balance was found. This may be due to the formation of methane which was not determined in these experiments. One milligram of methane per minute would have accounted for the largest discrepancies found. The formation of methane is not believed to have interfered with the oxidation measurements because, first, the observed rates of oxidation were the same at any temperature, regardless of the value of the ratio $H_2/(CO + 2CO_2)$ in the products, and, second, the concentrations of the products of reaction in the effluent gases were so small that the reaction between them must have been small by comparison with the reaction between hydrogen and the graphite with which it was in contact when it was formed.

Values of the heat of activation, which agree fairly well with those observed both for the steam and for the carbon dioxide oxidation reactions with graphite, may be calculated according to the principles enunciated by Hinshelwood.[2] The calculation involves the assumption that heats of adsorption found at room temperatures are valid at high temperatures. It also requires the assumption of mechanisms of reaction which may be subjected to experimental verification. The mere agreement of the experimental values of the heat of activation with such calculated values is not sufficient evidence for the acceptance of the assumptions, so detailed discussion of the mechanism of reaction will be deferred.

Summary

The rate of oxidation of graphite by steam has been measured under such conditions that the rate determining effect of diffusion has been eliminated. At about 745 mm. vapor pressure, the rate of gasification of carbon in micromoles per square cm. per second, in the high temperature range, from 1000 to 1160°, is given by

$$\log G_1 = 6.20 - (35{,}130/4.575\,T)$$

and in the low temperature range, from 850 to 1000°, by

$$\log G_2 = 8.42 - (49{,}720/4.575\,T)$$

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(2) C. N. Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," 3d ed., Oxford University Press, 1933, pp. 349–355.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA AND OF THE COLLEGE OF ST. THOMAS]

Titration of Chloride and Bromide with Mercurous Nitrate Using Brom Phenol Blue as Adsorption Indicator

BY I. M. KOLTHOFF AND W. D. LARSON

Short notes on the titration of chloride and bromide with mercurous nitrate as a reagent using adsorption indicators for the detection of the end-point have been published in the literature. Burstein[1] used sodium alizarine sulfonate as indicator in the titration of bromide. Von Zombory[2] recommended brom phenol blue and brom cresol purple in the titration of chloride and bromide with mercurous nitrate or in the reverse titration. Recently von Zombory and Pollak[3] have also recommended chlor phenol red and brom cresol green for the same purpose. Each of the last four indicators remains in the yellow form in the solution when there is an excess of chloride or bromide, and is adsorbed with a lilac color when mercury is in excess. The color change is reversible; hence, if the end-point is overstepped one can back titrate with halide solution. After examination of many dyes as adsorption indicators for the various titrations, it appeared that brom phenol blue yielded the best color change, especially for titrations of chloride.

A more detailed study was made of the practical applicability of the chloride and bromide titration under varying conditions with mercurous nitrate, using brom phenol blue as adsorption indicator. The analytical results are reported in the first part of this paper, and in the second part the mechanism of the indicator action is discussed.

Materials Used

Mercurous Nitrate.—Mallinckrodt Analytical Reagent grade was used.

Potassium Chloride.—A C. P. product twice recrystallized and dried at 200°.

Potassium Bromide.—A chloride-free product was obtained by heating pure potassium bromate until all the oxygen was driven off. The resulting salt was recrystallized three times from water and dried.

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(1) R. Burstein, *Z. anorg. allgem. Chem.*, **168**, 325 (1927).

(2) L. v. Zombory, *ibid.*, **184**, 237 (1929).

(3) L. v. Zombory and L. Pollak, *ibid.*, **215**, 255 (1933).

Brom Phenol Blue.—A 0.1% solution of the monosodium salt in water.

Standard Solutions.—Solutions of potassium chloride and bromide of known concentrations were prepared by weighing out the required amounts of the pure salts and diluting in a volumetric flask.

Mercurous Nitrate Solution.—About 2 to 3 g. portions of the salt were triturated with about 50 cc. of water, and the mixture was filtered. In this way a perfectly clear solution was obtained containing no added nitric acid. The free acid content of the approximately 0.1 *N* solution of the reagent prepared in the above manner was determined after removing the mercurous mercury with an excess of potassium chloride and was found to be 0.014 *N*.

