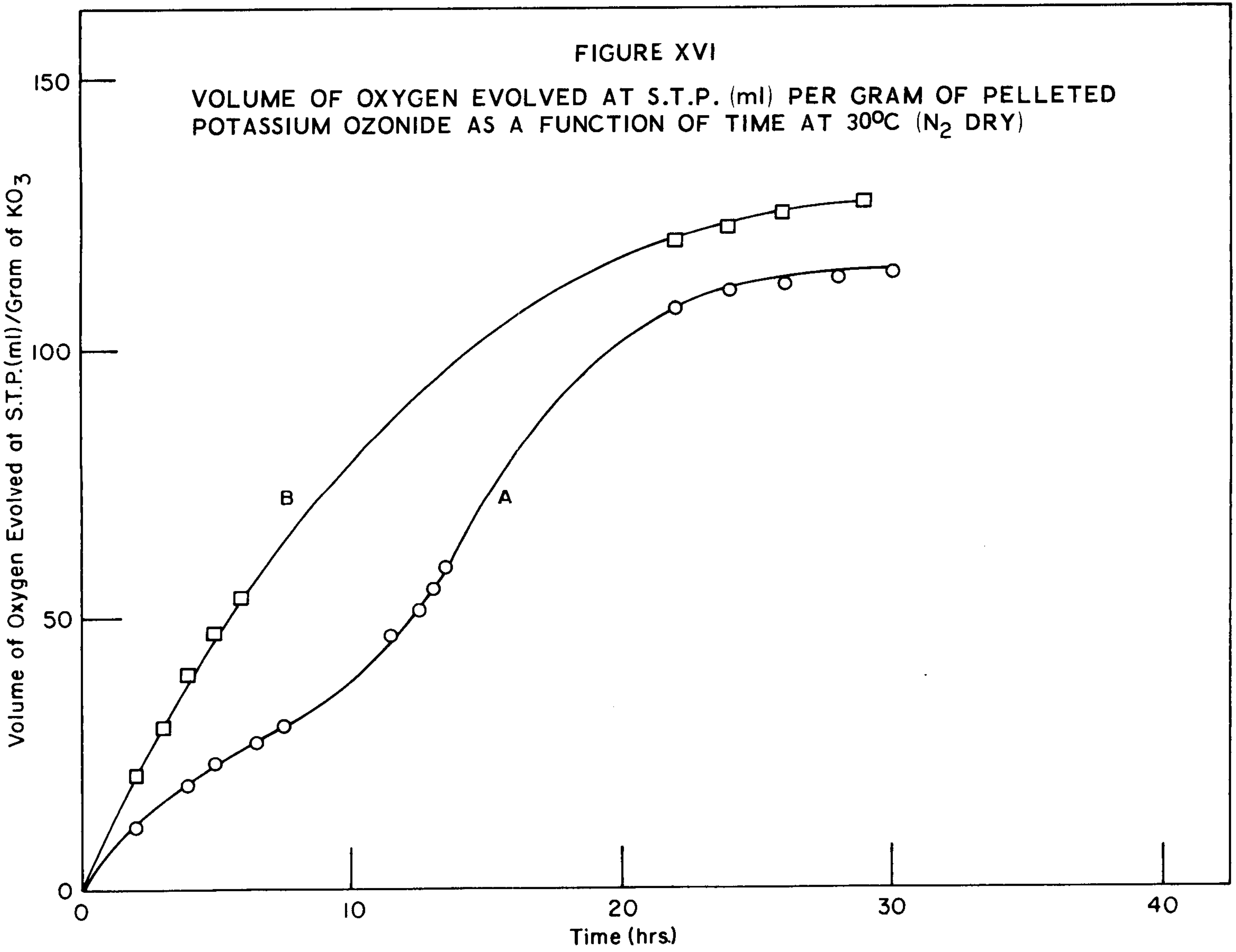


FIGURE XVI

VOLUME OF OXYGEN EVOLVED AT S.T.P. (ml) PER GRAM OF PELLETED POTASSIUM OZONIDE AS A FUNCTION OF TIME AT 30°C (N_2 DRY)

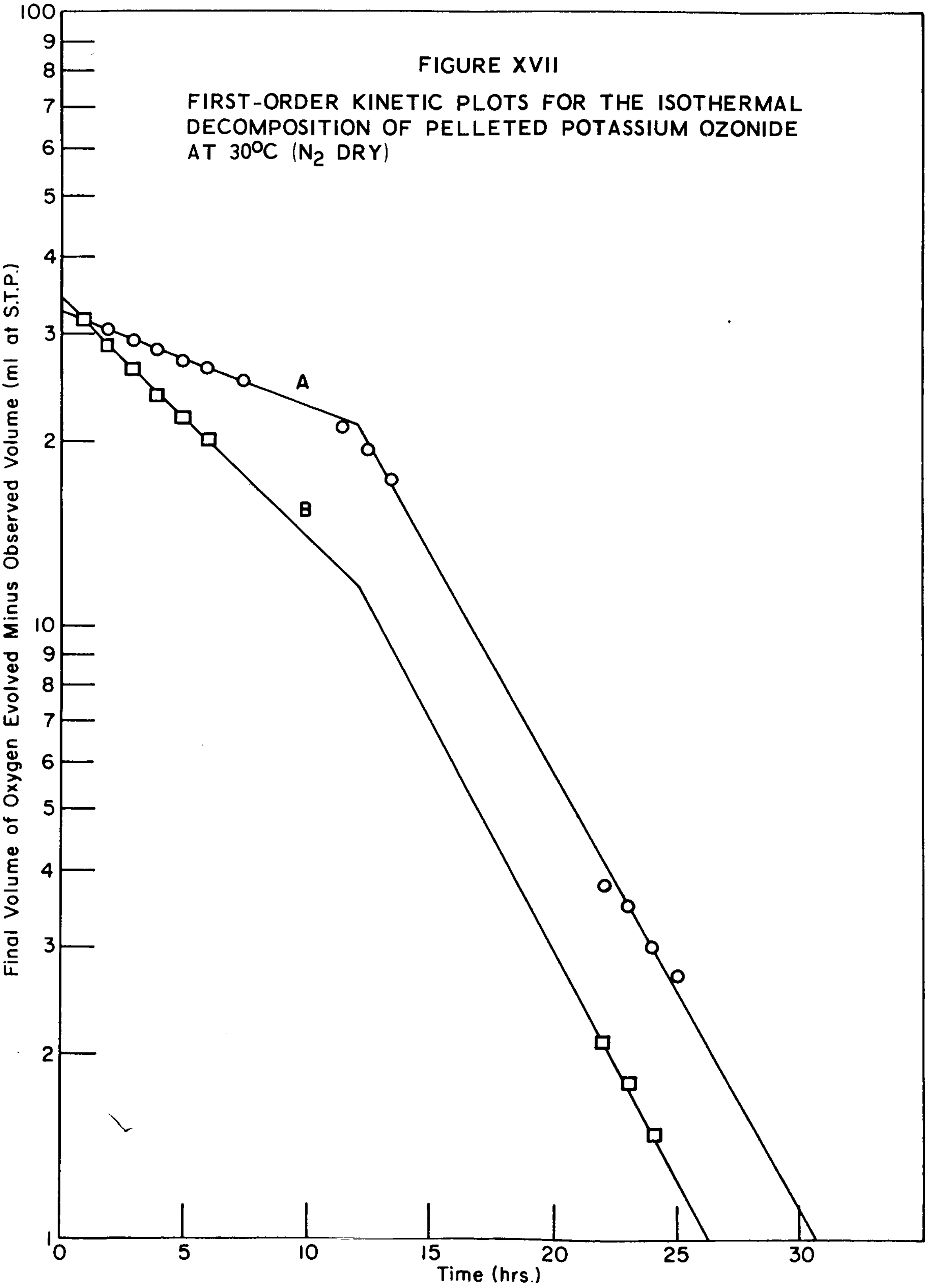


FIGURE XVII

FIRST-ORDER KINETIC PLOTS FOR THE ISOTHERMAL DECOMPOSITION OF PELLETED POTASSIUM OZONIDE AT 30°C (N_2 DRY)

3. Class III

As a result of the observations made during the second set of kinetic studies, it was decided to dry the reaction chamber with phosphorous pentoxide prior to sample loading. The operating procedures remained the same in all other respects. The results were dramatic. In these runs, induction periods were consistently observed. Figures XVIII and XIX illustrate the typical kinetic curves and first-order plots obtained for these data. For example, at 30°C, an induction period of 12 hours and average decomposition rates of 1.1 and 35.4%/hr for the induction and active periods, respectively, were observed. These data are contrasted to an induction period of nine hours and average decomposition rates of 5.1 and 17.5%/hr when nitrogen flushing was used. These results confirm the indications that nitrogen flushing was not effective in removing water vapor from the reaction system.

More important, our results indicate that under extremely dry conditions we are in essential agreement with the Soviet investigators. Moreover, the results serve to point out that, although the ozonides tend to gradually decompose upon standing to the superoxide and oxygen, the rates of their decomposition at temperatures 0°C and below are sufficiently slow so as to make the long term storage of these materials practical.

