efficients. The agreement hitherto found with Ostwald's dilution law, for weak electrolytes and for the lower concentrations of "transition" electrolytes, has been found to be due to a compensation of two effects. Arrhenius' method for computing degrees of dissociation yields too low values, and the activity coefficients have been tacitly assumed to be unity, whereas at all low concentrations such coefficients are less than one.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE LABORATORIES OF GENERAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

PROMOTER ACTION IN HOMOGENEOUS CATALYSIS. III. COBALT SALTS AS PROMOTERS IN THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE BY POTASSIUM DICHROMATE

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In a previous study,[3] wherein hydrogen peroxide was decomposed catalytically by cupric and ferric salts, the cause for the "promotion" effect was demonstrated to be due to the formation of cupric acid by the intermediate compound of this catalysis (ferric acid). The mechanism of promotion was provisionally defined as a change in the path of the catalytic reactions, with a concomitant displacement of the region of the steady state. It was felt that other systems should be studied in order to test this hypothesis more fully. Since no other promoters had been found for the system using ferric salts as a catalyst, a new system was sought. This was found in the catalytic decomposition of hydrogen peroxide by potassium dichromate.

This reaction has been known for some time. As a product of this reaction, there are distinguished two different perchromic acids. The blue perchromic acid has been studied more than the red, probably due to its use in analysis. However, it will not be considered here, since whenever it is formed there is reduction of chromium and the reaction is no longer catalytic.

Schönbein[4] considered the brown color formed when potassium dichromate was added to a hydrogen peroxide solution to be a chromium chromate. Berthelot[5] also held this view, but in addition showed that the reaction is catalytic in character. This was done by means of a calorimetric study, which showed that the heat of the catalytic reaction is 20.8 Calories. The heat of formation of hydrogen peroxide is —21.6 Calories,

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[1] Du Pont Fellow.

[2] Part of a thesis submitted to the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[3] Robertson, THIS JOURNAL, **47**, 1300 (1925).

[4] Schönbein, *J. prakt. Chem.*, **80**, 257 (1860).

[5] Berthelot, *Compt. rend.*, **108**, 24 (1889).

a practically identical value. In addition, Berthelot showed that a given amount of the dichromate decomposed an unlimited amount of the hydrogen peroxide and that there was no reduced chromium present when the concentration of the solution was about 0.0625 *N*. Later, Riesenfeld[6] confirmed the fact that the reaction was catalytic, as did Spitalsky.[7]

This last investigator studied the effect of potassium chromate-dichromate mixtures upon hydrogen peroxide and reported that the chromate was less active than the dichromate and that there was no simple mathematical relation to explain the effect of catalytic mixtures containing these salts. Sometime later, Riesenfeld[8] repeated this work and reported that the effect was the sum of the individual effects.

In preliminary investigations it was found that the reaction was indeed catalytic and gave good unimolecular constants under the conditions which were to be used in the promotion studies. The concentration of hydrogen peroxide was 0.190 *M* and that of the dichromate from 0.25 to 0.75 millimolar. After making the correction for temperature differences, the values obtained checked those of Spitalsky very closely.

The nature of the intermediate is not known definitely, but Schönbeins' chromium chromate seems improbable. Later and more exact work treats almost exclusively of the blue compound formed when acid is present—possibly because of the analytic importance of this substance. However, Riesenfeld's[6] work indicates that there is formed in ammoniacal solution a red salt of the formula $(NH_4)_3CrO_8$, which decomposes in alkaline or neutral solutions giving off oxygen with no reduction of chromium to the tervalent state. For the present, an analogous compound will be assumed to be the intermediate. Nearly all investigators upon the perchromates assume that the chromium in this compound has a valence of seven and not six. In this way it differs from other "per" salts in which the central elements are supposed not to possess a higher valence than the maximum fixed by their position in the periodic classification.[9]

Experimental Methods

The technique of experimentation was practically that followed in the research upon ferric salts, being a gasometric method. Considerably more care was exercised in preparing the reaction flasks, since the solutions were presumably neutral. The flasks were subjected to prolonged steaming in order to remove surface alkali. Another difference

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[6] Riesenfeld, Wohlers and Kutsch, *Ber.*, **38,** 1888 (1905).

