

all the solid had melted, the cooling bath was replaced and the evacuation was resumed. After all traces of air had been removed, the samples were sealed, and placed in an oil-bath, maintained at a predetermined temperature with an accuracy of $\pm 0.1^\circ$. At intervals, one ampule was removed from the oil-bath, chilled quickly and a 10-ml. sample of its contents was withdrawn and titrated.

Polymerization of Styrene—Raw Materials.—Styrene was obtained from The Dow Chemical Company and was distilled at room temperature immediately prior to use. The material boiled at 74° at 73 mm. and had d^{20}_4 0.907 and n^{20}_D 1.5468. Baker and Adamson thiophene-free reagent grade benzene from The General Chemical Division of Allied Chemical & Dye Corp. and Eastman Kodak Co. white label benzoyl peroxide of 98.8% purity were used without further purification. E. I. du Pont de Nemours & Co., Inc., reagent grade methanol was distilled over solid sodium hydroxide and the portion boiling at 64.5° (90%) was collected.

Polymerization of Styrene by Cyclohexyl Hydroperoxide.—A stock solution of cyclohexyl hydroperoxide in benzene having at least twice the final desired maximum concentration was made. This was diluted with styrene so that the final solution contained 50% by vol. of benzene-peroxide solution and 50% by vol. styrene. The peroxide concentration was checked by titration and 25-ml. samples were sealed in glass ampules as described above. The filled ampules were placed in a water-bath at $70 \pm 0.1^\circ$, removed after ninety minutes and quickly chilled. The ampules were then broken and weighed amounts of the solution were added to excess methanol. The precipitated polystyrene was allowed to settle overnight, then filtered on sintered glass crucibles, washed five times with methanol and dried at 70° to constant weight.

Rate Measurements in Benzene-Styrene.—The procedure used here was the same as in the polymerization experiment above except that only one concentration of cyclohexyl hydroperoxide was used. It was found more convenient to express the concentration as weight per cent. cyclohexyl hydroperoxide, since the polymerized styrene became quite viscous. For this reason, weighed samples of solution were used for analysis. The ampules were removed from the water-bath at various times and chilled. One weighed portion was analyzed for peroxide and the polystyrene precipitated from another weighed portion. Since some of these samples were quite viscous and a great deal of polystyrene was obtained, the polystyrene was re-dissolved in benzene and re-precipitated after the first

drying and weighing. Surprisingly little occlusion was found.

Viscosity Measurements.—Approximately 0.06 base molar solutions of polystyrene were made up in benzene. These were then diluted so that at least two concentrations were available for each sample of polystyrene. Viscosity was measured at $25 \pm 0.1^\circ$ with an Ostwald viscosimeter having a flow time for benzene of 59.4 sec. The molecular weights and degrees of polymerization were then calculated using the method of Gregg and Mayo.¹³

Analytical.—The method used was similar to that described by Wheeler.¹⁴ The sample to be analyzed for peroxide was placed in a 250-ml. iodine flask. To it was added 20 ml. of 50/50 acetic acid-chloroform solution and a few pieces of Dry Ice to sweep out air. After the Dry Ice had vaporized, 2 ml. of saturated potassium iodide was added quickly, admitting as little air as possible. The flasks were shaken for ten minutes, water was added, and the solutions titrated with standard thiosulfate. Blanks usually amounted to one or two drops of 0.1 *N* thiosulfate.

Summary

1. Cyclohexyl hydroperoxide was isolated in substantial purity from the oxidation products of cyclohexane and its structure was ascertained.

2. The rate of decomposition of cyclohexyl hydroperoxide was measured in various solvents. This decomposition was found to follow a first order law at low concentrations and had an activation energy of 34 kcal. per mole. In the presence of styrene the decomposition of cyclohexyl hydroperoxide was accelerated very considerably.

3. The rate of polymerization of styrene was studied in the presence of cyclohexyl hydroperoxide. The degree of polymerization of the polymer formed as determined by viscosity measurements was found to be about three times larger than the number of styrene molecules polymerized per peroxide molecule decomposed.

(13) Gregg and Mayo, *THIS JOURNAL*, **70**, 2373 (1948).

