[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Apparent Solubility Product of Chromous Hydroxide. The Significance of the Solubility Products of the Hydroxides of the Metals which Form Basic Salts[1]

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From *p*H measurements with a hydrogen electrode during the precipitation of basic chromous sulfate, Bennett[3] calculated the solubility product of chromous hydroxide as being 2×10^{-20}. As platinum black is a very active catalyst for the reaction between chromous ion and hydrogen ion, the use of such an electrode is a possible source of serious error. Further, as solubility products derived from studies on basic salts do not, as a rule, agree with those obtained from other sources, the writers felt that the results which he obtained should be checked by another method. Therefore, measurements were made with a glass electrode of both the *p*H of solutions in contact with basic chromous chloride and of solutions in contact with normal chromous hydroxide. It was found that the apparent solubility products of the two precipitates differ by a factor of about 200, the normal hydroxide being the more soluble.

Experimental

Because of the extreme sensitivity of chromous solutions to oxidation by the air, it was necessary to employ anaerobic technique throughout. The solutions were protected from air in closed systems by nitrogen which had been bubbled through chromous chloride solution to remove any traces of oxygen.

Chromous chloride stock solutions (about 0.1 *M* in chromous chloride and 0.2 *M* in hydrochloric acid) were prepared by a method which was essentially that of Balthis and Bailar.[4] These solutions, when protected from air, were quite stable, the chromous concentration changing less than 1% during a month. The presence of acetic acid or zinc could not be detected in the final product. The total chromium, chromous chromium, and total chloride concentrations were determined, permitting calculation of the chromic and hydrochloric acid concentrations. The concentration of chromic chromium in these preparations was always very small, being less than 1% of the total.

Titrations were carried out in an anaerobic titration apparatus similar to that of Crowell and Baumbach,[5] except that a glass electrode was used instead of a platinum indicator electrode. The standard half cell used was the "saturated" calomel electrode, and the measurements were made with a Beckman *p*H meter, laboratory model. The glass electrode was checked against standard biphthalate, acetate, and borax buffers. The readings were estimated to 0.01 *p*H unit and are probably reliable to within 0.02 unit.

Qualitative Experiments.—Preliminary qualitative experiments showed that gradual addition of dilute alkali hydroxide to a solution of chromous chloride resulted in the precipitation of a blue-white basic salt. Analysis of the precipitates formed in this way revealed a ratio of chromium to chlorine which varied with the concentration of the solutions and the rate of mixing during precipitation. Values of the molar ratio of chromium to chlorine of about 1.0 to 0.1 and 1.0 to 0.3 were obtained. The chloride was found to be very firmly held in the precipitate, not being removed by repeated washing. The same results were obtained using ammonia, ethylenediamine, and several aliphatic amines as the precipitating agent. In none of the latter cases were appreciable amounts of nitrogen base retained in the precipitate.

Addition of chromous chloride to an excess of alkali hydroxide resulted in the formation of a characteristic reddish-brown precipitate of normal chromous hydroxide. The product could very easily be washed free of chloride ions. When precipitated with excesses of sodium hydroxide of various concentrations, the chromous hydroxide assumed a variety of colors. This was presumably due to differences in hydration and particle size (Table I).

TABLE I

NaOH, *N*	Nature of ppt. when freshly made	Nature of ppt. after 24 hrs.
18	Orange-brown, small amounts peptized	Dark brown
12	Orange-brown, darker than above	Dark brown
6	Reddish-brown-violet, gelatinous	Dark greenish-brown
3	Violet, gelatinous	Dark greenish-brown
1	Brown, slightly violet	Dark greenish-brown
0.5	Brown	Dark brown
0.1	Brown	Dark brown

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[3] W. H. Bennett, *Trans. Faraday Soc.*, **28**, 889 (1932).

[4] J. H. Balthis and J. C. Bailar, THIS JOURNAL, **58**, 1474 (1936).

[5] W. R. Crowell and H. L. Baumbach, THIS JOURNAL, **57**, 2607 (1935).

Neither the pale blue nor the brown precipitates showed any tendency to change to the other when left standing. If sufficient acid were added to dissolve most but not all of a freshly-made brown precipitate, the product would change quickly to the blue form. Similarly, the blue precipitate would change to the brown if treated with a strong base. A slight excess of base did not do this at an appreciable rate. Both forms dissolved readily in dilute acids when freshly precipitated, but aged quickly on standing. After a few hours, they became very insoluble in acids and could no longer be changed from one to the other as just described. Each precipitate gave off hydrogen slowly when in contact with the mother liquor, but was much more stable after washing with water. Microscopic examination of each modification did not reveal any crystals.

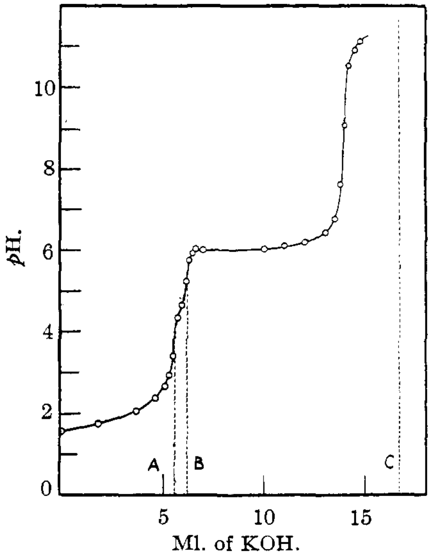

Fig. 1.—Titration of 5.09 ml. of chromous chloride solution (0.1816 M in $CrCl_2$, 0.005 M in $CrCl_3$ and 0.2060 M in HCl) with 0.1778 M KOH: A, calculated equivalence point for HCl present; B, for $CrCl_3$ present; C, for $CrCl_2$ present.

