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Investigations in the Chemistry of Rhenium. II. Lower Oxidation States¹

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We have previously reported our spectrophotometric and chemical studies of the solution chemistry of rhenium in the IV, V and VII states.² To extend these studies to lower oxidation states of rhenium, we have investigated the -I state and its oxidation products. It will be evident to the reader that the conclusions as to the reactions of rhenium(-I) that are reached in this paper have not been completely proved and that further experimental work is desirable. Since we are not in a position to continue these investigations, they are being reported in their present somewhat tentative state.

The -I state of rhenium was first prepared by Lundell and Knowles³ by running 0.0009-0.00018 *F* potassium perrhenate in 0.9 *F* sulfuric acid through a Jones reductor. The oxidation number was established by titration to $\text{Re}^{\text{VII}}\text{O}_4^-$. The existence of rhenium (-I) was confirmed by Tomiček and Tomiček⁴ and by Lingane^{5,6} and electronic structures were proposed by Lingane^{5,6} and by Pauling.⁷

Experimental

The preparation of reagents and the details of spectrophotometry have been given before.² Rhenium (-I) was prepared by passing perrhenic acid in hydrochloric acid over amalgamated zinc. The 20-mesh zinc was amalgamated by stirring with sufficient mercuric nitrate solution to form a 5% amalgam; a small amount of nitric acid was present to prevent formation of mercury oxides.⁸ The reductor was constructed so that it could be evacuated and filled with carbon dioxide and kept cooled by an ice-bath. Samples of the reduced rhenium solution were withdrawn from it into graduated centrifuge tubes for analysis. Drainage loss in the reductor was 0.5-1 ml. of solution.

Results and Discussion

Preparation of Re(-I) in Jones Reductor.—For our spectrophotometric experiments, it was desirable to prepare as concentrated a solution of Re(-I) as possible. Lundell and Knowles³ worked with solutions that were *ca.* 10^{-4} *F* and Lingane⁶ has prepared solutions that were *ca.* 8×10^{-4} *F* in Re(-I). These authors carried out their re-

ductions in sulfuric acid solutions. With the various experimental conditions we have tried in hydrochloric acid solution, it was not possible to quantitatively reduce Re(VII) to Re(-I) if the initial Re(VII) concentration was greater than 0.001 *F*.

In typical experiments, 10-40 ml. samples of a perrhenic acid solution in 4-6 *F* hydrochloric acid were treated in the reductor with 5% amalgamated zinc for two to five minutes. The hydrogen ion concentration was typically lowered to 0.5 *F* or less after this length of reaction with the zinc.

Analyses with cerium(IV) were done by running 2.0-ml. portions of the reduced rhenium solution into excess 0.0462 *F* cerium(IV) in 0.5 *F* sulfuric acid. The unreacted cerium(IV) was determined with 0.05 *F* iron(II) sulfate by titrating over a period of one to two minutes to an end-point with *o*-phenanthroline iron(II) complex indicator. No significant oxidation by the excess cerium(IV) of the chloride present in the rhenium solution was found at 0.5 *F* H^+ because no effect on the analyses was found when the volume of 0.0462 *F* cerium(IV) was varied from 1.5 to 2 ml., and the end-point was stable several minutes. As stated by Lingane,⁶ direct titration of the Re(-I) by cerium(IV) was less satisfactory because the rate of reaction was slow near the end-point. The reduced solutions were also analyzed by adding 2.0 ml. of rhenium solution to 2.0 ml. of 0.015 *F* potassium iodate. No color with starch was found, and the light green color of the mixture showed that iodine monochloride had formed in the chloride furnished by the rhenium solution. The excess oxidant was then determined by adding potassium iodide and titrating the iodine formed by thiosulfate. Some titrations were also done by running 2.0 ml. of reduced rhenium solution into excess iodine, using 0.085 meq. of iodine in a total volume of 3-30 ml.

