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# Target Chemistry of Zirconium and Yttrium; Isolation of Zr$^{89}$ in Pure State

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Radioactive Zr$^{89}$ obtained by bombardment of Y$_2$O$_3$ with deuterons, was separated without addition of stable zirconium in quantities $\sim 10^{-10}$ gram. Oxychloride solutions of Zr$^{89}$ mixed with inactive Zr were used for coagulation studies in the concentration range $1.5 \times 10^{-4}$—$1.5 \times 10^{-11}$ gA/l. It was found that the fraction coagulated increased with dilution under the constant conditions used ($p$H—4.0; NaCl—$2.5 \times 10^{-2}N$; $T$—25°), to $2.7 \times 10^{-6}$ gA/l. The log-log plot of zirconium concentration ($C$) in solution against coagulated part ($c$) closely approaches a straight line with exponent $n = 1.50$ and $k = 490$. At $1.5 \times 10^{-6}$ gA/l and lower concentrations the coagulated fraction reaches a maximum and becomes constant, $k = C/c = .45$. Within the range studied salt increases coagulation of zirconium above $10^{-5}$ gA/l; but below $10^{-6}$ gA/l the salt effect is reversed. Increase in $p$H results in increase in the fraction coagulated ($r$) in all concentrations studied. At a minute concentration $r = (p\text{H} - K)/m$, $K$ being 1.85 with NaCl, 0.05$N$ and 1.58 with NaCl, 0.005$N$ and $m$ being 3.15. The separation of Zr$^{89}$ in minute quantities without addition of stable zirconium is plausible if a Nernst distribution of zirconium between coagulated part and solution is postulated. The concept of the solubility of the hydrous oxide of zirconium as a constant quantity remaining in solution under specified conditions was not verified.

## I. INTRODUCTION

ISOLATION of artificial radioactive isotopes without dilution by inactive isotopes of the same charge number is pertinent to the solution of some problems in nuclear physics. Isotopes of a different charge number ($Z \pm 1, 2$) than those bombarded ($Z$) are produced by several nuclear reactions. However, the yields are minute quantities so their separation involves unconventional procedure and the little known behavior of elements in extreme dilution.

For instance, it has been shown in the past[1–6] that some natural radioactive isotopes which form slightly soluble hydrous oxides can be agglomerated at very low concentrations even when the amounts in solution are much below their solubilities. These agglomerates were termed radio-colloids while the phenomenon was treated mainly as adsorption in order to avoid conflict with the solubility product principle.[7]

In the field of artificial radioactivity the formation of radio-colloids has been used in the separation of yttrium isotopes (Y$^{87, 88}$) obtained by the reactions, Sr$^{86, 88, 87}$($d$, $n$ and $d$, $2n$)Y$^{87, 88}$, without addition of inactive yttrium as carrier.[8] It was found that partial agglomeration of yttrium takes place in solutions of minute* concentrations and its extent depends primarily upon two factors, the $p$H of the solution and the salt concentration. These two factors act in opposite directions and affect the splitting of yttrium between the solution and the radio-colloid.

The experiments showed furthermore, that with very dilute solutions the fraction coagulated at a given $p$H and salt concentration, increases with dilution to some limit. This, of course, is contrary to the behavior of yttrium in conventional concentrations.

The present work on the tetravalent element zirconium was undertaken as an extension of the previous studies of yttrium to confirm the basic

[1] Blau and Rona, Akad. Wiss. Wien **139**, 275 (1930).
[2] Chamie, J. Phys. Rad. **10**, 44 (1929).
[3] Chamie and Guillot, Comptes rendus **190**, 1187 (1930).
[4] Hahn, *Applied Radiochemistry* (Cornell University Press, Ithaca, New York, 1936).
[5] Hahn and Werner, Naturwiss. **17**, 961 (1929).
[6] Werner, Zeits. f. physik. Chemie **A156**, 89 (1931).
[7] In the literature there is considerable controversy on radio-colloid formation. One school of thought admits only an adsorption grouping while another supports independent coagulation. An example which has had contradictory explanations is the formation of radio-colloids of thorium

*B*, an isotope of lead, agglomeration of which has been observed in concentrations as low as $10^{-11}$ gA/liter while the solubility under the conditions of the experiment was $5 \times 10^{-5}$ gA/liter. Paneth, Mitt. Rad. Inst. Wien **34**, 47, 55 (1913); Zeits. f. Electrochemie **31**, 5 (1925).
[8] J. D. Kurbatov and M. H. Kurbatov, J. Phys. Chem. **46**, 441 (1942).
* Minute quantities are accepted arbitrarily as those less than $10^{-9}$ gram.

observation of increased coagulation with dilution, within certain limits. The radioactive isotopes of zirconium were selected mainly because of the convenient half-lives and strong radiation intensities of $Zr^{89}$ and $Zr^{93}$.