Quantitative Experiments.—Five ml. samples of the chromous chloride stock solutions were diluted to 50 ml. and titrated with 0.2 N potassium hydroxide. Inflections, agreeing well with the calculated, were obtained corresponding to the neutralization of the free hydrochloric acid and to the precipitation of the small amount of chromic chromium which was always present (Fig. 1). The equivalents of base actually needed to precipitate all the chromous chromium were always markedly less than the theoretical, the differences amounting to from 10 to 25%. The amount of base used depended on the rate of titration and the concentration of the chromous chloride.

Equilibrium was reached quickly during the neutralization of the free acid and after an excess of base had been added. While the basic salt was being precipitated, addition of base caused a rise in *p*H followed by a slow downward drift. Equilibrium was not established even after an hour's stirring, during which time the *p*H might fall as much as one unit. To obtain the curve shown, readings were taken after five minutes of stirring. By stirring the mixtures until the drift was quite slow (half an hour) it was estimated that the *p*H of precipitation of the basic salt was about 5.8 in 0.01 M solution. This corresponds to an apparent solubility product of about 5×10^{-19}, assuming the precipitate to be $Cr(OH)_2$ and using the extrapolation method of Britton.[6]

When samples of chromous chloride stock solution were added to a measured excess of standard base (forming the brown precipitate) and the excess titrated with standard acid, sharp inflections were obtained corresponding well with the calculated equivalence points assuming normal chromous hydroxide to be the product formed. The deviations were a few tenths of a per cent. On the addition of more acid, the precipitate was partly dissolved and began to be converted into the basic salt. If 10 to 20% of the acid theoretically needed to dissolve all the precipitate were added, constant and reproducible values of the *p*H of apparent equilibrium were obtained after short intervals of drifting. By assuming the acid added to have dissolved an equivalent amount of chromous hydroxide, the concentrations of chromous ion were estimated and the apparent solubility product $[K_{sp} = (Cr)(OH)^2]$ of the hydroxide calculated.

In one instance, 30.0 ml. of approximately 0.1 N potassium hydroxide was measured out into the titration apparatus under nitrogen and diluted to 49.0 ml. with oxygen-free water. Slowly and with efficient stirring, 5.00 ml. of stock chromous chloride solution (0.1358 M in chromous ion and about 0.3 M in free acid) was added and the resulting brown precipitate was stirred for about fifteen minutes after completion of the addition. The excess of base was then removed by titration with 0.09912 M hydrochloric

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[6] H. S. Britton, *J. Chem. Soc.*, **127**, 2110 (1925).

acid, a sharp break of about three pH units marking the end-point. This took place when 1.35 ml. of acid had been added. The titration was continued until a total volume of 4.00 ml. of acid had been added and the mixture was stirred until the pH became constant. This required about ten minutes, and the observed pH of 6.81 did not deviate at all during ten minutes of further stirring. At this point, the total volume of the mixture was 58.0 ml., giving a chromous ion concentration of 2.27×10^{-3} M, leading to a pK_{sp} of 17.00.

The weighted average of the values of the pK_{sp} [pCr + 2pOH] was 17.00 ± 0.02 or $K_{sp} = 1.0 \times 10^{-17}$. As the addition of acid was continued, the precipitate was converted to the basic salt and the apparent solubility product calculated in this way gradually changed to the 10^{-19} value characteristic of the basic salt.

Discussion

The application of the solubility product principle to the hydroxide of a divalent element involves the assumption that the normal hydroxide, $M(OH)_2$, is in equilibrium with its ions in the solution. A solubility product calculated from the pH of initial precipitation (the method of Britton) has no real significance if the precipitate formed is not the normal hydroxide but a basic salt having quite different properties. In some cases the solubility products calculated in such manner are not even of the same order of magnitude as those obtained in other ways. It is clear from the results of this investigation that a simple equilibrium is not established between even normal chromous hydroxide and chloride solutions. Instead there is a false equilibrium between the solution and the basic salt, and between the basic salt and the normal hydroxide. Hence, the simple solubility principle is not applicable.

If the basic salt were a definite substance, true equilibria could be established and the theoretical treatment would be simple. Nikurasin,[7] who obtained results similar to ours in a study of the precipitation of zinc sulfate with base, calculated a solubility product for the basic salt assuming it to be a definite compound having the formula $ZnSO_4 \cdot 3Zn(OH)_2$. We do not feel justified in postulating a formula for the basic chromous chloride because of the wide variation in composition with the conditions of preparation. We feel rather that it is probably a mixture of the chlorides of a number of complex heteropolybases[8] undergoing olation and oxo-formation[9] on standing in the solid state. Britton[6] has already shown that Mg^{++}, Fe^{++}, Mn^{++}, Co^{++}, Ni^{++}, Cu^{++}, and Zn^{++} form basic salts under the same conditions as Cr^{++}. Therefore solubility products calculated for the hydroxides of these and similar elements cannot be interpreted literally if the measurements are made in solutions containing other ions, although they may be useful from a practical standpoint.

Summary

From glass electrode measurements on normal chromous hydroxide, the apparent solubility product was calculated as being 1.0×10^{-17}. Measurements made upon a basic salt led to a lower value. Since there is formed a three phase mixture of normal hydroxide, basic salt and solution, the solubility product principle is not strictly applicable. This difficulty appears to be a general one with the hydroxides of the divalent elements.

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[7] A. I. Nikurasin, *J. Gen. Chem.* (*U. S. S. R.*), **8**, 1454 (1938).

[8] G. Jander and K. F. Jahr, *Kolloid Beihefte*, **43**, 295 (1936).

[9] Stiasny, *Collegium*, 265, 897 (1932).