Part of a standard 0.1 *N* solution was kept in a bottle containing several drops of mercury, and the remainder was kept without mercury. The solutions were standardized after various intervals. It appeared that the solution kept without mercury slowly decreased in strength. The original 0.1 *N* solution was 0.0988 *N* after one month and 0.097 *N* after two months. After this time a white precipitate, probably of basic mercurous nitrate, had separated from the solution. The solution kept in the presence of metallic mercury did not change its titer after six months of standing. It is therefore recommended to preserve the mercurous nitrate by addition of several drops of pure mercury.

The reagent was standardized potentiometrically by titrating known volumes with standard potassium chloride and bromide solutions, and also by performing the titrations in the reverse way. A platinum gauze electrode electrolytically coated with a thin layer of mercury served as indicator electrode. In the titration with bromide, a normality of 0.1197 (average of 5 determinations) was found; with potassium chloride, a normality of 0.11975 was found. The values of the individual standardizations agreed to within 0.1%.

Accuracy of the Titration with Brom Phenol Blue as Indicator.—The end-point in the titration of 0.1 *N* chloride and bromide with mercurous nitrate using brom phenol blue as indicator (color change from yellow to lilac), and with reverse titrations (color change from lilac to yellow) is sharp within one drop. In the titration of 25 cc. of 0.1 *N* chloride with mercurous nitrate using 4 to 6 drops of indicator a normality of the latter of 0.1196 was found; in the reverse titration, of 0.1198; whereas with bromide the values were 0.1197 and 0.1196, respectively. The average value agreed within 0.1% with that found potentiometrically. The procedure therefore gives exact and precise results.

Unfortunately the method cannot be applied to the titration of very dilute chloride and bromide solutions; 0.01 *N* bromide solution could be titrated with an accuracy of 0.5% with 0.01 *N* mercurous nitrate; identical results were found in the reverse titration. A good end-point is no longer obtained in the titration of 0.005 *N* or more dilute solutions.

Mercurous chloride has less adsorbent properties than the bromide. Consequently, in titrations of or with chloride no good end-point was found if the solutions were more dilute than 0.04 *N*.

Influence of Electrolytes.—Electrolytes not reacting with mercurous nitrate are considered only. Since there is no direct method for the titration of chloride in acid medium, the effect of nitric and sulfuric acids was first studied. It was found that chloride and bromide can be titrated with the same accuracy as in neutral medium if the nitric acid concentration at the end-point is less than 0.2 *N* and the sulfuric acid concentration less than 0.1 *N*. In the presence of acid the color change is from yellow in excess of halide to gray in excess of mercury. The color change is not reversible in acid solution and therefore it is not possible to titrate a fairly strongly acid mercurous solution with chloride or bromide using brom phenol blue as indicator.

Large amounts (up to 5 g.) of potassium nitrate did not interfere with the titration of 25 cc. of 0.1 *N* chloride or bromide. Good results were also obtained with 0.5 g. of potassium sulfate, but with 1 g. of this salt the color change appeared 0.8% late. The error increased with larger amounts of sulfate. Calcium and barium nitrate did not interfere.

Copper, cadmium and zinc interfere even if present in relatively small concentration. If 1 cc. of 0.1 molar cupric nitrate solution was added to 25 cc. of 0.1 *N* chloride, the end-point appeared 1.5% late, with 2.5 cc. of copper solution, 2% late. One cc. of 1 molar zinc or cadmium nitrate added to 25 cc. of 0.1 *N* chloride did not interfere; with 1.5 cc. of these metal solutions the end-point appeared 0.6 and 0.2% late; with 2 cc., 2 and 0.6%, respectively. With 3 cc. of 1 molar zinc nitrate present no visible color change was noticed. It is possible that the interference is explained by a precipitation of the indicator by the cations mentioned. If a few drops of the zinc or cadmium solution are added to the indicator, a deep purple precipitate is formed.

The interference by the above elements is not overcome by titrating in acetic acid medium.