Estimations of the activation energy of the thermal decomposition of potassium ozonide were made from Arrhenius plots of the kinetic data presented in Table IV. Figure XX illustrates the curve obtained for the case in which the potassium ozonide sample was a powder. A value of 15.6 Kcal was obtained for the activation energy. Estimates of the activation energy were also made for the other cases. The data obtained for pelleted samples yielded values of 17.8 Kcal when the reaction chamber was flushed with nitrogen and 13.5 Kcal when phosphorus pentoxide was used as the drying agent. These results are in general agreement with those of the Soviet investigators who have reported values of 21.6-23.4 Kcal for the temperature range of -18°C to 50°C.(34)

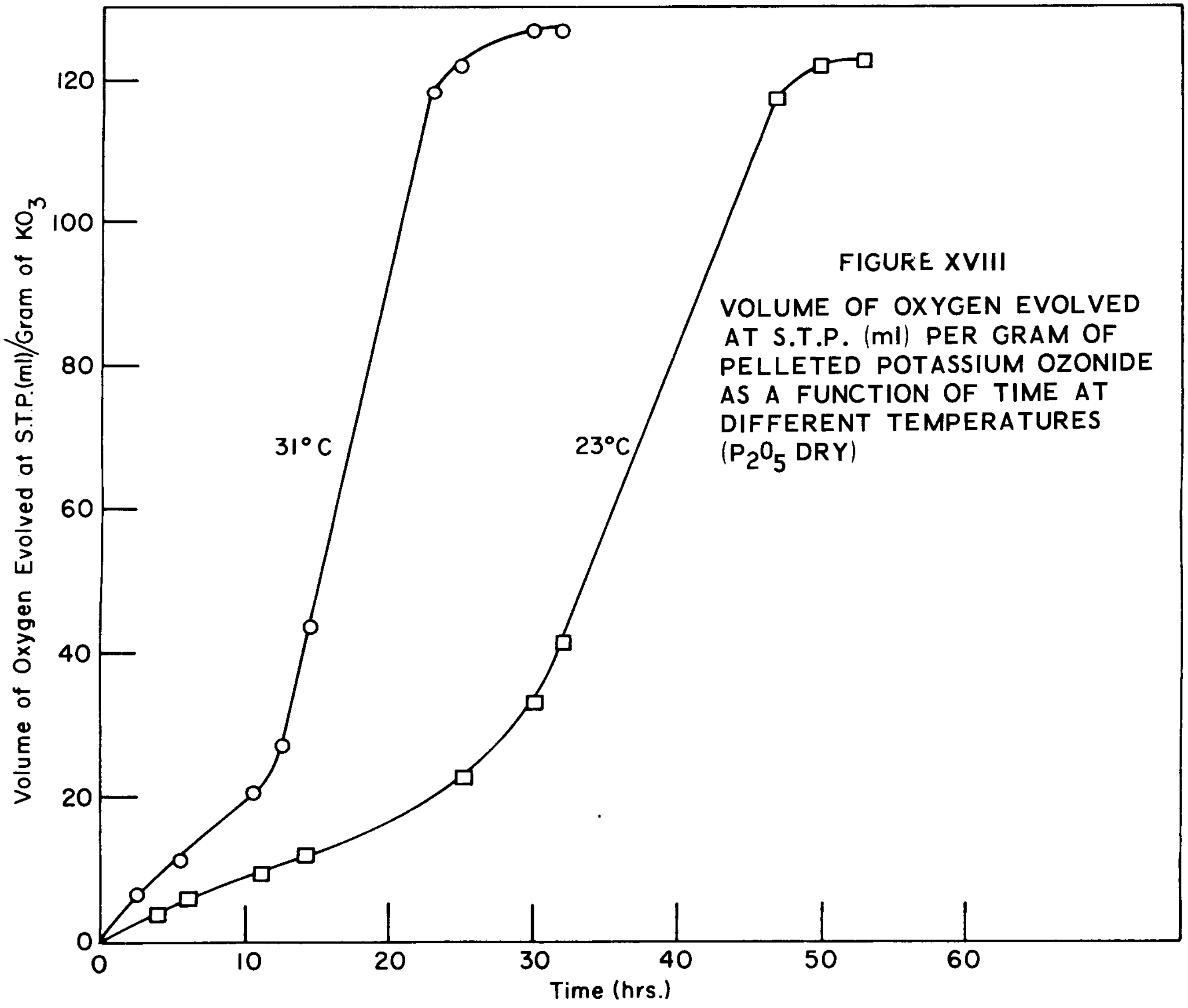


FIGURE XVIII

VOLUME OF OXYGEN EVOLVED AT S.T.P. (ml) PER GRAM OF PELLETED POTASSIUM OZONIDE AS A FUNCTION OF TIME AT DIFFERENT TEMPERATURES (P_2O_5 DRY)

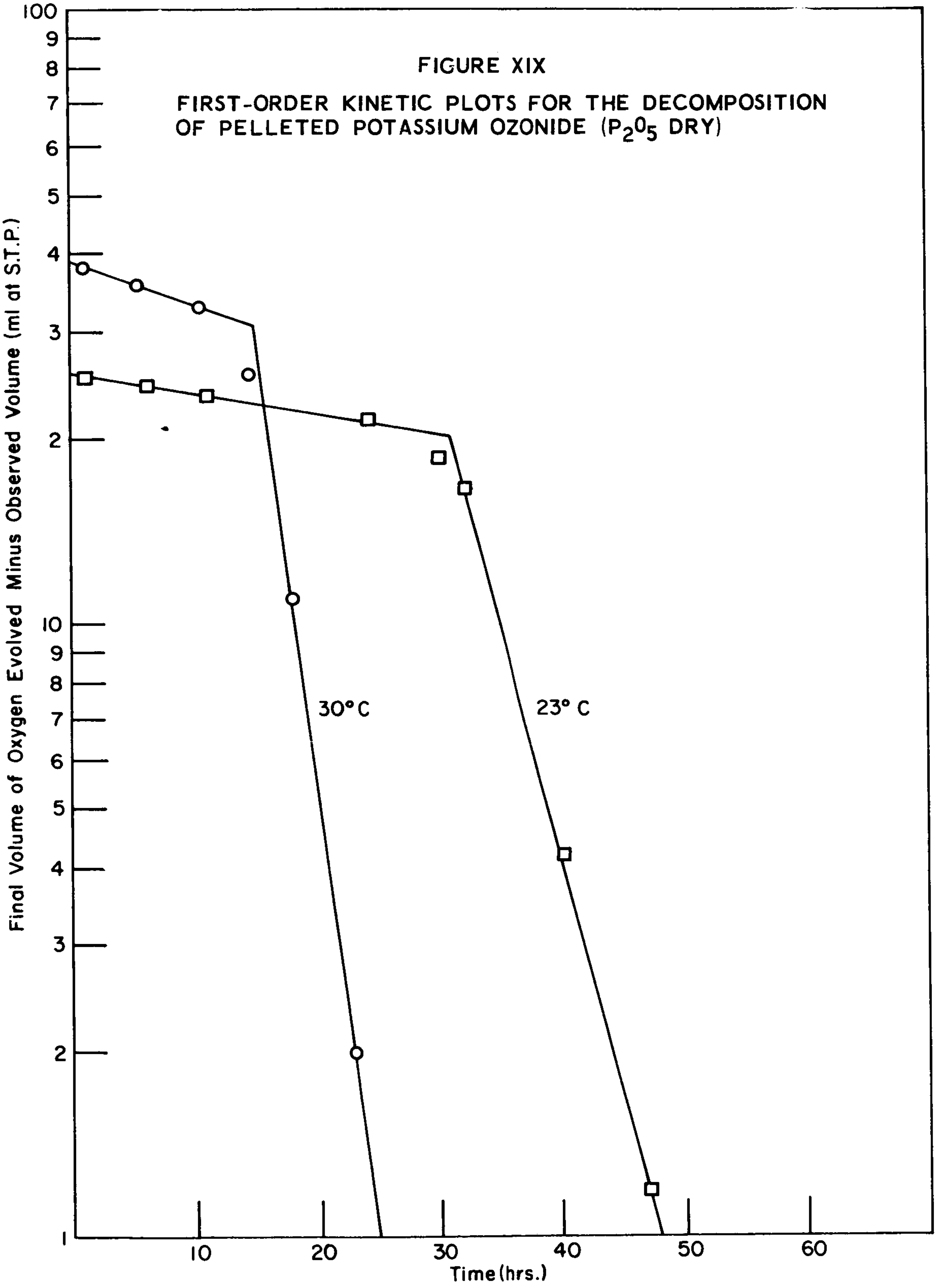
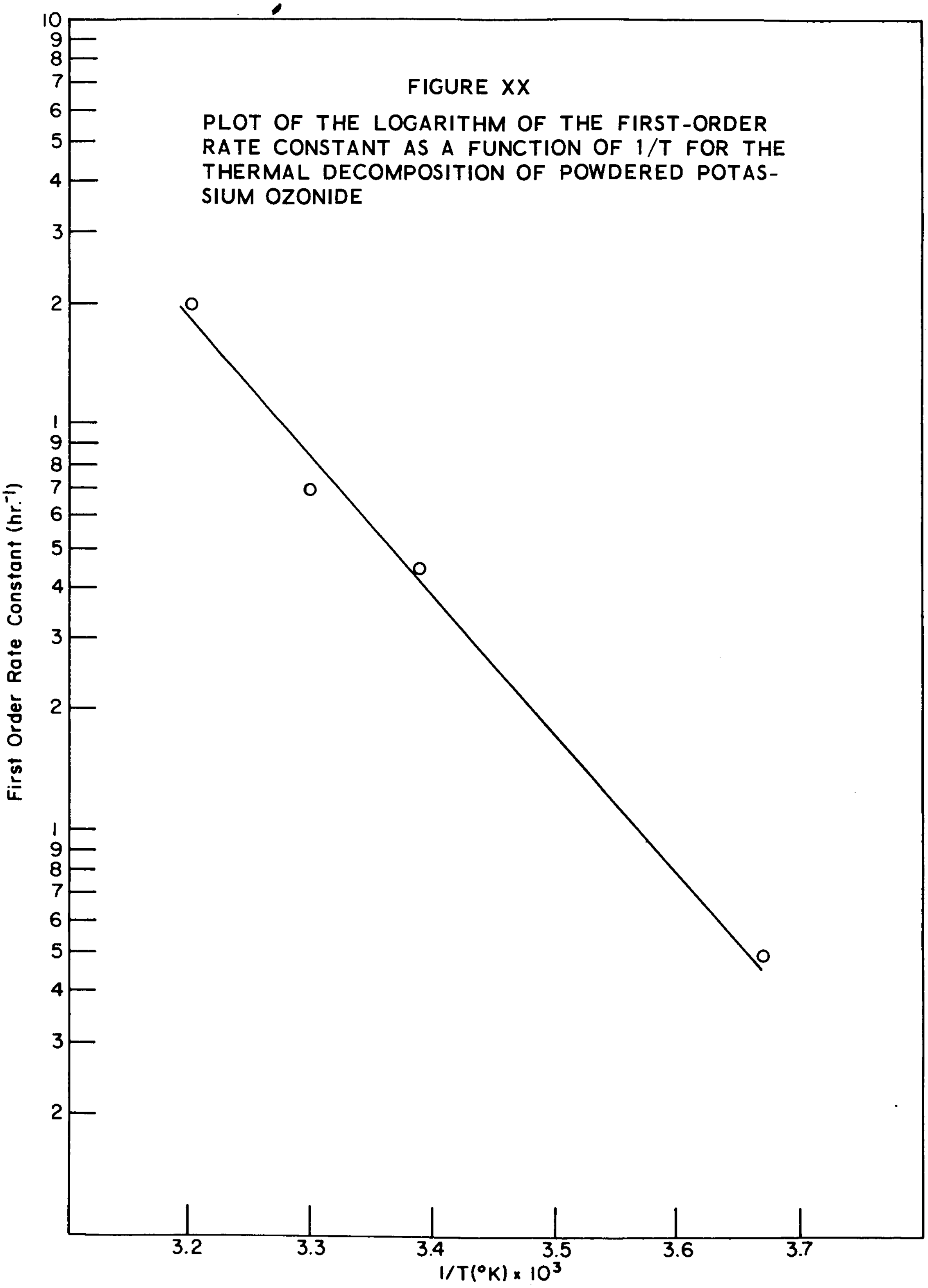


