Nernst approximation formula, but the values are certainly of the same order.

It should be noted that the largest factor in any case in determining the extent of dissociation is the *heat* of dissociation, and this seems to be more uncertain than any other factor. However, the method of calculation employed above should always permit the calculation of the degree of dissociation from any value of the heat of dissociation which may finally be selected, and conversely the heat of dissociation should be accurately calculable when more accurate data for the degree of dissociation become available.

Summary

1. The free energy of dissociation, the dissociation constant, and the degree of dissociation, of molecular hydrogen into atomic hydrogen, have been calculated from the entropies of the substances and published data for the heat of dissociation.

2. The results indicate, in accordance with the conclusions of Duffendack and of Saha, that hydrogen is much more highly dissociated at high temperatures than earlier calculations had indicated.

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[Contribution from the Bureau of Standards, United States Department of Commerce]

THE SEPARATION OF IRON AND ALUMINUM FROM MANGANESE AND CERTAIN OTHER ELEMENTS[1]

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Introduction

It is generally stated that the separation of iron and aluminum from manganese is not satisfactory when ammonia is used as the precipitant, and that special procedures, such as the basic acetate method or precipitation with barium carbonate, are necessary. There is no denial that these methods perform their function and are desirable in special cases; the question is as to their necessity in the analysis of such materials as silicate and carbonate rocks. All of the special procedures entail extra work, complications, and sometimes uncertainties, as in the basic acetate separation with its tedious neutralization, its uncertain precipitation of aluminum, and its non-precipitation of certain of the rare earths.[2] As to the necessity, in the case of manganese, for such methods, one of us has long entertained doubts. It seemed reasonable to expect that precipitations carried out under the conditions prescribed by Blum[3] for the

[1] Published by permission of the Director of the Bureau of Standards of the U. S. Department of Commerce.

[2] Hillebrand, U. S. Geol. Surv., *Bull.*, **700**, 109 (1919).

[3] Blum, Bur. Standards, *Sci. Paper*, **286** (1916); This Journal, **38**, 1282 (1916).

complete deposition of aluminum (a definite hydrogen-ion concentration, high concentration of ammonium salts, and very short period of boiling after the solution is alkaline) would yield nearly as good a separation from manganese as is obtained in the barium carbonate method. In other words, a proper precipitation of aluminum should favor a good separation from manganese. The conditions specified by Blum are easily met where light-colored solutions and precipitates prevail and they can be satisfactorily met in the presence of considerable quantities of colored precipitates, such as ferric hydroxide.

The succeeding experiments deal, therefore, chiefly with the application of Blum's method to the separation of iron and aluminum from manganese. To make the study more complete, the influence of vanadium and phosphorus was also tested, as well as the behavior of nickel, cobalt, copper, and zinc.

Experimental Part

Unless otherwise specified, all precipitations were made by adhering as closely as possible to the following procedure recommended by Blum for the precipitation of aluminum hydroxide.

> "To the solution containing 5 g. of ammonium chloride per 200 cc. of solution, or an equivalent amount of hydrochloric acid, add a few drops of methyl red (0.2% alcoholic solution)[4] and heat just to boiling. Carefully add dil. ammonium hydroxide dropwise until the color of the solution changes to a distinct yellow. Boil the solution for 1 to 2 minutes and filter at once. Wash the precipitate thoroughly with hot 2% ammonium chloride (or nitrate) solution."

When two precipitations were carried out, the first precipitate was washed moderately. In all cases the final precipitates were dissolved in hydrochloric acid, twice heated with sulfuric acid, until fumes appeared, and tested for manganese by oxidation with bismuthate after proper dilution and acidification with nitric acid. With small amounts of manganese, determinations were carried out colorimetrically; with appreciable amounts of manganese, titration with ferrous sulfate and permanganate was used. The accuracy of the procedures was checked against manganese obtained from a standard solution of permanganate. The results of the experiments are clearly shown in Table I.

