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THE KINETICS OF THE REACTIONS OF KO_2 AND KOH WITH WATER

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ABSTRACT

This report gives the results of a kinetic study of the reactions of potassium hydroxide and potassium superoxide with water vapor and carbon dioxide, describes the equipment used, and furnishes the mathematics required for calculating time dependent concentrations.

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THE KINETICS OF THE REACTIONS OF KO_2 AND KOH WITH WATER

Order and Rates

The kinetics of the reactions of potassium superoxide and potassium hydroxide with water have been determined to be first order with respect to water for the former and second order with respect to water for the latter according to Equations 1 and 2.

$$2KO_2 + H_2O \xrightarrow{k_o} 2KOH + 1.5\ O_2, \tag{1}$$

$$2\ [KOH + 2H_2O \xrightarrow{k_1} KOH \cdot 2H_2O]. \tag{2}$$

These two equations may be added to obtain Equation 3 which has been reported in the chemical literature.*

$$2KO_2 + 5H_2O \rightarrow 2\ (KOH \cdot 2H_2O) + 1.5\ O_2. \tag{3}$$

The reaction rate constants (Table I) were computed from time dependent measurements of the moisture remaining in the nitrogen atmosphere over the solid reactants KO_2 and KOH.

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*Mel' nikov, A. Kh., et.al., Zh. Neorgan. Khim 7, 1228, 1962; C. A. 57, 10766b.

TABLE I

REACTION ORDERS AND RATES AT 22 ($\pm$1)°C AND 20 PSIG N_2

Order	Rate Constants	Reaction
1st	$k_o = 0.351\ (\pm 0.006)\ hr^{-1}$	Eq (1)
2nd	$k_1 = 4.66\ (\pm 0.04) \times 10^{-2}\ hr^{-1}\ (m/1)^{-1}$	Eq (2)

Procedure and Results

Moisture was added to dry nitrogen by bubbling the nitrogen through an aqueous-sulfuric acid solution. When the water level had stabilized around 1000 ppm (by volume) the reaction chamber containing the KO_2 or the KOH was pressurized and, after a reaction time interval, the nitrogen was analyzed by means of a Consolidated Electrodynamics Corporation moisture monitor. Figure 1 shows a block diagram of the apparatus used in these experiments and Figure 2 shows typical curves for the reactions. In all cases the solid reactants were in large excess as compared to the amount of moisture in the nitrogen atmosphere and it is assumed that this will be the case in most practical applications.

The amount of water remaining, $\underline{b}$, after time $\underline{t}$, may be found by the integrated rate expression, Equation 4*, where $\underline{a}$ is the initial water concentration in moles/liter and $\underline{e}$ is the constant 2.7183:

$$b = \frac{k_o a}{e^{k_o t}(k_1 a + k_o) - k_1 a} . \tag{4}$$

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*See Appendix A for the derivation of Equation 4 and Appendix B for a sample calculation.

