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RESEARCH ON CHARACTERISTICS OF TRANSITION ELEMENTS IN SOLUTION

1. Studies on rhodium chemistry
   with a note on palladium

   by CLARA BERECKI-BIEDERMANN

2. Studies on ruthenium chemistry

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LARS GUNNAR SILLÉN
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TECHNICAL REPORT
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    by Clara Berecki-Biedermann

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TECHNICAL (FINAL) REPORT

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Contents   pages

The technical report consists of two independent units and it has been thought convenient to give them separate numbering of pages, figures and references.

Abstract

Rhodium

Systematic studies have been made on the preparation and characterization of halogenide-free rhodium sulfate and perchlorate solutions. Improved methods of preparation and analysis have been worked out.

Three oxidation states were met with.

Rhodium(III) (yellow) has a practically constant hydroxide number, $Z \approx 1.75$ in the range of $[H^+]$ studied, so that the formula is close to $Rh_n(OH)_{1.75n}^{1.25n+}$ in acid solutions. For rhodium(V) (green) other valencies were ascribed by earlier authors; evidence for the oxidation number 5+ was obtained by careful analysis. A third violet species has an oxidation number > 5. Because of its instability the oxidation number has not yet been determined.

Some redox emfs for Rh(III, V) mixtures are given. They do not correspond to real equilibrium, but the apparent standard electrode potential in $0.5 - 1$ M $HClO_4$ is around $+1.42$ V.

Absorption spectra are given for the solutions prepared. The work will be continued using, in addition to the other methods, conductivity and freezing-point measurements.

Palladium

Pure palladium(II) perchlorate and sulfate solutions were prepared by precipitating first - with $HClO_4$ - hydrous palladium oxide from a clear alkaline solution of $Pd(NO_3)_2$ and then dissolving the precipitate in cold $HClO_4$ (H_2SO_4).

Ruthenium

The preparative and analytical methods described earlier (Brito 1960) have been improved, and new ones introduced. Catalytic reduction with H_2 gas on a Pt catalyst proved a very useful tool. The various solutions obtained during the reactions are characterized by redox potential e, oxidation number X, color and spectra, and some often recurring solutions are denoted by letters as R_1, G_2 etc.

Redox reactions of Ru in 1 M H_2SO_4 medium were studied: X was varied stepwise by chemical means (Ti(III), Cr(II), Ce(IV)) or coulometrically, and e was measured. The resulting curves e (X) (schematic survey in Fig 1) bring out the existence of slow, irreversible reactions, and of polynuclear species of mixed oxidation number.

Relatively well-defined states are the red Ru(IV), "R_1", the green Ru(III) "G_2", and the pink Ru(II), "P_1". The Ru(II, III) redox potentials in 1 M H_2SO_4

are fairly well-defined with the $e_o \approx 180$ mV.

Between X = 3 and X = 4, dark-brown solutions (B_3, B_4, B_5 etc) are obtained which change their properties with time and may contain several species. The redox curves indicate one or several species with X $\approx$ 3.5, one with X $\approx$ 3.25, and one with X $\approx$ 3.7.

A mathematical analysis of some of the redox curves e(X) has been attempted. The tentative values for the oxidation number, and the number of Ru atoms in the various species, are by no means certain since most curves were irreversible. They may have some connection with reality, however.

For the red species R_1 analysis indicated the formula $Ru_n(OH)_{3n}^{n+}$. Tentative formulas are given also for some other species.

Absorption spectra are given, and possible lines for future work on ruthenium chemistry are indicated.

Studies on rhodium chemistry, with a note on palladium

by Clara Berecki-Biedermann

Introduction

This research project was undertaken in November 1958 with the intention to find experimental methods suitable for the determination of the fundamental properties of the simple rhodium species prevailing in aqueous solutions. We shall call simple species those which occur in solutions containing ligands of minimum tendency for complex formation such as ClO_4^-, SO_4^{2-} and NO_3^-.

Very little quantitative results have been reported on such solutions. The main reason for this lack of data seems to be the fact that the investigators working with solutions of the platinum group metals have been mainly concerned with the study of those robust rhodium species which can be easily obtained in the crystalline state and which do not undergo any reaction when dissolved. As a consequence the composition, the oxidation state, the absorption spectra and the electrochemical constants of the simple rhodium ions were not known with certainty. Thus Latimer[8] who reviewed the data available up to 1952, could give but rough estimates for the standard potentials of the rhodium ions and for the formation constants of the halide complexes.

As the present work proceeded it became evident that no adequate methods were at one's disposal for the preparation and analysis of the rhodium solutions. No successful study of ionic equilibria can be carried out before these problems are satisfactorily solved; thus some time had to be devoted to preparative and analytical questions.

In connection with the study of these problems it was discovered and confirmed that the dark green colored species formed when Rh(III) is oxidized has the oxidation number five.

The solutions prepared and analyzed according to the improved methods served for the study of the hydrolysis equilibria of Rh(III), Some redox potential measurements were carried out with the Rh(III) - Rh(V) couple. The characteristic absorption spectra of the Rh(III) and Rh(V) species are given as well as that of a violet colored Rh ion having an oxidation state exceeding five.

Some preliminary work has been made on the preparation and analysis of palladium(II) perchlorate and sulfate solutions. It was found that the principles worked out for rhodium solutions are of considerable value also for palladium.

Preparation of halogenide-free rhodium(III) perchlorate and sulfate solutions

Summary of the main results

Since the main scope of this work has been the investigation of the hydrolysis equilibria it was necessary to prepare rhodium(III) perchlorate and sulfate solutions of moderate acidity which should contain neither substances forming complexes with rhodium(III) ions nor protolyzing impurities in detectable amounts. None of the numerous methods used for the preparation of pure perchlorate solutions of the common metals proved to be applicable to rhodium. This failure is to be explained by the fact that the ionic species existing in solutions of rhodium halides - which had to be used as starting material for reasons given in ref. 1 - are extremely inert in most ligand displacement and redox reactions. Recognition of this difficulty made necessary a rather extensive study to find special experimental conditions rendering the rhodium complexes reactive. The results of this study are summarized in ref. 1 which is included in this report as Appendix No 1. In this paper two convenient methods are recommended for the preparation of pure rhodium(III) perchlorate and sulfate solutions.

Current work in this laboratory has given evidence that the principles utilized for the preparation of rhodium solution are also applicable to other members of the platinum group metals.

Additional attempts of preparation

a) Use of anion exchange resin. The scope of these experiments was to develop a method which would yield halogenide-free solutions without precipitating rhodium hydroxide. Dilute (0.1 to 1 mM) solutions of rhodium chloride were first slightly acidified and boiled for half an hour, and then slowly passed through an anion exchanger, saturated with perchlorate, of the quaternary amine type such as Dowex 2. Cl^- could not be detected in the eluate but a considerable part of the rhodium remained adsorbed on the resin causing a severe loss of rhodium. Washing with a large amount of HCl(6 M) was required to elute the rhodium from the resin face. Further experiments are needed to establish the potentialities of this method, which might find application to prepare very dilute rhodium(III) solutions, where the relative concentration of the anionic form becomes negligible.

b) Use of high temperature and pressure. These experiments were carried out to find whether the halide bound in the inert rhodium complexes could be transformed to halide ions by heating the solutions to a temperature exceeding by far that of the boiling point at atmospheric pressure. A series of rhodium chloride (bromide) solutions with excess perchloric or sulfuric acid were sealed into thick-walled quartz tubes and they were kept at 300^oC for one to two days. Then the tubes were suddenly cooled in an ice-water mixture, opened and the cold solutions were immediately ozonized to remove the free chloride (bromide) ions. It was found that in the suddenly cooled solutions maximally 50 % of the chloride is present as Cl^-. Moreover, additional complications seem

to arise at high temperatures and pressures. In the presence of sulfuric acid the rhodium precipitated as a slightly soluble salt which contained chloride as well as sulfate. On the other hand in perchloric acid solutions decomposition of ClO_4^- to Cl^- occured. In view of these difficulties it was decided to abandon this line.

c) Use of Tl^+. It was mentioned in ref. 1 that by adding Ag^+ to dilute rhodium halide solution a precipitate containing silver, rhodium and halogenide is formed. Attempts were therefore made to remove the halogenide by adding Tl^+ to rhodium halogenide solution. Unfortunately, Tl^+ also seems to form a rhodium salt which is still less soluble than that obtained with Ag^+.

Analysis

In connection with the equilibrium studies the need has arisen to work out a reliable and rapid volumetric method to determine the concentration of dilute rhodium solutions. The classical gravimetric procedure of Gilchrist and Wichers[6] is not practical for rhodium concentrations less than 100 mM because great precautions and special equipment are required to determine accurately mg amounts of rhodium metal.

It was found that under specified conditions Rh(III) may be quantitatively oxidized to green colored Rh(V) which can be determined by iodometry. Using amperometric end-point, rhodium in amounts exceeding 1 micromole, can be determined with an uncertainty less than 1 %. The detailed procedure of the analysis is given in Appendix No 2.

In ref. 1 a method is given for the detection and determination of halogenide present in rhodium and palladium solutions.

Rh(III) and Pd(II) were found to be easily reduced to the metals by H_2 and on the basis of these reactions a convenient method was suggested for the determination of $[Rh_{total}]$ and $[Pd_{total}]$ in concentrated solutions. For details see Appendix No 1. p. 008.

Rhodium in oxidation states higher than three

The dark green colored species: Rh(V)

The preparation of the rhodium(V) species as well as its stability, solubility and absorption spectra are discussed in ref. 2. It contains moreover a critical survey of earlier works concerned with rhodium species of the oxidation number higher than three, generally believed to be four.

The violet colored species: Rh(>V)

Addition of an excess of periodate or bismuthate to an acid rhodium(III) perchlorate or sulfate solution results in the formation of a red-violet colored rhodium species in an oxidation state higher than five. The oxidation proceeds in two steps: within some minutes the characteristic dark green color of rhodium(V) develops which

then gradually turns to violet. When the excess of oxidizing agent is removed (or consumed) the solution gradually turns back to green indicating the presence of Rh(V), and finally it becomes yellow, the characteristic color of Rh(III). On account of the high instability of the violet species no reliable method could as yet be found to determine its oxidation number. Work is now in progress to find the experimental conditions which render the violet species more stable. Moreover attempts are being made to achieve oxidation with electrolysis.

Hydrolysis studies

Experimental conditions

The mechanism of the hydrolysis of the rhodium(III) ion has been investigated at $25^{\circ}C$ by determining $\underline{h}$, the equilibrium concentration of hydrogen ions in a series of rhodium perchlorate solutions. These were made to contain 3 M ClO_4^{-}, by adding $NaClO_4$ in order to minimize the variation of the activity factors. The concentration of rhodium(III) (B) of the test solutions ranged from 0.001 to 0.1 M and for each value of B the hydrogen ion concentration interval 0.001 to 1 M was investigated.

Measurement of $[H^{+}]$

$\underline{h}$ was determined by measuring the emf of cells containing a glass electrode or a quinhydrone half-cell, as well as by conductivity measurements. The emf measurements could generally be reproduced within $\pm$ 0.2 mV, whereas the conductivity of solutions of identical composition were reproducible to within $\pm$ 0.02 %. The technique of the emf measurements and the formulas employed are described in details in ref. 3 (pages 7-13, Figs 2-4). The $\underline{h}$ values obtained by the conductivity data always agreed to within 1 % with those calculated on the basis of the emf measurements.