Table I shows the results of some of these experiments. The apparent average oxidation numbers listed there are calculated on the basis of the initial formality of perrhenic acid and the number of reducing equivalents in the solutions—these apparent oxidation numbers would be more positive than the true average oxidation number of the rhenium in solution if any rhenium were precipitated or otherwise removed in the reductor. It is evident from the table that the 0.00097 *F* Re(VII) solutions could be quantitatively reduced to Re(-I), but that the reduction was not quantitative at higher concentrations of rhenium. As regards the other experimental conditions in the reductor, no effect of the time of reduction upon the completeness of formation of Re(-I) was found from 2-10 min. with 10 to 20 ml. of 0.0010, 0.0024, or 0.0048 *F* HReO_4 in 2, 4, 5.4, or 6 *F* hydrochloric acid. Similarly no effect upon the extent of reduction was found when the total volume of solution taken was varied from 10-40 ml. within the range of other conditions given above, if sufficient amalgamated zinc was present so that all the solution was in contact with zinc. No specific effect of the concentration of hydrochloric acid was found from 2-6 *F*, but reduction was far from complete in 0.1-0.5 *F* acid. No improvement was found

(1) Presented before the Physical and Inorganic Division at the 115th meeting of the American Chemical Society, San Francisco, California, March 28, 1949. A more detailed account of these investigations is contained in the Thesis by E. K. Maun, submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, California Institute of Technology, June, 1949.

(2) E. K. Maun and N. Davidson, *THIS JOURNAL*, **72**, 2254 (1950).

(3) G. E. F. Lundell and H. B. Knowles, *Bur. Standards J. Research*, **18**, 629 (1937).

(4) O. and F. Tomiček, *Coll. Czech. Commun.*, **11**, 626 (1939).

(5) J. J. Lingane, *THIS JOURNAL*, **64**, 1001 (1942).

(6) J. J. Lingane, *ibid.*, **64**, 2182 (1942).

(7) L. Pauling, *Chem. Eng. News*, **25**, 2970 (1947).

(8) H. W. Stone and D. N. Hume, *Anal. Chem.*, **11**, 598 (1939); I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," 2nd ed., Macmillan Co., New York, N. Y., 1946, p. 598.

when an approximately 20% amalgam was used instead of a 5% amalgam.

TABLE I

APPARENT AVERAGE OXIDATION NUMBERS OF REDUCED RHENIUM SOLUTIONS

HReO ₄ , F	Average oxidation number		
	with Ce(SO ₄) ₂	with KIO ₃	with I ₂
0.00097 ^a	0.1		
.00097 ^a	-1.4		
.00097 ^a	-0.9		
.00242 ^b	-0.3		
.00242 ^b	0.5		
.00483 ^{a,d}	2.4		
.00483 ^c	-0.2, 0.1	-0.4, 0.4	0.6, 0.8
.00504 ^c	0.6, 0.7	0.8, 1.0	0.7, 0.8
.0097 ^a	2.9		

^a 10 ml. of solution in initially 4 F HCl reduced 3-5 min.

^b 10 ml. of solution in initially 6 F HCl reduced 2-3 min.

^c 20 ml. of solution in initially 4 F HCl reduced 3-5 min.

^d Noticed some brown solid in reduced solution.

There are three possible explanations for the incomplete reductions of Table I. (a) Some rhenium may have been precipitated in the reductor, so that the resulting solutions contain fairly pure Re(-I), but at a lower concentration than the initial Re(VII) concentration. (b) The solutions with average oxidation number 0-3 in Table I contain Re(-I) and Re(VII). (c) The incompletely reduced solutions contain varying amounts of Re(I), Re(II), Re(III), or Re(IV).

A few of the solutions (an example is given in Table I) with a high initial concentration of Re(VII) were brown after treatment in the reductor—due either to suspended solid matter or to colored ions in solution. These solutions typically had oxidation numbers of 2-4 and probably contained rhenium dioxide or some rhenium ions of an intermediate oxidation state. Most of the solutions emerging from the reductor, however, were colorless and for these solutions there is evidence that (a) is the correct explanation of the incomplete reductions of Table I at high rhenium concentrations. This evidence is essentially that the properties of the "incompletely reduced" solutions were identical with the properties of the completely reduced 0.00097 F Re(-I) solutions. All the solutions slowly became brown on standing in air. The most characteristic test found was the formation of a precipitate of copper when the reduced solutions at a hydrogen ion concentration of 0.5 F or less were slowly titrated by 0.07 F copper(II) sulfate. The solutions also gave a heavy black precipitate with mercury(II) nitrate solution, decolorized permanganate, and gave a blue coloration with ammonium molybdate or ammonium vanadate, as reported by Lundell and Knowles.³

The reduced solutions developed but little color on standing when air was excluded. As shown in a subsequent section, mixtures of perrhenate and the reduced solutions developed a

brown color which we have attributed to the intermediate oxidation states Re(+I) and Re(IV). Irrespective of the validity of this particular assignment of oxidation states, the fact that the reduced Re(-I) solutions did not develop color on standing shows that they do not contain Re(VII) or any of the strongly colored intermediate oxidation states.

