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MONITORING AGENCY DOCUMENT NO. AFCRL-TN-60-461

ASTIA DOCUMENT NO.

Notes on the preparation and analysis of ruthenium(III) and ruthenium(IV) in sulfate medium

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TECHNICAL NOTE NO. 1

CONTRACT NO. AF 61(052)-181

DATE OF REPORT: February 15, 1960

The research reported in this document has been sponsored by the AIR FORCE CAMBRIDGE RESEARCH CENTER of the AIR RESEARCH AND DEVELOPMENT COMMAND, UNITED STATES AIR FORCE, through its European Office.

Abstract

For equilibrium studies, pure solutions of ruthenium(III) and ruthenium(IV) perchlorates or sulfates are needed. A survey is given of synthetic and analytical methods reported in literature. Since none of them was suitable for our purpose, new or modified methods were worked out.

For the preparation of ruthenium(IV) sulfate solution, RuO_4 was reduced with H_2O_2 in dilute H_2SO_4 and the ruthenium(IV) cations separated from complex anions by a cation exchanger. For the preparation of ruthenium(III), RuO_4 was reduced with SO_2, the excess SO_2 removed and the sulfito complex decomposed.

Total ruthenium was determined by reducing to metallic ruthenium, using Mg metal, and then weighing.

For determining ruthenium(III) or ruthenium(IV), a redox titration method is proposed: a known excess of cerium(IV) sulfate in ~ 2 M H_2SO_4 is added, the RuO_4 formed is boiled off and the remaining cerium(IV) backtitrated with iron(II) + ferroin.

For the determination of H, the total analytical concentration of H^+, in purely cationic Ru(IV) solutions, the ruthenium may be either held back in a H^+-saturated ion exchanger or bound by adding acetylacetone. The H^+ set free can in both cases be titrated with standard NaOH. Concordant results were obtained using these two methods.

Notes on the preparation and analysis of ruthenium(III) and ruthenium(IV) in sulfate medium

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For some time, investigations have been made in this laboratory to study the hydrolysis of ruthenium(III) and ruthenium(IV) by means of the general methods that have been developed here. This work, which is still under way, has met with several experimental difficulties. It is thought, however, that some of our experience may be useful to others.

We tried first to use a perchlorate medium - it has been used in most other studies in this department and has the advantage that, usually, the complex formation with the medium ions is a minimum. Amber-red solutions of ruthenium in $HClO_4$ could be obtained by reducing RuO_4 with H_2O_2 and boiling off the excess of H_2O_2. However, it was found that these solutions precipitate $RuO_2(H_2O)_x$ on standing. For instance, in a filtered solution with $[H^+]$ as high as 150 mM, the total concentration, B, of Ru(IV) was finally less than 2 mM. Moreover, solutions of ruthenium(III) in perchloric acid, obtained by electrolytic reduction of a ruthenium(IV) perchlorate solution, proved to be unstable, Ru(IV) and Cl^- being formed. This agrees with the findings of Wehner and Hindman[1].

Four our purposes, it was desirable to have solutions with a low analytical H^+ concentration, H, and a large total concentration, B, of the oxidation state of Ru, the hydrolysis of which was to be studied. The reaction might be followed by measuring either the free concentration of H^+, h, with a glass electrode, or the remaining free concentration of Ru^{3+} or Ru^{4+}, b, using for instance a redox electrode.

Since there were disadvantages with other media, such as Cl^-, it was decided to use a sulfate medium despite certain difficulties, especially the formation of HSO_4^-, and the possibility of rather strong complexing.

Preparation and spectra (schema I). The starting material was commercial ruthenium chloride, from which a chloride-free ruthenium sulfate solution was prepared by repeated evaporation in 25 °/o sulfuric acid under an infrared lamp during which SO_3 fumes appeared - this ensured the removal of Cl^- and Os[1]. From this solution, RuO_4 was prepared by oxidation with $KMnO_4$ [2,3,4,6].

The RuO_4 was then collected and reduced in various ways; for clarity, the various solutions obtained will be denoted by letters: S, G_1, B_1, etc. (See schema I and figs.). Each of the experiments to be described has been repeated several times with various modifications.

Green solution G_1. To the initial ruthenium sulfate solution, S, an excess of $KMnO_4$ was added. The RuO_4 formed was distilled in an all-glass apparatus by heating and passing a slow stream of N_2. The vapor was caught in three ice-cooled receivers containing 0.5 - 1 M H_2SO_4 and an excess of H_2O_2. The solution, which was first yellow due to the RuO_4, gradually turned green ("G_1") with the evolution of O_2. The absorption spectrum of G_1 has a maximum at 3000 Å. (Fig 1). With time, G_1 gradually changed colour and after a couple of days had turned reddish brown ("B_1").