FIGURE XIX

FIRST-ORDER KINETIC PLOTS FOR THE DECOMPOSITION OF PELLETED POTASSIUM OZONIDE (P_2O_5 DRY)

FIGURE XX

PLOT OF THE LOGARITHM OF THE FIRST-ORDER RATE CONSTANT AS A FUNCTION OF 1/T FOR THE THERMAL DECOMPOSITION OF POWDERED POTASSIUM OZONIDE



In an attempt to determine the mechanism of the decomposition reaction and to characterize the nature of the induction period, the Russian investigators(34,37) followed the magnetic susceptibility of the ozonide sample simultaneously with the kinetic study. Their data was interpreted as confirming the intermediate formation of atomic oxygen, the magnetic susceptibility of which is several times larger than that of potassium ozonide and potassium superoxide. According to their interpretation, at the start of decomposition of the ozonide sample, the amount of atomic oxygen in the solid phase increased with time, passed through a maximum when the decomposition reaction was approximately 60% completed, then dropped to zero at 100% decomposition. The maximum relative amount of atomic oxygen was observed at a point corresponding to the end of the induction period or the start of the active period. These observations led Kazarnovskii, et al,(37) to propose an hypothesis based on the theory of defective crystal structures and the following decomposition mechanism:

$$KO_3 = KO_2 + O \qquad (20)$$

$$KO_3 + O = KO_2 + O_2 \qquad (21)$$

According to this hypothesis, the induction period is characterized by an accumulation of defects in the crystal lattice of potassium ozonide, i.e., by the formation of superoxide ions and atomic oxygen. When sufficient defects have accumulated, a critical point is reached where the initial structure decomposes to form the new lattice of potassium superoxide. This critical point corresponds to the end of the induction period and the beginning of the decomposition reaction.

If the Russian hypothesis is correct, it is possible that the slight differences between our results and theirs, with regard to actual values of rate constants and length of induction periods, may be due to differences in our handling or preparation of the potassium ozonide sample so that a degree of crystal defects exists at the start of the kinetic study. However, it must be emphasized that a critical review of the

Russian work on the simultaneous study of the decomposition and paramagnetic changes has led us to the conclusion that they are quite optimistic with respect to their analysis and interpretation of the data.

In order to obtain a measure of the heat of reaction associated with the thermal decomposition of potassium ozonide to the superoxide and molecular oxygen, reaction (19), a differential thermal analysis of a sample of potassium ozonide was made using a Perkin-Elmer Differential Scanning Calorimeter, Model DSC-1. The measurements were made at the Perkin-Elmer facilities in Norwalk, Connecticut.

The differential calorimetric scan recorded for a 10.56 mg sample of potassium ozonide (86.6% pure) is shown in Figure XXI. Qualitatively, this curve shows that a measurable decomposition rate is not observed until a temperature of about 52°C is reached and that the energy change for the decomposition reaction is exothermic. Quantitatively, the heat of the decomposition reaction is related to the area under the curve obtained. An external standard was used to calibrate the instrument. Indium metal was chosen because it has a well-known transition energy of 6.8 cal/gram and is available in high purity. The heat evolved during the decomposition of the potassium ozonide sample was thus determined to be 3.2 Kcal/mole in the temperature range from 325 to 373°K.

In determining the heat of the decomposition reaction, the purity of the potassium ozonide sample was taken into account. The assumption was made that the impurities in the sample did not undergo any transitions or reactions which would contribute to the energy change observed in the temperature range at which the measurements were made.

Our value is in qualitative agreement with the value of 5.8 Kcal/mole at 298.16°K reported by Kazarnovskii, et al.(34) Upon completion of the differential calorimetric scan, the decomposed potassium ozonide was cooled and reweighed. On the basis of the weight lost upon decomposition, the purity of the ozonide sample was determined to be 86.0%.

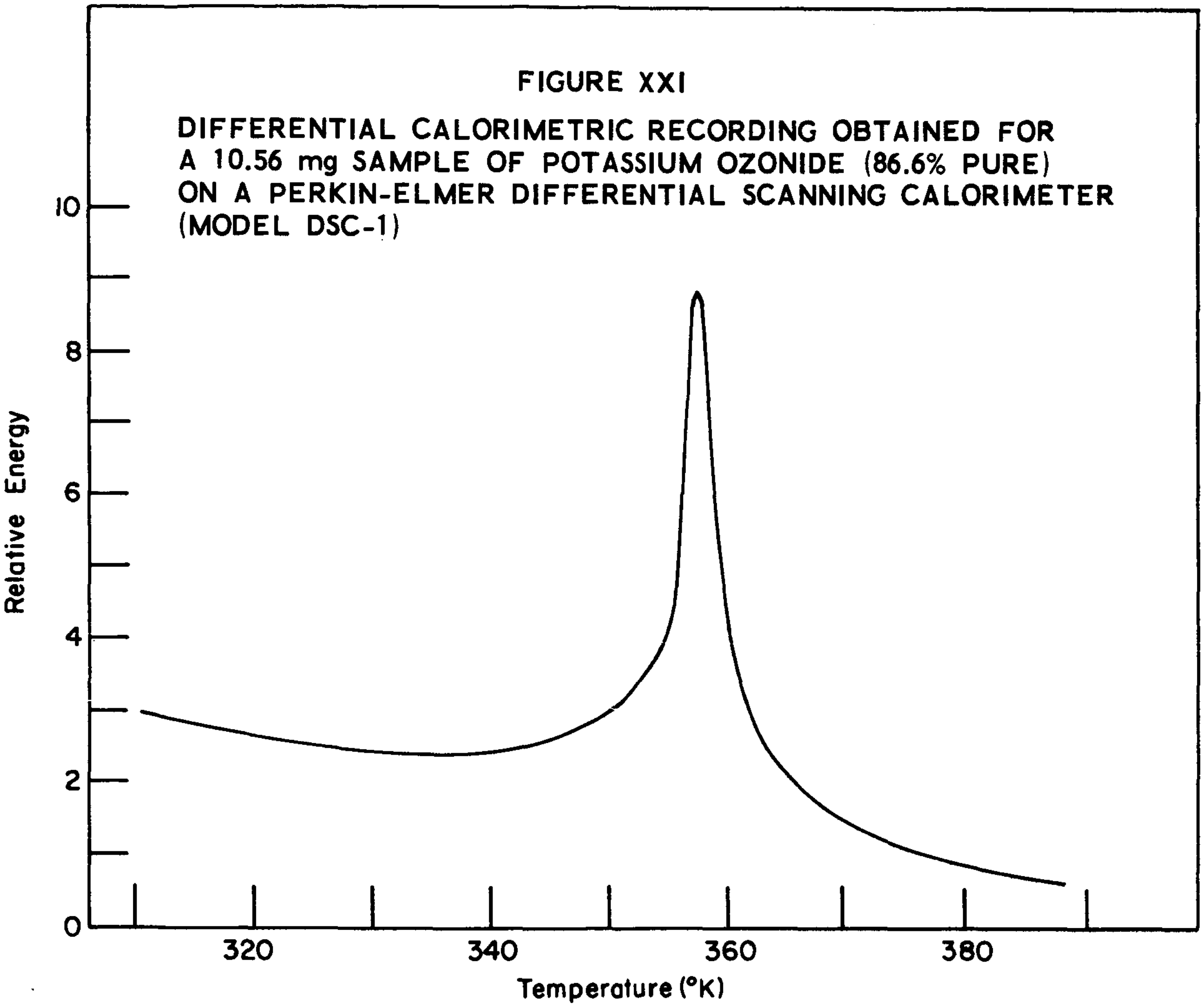


FIGURE XXI

DIFFERENTIAL CALORIMETRIC RECORDING OBTAINED FOR A 10.56 mg SAMPLE OF POTASSIUM OZONIDE (86.6% PURE) ON A PERKIN-ELMER DIFFERENTIAL SCANNING CALORIMETER (MODEL DSC-1)

This figure is in excellent agreement with the original analysis made following our standard technique.