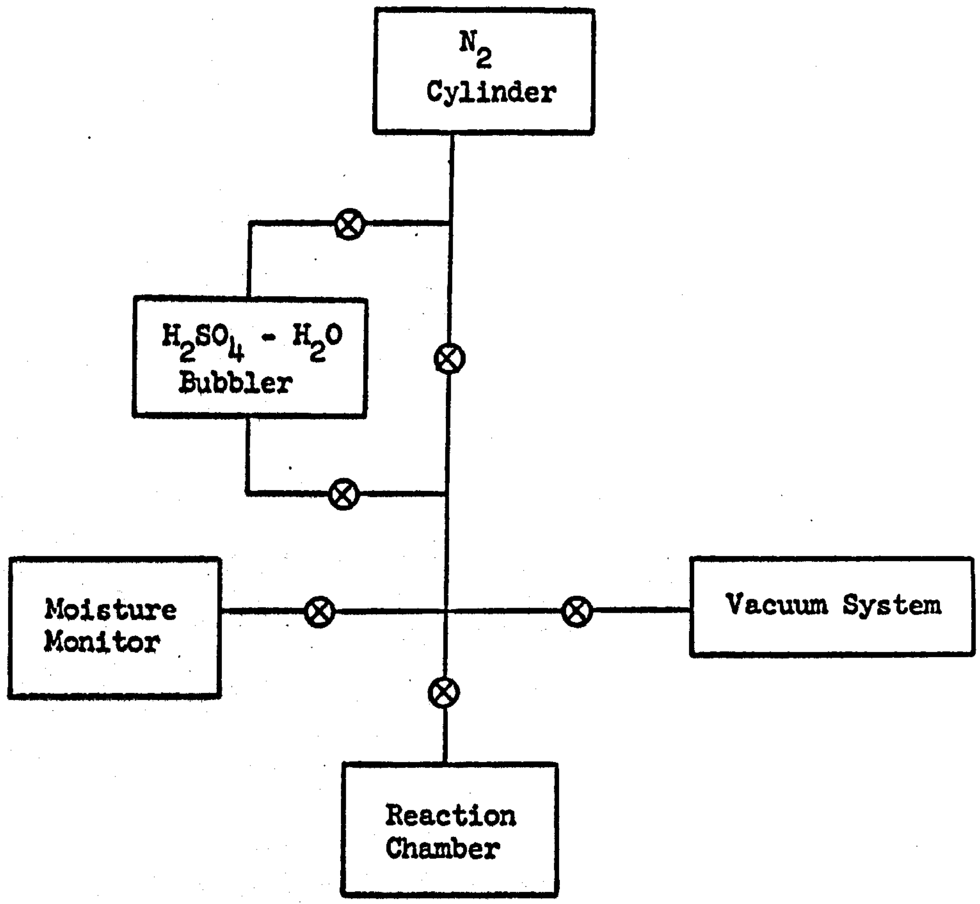

Figure 1. Diagram of Reaction Apparatus

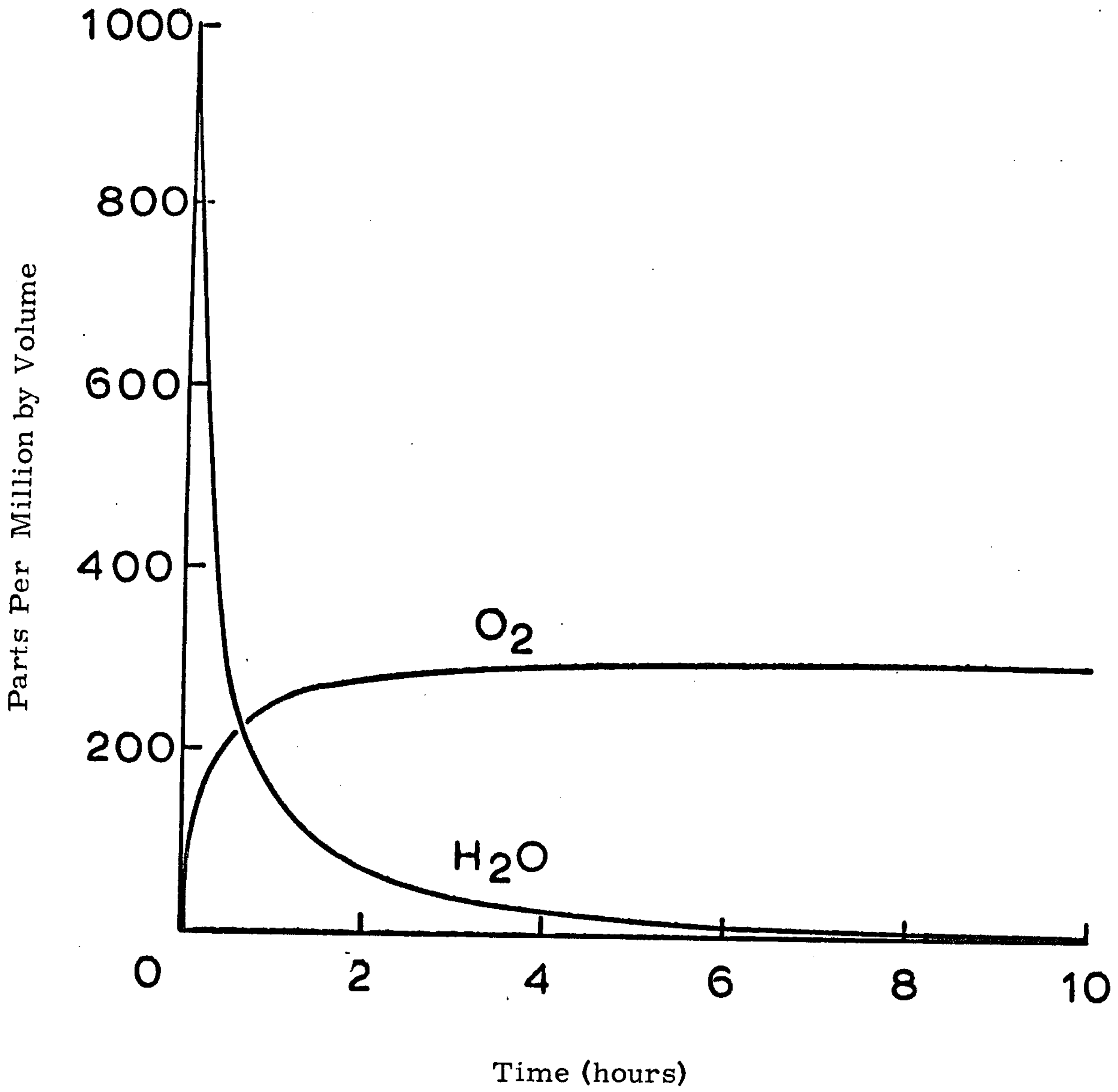

Figure 2. Reaction Curves

When the expression of concentration in terms of parts per million by volume is more convenient, the constant $\underline{k}_1$ in Equation 4 may be replaced by $\underline{k}'_1$. The latter may be computed by Equation 5,

$$k'_1 = \frac{Pk_1}{RT}, \tag{5}$$

where $\underline{P}$ is the absolute pressure in atmospheres, $\underline{R}$ is the gas constant, 0.08205, and $\underline{T}$ is the absolute temperature in degrees Kelvin. The first order constant k_o is independent of concentration units. The amount of oxygen evolved, $\underline{c}$, may be calculated by Equation 6 where $\underline{a}$ and $\underline{b}$ are as defined previously.

$$c = 0.3\,(a-b). \tag{6}$$

The average molecular weight of the potassium superoxide was determined titrimetrically to be 73.7, indicating a purity of about 96 percent as received from the supplier. The apparent density of the yellow solid was less than 1 g/cc, indicating a very large internal surface area (theoretical density = 2.14 g/cc). When small (1 cc) pieces of the superoxide were floated on water a considerable effervescence was noted as the reaction proceeded according to Equation 3. (Quantitative gas volumetric experiments confirm this stoichiometry.) There were no evidences of rapid combustion as would be expected if there had been unreacted potassium metal present, and it is thought safe to destroy potassium superoxide in this manner when the evolution of considerable quantities of oxygen does not present a hazard. An infrared spectrophotometric analysis of the oxygen evolved in the reaction showed no detectable infrared active species (H_2O_2 or organic impurities) at a cell pressure of 47 cm Hg.