Some attempts were made to determine the total concentration of rhenium in the solutions after reduction, to find whether there had been loss by deposition or by spray or otherwise. The method used was to oxidize all the rhenium in the solution to perrhenate, best by boiling with hydrogen peroxide, and then add excess chromium(II) chloride in 4 F hydrochloric acid. In this manner all the rhenium was converted into rhenium(IV) and the excess chromium(II) could be destroyed by bubbling oxygen through the solution for one to two min.² The rhenium(IV) was then titrated to perrhenate by cerium(IV) sulfate thus giving the total rhenium concentration in the solution. Portions of 0.00483 F perrhenic acid in 4 F hydrochloric acid were reduced in the reductor for 3-4 min. The amount of 0.05 F cerium(IV) sulfate consumed by 2.0 ml. samples ranged from 0.044 to 0.070 meq. in several runs. Two-milliliter samples were then oxidized by excess hydrogen peroxide, the excess removed by boiling, and the rhenium converted into rhenium(IV) by chromium(II). The cerium(IV) then required to titrate the rhenium(IV) to perrhenate was 0.0215 to 0.0235 meq., or 20-25% less than the amount expected (0.0291 meq.) from the 0.0097 mmole. of rhenium used in the experiment. However, when the chromium(II) chloride was used to analyze perrhenate not run through the reductor, results 5-10% low were found.² These results are therefore not accurate, but they do indicate a decrease in the total rhenium concentration of relatively concentrated rhenium solutions on passage through the reductor.

For most of the experiments described in the subsequent sections on the oxidation of Re(-I) it was desirable to work at an acidity of 4 F HCl to exclude the possibility of precipitation of rhenium dioxide. Since passage through the reductor lowered the acidity of the original solutions to 0.5 F or less, this required dilution of the reduced Re(-I) solutions with concentrated hydrochloric acid (11-12 F). In order to maintain the Re(-I) concentration sufficiently high, we have used initially 0.005 F perrhenate solutions in the reductor.⁹ The apparent average oxidation numbers of the reduced solutions as calculated assuming no loss of rhenium in reduction were 0.5-2.5. The evidence cited above supports the hypothesis that these solutions contain only Re(-I) at a concentration found by the cerium(IV) titrations. The quantitative interpretations of the results of the subsequent sections have been made assuming the validity of this hypothesis.

Accepting this hypothesis, several conclusions may be drawn about the reactions of Re(-I) from Table I; *viz.*, Re(-I) is quantitatively oxidized to Re(VII) by iodate and almost completely oxidized by iodine. It will be recalled² that Re(V) is almost quantitatively oxidized by iodine but that

(9) Addition of anhydrous hydrogen chloride would have avoided this dilution difficulty but would have introduced new experimental difficulties associated with (a) the problem of adding a prescribed quantity of the gas, and (b) the increased possibilities of air oxidation of Re(-I) during the extra manipulations.

Re(IV) is hardly attacked by this reagent. It may be that in the oxidation of Re(-I) by iodine, the reaction proceeds in a series of two-electron steps, that is, through the I, III and V oxidation states.

Curve A of Fig. 1 is the absorption spectrum of Re(-I) solutions. There is no strong characteristic absorption in the visible spectrum and we may say that Re(-I) is relatively colorless. The strong absorption below 400 $m\mu$ could be due to traces of the higher oxidation states of rhenium, many of which absorb very strongly in this region. Curve B of Fig. 1 shows that the light absorption of a 40 hr. old Re(-I) solution was similar to that of a fresh solution although somewhat higher.

