dilutions, $K_{sp} = m_0^2 = (0.01942)^2 = 3.77 \times 10^{-4}$. Using this value for K_{sp} and the solubility data in potassium nitrate solutions, the activity coefficients of potassium metaperiodate in potassium nitrate solutions may be calculated from the relation

$$\gamma = \sqrt{K_{sp}/[IO_4^-][K^+]}$$

The values for the activity coefficients are collected in Table III, and shown graphically in Fig. 2.

It should be noted that within our experimental error, the γ values in potassium nitrate solutions having concentrations higher than 0.2 m are the same as the γ values for potassium nitrate of the same total molality.

Our values for the solubility of potassium metaperiodate is 0.02248 molal compared to Hill's value of 0.0223. The other values recorded in Seidell[6] and in the "International Critical Tables[7]" at 13° are over 20% higher and are certainly in error. Pederson's[3] value at 18° of 0.01618 mole liter is a much more reasonable value.

Summary

The solubility of potassium metaperiodate in water and in aqueous solutions of lithium nitrate, sodium chloride and potassium nitrate have been determined at 25° up to ionic strengths of approximately one.

The activity coefficients of potassium metaperiodate have been computed for the saturated solution in water and the various salt solutions.

The activity product has been calculated.

[6] Seidell. "Solubilities of Inorganic and Metal Organic Compounds." p. 825.

[7] "International Critical Tables." Vol. 4, p. 239.

BLOOMINGTON, INDIANA RECEIVED NOVEMBER 7, 1946

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Reactions of the Hydroxyl Radical[1]

BY W. H. RODEBUSH, C. R. KEIZER, FRANCES S. MCKEE AND J. V. QUAGLIANO

Numerous investigators[2-5] have studied the reactions of the products of the glow discharge in water vapor. It is agreed that the principal dissociation products are hydrogen atoms and hydroxyl radicals. If the products of the discharge are conducted immediately into a liquid air trap considerable yields of hydrogen peroxide are obtained. If Dry Ice is substituted for liquid air no hydrogen peroxide is obtained and frequently very little water is condensed. Attempts to measure the concentration of the hydroxyl radical in the vapor from the discharge by spectroscopic or other means have always indicated that the hydroxyl radicals disappear rapidly by some sort of reaction (presumably a homogeneous one) but it has not been clear just what this reaction or reactions might be.

Recently we have had occasion to repeat some of these experiments in this Laboratory and it appears worthwhile to report some additional results which were obtained and the conclusions which may be drawn from them.

Experimental

The glow discharge operates at a much lower voltage in water vapor than in hydrogen (1000 volts at 60 cycles will maintain a good discharge in a 30-mm. tube, 2 meters in length). As is well known, the actual voltage drop varies only slightly with the length of tube but markedly with the diameter. So far as yield of hydrogen peroxide is concerned the optimum conditions appear to be a pressure of 0.1–0.2 mm. of water vapor in the discharge tube with as rapid a throughput as possible under the low pressure conditions.

Arrangement of Condensation Traps.—The prime factor in the variation of products and yields of the reaction is the arrangement and temperature of the condensation traps. Three different arrangements were studied.

A. A liquid-air cooled trap was placed in the closest possible position adjacent to the discharge tube.

B. The trap in arrangement A was cooled with Dry Ice and a second trap cooled with liquid air was placed immediately behind it.

C. The liquid air trap in arrangement A was moved to a distance of 1 meter from the discharge tube with a connecting tube of 25 mm. diameter.

In every case careful tests were made by means of additional traps to prove that products were not passing through the traps because of too rapid flow.

Products of the Reaction.—The products and yield obtained from the glow discharge vary greatly with the location and temperature of the condensation traps. If the discharge products are pumped rapidly through a liquid air trap placed in the closest possible position to the discharge (A) the maximum yield of peroxide is obtained. The condensate will show on analysis more than 60% hydrogen peroxide the remainder, of course, being water. Furthermore, practically all of the oxygen which entered the discharge tube as water is recovered in the form of water or hydrogen peroxide.

If Dry Ice is substituted for the liquid air as a cooling agent, arrangement B, no peroxide and only a small amount of water is collected. If a second trap cooled with liquid is placed beyond the Dry Ice trap no hydrogen peroxide and very little water is condensed.

Finally, if the products of the discharge are conducted through a meter length of tube and then into a liquid air no peroxide and practically no water is condensed in the trap.

Interpretation of Experimental Results.—The results obtained with the various arrangements described above can be accounted for if one makes the following postulates.

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[1] This article is based upon work performed for the Office of Scientific Research and Development under Contract OEMsr 1452.

[2] K. F. Bonhoeffer and T. G. Pearson, *Z. physik. Chem.*, **B14**, (1931).

[3] W. H. Rodebush and R. W. Campbell, *J. Chem. Phys.*, **4**, 293 (1936).

