CCXXXIV.—*The Adsorption of Thorium-B and Thorium-C by Ferric Hydroxide.*

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It has been found by McCoy and Viol (*Phil. Mag.*, 1913, [vi], **25**, 340) that "ferric iron precipitated by fumaric acid from a boiling, nearly neutral solution of thorium-*B* and thorium-*C* carries down all the -*C* and only a small part of the -*B*." By redissolving the precipitated iron with the radioactive matter adsorbed and repeating the process, it is claimed that thorium-*C* can be obtained in which no thorium-*B* can be detected after the decay of the former. This process is recommended by these authors as a method of separating thorium-*C* in a state of radioactive purity.

In view of the number of recent publications on the determination of acidity in weakly acid solutions, and the marked influence of the hydrogen ion on many reactions, it seemed desirable to investigate more closely this adsorption effect. Careful measurements have been made of the acidity of the solutions used, and of the ratio in which thorium-*B* and thorium-*C* were adsorbed, with a view to determine whether any connexion exists between these two factors.

The ratio of thorium-*B* to thorium-*C* is readily determined from the form of the decay curve. Pure thorium-*C* decays with the period of half change 1 hour, giving out α -rays; pure thorium-*B* shows no initial α -activity, but develops an activity that rises to a

maximum in $3\frac{2}{3}$ hours and then decays with the period of half change 10.6 hours. In a mixture of thorium-*B* and thorium-*C*, the amount of -*C* is proportional to the initial activity, whilst the amount of -*B* originally present can be calculated from the residual activity after the decay of the original thorium-*C*, that is, after about six hours.

In the following experiments the activities were measured throughout in the α -ray electroscope and the ratio of thorium-*B* to -*C* calculated from the form of the decay curve. The acid used was hydrochloric, a stock solution being diluted to the various strengths required. With a dilute solution of ferric chloride, about 2 grams per litre, it was found that in acid solution hydrolysis took place with precipitation of ferric hydroxide under the following conditions :

Volume of hydrochloric acid used	= 15 to 25 c.c.
Maximum normality of the acid	= $N/20$.
Volume of $N/10$ -fumaric acid solution, or sodium fumarate	= 3 c.c.
Volume of standard ferric chloride	= 3 c.c.

When the whole was raised to boiling, hydrolysis was complete in a few minutes.

In the first series of experiments the active deposit of thorium-*B* and thorium-*C*, obtained in the usual way by exposing a negatively charged plate to thorium hydroxide, was dissolved in 15 c.c. of hydrochloric acid each time, the strength of the acid being varied. Solutions of sodium fumarate and ferric chloride were added in the quantities stated above, and the whole boiled to precipitate the iron. The precipitate was washed, quickly dried, and the activity on the filter-paper determined for several hours. The actual decay curves obtained are shown in Fig. 1 along with the dotted curves (*a*) and (*b*), which are the theoretical curves for pure thorium-*C* and for the equilibrium mixture respectively. The scale of activities is so chosen that the initial activity in each case is 100. The results are tabulated below in a somewhat different form, the acidity being expressed as normality of hydrochloric acid used and the ratio given as atoms of thorium-*B* per atom of thorium-*C*. In the original active deposit, where the two members were present in radioactive equilibrium, this ratio had the value 10.6.

Normality of acid	0.029	0.014	0.007	0.004	0.003
Atomic ratio, Th- <i>B</i> /Th- <i>C</i>	3.1	17.7	18.3	33.7	37.7

From these figures it is apparent that, in the most strongly acid solution, thorium-*C* is adsorbed in considerable excess of the equilibrium ratio, and the decay curve (No. 1) is not very different

from that of pure thorium-*C*. But as the acidity is decreased the relative amount of thorium-*B* increases, until from the most weakly acid solution thorium-*B* is adsorbed in large excess, and the decay curve shows a maximum activity characteristic of thorium-*B*.

It was recognised, however, that in these experiments the normality of the acid as given represents the total hydrochloric acid added, but does not represent the concentration of hydrogen ion after the precipitation. Part of the hydrochloric acid would act

FIG. 1.

on the sodium fumarate to liberate free fumaric acid which, as an organic dibasic acid, would be only slightly ionised. The actual concentration of hydrogen ion would thus be lower than is indicated by the normality. Another and opposing factor is the hydrochloric acid liberated in the solution by the hydrolysis of the ferric chloride. The precipitate of iron contained about 6–10 mg. of ferric oxide, and the amount of hydrochloric acid liberated may readily be calculated as follows:

One gram-molecule, that is, 160 grams, of ferric oxide liberates

six equivalents of hydrochloric acid. If these equivalents are present in 25 c.c., the normality is raised by 240. Thus 10 mg. of ferric oxide raise the normality by 0.015*N*. This amount is very appreciable in view of the low acidities used.