At acidities higher than 0.1 M only the conductivity data could be used because the absolute undertainty of the $\underline{h}$ determination by emf measurements diminishes with increasing $\underline{h}$, while the relative uncertainty remains constant. This is due to the fact that the emf is a logarithmic function of $\underline{h}$. On the other hand, the conductivity is an approximately linear function of $\underline{h}$. No difficulty was found to obtain precise results in rhodium(III) perchlorate solutions. $Z(\log \underline{h})_B$ data obtained in a series of measurements where the acidity was successively increased were always found to coincide - within the limits of experimental uncertainty - with the $Z(\log \underline{h})_B$ data measured in a series in which the hydrogen ion concentration was gradually diminished by adding NaOH.

Conclusions

In the entire (B, $\log \underline{h}$) range studied, Z proved to be a constant = 1.75 $\pm$ 0.1. This result can be explained in the simplest way by assuming that in our solution Rh(III) predominantly exists as a single polynuclear species with the general composition $(Rh(OH)_{1.75 \pm 0.1})_n$ where n is an integer. The lowest values of n which yield integers for the number of OH bound to rhodium are 3, 4 and 5 corresponding to

$Rh_3(OH)_5^{4+}$, $Rh_4(OH)_7^{5+}$ and $Rh_5(OH)_9^{6+}$ respectively. Since Z proved to be a constant one cannot decide on the basis of emf and conductance data alone which value of n is to be preferred. In order to determine the prevailing n values one has to measure the molecular weight of the hydrolyzed rhodium species. A convenient titration method is now being worked out in this laboratory to measure the freezing-point lowering of a series of solutions. It is hoped that these data will furnish valuable information concerning the number of rhodium atoms present in the hydroxo complex.

Studies on the Rh(V)-Rh(III) half-cell

A considerable effort was made to find the optimum experimental conditions for the accurate measurements of the emf of cells containing the Rh(V)-Rh(III) couple in perchlorate solution. A study of the dependence of the potential of this half-cell on the acidity and the [Rh(V)] would enable us to ascertain the composition of the Rh(V) species once the hydrolysis equilibria of .Rh(III) were known. Moreover such a study would make it possible to treat quantitatively a number of important preparative and analytical methods involving Rh(V).

It is emphasized that the results presented in this section are preliminary ones. Nevertheless it is believed that the experimental approach developed is essentially correct and that continued work along the lines followed will lead us nearer to a more thorough understanding of the complicated reactions occurring in rhodium(V) perchlorate solutions.

Preparation of the test solutions

All the test solutions used for the emf (redox) measurements were of the general composition

$[Rh(V)]=B_5$ M, $[Rh(III)]=B_3$ M, $[H^+]=H$ M, $[Na^+]=(3.000-5B_5-3B_3-H)$ M, $[ClO_4^-]=3.000$ M =

= solution S

B_5 and B_3 were varied between 0.001 and 0.02 M, and the H values ranged from 0.25 to 1 M. The test solutions were prepared from a moderately acid stock solution of Rh(III) perchlorate containing 3 M ClO_4^-. To a known volume of this stock solution 2 M NaOH (containing also 3 M $NaClO_4$) was added until the $[OH^-]_{excess}$ became ~0.1 M. Ozone was passed through this alkaline solution at $1^\circ C$ which oxidized a substantial part of Rh(III) to Rh(V). Finally by adding 3 M $HClO_4$ the acidity of the ozonized solution was adjusted to a value between 0.2 and 1 M. In the last step nitrogen was passed through the test solution to expel the excess of ozone. By ozonizing for varying periods of time or by diluting the ozonized solutions with the Rh(III) perchlorate stock solution, the

ratio [Rh(V)]/[Rh(III)] could be conveniently varied. The [Rh(V)] of the test solution was determined by iodometry (cf. ref. 2). Since Rh(V) oxidises water at an appreciable rate, the actual [Rh(V)] was checked at regular intervals in the course of the emf measurements.

Experimental details of the redox measurements

The Rh(V)-Rh(III) couple was studied at 25°C by measuring the emf of the cell

$$- RE / solution S / Pt or Au + \tag{A}$$

where RE denotes the reference half-cell

Ag, AgCl / 2.990 M NaClO$_4$, 0.010 M NaCl/ 3 M NaClO$_4$/
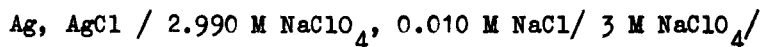
The emf of cell (A) may be written at 25°C

$$E_A = E'_{0,R} + 29.58 \log \frac{B_5}{B_3} - e_s - E_j \tag{1}$$

where $E'_{0,R}$ denotes the apparent standard potential of the Rh(V) - Rh(III) couple in the medium 3 M (Na$^+$)ClO$_4^-$, and e_s is a constant. E_j represents the liquid junction potential arising between solution S and 3 M NaClO$_4$. To evaluate the E_A data the E_j values given in Biedermann and Sillén's work[4] were used.

e_s was determined by measuring the emf of the cell

$$- RE / 0.100 \text{ M H}^+, 2.900 \text{ M Na}^+, 3.000 \text{ M ClO}_4^-/quinhydrone (s), Pt + \tag{B}$$
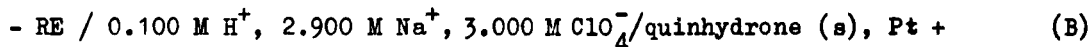
$$E_B = E_{0,Q} - e_s - 59.15 - E_j \tag{2}$$

To calculate e_s the value of $E_{0,Q} = 677.7$ mV according to Biedermann and Wallin[5] was used.

At 0°C the cell

$$- GE / solution S / Pt or Au + \tag{C}$$

was also studied. In (C) GE stands for the glass electrode half-cell. The emf of cell (C) can be written

$$E_C = E'_{0,R} + 27.14 \log \frac{B_5}{B_3} - 54.19 \log h - E_{G,0} \tag{3}$$

where $E_{G,0}$ denotes a constant. Its actual value, which changed slightly from day to day was obtained by measuring the emf of the cell

$$- H_2(1 \text{ atm}) / 0.100 \text{ M H}^+, 2.900 \text{ M Na}^+, 3.000 \text{ M ClO}_4^- / GE +$$
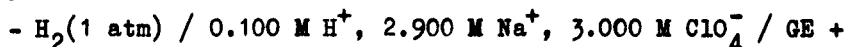
In the first instance different metals were tried as redox electrodes. The best results were found with bright platinum foil electrodes. These attained equilibrium with the test solutions within half an hour, and when several foils were immersed in the same solution they never differed more than 0.5 mV after one hour. Also gold plated platinum foils functioned satisfactorily, although they came much slower to equilibrium than the platinum foils. In all cases the E_A and

E_C values finally measured with gold and platinum electrodes agreed at least within 1 mV.

In a series of experiments the <u>reversibility</u> of the redox electrodes was tested. First of all no cathodic or anodic polarization could be detected when E_A was measured with a compensator (Leeds and Northrup type K3) and a galvanometer of a sensitivity of 2×10^{-9} A/mm. Thus charging and discharging of cell (A) for short periods with a current of 10^{-8} A are reversible processes. When the ratio B_5/B_3 was made to change by adding either the oxidized or the reduced form the value of E_A and E_C changed immediately in the direction predicted by equations (1) and (3).

<u>Conclusions</u>

The correct explanation of the E_A and E_C data is rendered difficult at the present because no truly constant values of emf could be obtained. All the plots of E_A (or E_C) <u>versus</u> time have shown a similar behavior. In a freshly prepared test solution the emf was found to decrease rapidly at first, then the rate of decrease diminished successively. After about two days E_A and E_C were found to decrease with 0.2 - 0.3 mV / hour and this rate was maintained for two weeks.

It was first attempted to ascribe the continuous decrease of the emf to the reduction of Rh(V) by water. To test this hypothesis the [Rh(V)] of the test solution was checked concurrently with the emf readings. The first period of rapid decrease could be well explained with the reaction Rh(V) + H_2O → Rh(III) + 1/2 O_2+ + 2 H^+, but after about one day only slight changes in [Rh(V)] could be observed while the emf proved to decrease uninterruptedly. It seems that Rh(V) undergoes a slow hydrolysis and under the present experimental conditions equilibrium is not attained within two weeks. Experiments are now in progress to study the emf of cells containing solutions preserved for several months.

Although it cannot be claimed that our emf data obtained after several days represent values corresponding to the equilibrium state they seem to be worth recording since they may be of some practical value for investigators working with fresh solutions of Rh(V). Some of our results are summarized in Table 1. The last column of this Table gives the values for the apparent standard potential $E'_{0,R}$, which would be equal to the standard potential of the Rh(V) - Rh(III) couple if the rhodium(V) and rhodium(III) species predominating in the perchlorate solutions would contain the same number of rhodium atoms and OH groups. All the $E'_{0,R}$ values obtained (not only those recorded) proved to be close to 1.42 V. We may thus conclude that Rh(V) is an oxidizing agent of somewhat higher strength than Cl_2; the standard potential of the Cl_2 + 2 e^- = 2 Cl^- half-cell is known to have the value of 1.37 V.

Table 1. A series of measurements with Rh(V)-Rh(III) half-cells

Rh(V) mM	Rh(III) mM	E_A mV	E_j mV	H mM	$E'_{0,R}$ mV
5.0	3.0	1069	16.5	1004	1407
14.09	5.91	1114	8.5	535	1433
13.51	6.49	1102	8.5	535	1422
13.3	6.7	1089	8.5	535	1418
6.9	3.9	1074	5.6	325	1402

Spectrophotometric measurements

In the course of this investigation the absorption spectra of the various test solutions were frequently determined. These data have been of value to follow slow reactions occuring in rhodium solutions such as the oxidation of rhodium(III) in acid solutions by ozone or by IO_4^-, the reduction of rhodium(V) by water or the removal of chloride from rhodium complexes. Moreover an effort was made to determine with some accuracy the spectra of the pure rhodium solutions prepared by the method described earlier.[1] These spectra may serve as a reliable basis for the study of the optical properties of the rhodium(III) and the rhodium(V) ions.

The author feels that the interpretation of the spectral data, in terms of ionic species, must be postponed until the exact composition of the rhodium ions prevailing under different experimental conditions will be determined with certainty by emf, conductance and freezing-point measurements. For this reason the solutions, for which spectra are given below, are characterized only by the way of preparation, by their stoichiometric composition and by their age.

Spectra of rhodium(III) in acid solutions

Fig.1 shows the logarithm of the molar extinction coefficient   ), in mole^{-1}cm^2, as a function of wavelength ($=\lambda$), in Ångström units, in acid perchlorate and sulfate solutions prepared by the method recommended in the note No1, section 4. The absorption spectra of freshly prepared solutions were found to change slowly with time. After about one month, extinction values were attained which did not show any appreciable change for 2 years. In aged solution (older than one month) Beer's law was found to be valid up to $[Rh(III)]_{total} = 50$ mM for the maxima at 3950 ± 10 Å (in perchlorate solutions) and at 4040 ± 20 Å (in sulfate solutions). The maxima at $\lambda < 2400$ Å were not quantitatively treated because the error caused by light scattering cannot be properly estimated at such low wavelengths.

Perchlorate solutions of Rh(III) prepared according to Klixbüll Jørgensen's method[7], which contain some Cl^- and ClO_3^- (see Appendix No 1, section 3.2), exhibit a different absorption spectrum (Fig.2). In the spectral region $\lambda < 3000$ Å, slow changes take place and within one year no evidence was found for the attainment of a steady state. It was observed that concurrently with the spectral changes a precipitate is also formed.

Perchlorate solutions prepared by our method and kept on a steam-bath for a period exceeding 120 h were found to show an absorption spectrum characterized by four maxima at the wavelength 3930 Å ($\varepsilon \sim 115$), 3000 Å ($\varepsilon \sim 200$), 2480 Å ($\varepsilon \sim 390$) and 2060 Å ($\varepsilon \sim 1380$). Thus in the region $\lambda > 3000$ Å it is rather similar to that found in Jørgensen's solution, shown in Fig.2. In these heated rhodium(III)

perchlorate solutions an appreciable amount of chloride could be detected. (cf. Appendix No 1, section 3.2).

