6. The values obtained by Kohlrausch, Holborn and Diesselhorst for potassium chloride solutions are shown to *average* about 0.15% high but the relative values are also in error. The maximum *absolute* error (in their 0.01 *N* solution at 0°) is shown to be 0.23% and the maximum *relative* error determined is 0.20%.

7. Values for the new solutions have been calculated to include temperatures as high as 30°, but for accurate measurements it is recommended that cells be standardized at 0°.

8. A new ice thermostat was used in these measurements where the cells were embedded and thoroughly packed in finely shaved ice, drainage being provided for the water.

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RUTHENIUM DICHLORIDE

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The blue color produced by the action of reducing agents on solutions of ruthenium appears to have been first noticed by Vauquelin[2] in 1804, and was later[3] attributed by him to the presence of the recently discovered osmium.

Thirty years later Claus discovered ruthenium, and noted this reaction as one of the most characteristic of this metal.[4] Since the blue color was produced by reducing agents, especially by zinc and by hydrogen sulfide, it was assumed by Claus and by later workers that it was occasioned by a lower chloride, $RuCl_2$, and as such has passed into the literature.

It may be noted that Claus[5] succeeded in chlorinating metallic ruthenium by heating in a current of dry chlorine, and considered that his analytical results substantiated this formula (then considered as RuCl).

Later, Joly[6] found that ruthenium could be more readily chlorinated by heating in a current of chlorine to which carbon monoxide was added. Under these conditions a very voluminous dark brown to black finely divided mass is obtained, to which Joly ascribed the formula $RuCl_3$. The chloride thus formed is insoluble in water, absolute alcohol, acids and alkalies, but dissolves readily in dil. alcohol, best about 25%, giving

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[1] This communication is an abstract of theses submitted by James L. Howe, Jr., in partial fulfilment of the requirements for the degree of Master of Arts (1921), and by S. C. Ogburn, Jr., in partial fulfilment of the requirements for the degree of Master of Science in Chemistry (1923) at Washington and Lee University.

[2] Vauquelin, *Ann. chim.*, **49**, 188, 219 (1804); **50**, 5 (1804).

[3] Vauquelin, *Ann.*, **89**, 150, 225 (1814).

[4] Claus, *Ann.*, **56**, 260 (1846).

[5] Claus, *Ann.*, **59**, 238 (1846).

[6] Joly, *Compt. rend.*, **114**, 291 (1892).

a deep azure-blue solution, apparently the same as that produced by reducing agents. Joly considered that on solution hydrolysis had taken place, with the formation of the substance $HORuCl_2$.

In an endeavor to determine whether ruthenium actually forms any simple compounds in which it acts as bivalent, Remy[7] has investigated the reduction of ruthenium trichloride by titrating its solution with sodium amalgam, and his results indicate that the ruthenium in the blue solution is present in bivalent form, although the reduction seems uniformly to go slightly further than that required for the dichloride.

In 1901[8] one of us investigated the blue solution produced by the electrolytic reduction of ruthenium trichloride, precipitating it with cesium chloride and with rubidium chloride, but failed to obtain results which could be considered trustworthy. In general, the ratio of chlorine to ruthenium was greater than that required for the formula $RuCl_2$, but less than that corresponding to the formula $RuCl_3$. In two cases the analysis of the precipitated salt pointed to the composition $3CsCl.2RuCl_2.2H_2O$. In the light of later work it appears that the difficulty of getting uniform analytical results may have been due to three different causes: (1) tendency of the salt to oxidize in acid solution, thus (2) making it difficult to wash the salt completely free from the mother liquor, and (3) the impossibility of determining when the reduction is complete. The solution used may still have contained unreduced trichloride, the brownish-red color being obscured by the intense blue of the dichloride, while Remy has suggested that the reduction may go further with the production of univalent ruthenium.

It has never been shown that the blue color produced by the reduction of trivalent ruthenium is due to the same cause as that given by the solution of the ruthenium chloride formed by chlorinating metallic ruthenium in the presence of carbon monoxide, and it therefore seemed worth while to study this latter chloride more fully. The details of its preparation are given in the experimental part of this paper.