Inspection of Table I shows that Blum's method for the precipitation of aluminum by ammonia gives as good a separation of manganese in a single precipitation (Expts. 2 and 5) as is obtained in a single basic acetate separation (Expts. 19 and 20). It is also seen that a double precipitation with ammonia under the same conditions gives a separation of manganese which is better than is required for all ordinary analytical purposes, even

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[4] There is no apparent reason why other indicators of approximately the same range of hydrogen-ion concentrations cannot be employed in colored solutions. Dibromo-*o*-cresol-sulfonephthalein (bromocresol purple) with a color change from yellow to purple and a P_H range of 5.2–6.8, is an example.

though as much as 1 g. of manganese is present at the start (Expts. 3, 4, and 6 to 10). Contrary to expectations, no advantage was gained by thoroughly boiling the hydrochloric acid solution of the first ammonia

TABLE I

THE SEPARATION OF IRON AND ALUMINUM FROM MANGANESE IN PRECIPITATIONS WITH AMMONIA

Expt.	Mn present G.	Other elements present G.	No. of pptns.	Mn retained by pptd. G.	Remarks
1	0.1	none	1	none	Solution remained perfectly clear
2	0.05	0.05 Al 0.05 Ti 0.05 Zr	1	0.00058	
3	0.05	0.05 Al 0.05 Ti 0.05 Zr	2	0.00003	Thorough boiling of the hydrochloric acid soln. of the first precipitate
4	0.05	0.05 Al 0.05 Ti 0.05 Zr	2	<0.00002	No boiling of the hydrochloric acid soln. of the first precipitate
5	0.05	0.05 Al 0.05 Ti 0.05 Fe	1	<0.00002	
6	0.05	0.05 Al 0.05 Ti 0.05 Fe	2	<0.00002	As in Expt. 3
7	0.05	0.05 Al 0.05 Ti 0.05 Fe	2	<0.00002	As in Expt. 4
8	0.5	0.05 Al 0.05 Ti 0.05 Fe	2	<0.00002	As in Expt. 3
9	0.5	0.05 Al 0.05 Ti 0.05 Zr	2	0.00004	As in Expt. 3
10	1.0	0.1 Al	2	<0.00002	As in Expt. 3
11	1.0	0.1 Al	1	0.0017	
12	0.05	0.05 Al 0.05 Ti 0.05 Zr	1	0.0114	Precipitation made with 5 cc. of NH_4OH (d., 0.9) in excess
13	0.05	0.05 Al 0.05 Ti 0.05 Zr	1	0.0069	As in Expt. 12, except that 4 times as much ammonium chloride was also added
14	0.05	0.05 Al 0.05 Ti 0.05 Zr	2	0.0001	First precipitation as in Expt. 12 Second precipitation according to Blum
15	0.05	0.15 Al	2	0.0080	Both pptns. made with 5 cc. excess of NH_4OH (d., 0.90)
16	0.05	0.05 Al 0.05 Ti 0.05 Fe	1	0.0185	As in Expt. 12

17	0.05	0.05 Al 0.05 Ti 0.05 Fe	2	0.0164	As in Expt. 15
18	0.05	0.05 Al 0.05 Ti 0.05 Fe	2	0.0020	As in Expt. 15, except that 4 times as much ammonium chloride was also added
19	0.05	0.05 Al	1	0.00054	Pptn. by basic acetate method as described in Ref. 2, p. 110
20	0.05	0.05 Fe	1	0.00018	As in Expt. 19

precipitate. The harmful effect of excessive ammonia in even a short boiling period (only 1–2 minutes while the solution is alkaline) is well shown in Expts. 12 and 15 to 17. Expt. 14 shows the beneficial effect

TABLE II

THE EFFECT OF VANADIUM AND PHOSPHORUS UPON THE SEPARATION OF IRON AND ALUMINUM FROM MANGANESE IN PRECIPITATIONS WITH AMMONIA

Expt.	Mn present G.	Other elements present G.	No. of pptns.	Mn retained by pptd. G.	Remarks
1	0.05	0.05 Al 0.05 Ti 0.05 Zr 0.05 P_2O_5	2	0.00042	
2	0.50	0.05 Al 0.05 Ti 0.05 Zr 0.05 P_2O_5	2	0.00046	
3	0.05	0.05 Al 0.05 Ti 0.05 Fe 0.05 P_2O_5	2	0.00024	
4	0.05	0.05 Al 0.20 P_2O_5	2	0.0081	
5	0.05	0.05 Al 0.20 P_2O_5	2	0.0205	Precipitation by basic acetate method, Ref. 2, p. 110
6	0.05	0.05 Fe 0.20 P_2O_5	1	0.0034	
7	0.05	0.05 Fe 0.20 P_2O_5	1	0.0215	As in Expt. 5
8	0.05	0.05 Al 0.05 Ti 0.05 Zr 0.05 V_2O_5	2	0.00015	
9	0.50	0.05 Al 0.05 Ti 0.05 Zr 0.05 V_2O_5	2	0.00022	
10	0.05	0.05 Al 0.05 Ti 0.05 Fe 0.05 V_2O_5	2	0.00003	

of a second careful precipitation following a preliminary careless one and Expts. 13 and 18 show the helpful effect of ammonium chloride.