[7] Spitalsky, *Z. anorg. Chem.*, **53,** 184 (1907).

[8] Riesenfeld, *ibid.*, **74,** 48 (1912).

[9] This point may be regarded as debatable. It is proposed to determine with Dr. D. M. Yost the valence not only in perchromates but in ferrates, pervanadates and cupric acid, by the method of x-ray absorption used by Lindh [*Compt. rend.*, **172,** 1176 (1921)] and others.

was the concentration of hydrogen peroxide, which was 190 millimolar instead of about 130.

When promoters were used the constants of the reaction were invariably calculated by the graphic method. By using a special plotting board 60 by 75 cm. this was found to be moderately rapid. The use of this method detected anomalies in the system where manganese chloride was used as the promoter, and made it possible to study this system thoroughly. This work will be published later.

The potassium dichromate used as the catalyst was prepared by recrystallizing some of the commercial c. p. product thrice and heating to 150°. A stock solution was prepared, 1 cc. of which was equivalent to 2 millimoles per liter in the reaction flask after dilution in the usual manner; since one-half millimole was the usual concentration, a second stock solution was prepared which gave a concentration of 0.05 millimole per liter. Little trouble was anticipated upon the score of a change in the concentration of the catalyst solutions, a stand that was justified since runs made at the end of the study gave constants which agreed well with those of the first few determinations.

Promotion by Cobalt Chloride

It had been found in preliminary experiments that salts of cobalt, copper, nickel, manganese and cerium, among others, promote the catalytic de-

TABLE I

EFFECT OF COBALT CHLORIDE UPON CATALYSIS OF POTASSIUM DICHROMATE

Concn. of $K_2Cr_2O_7$ Millimole per liter	Concn. of $CoCl_2$ Millimoles per liter	K_R	P. F.	"D"
0.25	0	55	1.00	104 (99)
	1	82	1.49	55 (50)
	5	99	1.80	24 (19)
	10	102	1.85	19 (14)
	20	109	1.98	6 (1)
	40	112	2.04	0 ...
0.50	0	110	1.00	78
	0.1	123	1.12	66
	1	151	1.37	41
	5	184	1.67	11
	10	194	1.76	2
	15	196	1.78	0
0.75	0	154	1.00	84
	0.1	174	1.13	71
	1	203	1.31	53
	5	245	1.59	25
	10	259	1.68	16
	20	284	1.84	0
0.50	10 Ni	134	1.22	
.00	50 Ni	1.8	..	
.00	10 Co	2.5	..	

composition of hydrogen peroxide by potassium dichromate. Cobalt was used for the most extensive work, since its salts do not hydrolyze quite so much as those of copper or manganese. The chloride was chosen because experience has shown that sulfates are very complex both in behavior and constitution.