Solutions similar to G_1 have been prepared by other workers. Martin[5] (schema II) reduced RuO_4 in H_2SO_4 using $NaNO_2$, Na_2SO_3, $FeSO_4$ etc, and obtained a green or greenish-brown solution, depending on the relative excess of Ru(VIII), which he suggested contained ruthenium(VI) and ruthenium(VI) + sulfate complexes. El Guebely and Haissinsky[6] (schema III) obtained a green solution by electrolytic oxidation of ruthenium(III) sulfate (E = 1.4 volt against a saturated calomel electrode) or by electrolytic reduction of RuO_4 in sulfate solutions (E = -0.2 volt). They claimed it contained ruthenium(VI). In neither case, however, were spectra given.

A S Wilson[7] reduced RuO_4 in H_2SO_4 with an excess of H_2O_2 and obtained a solution for which he gives the spectra obtained after various times. The spectrum after about 9 days has a maximum at 2900 Å and coincides approximately with that of G_1 (Fig 1). He ascribed it to ruthenium(III). Using less H_2O_2, Wilson obtained, following Martin, greenish-brown solutions. He suggested they might contain Ru in the valency states IV and VI. By considering the reactions to be described in the following, it seems likely that the ruthenium species in G_1 has a higher valency state than +4, probably +6.

The solutions B_1, B_2 and R_1. When G_1 was kept for two or three days, it turned into a reddish-brown solution B_1. This solution was boiled to remove H_2O_2, cooled and then passed through a H^+-saturated Dowex-50 ion exchanger. A brown solution, "B_2", passed through the resin - it probably contained an uncharged or anionic sulfate complex. When the resin was washed with a H_2SO_4 or Na_2SO_4 solution, a red solution, "R_1", was obtained. The spectra of B_2 and R_1 are given in figure 2.

For hydrolysis studies, a ruthenium(IV) sulfate solution of relatively low acidity can be prepared conveniently by eluting a cation exchanger, saturated with a red cationic species R_1, with a dilute Na_2SO_4 solution and then concentrating by careful evaporation under vacuum at room temperature.

Solutions R_2, V and Y. In another series of experiments, RuO_4 was collected in, say, 0.2 M H_2SO_4 saturated with SO_2. In this case, a rapid reduction was observed. The solution first turned reddish-brown with the same shade as R_2 (no spectra could however be taken because of experimental difficulties) and then gradually turned yellowish brown. However, if the excess SO_2 was not immediately boiled off, a violet solution, "V", was formed overnight, which was stable over a long time, even after the excess SO_2 had been boiled off. When V was evaporated slowly to dryness with an electric mantle in a N_2 atmosphere (free from O_2) and the dry residue dissolved, the solution was blackish brown when concentrated, and yellow, "Y", when diluted. The spectra of V and Y are given in Fig 1 and 2.

A similar yellow solution was obtained by El Guebeley and Haissinsky[6] who concluded that it contained ruthenium(III). We agree with their conclusion and consider that R_2 contains ruthenium(IV). The solution V is probably a strong sulfito complex of ruthenium(III).

Analysis.

The literature on the analysis of Ru is rather meagre. The volumetric redox titrations proposed are somewhat uncertain[8].

The most reliable method for finding the total Ru concentration is by transformation to metallic Ru. It was found convenient to add, to a known amount of solution, an excess of magnesium metal and dilute sulfuric acid. When the reaction has been almost completed at ordinary temperature, more H_2SO_4 is added and the solution is boiled in order to dissolve all excess of magnesium and to agglomerate any colloidal Ru that may have been formed. The Ru is carefully collected on a weighed porcelain filter crucible "Berlin 1A1", washed with 0.5 M H_2SO_4 and water, heated in H_2 and finally weighed.

The results were reproducible and agreed well with those obtained by precipitation of $RuO_2(H_2O)_x$ from a solution of Ru(IV), R_1, with $NaHCO_3$ at pH = 6 and handled in the same way as above. However, the reduction with metallic Mg is applicable to both Ru(III) and Ru(IV) and to cationic species as well as anionic ones whereas the precipitation of the hydroxide is feasible only if the solution contains cationic species or weak anionic complexes. For instance, from B_2, the precipitation of the hydroxide is not complete.