Of these, $Zr^{93}$ has characteristics which make it advantageous for studies of dilute solutions ($10^{-6}$ to $10^{-3}$ gram atom per liter) and $Zr^{89}$ for concentrations below $10^{-6}$ gram atom per liter.

The interrelation of the isotopes of yttrium, zirconium and columbium is shown in Fig. 1.

The half-lives ($T$) and upper limits of radiation energies in Mev are given according to latest data.[9,10] The radioactive isotopes used in the present work are shown in heavy lines.

## II. TARGET CHEMISTRY OF ZIRCONIUM

By activation of metallic zirconium with deuterons in the Ohio State University cyclotron, the radioactive isotope $Zr^{93}$ of $T-65.5$ days was secured for studies of dilute solutions.

In spite of the convenient half-life and strong radiation intensity $Zr^{93}$ has the disadvantage of chain disintegration into $Cb^{93}$, $T-38.7$ days, the latter an isomer of stable Cb. Therefore, a separation of Cb from Zr is required just prior

FIG. 1. Region of yttrium, zirconium, and columbium isotopes. Stable isotopes are shown in rectangles and radioactive in ovals.

to each series of experiments with dilute solutions of zirconium.

The target chemistry of the metallic zirconium (*ca.* 0.1 g) bombarded with deuterons consisted in dissolving the metal, separating the isotopes of columbium ($d$, $n$ and $d$, $2n$ reactions) and

yttrium ($d$, $\alpha$ reaction) and removing from the zirconium the usual active impurities Cu, Ni, Co, Na, etc.

After only the surface of the zirconium was dissolved in acids, stable yttrium was added and
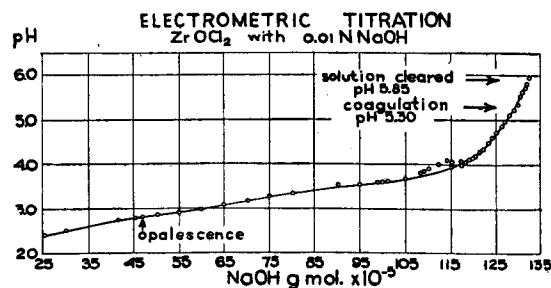
FIG. 2. Electrometric titration: final concentration of zirconium $4.4 \times 10^{-3}$ gA/l.

later separated by the hydrofluoric acid procedure.

The columbium isotopes were first separated, without addition of stable columbium, by means of the potassium carbonate procedure. The minute quantities of potassium hexacolumbate so obtained were used later as tracer for repeated purification of zirconium from accumulated $Cb^{93}$ since the minute $Cb^{92}$ has a strong radiation intensity.

The final separation of yttrium from the experimental solution of zirconium was made by partial and repeated coagulation of zirconium at $p$H, 4.0.

The common impurities were removed by the ammoniacal procedure.[11]

By direct dilution of the active zirconium obtained, as little as 0.06 mg could be used per experiment since it had sufficient activity for accurate measurement. However, since Zr is secured already mixed with stable isotopes the ratio of active to stable cannot be increased. Therefore, the properties of very dilute solutions could be studied only after separation of $Zr^{89}$ without carrier, from yttrium bombardment.

Since the target chemistry in this case is unconventional the properties of zirconium in dilute solution will be treated first, returning later to the isolation of $Zr^{89}$.

[9] M. L. Pool and J. E. Edwards, Bull. Am. Phys. Soc. 19, 7 (1944).
[10] G. T. Seaborg, Rev. Mod. Phys. 16, 13 (1944).

[11] Allen, Pool, Kurbatov, and Quill, Phys. Rev. 60, 425 (1941).

## III. EXPERIMENTAL PROCEDURE

When ten milliliters of a solution containing $6 \times 10^{-4}$ g of zirconium as oxychloride is titrated with sodium hydroxide ($0.01N$) opalescence appears at a $p$H as low as 2.8. The solution becomes increasingly cloudy as the $p$H rises then clears at a much higher $p$H than that at which coagulation started (Fig. 2). A continuous coagulation process is evident during the titration.

On the basis of these data a $p$H range well below that of quantitative precipitation was selected for studies of the behavior of more dilute solutions.

The method used for coagulation and separation of precipitate and filtrate was as follows: Samples of 20 to 40 ml of known zirconium concentration in known acid concentration were titrated to a desired $p$H with standardized sodium hydroxide solutions of various strengths depending upon the final concentration of zirconium and salt desired in the particular experiment. These titrations were carried out at 25° using a Leeds and Northrup $p$H meter. Then the samples were allowed to stand for an agglomeration period before removal of the coagulated part.

Since the quality of water is of primary significance in securing reproduceable results the following standardized conditions were used throughout: Portions of the freshly redistilled water to be used for a series of experiments were electrometrically titrated with sodium hydroxide to $p$H 9 and back titrated with hydrochloric acid of known normality to $p$H 2 to be certain that no buffering compounds were present. The initial $p$H of the water was regularly found to be not less than 6.6.*

The requirement of maintaining $p$H without change during the agglomeration period was met

by performing the experiments in a room free from other chemical work using a separate enclosed space having open vessels of soda-lime and provision for air exchange through filters with sodium hydroxide. A facilitating circumstance in avoiding carbon dioxide effect is the $p$H range of 3 to 4.5 when the admixture of sodium carbonate owing to the initial $p$H of the water constitutes less than 0.1 percent of the total salt (NaCl) concentration present in the experiment.