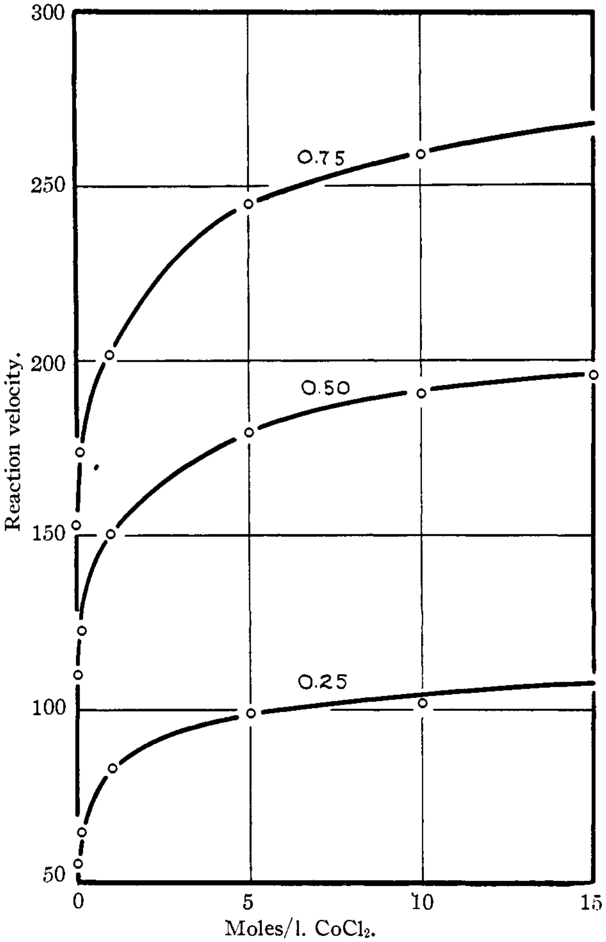

Fig. 1.—Effect of cobalt chloride upon the catalytic decomposition of hydrogen peroxide by potassium dichromate.

A sample of c. p. cobalt chloride was purified by recrystallization from water. The operation was thrice repeated, the last time at a low temperature, since it was found that otherwise some anhydrous blue salt was present. The required amount of the salt was weighed out to give a solution of which 1 cc. represented one millimole per liter. Experiments were run with concentrations of the dichromate of 0.25, 0.50 and 0.75

millimole per liter, without promoter and with various amounts of cobalt chloride. The cobalt chloride was found to be a moderately good promoter, but not so efficacious as the copper as in the case of the ferric salt catalysis. The results of these experiments are shown in Table I and Fig. 1. Several experiments were run with nickel chloride, which is a promoter of the same order as the cobalt, but the work was not investigated further due to the lack of time. A study of this system might be of interest because of the reported isomerism of the higher oxides of nickel.

Discussion of the Promotion Curves

It will be noticed that the curves showing the reaction rate as a function of the amount of added cobalt chloride are smooth with a gradually decreasing slope. They apparently approach a maximum at a decreasing rate and resemble exponential curves where the fractional change is proportional to successive added amounts of promoter. An approximate relationship is obtained when the reaction rate is plotted against the logarithm of the concentration of the promoter. A straight line is obtained which is useful for comparing results and extrapolation. A more exact equation has been developed,[10] but in order to test this relationship it is necessary to know the maximum promoted rate. The log. concn.—reaction rate graph is useful for this purpose.

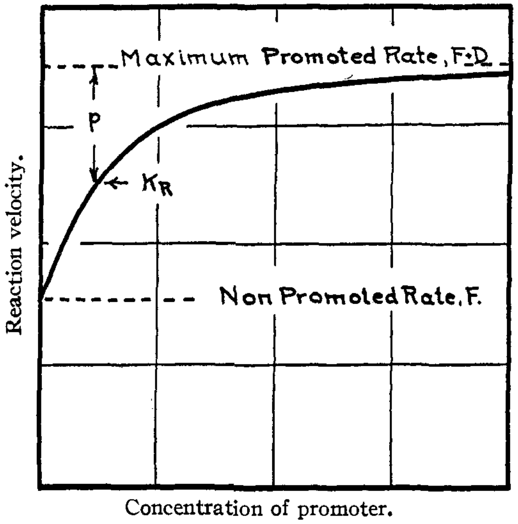

Fig. 2.

The explanation of the relationship shown in the equation is very interesting. The conception of activation has been abandoned since experience has shown that it is non-productive and actually misleading. As an analogy to the copper-iron system, the idea presented itself that there probably was the formation of a more highly oxidized compound of cobalt, which is more rapidly auto-reduced by hydrogen peroxide (though less rapidly formed) than the perchromic acid. The application of this idea

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[10] There is another relationship which is felt to be more nearly true but it cannot be easily expressed by a single equation. This relationship will be described in a later paper upon negative catalysis and promoter action with respect to the Steady State.

