theoretical objective is, of course, solely to have the weights accurately compared *inter se*. But there is also the desideratum, when the exercise is given to students who are using the balance for the first time, that the method should appeal to them as simple and easy to grasp.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA.]

# HYDROLYSIS OF ZIRCONYL CHLORIDE AND SULFATE AT ZERO AND TWENTY DEGREES.

BY F. P. VENABLE AND D. H. JACKSON.

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The hydrolysis of zirconyl chloride has been measured at room and higher temperatures by Ruer[1] and a partial table given by Ruer and Levin[2] for zirconyl sulfate at room temperature. It was thought desirable to repeat these for varying dilutions and to determine both the progress and extent of hydrolysis. To throw further light, if possible, upon the reaction, experiments were carried out with a precipitant, iodic acid, which forms a practically insoluble compound with a portion of the combined zirconyl radical and carries down with it the fully hydrolyzed zirconyl hydroxide. At least this is one explanation of its action.

The 2 stable salts, zirconyl chloride and zirconium sulfate, were chosen for the purposes of the investigation. The latter is readily hydrolyzed to the zirconyl sulfate on the addition of water. These salts were freshly prepared and their purity carefully tested. The hydrolysis depends upon 3 factors—concentration, temperature, and time. In these experiments the temperature was held constant and separate series were carried out for each degree of dilution.

The apparatus used in making the conductivity measurements consisted of a modification of the Arrhenius conductivity cell, a Wheatstone bridge, and a small induction coil with telephone receiver. The measurements were made with 0.2, 0.1 and 0.01 *M* solutions for the sulfate and chloride. Readings were taken at 5-minute intervals when the hydrolysis was fairly rapid, and at increasing intervals as it slowed down. The first reading was taken immediately after solution. At the expiration of 3 or 4 hours the changes were so slight that the readings were stopped, since it was difficult to maintain the constant temperature for many hours or days. The relative conductivity is given in reciprocal ohms.

It will be noticed that at both 0° and 20°, and especially at the higher concentration, there is a brief period of temperature adjustment. This

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[1] Ruer, *Z. anorg. Chem.*, **43**, 282 (1905).

[2] Ruer and Levin, *ibid.*, **46**, 449 (1905).

is more pronounced at 0° and is doubtless due to the heat of solution. After expiration of 3 to 4 hours the change in conductivity is so slow as to amount almost to an equilibrium in the reaction. This may be due to the reversing influence of the liberated acid or to the formation of some definite product of hydrolysis which is more resistant to the action of water. These results corroborate those of Ruer, who found that further notable increase in hydrolysis was brought about only after many hours or on heating to boiling. On standing for some time after boiling the resistance increased to a slight extent, showing a reversal of the reaction or partial removal of the free acid.

TABLE I.—EXPERIMENTS WITH $ZrOCl_2$.

| Time elapsed in minutes. | 0°. 35.50 g. in l. | 0°. 17.75 g. in l. | 0°. 1.775 g. in l. | 20°. 35.50 g. in l. | 20°. 17.75 g. in l. | 20°. 1.775 g. in l. |
|---|---|---|---|---|---|---|
| First reading. | 0.11307 | 0.05194 | 0.01014 | 0.16700 | 0.10799 | 0.01215 |
| 5 | 0.08877 | 0.04929 | 0.01008 | 0.16072 | 0.11055 | 0.01213 |
| 10 | 0.08500 | 0.04920 | 0.01009 | 0.15957 | 0.11292 | 0.01218 |
| 15 | 0.08383 | 0.05010 | 0.01014 | 0.15905 | 0.11545 | 0.01227 |
| 25 | 0.08356 | 0.05153 | 0.01027 | 0.16191 | 0.11672 | 0.01241 |
| 35 | 0.08469 | 0.05250 | 0.01041 | 0.16500 | 0.12220 | 0.01252 |
| 45 | 0.08500 | 0.05331 | 0.01055 | 0.16734 | 0.12472 | 0.01264 |
| 55 | 0.08560 | 0.05413 | 0.01066 | 0.17129 | 0.12806 | 0.01285 |
| 75 | 0.08681 | 0.05451 | 0.01080 | 0.17261 | 0.13057 | 0.01299 |
| 95 | 0.08763 | 0.05619 | 0.01090 | 0.17360 | 0.13251 | 0.01311 |
| 115 | 0.09053 | 0.05641 | 0.01096 | 0.17492 | 0.13392 | 0.01321 |
| 145 | 0.09245 | 0.05719 | 0.01103 | 0.17558 | 0.13586 | 0.01328 |
| 175 | 0.09282 | 0.05729 | 0.01104 | 0.17558 | 0.13670 | 0.01333 |
| 205 | 0.09436 | ....... | ....... | ....... | 0.13670 | 0.01333 |