The absorption of a rhodium(III) sulfate solution is affected considerably by heating. A new maximum arises at $\lambda = 3190 \pm 20$ Å, a behaviour similar to that observed in heated ClO_4^- and Cl^- solutions.

As it was discussed in ref.1 (section 5.2.) attempts were made to prepare rhodium(III) perchlorate at room temperature by adding $AgClO_4$ to $RhCl_3$ solution. It was found that addition of Ag^+ yields a solution in which $[Cl^-]_{total}/Rh[(III)]_{total} \approx 1$. It is likely that in this solution rhodium prevails as $RhCl^{2+}$ species; its spectra is given in Fig. 3.

Rh(III) in alkaline solutions

It is recalled that freshly precipitated rhodium(III) hydroxide is soluble in the excess of a strong base. Such alkaline rhodium solutions are stable, however, only for a limited time, its length depending upon the anion present, on the $[Rh]_{total}$, the $[OH^-]$ and on the method of preparation of the starting acid solution. The absorption spectra of clear alkaline solution containing a rhodium(III) species, previously[1,2] shown to be highly reactive, is illustrated in Fig. 4. It is seen that the spectra of both the perchlorate and sulfate solutions of pH 14 practically coincide. In such solutions a precipitate becomes visible after ~1 h at room temperature.

In $RhCl_3$ solutions of $[OH^-] = 5$ M, in which no visible precipitate could be detected for several days, rapidly changing absorption spectra were recorded. The spectra obtained after 18 hours, Fig.5, curve 4, seems to coincide with those given in Fig. 4. The spectral changes in the solution illustrate the slow formation of the hydroxo species from the robust rhodium complexes. The spectra of alkalized solutions of preheated rhodium(III) perchlorate or sulfate changed similarly to that of the chloride solution.

Spectra of the rhodium(V) species

Reference is made to Appendix No 2.

Spectrum of the rhodium species produced by oxidation with IO_4^-

In the visible range of the spectrum the violet colored rhodium (>V) ion (cf. page 1:3) has a high extinction shown in Fig. 6. At $\lambda < 4000$ Å the extinction increases sharply as the wavelengths decrease. Maximum extinction is attained 8 - 10 hours after the addition of the oxidizing agent. As long as an excess of periodate is present in the solution no appreciable fading of the color can be detected.

Figure 1.

Absorption spectra of Rh(III); $\log \varepsilon$ versus λ, in perchlorate (———) and in sulfate (———) solutions. [Rh(III)] was varied between 1.00 and 10.0 mM, [HClO$_4$] was kept at 1 M and [HSO$_4^-$] + [SO$_4^{2-}$] at 0.5 M.
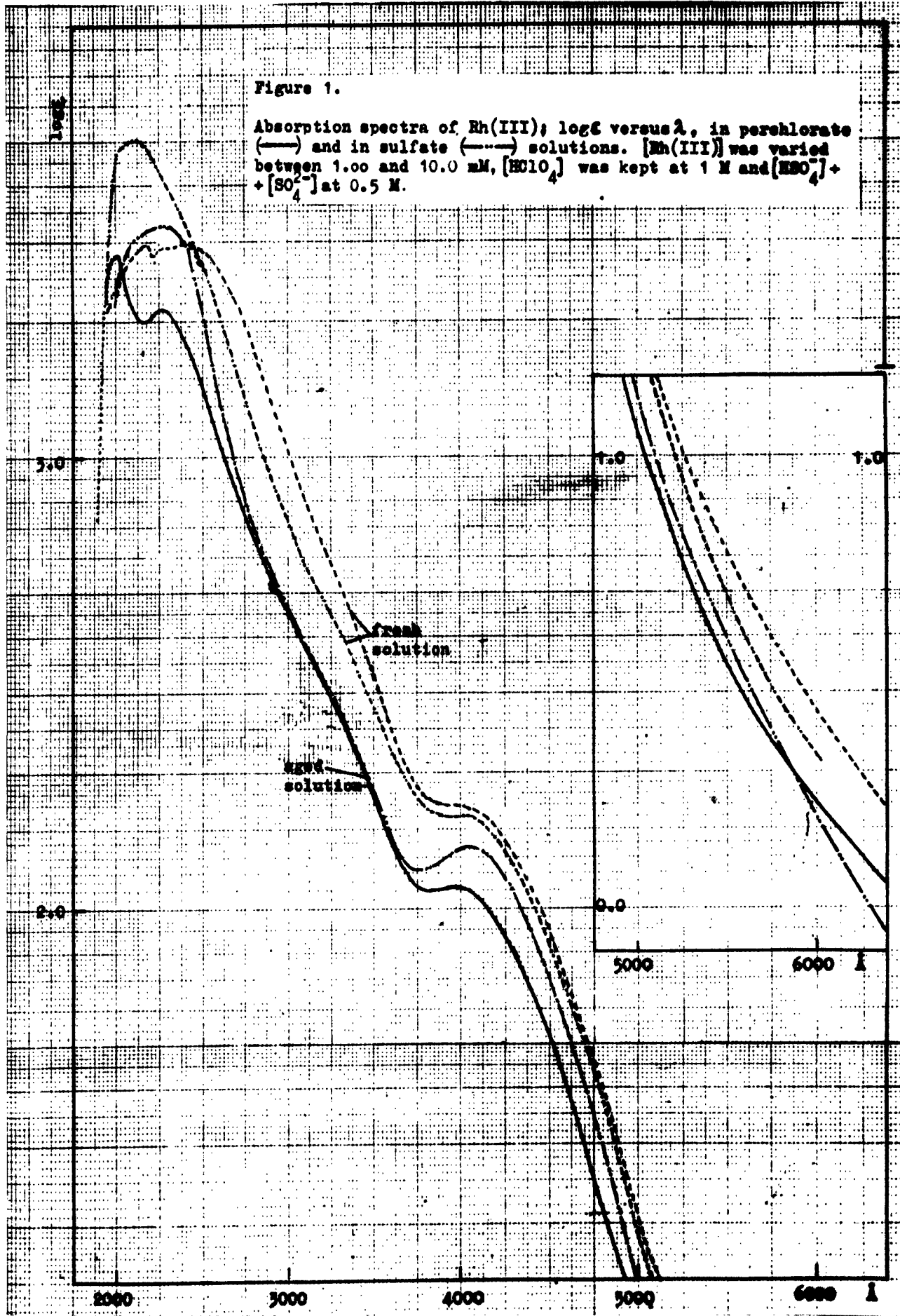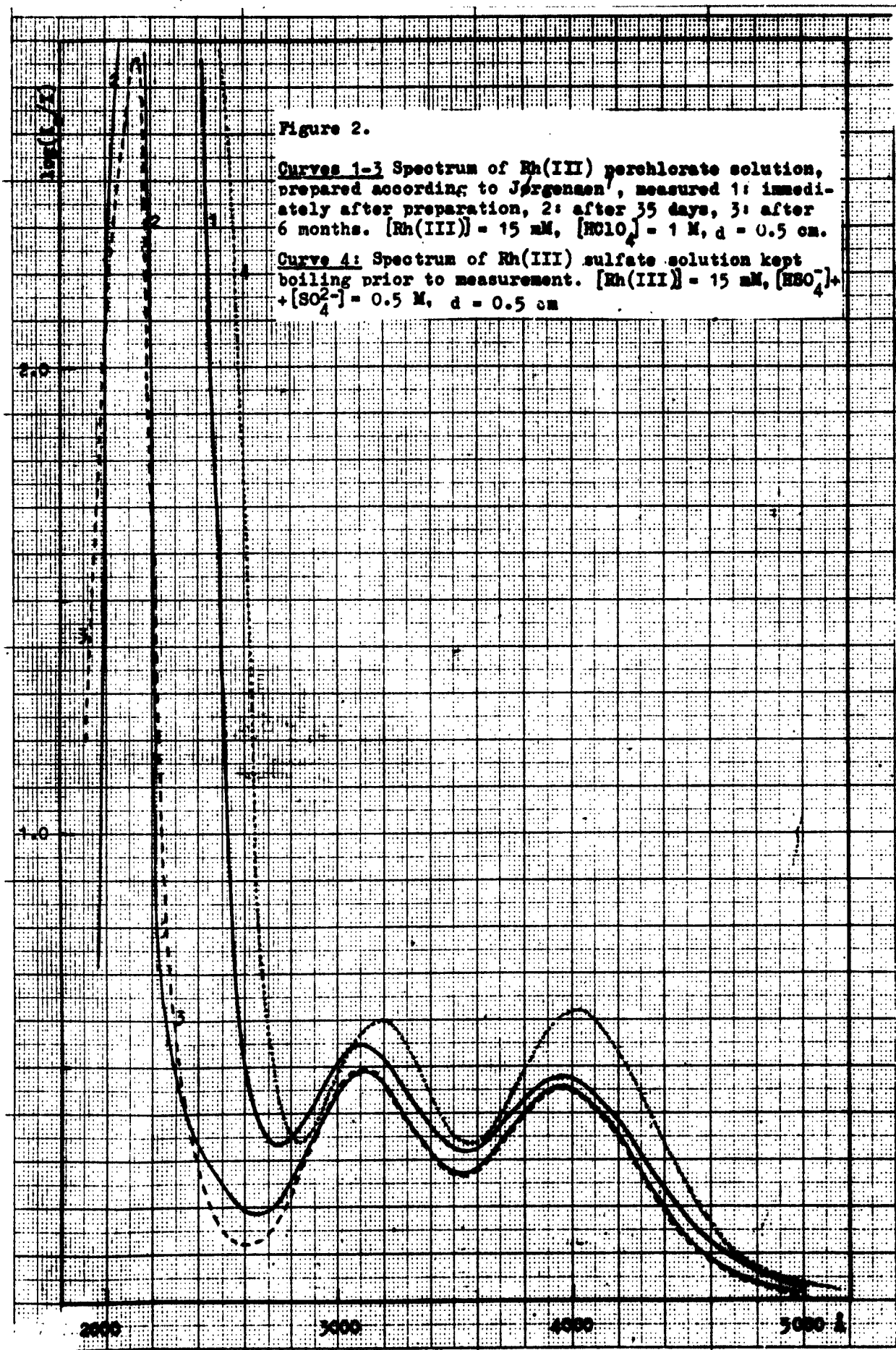
Figure 2.

Curves 1-3 Spectrum of Rh(III) perchlorate solution, prepared according to Jørgensen[1], measured 1: immediately after preparation, 2: after 35 days, 3: after 6 months. [Rh(III)] = 15 mM, [HClO$_4$] = 1 M, d = 0.5 cm.

Curve 4: Spectrum of Rh(III) sulfate solution kept boiling prior to measurement. [Rh(III)] = 15 mM, [HSO$_4^-$]+ +[SO$_4^{2-}$] = 0.5 M, d = 0.5 cm

Figure 5.

Curve 1: spectrum of aged Ti(III) chloride solution

Curve 2: spectrum of solution in water [Ti]/[Ti]er

Figure 4.

Spectra of Rh(III) species in alkaline solutions.

1: [Rh(III)] =1.00 mM, [OH⁻] =1.30 M, [NaClO₄] =0.10 M.