is best shown by reference to Fig. 2. The rate of the unpromoted reaction is given by F, that of the promoted reaction by F plus D where D is the difference between the rates of reduction of the first and second intermediates as the steady state. For any concentration of the promoter the rate of reaction differs from complete promotion by the amount p. As more promoter is added the amount of p changing is proportional to the amount left unchanged; $-\mathrm{d}p/\mathrm{d}P = k'p$, $-\mathrm{d}p/p = k'\mathrm{d}P$, $-\log p = k'P$; or $p = Ke^{-Pk}$, where in this case D may be set equal to K and the reaction rate expressed in the form, $K_R = F + D - De^{-Pk} = F + D(1 - e^{-Pk})$. F and D may be given in the form of "promotion factors" for convenience in comparing the results of promotion in different systems.

Formation of Cobaltous Acid and the Mechanism of the Reaction

McConnell and Hanes describe the formation of a monohydrated cobalt peroxide, H_2CoO_3, which they call cobaltous acid, by the action of hydrogen peroxide upon cobaltous hydroxide. It is soluble, giving a colorless solution, though solutions of its salts are said to be green. These investigators[11] noted that this substance reacts rapidly with an excess of hydrogen peroxide, though they do not make it clear whether they consider the effect to be purely catalytic, which their equation would indicate, or one of autoreduction. The latter by analogy with the reactions of copper peroxide seems more logical to the writer.[12]

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[11] McConnell and Hanes, *J. Chem. Soc.*, **71**, 584 (1897).

[12] The existence of this compound will be assumed for the purpose of this article, for while the composition of the second intermediate is interesting, it is not vital to the argument. Experiments seeking to prove the composition of this substance have been inconclusive and will be pursued further, together with a study of the chemistry of higher valenced cobalt. This field at present is in a most chaotic condition and the literature is very unreliable. Tervalent cobalt has been found to auto-reduce hydrogen peroxide, but its compounds are nearly impossible to prepare in the pure state, hence its presence has not been determined. A solution of cobaltic sulfate in sulfuric acid is easily prepared and is relatively stable. Its properties were investigated, but the use of this solution in spectrographic studies is rendered questionable, since it seems to the writer that the substance might be a cobaltisulfuric acid analogous to ferrisulfuric acid and have a different absorption of light for that reason. Marshall [*J. Chem. Soc.*, **59**, 760 (1891)] has noted that the alum is far more stable than the cobaltic sulfate alone, and a similar condition may exist here.

However reasonable it is to assume the presence of tervalent cobalt, there is good reason for believing that cobalt with a valence higher than three exists in the reaction mixture. Experiments to be described later show unmistakably that the cobalt produces an acid-forming compound in the promotion reaction. Now, the chemistry of tervalent cobalt is essentially that of a basic element; hence, it is reasonable to assume the presence of some acid-forming higher oxide of cobalt.

Some other higher oxides of cobalt are described in the literature. Since they are insoluble in water and are not formed by hydrogen peroxide, they will not be considered further. A critical review of several papers leads one to think that the product obtained by the action of hypo-iodites and similar reagents upon solutions of cobaltous

The formation of cobaltous acid from the hydroxide probably goes to completion.

$$H_2O_2 + Co(OH)_2 \longrightarrow H_2CoO_3 + H_2O \qquad (1)$$

Where the acid is made from cobalt chloride, the reaction is possibly an equilibrium reaction

$$H_2O_2 + CoCl_2 + H_2O \rightleftharpoons H_2CoO_3 + 2HCl \qquad (2)$$

but both reduction reactions go to completion.

$$H_2CoO_3 + H_2O_2 \longrightarrow Co(OH)_2 + H_2O + O_2 \qquad (3)$$

$$H_2CoO_3 + H_2O_2 + 2HCl \longrightarrow CoCl_2 + 3H_2O + O_2 \qquad (4)$$

Another reaction may accompany the latter

$$H_2CoO_3 + 2HCl \longrightarrow CoCl_2 + 2H_2O + \tfrac{1}{2}O_2 \qquad (5)$$

since the cobaltous acid is unstable in acid solution.