From the fact of its insolubility in water, acids, alkalies, and alcohol, but ready solubility in dil. alcohol, it had been inferred that the blue solution formed was colloidal, but it was found to diffuse readily through a collodion membrane and it was not precipitated by electrolytes. This substantiates the observations of Remy[9] on the blue solution from reduced ruthenium trichloride, which failed to show the Tyndall effect or to reveal any colloidal particles under the ultramicroscope.

On the other hand, the solution failed to give any immediate reaction for either chlorine or ruthenium ions, and its conductivity was very slight.

Analysis shows that ruthenium and chlorine are present in the blue solution in the ratio of 1:2, and that the same is true of that portion of

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[7] Remy, *Z. anorg. Chem.*, **113**, 229 (1920). This paper contains an excellent critical review of the subject.

[8] Howe, THIS JOURNAL, **23**, 782 (1901).

[9] Ref. 7, p. 246.

the chlorinated ruthenium which is dissolved out of the original mass. Hence, it must be concluded that ruthenium dichloride exists as a brown powder, formed by the direct chlorination of ruthenium in the presence of carbon monoxide, is insoluble in all ordinary solvents, but soluble in dilute alcohol and some other diluted organic hydroxy compounds, and that in such solutions it is not appreciably ionized.

Experimental Part

Chlorination of Ruthenium.—Two to four tenths g. of pure ruthenium, which had been reduced by hydrogen, was placed in a porcelain boat and the latter then inserted in a hard glass tube in a combustion furnace. A gentle stream of purified and dried chlorine was passed through the tube, and after the air had been expelled the furnace was heated. When the heat of the furnace was fairly high a small amount of pure and dry carbon monoxide was allowed to enter with the chlorine. Almost immediately there was apparent a distinct glow and a perceptible swelling of the ruthenium. After the reaction had proceeded for 15 to 20 minutes the heat and the current of carbon monoxide were cut off, and a moment later the entrance and exit tubes were closed, leaving the chlorinated ruthenium to cool in an atmosphere, but not in a current, of chlorine. It was found that when the chlorine stream was continued while the ruthenium was cooling there was danger of a little of the ruthenium becoming more highly chlorinated. This was evidenced by the mass giving a reddish-brown solution of the trichloride on treatment with water, as was early noticed by Claus. When chlorinated in the manner above indicated the product was completely insoluble in water and in strong alcohol.

In order to determine the most favorable conditions for chlorination, varying temperatures and amounts of carbon monoxide were tried, the amounts of chlorine absorbed by the ruthenium in different experiments being 23.2%, 32.7%, 39.5%, 36.1% and 41.1%. The last result corresponds to the calculated amount for complete chlorination to the dichloride. The most favorable condition was found to be a rather low temperature, a rapid stream of chlorine, and a very small amount of carbon monoxide, which seems to act here as a catalyst. When a high temperature was used, black lustrous crystals were obtained, apparently of metallic ruthenium, indicating the reversibility of the reaction, $Ru + Cl_2 \rightleftharpoons RuCl_2$.

Solution of the Chlorinated Ruthenium.—While the product of chlorination as above described is insoluble in water or in alcohol alone, it dissolves with more or less readiness in mixtures of the two solvents in almost any proportion. With some samples it was possible to get a very deep azure-blue solution by merely placing the chloride on a filter paper in a funnel and pouring dil. alcohol through it; in most cases, however, it dissolves more slowly, first giving a claret solution, which gradually becomes azure-blue, often almost black, in the course of a few hours. Deeply colored solutions were obtained with as low as 25% alcohol and as high as 90%.