(14) Wheeler, *Oil and Soap*, **9**, 89 (1932).

PHILADELPHIA 37, PENNSYLVANIA

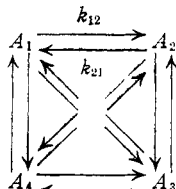
RECEIVED JANUARY 5, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND PHYSICS, THE UNIVERSITY OF TEXAS, AND TECHNICAL AND RESEARCH DIVISIONS, HUMBLE OIL AND REFINING CO.]

A General Theory of Coupled Sets of First Order Reactions

BY F. A. MATSEN AND J. L. FRANKLIN

The most general form for a coupled set of first order reactions is the one in which every component is reacting to form every other component. For four components



From the general form any simpler set may be obtained by setting certain of the rate constants equal to zero.

Application of the law of mass action to the

general *m*-component system yields the following set of rate equations

$$\dot{A}_i + \sum_{j=1}^m K_{ij} A_j = 0 \quad (i = 1, 2, \dots, m) \quad (1)$$

where $K_{ij} = -k_{ij}$ and $K_{ij} = \sum_p k_{ip}$ ($p = 1, 2, \dots, m$).

Equations of this form have been integrated by a number of authors¹ and the integral shown to be

$$A_i = \sum_{r=1}^m B_{ir} e^{-\lambda_r t}$$

(1) (a) Picard, "Traité d'Analyse," Paris, 1928; (b) Rakowski, *Z. physik. Chem.*, **67**, 321 (1907); (c) Zwolinski and Eyring, *THIS JOURNAL*, **69**, 2702 (1947); (d) Denbigh, Hicks and Page, *Trans. Faraday Soc.*, **44**, 479 (1948).

The problem is identical in form with the determination of the normal modes and frequencies of vibration of a polyatomic molecule,² and it is proposed to carry out the integration of the rate equations in the same manner.

The concentrations A_i may be considered to be components of an m dimensional vector in concentration space. A transformation to another set of coördinates, Q_r is defined as follows

$$Q_r = \sum_{i=1}^m B_{ri} A_i \quad (r = 1, 2, \dots, m) \quad (2)$$

with the inverse transformation

$$A_i = \sum_{r=1}^m B_{ir} Q_r \quad (3)$$

There are a large number of sets of coördinates which might completely describe the system. For the purposes of integration the set Q_r will be taken to be mutually orthogonal, with an orthogonality defined by the rate equations

$$\dot{Q}_r + \lambda_r Q_r = 0 \quad (4)$$

The Q_r will be called "eigenconcentrations." Integration of equation (4) yields

$$Q_r = Q_r^0 e^{-\lambda_r t} \quad (5)$$

If initially the concentrations A_i are such that all Q_r except one, Q_k , are zero, Q_k alone will describe the system for all time. Then

$$A_i = B_{ik} Q_k = B_{ik} Q_k^0 e^{-\lambda_k t} \quad (6)$$

On substitution of these expressions into the rate equations and dropping the dummy index, k , there is obtained the following set of simultaneous equations.

$$\sum_{j=1}^m (K_{ij} - \delta_{ij} \lambda) B_j = 0. \quad (i = 1, 2, \dots, m) \quad (7)$$

Applying the usual condition for a non-trivial solution for the B

$$|K_{ij} - \lambda \delta_{ij}| = 0 \quad (i, j = 1, 2, \dots, m) \quad (8)$$

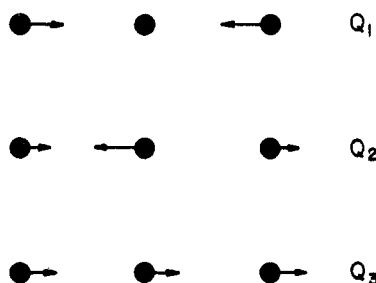
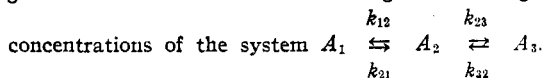


Fig. 1.—The normal coördinate analogs for the eigen-



(2) See for example Pauling and Wilson, "Introduction to Quantum Mechanics," McGraw-Hill Book Co., Inc., New York, N. Y., 1935, p. 282 ff.

there are obtained m values of $\lambda(\lambda_1 \dots \lambda_r \dots \lambda_m)$ and the above equations become

$$\sum_{j=1}^m (K_{ij} - \lambda_r \delta_{ij}) B_{jr} = 0 \quad (9)$$

which may be solved for ratios of the B_{jr} . The imposition of material balance, initial and terminal conditions determine the B_{jr} and consequently the integrals of the rate equations.