2: [Rh(III)] =1.00 mM, [OH⁻] =1.30 M, [Na₂SO₄] =0.10 M.
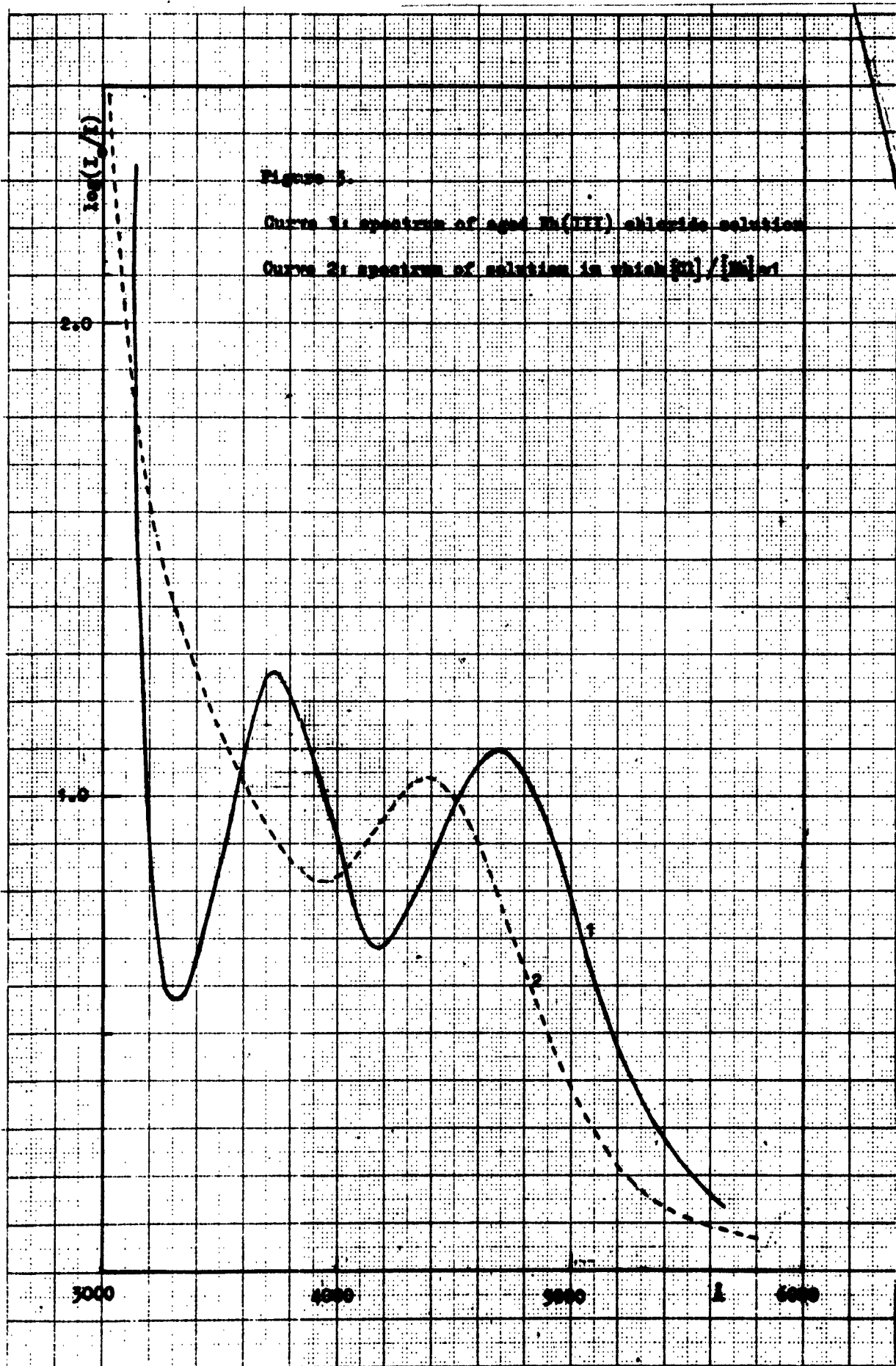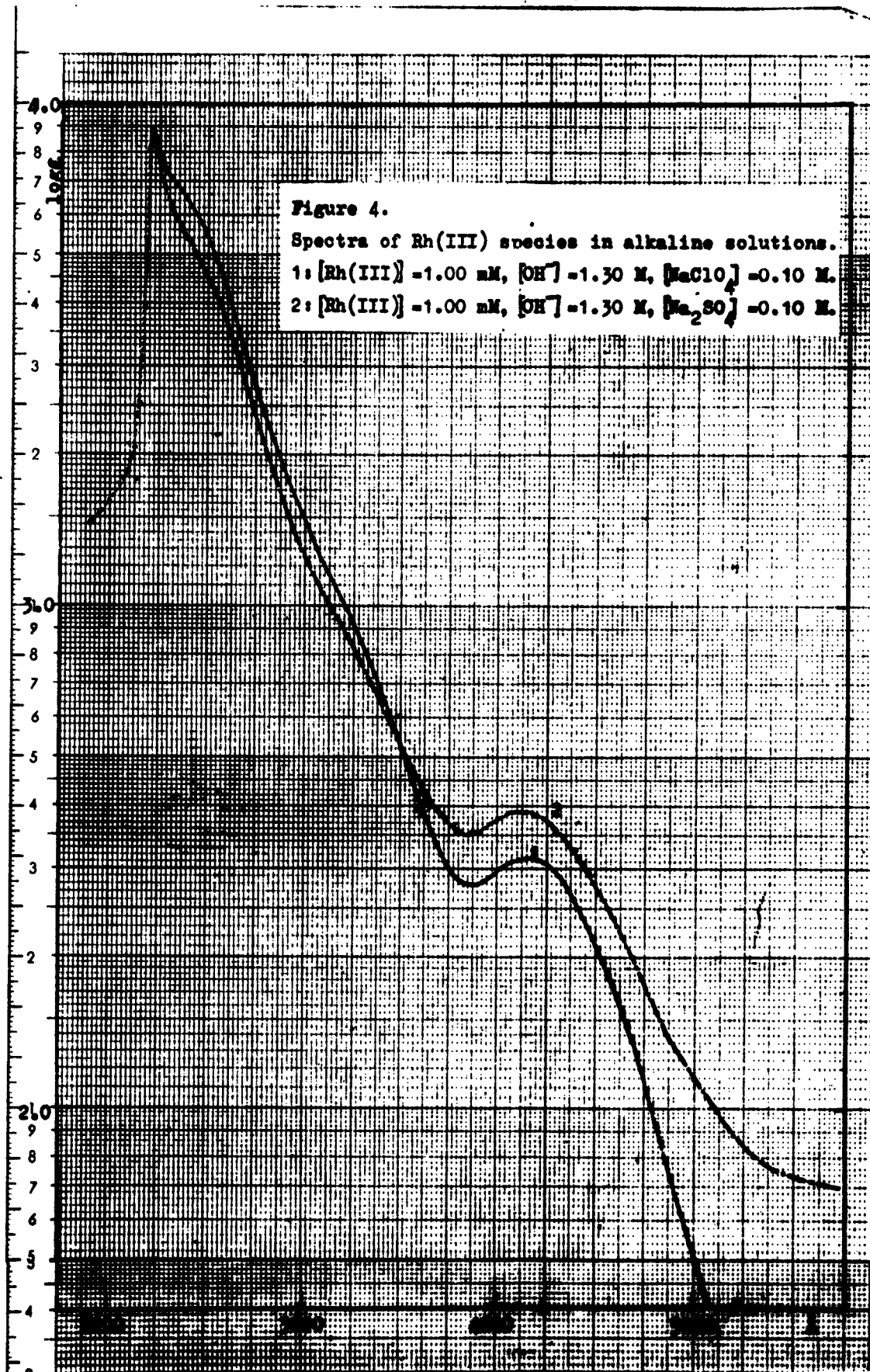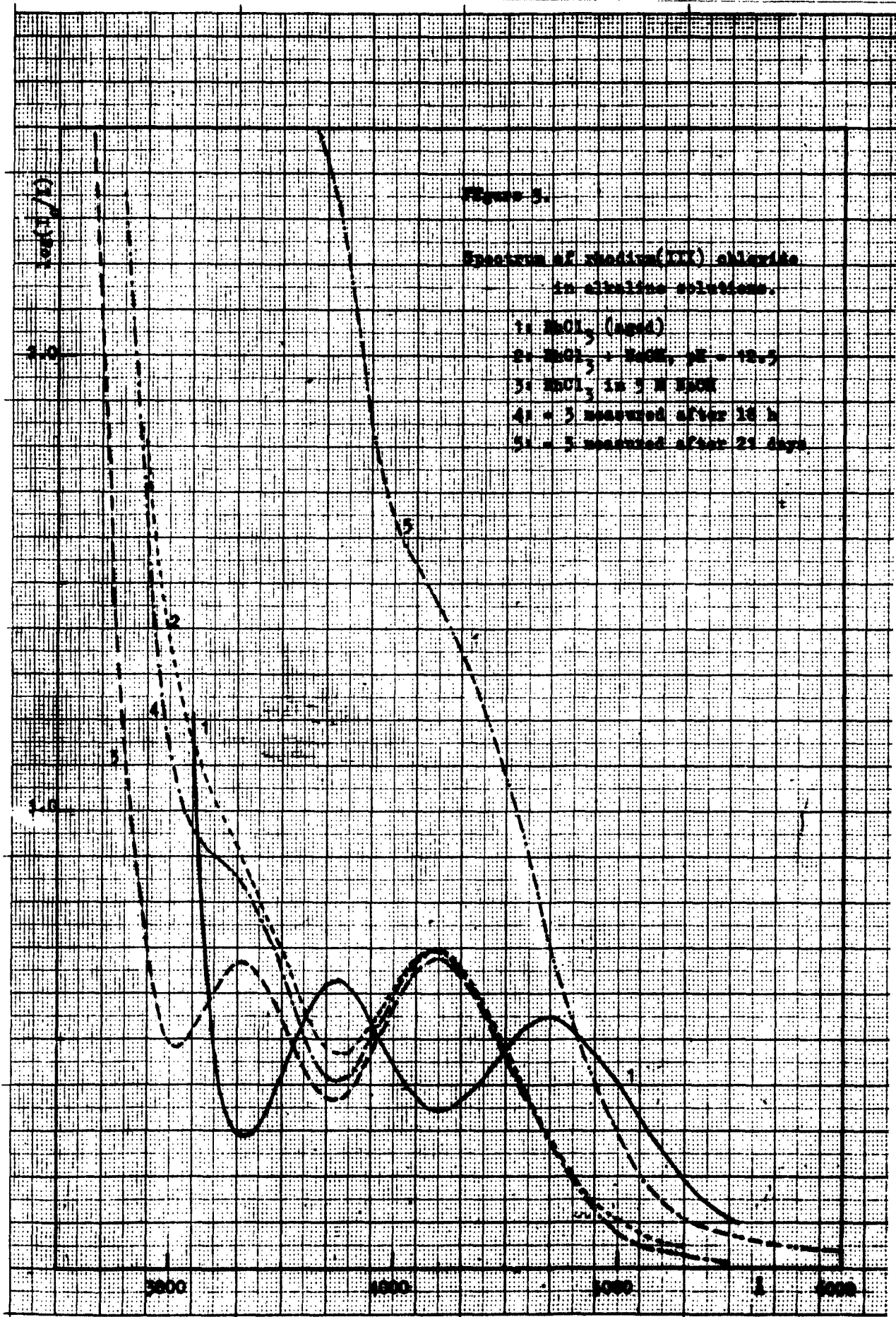
Figure 3.

Spectrum of sodium(III) chloride
in alkaline solutions.

1: MoCl₃ (aged)
2: MoCl₃ ..... pH= ....
3: MoCl₃ in ... M LiOH
4: ... 3 measured after 24 h
5: ... 3 measured after 21 days.

Figure 4.

Absorption spectrum of the red-violet colored rhodium(>V) species
in sulfate solution, measured 20 h after the addition of periodate.

