problem. A brief discussion of the deviations may be in order, however.

It may be seen that the absorption data tend to run somewhat higher than the desorption data. The reason for this is the limited formation of undissolved hydride. The initial H_2 pressure during the absorption runs was between 600 and 650 mm. Thus, at temperatures below 400°, the melt absorbed sufficient H_2 to saturate itself and, in addition, enough to coat the surface with a thin layer of sodium hydride. Since the system was static, this layer prevented further hydride formation,[10] and accounts for the slightly higher solubility figures reported.

The wide deviation of the point at 265° is explained by the fact that, at this temperature, the melt probably was not saturated with sodium oxide, and subsequent correction for anticipated saturation by this material resulted in a low hydride value. The 240° figure was not corrected for oxide, since no attack was in evidence and no alkalinity was found.

This solubility study was limited by the vapor pressure of sodium metal and the dissociation pressure of sodium hydride. Both become significant to these data at 425°. The desorption apparatus would not allow for operation at pressures in excess of one atmosphere, and excessive distillation of sodium vitiated higher temperature results in the absorption runs. Data were collected at 500°, but were not sufficiently reliable to be included in this report. There were indications, however, that the system was approaching a limiting solubility of approximately 5 wt. % NaH (under about 1 atmosphere H_2 pressure). Hence, extrapolation of the data herein reported is not recommended.

The results of this study demonstrate a possible source of error in present sodium analysis for oxygen by the amalgamation method. The error with respect to sodium hydride, as well as the likelihood that it will be present in most sodium systems, is particularly significant. The error will not necessarily be predictable in a sample drawn directly from saturated sodium unless precautions are taken to prevent dissociation of hydride during sample handling and cooling. Excessive local heating during amalgamation in the oxide analysis method can also result in hydride loss.

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[10] D. T. Hurd, "Chemistry of Hydrides," John Wiley and Sons, New York, N. Y., 1952, p. 31.

THE EFFECT OF D_2O ON THE RATE OF THE REACTION BETWEEN OXYGEN AND Pu(III)[1]

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It has been shown recently that the reaction between Pu(III) and oxygen in aqueous sulfate solutions is in termolecular: first order in the oxygen concentration and second order in the Pu(III) concentration.[2] One possible mechanism would involve an activated complex in which two Pu(III) sulfate complexes were linked by means of an oxygen bridge; this structure would be similar to that postulated for one of the Pu(IV)–H_2O_2 complexes.[3] Another possible mechanism would involve the transfer of a hydrogen atom from the hydration shell of each of two Pu(III)–$SO_4^=$ complexes to the oxygen molecule.[4] If a hydrogen atom transfer mechanism were the correct one, there should be a marked hydrogen isotope effect and a significant decrease in reaction rate in D_2O.[4] In the hope of deciding between these mechanisms, rates in H_2O and D_2O solutions were determined and compared at the same O_2, Pu(III) and free $SO_4^=$ concentrations. Only a moderate hydrogen isotope effect was observed.

The solubility of oxygen in D_2O was determined so that a correction for the concentration difference in the two solvents at the same partial pressure of oxygen could be applied. A known volume of water was saturated with oxygen, transferred to a vacuum line and distilled into a large bulb chilled with Dry Ice. The liberated gas was determined manometrically. For a partial pressure of O_2 of 1 atm. the solubility was found to be 1.28×10^{-3} *M* in H_2O and 1.41×10^{-3} *M* in D_2O. Three determinations in each solvent were made, the mean deviation was about 2.4%. No measurements have been made in salt solutions, but it is probably safe to assume the same solubility ratio and that O_2 is about 10% more soluble in D_2O solutions than in H_2O solutions.