An Example.—The reaction $A_1 \xrightleftharpoons[k_{21}]{k_{12}} A_2 \xrightleftharpoons[k_{32}]{k_{23}} A_3$

will now be treated in some detail: the rate equations for this reaction are

$$\begin{aligned} \dot{A}_1 + k_{12} A_1 - k_{21} A_2 &= 0 \\ \dot{A}_2 - k_{12} A_1 + k_{21} A_2 + k_{23} A_2 - k_{32} A_3 &= 0 \\ \dot{A}_3 - k_{23} A_2 + k_{32} A_3 &= 0 \end{aligned}$$

the secular equation is then

$$\begin{vmatrix} k_{12} - \lambda & -k_{21} & 0 \\ -k_{12} & k_{21} + k_{23} - \lambda & -k_{32} \\ 0 & -k_{23} & k_{32} - \lambda \end{vmatrix} = 0$$

with roots

$$\lambda^2 - (k_{12} + k_{21} + k_{23} + k_{32})\lambda + (k_{12}k_{32} + k_{12}k_{23} + k_{32}k_{21}) = 0$$

$$\lambda_3 = 0$$

this is the result obtained by Sherwood and Reed.³

It will be of interest to complete the problem for the situation $k_{ij} = k$. Then

$$\lambda_1 = k, \lambda_2 = 3k, \lambda_3 = 0$$

The integrals become

$$\begin{aligned} A_1 &= B_{11} e^{-kt} + B_{12} e^{-3kt} + B_{13} \\ A_2 &= -2B_{12} e^{-3kt} + B_{13} \\ A_3 &= -B_{11} e^{-kt} + B_{12} e^{-3kt} + B_{13} \end{aligned}$$

and the eigenconcentrations are

$$\begin{aligned} Q_1 &= (1/2B_{11})(A_1 - A_3) \\ Q_2 &= (1/6B_{12})(A_1 - 2A_2 + A_3) \\ Q_3 &= (1/3B_{13})(A_1 + A_2 + A_3) + \text{constant} \end{aligned}$$

Q_3 is determined only to an additive constant because its eigenvalue is zero.

It may be noted that the eigenconcentrations are identical to the normal coördinates for the parallel modes of a linear triatomic molecule when concentrations are replaced by displacements along the axis of the molecule. Q_1 becomes the symmetric stretching, Q_2 the unsymmetric stretching and Q_3 the translation coördinate (see Fig. 1).

The development has been based on the assumed existence of a set of orthogonal eigenconcentrations. Thus for a system initially described by Q_i alone, all other Q 's being zero, the system will continue to be described by Q_i alone for all time, and the system will adjust itself so that Q_i decays to zero with a rate constant λ_i .

When $A_1 = A_3$, Q_1 is zero and decays to this value with a rate constant $\lambda_1 = k$ when Q_2 and

(3) T. K. Sherwood and C. E. Reed, "Applied Mathematics in Chemical Engineering," McGraw-Hill Book Co., Inc., New York, N. Y., 1939.

Q_3 are set equal to zero, *i.e.*, $A_1 + A_3 = 2A_2$ and $A_1 + A_2 + A_3 = \text{constant}$. Setting Q_2 and Q_3 equal to zero imposes the condition for the steady state for A_2 .

Similarly Q_2 decays to its zero value with a rate constant $\lambda_2 = 3k$ when Q_1 and Q_3 are set equal to zero; *i.e.*, when $A_1 = A_3$ and $A_1 + A_2 + A_3 = \text{constant}$. This is the equilibrium condition between A_1 and A_3 .

Setting Q_1 and Q_2 equal to zero imposes the complete equilibrium condition $A_1 = A_2 = A_3$ so the system remains unchanged for any value of Q_3 . Consequently, Q_3 decays with a rate constant $\lambda_3 = 0$.