The results given by this method agreed with those obtained by a different one. To a Ru(IV) solution, R_1, a known amount of standard cerium(IV) sulfate solution was added so that $[H^+]$ was 3 - 4 M. Then, RuO_4 was removed by boiling and passing N_2 through the solution, after which it was cooled and back-titrated with Fe(II) + ferroin. In this way, it is possible to determine the total concentration of Ru(IV) in the solution.

To determine the total <u>sulfate</u> concentration, two methods were tried: a) the solution R_1 was passed through a H^+-saturated ion exchanger and the eluate titrated as $H_2^+SO_4^{2-}$ with standard NaOH and b) a slight excess of acetylacetone, AH, was added to the solution. Once again, ruthenium forms an uncharged complex, perhaps RuA_4 but more probably $RuOA_2$. The solution, as before, can be potentiometrically titrated as $H_2^+SO_4^{2-}$ with standard NaOH. The two methods gave concordant results which indicates that there is no serious error from the retention of sulfate in the ion exchanger.

To test the assignment of the oxidation number +3 to the "ruthenium(III)" solution Y, a sample of previously analysed Ru(IV) solution R_1, was reduced wi SO_2. The solution was then freed from the excess of SO_2 by bubbling and prolonged boiling. Now, using the previous method with Ce(IV) oxidation, it was found that one equivalent more of Ce(IV) was needed whick is evidence that Ru(III) had been formed.

<u>Conclusion</u>. The results obtained have confirmed our view that "R_1" is a Ru(IV) cationic species. "B_2" is an anionic species of Ru(VI) or Ru(IV). B_1 is a mixture of B_2 and R_1. It seems likely that G_1 contains a higher valenc state than +4, perhaps +6. In the transient solution, R_2, the main constituen is probably Ru(IV) whereas V and Y probably contain Ru(III). G_2, finally, may be Ru(II), or a Ru(III) + Ru(II) mixture.

Work is under way to confirm the tentative valencies given here and especially to study the hydrolysis reactions.