[4] A. A. Frost and O. Oldenberg, *ibid.*, **4**, 642 (1936).

[5] W. V. Smith, *ibid.*, **11**, 110 (1943).

I. The dissociation of water is nearly complete. Any undissociated water vapor escaping from the discharge tube would be condensed in the traps even when cooled with Dry Ice. Since very small amounts of water were condensed with arrangements B and C this conclusion is confirmed.

II. The products of dissociation are almost entirely hydrogen and hydroxyl. With a very intense discharge the hydroxyl radical can be dissociated but with a discharge of moderate intensity no atomic oxygen spectrum is obtained. It is known from previous work in this Laboratory that when oxygen atoms are produced in the discharge a considerable loss of oxygen as molecular oxygen takes place. When arrangement A was used practically all of the oxygen originally in the water vapor is recovered in the form of water or hydrogen peroxide. This fact also excludes the possibility of hydrogen peroxide decomposition.

III. The primary step in the formation of hydrogen peroxide is the condensation of hydroxyl radicals on the walls of the liquid air cooled trap. Hydrogen and hydroxyl radicals will be present in equal numbers in the gas entering the trap in arrangement A. If the hydroxyl radicals are immediately condensed on the cold walls, one may assume equal probability for the reactions

$$H + OH \longrightarrow H_2O \qquad (1)$$

$$OH + OH \longrightarrow H_2O_2 \qquad (2)$$

in which a hydroxyl radical already condensed on the trap wall reacts with the first radical which collides with it, either the hydrogen or hydroxyl. If the water vapor is 100% dissociated and one assumes reactions (1) and (2) equally probable one estimates a yield of 65% hydrogen peroxide. As was stated above yields of more than 60% hydrogen peroxide were readily obtained. This percentage is on the basis of the condensate in the trap but it should be remembered that practically all the water entering the discharge tube is recovered either as hydrogen peroxide or water in the trap.

As a matter of fact, one need not assume that reactions (1) and (2) are equally probable. There is a competing reaction

$$H + H \longrightarrow H_2 \qquad (3)$$

This reaction probably takes place at such a rate on the walls of the trap as to reduce the concentration of hydrogen atoms and favor reaction (2) above. The fact that bubbles of gas (which must be molecular hydrogen) are seen to form when the condensate in the liquid trap is warmed to near the melting point, confirms the conclusions.

The failure to obtain any hydrogen peroxide when the trap is cooled with Dry Ice is easily accounted for. The condensation point of hydroxyl radicals will be low since they do not form an associated condensed phase. This condensation point will be nearer that of hydrogen chloride than hydrogen peroxide for example. Actually because of the smaller molecular weight the condensation point will be below that for hydrogen chloride and hence liquid air cooling will be required to remove hydroxyl radicals from a gas stream.

IV. In the gas phase hydroxyl radicals disappear by the over-all reaction

$$OH + OH \longrightarrow H_2 + O_2 \qquad (4)$$

The results obtained with arrangements B and C make this conclusion inescapable. There is no direct evidence as to the character and mechanism of this reaction except that it must be rapid since the yield of hydrogen peroxide is rapidly reduced as the liquid air trap is removed away from the discharge tube and becomes negligibly small at a separation of one meter. The time required for the dissociation products to travel the distance is very short and the only reaction likely to be rapid enough to account for the disappearance would be a homogeneous mechanism. Hence we may conclude that the reaction (4) takes place as it is written.

The Reaction of Hydrogen Atoms with Molecular Oxygen

In the foregoing discussion, no account was taken of the reaction mechanism

$$H + O_2 \longrightarrow HO_2 \qquad (5)$$

This is presumably the initial step in the formation of hydrogen peroxide which always takes place when hydrogen atoms are introduced into molecular oxygen. In the mercury-sensitized photochemical reaction, nearly 100% conversion of hydrogen atoms to hydrogen peroxide can be obtained.

Since this reaction takes place readily at relatively high temperatures ($> 40°$), the fact that hydrogen peroxide is formed only by immediate condensation in a liquid-air trap indicates that the mechanism (5) is not involved. There is, of course, little or no molecular oxygen formed when arrangement A is used.

With arrangement C, there must be an opportunity for the reaction (5) to take place but, presumably, the collision efficiency of this reaction is low so that at these low pressures the amount of peroxide formed is too small to be detected.

The Disappearance of Hydroxyl Radicals

The disappearance of hydroxyl radicals in the discharge has been the subject of numerous spectroscopic investigations. As a result of their studies Bonhoeffer and Pearson[2] suggested that the disappearance was due to the reaction

$$OH + OH \longrightarrow H_2O + O$$

but this conclusion was shown to be untenable by Rodebush and Wahl.[6] Later Oldenburg and Frost[4] suggested a termolecular homogeneous mechanism but did not attempt to specify exactly what the reaction is.

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(6) W. H. Rodebush and M. H. Wahl, *J. Chem. Phys.*, **1** 696 (1933).