Steady State.—It is intuitively obvious that a closed reaction system will eventually reach a steady or equilibrium state. The theoretical basis for this statement for coupled first order reactions is as follows: Since the sum of the elements in each column of the determinant (K_{ij}) is zero, the determinant itself is zero which guarantees a zero root to the secular equation ($K_{ij} - \lambda\delta_{ij}$) = 0. A zero root leads to a constant in the integral for each component, all other terms decaying to zero at infinite time. The eigenconcentration associated with $\lambda = 0$ is the sum of the concentrations of all components. This is the condition of conservation of mass, which is imposed by closing the system.

Some reactions reach a steady concentration with respect to one or more components before reaching a steady state for all of the components. This condition is described by setting one or more of the eigenconcentrations equal to zero. If this condition is imposed initially, the particular component will be in steady state throughout the course of the reaction. In some systems a temporary steady state for one component is reached: This, however, does not have any particular significance with respect to the eigenconcentrations.

The absence of a zero root in a particular problem does not necessarily indicate that no steady state may be formed. The solution of the secular equation is simplified if the components which do not feed back into the system are omitted from the formulation. The concentration of these components may then be obtained in an unambiguous way by a straightforward integration of the concentration expressions of their precursors. The secular equation obtained by such a simplification might contain no zero roots but a time-independent state would nevertheless be obtained.

When pseudo first order reactions are included in the reaction, the determinant (K_{ij}) is not necessarily zero. The secular equation then has no zero root and a non-steady state results. The roots may all be positive in which case all the formal components vanish at $t = \infty$. One or more of the roots may be negative in which case one or more of the components increases without

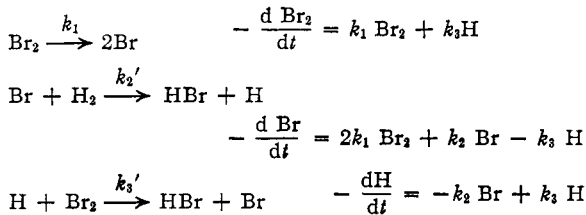
bound. Finally one of the roots may be imaginary in which case the one or more of the components oscillates. For further detail on such systems see reference 1d.

For certain first order systems the concentrations of the components may not be expressed as a sum of exponential terms, in which case the method of integration discussed above is not ap-

plicable. An example is the system $A_1 \xrightarrow{k} A_2 \xrightarrow{k} A_3$, where $A_2 = \text{constant } e^{-kt}$. This system when treated in the manner described here leads to degeneracy with $\lambda_1 = \lambda_2 = \lambda_3 = 0$, and $B_{11}/B_{21} = B_{12}/B_{22} = 0$. The latter set of equations indicates that A_1 and A_2 cannot be expressed in terms of the same set of coordinates. Further, it is not possible to form "correct zero order functions" as is done in other degenerate problems.

Applications.—The equations for several simple systems have been integrated with exact results. There do not appear to be many coupled systems which are strictly first order. Radioactive decay series come to mind but these rarely involve feed-back. If feed-back is not involved, the equations can be integrated by traditional means.

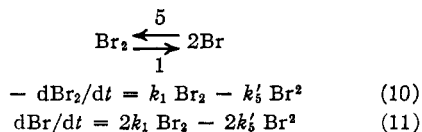
The reactions in the early stages of a self-initiating chain are all first order. For example



where $k_2 = k_2'/\text{H}_2$ and $k_3 = k_3'/\text{Br}_2$. The atom and molecule symbols represent concentrations.

However, the recombination reactions, particularly $2\text{Br} \xrightarrow{k_5'} \text{Br}_2$, quickly become important. This type of reaction cannot be handled by the method of integration proposed here unless approximations are made.

