suggestions. The last named made the indicator measurements of acidity which are referred to in the paper.

Summary

1. The customary separation of rhodium from platinum by means of ammonium chloride is unsatisfactory unless regarded merely as a preliminary fractionation.

2. Rhodium can be separated from quadrivalent platinum by hydrolysis in faintly alkaline chloride solutions.

3. Data are given for the separation of rhodium by means of sodium hypobromite and by means of barium carbonate. The latter is the more satisfactory reagent, particularly because it readily maintains the desired alkalinity. Two precipitations are sufficient for most purposes, but a third should be made when high accuracy is desired.

4. Experiments were made to determine the behavior of bivalent platinum chloride, as well as of the other platinum metals and gold, with respect to hydrolysis.

5. A procedure is recommended for the separation of rhodium from platinum in the absence of other platinum metals and of certain undesirable salts.

WASHINGTON, D. C.

NOTES

The Atomic Weight of Zirconium.—Results of our investigation of the atomic weight of zirconium were published in THIS JOURNAL in 1917.[1] The compound selected for analysis was zirconium tetrachloride. Determinations of zirconium as the oxide gave an average of 92.1 and those of the chlorine an average of 91.76 for the atomic weight of zirconium. The divergences in the individual determinations were too large for atomic weight work. At the time we could offer no explanation for these divergences, though the suggestion was made that in the case of the weighings of zirconia they might be due to the retention of chlorine even after 50 to 60 hours of heating at about 1000°. We were at quite a loss to explain those found in the chlorine determinations.

The war interrupted our work. Later, various methods of removing the chlorine supposed to be present yielded no results. The discovery of hafnium by Hevesy and the proof that it accompanied zirconium in all of its minerals has at last revealed the cause of our difficulties. Dr. Hevesy has very kindly examined three mixed samples of the zirconia from bulbs such as were used by us and has reported the amount of hafnium oxide present in each. In No. 1 he found 1% of hafnium dioxide, HfO_2; in No. 2, 0.95%; in No. 3, 0.7%. He states that by his method it is scarcely

[1] THIS JOURNAL, **39**, 1598 (1917).

possible to determine accurately so slight a difference as that between 1.0% and 0.95%. Of course we cannot state positively the relation of these percentages to that in the individual bulbs used by us for analysis nor to the average obtained from these separate bulbs. Our process of distillation from bulb to bulb would probably bring about variations in the content of the separate bulbs, as it is not at all probable that zirconium tetrachloride and hafnium tetrachloride would have the same volatilization point.

Introducing the factors given by Dr. Hevesy for the correction in the averages from our results, we find that for the zirconia average of 92.1 for the atomic weight of zirconium, the corrected result for 1% of hafnium dioxide would be 91.22; for 0.7% it would be 91.49. For the chlorine average of 91.76 for the atomic weight the corrected results would be 91.19 and 91.34, respectively. The average of the zirconia results would be 91.36 and for the chlorine results 91.26. These values are calculated on the basis of Hf = 180, which Dr. Hevesy says is very close to the true atomic weight. It seems probable, therefore, that the atomic weight of zirconium is very close to 91.2. Dr. Hevesy informs us that preliminary determinations by Hönigschmid made on preparations that had been found free from hafnium are in close accord with this number.

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Calculation of Degree of Photolysis of Potassium Nitrate.—On p. 801 of the April, 1924, number of This Journal, appears a statement by W. T. Anderson, Jr., in his paper on the "Photolysis of Potassium Nitrate," to the effect that "it is not possible by the experimental methods employed to determine the total amount of nitrate decomposed in any interval of time," by which it is understood to mean all of the nitrate that has been changed to nitrite, including that which has been changed back to nitrate again. On p. 1066 of the same number of This Journal, a book was reviewed, on p. 52 of which may be found a method by which it is possible to calculate the total nitrate decomposed using the data already determined by the author. The following indicates the method by which this may be done.

Let x = concentration expressed in equivalents of nitrate at any time Θ.
y = concentration of nitrite expressed in the same way.

Since under the conditions the active oxygen is probably equivalent to the nitrite (that this assumption is justified, is shown by the plot in Fig. 1), there may be written

$$dy/d\Theta = k_1x - k_2\,y^2 \qquad (1)$$

where k_1 and k_2 are the velocity constants of the reactions to the right and left, respectively.