The Oxidation of Rhenium(-I) to Intermediate Oxidation States.—In this section we shall present evidence that Re(-I) in 4 *F* hydrochloric acid is oxidized by oxygen, Re(VII), and by Cu(II) to a yellow-brown Re(+I). The Re(+I) can be oxidized to Re(IV) by oxygen or Re(VII), and is also further oxidized by Cu(II). Lundell and Knowles³ found indications that reaction of dilute Re(-I) solution with sulfuric acid formed Re(+I). These authors also found evidence for the formation of Re(+I) in potentiometric titrations of Re(-I) by permanganate. Lingane⁶ confirmed an average oxidation number of +I for partly oxidized solutions in warm sulfuric acid, but concluded from polarographic studies that the sequence of electrolytic oxidation of Re(-I) was through the states +II, +III, and +V to +VII. The preparation of a compound $Re_2O \cdot H_2O$ has been reported,¹⁰ and a solution possibly containing Re(+I) from reduction of Re_2Cl_6 has been described.¹¹

The light absorption of a Re(-I) solution exposed to air went through three stages, as shown in Fig. 1, with the approximate periods of time involved given in the legend to the figure: (1) gradual formation of a yellow-brown substance with absorption peak at 610 $m\mu$ (curve C), (2) formation of a yellow-green product with peak at 690 $m\mu$ while the absorption at 610 $m\mu$ decreased (curve D), and (3) decrease in the absorption of the yellow-green product upon long exposure to air (E).

When oxygen was bubbled through Re(-I) solutions, they rapidly turned brown. As shown in Table II, the change in reduction titer of the solutions after five minutes of oxygenation corresponds to the oxidation of Re(-I) to Re(+I). The data in Table II indicate that further oxidation is probably slower, because an additional twenty-five minute oxygenation caused only 8% decrease in reducing titer compared to 23% for the first five-minute oxygenation (theory 25% for Re(-I) to Re(+I)). This result strongly suggests that curve C of Fig. 1 represents the absorption spectrum of Re(I). The force of this argument is

(10) R. C. Young and J. W. Irvine, Jr., *THIS JOURNAL*, **59**, 2648 (1937).

(11) W. and I. Noddack, *Z. anorg. Chem.*, **215**, 129 (1933).

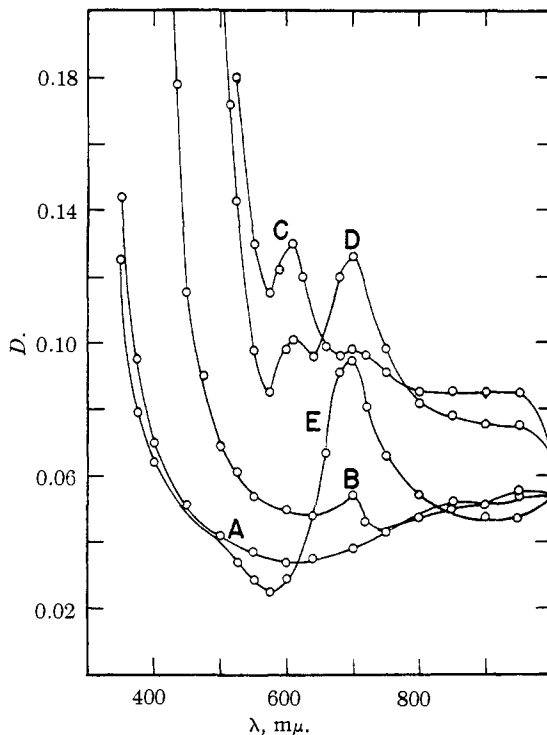


Fig. 1.—Light absorption of solutions that were initially 0.0013 *F* Re(-I) in 4 *F* HCl: A, 22–44 min. after preparation; B, 40 hr. after preparation; C, after 182 min. exposure to air; D, after 15 hr. exposure to air; E, after 40 hr. exposure to air.

somewhat weakened by the fact that the titration experiment and the spectrophotometric experiment were carried out at different acidities (*ca.* 0.5 *F* and 4 *F*) and it is possible that this variable affects the course of the reaction.

TABLE II
EFFECT OF OXYGEN UPON Re(-I)^a

Re(-I), ^b	Time oxygen bubbled through rhenium solution, min.	% decrease ^b in reducing titer
0.0026	5	21
.0030	5	24
.0042	5	22
.0042	30	31

^a The solutions were taken directly from the reductor without adjusting the HCl concentration; therefore, they were *ca.* 0.5 *F* in acid. ^b Based on titrations of 2.0-ml. portions with Ce(IV).