A second series of experiments was accordingly undertaken, in which the actual concentration of hydrogen ion was measured in place of the normality of the hydrochloric acid. The active deposit was dissolved as before in hydrochloric acid of varying strength, fumaric acid and ferric chloride were added, and the iron was precipitated by boiling. The filtrate from each experiment was collected and the concentration of hydrogen ion in it determined by the hydrogen cell. The final acidity thus measured is a complex quantity, being the sum of three factors—the hydrochloric acid used, the fumaric acid added, and the hydrochloric acid liberated by the hydrolysis of the ferric chloride. It is therefore not strictly comparable with the figures in the previous table, which refer only to the normality of the hydrochloric acid used. Indeed, when the active deposit is removed from the plate by simply warming in ferric chloride solution without the addition of any acid, the resulting filtrate is distinctly acid. To reach lower acidities it is necessary to add dilute alkali to the ferric chloride, and care has to be taken to avoid local precipitation of ferric hydroxide during the addition.

The results of this series of experiments are given in the following table, and the decay curves obtained are shown in Fig. 2.

Final hydron concentration in grams per litre	0.0085	0.0068	0.0063	0.0055	0.0049	0.0046	0.0037
Atomic ratio, Th- <i>B</i> /Th- <i>C</i>	1.2	2.25	3.8	7.8	10.6	13.9	16.9

The same transition from excess of the *C*-member to excess of the *B*-member is again evident, and Fig. 3 shows graphically the increase of the ratio Th-*B*/Th-*C* with diminishing acidity. The flat portions of the graph can be prolonged at either end, and experimental points have been obtained corresponding with higher and lower acidities than those shown. As the middle part of the graph is the most interesting, it only has been shown on a larger scale than would otherwise be possible. The top portion of this graph is the more difficult to realise experimentally, and in order to control better the lower acidities, an attempt was made to use the buffer mixtures of hydrochloric acid and sodium acetate given by Walpole (T., 1914, 105, 2501, 2521). The active deposit was dissolved in a mixture of hydrochloric acid and sodium acetate having a known hydron concentration, and ferric chloride added

so as to precipitate basic ferric acetate as adsorbent. Unfortunately, with the low concentration of acetic anion in these mixtures and the small quantity of iron permissible as adsorbent, it was not found possible to precipitate basic ferric acetate at an acidity greater than $[H^+] = 10^{-6}$. At this very low acidity thorium-*B* was

FIG. 2.

adsorbed in large excess. At the lower end, the curve is limited by the strength of acid in which ferric hydroxide can be formed by hydrolysis. In no experiment was pure thorium-*C* adsorbed, the nearest approach to it being a mixture for which the atomic ratio Th-*B*/Th-*C* was 0.4. It should be noted that even when thorium-*B* and thorium-*C* are present in equal quantity, the decay curve for the mixture differs from that of pure thorium-*C* only very slightly

during the first three hours, and only after four hours does the difference due to the thorium-*B* become really appreciable.

It is worth while comparing the graph of Fig. 3 with that published by von Hevesy (*Phil. Mag.*, 1912, [vi], **23**, 628) in his investigation of the electrochemical properties of thorium-*B* and thorium-*C*, in which he deposited both these elements on metallic electrodes at varying potentials. By dipping a noble metal in a solution of one of its salts, for example, silver in silver nitrate, a positive potential was obtained; similarly by dipping such a metal as magnesium or zinc in a solution of its sulphate the electrode took up a negative

FIG. 3.

potential towards the solution. At a positive potential thorium-*C* was deposited on the electrode almost pure, whilst at a sufficiently negative potential thorium-*B* was deposited in large excess; at intermediate potentials the two members were deposited in varying ratios, the proportion of thorium-*C* diminishing as the potential became more negative, and at -0.6 volt against the calomel electrode the two were deposited in radioactive equilibrium. The graph showing the ratio of thorium-*B* to thorium-*C* as ordinate and the electrode potential as abscissa has the same general form as that of Fig. 3, and both curves show an inflexion at the point corresponding with the radioactive equilibrium.