If x_0 and y_0 represent the concentrations at the start of the reaction and x_∞ and y_∞ those at equilibrium, represented approximately by the time 360 minutes in the table on page 798 of the reference cited, let

$$\beta = \frac{k_1 + k_2\,y_\infty}{k_2} = \frac{(x_0 + y_0)\,y_\infty}{x_0 + y_0 - y_\infty} \tag{2}$$

and since $x = x_0 + y_0 - y$, by stoichiometry, Equation 1 reduces to the form

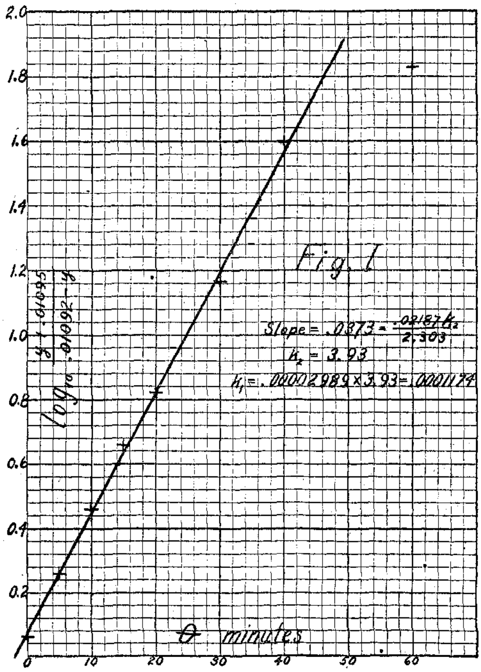
$$\mathrm{d}y/\mathrm{d}\Theta = k_2\,(y_\infty - y)(y + \beta) \tag{3}$$

the integral of which is

$$ln\,\frac{y + \beta}{y_\infty - y} - ln\,\frac{\beta}{y_\infty} = (\beta + y_\infty)k_2\,\Theta \tag{4}$$

and k_1 and k_2 may then be calculated with the experimental data given by the author, from Equations 2 and 4, in the usual manner.

The writer has done this for the first set of data given by the author in his Table I. From Equation 4, plotting log $\frac{y + \beta}{y_\infty - y}$ against Θ on normal plotting paper should give a straight line. This has been done in Fig. 1. The last point shows a large deviation, undoubtedly due to being so near equilibrium, where a small error in measurement would make a much larger deviation from the line. From the slope of this line the value of the velocity constant k_1 of the decomposition reaction was found to be 0.000117, when the data were expressed in milli-equivalents and minutes. This value of k_1 is all that is needed to make the quantum calculations to which the author refers. If the actual amount of nitrate decomposed is also desired, it may be determined by the following method.



Let N represent the total amount of nitrate decomposed at any time Θ, including that which has gone back to nitrate again, expressed in equivalents. The nitrate decomposes according to the equation

$$\mathrm{d}N/\mathrm{d}\Theta = k_1 x \tag{5}$$

and the total nitrate decomposed is given from the equation

$$\int_0^{\Theta} \frac{dN}{d\Theta}\, d\Theta = \int_0^{\Theta} k_1 x d\Theta \qquad (6)$$

Transform Equation 4 to the form

$$\frac{(y+\beta)y_\infty}{(y_\infty - y)\beta} = e^{(\beta + y_\infty)k_2\Theta} \qquad (7)$$

in which the constants β, y_∞ and k_2 are all known, and which will be simplified by the substitution of the numerical values. Then solve (7) for y and substitute for y, $x_0 + y_0 + x$, giving the relation between x and Θ, which when substituted in Equations 5 and 6 will give Equation 6 with two variables only, N and Θ.

Equation 6, simplified by the introduction of numerical values, may now be integrated between any two limits of Θ, the amount of nitrate decomposed being most readily calculated by evaluating the integral by the graphical method.

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CATALYTIC ALKYLATION OF ANILINE

BY A. B. BROWN AND E. EMMET REID

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Introduction

The efficiency of the high grade silica gel prepared in this Laboratory as a catalyst for the amination of alcohols[1] made desirable a study of its effectiveness as a catalyst in the N-alkylation of aniline. Mailhe and de Godon have shown that thoria[2] and zirconia are effective in methylating aniline, and that alumina[3] is exceptionally suitable for methylating aniline, *o*-, *m*- and *p*-toluidine.

The present investigation has for its purpose the quantitative study of the extent of N-alkylation of aniline by methyl, ethyl, *n*-propyl and *n*-butyl alcohols with silica gel as catalyst over the temperature range 300–500°.

Apparatus

The apparatus and method of operating were the same as used for the study of the alkylation of ammonia.[1]

Reactants

The aniline was fractioned through a 60cm. Vigreaux column from a commercial C. P. sample, and the portion boiling constantly within 0.2° taken.

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[1] Articles to appear in *J. Phys. Chem.*

[2] Mailhe and de Godon, *Compt. rend.*, **166**, 467 (1918).

[3] *Ibid.*, **166**, 564 (1918).