2.3.2 Reaction with Water Vapor

One of the most important chemical properties of the alkali metal ozonides with respect to their usefulness in air revitalization systems is their reaction with water vapor. Investigations to date, though not kinetic in nature, are in essential agreement that the ozonides react with water, either in the liquid or gaseous state, to form oxygen and the corresponding hydroxide:

$$2MO_3 + H_2O\ (g,\ l) = 2\ MOH + 5/2\ O_2 \tag{22}$$

We have investigated the kinetics of the reaction of potassium ozonide with water vapor at 24 and 31°C at conditions of 50 and 100% relative humidity. These studies have served to establish relative trends at the various experimental environments.

The apparatus used in these studies is shown in Figure XXII. Potassium ozonide pellets were prepared as described above and loaded into the reaction chamber in a dry box. The vial containing the sample was stoppered and the apparatus removed from the dry box. Approximately 15 ml of the solution required to maintain the desired humidity was added through the side arm. Pure water was used to maintain the atmosphere at 100% relative humidity; a 43.1% aqueous solution of sulfuric acid was needed to produce an atmosphere of 50% relative humidity. The reaction chamber was set in a thermostated bath and the gas burette attached to the side arm. When equilibrium had been attained, the sample was exposed to the water vapor atmosphere by raising the glass rod through the mercury seal. The rod was clamped in position with the rubber stopper located above the sample vial. The volume of oxygen evolved during the reaction of potassium ozonide with water vapor was monitored with time. The results obtained are summarized in Table V and illustrated in Figures XXIII and XXIV.

FIGURE XXII

APPARATUS USED FOR THE KINETIC STUDY OF THE REACTION OF ALKALI METAL OZONIDES WITH WATER VAPOR AT CONTROLLED HUMIDITIES

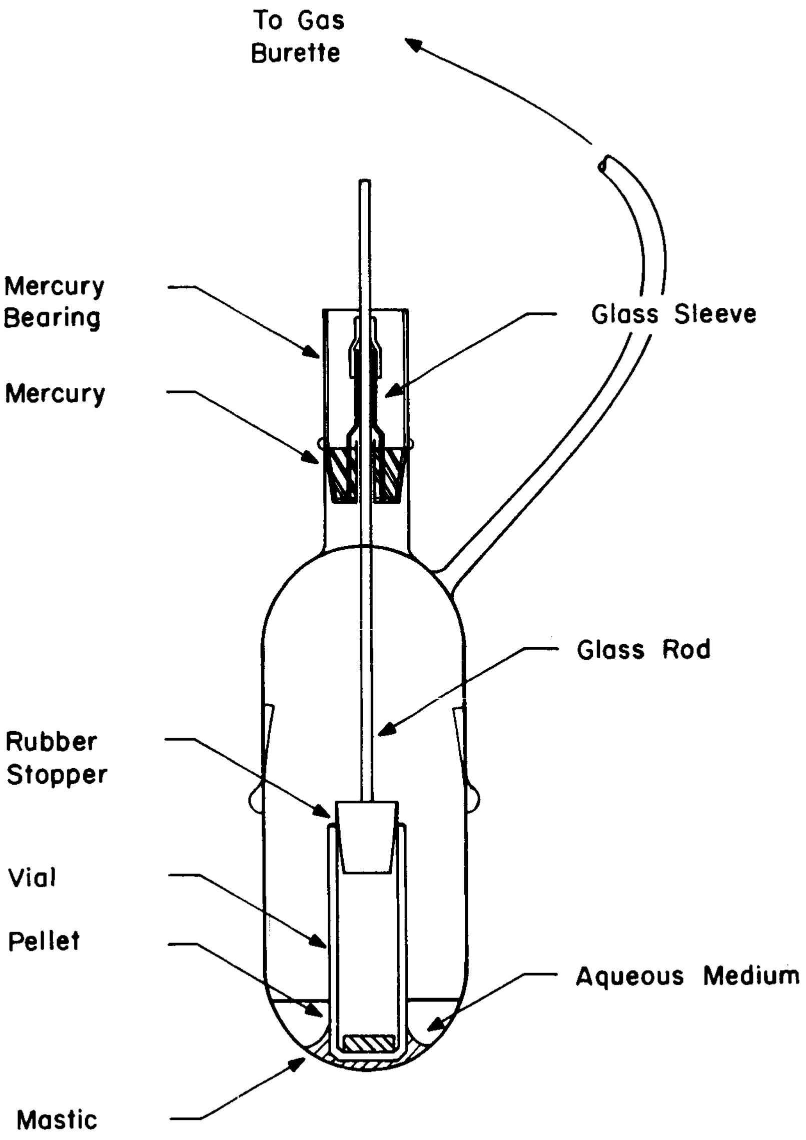
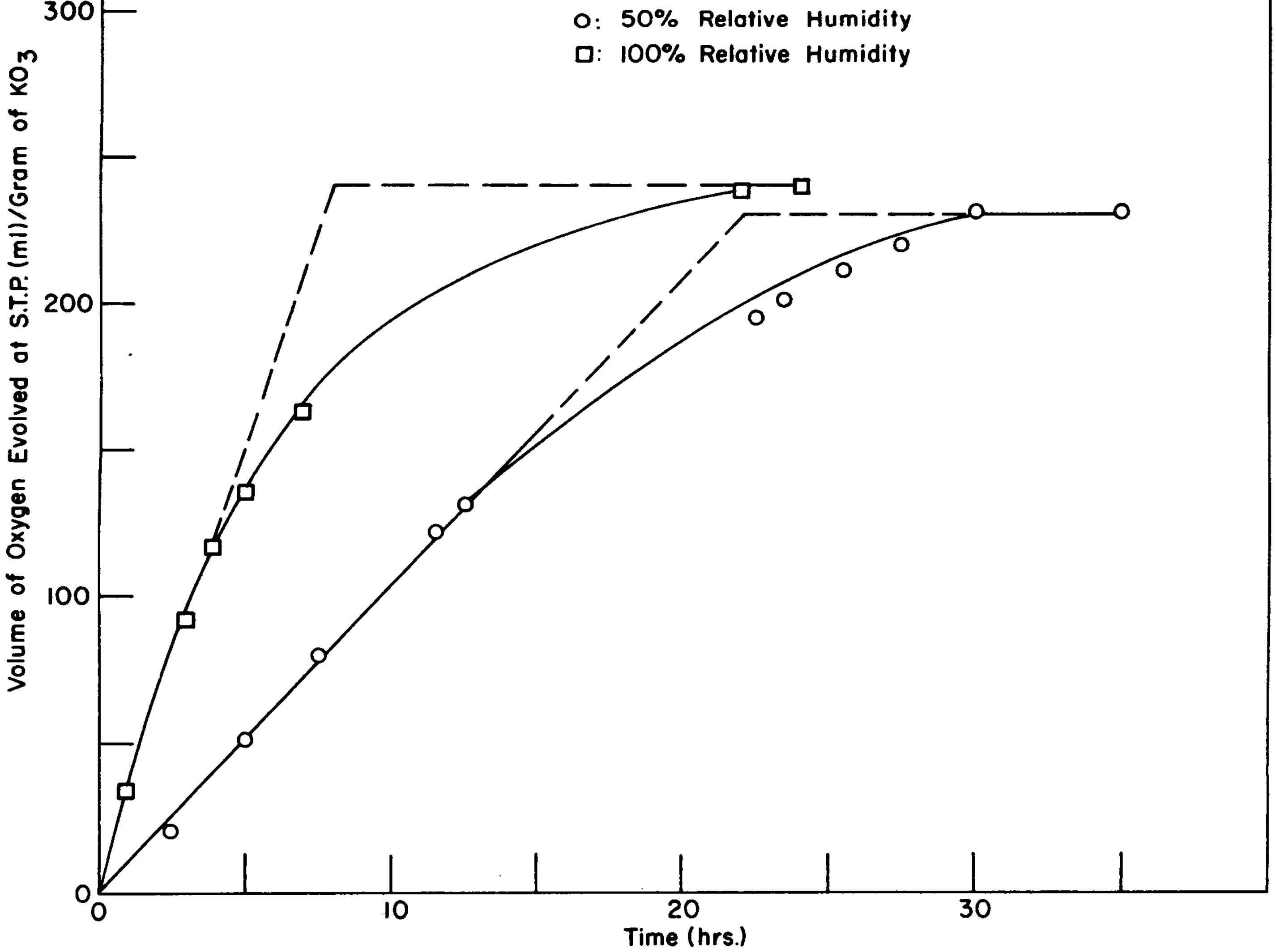