When perrhenate is added to a Re(-I) solution in 4 *F* HCl (the perrhenate solution being sufficiently concentrated so that the acidity is not lowered by dilution), the same sequence of color changes is observed as in the air oxidation of Re(-I). Figure 2 is a spectrophotometric record of a typical set of reactions. The experiments were done by adding deaerated perrhenate to fresh Re(-I) solutions in capped spectrophotometer cells protected by an atmosphere of carbon dioxide. For a resulting solution with an average

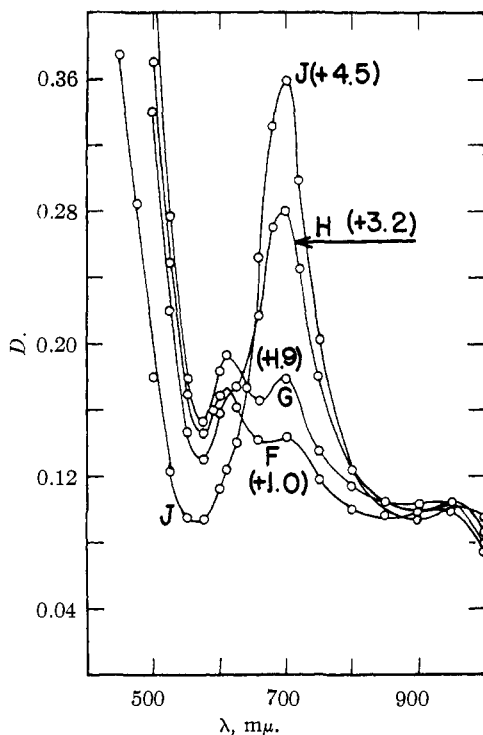
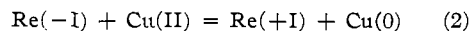


Fig. 2.—Absorption spectra of reaction mixtures of 3 ml. of 0.0013 *F* Re(-I) in 4 *F* HCl with: F, 0.030 ml. of 0.0431 *F* HReO₄ to give av. ox. no. +1, measured 40 hr. after preparation; G, 0.020 ml. of 0.0431 *F* HReO₄ added to 44 hr. old solution F to give av. ox. no. +1.9 and measured 18 hr. after preparation; H, 0.10 ml. of 0.0431 *F* HReO₄, av. ox. no. + 3.2, 40 hr. after preparation; J, 0.20 ml. of 0.0431 *F* HReO₄, av. ox. no. + 4.5, 40 hr. after preparation.

oxidation number of +1.0 (curve F, Fig. 2), the absorption spectrum had a peak at 610 *mμ* and was similar to the absorption spectrum (C, Fig. 1) of the first colored product in the air oxidation of Re(-I). This absorption, which we believe is due to Re(+I), developed almost completely within ten to thirty minutes after addition of perrhenate, and did not change appreciably on standing for forty hours. When much more perrhenate is added (H and J, Fig. 2) the peak at 610 *mμ* disappears and a peak at 690 *mμ* forms. For solutions with an intermediate oxidation number (curve G) absorption maxima at both 610 *mμ* and 690 *mμ* are present. It should be mentioned that the 690 *mμ* peak requires a period of twenty to forty hours to form completely.

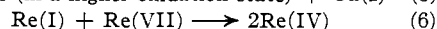
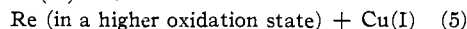
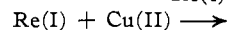
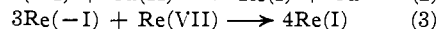
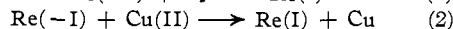
Before attempting to interpret in detail the oxidation of Re(-I) with perrhenate, it is convenient to discuss the oxidation of Re(-I) by copper(II) ions. In these experiments, Re(-I) in 0.8 *F* HCl was titrated with 0.070 *F* copper(II) sulfate. An external test was made for Cu(II) or Cu(I) with starch-iodide solution. The first addition of copper(II) sulfate to Re(-I) gave a black metallic precipitate and a strongly brown solution which