The experiments listed in Table II are self-explanatory and were made to ascertain the effect of the commonly occurring elements vanadium and phosphorus on the separation of iron and aluminum from manganese.

It is seen that the separation of iron and aluminum from manganese is fairly good when moderate amounts of phosphorus and large amounts of the former are involved (Expts. 1 to 3); when the reverse conditions prevail, the separation is worthless (Expts. 4 and 6). This was expected on account of the insolubility of manganese phosphate in weakly acid or alkaline solutions; for this reason the basic acetate method also fails in similar circumstances (Expts. 5 and 7)—a difficulty not mentioned in the literature. Vanadium behaves like phosphorus, though to a lesser degree (Expts. 8 to 10).

The data given in Table III are presented for the sake of completeness, and show: (1) the behavior of nickel, cobalt, copper, and zinc in precipitations with ammonia as in Blum's method, (2) the effect of excess ammonium chloride, and (3) the effect of an excess of both ammonia and ammonium chloride.

TABLE III

THE SEPARATION OF IRON AND ALUMINUM FROM NICKEL, COBALT, COPPER AND ZINC IN PRECIPITATIONS WITH AMMONIA

0.1 g. of aluminum was used in all experiments except 13–16, in which 0.1 g. of iron was substituted

Expt.	Elements present G.	No. of pptns.	Wt. of element retained by the pptd. G.	Remarks
1	0.05 Ni	1	0.0006 Ni	
2	0.05 Co	1	0.0041 Co	
3	0.05 Cu	1	0.0211 Cu	
4	0.05 Zn	1	0.0216 Zn	Precipitation was carried out by Blum's method in Expts. 1–8
5	0.05 Ni	2	none	
6	0.05 Co	2	0.0012 Co	
7	0.05 Cu	2	0.0077 Cu	
8	0.05 Zn	2	0.0108 Zn	
9	0.05 Ni	2	none	In Expts. 9–12, Blum's method was employed after adding 4 times the specified amount of ammonium chloride
10	0.05 Co	2	0.0009 Co	
11	0.05 Cu	2	0.0017 Cu	
12	0.05 Zn	2	0.0043 Zn	
13	0.05 Ni	2	0.00047 Ni	In Expts. 13–16, 5 cc. of ammonia (d., 0.90) in excess was used in each precipitation in addition to the excess ammonium chloride used in Expts. 9–12
14	0.05 Co	2	0.0030 Co	
15	0.05 Cu	2	0.0003 Cu	
16	0.05 Zn	2	0.0005 Zn	

Expts. 1, 5, and 9 in Table III show that the separation of iron and aluminum from nickel is as satisfactory as that of manganese under like conditions. It is also apparent that the separation from cobalt, copper, and zinc is not satisfactory in any case and that the retention of the elements increases with the atomic weight. An increase in the concentration of ammonium chloride betters the separation somewhat (Expts. 10 to 12). With an increase of both ammonium chloride and ammonia (which cause incomplete precipitation of aluminum) the separation from copper and zinc is improved; under the same conditions nickel and cobalt resemble manganese in that the retention is greater. The retention does not, however, appear to be due to oxidation, as the precipitates yield but very little iodine upon treatment with hydrochloric acid and potassium iodide.

The data given in Table III show why it is necessary to separate zinc before iron in analyses such as that of brass; it is also apparent that the practice of separating iron before nickel in such analyses is sound.

Summary

1. Moderate amounts of iron and aluminum can be separated from manganese and nickel as satisfactorily by precipitation with ammonia as by the basic acetate or barium carbonate methods. The only requirement is the procedure recommended by Blum for the complete precipitation of aluminum, namely, presence of ammonium chloride, very low alkalinity (P_H = 6.5 to 7.5, as indicated by methyl red or other suitable indicator), and only 1 to 2 minutes' boiling of the alkaline solution.

2. Phosphorus and vanadium interfere but slightly in the separation when iron or aluminum is preponderant. When the reverse holds, they form insoluble compounds with manganese and interfere not only in separations by ammonia but also in the methods using basic acetate or barium carbonate.

3. Under the above conditions the separation of iron and aluminum from cobalt, copper and zinc is incomplete. A large excess of ammonium chloride improves the separation.

4. An excess of both ammonia and ammonium chloride gives a better separation from copper and zinc. Under these conditions, however, the precipitation of aluminum is incomplete and the separation from manganese, nickel and cobalt is less satisfactory.

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