The heat of solution of solid glycine in the saturated solution is

$$\Delta H = \bar{L}_2 \text{ (satd.)} - L_2(s) = -354 + 3765 = 3411 \text{ cal.}$$

whence the entropy of solution in the saturated solution is

$$\Delta S = 3411/298.16 = 11.4 \text{ E. U.}$$

Summary

We have measured the heats of dilution of aqueous solutions of glycine from 3 *m* to 0.005 *m* and of glycolamide from 6 *m* to 0.01 *m*. The apparent relative molal heat content in each case may be represented satisfactorily by a cubic equation in the molality. From the heat capacity data we have obtained equations for the apparent relative molal heat contents as cubic functions of the temperature.

We have used these data to calculate ϕ, the osmotic coefficient of glycine at 25°, from freezing point measurements and find that these values agree within about 0.004 with the results of precise vapor pressure measurements at 25°.

From known values of the heats of combustion and entropy of glycine we have calculated the standard heat, entropy and free energy of formation of glycine in the solid state and also in the hypothetical 1 *m* solution.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

The Reducibility of Quadrivalent Zirconium[1]

BY A. W. LAUBENGAYER AND R. B. EATON

Although the normal valence for elements of the fourth periodic group is four, titanium and zirconium have been shown to form compounds in which they exhibit a lower state of oxidation. Compounds of trivalent titanium have been obtained under both aqueous[2] and anhydrous[3] conditions, and compounds of divalent titanium, anhydrously prepared, have been found[4] to be relatively stable in water. For zirconium, however, the oxidation states of +2 and +3 have been obtained[5,6] only in the absence of water.

No thorough study has been reported concerning the reduction of zirconium in aqueous solution, with special reference to intermediate valence states. Such investigations among elements closely related to zirconium have provided interesting and valuable information. This paper discusses electrolytic and polarographic investigations upon the reducibility of quadrivalent zirconium in aqueous solution.

Experimental

Materials.—Zirconyl chloride was purified by recrystallization from hydrochloric acid solution until spectroscopic analysis showed no metals other than hafnium to be present. Zirconium tetrachloride was prepared by passing a dry mixture of chlorine and carbon monoxide over anhydrous zirconyl chloride or zirconium dioxide, heated to around 450°. The tetrachloride was purified by resublimation in a slow stream of nitrogen. Analysis indicated less than 1% of hafnium in the zirconium preparations.

Electrolysis of Zirconium Solutions.—For the study of the reduction of quadrivalent zirconium by simple electrolysis, solutions and conditions were so chosen as to avoid, so far as possible, hydrolysis and the formation of stable oxy-ions of zirconium. In some cases organic solvents were used in the hope of approaching the normal Zr^{+4} ion. Electrolyses were carried out in the usual manner, with a glass cell and protecting the main body of the solution to be reduced from anodic oxidation products by an unglazed porcelain cup which enclosed the platinum anode. To take advantage of the differences in hydrogen overvoltage, platinum, lead and mercury were used successively as cathodes. The solutions and any products of electrolysis were examined for reducing properties at intervals during the electrolysis. Measurements of current and applied voltage were made with standard equipment.

The solutions studied by electrolysis were the following: zirconium acetate in glacial acetic acid; zirconuim sulfate in both concentrated and dilute sulfuric acid; zirconium fluoride in hydrofluoric acid; and zirconium chloride in water, concentrated and dilute hydrochloric acid, hydrochloric acid saturated with hydrogen chloride at 0°, methyl alcohol, ethyl alcohol and pyridine. These solutions were electrolyzed for from one to fifteen hours at a potential sufficient to produce a steady slow discharge of hydrogen. Reduction of the zirconium to a state of di- or trivalency was not obtained in any case, although in the case of the sulfate solutions, metallic zirconium deposited at the platinum electrode. This metal deposition from

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(1) Presented before the Division of Physical and Inorganic Chemistry, American Chemical Society, at Cincinnati, Ohio, April, 1940.

(2) Diethelm and Foerster, *Z. physik. Chem.*, **62**, 129 (1908).

(3) Ruff and Neumann, *Z. anorg. allgem. Chem.*, **128**, 81 (1923).

(4) Forbes and Hall, THIS JOURNAL, **46**, 385 (1924).

(5) Ruff and Wallstein, *Z. anorg. allgem. Chem.*, **128**, 96 (1923).