A Useful Approximation.—A coupled multi-reaction system is quite stable to small changes in rate constants. It is therefore proposed to replace a second order reaction by a first order reaction with a variable rate constant. This constant will contain a concentration term and will be evaluated by successive approximation. The formulation will be tested on a simple system for which an exact integration is possible. Since the H_2 - Br_2 reaction is to be discussed in some detail in the next section, it will be of interest to take the Br_2 dissociation as an example



by stoichiometry

$$\text{Br}_2^0 = \text{Br}_2 + \text{Br}/2$$

Upon integration of (11) between the limits 0 and Br and 0 and t for Br and t , respectively, we get

$$\frac{1}{4\text{Br}_2^0 - \text{Br}_0} \ln \frac{4\text{Br}_2^0(\text{Br}_0 + \text{Br}) - 2\text{Br}_0\text{Br}}{4\text{Br}_2^0(\text{Br}_0 - \text{Br}) - \text{Br}_0(\text{Br}_0 - \text{Br})} = \frac{k_1 t}{\text{Br}_0}$$

Br_0 and Br are small compared to Br_2^0 and so we may write

$$\frac{\text{Br}_0^2}{\text{Br}_2^0} = K = \frac{k_1}{k_5'}$$

and

$$\ln \frac{1 + \text{Br}/\text{Br}_0}{1 - \text{Br}/\text{Br}_0} = 4k_5'\text{Br}_0 t \quad (12)$$

To apply the approximation, discussed above, equations (10) and (11) are written

$$(d\text{Br}_2/dt) + k_1\text{Br}_2 - k_5\text{Br} = 0 \quad (13)$$

$$(d\text{Br}/dt) - 2k_1\text{Br}_2 + 2k_5\text{Br} = 0 \quad (14)$$

Here $k_5 = k_5'\text{Br}$, then

$$\text{Br}_2 = \frac{\text{Br}_2^0}{k_1 + 2k_5} [k_1 e^{-(k_1 + 2k_5)t} + 2k_5] \quad (15)$$

$$\text{Br} = \frac{2k_1\text{Br}_2^0}{k_1 + 2k_5} [1 - e^{-(k_1 + 2k_5)t}] \quad (16)$$

The two forms give almost identical results for Br (see Fig. 2) and Br_2 , the approximate form approaching equilibrium more slowly. The approximate form gives $\text{Br}_2 = \text{Br}_2^0$ at $t = 0$ and to a very close approximation at $t = \infty$ and values very slightly less than Br_2^0 at intermediate times. In preparing Fig. 2, a Br_2^0 of 2.24×10^{-6} mole/cc. was assumed and k_5 was replaced by $k_5'\text{Br}$ and the equation solved for t at various values of Br (or Br_2). It appears possible, therefore, to replace second order expressions by equivalent first order expressions with variable rate constants in certain cases. It is obvious that the equation should be studied with some care before the approximation is used.

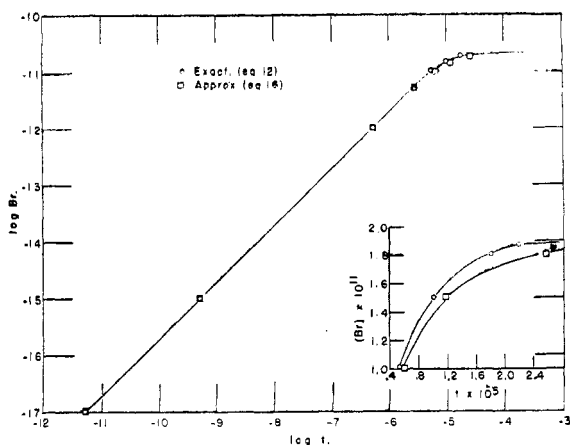
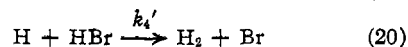
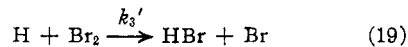
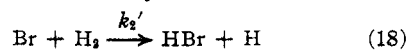
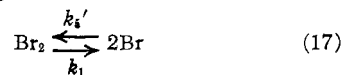


Fig. 2.

The H_2 - Br_2 Reaction.—The following mechanism has been shown to account for the rate of reaction of hydrogen and bromine



In the early stages the HBr concentration is small and equation 20 may be neglected. The H_2 and Br_2 are substantially constant and may be incorporated in the corresponding rate constants. In addition, k_5 is set equal to $k_5'\text{Br}$. The rate equations can then be integrated as above and the concentrations of bromine and hydrogen atoms expressed as functions of time. At $t = \infty$ there are obtained the steady state concentrations

$$\text{Br} = \sqrt{\frac{k_1\text{Br}_2}{k_5'}} \quad \text{and} \quad \text{H} = \frac{k_2'\text{H}_2}{k_3'} \sqrt{\frac{k_1}{k_5'\text{Br}_2}}$$

These are identical with the values obtained by the conventional steady state treatment for HBr = 0. It is felt that this identity of results strengthens the steady state concept.