TABLE II.—HYDROLYSIS OF ZIRCONYL SULFATE, $ZrOSO_4$.

| Time elapsed in minutes. | 0°. $ZrOSO_4$=20.26 in 1000 cc. | 0°. $ZrOSO_4$=2.026 in 1000 cc. | 20°. $ZrOSO_4$=40.52 in 1000 cc. | 20°. $ZrOSO_4$=20.26 in 1000 cc. | 20°. $ZrOSO_4$=2.026 in 1000 cc. |
|---|---|---|---|---|---|
| First reading. | 0.10067 | 0.01275 | 0.24800 | 0.13178 | 0.01389 |
| 5 | 0.10000 | 0.01263 | 0.24550 | 0.13108 | 0.01385 |
| 10 | 0.10000 | 0.01272 | 0.24550 | 0.13190 | 0.01385 |
| 15 | 0.10044 | 0.01313 | 0.24700 | 0.13322 | 0.01389 |
| 25 | 0.10209 | 0.01328 | 0.24875 | 0.13553 | 0.01408 |
| 35 | 0.10297 | 0.01353 | 0.25167 | 0.13678 | 0.01430 |
| 45 | 0.10418 | 0.01376 | 0.25500 | 0.13822 | 0.01449 |
| 55 | 0.10528 | 0.01397 | 0.25750 | 0.13982 | 0.01469 |
| 75 | 0.10682 | 0.01401 | 0.26167 | 0.14107 | 0.01481 |
| 95 | 0.10803 | 0.01408 | 0.26582 | 0.14196 | 0.01495 |
| 115 | 0.10880 | 0.01414 | 0.26822 | 0.14232 | 0.01507 |
| 145 | 0.10935 | 0.01421 | 0.27166 | 0.14286 | 0.01511 |
| 175 | 0.11011 | 0.01423 | 0.27332 | 0.14335 | 0.01514 |
| 205 | 0.11011 | 0.01425 | 0.27332 | 0.14335 | 0.01514 |

Zirconium sulfate, $Zr(SO_4)_2$, was used for the next series of experiments. It has been shown that on the addition of water this immediately hydrolyzes, forming a crystalline substance. The reaction is $Zr(SO_4)_2 + 4H_2O \longrightarrow ZrOSO_4.H_2SO_4.3H_2O$. This appears in the older literature as $Zr(SO_4)_2.4H_2O$. As the sulfate is less soluble than the chloride, it was found impossible to make a 0.2 *M* solution at 0°. In this series the temperature adjustment is noticed again but is slighter. The equilibrium is reached after the same lapse of time.

## Precipitation with Iodic Acid.

These experiments were carried out with zirconyl chloride only. Solutions of known strength were prepared and 25-cc. portions were withdrawn at definite time intervals. In these the iodic acid solution was added from a buret until a drop gave no further precipitate. This does not give the end-point with great accuracy, but sufficient to mark the change of ratio of the iodic acid to the zirconyl radical present. The results obtained give an indication of the extent of the hydrolysis.

TABLE III.—PRECIPITATION WITH IODIC ACID.

| Time elapsed | 0°. ZrO=0.5330. | | 0°. ZrO=0.2665. | | 0°. ZrO=0.02665. | | 20°. ZrO=0.5330. | | 20°. ZrO=0.2665. | |
|---|---|---|---|---|---|---|---|---|---|---|
| in minutes. | $IO_3$. | $ZrO/IO_3$. | $IO_3$. | $ZrO/IO_3$. | $IO_3$. | $ZrO/IO_3$. | $IO_3$. | $ZrO/IO_3$. | $IO_3$. | $ZrO/IO_3$ |
| 1st measure | 1.242 | 0.421 | 0.752 | 0.353 | 0.192 | 0.134 | 0.875 | 0.609 | 0.542 | 0.492 |
| 10 | 1.189 | 0.448 | 0.664 | 0.400 | 0.175 | 0.152 | 0.664 | 0.803 | 0.472 | 0.564 |
| 20 | 1.101 | 0.483 | 0.577 | 0.462 | 0.158 | 0.169 | 0.612 | 0.871 | 0.437 | 0.609 |
| 30 | 1.066 | 0.500 | 0.560 | 0.476 | 0.140 | 0.190 | 0.577 | 0.923 | 0.402 | 0.663 |
| 50 | 1.031 | 0.517 | 0.542 | 0.492 | 0.123 | 0.216 | 0.551 | 0.966 | 0.367 | 0.726 |
| 70 | 0.997 | 0.534 | 0.533 | 0.500 | 0.114 | 0.233 | 0.525 | 1.011 | 0.350 | 0.757 |
| 90 | 0.979 | 0.544 | 0.525 | 0.511 | 0.105 | 0.253 | 0.508 | 1.049 | 0.341 | 0.775 |
| 120 | 0.962 | 0.554 | 0.507 | 0.525 | 0.105 | 0.253 | 0.491 | 1.081 | 0.338 | 0.788 |
| 150 | 0.962 | 0.554 | 0.498 | 0.535 | ..... | ..... | 0.483 | 1.106 | ..... | ..... |