[Rh] = 1.1 mM; d = 1.00 cm
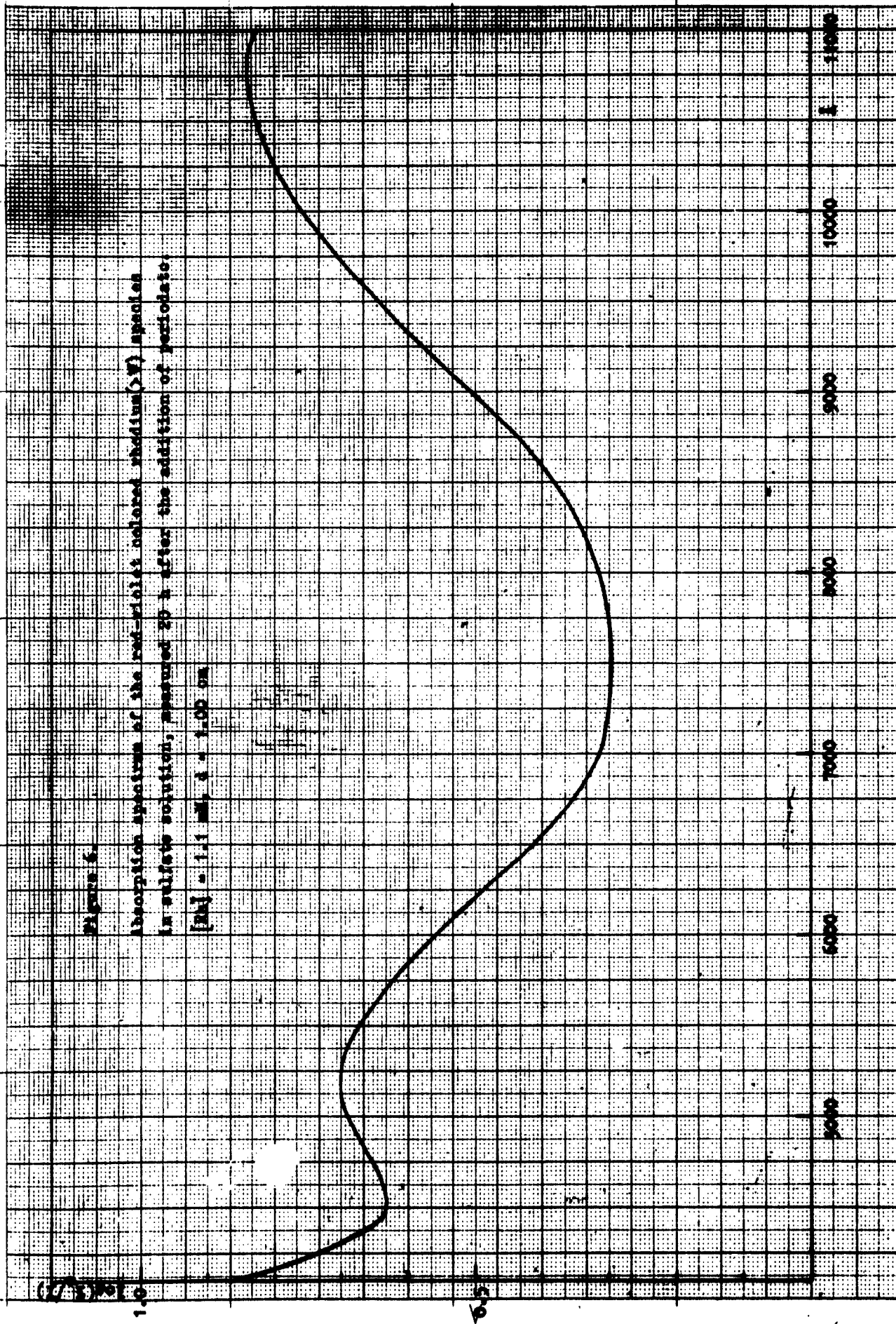
If rhodium(III) could be quantitatively transformed to the highest oxidation state a convenient colorimetric method would be available for the determination of rhodium in solutions so dilute that iodometry cannot yield accurate results. Moreover, there is experimental evidence that oxidation to the violet colored state is a reaction characteristic for rhodium, thus it could serve for the detection and determination of rhodium in the presence of other metals of the platinum group.

Work is now in progress to find the optimal experimental conditions for the quantitative reaction between rhodium(III) and periodate.

The measurements were carried out with a Hilger spectrophotometer of model UVISPEK which was placed in a thermostated room kept at $25.0 \pm 0.5^{\circ}$C. Silica cells (of optical paths 0.10 to 4.00 cm) were used. The absorption curves were constructed from readings at every 50 Å. In the vicinity of the extrema measurements were made at every 10 Å.

Note on the preparation and analysis of palladium(II) perchlorate and sulfate solutions

It has been claimed[9] that pure palladium(II) perchlorate solution can be prepared by fuming $Pd(NO_3)_2$ with an excess of cc $HClO_4$. It was found, however, in this laboratory that boiling 11 M $HClO_4$ is capable of oxidising Pd(II) to Pd(IV) at a considerable rate and at the same time perchlorate is reduced to Cl^- and Cl_2. The chloride produced is bound by the palladium forming a robust complex and consequently it will remain in the solution.

For the preparation of halogenide-free palladium(II)perchlorate and sulfate solution use was made of the principle found to be of great value for the investigation of rhodium: the palladium(II) species present in alkaline solutions proved to be reactive in contrast to those existing in acid solutions. Pd metal, purified by repeated precipitation with H_2 from alkalified nitrate solution was dissolved in freshly distilled nitric acid. The greatest part of the excess acid was distilled off in vacuum (at $\sim$14 Hg mm) and then the concentrated $Pd(NO_3)_2$ solution was dropwise added to a great excess of 1 M NaOH. In solutions of $[OH^-]$ = 1 M the palladium(II) forms hydroxo complexes which after a few days are transformed to colloidal palladium(II) hydroxide. For the preparation fresh alkaline solutions were used, from which palladium(II) hydroxide was precipitated by adding $HClO_4$ in successive portions until the pH of the supernatant attained a value of 9 . During the precipitation the solution was cooled and vigorously stirred. Palladium(II) hydroxide precipitated in this way settles rapidly and it can be easily washed with water and separated by centrifugation. No trace of nitrate could be detected in this palladium(II) hydroxide precipitate. It dissolved easily in cold dilute $HClO_4$ (H_2SO_4).

Palladium can be quantitatively removed from such solutions by passing through H_2 at $50^\circ C$, using the reduction vessel described in ref. 1. The supernatant can be used for the determination of analytical concentration of H^+ as well as for the detection of impurities e.g Cl^-.

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Studies on ruthenium chemistry

by Felipe Brito and Derek Lewis.

Introduction

In a previous report (Brito 1960) a survey was made of preliminary work on solutions of ruthenium in perchlorate and sulfate media. The present report, which is an extension of this work deals exclusively with ruthenium chemistry in sulfate media. Sulfate was preferred to perchlorate because, in its lower oxidation states, ruthenium seems to reduce ClO_4^- to chloride. In the following, we shall occasionally refer to results and methods from the earlier report (Brito 1960) so as not to repeat experimental and other details unnecessarily.

The solution chemistry of ruthenium (like that of several other platinum metals) is complicated by the fact that reactions are often slow, so that in many regions it is hard to obtain a true equilibrium state. The formation of stable halogeno complexes, which is one of the main difficulties with rhodium (see Berecki-Biedermann 1960, 1962, 1963) is more easily overcome with Ru, since in the preparative work one can let it pass through the state of halogen-free volatile RuO_4. On the other hand, in perchlorate and sulfate solutions a number of slow-reacting polynuclear Ru complexes are formed, many of them with a non-integral oxidation number, which introduces further complications.

Since the previous report, Atwood and De Vries (1962) have published a polarographic study on Ru solutions in 0.1 M $NaClO_4$ and at various pH. Reading it superficially one might get the impression that this is a relatively simple system with mononuclear Ru^{3+} and Ru^{4+} forming a mixed binuclear complex. Potential diagrams for Ru, published earlier by other authors, also give an impression of relative simplicity. However, the real complexity of the Ru system is made clear by extended redox studies such as those reported in Fig 1.

For chloro ruthenium complexes, the existence of a binuclear complex $Cl_5RuORuCl_5^{4-}$ has been demonstrated in a crystal structure (Mathieson, Mellor and Stephenson, 1952) and recently Fletcher and Woodhead (1962) claim evidence for a series of polynuclear chloro complexes. The present work, however, is concerned only with complexes in sulfate medium.

Notation

    B = total concentration of Ru, in M

    C = total concentration of SO_4 (including HSO_4^- and SO_4 bound in complexes), M

    c (index) = concentration

    c_{pqx} = concentration of species

$D = x' - x''$, eqn (9)

E = emf measured in cell, usually in mV

E_o = constant

E_j = liquid junction potential

e = redox potential of solution, against electrode Pt, $H_2/1$ M $H_2SO_4/$

e_H = electrode potential of hydrogen electrode ($= \underline{e}$ at equilibrium with H_2 at 1 atm)

e_R = redox potential as measured with inert electrode. At non-equilibrium, $e_H \neq e_R$
  and sometimes even different inert metals may catalyze different redox systems
  so that $e_{Pt} \neq e_{Au}$ etc.

$f = (E - E_o' + E_j')/59.15$

H = excess of H^+ over reference state with Na^+, Ru^{X+}, SO_4^{2-} and H_2O; often negative.

H_+ = $H + HX$, H^+ excess after reduction of Ru to metal with H_2

h = concentration of free H^+, or, more strictly, $H^+ + HSO_4^-$

h^* = true concentration of H^+ (hydrated), thus corrected for HSO_4^-

j = constant in $E_j = jh$

j^* = constant in $E_j = j^* h^*$

M = mole/liter

M^* = mole/kg solution (practical for weight titration)

n = number of faradays added per Ru on anodic oxidation of solution

n_e = n at equivalence point

p = number of OH bound in species $Ru_q(OH)_p^{(qx-p)+}$

$pE = eF/(RT \ln 10) = -\log \{e^-\}$

V_o = original volume of solution

v = volume of titration solution added

v_e = v at equivalence point

x = average oxidation number of Ru in complex

X = average oxidation number of Ru in solution

$y = -\Delta X$ = number of faradays added per mole dissolved Ru on cathodic reduction

Z = average number of OH bound per Ru in solution

Z(index) = p/q for species

Since all the measurements have been made in sulfate medium, we may (as usual in ionic medium work) neglect the complex formation with the medium ions, and thus let $[H^+]$ stand for what is really $[H^+] + [HSO_4^-]$ and so on.

Each complex, $Ru_q(OH)_p^{(qx-p)+}$ is characterized by three quantities q, p and x, q, p and qx are integer, whereas x may often be non-integer.

If we let c_{pqx} stand for the concentration of the individual species, then we

have

$$B = \Sigma \, qc_{pqx} \, ; \quad BZ = \Sigma \, pc_{pqx} \, ; \quad BX = \Sigma \, qxc_{pqx} \, ; \tag{1}$$

where the sums are taken over all ruthenium species.

The relationship between free and total excess H^+ is

$$h = BZ + H \tag{2}$$

where H is often negative. If all Ru in the solution is reduced to metal by $H_2(Pt)$ and the excess $H^+(H_+)$ is determined in the reduced solution, we have, considering $X \, H^+$ would be set free on the reduction of Ru^{X+}:

$$H_+ = H + BX \tag{3}$$

In the reduction titrations the solution was reduced either electrolytically or by adding a reducing substance. If X_{init} is the initial oxidation number, and X the value after the addition of y equivalents per Ru, then we have

$$\Delta X = X - X_{init} = - y \tag{4}$$

In case X_{init} is considered as certain, the data are given in the form of $e(X)$ otherwise as $e(y)$.