With the higher concentrations of zirconium, $10^{-5}$ gA/l and with the higher $p$H, 4.5, it was observed that on standing within the first half hour the $p$H drops to the extent of 0.1 to 0.2. On the contrary, no experimentally observable change in $p$H takes place during the agglomeration period with the very dilute solutions of zirconium. The observation of $p$H lowering on standing only with higher concentrations of zirconium was attributed to the fact that the agglomeration process requires some time. The duration of agglomeration was standardized at six hours, this period having been selected upon evaluation of the attainment of full agglomeration after titration of a sample to a definite $p$H. Separations were made after six hours and fourteen hours with $2.78 \times 10^{-4}$ gAZr/l giving the following results:

| $p$H | Percent coagulated 6 hr. | Percent coagulated 14 hr. |
|------|--------------------------|---------------------------|
| 3.5  | 13.0                     | 12.8                      |
| 4.5  | 26.3                     | 25.4                      |

Since radioactivity measurements, owing to the geometry of samples relative to the G-M counter tube or ionization chamber, vary to the extent of ±3 percent of the activity measured the above figures indicate that extension of agglomeration time beyond six hours is not required if there is no removal of coagulated fraction and no distortion of other conditions. It was found that an hour and a half was insufficient since the results vary especially at high concentrations.

After the six-hour agglomeration period the solutions were filtered through Schleicher and Schull blue ribbon paper, and the deposits on

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* Agglomeration of radio-colloids has been previously reported in the literature as attributable entirely to the purity of the water used and experiments were described using water prepared by centrifuging. In the present work, accordingly, centrifuged water was tested in control experiments with minute concentrations. However, no observable effect was found with the centrifuged water as compared to the redistilled water maintained free from carbon dioxide. (Table II.) In addition, the formation of radio-colloids was described previously without reference to control of the $p$H of the solutions or the salts present. Consequently the observations made were found to be inconclusive. O. Werner, Zeits. f. physik Chemie **A156**, 89 (1931).

the paper subsequently dissolved by washing first with $2N$ hydrochloric acid and then several times with $0.1N$ hydrochloric acid until the papers were inactive.

The method of removing the coagulated part by means of filter paper was chosen after a comparison of data obtained on agglomeration of yttrium,[8] cerium,[12] and zirconium.* Filter papers were washed before using with salt and hydrochloric acid solutions of $p$H corresponding to that of the experimental series of zirconium. No washing, in the analytical sense, can be done on the agglomerated fraction on the papers even with wash water of corresponding $p$H and salt concentration, therefore, the volume of solution left on the filter paper was reduced to an amount not exceeding 2 percent by use of 6-cm filter papers.

The effect of filter paper on agglomeration was evaluated by arranging consecutive filtrations, that is, the filtrate from one funnel immediately filling a second paper placed below the first funnel. It was found that in minute concentrations the amount of coagulation on the second paper does not exceed 5 percent of the agglomerated fraction on the first paper.

While the effect of the filter paper undoubtedly cannot be excluded as a part of the process of separation, the experimental data suggest that the agglomeration of radio-colloids begins with adjustment of $p$H and after a period of time the filtration facilitates the removal of coagulated particles by localizing their accumulation on the paper.

With concentrations of $10^{-5}$ gA/l of zirconium and less no coagulated fraction is visible. Consequently the experimental procedure cannot be followed by common analytical methods. The complete transfer of agglomerated phase to filter

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[12] J. D. Kurbatov and M. L. Pool, Phys. Rev. **65**, 61 (1944).

* It was found that agglomeration and settling of radio-colloids takes place even in concentrations below $10^{-6}$ gA/l without filtration. Samples were titrated to the desired $p$H values and allowed to stand for eight days in stoppered graduated cylinders. A top portion (about 25 percent) of the liquid was slowly pipetted, and the quantity of material found in the upper liquid phase was always lower than that of the original. However, the concentration of the liquid separated by pipette, without filtration, varied considerably ($\pm16$ percent). Similar observations were made by centrifuging samples after elapse of an agglomeration period.

paper and complete solution from the filter paper into a vessel for measuring on the G-M counter was controlled by means of activity determinations. Secondary treatment was made of the beakers and filter papers with weighable quantities of zirconium. When zero activity was found on the beakers and papers the procedure with very dilute solutions was considered to have been adequately performed. Careful performance of a standardized technique which is entirely controlled by instruments is required instead of the visual judgment of the experimenter, when working with concentrations below $10^{-5}$ gAZr/l.