Reactions 2 and 4 together constitute the "catalytic pair" for the decomposition of hydrogen peroxide by cobalt chloride. This is quite a slow reaction, the constant being in the order of 2 for a concentration of 10 millimoles per liter of cobalt chloride.

The reactions for the catalytic decomposition of hydrogen peroxide by the dichromate are written thus:

$$K_2Cr_2O_7 + H_2O_2 \longrightarrow 2KCrO_4 + H_2O \qquad (6)$$

$$2KCrO_4 + H_2O_2 \longrightarrow K_2Cr_2O_7 + H_2O + O_2 \qquad (7)$$

not because the formula $KCrO_4$ represents the composition of the perchromic acid, but because it indicates that the intermediate possesses a higher valence than six.

One would suppose that if a more active oxidizing agent than hydrogen peroxide were used—such as perchromic acid, let us say—the cobalt chloride would be oxidized to cobaltous acid more rapidly than otherwise. The reaction could proceed in the sense of the following reaction,

$$2KCrO_4 + CoCl_2 + 2H_2O \longrightarrow H_2CoO_3 + K_2Cr_2O_7 + 2HCl \qquad (8)$$

with the regeneration of potassium dichromate as one of the reaction products. The cobaltous acid thus produced is rapidly auto-reduced by the hydrogen peroxide, as indicated by Reaction 4, the dichromate forms more intermediate, and so the reactions proceed, the catalytic decomposition as a whole being increased by virtue of this change in path.

The promotion effect may, therefore, be explained as before upon the basis of a change in the path of the reaction. If it is assumed that Reaction 8 is "instantaneous," or a great deal more rapid than Reactions 2, 4, 6 or 7, it is evident that the promoted reaction may be considered as following the path of Reactions 6 and 4 instead of Reactions 6 and 7. Reaction 4 is more rapid than 7 and hence the rate as a whole is increased.

The quantitative consequences of this idea have been developed. The

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salts leads to the formation of insoluble cobaltous cobaltite, which adsorbs the alkali cobaltites and not only removes them largely from solution, but increases the "available oxygen" in the precipitate.

results of the experiments are shown in Table I and Fig. 3. There is a deviation from the straight line which should result, which may be due to the fact that Reaction 8 is so slow that its reaction time is not negligible in comparison with the others.[13] It must be mentioned that in this logarithmic plot the small differences for larger concentrations of promoter are near the limit of experimental error and are greatly exaggerated. For instance, the series for 0.25 millimole of potassium dichromate gives far better results when a maximum promotion factor of 199 is used instead of 204.

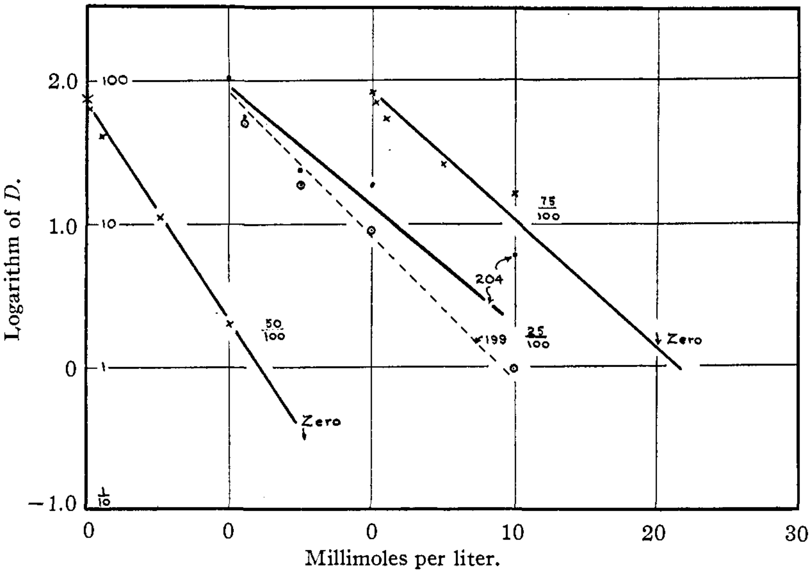

Fig. 3.—Concentration of added $CoCl_2$.