Preparation

In the earlier report (Brito 1960) the starting material was commercial ruthenium chloride, which was first transformed to sulfate, and then to volatile RuO_4, which was absorbed in dilute H_2SO_4 to which was added H_2O_2 or SO_2. In the further treatment of Ru, two green solutions (G_1, G_2), two red solutions (R_1, R_2), one violet (V), and one yellow (Y) were described. The methods of preparation were given in the form of a diagram and compared with corresponding diagrams for earlier workers.

The present work was based on the experience from the earlier report. Since with the earlier methods of reduction, there was some risk of the formation of sulfito or peroxo complexes, preparative reduction was usually carried out either electrolytically or with H_2 on a catalyst of platinized Pt. Similarly oxidation was usually carried out with air, or oxygen gas, or anodically.

The methods of preparation of the various solutions studied in the present work are given in the schema below. Again, for brevity and clarity, the solutions have been denoted by letter symbols, which are intended to refer to the Ru species, or group of Ru species, existing in the solution. The same symbol is retained so long as there is no reason to believe that the set of Ru species has been essentially changed.

Symbol	Product	Treatment
	Ru(III,IV)chloride (s)	
	Ru(III, IV) sulfate	H_2SO_4, infrared lamp
		$S_2O_8^{2-}$, Ag^+ distil into dilute H_2SO_4
	RuO_4	

Symbol	Product	Treatment
X=8	RuO_4	
G_1 (X=6?)	green	0.2 M H_2SO_4, electrolytic reduction
B_1	reddish brown + RuO_2	"
G_2 (X=3)	green, e ≈ 300	H_2(Pt) "
B_3	dark brown e ≈ 400-600	Filter, 2 months in contact with air
B_3, X=3.5	dark brown e ≈ 785	(B=9.22 mM, 148.1 mM SO_4^{2-}) ... 1 ... H_2SO_4
X=3.25	clear brown, e = 510	add 1 M H_2SO_4
		Ti^{3+}, ΔX = - 0.25
G_2, X=3	green, e ≈ 300	Ti^{3+}, ΔX = - 0.50
X=8	RuO_4	
G_1, X=6?	green	0.5 M H_2SO_4 + H_2O_2
B_1?	reddish brown	"
G_2 X=3	green	H_2(Pt)
B_4	dark brown	O_2
X=8	RuO_4	
B_1	reddish brown	1 M H_2SO_4, H_2O_2, stand, heat
X=4	Ru resin	H^+ resin Dowex 50, throw eluate
R_1, X=4	amber red	elute with 1 M Na_2SO_4
R_1, X=4	amber red	evaporate in vacuum, + Na_2SO_4(s), filter
B_5	brown, e ≈ 330	H_2(Pt), h ≈ 100 mM
X=4	Ru resin	
R_1, X=4	amber red	elute with 1 M H_2SO_4
	brown, e ≈ 400-600	H_2(Pt)
G_2, X=3	green, e ≈ 300	"
P_1, X=2	pink, e ≈ 100	"
Y_2	yellow, e ≈ 820-870	O_2, then N_2

G_2, X=3   green

anodic oxidation

Y_3, X=5,7 golden yellow, e ≈ 790

cathodic reduction

G_2, X=3   green

- - - - - - - - - -

Color in itself is obviously not a sufficient characteristic for a Ru solution but has to be supplemented by his-tory and redox potential. We have met with a number of different brown solutions, as seen from the schema and Fig (. For example, the dark brown solutions B_3 and B_4 were prepared in a very similar way. The differences observed in their behavior on redox treatment may be connected with the fact that H_2O_2 was used in the preparation of B_4. They may also be connected with a difference in age: B_3 was studied a few weeks after preparation, B_4 had been kept for several months. It is possible that B_5 is identical with B_3.

G_2 is used here as the symbol for a green solution, c ≈ 0.3 V, in all probability Ru(III), and P_1 is a pink solution, e ≈ 0.1 V, probably Ru(II). The solution denoted "G_2" in the previous report (Brito 1960) probably contained a mixture of G_2 and P_1.

Catalytic reduction.

Hydrogen gas in contact with platinized Pt, or another finely-divided Pt group metal, is an excellent source for electrons in preparing lower valency states, provided the standard potential of the system to be reduced is at least 200 mV higher that that of H^+, H_2. The alternative way of preparing such solutions is electrolysis or addition of strong chemical reducters, which usually intro-duces undesirable impurities. With H_2 as reducing agent, the product H^+ causes no disturbance and one can prepare a solution of low valency of known B and H provided one has a solution of the higher valency (usually stable in air) of known B and H.

The experimental arrangement is much the same as for the usual emf titra-tions in this laboratory. The solution contained a foil or net of large surface, and the reaction was followed by means of glass and redox electrodes. It was possible to vary Z - the number of OH bound per metal atom - by adding acid or base. One could also vary X, the average oxidation number of the metal, by adding redox reagents, or preferably by coulometry at constant current or constant voltage.

The redox potential e measured during the catalytical reduction is really a mixed potential of the ruthenium system and the hydrogen electrode, and its value at each moment is such as to make equal the rate of oxidation of the H_2 to H^+, and the rate of reduction of the metal.

We shall replace $\underline{e}$ by Jörgensen's pE (1945)

$$pE \sim e(RT \ln 10/F)^{-1} = - \log \{e^-\} \tag{5}$$

During reduction, since the metal system is not at equilibrium, we must consider two different values, the e_R with regard to ruthenium system, and e_H with regard to the H_2, H^+ system.

It can be shown that to attain 99.9 % efficiency we must have at the end of the H_2-Pt reduction,

$$pE_o > 3/(\Delta X) + \log (H + B\Delta X)$$

where B is the total metal concentration, H is the initial total H^+ and ΔX, the difference in oxidation numbers.

By hydrogen reduction, with various experimental arrangements and ionic media, solutions of vanadium(III) have been prepared from vanadium (IV) or (V) (F Brito to be published), uranium (IV) has been prepared from uranyl, vanadate (IV) from vanadate (V). In the present report, H_2 reduction has been used for preparing Ti(III), Fe(II), Ce(III), Tl(I), and especially various lower valences of Ru.

The starting solutions of Ru were Ru(IV) solutions, R_1, ruthenium B_3 or B_4 solutions and RuO_4 solutions, in H_2SO_4 medium. The mixed potential, and the redox potential e_R after expelling H_2, was followed by means of Au or Pt electrodes, and when $[H^+]$ was small, h was measured by a glass electrode.

More details will be given in the various sections below.

Analytical methods.

Total Ru concentration, B. Ru was determined by weighing as the metal. Either, the metal was reduced from the solution by the addition of Mg metal, (Brito 1960), or hydroxide was first precipitated with $NaHCO_3$ solution, and this hydroxide was ignited in H_2 and resultant metal weighed. B_4 and B_3 were determined by the addition of a measured quantity into an excess of fresh NH_3 solution contained in a weight crucible. It was carefully evaporated and finally ignited in H_2, and weighed. Test for chloride. After the elimination of Ru with Mg, the stock solutions were tested with HNO_3 and $AgNO_3$ to see whether any Cl^- was left. Usually the reaction was negative. In one typical example it was found that the ratio Cl/Ru was less than 0.002.

Average oxidation number, X.

The oxidation number X was determined in the main as already described by Brito (1960). We used two stock solutions of cerium(IV) which had been standardised against a Ti(III) solution, which in its turn had been standardised by dichromate and Mohr's salt. The Fe(II) solutions were prepared by diluting a solution of Mohr's salt in 2 M H_2SO_4; they were kept under CO_2 in a buret with half-automatic filling. They were always standardised against Ce(IV) before and after the determination

of X.

For the latter, known excess amount of Ce(IV) was added to the unknown Ru solution, which was oxidized to RuO_4; the tetraoxide was expelled as completely as possible by boiling, and by bubbling N_2. Finally, the remaining excess of Ce(IV) was determined by titration with Fe(II).

The following values for X were obtained, for a number of solutions:

R_1: 3.91, 4.11, 3.94. B_3: 3.35, 3.41, 3.39. B_4(fresh) 3.08, 3.22, 3.30, 3.39. B_4(after 6 months) 3.53, 3.55, 3.52, 3.57, 3.50.

G_2: 2.90 (e ≈ 133 mV), 3.03 (e ≈ 184 mV).

For a few points obtained by oxidation of G_2, the results are given in the diagram, Fig 1.

Analytical hydrogen ion excess H.

The redox experiments were all made in 1 M H_2SO_4. To determine Z, it was necessary, however, to study Ru solutions of lower acidity. According to (2), the hydroxide number Z is related to the apparent hydrogen ion concentration h by h = H + BZ. Since h can be determined by emf measurements, to determine Z it is necessary to find H. Several batch methods are available, each of which gives H + some multiple of B:

a) To the sample, known excess of $NaHCO_3$ *is* added, solid, or in solution. The precipitate is removed, and the excess HCO_3^- is back-titrated with standard acid. If the precipitate contains no anions but OH^-, the reaction formula is:

$$X\ HCO_3^- + Ru^{X+} \rightarrow Ru(OH)_X(s) + X\ CO_2(g)$$

Each Ru is then equivalent to X moles H^+, and the total acidity determined is H + BX.

/with $[H^+]$ = 5 - 10 mM/

b) Ru is reduced catalytically to the metal,/using H_2 on a Pt catalyst, and the acidity of the remaining solution determined by titration. The reaction formula is:

$$0.5\ X\ H_2 + Ru^{X+} \rightarrow X\ Ru(s) + X\ H^+$$
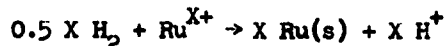
The resulting acidity of the solution is again, H + BX.

c) The solution is titrated with standard NaOH to pH ≈ 6, using bromocresol purpur as indicator, as described in the earlier report (Brito 1960, p 13). This gives H + BX, if the reaction is

$$X\ OH^- + Ru^{X+} \rightarrow Ru(OH)_X(s)$$
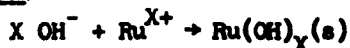
This works well for X=4, but sometimes (e.g. for B_4) gives discordant results, probably because of side reactions.

d) Excess Br_2 is added, and Br_2 + RuO_4 distilled away. The remaining solution is titrated with NaOH. This gives H + 8B since the reaction is $Ru^{X+} + (4-0.5X)Br_2 + 4H_2O \rightarrow RuO_4(g) + 8H^+ + (8-X)Br^-$.

e) To the sample is added a small excess of solid $KBrO_3$. RuO_4 and Br_2 are expelled by boiling the solution, and the total concentration, H_{Br}, of acid determined by titration with standard NaOH. The reaction is:

$$Ru^{X+} + (1.6 - 0.2X)BrO_3^- + (0.6X - 0.8)H_2O \rightarrow RuO_4(s) + (0.8 - 0.1X)Br_2 + (1.2X - 1.6)H^+.$$
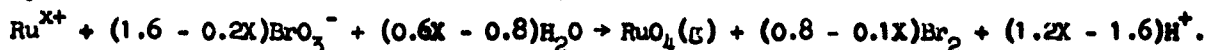
Thus, for each Ru present in the solution, $(1.2X - 1.6)$ H^+ are set free, so that the measured acidity of the final solution is $H_{Br} = \underline{H + (1.2X - 1.6)}$.

Determination of h by emf methods.

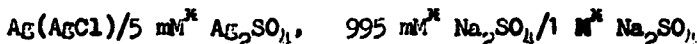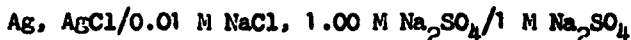In order to determine the hydroxide number, Z, it was necessary to determine $h = [H^+]$ in less acidic solutions than the ones used in the redox experiments. This was done by emf measurements, using the cell

reference electrode /Ru solution/glass electrode

As a reference electrode we used either

$Ag(AgCl)/5$ mM^X Ag_2SO_4,   995 mM^X Na_2SO_4/1 M^X Na_2SO_4

or

$Ag, AgCl/0.01$ M NaCl, 1.00 M Na_2SO_4/1 M Na_2SO_4

In either case, the cell was calibrated by using solutions without Ru:

reference electrode/h M H^+, (2 - h) M Na^+, 1 M SO_4^{2+}/glass electrode or H_2(Pt).