(6) Young, THIS JOURNAL, **53**, 2148 (1931).

sulfate solutions is in general agreement with the findings of Bradt and Linford.[7]

Reduction Potential Studies.—In order to study more carefully the cathodic processes involved in electrolysis of zirconium solutions, current density–cathode potential curves were determined for zirconium tetrachloride in hydrochloric acid. The measurements were taken in the customary way using a standard potentiometric circuit. A static mercury surface served as cathode. The solutions studied were 0.169, 0.383 and 0.544 *M* with respect to zirconium tetrachloride in 6 to 8 *N* hydrochloric acid, so chosen as to avoid hydrolysis of the tetrachloride and the formation of the stable zirconyl ion, ZrO^{++}.

In these experiments only hydrogen was produced, beginning at a cathode potential of around 0.45 v. (against 1 *N* calomel half-cell), and the rate of discharge increased steadily with current density up to around 3 milliamp./sq. cm. The current density–cathode potential curves showed no characteristics other than those for the hydrogen discharge from hydrochloric acid solution. No evidence suggested the reduction of quadrivalent zirconium in these acid solutions.

Polarographic Studies.—A systematic investigation of the reduction potential for dilute zirconium solutions at a dropping mercury cathode employed the recently developed polarographic technique, which has been well reviewed by Kolthoff and Lingane[8] and by Perley.[9] Zirconium solutions were electrolyzed in a cell in which the cathode consisted of small drops of mercury falling from a glass capillary and the anode consisted of a large static mercury surface. A Nejedley Polarograph was used which photographically recorded current–voltage curves as the electrolysis proceeded at a uniformly increasing applied electromotive force. For the reduction processes, indicated by "waves" in the current–voltage curves, "half-wave" potentials were taken as characteristic. These were determined by subtracting the anode potential from the applied voltage at the half-wave point, the anode potential being measured against a normal calomel electrode on an auxiliary potentiometric circuit.

Series of polarographic curves were determined for several solutions of zirconyl chloride differing tenfold in zirconium concentration. For each series the hydrogen ion concentration was varied as widely as feasible by the addition of solutions of potassium hydroxide or hydrochloric acid. The *p*H was determined by measuring the potential of the solutions against a calibrated glass electrode. The zirconium concentrations and *p*H were so chosen and varied to afford the greatest opportunity for the separation and identification of the polarographic waves obtained.

All solutions were 0.1 *M* with respect to potassium chloride as the indifferent electrolyte. Measurements were made at 25° and with an initial drop time of two seconds. The sensitivity of the galvanometer was such that a deflection of 1 mm. upon the recorded curves denoted a current of 2.4×10^{-9} amp. Representative data are summarized in Table I.

TABLE I

Series	Curve	*p*H	Half-wave potential, v. First	Half-wave potential, v. Second	Height first wave,[a] cm.
I 0.01 *M* $ZrOCl_2$ in 0.1 *M* KCl, adding 0.1 *M* KOH	1	2.03	1.667		10,000
	2	2.13	1.628	Not measurable	7,000
	3	2.28	1.660		5,000
	4	2.40	1.629		4,000
	5	2.54	1.723		2,500
IIA 0.001 *M* $ZrOCl_2$ in 0.1 *M* KCl, adding 1.0 *M* HCl	1	2.96	1.548		750
	2	2.72	1.559	None present	1,320
	3	2.54	1.591		1,830
	4	2.45	1.595		2,650
IIB 0.001 *M* $ZrOCl_2$ in 0.1 *M* KCl adding 0.01 *M* KOH	1	2.99	1.560	1.792	750
	2	3.18	1.533	1.740	495
	3	3.33	1.520	1.742	360
	4	3.56	1.512	1.683	210
	5	3.66	1.511	1.682	175
	6	3.82	1.529	1.577	212
IIIA 0.0001 *M* $ZrOCl_2$ in 0.1 *M* KCl adding 1.0 *M* HCl	1	4.05	1.560		87
	4	3.28	1.609	None present	335
	6	2.86	1.628		825
IIIB 0.0001 *M* $ZrOCl_2$ in 0.1 *M* KCl adding 0.01 *M* KOH	1	4.02	1.567		96
	2	4.40	1.518	None present	63
	3	4.62	1.460		48

[a] At full galvanometer sensitivity.

From these data it is seen that all polarographic curves possess at least one reduction step and some, within a limited range of *p*H and zirconium concentration, have two steps, indicating two reduction processes. In Fig. 1 is shown the polarogram of Curve 1 series IIB, Table I, upon which two measurable waves appear.

