species or the total amount of a product formed at infinite time.

Most chemical reactions may be represented by a first order, first degree differential equation expressing the rate, dx/dt, as a function of x, where x is a linear function of the degree of advancement or extent of reaction. The elimination of x between the differential equation and its integrated forms results in an expression for dx/dt as a function of t. Therefore, since the amount of non-reactive product formed in a reaction is ordinarily a linear function of the degree of advancement, experimental determination of the rate of formation of an inactive product permits a test for differential rate equations.

Chemical reactions in which the rate is proportional to a power of the concentration of a single reactant may be represented by the equation

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k(a - x)^n \tag{1}$$

where k and a are constants that may contain stoichiometric relationships and initial concentrations, and n is defined as the order of the reaction. The rate equations for chemical reactions, in which several reactants contribute to the rate in proportion to powers of their concentrations, may be reduced to equation 1 when contributing reactants are present in stoichiometric amounts. Firstorder reversible reactions and simultaneous zero and first-order reactions also may be reduced to equation 1.

From the elimination of (a - x) between equation 1 and its integrated form, one obtains

$$\log \frac{dx}{dt} = 0.4343kt + \log ak \ (n = 1)$$
(2)

and

$$\frac{\mathrm{d}x^{1-n/n}}{\mathrm{d}t} = (n-1)k^{1/n}t + k^{1-n/n} a^{1-n} \ (n \neq 1) \quad (3)$$

Therefore, if the rate of formation of a product can be determined as a function of time, a straight line relationship between the time and an appropriate function of this rate will constitute a test for a particular order. Values of k and a can be obtained from the slope and intercept of this straight line.

This method may be applied to data obtained from the irradiation of dried purified cellulose in a vacuum with 2537 Å. light.<sup>3</sup> The pressure of the evolved hydrogen was measured manometrically in a system which was alternately evacuated and closed off for five-minute periods during the six hours of irradiation. Thus, the hydrogen pressure was kept below 0.03 mm. to avoid a pressure dependent inhibition. Figure 1 indicates a linear relationship between the square of the reciprocal of the rate of hydrogen evolution and the time. Therefore the rate of hydrogen evolution follows the parabolic law, (n = -1)

$$\frac{dx^{-2}}{dt} = -\frac{2t}{k} + \frac{a^2}{k^2}$$
(4)

For the particular conditions of the experiment a = -0.300 mm.,  $k = -3.80 \times 10^{-5}$  (mm.)<sup>2</sup>/sec., and equation 1 becomes

(3) Unpublished work of the author.



Fig. 1.—(Rate of hydrogen pressure increase)<sup>-2</sup>  $v_s$ . time of irradiation of cellulose in a vacuum with 2537 Å. light.

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{3.80 \times 10^{-5}}{0.300 + x} \tag{5}$$

indicating a zero-order rate of hydrogen formation, inhibited by a product of the irradiation.

## THE HEATS OF FORMATION OF Na<sub>2</sub>O<sub>2</sub>, NaO2 and KO21,2

### BY PAUL W. GILLES AND JOHN L. MARGRAVE<sup>3</sup>

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The alkali metals and oxygen form more than the usual variety of compounds. There are  $M_7O_1$ , M4O, M3O, M7O2 suboxides, M2O normal oxides,  $M_2O_2$  peroxides,  $M_2O_3$  sesquioxides,  $MO_2$  superoxides and MO<sub>3</sub> ozonides. For an excellent summary of the properties of these compounds and literature citations, reference to the recent review by Brewer<sup>4</sup> should be made.

The superoxides of potassium, rubidium and cesium are obtained by combustion of the metals or lower oxides, and have been known for many years, but only recently have attempts to prepare  $NaO_2$  been successful.<sup>5-7</sup>

Because of our proximity to this work, we became interested in the stabilities of the superoxides, their dissociation behavior and the best

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(2) Presented before the Division of Physical and Inorganic Chemistry at the 117th Meeting of the American Chemical Society, Detroit, Michigan, April 19, 1950, and at the 118th Meeting of the American Chemical Society, Chicago, Illinois, September 7, 1950.

(3) University of Wisconsin, Madison, Wisconsin.

(4) L. Brewer, Chem. Revs., 52, 1 (1953).
(5) W. H. Schechter, H. H. Sisler and J. Kleinberg, J. Am. Chem. Soc., 70, 267 (1948).