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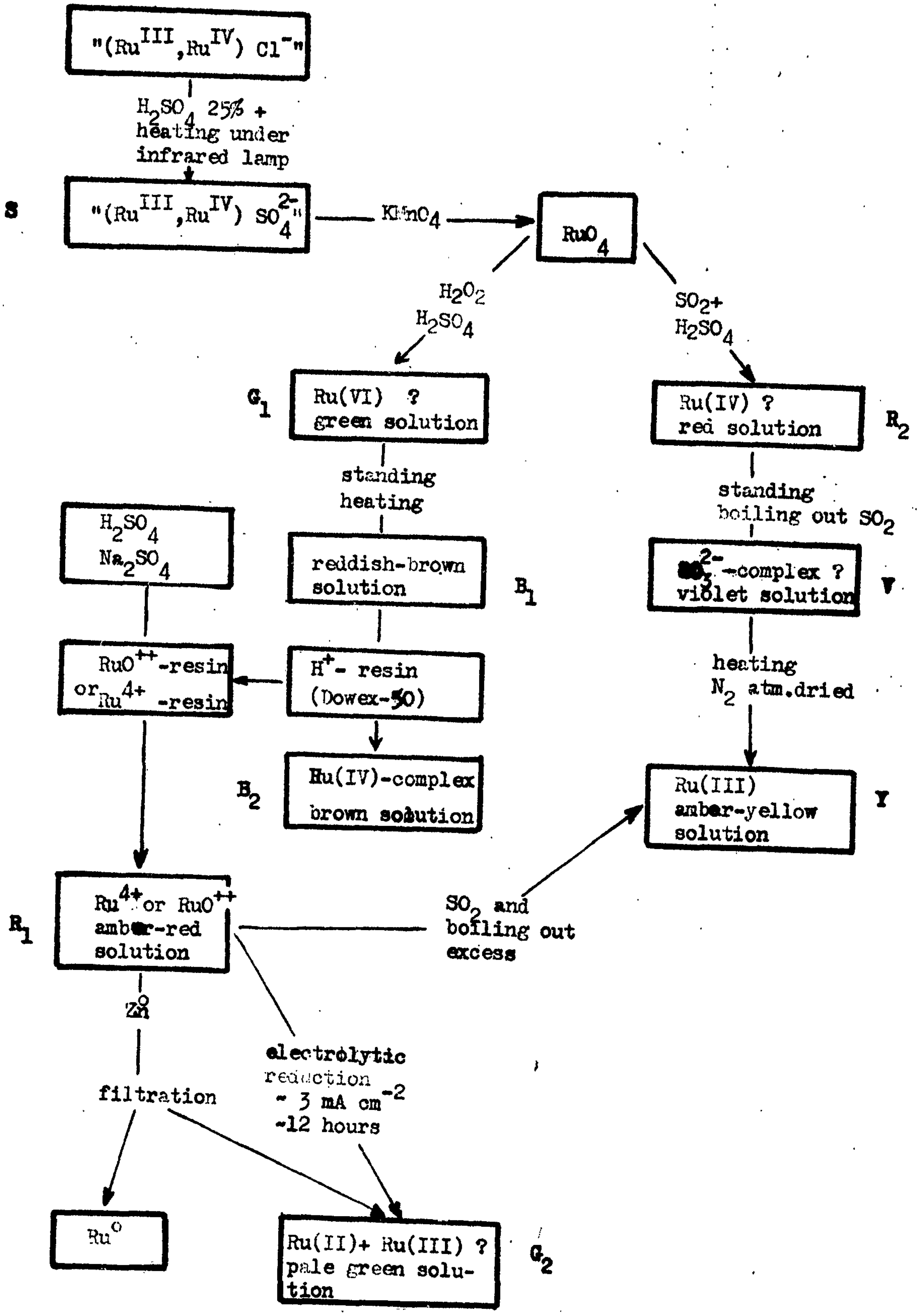
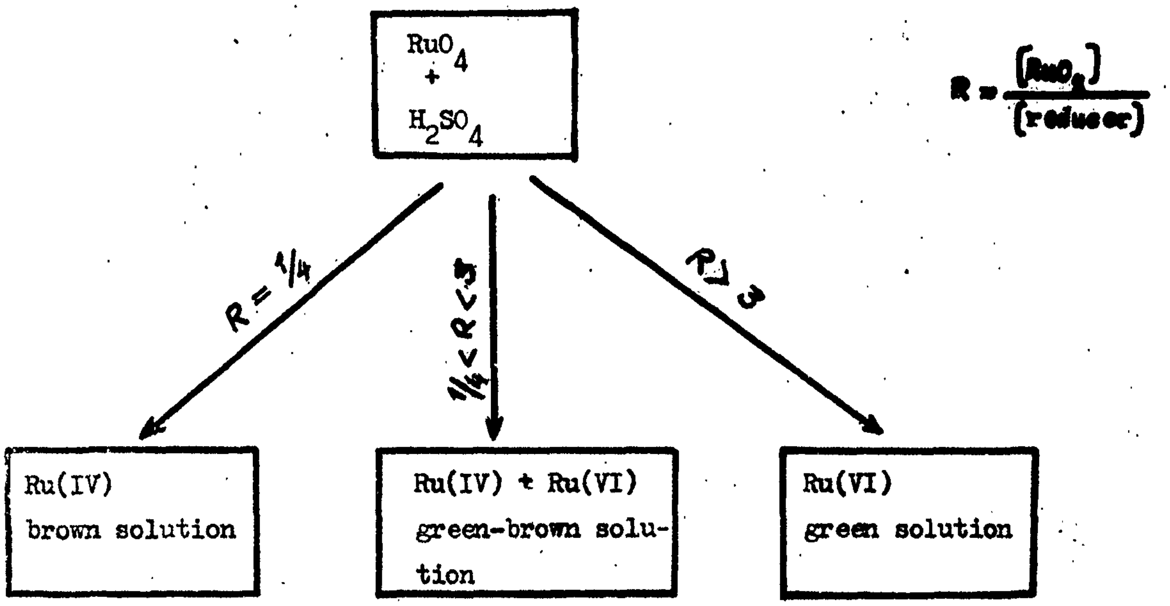
Schema I


"(Ru^III,Ru^IV) Cl⁻"
H2SO4 25% + heating under infrared lamp
S
"(Ru^III,Ru^IV) SO4^2-"
KMnO4
RuO4
H2O2 H2SO4
SO2+ H2SO4
G1
Ru(VI) ? green solution
Ru(IV) ? red solution
R2
standing heating
standing boiling out SO2
H2SO4 Na2SO4
reddish-brown solution
B1
SO3^2- -complex ? violet solution
V
RuO++-resin or Ru4+ -resin
H+- resin (Dowex-50)
heating N2 atm.dried
B2
Ru(IV)-complex brown solution
Ru(III) amber-yellow solution
Y
R1
Ru4+ or RuO++ amber-red solution
SO2 and boiling out excess
Zn°
filtration
electrolytic reduction ~ 3 mA cm^-2 ~12 hours
Ru°
Ru(II)+ Ru(III) ? pale green solution
G2