The emf of the latter cell was found to follow the expected equation

$$E = E_o + 59.15^4 \log h + jh \tag{6}$$

For the first half-cell $E_o = -692.65 \pm 0.05$ mV, $j = 6.0 \pm 0.1$ mV/M^X (H_2 electrode). With a glass electrode, E_o varied somewhat as usual, and $j = 14 \pm 1$ mV/M^X. For the second half-cell, $j = 5.85$ mV/M (H_2 electrode $\approx$ glass electrode).

The glass electrode used was calibrated against a hydrogen electrode over the range of log h that was encountered in the Ru studies.

Before each titration of a Ru solution, the value of E_o was determined by measuring E for a cell made up with a standard solution to the right, in which B = 0 and h = 200 mM; no significant change in E_o was found to occur when the glass electrode was transferred from the standard solution to the titration vessel.

For the solutions containing Ru, the value for h was calculated from equation (6) by means of successive approximations.

Preliminary titrations with the usual technique had indicated that the quantity sought for, BZ (the concentration of bound OH per liter) came out as the difference between two large numbers. Since we had to start with a rather acidic solution, h ≈ 0.90 M, and in addition had to add a second Ru solution in order to keep B constant, it would have been necessary to have a base solution of inconveniently high concentration, say around 0.3 - 0.4 M. So it was decided, instead, to vary H in the solutions by adding a solid base, $NaHCO_3$. In comparison with, for instance, using a weight buret, the addition of $NaHCO_3$ was economical of primary stock solution of ruthenium, the preparation and analysis of which was expensive, time consuming and difficult.

Equilibria of HSO_4^-. We should remember that all the work has been done in a 1 M SO_4^{2-} medium, and that the h measured is really the sum of $[H^+] + [HSO_4^-]$. Let us consider the equilibrium

$$H^+ + SO_4^{2-} \rightleftharpoons HSO_4^-, \quad [HSO_4^-] = Kh^x [SO_4^{2-}]$$
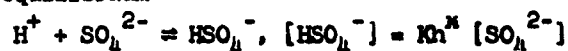
here, h^x is the true concentration of H^+ [hydrated].

If, now, $[HSO_4^-] + [SO_4^{2-}] = C$ we find

$$h = [H^+] + [HSO_4^-] = h^x + CKh^x/(1 + Kh^x) \approx h^x (1 + KC) \tag{7}$$

If we use, instead of h, the true H^+ concentration, h^x, then E can be expected to follow the equation

$$E = E^x_0 + 59.154 \log h^x + E_j^x \tag{8}$$

Peterson (1961) has shown experimentally and by application of the Henderson equation, that E_j gives a straight line versus h = H, when h is small. This has also been confirmed by our experiments. From the present data in sulfate medium, it is not possible to obtain an independent value for K. Following Peterson we shall use the results of Baes (1957) to estimate K in 1 M H_2SO_4. With this estimate, $K^{-1} = 0.29$ M one may calculate h^x. Such calculations show that the limiting values of $\log h^x$ in this investigation are about -1 and -3.

Redox reactions of ruthenium.

A considerable effort was made to study redox reactions of ruthenium, especially with oxidation number X < 4, in the medium 1 M H_2SO_4. With this high acidity, the changes in $[H^+]$ accompaning the redox reactions are negligible. The results are reported in the form of curves e(X), where e is the electrode potential, and X is the apparent oxidation number. (See "notation").

The variation of e with B (the total Ru concentration), and with temperature was also studied to some extent.

We define the redox potential, e, in the solution as the emf between an "inert" metal such as Pt or Au in the solution on one side, and on the other side, the electrode 1 M H_2SO_4/H_2(1 atm). Like several earlier authors we noticed that in certain ranges of X, particularly between X = 3.5 and 3, the e values measured by probe electrodes in Ru solutions are unstable and drift steadily over considerable periods of time. This drifting was observed although careful precautions were taken to exclude oxidizible or reducible impurities. Thus far, attempts to eliminate it, e g by working at temperatures other than $25°C$, have not been successful. The obvious interpretation is that the solutions contain several redox couples which are not in true equilibrium. What is measured is then a "mixed potential", which is mostly influenced by the couple (couples) with the fastest electrode reactions.

Although the e values did not always correspond to the final equilibrium state, a considerable number of careful measurements were made in the ranges of instability

since it was thought that they could give at least some information on the reactions going on.

For varying X, both chemical and electrolytic methods have been used. The chemical methods - reduction with Ti(III) or Cr(II), and oxidation with Co(IV) - have the advantage that one can easily and very quickly traverse the whole range of X whereas on the other hand there is a risk that the substance introduced may give rise to complications, for instance mixed polynuclear complexes. On the other hand, the electrolytic method has the advantage that no foreign substance need be introduced into the solution being investigated, but has the drawback that one has to work slowly; also, one can not be quite certain that side reactions do not occur.

Survey of redox titrations.

Fig. gives a survey of the redox experiments made with the medium 1 M H_2SO_4.

The coordinates are $\underline{e}$, the redox potential defined with H_2(1 atm)/1 M H_2SO_4 as the reference zero electrode and X, the apparent oxidation number of Ru. Most of the curves refer to reduction, either with chemical reagents (Ti^{3+}, Cr^{2+}), or by cathodic reduction (e^-). A few curves refer to experiments in which Ru was oxidized: they are denoted by arrows pointing to higher $\underline{e}$. These curves are for the oxidation of O_2 anodically (e^-), and P_1 anodically in the presence of Co^{3+} (e^-, Co^{3+}) or Tl^+ (e^-, Tl^+).

A few single points refer to various steps of oxidation of O_2 solution by O_2 in which X was determined analytically.

It would be a gross exaggeration to say that all points lie on the same curve, or that we are working always with reversible reactions. In fact, the Ru system is the most recalcitrant we have ever met. It is some consolation that all other workers who have tried to work on this system, have met with similar difficulties, whether they noticed it or not.

Obviously there are irreversible reactions going on, and considerable aging effects were noticed. In a solution with the same apparent oxidation number X, the average composition of the species - the average number $\bar{q}$ of Ru atoms per complex and $\bar{Z}$ of OH groups per Ru - may thus vary with time. It should also be remembered that there may be peroxo and hydrido ligands (O_2^{2-} or H^-) which may give Ru an apparent oxidation number different from that of the Ru atoms alone. This gives still more possibilities for the existence of a number of different solutions with the same apparent X.

The range between X=0 and 4 will not be treated here. The dark green color that occurs during the catalytical or electrolytic reduction at $e_H = 1.34$ volt seems to be due to an unstable state, which may have X=6 (Martin 1952), but which

Fig 1
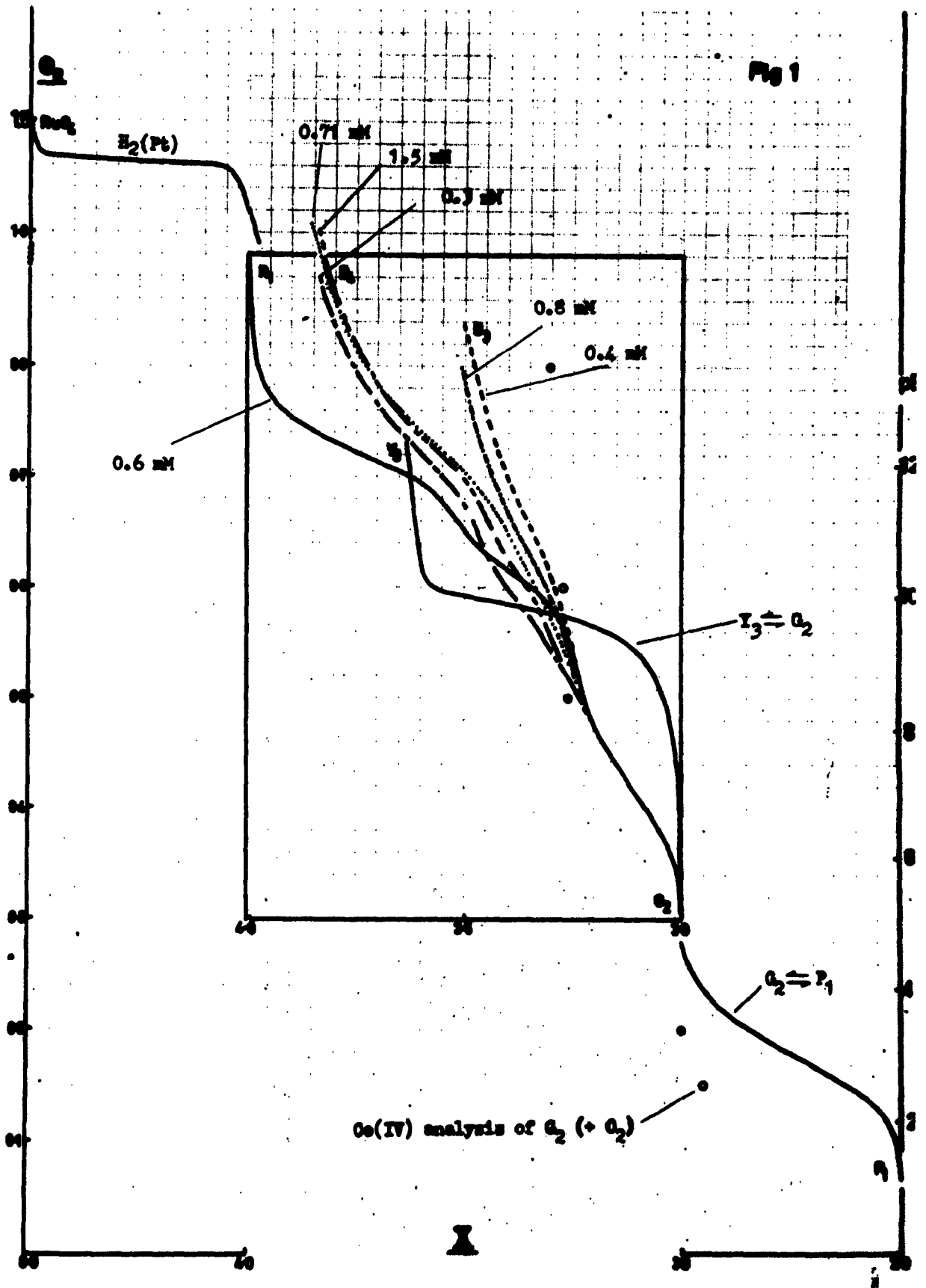
gradually decomposes to RuO_4 and lower oxidation states on standing. There are indications in the literature of a state with $X \approx 4.2$ or 4.4 (Wehner and Hindman 1952, Cady 1957).

Between $X=2$ and $X=3$, the potential seems to be fairly well-defined, and in fact, this part of the system can be described quantitatively by assuming the reaction, $Ru^{3+} + e^- \rightleftharpoons Ru^{2+}$ (omitting OH and SO_4 complex formation) with a standard potential, in 1 M H_2SO_4, of $e_o \approx 180$ mV.

The most complicated picture is between $X=3$ and $X=4$. It is our impression that the red solution R_1 and the green solution G_2 are fairly well-defined states of Ru.

The "anchoring" of the $e(X)$ curves along the X axis might be open to discussion. In general, curves from experiments beginning with the R_1 state were fixed to begin at $X=4.0$ as indicated by our earlier analysis of R_1 (Brito 1960). Those curves that went through the green G_2 state were fixed so that the corresponding point was at $X=3.0$. It is, however, remarkable that the change in X from B_1 to G_2 was found to be ≈ 1.15 on cathodic reduction, but ≈ 1.0 from chemical reduction; one explanation might be the formation of hydrido or peroxo complexes in the former case.