In Fig. 3 are plotted the calculated values for the concentrations of hydrogen and bromine atoms making use of the constants tabulated by Hirschfelder, Henkel and Spaulding.⁴ It will be

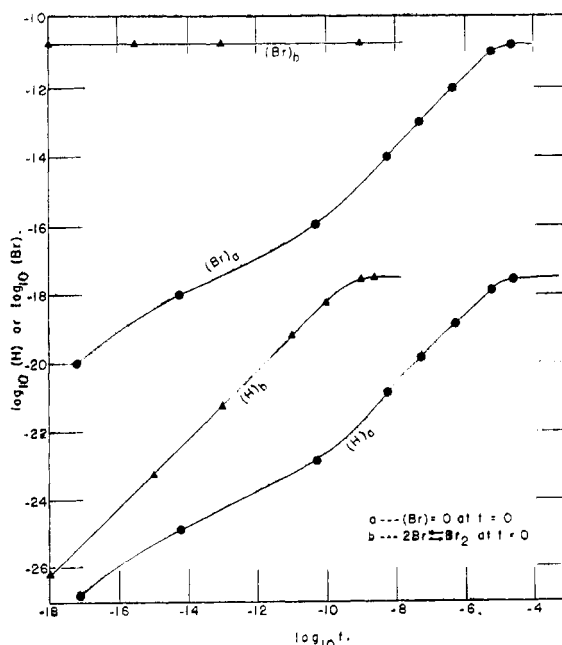


Fig. 3.

(4) Hirschfelder, Henkel and Spaulding, "Equations for Hydrogen-Bromine Flame Propagation," University of Wisconsin, Naval Research Laboratory, Report CF 1112; temperature 574.4°K.; $k_1 = 4.5 \times 10^{-2}$; $k_2 = 3.06 \times 10^2$; $k_3 = 1.95 \times 10^3$; $k_4 = 2.9 \times 10^{10}$ Br; $\text{Br}_2 = \text{H}_2 = 2.24 \times 10^{-6}$ mole/cc.

noted that steady state is reached in 10^{-5} and 10^{-9} second for an initial concentration of bromine atoms equal to zero and $\sqrt{k_1\text{Br}_2/k_5}$, respectively.

Summary

The rate equations for a coupled set of first order reactions are integrated by a method similar

to that used in the determination of the normal coordinates of vibration of molecules.

The equations for the $\text{H}_2\text{-Br}_2$ reaction are integrated approximately. The steady condition for H atoms and Br atoms is predicted as well as their respective steady state concentrations.

AUSTIN, TEXAS
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RECEIVED OCTOBER 31, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Some Chemical and Physical Properties of Uranium Peroxide

BY GEORGE W. WATT, SIEGRIED L. ACHORN AND JACK L. MARLEY

In the course of certain studies in progress in these laboratories we have accumulated considerable data relative to the solid product that results from the action of hydrogen peroxide upon aqueous solutions of uranyl salts and which has been designated as a peroxyhydrate of uranium (VI) oxide,¹ as peruranic acid,² but more commonly as uranium peroxide.³⁻⁷ Since further studies on this product are not planned, it seems worthwhile to record certain of the experimental data which we have obtained. The present studies are concerned primarily with conditions favorable to complete precipitation of uranium as a peroxide, and with the nature of the reaction between uranium peroxide and sulfites.

Experimental

Materials.—All of the chemicals used in this work were reagent grade. The uranium salts taken as starting materials consisted of uranyl nitrate 6-hydrate (Baker and Adamson) and the 2-hydrate prepared by drying the 6-hydrate *in vacuo* over concentrated sulfuric acid.

Anal. Calcd. for $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$: U, 47.4. Found: U, 47.6. Calcd. for $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$: U, 55.4. Found: U, 55.3.