The activities of the solutions so obtained and the original filtrates were determined either (a) directly by means of a Geiger-Mueller counter with immersion tube for liquids or (b) by means of a Wolf unifilar electrometer. In the latter case the solutions were evaporated to dryness in Petri dishes of 4-cm diameter and the activities measured with an ionization chamber filled with freon at 20-lb. pressure.

Both methods have certain disadvantages. Zirconium can be kept in solution only in strong acid and the very thin glass of the G-M counter immersion tube cannot be used long. The electrometer measurements require preparation of solid samples of uniform geometry and there is a loss in total activity owing to the depth of the measured material.

In all cases where the ratio of beta- and gamma-radiation intensities was required to establish the purity of an isotope the electrometer was used.

## IV. SOME PROPERTIES OF ZIRCONIUM IN DILUTE SOLUTION AT $p$H 4.0 AND 4.5

After purification, the oxychloride solutions of bombarded zirconium were diluted as previously mentioned so that 20 ml of solution had an activity of approximately 400 counts per minute, measured on the G-M counter.*

The concentration of such a solution was found by usual analysis of undiluted zirconium to be $1.23 \times 10^{-5}$ gA/l. The more concentrated solutions were obtained then by adding the desired amount of stable zirconium; the actual quantities

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* The activity of these solutions, expressed in counts, was correlated with electrometer measurements expressed in units of a constant source of activity.
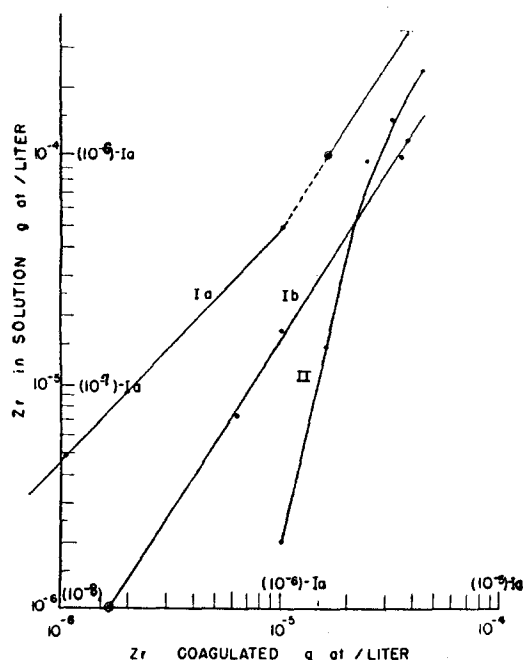
FIG. 3. Coagulation of zirconium at $pH$, 4.0.

| Curve No. | NaCl conc. $N$ | Final conc. Zr gA/l | Zr Coagulated gA/l |
|---|---|---|---|
| Ia | .025 | $10^{-8}$ to $10^{-6}$ | $10^{-7}$ to $10^{-6}$ |
| Ib | .025 | $10^{-6}$ to $10^{-4}$ | $10^{-6}$ to $10^{-5}$ |
| II | .005 | $10^{-6}$ to $10^{-4}$ | $10^{-5}$ |

(Curve Ib is a continuation of Curve Ia).

of zirconium used in this series of experiments being from $4.1 \times 10^{-5}$ to $1.0 \times 10^{-3}$ g.

Agglomeration was obtained in the two $pH$ regions, 4.0 and 4.5 while the sodium chloride concentration was maintained approximately 0.005$N$.

The deviations in measurements of the activities of filtrates and solutions of coagulated part did not exceed ±2 percent of the total counts taken for experiment.

In Table I the results are given for the coagulate. The log-log plot of coagulated Zr and final concentration (Fig. 3, Curve II) approaches a straight line only below $1.2 \times 10^{-4}$ gAZr/l. If the distribution of zirconium between solution and coagulate in this region is expressed as

$$C/c^n = K,$$

where $c$ is the amount coagulated per liter of solution and $C$ is the final concentration, the value of $n$ is 4.1 at 25° with sodium chloride concentration $\sim 0.005N$ and $pH$ 4.0.

At higher concentrations than $1.2 \times 10^{-4}$ gA/l

at $pH$ 4.0 and 4.5 the log-log plot of coagulate against final concentration does not hold as a straight line. However, the log-log plot of coagulate against initial concentration (shown in Fig. 4) gives a straight line with exponent $n = 0.48$ ($pH = 4.0$) and 0.58 ($pH = 4.5$) and proportionately constant, $k = 2.2 \times 10^{-3}$ and $8.0 \times 10^{-3}$ respectively.

Thus the interpretation of zirconium coagulation as a distribution phenomenon with the above dilutions and under the condition that the duration of the experiments be maintained constant is limited to the lower concentrations. The time allowed for coagulation was found to be significant so, to make results comparable, these and following separations of the coagulated fraction were performed six hours after titration.

From the tabulated data it is evident that (a) the coagulated fraction increases with dilution in this zirconium concentration range, at a given salt, $pH$, and temperature and (b) that the fraction of zirconium removed depends on $pH$ at this temperature and salt concentration.