(6) W. H. Schechter, J. K. Thompson and J. Kleinberg, ibid., 71, 1816 (1949).

(7) S. E. Stephanou, W. H. Schechter, W. J. Argersinger, Jr., and J. Kleinberg, ibid., 71, 1819 (1949).

	TIEATS OF REACTION	N OF $\operatorname{INAO}_2$ , $\operatorname{INA}_2\operatorname{O}_2$ AND I	AU2 WITH WATER	
Compound	Analyses b (wt. %)	cal./g. obsvd.	ΔH reaction, c kcal./mole (for pure oxide)	Concn. of final soln,. moles H <sub>2</sub> O/mole MOH
NaO <sub>2</sub>	$\begin{array}{l} NaO_2 \ = \ 94\% \\ Na_2O_2 \ = \ 6\% \\ Na_2CO_3 \ = \ not \ done \end{array}$	$300.8 \pm 1.8$ (5 runs)	$16.3 \pm 0.6$	3500
NaO <sub>2</sub>	$NaO_2 = 93.8\%$ $Na_2O_2 = 6.2\%$ $Na_2CO_3 = not done$	$288.4 \pm 0.3$ (3 runs)	$15.6 \pm 0.3$	3800
$\mathrm{NaO}_{2}^{a}$	$NaO_2 = 94.0\%$ $Na_2O_2 = 4.4\%$ $Na_2CO_3 = 1.6\%$	$302.1 \pm 1.2$ (2 runs)	$16.7 \pm 0.3$	4800
NaO2ª	$NaO_2 = 92.5\%$ $Na_2O_2 = 6.0\%$ $Na_2CO_3 = 1.5\%$	$275.5 \pm 1.2$ (2 runs)	$14.6\pm0.3$	9000
NaO2ª	not done, but same sample as above	294.7 (1 run)	$15.9 \pm (0.3)$	6770
Na <sub>2</sub> O2 (white)	$Na_2O_2 = 99.2\%$ $Na_2O = 0.8\%$ $Na_2CO_3 = not done$	$437.9 \pm 4.1$ (3 runs)	$34.0 \pm 0.3$	3800
KO2	$\begin{array}{l} \mathrm{KO}_2 \ = \ 92.4\% \\ \mathrm{K}_2\mathrm{O} \ = \ 3.2\% \\ \mathrm{K}_2\mathrm{CO}_3 \ = \ 2.8\% \\ \mathrm{Na}_2\mathrm{O}_2 \ = \ 1.6\% \end{array}$	$193.5 \pm 0.9$ (2 runs)	$12.5\pm0.6$	6850
KO2ª	$\begin{array}{l} \mathrm{KO}_2 \ = \ 91.1\% \\ \mathrm{K}_2\mathrm{O} \ = \ 3.4\% \\ \mathrm{K}_2\mathrm{CO}_3 \ = \ 2.2\% \\ \mathrm{Na}_2\mathrm{O}_2 \ = \ 3.3\% \end{array}$	$204.1 \pm 8.1$ (2 runs)	$12.8 \pm 1.1$	13, 100
$\mathrm{KO}_2{}^a$	$KO_2 = 93.4\%$ $K_2CO_3 = 4.2\%$ $Na_2O_2 = 2.4\%$	$207.9 \pm 8$ (1 run)	$15.2 \pm 0.8$	11, 700

TABLE I

HEATS OF REACTION OF NaO2, Na2O2 AND KO2 WITH WATER

<sup>a</sup> Runs made with Berkeley calorimeter. <sup>b</sup> Maximum error in analyses is  $\pm 1\%$  except for the first NaO<sub>2</sub> sample used for the first 5 runs where the error in analysis may be  $\pm 2\%$ . <sup>c</sup> The maximum limit of error stated for the heat of reaction of the pure compound includes allowance for both the error in the analysis and the error in observing the heat of reaction.

conditions for their preparation. This note presents the results of measurements of the heats of reactions of  $Na_2O_2$ ,  $NaO_2$  and  $KO_2$  with water. The values are used with available thermochemical data<sup>8</sup> to calculate the heats of formation.