FIGURE XXIII

VOLUME OF OXYGEN EVOLVED AT S.T.P. (ml) PER GRAM OF PELLETED POTASSIUM OZONIDE DURING REACTION WITH WATER VAPOR AT 24°C



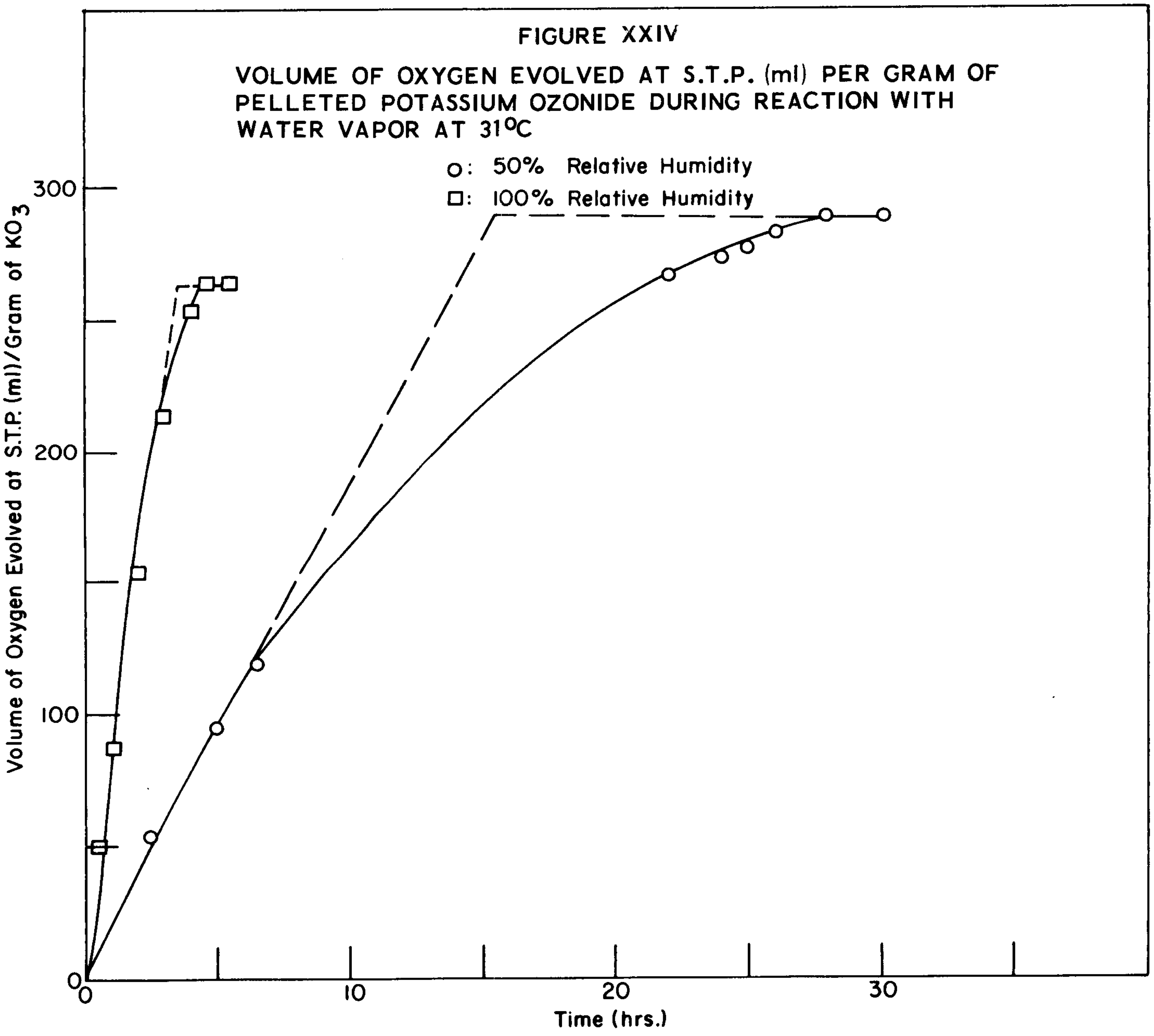


FIGURE XXIV

VOLUME OF OXYGEN EVOLVED AT S.T.P. (ml) PER GRAM OF PELLETED POTASSIUM OZONIDE DURING REACTION WITH WATER VAPOR AT 31°C

TABLE V

SUMMARY OF KINETIC DATA FOR THE REACTION OF PELLETED POTASSIUM OZONIDE WITH WATER VAPOR AT VARIOUS TEMPERATURES AND HUMIDITIES

Temperature (°C)	Relative Humidity (%)	Average Rate of Oxygen Evolution During Active Period (ml/g/hr)	Total Reaction Time (hr)
24±1	50	10.9	30
	100	29.6	22
31±1	50	35.0	27.5
	100	60.1	4.5

At 24°C and 50% relative humidity, the reaction of pelleted potassium ozonide with water vapor is complete in 30 hours. In the first 22 hours, 87.0% of the available oxygen is evolved. The average rate of oxygen evolution during this active period is 10.9 ml/g/hr. At the same temperature, but at 100% relative humidity, the average rate of oxygen evolution is 29.6 ml/g/hr for only eight hours, at which time 74.2% of the available oxygen has been released. Under these conditions, the total reaction time is 22 hours.

At 31°C and 50% relative humidity, the reaction between pelleted potassium ozonide and water vapor proceeds at an average rate of 35.0 ml/g/hr for eight hours and is complete after 27.5 hours. After eight hours, the reaction is 77.4% complete. At the same temperature, but at 100% relative humidity, the reaction is complete in 4.5 hours. In the first 3.5 hours, 92.4% of the available oxygen is evolved. The average rate of oxygen evolution during this period is 60.1 ml/g/hr.

The reaction by which the ozonides are expected to replenish oxygen in a space cabin has thus been experimentally verified. These studies have confirmed the opinion that the rates of oxygen production by the reaction of potassium ozonide pellets with water vapor, in the temperature and relative humidity ranges of interest, are of such a magnitude that unusual safety problems will not arise.

2.3.3 Reaction with Carbon Dioxide

Extensive studies have been performed for the reactions of carbon dioxide with alkali metal hydroxide, oxides, peroxides, and superoxides.(38,39,40,41,42) Sodium and potassium superoxides have been shown to react with carbon monoxide.(43) The latter reaction is of interest because Bogatov, et al,(44) have confirmed the presence of carbon monoxide in the atmosphere of confined chambers inhabited by mixed groups of smokers and non-smokers. After approximately ten days, the air of the test chamber inhabited by three persons contained 0.023-0.027 mg/ℓ of carbon monoxide. The Russian investigators have reported that sodium superoxide reacts with dry carbon monoxide only above 100°C to form the carbonate:(44)

$$2\ NaO_2 + CO = Na_2CO_3 + O_2 \tag{23}$$

accompanied by the reaction:

$$2\ NaO_2 = Na_2O_2 + O_2 \tag{24}$$

Potassium superoxide, on the other hand, forms the carbonate with dry carbon monoxide at only 95°C.(44)

With regard to carbon dioxide absorption, it has been shown that in all cases, water vapor plays a vital role in the reaction rate.(39,41) The reactions between pure, dry, solid oxides and an anhydrous carbon dioxide atmosphere are thermodynamically favorable; however, reasonable rates of reaction are not obtained unless water is introduced into the system. The role of water in these reactions has not been clearly established.

For hydroxides, it is possible to explain the function of water by considering its role in providing the ionic species necessary for reaction according to the following scheme:

$$MOH \overset{H_2O}{=} M^+ + OH^- \tag{25}$$

$$CO_2 + H_2O = CO_3^= + 2H^+ \tag{26}$$

$$2M^+ + 2OH^- + CO_3^= + 2H^+ = M_2CO_3 + 2H_2O \tag{27}$$

For superoxides, an analogous reaction scheme may be written:

$$2MO_2 + H_2O = 2M^+ + 2OH^- + 3/2\ O_2 \tag{28}$$

$$CO_2 + H_2O = CO_3^= + 2H^+ \tag{29}$$

$$2M^+ + 2OH^- + CO_3^= + 2H^+ = M_2CO_3 + 2H_2O \tag{30}$$

On the basis of the trends outlined above, it is reasonable to assume that some water will also be necessary to initiate the reaction between an alkali metal ozonide and gaseous carbon dioxide. Analogous to superoxide chemistry, therefore, the over-all reactions might be written as:

$$2\ KO_3 + H_2O = 2KOH + 5/2\ O_2 \qquad (31)$$

followed by:

$$2\ KOH + CO_2 = K_2CO_3 + H_2O \qquad (32)$$

However, no experimental justification for the above assumptions relative to the ozonides was available, and as a result, a study was initiated in our laboratories to investigate the kinetics of the reaction of potassium ozonide with gaseous carbon dioxide.