contained neither Cu(II) nor Cu(I). The metallic precipitate was dissolved in nitric acid, and this solution gave a blue color with ammonium hydroxide. The metallic precipitate was shown to be all copper in a roughly quantitative precipitation by potassium ferrocyanide; the strong brown color remaining in the reaction mixture of the Re(-I) and the Cu(II) was thus due to an oxidation state of rhenium since no Cu(II) or Cu(I) remained in the solution. Further addition of Cu(II) decolorized the solution and formed Cu(I). The decolorization showed that the rhenium was oxidized from the brown form to a weakly absorbing form by further addition of Cu(II). In one experiment, 3.4 ml. of 0.070 *F* copper sulfate was slowly added to 23 ml. of 0.0029 *F* Re(-I) in 0.8 *F* HCl. The copper formed was 0.068 mmole. or a 1:1 ratio with the mmole. of Re(-I) taken; some Cu(I) remained in the solution. In another similar experiment, 0.098 mmole. of copper formed from reaction with 0.086 mmole. of Re(-I). The reaction



explains the amount of copper formed and the brown color of the solution within the experimental error. Excess Cu(II) was reduced only to Cu(I) while the rhenium was oxidized to a less colored form.

On the basis of all these results, we believe there is evidence for the reactions



We tentatively attribute the absorption spectrum with a maximum at 610 *mμ* to Re(I) and that with a maximum at 690 *mμ* to Re(IV). It would have been desirable to extend the experiments by analyses on the solutions used since the spectrophotometric data are not sufficiently accurate or clean cut to prove these identifications. However, these identifications do explain the totality of our results in a unified way. Curves C and F (Figs. 1, 2) represent the absorption spectrum of Re(+I) and J is that of Re(IV) obtained by oxidation of Re(I). (It must be recalled² that there is evidence that several varieties of Re(IV) can exist in 4 *F* HCl and that these have different absorption spectra.)

We have already discussed the evidence for reactions (1), (2), (4) and (5). The evidence for (3) is principally the similarity between curve (C) (reaction 1) and curve F (reaction 3). Furthermore, F is somewhat higher than C as expected if rhenium from the Re(VII) state as well as from the Re(-I) forms the colored Re(I) state. The color of the solutions obtained by reaction (2) where analysis indicates the product is Re(I) was

qualitatively similar to the color of the solutions that gave the absorption spectra C and F. In curve G, Fig. 2, for a solution with an average oxidation number of 1.9, the peak at 690 $m\mu$ is apparent as expected, but the 610 $m\mu$ peak is greater than that for curve F, in contradiction to our hypothesis that some of the Re(-I) in solution F has been oxidized to Re(IV) in solution G. One can avoid this contradiction by assuming that reaction (3) does not readily go to completion or that there are analytical errors or that small amounts of other highly colored oxidation states (say Re(III)) are formed in some of the solutions. Although it is possible that the absorption spectra of Fig. 2 could be due to other oxidation states, say Re(II) and Re(III), the titration evidence for Re(I) by reactions (1) and (2) and the similarity between curves F and C agree with reaction (3). The identification of the oxidation product of Re(I) by oxygen or Re(VII) as Re(IV) is partly based on the fact that curve J (av. ox. no. 4.5) is higher than curve H (av. ox. no. 3.2) while several solutions of av. ox. no. 4-5 had absorption comparable to that of curve J. Curve J gives extinction coefficients and an absorption spectrum for Re(IV) that are comparable to those for other Re(IV) solutions obtained by dissolving ReO_2 in 4 F HCl^2 and this is additional evidence for attributing this curve to Re(IV).

Re(-I) does not react appreciably with K_2ReCl_6 because the light absorption of a mixture of 0.0021 F K_2ReCl_6 and 0.0011 F Re(-I) in 6 F HCl was sufficiently close to the sum of the separate component absorptions that not more than 10-15% of the K_2ReCl_6 could have reacted in 1-2 hr.

Other Chemical Studies on Re(-I).—Since the low concentration of Re(-I) obtained was a limitation on experimental study of this state, other conditions were tried to see if higher concentrations could be obtained. No reducing agent was formed when 0.005 F perrhenate in 1 F sodium hydroxide was left in the Jones reductor under nitrogen 5 min., when hydrogen was bubbled over rhenium powder in 6 F hydrochloric acid or in 6 F sodium hydroxide, or when 0.01 F perrhenic acid in 4 F hydrochloric acid was shaken with mercury. An interesting result was found after 20 ml. of 0.0050 F K_2ReCl_6 in 4 F HCl had been left in the reductor for four minutes because the nearly colorless solution was then 0.013 N in reducing agent as determined with cerium(IV). Since ReCl_6^- is not affected by short treatment with cerium(IV) sulfate,² this shows the presence of either a reactive form of rhenium(IV) or some reduced state. Addition of cesium chloride solution gave considerable yellow precipitate (Cs_2ReCl_6), indicating that much ReCl_6^- remained unreacted²; therefore it was concluded that high percentage yields of the reactive state could not readily be obtained.