Preparation of Uranium Peroxide 2-Hydrate.—A solution (100 ml.) which was 0.1 M in uranyl nitrate and 0.1 M in nitric acid was heated to ca. 90°, stirred, and treated dropwise with 15 ml. of 10% hydrogen peroxide solution (*i. e.*, a quantity insufficient to precipitate all of the uranium as the peroxide). The resulting light yellow precipitate (hereafter designated product A) was digested for one hour at 90°, centrifuged, and washed free of nitrate ion with distilled water. Although different conditions of drying were employed (*e. g.*, air-drying, drying over calcium chloride at atmospheric pressure, drying *in vacuo* over concentrated sulfuric acid, and drying in an oven at 110°), the final product in all cases was the 2-hydrate. All attempts to effect further dehydration at more elevated temperatures led to partial or complete conversion to uranium(VI) oxide.

(1) Hüttig and Schröder, *Z. anorg. allgem. Chem.*, **121**, 243 (1922).
(2) Sievert and Müller, *ibid.*, **173**, 297 (1928).

(3) Fairley, *J. Chem. Soc.*, **31**, 127 (1877).

(4) Alibegoff, *Ann.*, **233**, 117 (1886).

(5) Melikoff and Pissarjewsky, *Z. anorg. allgem. Chem.*, **18**, 59 (1898).

(6) Pissarjewsky, *J. Russ. Phys.-Chem. Soc.*, **35**, 42 (1903).

(7) Rosenheim and Daehr, *Z. anorg. allgem. Chem.*, **181**, 177 (1929).

Anal. Calcd. for $\text{UO}_4 \cdot 2\text{H}_2\text{O}$: U, 70.4; peroxidic oxygen, 9.4. Found: U, 69.8; peroxidic oxygen,⁸ 9.3.

Uranium peroxide 2-hydrate was also formed by adding, with stirring, 25 ml. of 0.1 M uranyl nitrate solution to an excess (20 ml.) of 10% hydrogen peroxide solution previously made 0.1 M in nitric acid and warmed to 40–50°. This precipitate (product B) was subsequently treated as described above except that it was digested at room temperature. It appeared to be less dense and somewhat more intensely colored than product A.

Anal. Calcd. for $\text{UO}_4 \cdot 2\text{H}_2\text{O}$: U, 70.4; peroxidic oxygen, 9.4. Found: U, 70.5; peroxidic oxygen, 9.0.

In view of the apparent difference between the product formed with uranium in excess and that produced with hydrogen peroxide in excess, electron projection and diffraction patterns were obtained⁹ using an RCA Type EMU-1 electron microscope and standard techniques of mounting and recording.¹⁰ The diffraction patterns establish the identity of the uranium-uranium distance in the crystals of the two products, and this suggests that the differences readily apparent in the projection patterns (product A: distinct cubes; product B: largely clusters of fine needle-like crystals) reflect only a difference in crystal habit. From numerous projection patterns, it appears that the clusters of crystals present in product B are in no case obtained exclusively and it is therefore not known whether they contribute to the diffraction process.

TABLE I

ELECTRON DIFFRACTION MAXIMA FOR URANIUM PEROXIDE

<i>d</i> , Å.	Product A		<i>d</i> , Å.	Product B	
		Rel. intensity			Rel. intensity
5.13	Strong		5.21	Strong	
4.29	Weak		4.29	Weak	
3.84	Medium		3.84	Medium	
3.47	Strong		3.47	Strong	
3.20	Medium		3.20	Medium	
2.64	Weak		2.66	Weak	
2.42	Weak		2.36	Weak	
2.07	Medium		2.07	Medium	
1.92	Strong		1.93	Strong	
1.74	Weak		1.75	Weak	
1.63	Weak		1.62	Weak	
1.48	Weak		1.48	Weak	
1.34	Weak		1.34	Weak	

(8) Determined by titration with standard potassium permanganate solution following acidification with dilute sulfuric acid.

(9) The assistance of Mr. L. L. Antes is gratefully acknowledged.

(10) Zworykin, *et al.*, "Electron Optics and the Electron Microscope," John Wiley and Sons, Inc., New York, N. Y., 1945.