Scheme II

F.S. Martin[5] (1952)



$$R = \frac{[RuO_4]}{(reducer)}$$

$$\begin{tikzcd}
RuO_4 + \text{reducer (} Fe^{++}, SO_3^{=} \text{, etc.)} \arrow[r] & Ru(IV) \\
& + \\
& RuO_4 \text{ (excess)} \arrow[d, shift left] \\
& Ru(VI) \arrow[u, shift left]
\end{tikzcd}$$

Schema III

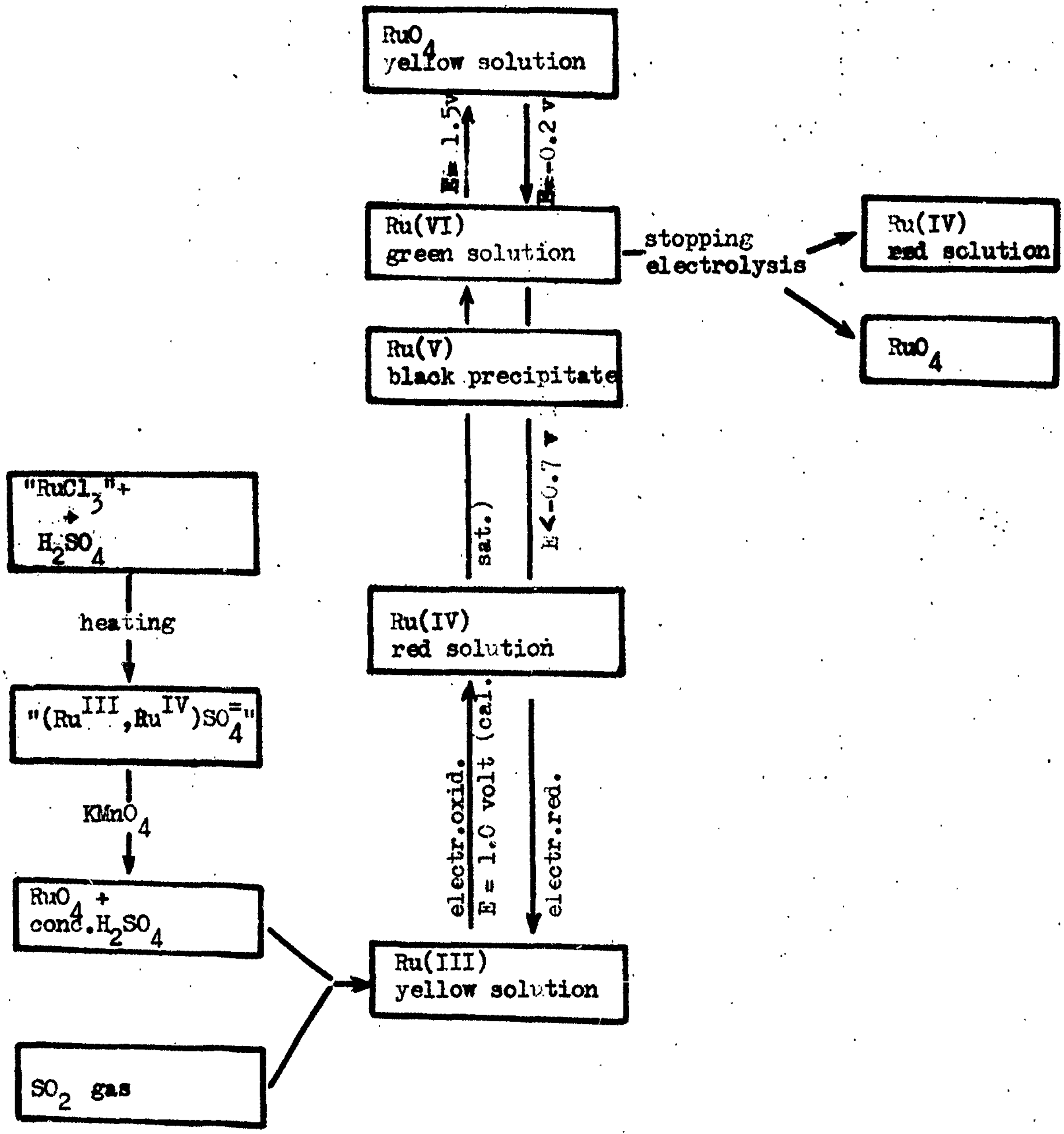

RuO4 yellow solution
E= 1.5v
E=-0.2 v
Ru(VI) green solution
stopping electrolysis
Ru(IV) red solution
RuO4
Ru(V) black precipitate
sat.)
E<-0.7 v
"RuCl3" + H2SO4
heating
"(RuIII,RuIV)SO4="
KMnO4
Ru(IV) red solution
electr.oxid.
E = 1.0 volt (cal.
electr.red.
RuO4 + conc.H2SO4
Ru(III) yellow solution
SO2 gas

