Kilpatrick and Rushton's experiments in which the viscosity of the acid solution was changed by adding cane sugar are also in error. This is shown in Table III.

TABLE III

SOLUTION RATE OF MAGNESIUM CYLINDER 2.04 CM. IN DIAMETER, 2.50 CM. LONG, IN 500 CC. OF 0.02725 *M* ACETIC ACID AT 25°

R. p. m.	*k* (no sugar)	*k'* (0.6 *M* sugar)	*k'* calcd. (= 0.55*k*)
1200	0.448	0.264	0.246
		.259	
1000	.378	.230	.207
	.378	.220	
600	.273	.150	.150
300	.179	.103	.099

Kilpatrick and Rushton, in interpreting their work with magnesium, have disregarded a fundamental law of kinetics, namely, that the observed rate of a reaction must be that of the slowest reaction which occurs. Since in this case transport of acid to the magnesium surface is the slowest process, rate measurements give no indication whatever of the mechanism of the chemical process.

In conclusion, the author wishes to acknowledge his obligation to Professor Henri Mouquin and to Mr. Aaron Spector, whose critical discussions have been of great assistance in preparing this paper.

Summary

Recent experimental studies of fluid motion near a solid surface have made it possible to compare semi-quantitatively the convective transport of fluid toward the surface with the solution rates of magnesium and zinc in acids, under identical conditions. The conclusion is reached that diffusion constitutes the last step in transport of acid to the metal surface.

It is shown that two of the original postulates of the Nernst "diffusion layer" theory of solution rates are untenable but unnecessary in the application of the theory. A rational modification of the Nernst theory is shown to be necessitated by hydrodynamics in the case of a limited number of systems.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Detection and Colorimetric Estimation of Micro Quantities of Bromide

BY V. A. STENGER AND I. M. KOLTHOFF

The reaction of bromide and a suitable oxidizing agent with fluorescein, giving rise to the formation of eosin, has been employed[1] for the colorimetric determination of small quantities of bromide in the presence of chloride. In a study of other indicators for the purpose we have found that phenol red has distinct advantages over fluorescein. They are (1) that it serves also as indicator in the adjustment of the *p*H of the liquid, (2) that the color change is more pronounced and (3) that amounts of bromide from 1 to 18 micrograms can be determined with greater relative accuracy.

Phenol red, with a color change from yellow to red over the *p*H interval 6.4–8.0, reacts with very dilute hypobromite in weakly alkaline solution to form an indicator of the brom phenol blue type, which changes from yellow to blue-violet over the *p*H range 3.2–4.6. We have found that the oxidation of bromide and the bromination of phenol red take place readily with the use of calcium hypochlorite in a borax buffer at *p*H 8.7–8.8. In the absence of bromide very small amounts of chlor phenol red are formed, with a *p*H range 5.0–6.6. By making the color comparison at a *p*H of 5.0–5.4, all the unbrominated phenol red and any trace of chlor phenol red will be in the yellow form, whereas the brominated compound will be reddish to violet depending upon its concentration. Thus, a sharp differentiation may be made between varying amounts of bromide originally present. With a given amount of phenol red, the violet color will have its maximum intensity when four atoms of bromide are available for each molecule of indicator, indicating that tetrabromphenolsulfophthalein is formed.

Reagents

Calcium Hypochlorite.—"H. T. H." from the Mathieson Alkali Works, New York, was extracted with water and

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(1) H. Baubigny, *Compt. rend.*, **125**, 654 (1897); F. L. Hahn, *ibid.*, **197**, 245 (1933). See also R. Lorenz, E. Bergheimer and E. Grau, *Z. anorg. allgem. Chem.*, **136**, 90 (1924); M. A. Labat, *Bull. soc. chim.*, [4] **9**, 393 (1911); A. V. Pavlinova, *Chem. Abstr.*, **25**, 2076 (1931).

the filtrate made to about 0.1 *N* oxidizing strength, determined iodimetrically by titration with standard thiosulfate. The concentration may vary by at least 10% without affecting the results appreciably. The solution was diluted as needed, 0.01 *N* hypochlorite being less stable.

Phenol Red.—Ten mg. of a good commercial product dissolved in 1 cc. 0.1 *N* sodium hydroxide and diluted to 100 cc.

Borax Buffer.—A solution saturated with sodium tetraborate at approximately 25°. A sample of commercial borax was found to contain 0.0004% bromide, this being completely removed by one recrystallization.

Acetate Buffer.—A solution containing 30 cc. of C. P. glacial acetic acid and 68 g. of sodium acetate trihydrate per liter. It should have a *p*H of 4.6–4.7, but need not be free from bromide.

Sodium Arsenite.—An approximately 0.1 *N* solution of commercial sodium arsenite. It should be practically neutral but need not be bromide free. Several other reducing agents, such as hydrogen peroxide, are equally useful for destroying the excess hypochlorite.