The explanation of this similarity between the curves for electro-deposition and adsorption probably lies in the application of von

Lerch's rule, that the successive products in a disintegration series become more "noble," and in the fact that thorium-*B* and thorium-*C* are known to exist both as colloids and ions. Thorium-*B* exists as a negatively charged colloid and thorium-*C* as a mixture of negative and positive colloid, the amount of positive decreasing with the acidity of the solution. In very weakly acid solution both exist mainly as negative colloids. As the acidity gradually increases, it is suggested that thorium-*B*, as the less noble element, with the greater tendency to form positive ions, passes first into the ionic state, while thorium-*C* remains colloidal. Hence, in the most acid solutions, thorium-*C* is adsorbed almost pure by the positively charged ferric hydroxide, but as the acidity diminishes and thorium-*B* passes into the colloidal state, the latter is adsorbed in increasing ratio and finally in excess of the equilibrium ratio. This reasoning also explains why thorium-*B* cannot be adsorbed in the same high degree of purity as thorium-*C*, for in weak acid that part of the thorium-*C* which is present as negative colloid is adsorbed along with the thorium-*B*.

To test the validity of this colloidal theory a third series of experiments was undertaken in which colloidal ferric hydroxide was used. The active deposit was dissolved as before in 25 c.c. of hydrochloric acid, the strength of which was gradually diminished in successive experiments. Below about $N/10,000$ -acid it is not possible to dilute hydrochloric acid with accuracy, and for these low acidities hydrochloric acid was replaced by mixtures of potassium dihydrogen phosphate and disodium hydrogen phosphate, for which the hydrogen-ion concentration is accurately known (see Prideaux, "Theory and Use of Indicators"). To the solution of the active deposit was added 1 c.c. of ferric hydroxide hydrosol (dialysed free from hydrochloric acid) and the iron was precipitated by addition of a drop of sodium sulphate solution. The precipitated iron carried down thorium-*B* and thorium-*C* in varying proportions, the relative amount of thorium-*B* increasing as before with diminishing acidity. The results are shown in the following table. The acidity of the solutions is given for convenience in the form of $\log [H^+]$; thus, for $N/100$ -acid, $\log [H^+] = -2$.

$-\log [H^+]$	1.7	2.0	2.3	2.7	3.0	4.0	4.94	5.91
Atomic ratio, Th- <i>B</i> /Th- <i>C</i>	0.45	0.97	2.0	3.5	7.0	15.0	15.6	16.2

The variation of the ratio of thorium-*B* to -*C* is shown in Fig. 4; the acid end of the curve is limited, of course, by the strength of the acid in which ferric hydroxide can be precipitated. Although not identical with the curve of Fig. 3, this graph shows the same general shape, with a well-defined transition from excess of the

C-member to excess of the *B*-, and has the same inflexion at the point of radioactive equilibrium.

These results obtained with colloidal iron appear to bear out the colloidal hypothesis previously outlined. Although the concentration of the radioactive matter is insufficient to coagulate the colloidal iron, once this coagulation is effected by addition of a suitable electrolyte the positively charged iron adsorbs that part of the radioactive matter which exists as negative colloid, the electric charges neutralising one other. The inflexion pointed out by von Hevesy and noted again in Figs. 3 and 4 is not so easily

FIG. 4.

explained. Why should these curves, relating to different phenomena, both show an inflexion at the same point, and that the point corresponding with the radioactive equilibrium? One is tempted to look for some connexion between the electrical and colloidal properties of these elements and their atomic stabilities as expressed by their equilibrium ratio.

Further experiments are being carried out in order to obtain more data on this point.

Summary.

1. It has been shown that ferric hydroxide adsorbs thorium-*B* and thorium-*C* in proportions varying regularly with the acidity

of the solution. The method is suitable for separating pure thorium-*C* only if the acidity is kept above a certain limit.

2. The variation of the ratio of thorium-*B* and thorium-*C* is continuous, so that the effect seems to be true adsorption and not the formation of a chemical compound between the active matter and the iron.

3. A colloidal theory has been suggested to explain the experimental results; it involves the passage of the radioactive matter from the ionic to the colloidal state, the change being governed by the acidity of the solution.

4. A parallelism has been pointed out between the results reported here and those of von Hevesy for electrode deposition of the same elements. From this parallelism some evidence has been obtained that suggests a connexion between the atomic stabilities of thorium-*B* and thorium-*C* and their electrochemical properties.

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