So far the proof follows closely that of a former article[14] and the question of promoter action and the steady state can be considered in an exactly analogous manner which will be apparent by reference to Fig. 5 of that paper.

Effect of Hydrogen Ion Upon the Promotion and the Mechanism of the Promoted Reaction

Due to some peculiarities of this reaction, it was possible to show in another way that the change in the course of the reaction was the cause of the promotion effect. Reaction 4 indicates that acid is necessary during the course of the "reduction" reaction of the catalytic pair for cobalt.

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[13] The results of previous researches upon the promoting effect of copper upon iron salts give good results when thus treated. In that case the reaction analogous to (8) is presumably very fast in comparison with the others.

[14] Ref. 3, pp. 1302, 1309.

This fact suggested that it would be interesting to try the effect of buffer solutions upon the catalytic solutions. The most practical buffer is the sodium acetate-acetic acid mixture. The choice is limited to this because of the range desired and the fact that many other buffer solutions would precipitate the cobalt used as the promoter. Accordingly some non-promoted reactions were carried on in the presence of 100 millimolar sodium acetate and 10 millimolar acetic acid. The reaction velocity was higher than in presumably neutral solutions, being 185 instead of 110. When five millimoles per liter of cobalt was added, the reaction rate was altered very little indeed. A typical log. concn.-time graph is shown in Fig. 4. Instead of being a straight line of about 65% greater slope, that being the promotion factor in the absence of the buffer, it is of the same slope as the non-promoted reaction for the greater part of its course, is nearly coincident and then deviates slightly. This last effect is not easily explained, but probably is due to decomposition of the cobaltous acid with the formation of partially dehydrated cobalt hydroxide or even Co_2O_3, which causes the reaction to be heterogeneous and autocatalytic. When the buffer consists of 100 millimoles sodium acetate and 100 millimoles acetic acid this autocatalytic effect is not apparent, which fact lends support to the idea that the solution is heterogeneous and the solid phase is basic and separates because the solution is not sufficiently acid. In this more acid solution, promotion exhibits itself. However, there is reduction of chromium and it is not practical to study this region further. This autocatalytic effect is most pronounced when sodium acetate is used alone, the solution then being slightly basic. A curve for that condition is also shown in the figure.

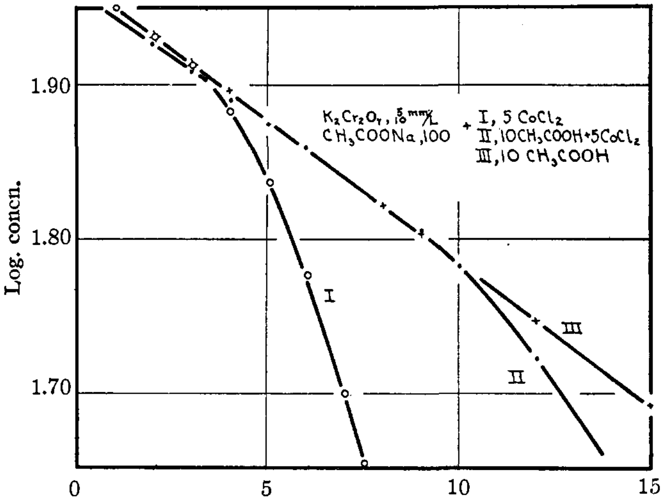

Fig. 4.

From this it may again be concluded that in the promotion here considered, Reaction 4 is the cause of the increase in total reaction rate. A preliminary value of the necessary hydrogen-ion concentration lies between 2.4×10^{-5} and 1.7×10^{-6} equivalent per liter (0.02 and 0.002 millimole per liter), or *P*H 4.6 and *P*H 5.8. It would thus seem that promotion may again be explained upon the basis of a change in the path of reaction. The non-promoted reaction follows the cycle of Reactions 6 and 7, while the promotion effect is due to the cycle through Reactions 6, 8 and 4.