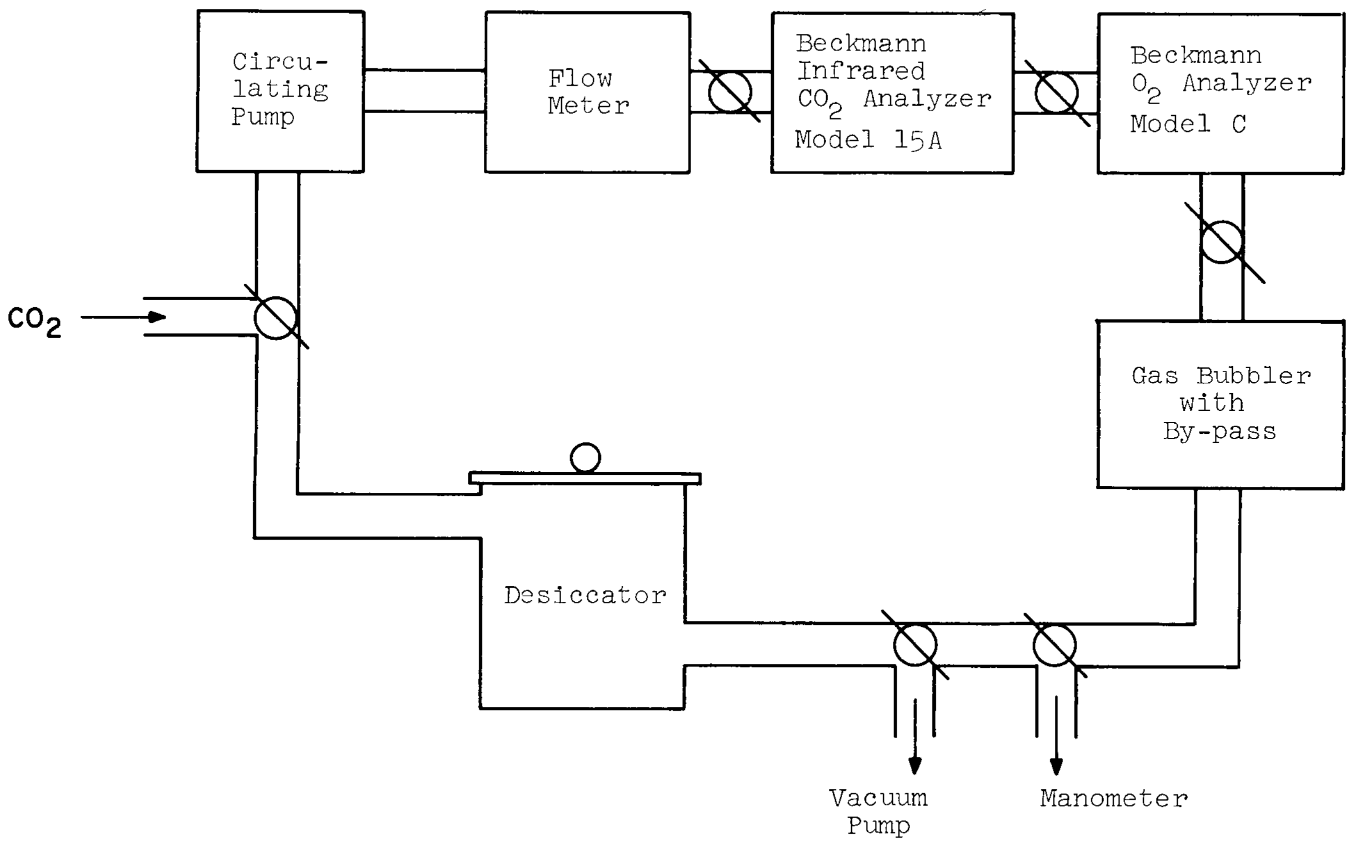
The experimental set-up used to study the rates of carbon dioxide absorption and oxygen evolution at various conditions of relative humidity is shown in Figure XXV.

The weighed, powdered ozonide sample was placed in the desiccator and the system evacuated. A gaseous mixture of carbon dioxide in nitrogen, of known composition, was then introduced into the system and circulated over the sample while being bubbled through a gas-washing column which contained a dilute sulfuric acid solution to provide the desired conditions of relative humidity. This design is advantageous because it is a closed system and therefore representative of an actual test chamber or manned space cabin. The concentrations of carbon dioxide and oxygen were monitored with time. The results are summarized in Table VI and illustrated in Figure XXVI and XXVII.

At 0% relative humidity, some reaction apparently occurs between the ozonide and carbon dioxide but may be attributed to the presence of residual moisture in the system or in the sample. At 37 and 70% relative humidity, carbon dioxide is absorbed by powdered potassium ozonide. The rates of carbon dioxide absorption and oxygen evolution at these humidities are given in Table VI.

FIGURE XXV

EXPERIMENTAL SET-UP USED FOR THE KINETIC STUDY OF THE REACTION OF ALKALI METAL OZONIDES WITH GASEOUS CARBON DIOXIDE AND WATER VAPOR AT CONTROLLED HUMIDITIES



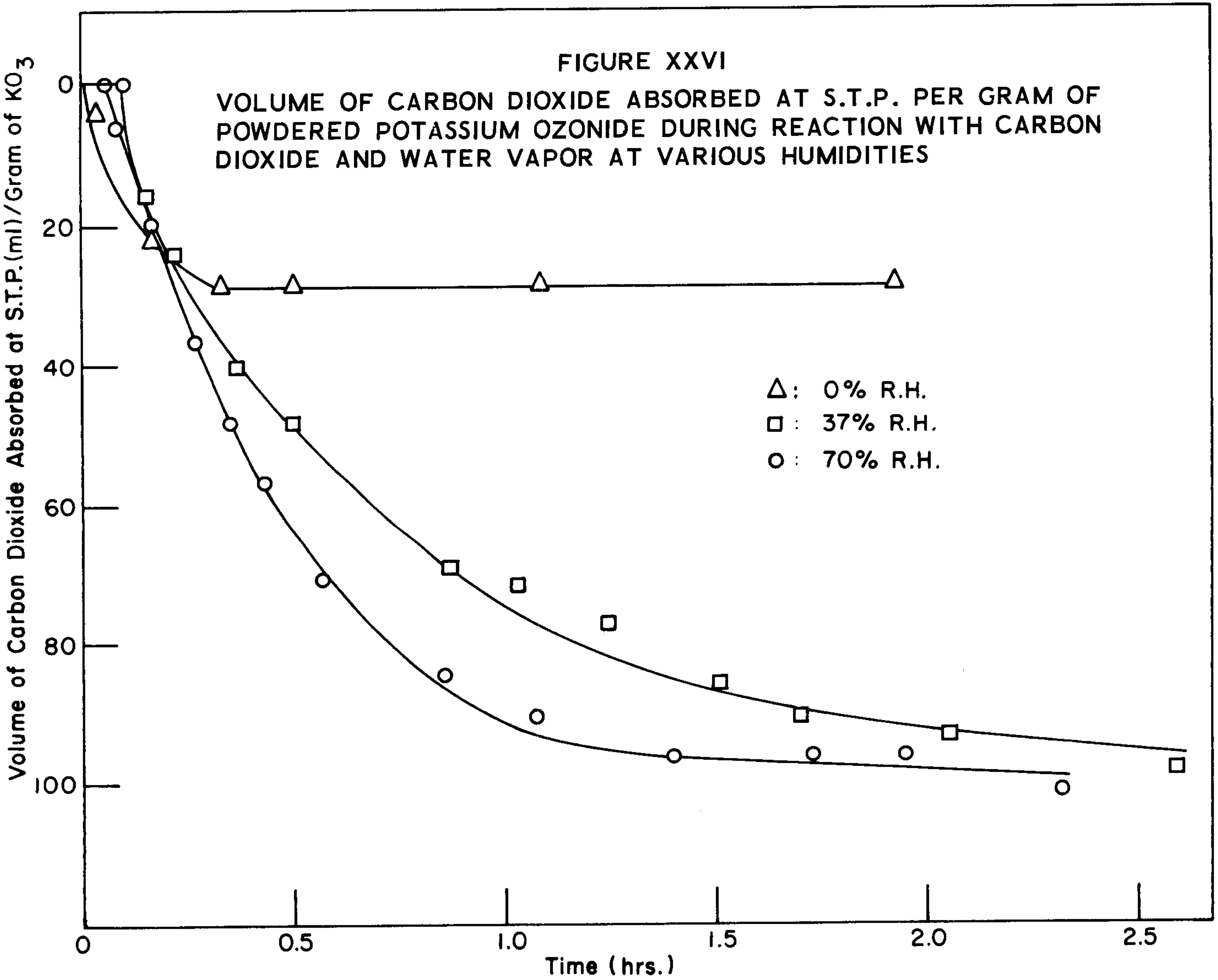


FIGURE XXVI

VOLUME OF CARBON DIOXIDE ABSORBED AT S.T.P. PER GRAM OF POWDERED POTASSIUM OZONIDE DURING REACTION WITH CARBON DIOXIDE AND WATER VAPOR AT VARIOUS HUMIDITIES