This solubility in a mixed solvent of a substance insoluble in either of the constituents naturally suggested[10] colloidal dispersion, and the effect

[10] Compare Galeotti, *Z. Chem. Ind. Kolloide*, 3, 118 (1908), regarding the solubility of zein.

of other solvents was tried. Traces of a blue solution were obtained with dilute methanol, phenol, acetic acid (10%), and with 50% glycerol; a more decided solution with glycerol (d., 1.25) and with dilute sucrose; no effect was produced by glacial acetic acid nor by dil. amyl alcohol. The thought that the solution might be colloidal had occurred in connection with the variable composition of the precipitate earlier obtained by cesium chloride from the blue solution prepared by the electrolytic reduction of ruthenium trichloride, and hence the solution in dilute alcohol was tested for evidence of the presence of a colloid. A collodion thimble, which had previously been proved leak-proof by water and by congo-red, was filled with the blue ruthenium solution and immersed in dil. alcohol of the same strength as the solvent. Within about fifteen minutes a slight blue color was imparted to the alcohol; gradually this deepened and at the end of 26 hours the solution inside and outside the dialyzer was uniformly blue. This latter was again tested after the experiment and found intact.

As a second experiment four separate portions of the blue solution were treated with solutions of aluminum chloride, potassium ferrocyanide, potassium ferricyanide and colloidal silicic acid, respectively. No appreciable action was produced by any of these coagulating agents until the solutions had stood for several days, and even then the action was slight. It may be assumed, therefore, that the solution is not colloidal, and this is confirmatory of Remy's results with the blue solution produced by the reduction of ruthenium trichloride by sodium amalgam.

Since Joly believed that the chlorinated ruthenium obtained by him in a manner similar to ours was the trichloride, and attributed the formula $Ru(OH)Cl_2$ to the blue solution, it is obvious that hydrolysis must have taken place if his view was correct: $RuCl_3 + HOH \rightleftharpoons Ru(OH)Cl_2 + HCl$. The solution, however, did not react to litmus; therefore no hydrolysis had taken place and the formula proposed by Joly must be incorrect.

Analysis of the Blue Solution.—It was first thought that by evaporating the solution to dryness and heating the residue in a current of hydrogen, as in the usual method of analysis of ruthenium compounds, it might be possible to obtain the ratio of chlorine to ruthenium in the blue compound. In the first experiments the solution was evaporated in a porcelain boat on a water-bath and then transferred to a hard glass tube in a combustion furnace and heated in a current of hydrogen, the hydrogen chloride formed being led into a solution of silver nitrate. As evaporation proceeded the solution became green and when nearly dry a brown-red. Silver nitrate gave a precipitate. It appears that under these conditions hydrolysis takes place. The analysis was then repeated, but the whole evaporation was conducted in a current of hydrogen in the combustion tube. This time the atomic ratio Cl : Ru was found to be 1.99 : 1. Two other analyses gave the ratios 1.9 : 1 and 1.8 : 1. The compound which gives the blue solution may, therefore, be considered to be the dichloride $RuCl_2$.

In order to establish the existence of ruthenium dichloride in the mass of chlorinated ruthenium and that no change had taken place on treating it with dil. alcohol, it was felt necessary to repeat the work in such a way as to account for all the chlorine taken up by the ruthenium on chlorination. These experiments were carried out as follows.

The weighed ruthenium was chlorinated in the usual manner in a porcelain boat and the amount of chlorine absorbed also weighed. After a rapid (but incomplete) extraction with a minimum quantity of dil. alcohol, the insoluble portion was filtered on a Gooch crucible, the precipitate transferred to a porcelain boat and analyzed in the usual way. This gave the amount of ruthenium dichloride which had been dissolved. The alcoholic solution was evaporated to dryness under suction, all the vapor being led through a solution of silver nitrate, in order to retain the chlorine which is evolved as hydrogen chloride in the final stages of evaporation. This material was then analyzed as usual.

The results are given in Analyses 1 and 2.

In order still further to ensure a correct analysis of the chlorine in the blue solution, an analysis was made in which the blue solution was evaporated to dryness with anhydrous sodium carbonate in an electric oven at 120°.

After dryness was reached, the temperature was raised to 185°, after which the residue was removed from the oven and heated to about 400°. The mass was then extracted with water and the chlorine determined. Owing to the fact that some of the ruthenium is oxidized to the ruthenate by heating with alkali, it is difficult to avoid loss in the extra manipulation, so that the ruthenium is more accurately calculated from the amount dissolved from the chlorinated ruthenium.