Sodium Nitrite.—A commercial product twice recrystallized, used in about 0.5 *M* solution.

Potassium Bromide.—A solution containing 14.9 mg. of C. P. potassium bromide per liter was used as a standard, 0.10 cc. being equivalent to 1.0 microgram of bromide.

Other reagents used were of C. P. quality, and redistilled water was employed throughout.

Preliminary Neutralization of the Sample.—If the sample is not neutral, add enough phenol red so that the proper amount indicated in the procedure will be present in the final test volume, and adjust with hydrochloric or sulfuric acid and sodium or potassium hydroxide just to the yellow color, being careful that no excess of acid is present. The base used should be nearly carbonate-free or else carbon dioxide should be boiled out of the slightly acid solution, as it may interfere with the buffer action. If buffer compounds such as phosphates are present, separate experiments will be necessary to determine the amounts of acid and base needed to obtain a *p*H of 8.8 during the oxidation and 5.4 during the color comparison. In any case, careful blanks must be made with the same amounts of all reagents, since traces of bromide may be introduced. It is essential that unknowns and standards have the same *p*H at the time of comparison.

Procedure.—For 0–4 micrograms of bromide. To 1.0 cc. of neutral sample in a 5-cc. vial add 0.05 cc. of phenol red and 0.20 cc. of borax solution. Add 0.20 cc. of 0.01 *N* hypochlorite and allow to stand for exactly four minutes with occasional shaking; then add 0.05 cc. of 0.1 *N* sodium arsenite followed by 0.20 cc. of acetate buffer, and compare with standards prepared in the same way. The color obtained will be yellow with less than 1 microgram of bromide, reddish from 1.5 to 2, and blue violet above 2.5. One can estimate the amount of bromide present with an accuracy of 15–20%. The test should not be made in direct sunlight.

For 3–18 micrograms of bromide. Observe exactly the same procedure with the following quantities: 10-cc. sample in a 20–25 cc. vial, 0.20 cc. of phenol red, 2.0 cc. of borax, 0.20 cc. of 0.1 *N* hypochlorite, 0.50 cc. of arsenite and 1.50 cc. of acetate buffer. An accuracy of about 10% is attainable. Amounts of bromide over 18 micrograms give nearly a constant color unless more than 30 micrograms is present; with larger amounts the indicator is attacked and fades. Therefore, if over 16 micrograms is indicated, the test should be repeated with a more dilute sample. Standards prepared in this way fade slightly after a few days; consequently a permanent set can be used only to indicate the approximate bromide concentration.

For the detection of smaller amounts of bromide a spot test may be made with 0.10-cc. sample, 0.02 cc. each of phenol red, borax and 0.01 *N* hypochlorite, 0.01 cc. of arsenite and 0.05 cc. of acetate buffer. By comparing within five minutes one may distinguish between 0, 0.2, 0.4, 0.6, 0.8, 1.0 and 1.5 micrograms. The standards change rapidly due to evaporation.

Interfering Compounds.—Reducing agents, including ammonium salts, interfere by reacting with hypochlorite. Their removal or oxidation will usually be quite simple, by evaporation and ignition of an alkaline solution of the sample. Iodide interferes by behaving qualitatively the same as bromide, as is also the case in the fluorescein method. It may be removed by boiling with sodium nitrite in dilute acid solution. The following procedure is convenient for samples containing 10 to 35 micrograms of bromide, and modification will be apparent for other amounts.

To 10–15 cc. of solution in a 50-cc. Erlenmeyer flask add for every 60 mg. of iodine expected 2 cc. of 1 *N* sulfuric acid and 1 cc. of 0.5 *M* sodium nitrite. Boil gently while shaking the flask until the solution becomes colorless, then wash the sides of the flask with water to replace that lost by evaporation and add a few more drops of acid and nitrite. If a color appears more should be added and the boiling repeated. When the solution finally remains colorless, boil two minutes longer, wash the sides of the flask and cool. Add 0.5 cc. of phenol red, adjust the *p*H as above and dilute to 25 cc. Pipet 10 cc. into a vial and proceed with the determination, the solution already containing the proper amount of indicator.

Using bromide-free potassium iodide prepared by reduction of resublimed iodine with hydrogen sulfide and crystallization from potassium hydroxide solution, we have found that the above procedure will remove the iodide quantitatively from as much as 200 mg., and have been able easily to detect 0.003% of bromide added to pure iodide. It is advisable to treat standards by the same procedure since traces of bromide may be present in the acid, base or nitrite employed. A sample of Mallinckrodt Analytical Reagent potassium iodide, labelled to contain 0.01% Cl + Br, calculated as Cl, was found in this way to contain less than 0.002% of bromine.