These results were used as a basis for the separation of pure Zr[89] from bombarded yttrium.

## V. TARGET CHEMISTRY OF YTTRIUM AND SEPARATION OF Zr[89] WITHOUT CARRIER

Yttrium oxide, Hilger's spectroscopically pure, was bombarded with deuterons for four and a half hours in the Ohio State University cyclotron. The main nuclear reactions are: $Y^{89}(d, p)Y^{90}$, $Y^{89}(d, 2n)Zr^{89}$, and $Y^{89}(d, \alpha)Sr^{87}$ and owing to the

Table I. Coagulation of zirconium from dilute solutions at 25°. (Final volume approximately 40 ml per experiment.)

| Initial conc. Zr gA/l $\times 10^4$ | $pH$ | NaCl normality $\times 10^3$ | Zr coagulated gA/l $\times 10^4$ | Percent |
|---|---|---|---|---|
| | | $pH$ 4 | | |
| .124 | 3.90 | 4.9 | .103 | 83 |
| .305 | 4.01 | 5.0 | .162 | 53 |
| .612 | 4.02 | 5.0 | .220 | 36 |
| 1.20 | 3.97 | 5.1 | .252 | 21 |
| 1.74 | 4.04 | 5.2 | .331 | 19 |
| 2.78 | 3.88 | 5.4 | .445 | 16 |
| | | $pH$ 4.5 | | |
| .306 | 4.43 | 5.0 | .211 | 69 |
| .606 | 4.53 | 5.0 | .285 | 47 |
| 1.18 | 4.44 | 5.1 | .413 | 35 |
| 1.74 | 4.53 | 5.2 | .574 | 33 |
| 2.76 | 4.34 | 5.5 | .690 | 25 |

presence of fast neutrons $Y^{89}(n, 2n)Y^{88}$, and $Y^{89}(n, p)Sr^{89}$ may occur.

Since $Zr^{89}$ disintegrates with emission of positrons and gamma-radiation and $Y^{90}$ by emission of electrons and no gamma-rays, the extent of separation of zirconium from yttrium without the addition of stable yttrium can be observed from the beta-gamma ratio in $Zr^{89}$ and the presence or absence of gamma-radiation in $Y^{90}$.*

In Fig. 5 is a condensed outline of the procedure used in the isolation of $Zr^{89}$. It may be noted that after solution and purification of yttrium by the ammonia procedure (not shown on chart) yttrium was again purified by solution in hydrochloric acid and precipitation with sodium hydroxide and finally electrometrically titrated to $p$H 4.0. Because of the high salt concentration and large quantity of yttrium, $Zr^{89}$ was coagulated to the extent of 58.7 percent; 41.3 percent remaining in solution with the yttrium. All the yttrium, within the limits of the experimental procedure, was found to be left in solution.

On the right side of the chart are shown the results on the purification of zirconium. At the lower salt concentration 94.2 percent of zir-

FIG. 4. Coagulation of zirconium in the region of concentrations from 2.8 to $0.12\times10^{-4}$ gA/l with NaCl concentration $0.005N$. (Plot against initial concentration of Zr.)

* Identical geometry of samples and thickness of precipitates were easily maintained due to the small quantities of material. Radiation contributed by x-rays was included in the ratio of beta- and gamma-intensities no separation of x-ray intensities being necessary for observation of purity of fractions.

conium was coagulated. The beta-gamma ratio remained constant and was not decreased by all subsequent coagulations. The purity of the zirconium was also confirmed by following its disintegration for several half-lives.
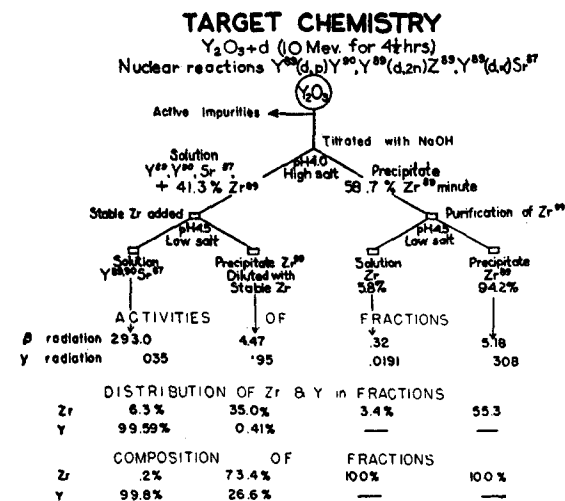
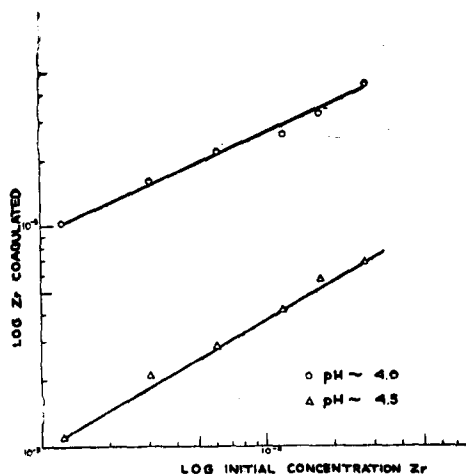FIG. 5. Scheme of purification of bombarded yttrium and isolation of $Zr^{89}$ in pure state.