	Analyses			
	1	2	3	
Ru taken	0.1672	0.2336	0.5294	
Cl absorbed	.0591	.0625	.1389	
Weight of chlorinated Ru	.2263	.2961	.6683	
Undissolved portion. Ru	.0920	.1592	.3633	
Cl	.0111	.0170	.0216	
Total residue	.1031	.1764	.3849	
Dissolved portion Ru	.0743	.0740	.1601	0.1661 (by difference).
Cl	.0491	.0448	.1171	
Total dissolved	.1234	.1188	.2772	0.2832
Total Ru recovered	.1663	.2334	.5234	
Total Cl recovered	.0602	.0618	.1387	
Total Ru + Cl recovered	.2265	.2952	.6621	
Loss or gain	+ .0002	− .0009	− .0062	
% Cl in dissolved compound (calc. for $RuCl_2$, 41.1)	39.8	37.7	42.25	41.3
Formula of dissolved compound from analysis	$RuCl_{1.9}$	$RuCl_{1.8}$	$RuCl_{2.09}$	$RuCl_2$

Both calculations are given in Analysis 3, which was carried out by this method.

The analyses leave no doubt that the compound extracted from the chlorinated ruthenium and that which gives the blue color to the solution are identical, and have the formula, $RuCl_2$.

Properties of a Solution of Ruthenium Dichloride in Dilute Alcohol.—When the chlorinated ruthenium is treated with concd. alcohol no change takes place, but on the addition of water it immediately begins to dissolve, giving a deep reddish-purple color, which soon changes over into azure-blue, sometimes so dark as to appear black. This solution is neutral to litmus, and appears to contain no appreciable quantity of electrolytes. With platinum electrodes of a centimeter area and placed a centimeter or so apart in a U-tube an 8-volt battery gave about one milliampere of current. When the current is passed for some time ruthenium is very gradually deposited on the cathode.

Sodium hydroxide solution (0.1 *N*) gives no immediate reaction in the cold; after several days, or sooner when the solution is heated, a green color develops and a black precipitate settles.

When the blue solution is saturated with hydrogen sulfide there is at first no change, but in the course of some minutes a slight black precipitate begins to appear, which later becomes voluminous and leaves a pale wine-colored supernatant liquid (probably the aquo chloride).

Silver nitrate gives no immediate reaction, but at the end of about fifteen minutes a faint white cloud of silver chloride begins to appear, which in time increases and finally settles as a gray precipitate.

On saturation with sulfur dioxide the solution remains unchanged for some time, but after several days becomes decolorized; later it assumes a reddish-violet color and by the end of a month is deep rose.

Hydrogen peroxide gives no color change for several days but later the solution becomes decolorized.

Bromine water causes the solution to become deep red. Chlorine in small quantity changes the color to green, which after some days becomes yellow.

When the solution is made alkaline with sodium hydroxide, the above-mentioned oxidizing agents cause a dark precipitate to form, probably of hydrated ruthenium oxide, Ru_2O_3.aq.

Neither dil. nor concd. hydrochloric acid causes any immediate change, but gradually the color fades, becoming a pink (aquo chloride). If to a concentrated blue solution concd. hydrochloric acid is added and then cesium or rubidium chloride, an olive-green precipitate is formed, the composition of which is variable. The same precipitate is formed in the blue solution obtained by the electrolytic reduction of ruthenium trichloride, and the analyses[11] indicate that the precipitate is contaminated by a double salt of the aquo-chloride, $Ru(H_2O)Cl_3$. The filtrate from this precipitate oxidizes very rapidly to a rose color, and from it the aquochloro ruthenate, $Cs_2Ru(H_2O)Cl_5$, crystallizes in rose-colored prisms.[12]

An effort was made to determine the state of oxidation of the ruthenium in the blue solution by the use of oxidizing agents. In a solution acidified by sulfuric acid the ruthenium is rapidly oxidized by potassium permanganate, but no satisfactory end-point could be obtained, owing to the action of the permanganate on the alcohol present. This oxidation of alcohol, normally slow, seems to be much accelerated by the presence of the ruthenium, doubtless as a catalytic agent. Efforts to remove the alcohol by evaporation under reduced pressure at 60° resulted in the solution gradually turning greenish-brown and eventually giving a brownish-black precipitate. It was evident that oxidation had taken place. By allowing the blue solution to evaporate spontaneously at ordinary temperature a blue varnish was obtained, which was readily soluble in water. The results of a single experiment are given.