It is noteworthy that there is here also indication of the initial effect of temperature adjustment and that there is a decrease in the amount of iodic acid necessary for precipitation until at the expiration of about 3 hours the change becomes very slight. The iodic acid forms a compound with the zirconyl radical, liberating the hydrochloric acid. This compound is practically insoluble in water or weak mineral acids. When precipitated this carries with it such of the colloidal zirconyl hydroxide as may have been formed by hydrolysis. It has been shown by Venable and Smithey[1] that when this precipitate is treated with hot or cold water much of the iodic acid may be washed out. It is interesting to note that after the lapse of 2 or 3 hours a practical equilibrium or period of slow change is reached in all 3 dilutions. When the rate of change per minute is examined it will be found that there are fluctuations. Sometimes these show a reversal from increase to decrease, and again the opposite is indicated. This is true both of the resistance and extent changes.

In examining Table V the recurrence of certain ratios will be observed,

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[1] Venable and Smithey, THIS JOURNAL, 41, 1722 (1919).

for instance, the end-points in the first 2-ratio columns and the ratios between 0.450 and 0.480. Some light is thrown on these by the experiments of Venable and Smithey. The ratio 0.456 would correspond to a hydrolyzed product $ZrO(OH)_2.2ZrO(IO_3)_2$, or to a zirconyl iodate in which $^1/_3$ of the molecules had undergone hydrolysis. Such a product was obtained by these investigators when the precipitation was made in cold, concentrated solutions and the precipitate was freed from the filtrate by suction without washing. The ratio 0.533 corresponds to a product $3ZrO(OH)_2.4ZrO(IO_3)_2$, in which 3 out of 7 molecules had been hydrolyzed. This was obtained when the precipitate was formed from dilute solutions and washed with a limited amount of water at room temperature. The ratio 0.914 corresponds in the same way to $2ZrO(OH)_2.ZrO(IO_3)_2$, in which 2 out of 3 molecules have been hydrolyzed. Here the precipitate was washed with hot water in increased amount. A ratio 1.218, corresponding to $3ZrO(OH)_2.2ZrO(IO_3)_2$, where 3 out of 4 molecules had been hydrolyzed, was obtained after prolonged washing with hot water.

## Summary.

1. The hydrolysis of zirconyl sulfate and chloride has been examined both by relative conductivity and by a precipitation method. The temperatures were 0° and 20°, respectively. Three different dilutions were used and the effect of the time factor noted.

2. There appears to be an initial temperature adjustment on dissolving the salts. Afterwards there is a decrease in the resistance until after about 3 hours an equilibrium or period of very slow change is reached.

3. In the experiments with iodic acid there is also indication of an initial adjustment. The extent of the hydrolysis is indicated. The equilibrium or period of slow change is reached in 2 to 3 hours.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

# SURFACE TENSION AND MOLECULAR ATTRACTION: ON THE ADHESIONAL WORK BETWEEN MERCURY AND ORGANIC LIQUIDS.[1]

BY WILLIAM D. HARKINS AND E. H. GRAFTON.

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Most of the papers on molecular attraction make use of one of the equations of state in order to calculate the internal pressure of pure substances in the liquid state. It is evident that such equations give a very uncertain basis for the determination of results which represent more

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[1] Published in abstract in *Proc. Nat. Acad. Sci.*, **5**, 569–73 (1919). For similar work with water and organic liquids see Hardy, *Proc. Roy. Soc. London* (A) **88**, 303–33 (1913); Harkins, Brown and Davies, THIS JOURNAL, **39**, 354–64 (1917); and Harkins, Clark, and Roberts, *ibid.*, **42**, 700–12 (1920).