During this work an evaluation of the half-life of $Zr^{89}$ was made and found to be slightly longer than previously reported owing mainly to better removal of yttrium from the zirconium fraction. In addition, the nuclear reaction $Y^{89}(d, 2n)Zr^{89}$ was established.

On the left-hand side of the chart are the results on separation of yttrium and zirconium with zirconium carrier added in quantity equivalent to the yttrium. The yttrium left in solution in this case was uncontaminated by zirconium but the precipitate of zirconium (41.3 percent of total) contained 26.6 percent of yttrium.

At the bottom of the chart are shown relative beta- and gamma-intensities for each fraction and the percentages of zirconium and yttrium as deduced from these measurements.

The precision of common gravimetric separation of two substances is usually determined by a comparison of weights found and known weights originally mixed in the sample. In case some of each constituent appears mixed with the other there is no measure of the purity of the fractions. However, with the aid of tracer procedure it can be seen that by means of electro-

TABLE II. Coagulation of zirconium from dilute and minute concentrations at 25° and $pH = 4$.

| Zr conc. gA/l | $pH$ | NaCl normality $\times 10^2$ | Zr coagulated gA/l | Percent |
|---|---|---|---|---|
| Minute | 4.01 | 2.38 | — | 69* |
| $1.54 \times 10^{-7}$ | 4.00 | 2.41 | $1.06 \times 10^{-7}$ | 69** |
| $1.54 \times 10^{-6}$ | 4.00 | 2.46 | $1.06 \times 10^{-6}$ | 69 |
| $2.69 \times 10^{-6}$ | 4.00 | 2.54 | $1.67 \times 10^{-6}$ | 62 |
| $1.35 \times 10^{-5}$ | 4.00 | 2.53 | $6.35 \times 10^{-6}$ | 47 |
| $2.69 \times 10^{-5}$ | 4.00 | 2.51 | $1.02 \times 10^{-5}$ | 38 |
| $1.34 \times 10^{-4}$ | 4.01 | 2.54 | $3.62 \times 10^{-5}$ | 27 |
| $1.54 \times 10^{-4}$ | 4.00 | 2.40 | $3.85 \times 10^{-5}$ | 25 |

\* Centrifuged water.
\*\* Water not centrifuged: freshly redistilled.

metric titration pure zirconium can be secured even in minute concentration but part will remain in the yttrium fraction. An yttrium fraction free of zirconium can be obtained if part of the yttrium is left in the zirconium. This is caused by the overlapping of the $pH$ ranges of coagulation of these two elements.

## VI. PROPERTIES OF ZIRCONIUM IN CONCENTRATIONS BELOW $10^{-6}$ gA/l

Using the radioactive $Zr^{89}$, a series of solutions was prepared by adding stable zirconium in known quantities, and in order to link these experiments with those previously described the highest concentration prepared was $1.54 \times 10^{-4}$ gA/l. The lowest concentration of $Zr^{89}$ was approximately $10^{-11}$ gA/l. This did not contain common zirconium and is referred to later as minute.*

. The same standardized procedure used on zirconium concentrations above $10^{-6}$ gA/l was followed with the lower concentrations. This included the precautions as to the purity of the water and reagents as described above; prevention of change in $pH$ during the agglomeration by maintaining the samples in an enclosed space free from carbon dioxide, other gas impurities and laboratory dust and especially care with regard to the temperature of experiments and duration of agglomeration time. The variation in temperature allowed in a complete series of experiments did not exceed $\pm 0.5°$ from the 25° selected.

* The total yield of purified $Zr^{89}$ was estimated by comparison of activity with known natural sources to be of the order of magnitude of $10^{-10}$ g.

Coagulations were carried out at $pH$ 4 with a salt concentration of $\sim 0.025N$ giving the results shown in Table II. It can be seen that the fraction coagulated increases with dilution to a certain limit, in this case, $1.54 \times 10^{-6}$ gA/l. Below this concentration the percent of zirconium coagulated remains constant.

The log-log plot of coagulated and final concentration of zirconium from $1.5 \times 10^{-4}$ to $2.7 \times 10^{-6}$ gA/l approaches a straight line (Fig. 3, Curve Ib). The constant, $n$, for this curve at $pH$ 4 and $0.025N$ salt concentrations is 1.5.

These values can be compared with those given previously for $pH$ 4: the fivefold increase in salt concentration resulting in less increase in coagulation with dilution.

Within a narrow range of concentrations 2.6 to $1.54 \times 10^{-6}$ gA/l the slope, $n$, decreases to unity and becomes constant and $k$ decreases to 0.45 (Curve Ia, Fig. 3).