Additional tests were made to determine whether the superoxide would react with dry CO_2 at an appreciable rate. Carbon dioxide, which had been dried over phosphorus pentoxide for 24 hours, was admitted to the reaction chamber (one atmosphere of pressure and $23^{o}C$) where the gas remained in contact with powdered KO_2. There was an initial decrease in pressure that was only slightly greater than the reading error and no change thereafter during a 24-hour period. The initial reaction was assumed to be the neutralization of impurity potassium hydroxide according to Equation 7.

$$2\,KOH \cdot n\,H_2O + CO_2 \rightarrow K_2CO_3 \cdot (n + 1)\,H_2O. \qquad (7)$$

Conclusions and Recommendations

Potassium superoxide was found to be a very active desiccant (0.633 lb H_2O/lb KO_2) capable of rapidly producing oxygen according to Equation 3 (0.337 lb O_2/lb KO_2). When the KO_2 is exhausted, the $KOH \cdot 2\,H_2O$ formed will continue to serve as a desiccant and, in the presence of CO_2, will react according to Equation 7 to yield the hygroscopic (but nondeliquescent) carbonate.

In view of the reported explosive nature of potassium superoxide when in contact with certain organic chemicals, it is recommended that the KO_2 be stored in tightly closed containers when not in use and be protected from organic solids and vapors in vibration-tested containers when used as a desiccant or source of oxygen.