It may be demonstrated that the first wave is due to hydrogen discharge, since the height of this wave is directly proportional to the hydrogen ion concentration.

It is concluded that the second wave, measurable in Series IIB and present but not measurable in Series I, is characteristic of a reduction

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[7] Bradt and Linford, *Trans. Am. Electrochem. Soc.*, **70**, 431 (1936).

[8] Kolthoff and Lingane, *Chem. Rev.*, **24**, 1 (1939).

[9] Perley, *Trans. Electrochem. Soc.*, **76**, 91 (1939).

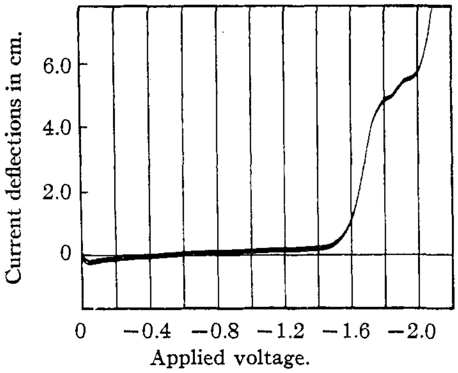

Fig. 1.—Current–voltage curve for 0.001 *M* $ZrOCl_2$ in 0.1 *N* KCl at *p*H 2.99: galvanometer sensitivity $^2/_{300}$; Curve 1, Series IIB in Table I.

of quadrivalent zirconium. The average half-wave potential for this reduction is 1.689 volts. No constant value for the half-wave potential could be obtained for this second wave, since the potential varied with the *p*H. This variation might be accounted for on the basis of changes in zirconium ion concentration brought about by hydrolysis, by changes in the nature of the zirconium ion complex, or by inherent obstacles in the measurement of a potential for a reduction occurring so close to that for hydrogen and while hydrogen bubbles are forming at the cathode. Since no evidence for stepwise reduction was observed, and since it has been found possible to deposit zirconium metal electrolytically, the logical conclusion is drawn that this second wave represents the reduction of quadrivalent zirconium to the metal.

Discussion

These experiments indicate that, unlike its neighbors, zirconium is not reduced in solution from quadrivalency to a state of intermediate valency, but may under some conditions be reduced to the metal. In this respect zirconium is more similar to tantalum than to its close neighbors, the rare earth elements, titanium, vanadium and columbium, all of which exhibit stepwise reduction in aqueous solution.

The polarographic and electrolytic experiments suggest that high zirconium concentration and high *p*H favor electrodeposition of zirconium. This conclusion is in general agreement with the findings of Bradt and Linford.[7]

The polarographic curves may be interpreted to yield a value for the polarographic deposition potential for zirconium of about 1.69 volts. This is a high potential, slightly above that for hydrogen, and is compatible with the difficulty experienced in electroplating zirconium. This also suggests extreme stability for the complex ions in which zirconium exists in aqueous solution, undoubtedly accounting for the non-stepwise reduction of zirconium in such ions. The variation of the deposition potential with *p*H seems to indicate changes in the nature of the complex ions with changing solution conditions; this is in general agreement with the observations of Adolf and Pauli.[10]

It is interesting to note the *p*H of those zirconyl chloride solutions used in the polarographic experiments to which no acid or base had been added (number 1 in each series, Table I). The close correspondence between the zirconium and hydrogen ion concentrations in each case seems to indicate 50% hydrolysis for all these solutions, or the formation of a complex of the ratio $ZrO_2 \cdot HCl$.

Acknowledgment.—The Nejedley Polarograph used in these experiments was made available by the Cornell Agronomy Department. Appreciation is expressed to Professor R. W. Cummings whose generosity and kind assistance made possible the polarographic work.

Summary

Investigations of the reducibility of quadrivalent zirconium in aqueous solution by electrolysis and by the polarographic method indicate:

1. Quadrivalent zirconium cannot be reduced to a state of intermediate valence by electrolysis of solutions of zirconium salts.

2. Non-stepwise reduction to the metal appears to take place at a potential of about 1.69 v. (Polarographic deposition potential against 1 *N* calomel.)

3. Metal deposition potential varies with the *p*H of the solution, probably due to the variation of the nature of the complex ions formed by zirconium.

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[10] Adolf and Pauli, *Kolloid Z.*, **29**, 173 (1921).