It is well known that electrolytes aid in the coagulation of colloids and this is true in the case of zirconium in concentrations greater than $10^{-5}$ gA/l. In Table III are given the results on coagulation at three different $pH$ values and two salt concentrations and it can be seen that the higher salt results in consistently higher fractions coagulated.

However, with minute concentrations the effect of salt is reversed. In Table IV it is shown that at a given $pH$ a tenfold increase in salt results in a smaller fraction coagulated.

It should be expected therefore, that at some intermediate concentration of zirconium and at a certain $pH$ a change in salt concentration would be without apparent effect. This is found in the zirconium concentration range of $7 \times 10^{-5}$ and $10^{-6}$ gA/l at $pH$ 4 when the salt concentrations are as shown:

| Zr conc. gA/l | NaCl $N$ | Percent coag. | NaCl $N$ | Percent coag. |
|---|---|---|---|---|
| $1.54 \times 10^{-6}$ | .0246 | 69 | .503 | 70 |
| $7.25 \times 10^{-5}$ | .025 | 31 | .005 | 31* |

\* Data read from crossing of curves Ib and II, Fig. 3.

The curves in Fig. 6 show that at the same minute concentration the fraction coagulated within the limits of the experiments is directly proportional to the $pH$, that is, $r = (pH - K)/m$,

$r$ being the coagulated fraction, $m$, the slope and $k$ the intercept. The constants are $m=3.15$ for both curves and $k=1.85$ and $1.58$ for 0.05 and $0.005N$ salt respectively.

The effect of $p$H on coagulation of zirconium throughout the range of concentrations studied, has been observed to be in the same direction in all cases, that is, increase in $p$H increase coagulation, salt being constant.

The basic observation on the coagulation of zirconium from very dilute solutions which is in line with the results previously observed with yttrium, is that this hydrous oxide does not exhibit a constant solubility value.

This has been confirmed by experiments extended for eight days. Two different concentrations of zirconium were coagulated at three different $p$H values. The results are shown in the left column of Table V. After eight days the $p$H was redetermined and a second coagulated part



Fig. 6. Effect of salt and $p$H on a minute concentration of zirconium at 25°.

TABLE III. Effect of salt concentration and $p$H on dilute solutions of zirconium. (Final volume ~45 ml/ experiment.)

| Zr conc. gA/l ×10⁴ | NaCl conc. $N$×10³ | $p$H | Percent coag. | Zr conc. gA/l ×10⁴ | NaCl $N$×10² | $p$H | Percent coag. |
|---|---|---|---|---|---|---|---|
| 2.86 | 5.3 | 3.43 | 13 | 2.55 | 1.91 | 3.47 | 17 |
| 2.78 | 5.4 | 3.92 | 16 | 2.50 | 1.88 | 4.00 | 28 |
| 2.76 | 5.5 | 4.47 | 25 | 2.44 | 1.82 | 4.43 | 98 |

TABLE IV. Effect of salt and $p$H on coagulation of minute concentrations of zirconium.

| NaCl conc. $N$×10³ | $p$H | Percent coag. | NaCl conc. $N$×10² | $p$H | Percent coag. |
|---|---|---|---|---|---|
| 4.57 | 2.50 | 29 | 5.01 | 2.50 | 20 |
| 5.53 | 3.01 | 47 | 5.35 | 3.00 | 35 |
| 5.85 | 3.51 | 60 | 5.40 | 3.52 | 53 |
| 5.93 | 4.00 | 77 | 5.43 | 4.02 | 63 |
|  |  |  | 5.43 | 4.25 | 76 |

TABLE V. Two successive coagulations of zirconium.

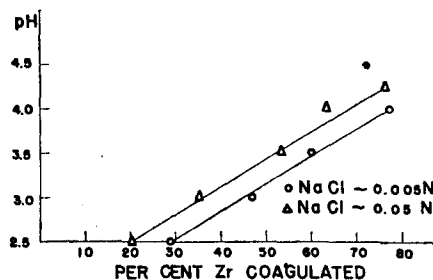| First coagulation separation after 6 hours | | | | Second coagulation from filtrate. Separation after 8 days | | | |
|---|---|---|---|---|---|---|---|
| Conc. Zr gA/l ×10⁴ | $p$H | Per-cent coag. | NaCl conc. $N$×10³ | Conc. Zr gA/l ×10⁴ | $p$H | Per-cent coag. | NaCl conc. $N$×10² |
| .622 | 3.48 | 24 | 4.9 | 1.29 | 3.25 | 11 | 1.18 |
| .612 | 4.02 | 36 | 5.0 | .950 | 3.62 | 37 | 1.06 |
| .606 | 4.53 | 47 | 5.0 | .795(1) | 3.97 | 73 | 1.07 |
| 1.80 | 3.52 | 8 | 5.1 | 4.07 | 3.34 | 7 | 1.1 |
| 1.74 | 4.04 | 19 | 5.2 | 3.46 | 3.73 | 14 | 1.1 |
| 1.74 | 4.53 | 33 | 5.2 | 2.86(2) | 3.98 | 77 | 1.1 |

removed from which it can be seen that at essentially identical salt concentration and $p$H ($p$H $-3.97$:NaCl$-.011N$) a three and a half-fold increase in concentration of zirconium in solution has negligible effect on coagulation.*

The experiments described may be partially interpreted if the phenomenon of distribution of zirconium between solution and coagulate be accepted as a Nernst distribution. The law holds well for concentrations below $10^{-6}$ gA/l and up to $1\times10^{-4}$ gA/l if the salt concentration is as high as $2.5\times10^{-2}N$.