In previous discussions it has been assumed that the reaction

$$OH + OH \longrightarrow H_2 + O_2$$

would have too high a heat of activation to take place. The argument for this is somewhat involved but starts with the fact that no reaction is observed between hydrogen and oxygen at room temperatures. Possible reactions are

$$\begin{aligned} H_2 + O_2 &\longrightarrow H_2O + O && (6)\\ &\longrightarrow OH + OH && (7)\\ &\longrightarrow H_2O_2 && (8) \end{aligned}$$

One may believe that the heats of activation for reactions (6) and (8) are high but these reactions are also inherently improbable and do not concern us here.

Reaction (7), on the other hand, is probably endothermic by 20 kcal. or more so that the failure to observe any reaction between hydrogen and oxygen is not surprising. If the heat of dissociation of the hydroxyl radical is less than 100 kcal. the heat of activation for the reverse reaction may be very small indeed.

There is no direct determination of the heat of dissociation of hydroxyl but the recent work of Dwyer and Oldenberg[7] gives the heat of the reaction

$$H_2O = H + OH, \ \Delta H = 118 \text{ kcal.}$$

When this datum is combined with the heat of formation of water, we obtain 100 cal. as the heat of dissociation of hydroxyl. In the opinion of the authors, this is an upper limit for the value. The oxygen–hydrogen bond in water has 110 kcal. as its dissociation energy. The loss of one electron could easily reduce the bond strength by 20 kcal. or more.

There is no implication in the foregoing as to the mechanism of the reaction (4) but there are good reasons for assuming that it is a homogeneous reaction. The walls of the apparatus are rendered inactive toward hydrogen atoms by an absorbed layer of water vapor. The recombination of hydrogen atoms has been shown to be due to triple collisions under these conditions. There is no reason, as has been pointed out earlier, to assume that hydroxyl radicals would condense on the walls or that the walls would exert any catalytic activity.

Summary

The formation of hydrogen peroxide from the products of the glow discharge in water vapor is a heterogeneous reaction.

Hydroxyl radicals react rapidly in the vapor phase to form molecular hydrogen and oxygen. This indicates that the heat of dissociation for hydroxyl may be 100 kcal. or less.

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[7] R. J. Dwyer and O. Oldenberg, *J. Chem. Phys.*, **12**, 351 (1944).

[CONTRIBUTION FROM THE NEWARK COLLEGE OF ENGINEERING, NEWARK, N. J.]

A New Equation of State for Gases

BY JOSEPH JOFFE

A new equation of state for gases is proposed in which all the constants are determined from the values of the critical pressure and critical temperature. The equation may be written in generalized form and may be regarded as an analytical expression of the law of corresponding states. This equation differs from generalized equations which have recently been proposed[1,2] in that no fitting of experimental data is required to obtain the values of the constants in the equation.

It is assumed that the equation of the critical isothermal is

$$p = RT/(V - b) - a/V(V - b) + c/V(V - b)^2 - d/V(V - b)^3 + e/V(V - b)^4 \quad (1)$$

The equation is seen to be of the fifth degree in the volume. In this respect it differs from the equations of van der Waals, Clausius, and Berthelot which are of the third degree in the volume, and from the equation of A. Wohl[3] which is of the fourth degree. To obtain the values of the constants the condition is imposed that this fifth degree equation in the volume have five equal roots at the critical point. This leads to the relations

$$\begin{aligned} RT_c &= bp_c + 5p_c(V_c - b)\\ a &= RT_cb + 10p_c(V_c - b)^2\\ c &= 10p_c(V_c - b)^3\\ d &= 5p_c(V_c - b)^4\\ e &= p_c(V_c - b)^5 \end{aligned} \qquad (2)$$

Any one of the constants in this set of equations may be assigned an arbitrary value whereupon the values of the other constants and of the critical ratio RT_c/p_cV_c are fixed. It was decided to arbitrarily assign a value to the constant b. Comparison of calculations with experimental data demonstrated that the value $b = V_c/4$, appearing in Berthelot's and Wohl's equations, is more satisfactory than either the van der Waals value $b = V_c/3$, or the Dieterici value $b = V_c/2$, in connection with equation (1) and (2). Substituting $b = V_c/4$ in (2) the following equations are obtained

$$\begin{aligned} RT_c &= 4p_cV_c\\ a &= 53p_cV_c^2/8\\ c &= 270\ p_cV_c^3/64\\ d &= 405p_cV_c^4/256\\ e &= 243p_cV_c^5/1024 \end{aligned} \qquad (3)$$

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[1] S. H. Maron and D. Turnbull, THIS JOURNAL, **64**, 2195 (1942).

[2] G. J. Su and C. H. Chang, *ibid.*, **68**, 1080 (1946).

[3] A. Wohl, *Z. physik. Chem.*, **87** 1 (1914); **99**, 207, 226, 234 (1921).