APPENDIX A

DERIVATION OF THE RATE EXPRESSION

When both KO_2 and KOH are present in a solid desiccant (i.e., the KO_2 has been exposed previously to small amounts of water vapor) and are in large excess with respect to the amount of water vapor, then reactions according to Equations A-1 and A-2 will occur simultaneously and independently.

$$2KO_2 + H_2O \xrightarrow{k_o} 2KOH + 1.5\ O_2, \qquad \text{(A-1)}$$

$$KOH + 2H_2O \xrightarrow{k_1} KOH \cdot 2H_2O. \qquad \text{(A-2)}$$

The reactions were found to be first and second order with respect to water and the rate constants $\underline{k}_o$ and $\underline{k}_1$ were evaluated separately. The rate expression may be formulated as in Equation A-3:

$$\frac{dx}{dt} = k_1 (a-x)^2 + k_o (a-x), \qquad \text{(A-3)}$$

where $\underline{a}$ is the initial water concentration and $\underline{x}$ is the decrease in water concentration due to the reactions in time $\underline{t}$.

Rearranging Equation A-3 gives

$$\frac{dx}{dt} = k_1x^2 + (-k_o - 2\ k_1a)\ x + (k_1a^2 + k_oa). \qquad \text{(A-4)}$$

Let

$$A = k_1, \; B = (-k_o - 2k_1a), \text{ and } C = (k_1a^2 + k_oa)$$

and, by substituting Equation A-4 and rearranging, the expression to be integrated is Equation A-5.

$$\frac{dx}{Ax^2 + Bx + C} = dt. \tag{A-5}$$

The expressions $B^2 - 4AC = k_o^2$, and $k_o^2 > 0$ indicate the logarithmic solution for the integral.*

$$\frac{1}{(B^2 - 4AC)^{1/2}} \ln\left[\frac{2Ax + B - (B^2 - 4AC)^{1/2}}{2Ax + B + (B^2 - 4AC)^{1/2}}\right] = t. \tag{A-6}$$

By substitution and rearrangement

$$t = \frac{1}{k_o} \ln\left[\frac{k_1 (a-x) + k_o}{k_1 (a-x)}\right]. \tag{A-7}$$

The evaluation of Equation A-7 between the limits x = 0, t = 0, and x = x, t = t and subsequent rearrangement gives Equation A-8,

$$(a-x) = \frac{k_oa}{e^{k_ot} \cdot (k_1a + k_o) - k_1a}. \tag{A-8}$$

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*Abramowitz, M. and Stegun, I. A., Handbook of Mathematical Functions with Formulas, Graphs and Mathematical Tables, National Bureau of Standards, Applied Mathematics Series 55, 1964, p. 12, sec. 3.3.17.

The term (a-x) is equivalent to b in the text and represents the water vapor concentration after reaction time t.

APPENDIX B

SAMPLE CALCULATIONS

The moisture concentration in parts per million by volume remaining in an enclosure after a given reaction time may be calculated by Equation 4 after first finding k_1' by Equation 5 of the text. For example, at 20 psig, 25°C, 2 hours reaction time, and an initial moisture level of 1000 ppm, the calculation would be made as follows:

$$k_1 = 4.66 \times 10^{-2} \text{ hr}^{-1} (\text{m}/1)^{-1}$$

$$P = \frac{20 \text{ psig}}{14.7 \text{ psig/atm.}} + 1.0 \text{ atm.} = 2.36 \text{ atmospheres}$$

$$R = 0.08205 \text{ atm. deg.}^{-1} (\text{m}/1)^{-1}$$

$$T = 273.2 + 25.0^{\circ}\text{C} = 298.2^{\circ} \text{ Kelvin}$$

$$k_1' = \frac{Pk_1}{RT} = \frac{(2.36)\ (4.66 \times 10^{-2})}{(0.082)\ (298.2)} = 4.49 \times 10^{-3} \text{ hr}^{-1}$$

$$k_o = 0.351 \text{ hr}^{-1}$$

$a = 1000$ ppm initial H_2O

$e = 2.7183$

$t = 2$ hrs

$$b = \frac{k_o a}{e^{k_o t}\,(k'_1 a + k_o) - k'_1 a}$$

$$b = \frac{(0.351)\,(1000)}{(2.72)^{0.351 \times 2}\,(4.49 \times 10^{-3} \times 1000 + 0.351) - 4.49 \times 10^{-3} \times 1000}$$

$b = 66.8$ ppm H_2O remaining.

The amount of oxygen generated in this period may be calculated by Equation 6 of the text.

$c = 0.3\ (a-b)$

$c = 0.3\ (1000 - 66.8)$

$c = 933.2$ ppm O_2 generated.

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