It has been pointed out that in heterogeneous systems the distribution law holds well only for dilute conditions. With the lowest concentrations of zirconium studied, it was found that the amount coagulated is directly proportional to the amount left in solution. In the light of classical concepts of distribution this would mean only one molecular species of zirconium in such dilute solutions under the conditions specified.

In the region of $10^{-6}$ to $10^{-4}$ gAZr/l in which the log-log plot of zirconium in solution against zirconium coagulated closely approaches a straight line the exponent $n$, is 1.5 with $0.025N$ salt and 4.1 with $0.005N$ salt. This may indicate that the zirconium left in solution exists in more than one form in this range or that the coagulated part is more associated.

The log-log plot of coagulated Zr against final concentration of Zr does not give a straight line for concentrations $>10^{-4}$ gA/l. This indicates a more rapid change in the composition of zir-

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* If the solubility were constant and these solutions saturated the coagulated fraction, for example, from the solution numbered (2) should be 92 percent instead of 77 percent if the solution numbered (1) were considered saturated.

conium in solution or coagulate than that observed in the range immediately above $10^{-6}$ gA/l.

It has been established that coagulation of Zr will take place at any concentration under the conditions described. Accordingly, it was shown above that for consecutive coagulations a second addition of hydroxyl ions is not required. The process proceeds at somewhat lower $pH$ values but extremely slowly.

The observation that the fraction coagulated increases with dilution to some limit is well supported by the effect of hydroxyl ions on hydrolysis.

Below $10^{-6}$ gA/l the coagulation of zirconium reaches a maximum and the fraction remains constant consequently the separation of $Zr^{89}$ in pure state, in quantities of the order of $10^{-10}$ g, was possible.

# The Elastic Scattering and Neutralization of Low Velocity Hydrogen Ions in Methane

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The low velocity scattering of $H^+$, $H_2^+$, and $H_3^+$ in methane was measured at voltages between about 1 and 150. Neutralization is found in all three cases, being much greater for $H_2^+$ and $H^+$ than for $H_3^+$. The elastic scattering is also relatively high compared to hydrogen and helium. It was found that there was an effect of pressure at constant voltage on the experimental determination of effective cross section for elastic scattering. This has been explained on the basis of multiple scattering. Approximate potential laws for the interactions have been evaluated.

THE experience gained in previous experimental[1] work on the measurement of low velocity ion scattering and the techniques developed in this work enabled the measurements of the scattering of low velocity hydrogen ions in hydrocarbons to be approached with confidence. In particular, the techniques of the determination of neutralization[1(d)] and of the removal of carbonaceous films[1(c)] provided procedures which enabled such measurements to be made. Methane was the choice for the first hydrocarbon to be studied because of its simplicity and gaseous nature.

In the same apparatus and using the same experimental methods and analytical correlations as have been previously described,[1] the elastic scattering and neutralization in methane of all three hydrogen ions, $H^+$, $H_2^+$, and $H_3^+$, have been measured from approximately 1 to 150 volts. The formation of carbonaceous films from the methane required their frequent removal (between every several experiments) by the method of a discharge in oxygen. The results are given in Table I and shown graphically in Figs. 1–3.

In the text, $R_T$ represents the ratio of the unscattered current to the total ion current entering the scattering chamber; and $R_S$ represents the ratio of the unscattered current to the total current minus that deflected by neutraliza-

[1] (a) A. S. Russell, C. M. Fontana, and J. H. Simons, J. Chem. Phys. **9**, 381 (1941). (b) J. H. Simons, H. T. Francis, C. M. Fontana, and S. R. Jackson, Rev. Sci. Inst. **13**, 419 (1942). (c) J. H. Simons, C. M. Fontana, E. E. Muschlitz, Jr., and S. R. Jackson, J. Chem. Phys. **11**, 307 (1943). (d) J. H. Simons, C. M. Fontana, H. T. Francis, and L. G. Unger, J. Chem. Phys. **11**, 312 (1943). (e) J. H. Simons, H. T. Francis, E. E. Muschlitz, Jr., and G. C. Fryburg, J. Chem. Phys. **11**, 316 (1943). (f) J. H. Simons, E. E. Muschlitz, Jr., and L. G. Unger, J. Chem. Phys. **11**, 322 (1943).