Aluminum does not interfere when present in fairly large quantities. Even with 10 cc. of 0.1 molar aluminum nitrate in 25 cc. of 0.1 *N* chloride the color change occurred within 0.3% of the theoretical end-point. A peculiar purplish coloration was noticed before the end-point, but the color change was still distinct. With 3 cc. of 1 molar ferric nitrate no difficulties were encountered in detecting the end-point, but with larger amounts of iron the color change became indistinct. In the latter case the interference can be overcome by the addition of potassium fluoride until no further fading of the color due to ferric ion is seen. In this way good results were obtained in the titration of a mixture of 25 cc. of 0.1 *N* chloride and 20 cc. of 1 molar ferric nitrate.

Mechanism of the Indicator Action

The classical interpretation of the indicator action as developed by Fajans[4] is that chloride ions are primarily adsorbed by the mercurous chloride as long as the former are in excess in the solution. Slightly after the end-point a primary adsorption of mercurous ions occurs with a

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[4] K. Fajans and H. Wolff, *Z. anorg. allgem. Chem.*, **137**, 221 (1929).

secondary adsorption of the indicator anions, resulting in a deformation of the latter at the surface, accompanied by the color change. Recent work done in this Laboratory has made it doubtful whether this interpretation is correct. In general, it has been found that an ion which is strongly adsorbed at the surface of an ionic lattice competes with the lattice ion of the same electrical sign for a position on the surface. If pure mercurous chloride is shaken with a solution of brom phenol blue (B. P. B.)—it may be expected that the following exchange reaction will take place at the surface of the precipitate

$$\underset{\text{surface}}{Hg_2^{++}(Cl^-)_2} + \underset{\text{solution}}{2(B.P.B^-)} \longrightarrow \underset{\text{surface (lilac)}}{Hg_2^{++}(B.P.B^-)_2} + \underset{\text{solution}}{2Cl^-}$$

If the chloride ions are in excess in the solution the surface layer will be mainly built up from mercurous chloride and only a few indicator ions have a chance to be adsorbed. At the equivalence point and especially in the presence of an excess of a slight amount of mercurous ions, the chloride ion concentration in the solution is so small that the exchange reaction at the surface can take place to a considerable extent. This exchange results in a color change. The indicator effect therefore is not to be attributed to a simultaneous adsorption of mercurous and dye ions on the surface of the precipitate, but to an exchange between chloride and dye ions on the surface. The same mechanism occurs in all other cases in which we are dealing with adsorption indicators.

It can be shown experimentally that the above exchange reaction takes place on the surface of mercurous chloride. Experiments in which well-washed mercurous chloride was shaken with brom phenol blue solutions were unsuccessful, since the freshly prepared adsorbent ages very rapidly, resulting in a large diminution of the surface. The rapidity of this aging process immediately after the formation of the precipitate is shown by the following experiments.

An equivalent amount of 0.1 *N* mercurous nitrate was added with a constant speed (from 75 to 85 seconds) to 25 cc. of 0.1 *N* potassium chloride, the latter being stirred mechanically. The age of the precipitate just after the addition of the mercurous nitrate was taken equal to zero. After a definite time of stirring, 5 cc. of 0.2% solution of the monosodium salt of brom phenol blue was added, and the mixture shaken for fifteen minutes. No change in the amount of dye adsorbed took place upon longer shaking, showing, in the first place, that adsorption equilibrium is reached within fifteen minutes, and, in the second place, that the adsorbed dye protects the precipitate from further aging.

After shaking, the mixture was diluted to 250 cc., and the excess dye was determined colorimetrically in the filtrate after addition of sodium carbonate to convert all of the dye to the alkaline form. Some experiments were also made in which the dye was added to the chloride solution before the precipitation (age of precipitate zero minutes). The results are given in Table I.

TABLE I

DECREASE OF DYE ADSORPTION WITH AGE OF MERCUROUS CHLORIDE

Age of ppt., min.	0	1	5	10	15	30
Dye adsorbed, %	38	32	24	11	5	4

In qualitative agreement with our results, Otto Hahn and Imre[5] found that the adsorption of thorium B by mercurous chloride in the presence of an excess of chloride, and by mercurous bromide in the presence of an excess of bromide, is reduced to zero very soon after the precipitations. They attribute this to a change from a polar to an apolar nature of the precipitates with consequent disappearance of active spots on which the adsorption may take place. However, the decrease in the adsorption may be more simply accounted for by the agglomeration of the particles, resulting in a diminution of the surface. Thus, if the dye was added to the fifteen-minute old mercurous chloride, the precipitate was easily filtered, while a one-minute old sample was much more difficult to filter, and part of it ran through as a highly dispersed suspension. Adsorbed dye on the surface protects the precipitate from further aging, and prevents or inhibits the formation of larger agglomerates.