In an attempt to prepare a solid compound of Re(-I), say KRe , K_2ReCl_6 in an evacuated tube was treated with distilled potassium vapor at 250-

350°. Part of the K_2ReCl_6 was converted to a metallic black solid. The solid was probably rhenium metal as indicated by its insolubility in hydrochloric acid and by its reaction with hydrogen peroxide. Rhenium metal was also formed from K_2ReCl_6 with distilled liquid potassium under argon at 250° in a quartz tube.

The possibility of concentrating Re(-I) by volatilization or by evaporating the solutions was studied by evacuation of 2-6 ml. of 0.0015 F Re(-I) in 6-8 F hydrochloric acid, using a mechanical pump. The vapors were condensed in a Dry Ice trap, and no reducing agent was found with cerium(IV) in this condensate. Hence no volatility of Re(-I) resulted in these experiments. A brown solid residue was left after volatilizing the hydrochloric acid and water from the rhenium solution, and analysis of this residue by cerium(IV) showed a decrease in the amount of reducing agent originally added as Re(-I). Therefore, the Re(-I) was destroyed in the process of concentration.

The proposed analogy⁷ between the electronic configurations of Re(-I) and of Pt(II) motivated an attempt to form a carbon monoxide complex of Re(-I). This complexing agent was selected because of its neutral charge and known reactivity with Pt(II) salts. The gas phase above a Re(-I) solution was evacuated and a known amount of carbon monoxide was admitted to the container with the Re(-I). The pressure in the system was then measured by a manometer. In this manner it was found that no detectable reaction occurred when 6 ml. of 0.0030 F Re(-I) in *ca.* 0.5 F H^+ was shaken with 0.437 mmole. of carbon monoxide at a pressure of 20 cm. of mercury at 25°. No effect was found for 10 ml. of 0.0052 F Re(-I) in 4 F HCl under similar conditions. The experimental uncertainties were such that formation of a compound such as Re(-I)CO might have escaped detection, but any complex with a greater ratio of carbon monoxide to rhenium would have been observed.

Acknowledgment.—We are indebted to Professors Ernest H. Swift and Linus Pauling for helpful suggestions.

Summary

Rhenium(-I) was prepared by passing 0.001 F perrhenic acid in 4 F hydrochloric acid through a Jones reductor. Reduction was incomplete with higher concentrations of rhenium. The rhenium(-I) was completely oxidized to perrhenate by cerium(IV) sulfate or potassium iodate, and largely oxidized by iodine. Light absorption measurements of the rhenium(-I) solutions showed no strong characteristic absorption in the visible spectrum.

Highly colored intermediate oxidation states were formed when rhenium(-I) was treated with copper(II) sulfate, perrhenate, or oxygen. From spectrophotometric study of the reactions of Re(-I) with perrhenate and oxygen, and from analy-

ses on the reaction of Re(-I) with copper(II) sulfate or oxygen, it is probable that the first product of oxidation is Re(+I), followed by formation of Re(IV) with excess oxidant.

Attempts to prepare a solid compound of

Re(-I) by reduction of K_2ReCl_6 by potassium gave only rhenium metal. No indication of volatility of Re(-I) or of reaction of Re(-I) with carbon monoxide was found.

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[CONTRIBUTION FROM GENERAL ELECTRIC RESEARCH LABORATORY]

The Solubility of Iron in Mercury at 25–700°

BY A. L. MARSHALL, L. F. EPSTEIN AND F. J. NORTON

Various developments involving the contact of iron with mercury over extended temperature ranges rendered necessary a study of the equilibrium solubility relationships.

The primary difficulty in this solubility determination is to secure initial, preliminary *wetting* of the iron by mercury. Iron broken under mercury will show wetted surfaces at the fracture. This wetting is lost after exposure to air.

Experimental

To have pure iron wetted by pure mercury with no other amalgamating material present, all oxide must be removed, the iron must be degassed and no access of oxygen allowed. The stringent requirements of attaining and maintaining exclusion of oxygen to a high degree were met by the following experimental arrangements.