The samples used in this work were furnished through the courtesy of Drs. C. B. Jackson and W. H. Schechter of the Callery Chemical Company. The KO<sub>2</sub> was prepared by atomizing liquid potassium into an oxygen atmosphere at about 300°; the Na<sub>2</sub>O<sub>2</sub> by oxidation of sodium metal; and the superoxide by high pressure oxidation of the peroxide. Prof. Jacob Kleinberg and Dr. Edgar Seyb kindly furnished some NaO<sub>2</sub> samples. Unfortunately, the quality of peroxides and superoxides was not high. There is, as yet, no simple way to determine just what the major contaminants in these materials are, although hydroxides, hydroxide hydrates, carbonates and peroxide hydrates appear likely. The samples were analyzed by (1) measuring the volume of oxygen evolved by a known weight of compound dissolved in water in the presence of  $MnO_2$ ; (2) titrating the resulting solution to the phenolphthalein and methyl orange points; (3) spectroscopic analysis; (4) X-ray diffraction; and (5) quantitative analysis for metals. Final analyses represent the best set of substances and percentages for agreement with the analytical data.

The materials were received in sealed containers in the form of lumps weighing 5-25 g. or in the form of powder. Different lumps in the same shipment were sometimes different in appearance, and even within the same lump inhomogeneity was often indicated by variations in color. In order to achieve rapid reaction in the calorimeter, the samples were crushed to about 250 mesh. The materials were handled in a dry box in a nitrogen or argon atmosphere.

(8) "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Circular 500 (1952).

Nevertheless, the possibility of contamination by atmospheric water or carbon dioxide, and the uncertainty as to the nature of the impurities present make the analysis of these materials the major uncertainty in this work.

Final interpretation of the thermodynamic properties of these substances must wait until highly pure samples are obtained, or until available contaminated samples can be completely analyzed.

The thermal measurements were carried out in two different calorimeters. One was constructed for this investigation. It consisted of a 1.5-1. Dewar flask fitted with a rubber stopper through which the stirrer, breaking mechanism, gas escape tube and electrical leads passed. The copper thermometer and manganin heater were wound between two silver cylinders. Both electrical and chemical calibrations of the calorimeter were made in the usual way. While one of us (JLM) was an AEC postdoctoral fellow, additional measurements were made with the calorimeter in the Department of Chemistry at the University of California at Berkeley, which has been described previously.<sup>9</sup>

In the presence of  $MnO_2(s)$  to catalyze the decomposition of peroxides in solution, the substances react with water according to the reactions

$$\begin{split} M_2O_2(s) \,+\, H_2O(l) \,=\, 2MOH(soln) \,+\, 1/2 \,\, O_2(g) \quad (1) \\ 2MO_2(s) \,+\, H_2O(l) \,=\, 2MOH(soln) \,+\, 3/2 \,\, O_2(g) \quad (2) \end{split}$$

The results are given in Table I. The third column gives the values of the heat evolved per gram of sample. The fourth column contains the values of  $\Delta H$  for the solution reaction as given in one of the two equations above. The value has been corrected for the impurities listed in the

(9) W. M. Latimer and H. W. Zimmerman, J. Am. Chem. Soc., 61, 1550 (1939); B. J. Fontana, "NNES IV-19B," McGraw-Hill Book Co., New York, N. Y., 1950, p. 321.

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second column. If other impurities are assumed, different heats will be obtained.

The NaO<sub>2</sub> results show discrepancies among the different groups of runs far beyond the expected experimental error. These arise either because the analytical sample was not the same, in all cases, as the calorimetric sample, or because the calorimetric sample underwent a reaction after the analysis. A reaction with water to form NaOH causes the heat of solution per gram to become smaller. A decomposition to Na<sub>2</sub>O<sub>2</sub> causes the heat of solution per gram to increase.

The second and third group of NaO<sub>2</sub> samples were from the same stock. The experiments were by a three-month interval. separated The fourth and fifth groups of samples were sealed into calorimetric bulbs at the same time from the same stock. The experiments were separated by a fourmonth interval. The results appear to indicate that a slow decomposition to Na<sub>2</sub>O<sub>2</sub> may occur and that low heat of solution values should be the most nearly correct. On the other hand, samples stored in sealed containers over long periods showed no great increase in pressure as would result from such decomposition. To obtain the final value, all the results have been averaged. For reaction (2) involving NaO<sub>2</sub>,  $\Delta H = -15.9 \pm$ 0.7 kcal./mole.

The different groups of samples of KO<sub>2</sub> show wide variation also, attributable to similar causes. The average of the five runs gives  $\Delta H = -13.2 \pm 0.8$  kcal./mole for reaction (2) involving KO<sub>2</sub>.

The results have been used together with existing data to calculate the heats of formation given in Table II.