Spectrographic Studies

This hypothesis concerning the change in path is supported by studies of absorption spectra of promoted and non-promoted reactions. The determinations were made with a Gaertner spectrometer equipped with a dense prism and calibrated by the flame spectra of compounds having suitable wave lengths. A Tungsarc lamp was used as a source of light for a Nutting photometer made by Hilger. The results are plotted with Bunsen's extinction coefficients as ordinates against the wave length in Ångström units as abscissas.

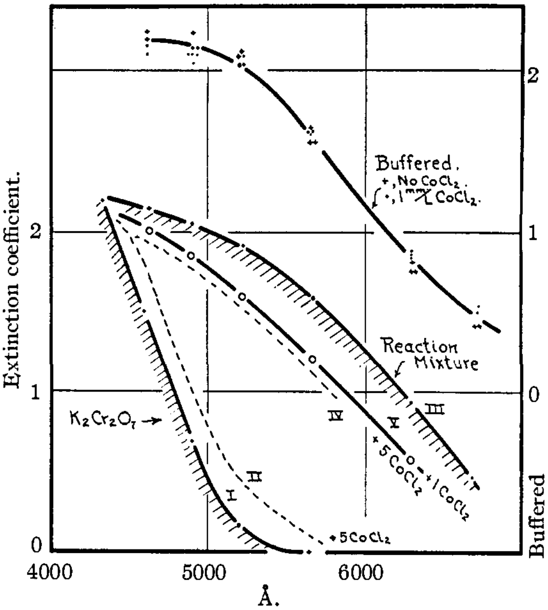

Fig. 5.

Curve I in Fig. 5 shows the absorption due to solutions of potassium dichromate. This is identical with the same solution containing buffer mixtures of one millimole per liter of cobalt chloride. The presence of more cobalt is apparent, as in Curve II, which represents a solution containing 5 millimoles per liter. Upon the addition of hydrogen peroxide to the dichromate solutions the absorption increases as shown in Curve III. However, if cobalt is present Curves IV and V illustrate the results. It is apparent that less of the "first intermediate" is present in the promoted reactions. Indeed, measurements indicate that for one millimole per liter of added cobalt about 30% is removed, the extinction coefficient being roughly proportional to the concentration of the intermediate as shown by separate experiments not recorded here.

In a buffered solution containing 100 millimoles of sodium acetate and 10 millimoles of acetic acid per liter, which shows no promotion in kinetic experiments, there was no change in the concentration of the first intermediate as indicated by the absorption spectrum measurements. This fact confirms the view that Reaction 4 is the basis of the promotion effect. Studies made upon the cobalt-rich portion of the system are so far inconclusive in identifying the second intermediate for reasons noted before, but are being continued in hope of success. By an extension of this method, absolute values may yet be obtained for the amount of hydrogen peroxide going through the more rapid reactions.

The major portion of this work was done at the University of Wisconsin with Professor J. H. Walton, whom the writer wishes to thank for his kindly help and interest in the problem. The material was arranged for publication and the spectrographic studies were made while the author was at the California Institute of Technology as a National Research Fellow.

Summary

1. Promotion has been studied in the catalytic decomposition of hydrogen peroxide by potassium dichromate. Cobalt chloride was used in this study, though salts of copper, nickel, manganese and cerium among others will show this effect.

2. The promotion is an exponential function of the amount of cobalt chloride added.

3. This fact has been explained upon the basis of a change in the path of the catalytic reaction. Oxidation of the cobalt is indicated by a decrease in the concentration of perchromic acid in the promoted reactions. It is not yet possible to say whether the cobalt is in the ter- or quadrivalent form during the promotion.

4. A definite hydrogen-ion concentration is necessary for promotion in this system, as is shown by studies of absorption spectra and by kinetic measurements. This fact is in agreement with the mechanism adopted to explain the promotion.

PASADENA, CALIFORNIA