Twenty mil pure Swedish iron was arranged as a cylinder in a quartz vessel in a vacuum system. The iron was heated by high frequency and degassed in a good vacuum¹ at about 800°, then fired in hydrogen. The hydrogen was purified by being passed through degassed, activated charcoal at liquid air temperatures.

When pure liquid mercury at room temperature was admitted suddenly to such a piece of hot iron, complete

wetting occurred. This is permanent for many months if air is not admitted to the iron.

The arrangement for heating iron in very pure hydrogen, then admitting mercury, is shown in Fig. 1. The portion enclosed by dotted lines was in a bake-out oven so all of the glassware and the iron could have a preliminary bake out in a good vacuum at 450°. At A, the point of admission of hydrogen, is a furnace with platinized asbestos in the line to assure reaction of traces of oxygen. At B is the degassed, activated charcoal which had liquid air on when the hydrogen was admitted. This removed the traces of air and also traces of other impurities in the hydrogen. The high frequency heating coil C surrounded the iron sample which was in the form of a thin cylinder. The thickness was such to give uniform heating by high frequency. Small prongs bent out at the extremities of the cylinder supported it in the quartz container with minimum contact. The quartz bulb holding the iron cylinder had graded seals at top and bottom. These led to the rest of the apparatus which was of Nonex glass.

Redistilled mercury of good purity initially was distilled again from the barometric reservoir E into F, after bake out and evacuation. Then on sealing off at G, nitrogen pressure raised the mercury over the iron sample.

The various by-passes enabled the sample bulb to be sealed off in a good vacuum at top and bottom. The quartz container had two sections with a constricted neck between. The upper one held the wetted iron and the lower the pure mercury. On rocking the container the mercury passed over the iron and back.

The sample container was placed in a steel bomb of one inch wall thickness, steel wool keeping the bulb in position. Mercury was placed in the bomb on the outside of the container so the pressure at high temperatures would be equalized inside and out. The steel bomb was then welded shut.

After various periods of agitation in an oscillating constant temperature furnace, the furnace was left in a slanted position so all of the mercury drained down off the iron into the lower section of the container. All this was done at the temperature of the experiment. Then on cooling down to room temperature any iron separating out from the mercury was in contact with quartz only. In the analysis, all the iron—in the mercury and on the wall—was determined.

Another point of interest is that at room temperature, mercury passed over wetted iron attained its equilibrium solubility in a few seconds.

In general, runs were made for several hours at temperature, and one run was made for one month. This gave the same result as shorter runs.

After equilibration the sample bulb was opened, the iron cylinder removed and the mercury slowly distilled in vacuum away from the bulb, and weighed. The residue was washed from the bulb with acid and iron determined.

This was done by oxidizing the iron and determining it by the red color which develops with KCNS. This colorimetric determination was made on the General Electric recording spectrophotometer.² The absorption

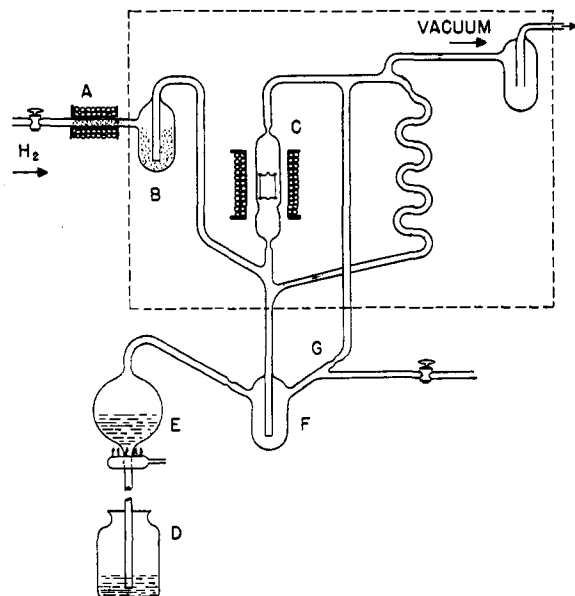


Fig. 1.—Apparatus for heating iron cylinder in pure hydrogen and in vacuum.

(1) F. J. Norton and A. L. Marshall, *Trans. Am. Inst. Min. Met. Eng.*, **156**, 351 (1944).

(2) J. L. Michaelson and H. A. Liebhafsky, *General Electric Review*, **39**, 455 (1936).