Two cc. of a blue ruthenium solution containing by analysis 0.12 mg. per cc. was allowed to evaporate spontaneously, the residue dissolved in water, and after acidification with sulfuric acid titrated with a 0.01409 *N* solution of potassium permanganate; 0.2 cc. was required to give a distinct pink. This corresponds to 0.14 mg. of ruthenium per cc., assuming that the ruthenium was oxidized from Ru^{II} to Ru^{III}. Other experiments gave similar figures.

These results are not sufficiently accurate to stand by themselves, but are confirmatory of the results obtained in the rest of the work.

In comparing the properties of our blue solution with those of Remy's solution,[13] account must be taken of the facts that his solution was produced by the reduction of an acid solution of trivalent ruthenium (this solution probably contains its ruthenium as H_2RuCl_5), while ours was prepared by dissolving ruthenium dichloride out of ruthenium which had been chlorinated by the action of chlorine in the presence of carbon monoxide, and that our solution contained the dichloride in a very slightly ionized condition. When our solution was acidified with hydrochloric acid it gave reactions very similar to those noted by Remy. It seems probable that in this acid solution the ruthenium is present as chlororuthenous acid, H_2RuCl_4.

Summary

The blue solutions produced by the reduction of ruthenium solutions, and also by the treatment of chlorinated ruthenium with dilute alcohol

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[11] A number of these analyses are given in the article previously mentioned (Ref. 8, p. 788). At that time it was suggested that the figures pointed to a formula $3CsCl.2RuCl_2.2H_2O$; it is more probable that the formula of the compound should be Cs_2RuCl_4.aq.

[12] Ref. 8, p. 785.

[13] Ref. 7, p. 249.

have been studied. Both solutions contain ruthenium in the bivalent condition.

When chlorine and carbon monoxide are passed over hot ruthenium, the dichloride is formed, but it is difficult to chlorinate the ruthenium completely.

Ruthenium dichloride is insoluble in the ordinary solvents, but is soluble in dil. alcohol, and to some extent in diluted organic hydroxides and acids.

The solution of the dichloride in dil. alcohol is not colloidal, but is very slightly ionized.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 155]

THE PRESSURE-VOLUME-TEMPERATURE RELATION FOR GASEOUS ETHYL ETHER

BY JAMES A. BEATTIE[1]

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This investigation was begun with the purpose of studying the mechanism of vaporization by a consideration of the pressure-volume-temperature data on the liquid and gaseous phases of a substance, and of studying the accuracy with which the equation of state suggested by Keyes[2] represents the experimental data. The particular form which the equation takes when no change is occurring in the molecular species of the substance under consideration, is $p = \frac{RT}{v-\delta} - \frac{A}{(v+l)^2}$, $\delta = \beta e^{-(\alpha/v)}$. H. B. Phillips pointed out to the author that the potential energy term $A/(v+l)^2$ in the above quotation was almost equivalent to $A/v^2\, e^{-m/v}$ where $m = 2\,l$. This latter term has been found to fit the data slightly better[3] than the algebraic form, especially for the liquid phase, and also to have a better theoretical significance. For future work the equation will be used in this modified form.

It will be noticed that this equation, which was deduced for the case that the molecular complexity of the fluid is not changing (neither association nor dissociation taking place) requires that the pressure be a linear function of the temperature when the volume is held constant. For testing the correctness of this condition, it is better to measure isometrics directly, rather than to calculate them from isothermal data, and hence in this work the isometric method was used.

Ethyl ether was the substance chosen for this study, since there is a large

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[1] National Research Fellow in Chemistry.

[2] Keyes, *Proc. Nat. Acad. Sci.*, **3**, 323 (1917).

[3] See Tables IV and V of this article and also Smith and Taylor, THIS JOURNAL, **45**, 2107 (1923).