### TABLE II

# HEATS OF FORMATION AT 298°K. IN KCAL./MOLE Kazar-

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Com- pound	de Forcrand¢	Kaule and Roth b	Kazar- novskii¢	This work
$Na_2O_2$	$-119.3^{d}$	$-121.2^{d}$		$-122.1 \pm 1.2$
NaO2	$(-65.0)^{e}$			$-62.1 \pm 0.7$
KO2	$-66.8 \pm 0.8^{d}$		-67.9	$-67.6 \pm 0.8$

<sup>a</sup> R. de Forcrand, Compt. rend., 127, 514 (1898); 158, 843, 991 (1914). <sup>b</sup> H. Kaule and W. Roth, Z. anorg. Chem., 253, 352 (1947); 255, 324 (1948). <sup>c</sup> L. Kazarnovskaya and I. Kazarnovskii, Zhur. Fiz. Khim., 25, 293 (1951). <sup>d</sup> Values recalculated from original experimental data but with heats of formation of aqueous solutions taken from NBS tables. <sup>e</sup> Indicate estimated values.

Through the courtesy of K. K. Kelley of the Pacific Experiment Station of the Bureau of Mines, the low temperature heat capacities of some of these samples have been measured by Todd<sup>10</sup> who reported the entropies at 298°K. In spite of the entropies and the heats of formation that are now available, it does not appear to be possible to establish unequivocally the decomposition behavior of the sodium oxides. The reasons for this situation are (1) high temperature heat capacity data are lacking, and (2) the nature of the solid phases produced by decomposition of the superoxide is not clear. The crystal structure of pure Na<sub>2</sub>O<sub>2</sub> is not definitely known, and published lattice con-

(10) S. S. Todd, J. Am. Chem. Soc., 75, 1229 (1953).

Notes

stants for  $NaO_2(s)$  indicate a possibility for extensive solid solution.

We are pleased to acknowledge the financial assistance of the Atomic Energy Commission. We are indebted to Drs. Jackson, Schechter, Kleinberg, and Seyb for the samples, and to the late Prof. W. M. Latimer for the use of the University of California calorimeter.

## VERIFICATION BY CHROMATOGRAPHY OF THE THERMAL FORMATION OF BARIUM AND LEAD TETRAPOLYPHOSPHATES

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#### Received March 16, 1956

In an earlier article,<sup>2</sup> thermal analysis and X-ray diffraction data were used to show that lead tetrapolyphosphate was the only crystalline polyphosphate to form thermally between the lead pyrophosphate and lead tetrametaphosphate compositions. An attempt was made during that study to investigate the reactions occurring in the barium pyrophosphate—barium tetrametaphosphate system. A phase diagram could not be constructed for the system as high temperatures were required which could not be attained with the thermal analysis equipment available. X-Ray diffraction data did show that a barium polyphosphate formed within the system, but the X-ray data were insufficient to identify it.

Recently, chromatographic techniques have been developed which can be used to distinguish the various species of phosphates.<sup>3</sup> This method has been used to establish the identity of the barium polyphosphate and to confirm the identity of the lead tetrapolyphosphate.

### Experimental

Mixtures of barium monohydrogen and dihydrogen orthophosphate were heated to constant weight at 550°, a temperature above the thermal decomposition temperatures of the individual reactants, but below the temperature of appearance of any liquid phase. The products were ground thoroughly and reheated at 550° for 12 hours to ensure complete reaction.

The sample of lead tetrapolyphosphate was one of the series of samples used to obtain the thermal analysis data reported in the earlier paper.

Samples of the reaction products corresponding in composition to barium tripolyphosphate and tetrapolyphosphate were taken for chromatographic analysis, since these compounds might be expected to form in the barium system in the composition range studied. These samples were converted to the sodium salts in solution by use of the sodium form of Amberlite IR-120 cation-exchange resin. The lead tetrapolyphosphate was converted to the sodium salt by reaction in solution with sodium carbonate.

One- and two-directional paper chromatograms were run on the samples. The developed chromatograms showed

(1) Inorganic Chemicals Division Research, Monsanto Chemical Company, Dayton 7, Ohio.

(2) R. K. Osterheld and R. P. Langguth, THIS JOURNAL, 59, 76-80 (1955).

(3) J. P. Ebel, Bull. soc. chim. France, 20, 991, 998 (1953); E. Karl-Kroupa, article submitted to Anal. Chem. for publication.