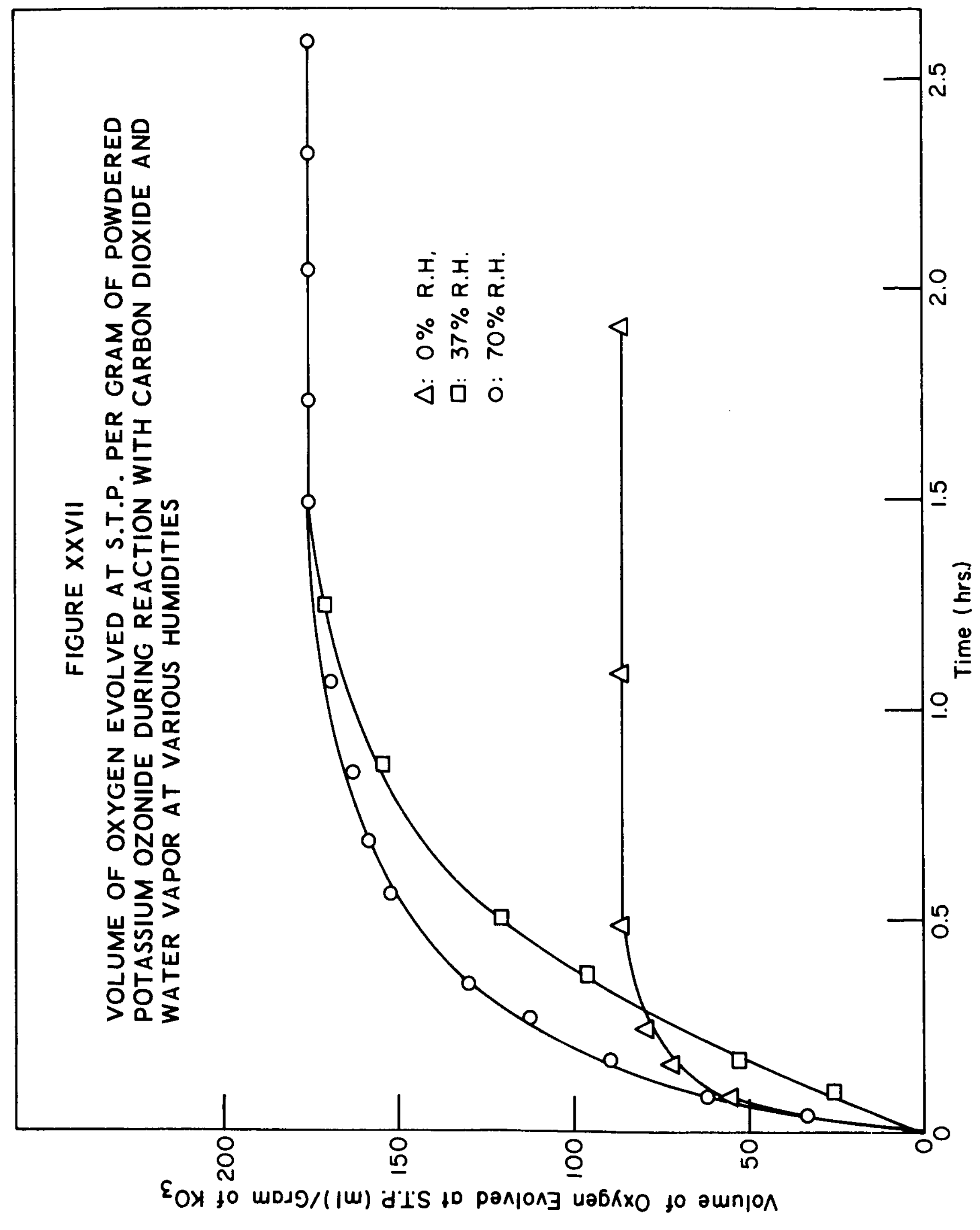


FIGURE XXVII

VOLUME OF OXYGEN EVOLVED AT S.T.P. PER GRAM OF POWDERED POTASSIUM OZONIDE DURING REACTION WITH CARBON DIOXIDE AND WATER VAPOR AT VARIOUS HUMIDITIES

TABLE VI

SUMMARY OF KINETIC DATA FOR THE REACTION OF POWDERED POTASSIUM OZONIDE WITH GASEOUS CARBON DIOXIDE AT VARIOUS HUMIDITIES

Relative Humidity (%)	Temperature (°C)	Rate of Reaction (%/hr)		Reaction Time (min.)	
		Oxygen Evolution	Carbon Dioxide Absorption	Oxygen Evolution	Carbon Dioxide Absorption
0	23±1	no reaction		no reaction	
37	25±1	4.7	2.5	90	120
70	28±1	5.2	3.7	70	85

These studies have established that in the presence of water vapor, potassium ozonide does react with gaseous carbon dioxide. As noted in the introduction, however, for air revitalization purposes, the alkali metal ozonides are not capable, by themselves, of completely removing carbon dioxide from a breathing atmosphere, but require an auxiliary scrubber to maintain the proper Respiratory Quotient.

The Respiratory Quotient calculated from the data obtained at 70% relative humidity is 0.63. On the bases of the purity of the original potassium ozonide sample and the stoichiometry of reactions (31) and (32), the predicted value for the Respiratory Quotient is 0.48. A probable explanation for the higher value obtained is the formation of bicarbonates as well as carbonates during the reaction of potassium ozonide with carbon dioxide and water vapor. If only potassium bicarbonate were formed, the expected Respiratory Quotient would be 0.80. Samples of the reaction products were titrated potentiometrically with hydrochloric acid. The results of these titrations clearly establish the presence of potassium bicarbonate in the reaction products in quantities 2.5-3 times greater than that of potassium carbonate. A Respiratory Quotient of 0.66 was calculated on the basis of the amount of potassium carbonate and bicarbonate found in the reaction product for the example cited above at 70% relative humidity. This value is in excellent agreement with the value calculated from the volumes of oxygen evolved and carbon dioxide absorbed during the reaction.

The implications of these results are extremely important. The apparent ease of bicarbonate formation increases the potential of alkali metal ozonides as air revitalization materials. The possibility that the following reaction takes place:

$$2KO_3 + H_2O + 2CO_2 = 2KHCO_3 + 5/2\ O_2 \qquad (33)$$

opens the door to a more favorable Respiratory Quotient than originally anticipated strictly on the basis of carbonate formation alone.

III

SUMMARY

A summary of the work accomplished under NASA contract NASw-559 is given below:

1. Potassium ozonide (88-97% pure) has been consistently prepared in laboratory (1 to 2 grams) via the gaseous ozone-solid hydroxide reaction path. The apparatus, experimental technique, and operating conditions necessary for optimum yields have been established along with the precautions that must be taken in the handling and the storage of these samples. It has been found that good yields (ca.7%) for a single ozonization are obtained when the following procedures are observed:

    a. An excess of anhydrous potassium hydroxide is used to tie up the water formed by the synthesis reaction, thus preventing the reaction between water and potassium ozonide.

    b. The reaction chamber is agitated frequently to insure continual exposure of a fresh surface area of potassium ozonide.

    c. Low concentrations of ozone at high flow rates are used.

    d. The length of time that the ozonization reaction is allowed to run is kept within 2.5 to 4.5 hours.

2. A reliable thermogravimetric method has been developed for the determination of alkali metal ozonides in the presence of lower oxides. The ozonide sample is thermally decomposed to the superoxide in an inert atmosphere and the purity calculated on the basis of the weight lost. This procedure has proven very reproducible and precise within 0.5%. For example, three analyses of a given batch of potassium ozonide yielded values of 92.0, 92.1 and 92.2%.

3. Discordant results have appeared in the literature relative to the thermal decomposition characteristics of potassium ozonide. Some investigators have reported an induction period during which the ozonide sample decomposes at a much slower rate than the ensuing active decomposition period. Other investigators have failed to observe this phenomon. The results obtained in our laboratories have resolved this discrepancy. When the thermal decomposition studies were carried out under extremely anhydrous conditions, induction periods of the nature described above were observed for pelleted potassium ozonide samples. This induction phenomenon was not observed when less stringent drying procedures were followed.

4. The kinetics of the thermal decomposition of potassium ozonide, in pellet and powdered forms, have been determined at various temperatures. For example, at 30°C, an induction period of 12 hours is observed for the thermal decomposition of pelleted potassium ozonide. The average rate of decomposition is 1.1%/hr. for the induction period which is followed by an active period of decomposition which proceeds at an average rate of 35.4%/hr. The decomposition of potassium ozonide at 30°C to the superoxide is complete in 24 hours. At 0°C and below, the rate of decomposition of potassium ozonide is sufficiently slow (less than 0.6%/hr) so as to make the long term storage of these materials practical at these temperatures.

5. A differential thermal analysis study of potassium ozonide, using a Perkin-Elmer Model DSC-1 Differential Scanning Calorimeter, has been carried out to determine the order of magnitude of its heat of decomposition. The heat evolved was determined to be 3.2 Kcal/mole in the temperature range from 325 to 373°K.

6. Kinetic studies have been carried out for the reaction of pelleted potassium ozonide with water vapor at 24 to 31°C

and at conditions of 50 and 100% relative humidity. These studies have verified the reaction by which the ozonides are expected to replenish oxygen in a space cabin. At 24°C and 50% relative humidity, the reaction of pelleted potassium ozonide with water vapor is complete in 30 hours. In the first 22 hours, 87.0% of the available oxygen is evolved. The average rate of oxygen evolution during this active period is 10.9 ml/g/hr. At the same temperature, but at 100% relative humidity, the average rate of oxygen evolution is 29.6 ml/g/hr for only eight hours, at which time 74.2% of the available oxygen has been released. Under these conditions, the total reaction time is 22 hours. At 31°C and 50% relative humidity, the reaction between pelleted potassium ozonide and water vapor proceeds at an average rate of 35.0 ml/g/hr for eight hours and is complete after 27.5 hours. After eight hours, the reaction is 77.4% complete. At the same temperature, but at 100% relative humidity, the reaction is complete in 4.5 hours. In the first 3.5 hours, 92.4% of the available oxygen is evolved. The average rate of oxygen evolution during this period is 60.1 ml/g/hr.