Chlorides do not interfere in any amount and the method is very suitable for the detection and determination of traces of bromide in commercial chlorides, even of analytical grade.

Summary

Phenol red upon treatment with hypochlorite in the presence of small amounts of bromide forms brom phenol blue. Procedures have been developed for the determination of 0.2 to 1.5

micrograms of bromide in 0.1 cc. of solution, 1 to 4 micrograms in 1.0 cc., and 3–18 micrograms in 10 cc. Chlorides do not interfere, while iodides may be removed with nitrite and acid. Reducing agents must be removed or oxidized.

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[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES]

The Role of Methyl and Methylene Radicals in the Decomposition of Methane[1]

BY LOUIS S. KASSEL[2]

The rate of thermal decomposition of methane in the absence of appreciable hydrogen is controlled by a unimolecular process with an activation energy of 79,000 cal. When hydrogen is present the reaction is very strongly retarded, and with sufficient hydrogen the rate can be represented as $k(CH_4)^2/(H_2)^3$.[3] These results were shown to agree well with the mechanism

$$\begin{aligned} CH_4 &= CH_2 + H_2 & (1)\\ CH_2 + CH_4 &= C_2H_6 & (2)\\ C_2H_6 &= C_2H_4 + H_2 & (3)\\ C_2H_4 &= C_2H_2 + H_2 & (4)\\ C_2H_2 &= 2C + H_2 & (5) \end{aligned}$$

which gives the rate equation

$$-\,d(CH_4)/dt = 2\,\frac{k_1k_2k_3k_4k_5(CH_4)^2 - r_1r_2r_3r_4r_5(H_2)^4}{r_1r_2r_3r_4(H_2)^3 + r_1r_2r_3k_5(H_2)^2 + r_1(r_2 + r_3)k_4k_5(H_2) + k_2k_3k_4k_5(CH_4)}$$

where k and r refer to the forward and reverse reaction, respectively. Important support for this scheme was furnished by the experiments of Storch,[4] which definitely established the sequence of products $C_2H_6 \longrightarrow C_2H_4 \longrightarrow C_2H_2 \longrightarrow C$. Subsequently Belchetz[5] reported confirmation of the production of methylene by flowing methane at 0.1 mm. pressure past a heated platinum filament and then over iodine or tellurium mirrors at a distance of 3 mm. from the filament. With tellurium mirrors a product was obtained which reacted with bromine to give CH_2Br_2; this product could not have been $Te_2(CH_3)_2$, which would have been formed from methyl groups, but could have been $TeCH_2$ or a polymer thereof. With iodine mirrors, CH_2I_2 was formed, and at filament temperatures above 1423°K., HI as well. These experiments thus seemed to indicate that the primary decomposition of methane produces methylene and no atomic hydrogen, and hence must be

$$CH_4 = CH_2 + H_2$$

These results and this conclusion have been attacked recently by Rice and Dooley,[6] who passed methane through a heated quartz tube and over mirrors of tellurium or antimony at a minimum distance of 1 cm. from the furnace. With tellurium mirrors they obtained $Te_2(CH_3)_2$, and no trace of the bright red, nonvolatile $(TeCH_2)_x$ which Rice and Glasebrook[7] found when similar experiments were made with diazomethane at furnace temperatures up to 600°. Rice and Dooley conclude that since the tellurium product of Belchetz was obviously not the $(TeCH_2)_x$ of Rice and Glasebrook, it was not any form of $TeCH_2$, and suggest that it was sublimed Te. Ignoring the CH_2Br_2 produced from Belchetz's product, and the CH_2I_2 he obtained with iodine mirrors, they reject reaction (1) and propose $CH_4 = CH_3 + H$ in spite of their own failure to find any atomic hydrogen. Further unpublished work of Rice[8] casts doubt upon the correctness of Belchetz's analytical results; this work did not include a repetition of Belchetz's experiments.

It is not the purpose of this discussion to reconcile these conflicting experiments, though it may be in order to point out that the temperature gradient in the arrangement of Belchetz was far steeper than that of Rice and Glasebrook and that this, or some other technical difference, may have led to different polymers of $TeCH_2$ in the two cases. Whatever radicals may be detectable, however, it does not appear possible to account for the observed kinetics of methane decomposition by a mechanism which involves methyl radicals. Attention is confined

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(3) Kassel, THIS JOURNAL, **54**, 3949 (1932).

(4) Storch, *ibid.*, **54**, 4188 (1932).

(5) Belchetz, *Trans. Faraday Soc.*, **30**, 170 (1934).

(6) Rice and Dooley, THIS JOURNAL, **56**, 2747 (1934).

(7) Rice and Glasebrook, *ibid.*, **56**, 2381 (1934).

(8) Rice, private communication.