Fig. 2

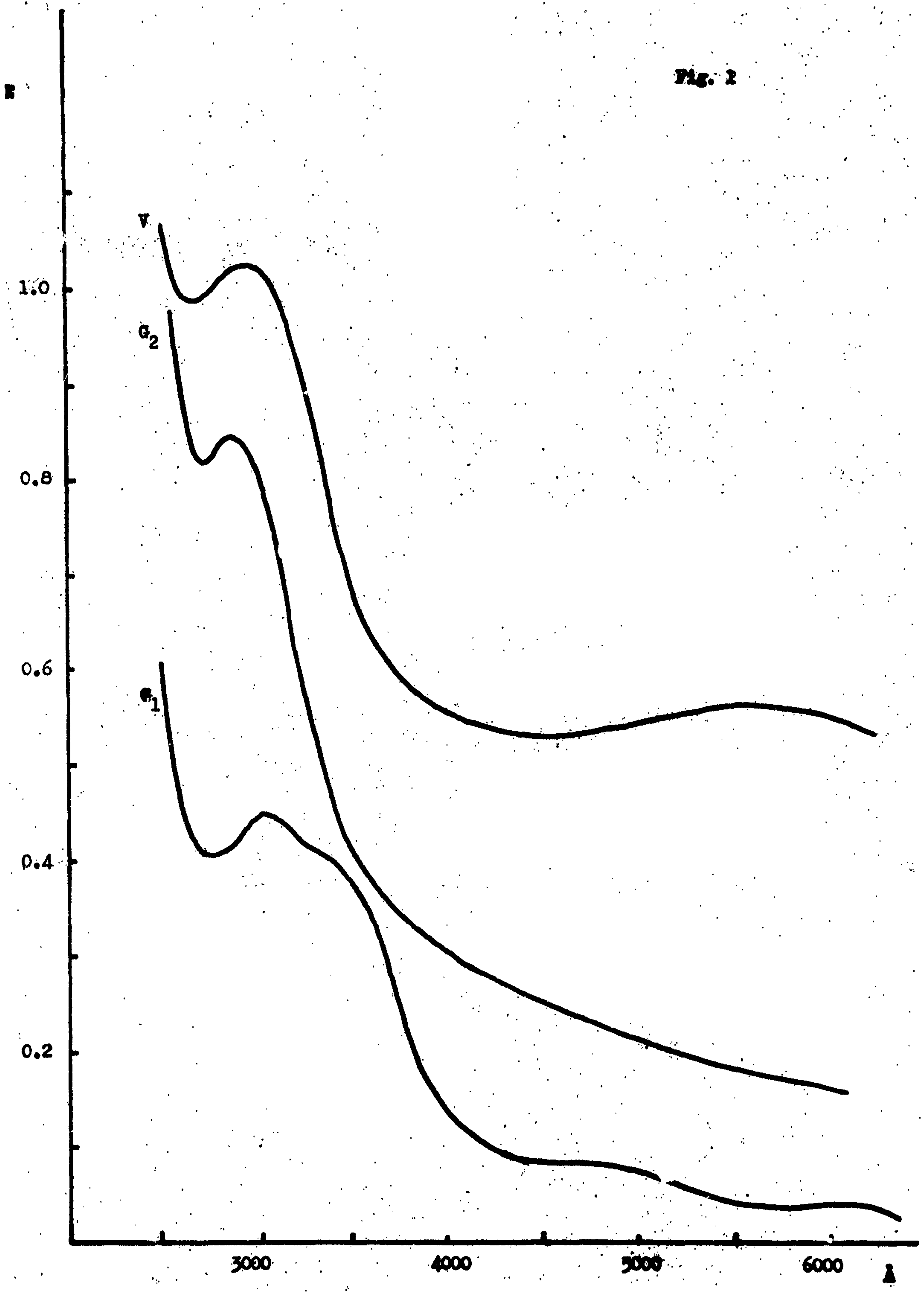


Fig. 2