7. Kinetic studies have been carried out for the reaction of pelleted potassium ozonide with carbon dioxide at 0, 50, and 100% relative humidity at 25°C. No reaction was observed between the ozonide and carbon dioxide under dry conditions. The Respiratory Quotient calculated from the data obtained at 70% relative humidity was 0.63. The stoichiometry of the reactions of potassium ozonide with water vapor and gaseous carbon dioxide to form the expected potassium carbonate leads to a Respiratory Quotient of only 0.40. Stoichiometric reactions in which the product is the bicarbonate lead to a Respiratory Quotient of 0.80. The presence of potassium bicarbonate in significant amounts in the reaction products was confirmed quantitatively by potentiometric titration with acid, thus accounting for the observed Respiratory Quotient

of 0.63. The implications of these results are extremely important. The apparent ease of bicarbonate formation increases the potential of alkali metal ozonides as air revitalization materials, since a higher Respiratory Quotient is obtainable than originally anticipated on the basis of carbonate formation alone.

8. Investigations of the syntheses of sodium and lithium ozonides have been carried out. Our observations tend to confirm literature reports concerning the synthesis and stability of sodium ozonide. Sodium ozonide prepared at room temperature by the passage of gaseous ozone through powdered sodium hydroxide is relatively stable but insoluble in liquid ammonia. On the other hand, sodium ozonide prepared at temperatures between - 50 and -60°C is soluble in liquid ammonia but unstable at room temperature. Literature reports emphasize the difficulty encountered in the attempts to prepare lithium ozonide by the action of gaseous ozone on solid lithium hydroxide. Some investigators have postulated that the formation of lithium ozonide is thermodynamically unfavorable; however, the validity of their thermodynamic values have been questioned. A transitory yellow color was observed in these laboratories when solid lithium hydroxide was exposed to gaseous ozone. This yellow product was not isolated.

9. In the course of this work, the following have been presented:

   a. Theoretical discussions of alkali metal ozonide chemistry.

   b. Discussions of the free-radical mechanisms involved in the synthesis and chemical reactions of alkali metal ozonides.

   c. Thermodynamic and kinetic data relative to the characterization of alkali metal ozonides.

d. General discussions of air revitalization systems employing solid chemical oxygen storage media.

e. Reviews of Soviet activity in the area of unfamiliar oxidation state chemistry with regard to air revitalization systems.

IV

CONCLUSIONS

Thus far, the work completed on the study of alkali metal ozonides clearly establishes the potential of these materials for use in non-regenerative air revitalization systems. The fundamental work has served to remove the fear that the materials are unusually dangerous to handle or so unstable as to make their engineering use impractical. It has been shown that although potassium ozonide does decompose to the superoxide and oxygen, the rate of such decomposition is not excessive at normal cabin temperatures, and that this material can be safely stored for extensive periods of time at temperatures below 0°C. The fact that this material does gradually decompose at cabin temperatures to yield breathing oxygen offers the possibility of engineering innovations in employing these materials which are not possible with similar oxygen source compounds. The discovery that bicarbonates are formed by the reaction of potassium ozonide with water vapor and carbon dioxide increases the attraction of this compound in an air revitalization system because of the favorable Respiratory Quotient obtained. To capitalize on the potential of alkali metal ozonides, continuation of fundamental studies is recommended. The directions that these studies should take are outlined in Section V, "Recommendations."

V

RECOMMENDATIONS

It is recommended that:

1. Systematic studies of the novel reaction paths developed in the course of this work be pursued in an effort to find a method for producing potassium ozonide in large yield. Until such a process is developed, engineering studies on systems employing this material for air revitalization purposes will be limited to bench scale tests.

2. Physico-chemical characterization studies of alkali metal ozonides be continued to definitively establish the heats associated with their pertinent chemical reactions. Determinations must be made of the handling characteristics of ozonides in bulk quantities; i.e., in quantities greater than the experimental yields presently obtained.

3. The search for methods of synthesizing stable sodium and lithium ozonides be continued. The results obtained thus far indicate that the reaction of gaseous ozone with solid lithium and sodium hydroxide leaves much to be desired. At this time, however, the evidence is far from conclusive that stable forms of these lower molecular weight ozonides can not be synthesized.

4. The studies of the reaction of potassium ozonide with water vapor and gaseous carbon dioxide to form potassium bicarbonate be further investigated since the optimization of this reaction could lead to a chemical air revitalization system with a Respiratory Quotient of 0.8.

5. The kinetic and thermodynamic characteristics of the reaction of potassium ozonide with gaseous carbon monoxide be determined.

VI

REFERENCES

1. Petrocelli, A.W., and R.V. Chiarenzelli, J. Chem. Ed. 39, 557 (1962).

2. Keating, D.A., and K. Weiswurm, WADD Technical Report, ASTIA AD No. 252127.

3. Ordway, F.I., et al., Basic Astronautics, Prentice Hall, Inc., New Jersey (1962).

4. Sisakyan, N.M., Problems of Space Biology, Vol. I, Moscow (1962), NASA Technical Translation F-174 (1963).

5. Sisakyan, N.M., and V.I. Yazdovskii, Problems of Space Biology, Vol. II, Moscow (1962), U.S. Dept. of Commerce, Offices of Technical Services Translation JPRS: 18395 (1963).

6. Volynkin, Yu.M., et al, "The First Manned Space Flights," Moscow (1962), English translation prepared by Translation Services Branch, Foreign Technology Division, WP-AFB, Ohio, ASTIA AD No. 294537.

7. Seryapin, A.D., Problems in Space Biology, Vol. I, NASA TT F-174 (1963), p. 339.

8. Semenov, A.D., "Toward New Acheivements in Soviet Chemistry," ASTIA AD No. 400418.

9. Petrocelli, A.W., and A. Capotosto, Jr., "Some Notes on the Use of Superoxides in Non-Regenerative Air Revitalization Systems," Paper to be delivered at the Maimi meeting of the Aerospace Medical Association in May, 1964, is press, Aerospace Medicine.

REFERENCES (Cont.)

10. Item of Interest, "Derivatives of Ozone", ASTIA AD No. 257921.

11. Makarov, S.Z., and E.I. Sokovnin, Doklady Akad. Nauk SSSR 137, 612 (1961).

12. Kazarnovskii, I.A., et al, Doklady Akad. Nauk SSSR 64, 69 (1949).

13. Nikolskii, G.P., et al, Doklady Akad. Nauk SSR 72, 713 (1950).

14. Field, F.H., and J.L. Frankling, Electron Impact Phenomenon, Academic Press, New York, 1957, p. 129.

15. NBS Circular 500 (1952).

16. JANAF Thermochemical Tables, ASTIA AD No. 286470.

17. Kacmarek, A.J., AFOSR 2983, Final Report, June, 1962.

18. Vol'nov, I.I., et al, Izv. Akad. Nauk SSSR Otd. Khim. Nauk, 1127 (1962).

19. Nikolskii, B.P., et al, Doklady Akad. Nauk SSSR 77, 69 (1951).

20. Solomon, I.J., and A.J. Kacmarek, J. Phys. Chem. 64, 168 (1960).

21. Whaley, T.P., and J. Kleinberg, J. Am. Chem. Soc. 73, 79 (1951).

22. Davis, I., ASTIA AD No. 267249.

23. Vol'nov, I.I., and V.V. Mateev, Izv. Akad. Nauk SSSR Otd. Khim. Nauk, 1136 (1963).

24. Nikolskii, G.P., et al, Doklady Akad. Nauk SSSR 77, 69 (1951).

25. Kuznetsov, V.G., et al, Russ. J. Inorg. Chem. 7, 499 (1962).

26. McLachlan, A.O., et al, J. Chem. Soc., 952 (1959).

REFERENCES (Cont.)

27. Smith, P., J. Phys. Chem. 60, 1471 (1956).

28. Kacmarek, A.J., et al, Inorg. Chem. 1, 659 (1962).

29. Solomon, I.J., et al, J. Am. Chem. Soc. 84, 34 (1962).

30. Chretian, A., et al, Bul. soc. chim. France, 49 (1960).

31. Milas, N.A., and S.M. Djokic, J. Am. Chem. Soc. 84, 3098 (1962).

32. Kraus, D.L., and A.W. Petrocelli, J. Phys. Chem. 66, 1225 (1962).

33. Petrocelli, A.W., General Dynamics/Electric Boat, Report U413-61-023 (1960), p. 58.

34. Kazarnovskii, I.A., et al, Doklady Akad. Nauk SSSR 108, 641 (1956).

35. Petrocelli, A.W., General Dynamics/Electric Boat, Report U413-62-219 (1962).

36. Seyb, E., and J. Kleinberg, Anal. Chem. 23, 115 (1951).

37. Kazarnovskii, I.A., et al, Doklady Akad. Nauk SSSR 123, 475 (1958).

38. Makarov, S.Z., and I.I. Vol'nov, Izv. Akad. Nauk SSSR, 370 (1951).

39. Markowitz, M.M., AF 33(657)-9124, Final Report, September, 1963.

40. Mel'nikov, A.Kh., et al, Russ. J. Inorg. Chem. 7, 633 (1962).

41. Mel'nikov, A.Kh., and T.P. Firsova, Zhur. Neorg. Khim. 6, 2470 (1961), ASTIA AD No. 269788.

42. Miller, R.R., and W.C. Lanning, ASTIA AD No. 236410.

43. Tsentsiter, A.B., and S.A. Tokareva, Fhur. Neorg. Khim. 6, 2474 (1961), ASTIA AD No. 269788.

44. Bogatov, P.I., et al, Voyenno-med. Zhur. 2, 37 (1961), ASTIA AD No. 257922.

NASA-Langley, 1964 CR-135