In order to show that the adsorption of the dye is to be attributed to an exchange between chloride and dye ions in the surface of the mercurous chloride, the following experiments were performed. An equivalent amount of mercurous nitrate was added to 25 cc. of 0.1 *N* potassium chloride, and the potential of the mercury electrode in the mechanically stirred mixtures was measured against a saturated calomel electrode. The potential increased slightly (5 to 10 millivolts) during the first fifteen minutes after precipitation, indicating a slight desorption of mercurous ions,

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(5) O. Hahn and L. Imre, *Z. physik. Chem.*, **144**, 161 (1927).

and then became virtually constant. This is in agreement with the results in Table I, which show that the most drastic aging occurs during the first fifteen minutes after precipitation. Similar experiments were made in which 5 cc. of a 0.2% solution of the monosodium salt of brom phenol blue was added at various times after the precipitation of the mercurous chloride. Blanks were made in which 5 cc. of water instead of dye was added. In all cases it was found that after the addition of the dye the potential of the electrode became more negative, indicating an increase in the chloride ion concentration of the solution. In all cases the potential became constant after fifteen minutes of stirring. The effect of the dye upon the change of the potential became less pronounced with increasing age of the precipitate, as was to be expected, and is shown in Table II.

TABLE II

EFFECT OF DYE UPON THE POTENTIAL OF THE MERCURY ELECTRODE IN MERCUROUS CHLORIDE SUSPENSION

Age of precipitate in minutes	2	5	12
Change of e. m. f. in mv. after addn. of dye	60	40	5
Corresponding decrease in *p*Cl in soln.	1.0	0.66	0.09

These results show conclusively that the adsorption of the dye is to be attributed to an exchange reaction between chloride and dye ions on the surface of mercurous chloride. The amount of exchange decreases rapidly with increasing age of the precipitate. With a fifteen-minute old precipitate the exchange is about ten times less than with a fresh product. Naturally the amount of exchange decreases with an excess of chloride ions, and increases with an excess of mercurous ions in the solution. Experimentally this was shown to be the case by adding to a mixture of 25 cc. of 0.1 N potassium chloride and 0.5 cc. of the brom phenol blue solution 24.0, 25.0 and 26.0 cc. of 0.1 N mercurous nitrate, respectively. The amounts of dye adsorbed were 60, 71 and 100%, respectively. When the experiments were repeated with 5 cc. of the dye solution instead of 0.5 cc. the differences became much less pronounced.

Attempts have been made to repeat all experiments with mercurous bromide. Unfortunately, the freshly prepared precipitate appeared to be so finely divided that it was impossible to obtain clear filtrates or centrifugates. Measurements of the change of potential of the mercury electrode in the suspension showed again that we are dealing here with an exchange mechanism. However, the potential in the freshly prepared suspension without dye changed in an irregular way on aging, and the results obtained were not as conclusive as those with mercurous chloride.

Summary

1. Chloride and bromide in concentrations greater than 0.04 N and 0.01 N, respectively, can be titrated accurately with mercurous nitrate using brom phenol blue as adsorption indicator. It is also possible to titrate mercurous mercury with chloride or bromide.

2. The titrations can be carried out in the presence of small amounts of nitric and sulfuric acids and sulfates, large amounts of calcium, potassium, sodium, barium, aluminum, ferric iron (with fluoride). Moderate amounts of copper, zinc and cadmium interfere.

3. The preparation of a stable mercurous nitrate solution has been described.

4. Freshly precipitated mercurous chloride undergoes a very rapid aging process resulting in a large decrease of the surface by agglomeration of the particles.

5. The mechanism of the indicator action is to be attributed to an exchange reaction, and not to a secondary adsorption with mercurous ions.

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