The acid dissociation quotient of DSO_4^- in D_2O solutions was needed for the calculation of the free $SO_4^=$ concentrations in those solutions. It was determined by making optical measurements on the Ce(III)–$SO_4^=$ system. Absorbancies were determined for a series of Ce(III) solutions which were 0.012 *M* in $HClO_4$ and with Na_2SO_4 ranging from 0 to 0.05 *M*. In these solutions, the acid concentration was low enough so that an approximate value for the acid dissociation quotient was sufficient for the determination of free sulfate concentration as a function of absorbancy. Using the same Ce(III) concentration, absorbancies were determined for a series of solutions all 0.05 *M* in Na_2SO_4, but with $HClO_4$ concentrations ranging up to 0.11 *M*. Free $SO_4^=$ concentrations were estimated from the absorbancy *vs.* $SO_4^=$ function and the acid dissociation quotients were calculated. The results of such determinations in both H_2O and D_2O solutions of unit ionic strength are given in Table I. The fact that the values obtained in the H_2O solutions are in good agreement with those obtained potentiometrically[5] indicates that the optical method for determining the acid dissociation quotients is valid. Assuming that the effect of D_2O is linear in its concentration, the data lead to the estimate that the acid dissociation quotient of DSO_4^- in pure D_2O solutions at 25° and unit ionic strength is 0.051 ± 0.003. The ratio of acid dissociation quotients found here is in substantial agreement with the ratios which have been re-

TABLE I

DETERMINATIONS OF THE ACID DISSOCIATION QUOTIENT OF THE BISULFATE ION IN SODIUM PERCHLORATE SOLUTIONS OF UNIT IONIC STRENGTH AT 25°

Fraction D_2O	Na_2SO_4, *M*	No. of soln.	$HClO_4$ range, *M*	Acid dissociation quotient
0	0.05	5	0.05 to 0.11	0.091 ± 0.006
0.892	.05	4	.05 to .11	.052 ± .004
0.876	.05	5	.03 to .11	.055 ± .003

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[1] This work was done under the auspices of the U. S. Atomic Energy Commission.

[2] T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **60**, 1417 (1956).

[3] R. E. Connick and W. H. McVey, paper 4.12 in "The Transuranium Elements," edited by G. T. Seaborg, J. J. Katz and W. M. Manning, "National Nuclear Energy Series," Division IV, Vol. 14B, McGraw-Hill Book Co., Inc., New York, N. Y., 1949.

[4] This was suggested to us by Professor Norman Davidson, see also R. E. Huffman and N. Davidson, *J. Am. Chem. Soc.*, **78**, 4836 (1956).

[5] E. Eichler and S. W. Rabideau, *ibid.*, **77**, 5501 (1955).

ported for other weak acids.[6] It was found to be impossible to make reliable measurements at an ionic strength of 2 due to the formation of a precipitate. However, it is probably safe to assume that the ratio is essentially the same at the two ionic strengths.

Three experiments have been made in which the rates of the reaction between Pu(III) and oxygen (in the presence of Fe(II) to eliminate complications from the reactions of H_2O_2) were compared in H_2O and D_2O solutions. The rates were determined as previously described.[2] The results of these experiments are shown in Table II.

TABLE II

EFFECT OF D_2O ON THE RATE OF REACTION BETWEEN Pu(III) AND OXYGEN IN $NaClO_4$ SOLUTIONS OF IONIC STRENGTH 2 AND 23°

$HClO_4$, *M*	Na_2SO_4, *M*	$NaClO_4$, *M*	Fraction D_2O	*Ka*	$SO_4^=$, *M*	R_H/R_D[a]	k_H/k_D[b]
0.131	0.06	1.75	0	0.10	0.03	1.84 ± 0.05	1.17
.131	.06	1.75	0.98	.056	$.022_6$		
.17	.14	1.55	0	.10	.07	1.53 ± .03	1.23
.17	.14	1.55	0.87_2	.059	$.056_7$		
.17	.14	1.55	0	.10	.07	1.15 ± .01	1.30
.219	.189	1.45	0.87_2	.059	.07		

[a] Observed rate ratio at the same Pu(III) concentrations. [b] Rate ratio corrected to the same free $SO_4^=$ and oxygen concentrations.

For our purposes, the rates should be compared not at the same stoichiometric concentrations of the reactants but at the same concentrations of the reactive intermediates. Since $PuSO_4^+$ and $Pu(SO_4)_2^-$ are believed to be the reactive intermediates, the possibility that their association quotients are different in the two solvents was considered. Preliminary spectrophotometric determinations of the association quotient of $CeSO_4^+$ in D_2O indicate that the association quotient is the same, within 10%, in H_2O and D_2O solutions. This lack of effect probably applies to the Pu(III)–$SO_4^=$ complexes as well.

In general a hydrogen isotope effect usually depends on the strength of the bonds to hydrogen both in the reactants and the activated complex, and a large range of rate ratios has been observed.[7] In comparing rates in H_2O and D_2O solutions the solvent effect cannot be ignored since it may give rise to rate ratios as large as 1.4.[8] Thus a rather large rate ratio is necessary if it is to be considered as evidence for hydrogen atom transfer.[9] The rather small rate ratio of 1.23 found for the oxidation of Pu(III) does not support a mechanism involving transfer of a hydrogen atom, but instead supports an electron transfer mechanism.

(6) C. K. Rule and V. K. LaMer, *ibid.*, **60**, 1974 (1938).

(7) K. B. Wiberg, *Chem. Revs.*, **55**, 713 (1955).

(8) H. Taube, personal communication, has reported that the Cl-atom transfer reaction

$$Cr(NH_3)_5Cl^{++} + Cr^{*++} = Cr^{++} + 5NH_3 + Cr^*Cl^{++}$$

is 1.4 times faster in H_2O than in D_2O solutions.

(9) For example, J. Hudis and R. W. Dodson, *J. Am. Chem. Soc*, **78**, 911 (1956), found the rate ratio to be 2 for the Fe(II)–Fe(III) exchange in H_2O and D_2O solutions, and considered this to support a H-atom transfer mechanism.

DECOMPOSITION STUDY OF CONCENTRATED HYDROGEN PEROXIDE

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Many investigations have been made on the liquid phase decomposition of H_2O_2. Practically all of this early work was done in dilute solution and on catalytic decomposition of H_2O_2. The kinetics of decomposition of very concentrated H_2O_2 has received little attention. Our primary objective was to study the homogeneous thermal decomposition in the concentration range of 100% H_2O_2 and arrive at a reasonable mechanism for the decomposition. After considerable effort to keep the experiments dust-free and make quartz surfaces catalytically inactive it was found that homogeneous decomposition was still not achieved. Because of this result the work was not continued beyond the first stages of a kinetic study.

Experimental

Spherical ampules of fused quartz having a capacity of about one ml. and weighing about 0.4 g. were constructed from selected quartz tubing which previously had been cleaned by the procedure recommended by Schumb.[1] The upper end of the ampule was drawn out into a thin capillary tube about 5 cm. in length with an inside diameter of 5–10 mils. The end was bent into a hook and left open. When this vessel was half filled it gave a surface to volume ratio of 4.83 cm.$^{-1}$. This ratio was about the same relative to the wetted surface of the vessel as well as the non-wetted surface, and does not include the liquid–gas interface. A small hook was attached to the bottom of the ampule so that it could be inverted for filling in a special apparatus. After filling about one-half full of sample the ampule was suspended on a calibrated quartz helix in a dry 25 mm. i.d. glass well. The weight loss of sample was measured by observing the change in helix length. The assembly was thermostated at the desired temperature inside a dry well immersed in an oil-bath (Corning cylindrical jar 12″ deep No. 870). *The length of the helix was observed through the* walls of the bath and well with a Gaertner model M-901 cathetometer. In order to reduce errors due to aberrations in the glass surfaces a flat vertical strip was ground and polished on the outside of the bath jar for a viewing window. Aberrations on the inner surfaces were effectively eliminated by choosing a bath fluid having nearly the same refractive index as Pyrex glass (White paraffin oil, 1.475^{20}). The tubing selected for the well had no appreciable optical aberrations.

Purification of Hydrogen Peroxide Solutions.—Hydrogen peroxide used in this work was purified by repeated recrystallization of concentrated 97.85% stabilizer-free material obtained from Buffalo Electric Co.[2,3] The material was handled in all quartz glassware under dust-free conditions. The quartz vessels were cleaned and conditioned before use by the previously mentioned procedure of Schumb.[1] The hydrogen peroxide was purified by six crystallizations which were carried out in a closed system constructed in such a way that the crystals always remained in the same flask. After crystallization the material gave an analysis of 99.8% hydrogen peroxide by weight using a method of direct titration against potassium permanganate in dilute sulfuric acid solution. Analyses indicating 100.0% of hydrogen peroxide were obtained by volumetric measurement of total oxygen obtained from complete decomposition of a weighed quantity of material. Since both methods are subject to errors it was felt that the correct value probably lies somewhere between the values given. The material was

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(1) W. C. Schumb, *Ind. Eng. Chem.*, **41**, 992 (1949).

(2) O. Maass and W. H. Hatcher, *J. Am. Chem. Soc.*, **42**, 2548 (1920).

(3) D. M. Yost and H. Russell, "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1946, p. 367.