It is advisable to compare reduction curves with different reducing agents: with chemical agents one might fear the formation of mixed complexes between Ru and say, Ti or Cr, whereas with cathodic reduction one might fear other side reactions. It is then reassuring that the reduction curve from $X=4$ to $X=3.5$ is fairly reproducible and has practically the same shape, using Ti^{3+}, or cathodic e^- as reducing agent. An analysis of this curve, as shown below, would indicate species, Ru_3^{12+} or Ru_4^{16+} (omitting OH and SO_4) for $X=4$ and Ru_2^{7+} for $X=3.5$. It is, however, thought-provoking that on back-titration of reduced $Ru(X=3)$ with R_1, when both solutions were fresh, a curve was obtained which could be quantitatively explained assuming mononuclear Ru^{3+} and Ru^{4+}, and a very large complex $Ru_n^{3.5n+}$. A possible explanation is discussed below.

The curves for the reduction of R_1, B_3 and B_4 (Cr^{2+} or Ti^{3+}) seem to coincide roughly for $X < 3.3$. In all of them, one can notice at least one more break, around $X=3.25$, which would indicate that there is at least one more complex of mixed valency.

Quite different from this group of reactions is the practically reversible curve obtained on repeated anodic oxidation and cathodic reduction of G_2 to Y_3. It seems that Y_3 corresponds to $X=3.7$.

In none of the experiments carried out so far, has it been possible to regenerate the well-defined red $Ru(IV)$ solution R_1 by oxidation of solutions derived from the reduction of the red sulfate.

Methods of redox titration

Cathodic reduction.

Both constant current and controlled-potential methods were employed.

In the constant-current work we used a Leeds and Northrup type 7960 coulometric analyzer, which indicates directly the number of faradays passed. This method is very convenient and especially useful during the early stages of reduction when the standard potentials of the possible redox processes are so well separated that no mixed reactions, such as the simultaneous reduction of Ru and deposition of H_2 will occur in spite of the rather high overpotential applied.

In some experiments, on the reduction of R_1, the coulometer was not available, and a simpler set-up was used which was still adequate for our purpose. The electrolytic current was then taken from a 6 V battery of storage cells in series, with a variable resistor. The current was measured by a milliammeter with a long scale, which was calibrated by measuring the potential drop across a known resistance by means of a potentiometer. The current was in general between 1 and 2.5 mA and was kept constant during the course of experiments by manual control. The time was measured by a cronometer.

In the controlled-potential experiments, the source of current was a lead-storage cell of high capacity, and the potential applied to the electrolysis cell was controlled by means of a simple potential divider. The number of faradays passed was determined by means of a calibrated milliammeter, having a accuracy of 0.5 %, and a stop-watch. In most of these experiments, the applied potential was adjusted to such a value that the cathodic over-potential was $\approx$ 0.1 V at the mid-point of the first shelf of the redox potential curves, and then left unchanged.

A variety of cathode materials have been used in various experiments, but usually, large Pt mesh electrodes have been employed, so that the current density was low at the cathode; they were coated with Pt black in the constant-current experiments. In a typical experiment, the cathode was a platinized Pt net of about 25 cm^2, half immersed in the solution so that the current density was 0.1-0.2 mA/cm^2.

The bubble overvoltage of H_2 on a Hg cathode in the Ru solutions was found to be very little different from that on the platinum electrodes (in each case about 0.1 V). Hg cathodes were not further tested.

The several different electrolytic cells employed may be exemplified by that used in most of the experiments with controlled potential. The cathode compartment consisted of a seven-neck flask containing the solution to be investigated, the cathode, and the probe and reference electrodes. The cathode compartment was connected through a bridge with 1 M H_2SO_4, to the anode compartment, which contained 1.0 M H_2SO_4, saturated with Ag_2SO_4(s), and a silver electrode. The whole assembly was kept in a paraffin oil thermostat (experiments at 25°C), an ice-water bath (experiments at

0.5°C), or a special oil thermostat (experiments at 40°)

As <u>reference electrodes</u> we used either a hydrogen electrode in 1.0 M H_2SO_4 connected through a ground glass joint to the Ru solution, or a Beckmann type 1190-60 glass electrode which had been calibrated against a H_2 electrode in 1 M H_2SO_4. As the hydrogen electrode, we sometimes used the platinized Pt anode itself, after O_2 had been removed and the electrode had been saturated with H_2.

For the <u>probe electrode</u> several different materials were tested, but in most experiments, e was measured with either bright Pt or gold-plated Pt electrodes or both: the cathode itself, a large platinized Pt electrode, was sometimes used, of course after the current had been switched off. In the controlled current runs, it usually agreed well with the other probe electrodes. In the controlled potential runs, a persistent polarisation was often observed with the bright Pt cathode used.

In all experiments, a slow stream of pure nitrogen was used to stir the cathode solution, and eliminate O_2. The N_2, which was delivered from a commercial cylinder, was purified by passing it through successively 10 % NaOH, 5 % pyrogallol in 12 % KOH, concentrated H_2SO_4, a column of hot copper, dispersed on asbestos, (to eliminate the last traces of oxygen) and 1.0 M H_2SO_4.

In order to ensure that no atmospheric oxygen entered the cell, the exhaust gas from the tightly stoppered electrolysis cell was led through a Bunsen valve or through an exit tube immersed in the thermostat bath.

Anodic oxidation.

For the anodic oxidation of solutions, the same apparatus was used, as for cathodical reduction, the current being reversed. Platinized platinum was used for the anode in the experiments at constant current in this case, the anode could be used immediately as a reference H_2 electrode. In the experiments at controlled potential, bright platinum was used for the anode.

The anodic oxidation was made at constant current, or with controlled potential, sometimes after the addition of the reduced form of an auxiliary system, $Tl^+ + Tl^{3+}$, or $Ce^{3+} + Ce^{4+}$. Thallium(I) sulfate solution was obtained from a weighed amount of Tl_2CO_3 pa. Cerium(III) sulfate solution was obtained by reduction with H_2(Pt) of cerium(IV)sulfate solution in H_2SO_4 of the concentration wanted.

Chemical reduction.

<u>Titanium(III) solutions</u> in 1 M H_2SO_4 were prepared by one of the following three methods:

a) Catalytic reduction of a titanium(IV)sulfate solution by H_2(Pt). The reaction was carried out in the storage vessel of a microburet with semi-automatic filling, which was especially constructed for solutions sensitive to air. Hydrogen gas was bubbled past a foil of platinized Pt dipping into the solution. In this way, Ti(IV) was partially reduced to Ti(III) and moreover the concentration [Ti(III)] was kept

constant. Even when the Ti(III) solution was stored, a slow stream of H_2 was bubbled into it, to make it circulate past the Pt foil.

b) Metallic Ti was dissolved in boiling dilute H_2SO_4, the SO_2 was expelled by means of CO_2, and the solution was stored like a)

c) A cation-exchange resin, saturated with Ti^{3+} was eluted with 1 M H_2SO_4. A column of Dowex-50 was first washed with 1 M KSCN, then repeatedly with 3 M HCl, with water, and finally it was saturated with Ti^{3+} by passing a solution of $TiCl_3$ in 3 M HCl. The preparation was free from iron. Under these conditions Ti(IV) is not held by the resin. The solution was stored like a).

Analysis. For analysing Ti(III) solutions an iron(III) solution was prepared by dissolving Fe (99.99 %) in boiling 1 M H_2SO_4, adding 30 % H_2O_2 dropwise, and boiling. A known amount of iron(III) solution was kept in the main vessel of a cell like the one described below, and the Ti(III) solution added from a buret. The redox potential $e(Fe^{3+}, Fe^{2+})$ was measured by means of an Au electrode, and the data were plotted in the form of $10^{pE}(v^{-1})$ to give the equivalence point v_e (v=volume of Ti^{3+} solution added). This gave v_e^{-1}. (This is a generalized Gran plot; other forms are also possible.) Identical values for $[Ti^{3+}]$ in the initial solution were obtained when the same method was used except that a certain amount of Ti^{3+} + excess of Fe^{3+} was back-titrated by the same cerium(IV) solution as was used for titration of the Ru(IV), R_1.

Chromium(II) solution was prepared by electrolytic reduction on a Hg cathode, of a chromium(III)sulfate solution in 1 M H_2SO_4. The anode was a Pt electrode in 1 M H_2SO_4, kept in a narrow tube, which ended in sintered-glass disk, across which the liquid junction was made. All operations were carried out in oxygen-free CO_2, which was also used, after the reduction, for pressing the solution into a buret similar to the one used for Ti(III). The chromium(II) solution was also standardized with iron(III).

Measurement of redox potential. The following cell was used: $H_2(Pt)/1$ M H_2SO_4/Ru solution, 1 M H_2SO_4/Pt or Au.

Usually, a bright Pt electrode and an Au electrode were used. The Pt electrodes were boiled in hot 1:1 HNO_3 and ignited in an ethanol flame. The Au electrodes were massive or prepared by electrodeposition on Pt; they were treated in an analogous way.

The reference half-cell consisted of a platinized Pt electrode in a tube of 12 cm length and 1.5 cm diameter. The tube had a stopper with holes for electrodes and inlet and outlet for H_2. The low end of the tube was narrowed and ground to form a cone-joint. The end was sealed, but there was a small hole in the side. The cone-joint was covered by a ground socket-joint, and the liquid junction was across

the joint. The resistance was of the order of 4000 ohms. The E of the cell was measured by a Radiometer pHM4.

During the experiments, a stream of N_2 was passed through the solution. It was first passed through a column with active Cu, then through 10 % H_2SO_4, 10 % NaOH and finally 1 M H_2SO_4. The H_2 gas for the reference cell was treated in an analogous way.

In the start of an experiment, the Ru solution was introduced into the titration vessel after which N_2 was bubbled for several hours, usually all the night. After this, Ti^{3+} or Cr^{2+} was added.

The emf measured with Pt and Au electrodes might differ by a few mV in the beginning of a titration but in the buffered solutions they were usually identical within $\pm$ 1 mV. In certain ranges of the titration, the emf of one or both electrodes was found to creep; in such cases the E was read when a given time, usually 5 minutes had passed after each addition from the buret.

The concentration of the Ti(III) or Cr(II) solution was always chosen such as to make the volume change during the titration less than 2 %. The concentration of the buret solution was always determined immediately after the redox titration, against Fe(III) or Ce(IV) + Fe(III).

General equations for e(y) curve in two-species region.

Let us assume that in a certain region - a "shelf" on the redox titration curve - practically all Ru is present as one of two complexes, one with oxidation number x' and q' Ru atoms per complex, the other with oxidation number x'' and q'' Ru atoms. The difference in oxidation numbers we may call D:

$$x' - x'' = D \tag{9}$$

We may assume that D is positive and will express ourselves accordingly although all the argument is also valid for negative values for D and y below.

The redox potential would thus be determined by the equilibrium (omitting in the formulas OH and SO_4 complexing)

$$q'' Ru_{q'}^{x'q'+} + q'q''D\ e^- = q' Ru_{q''}^{x''q''+} \tag{10}$$

The Nernst expression for the electrode potential gives

$$e = e_o + \frac{RT \ln 10}{Fq'q''D} (q'' \log c' - q' \log c'') \tag{11}$$

where c' and c'' are the concentrations of the two species. The expression (11) is simplified if we divide by the factor $(RTF^{-1} \ln 10)$ and replace e by pE:

$$pE = pE_o + \frac{q'' \log c' - q' \log c''}{q'q''D} \tag{12}$$

Equation (12) may be transformed to

$$q'q''D(pE - pE_o) = q'' \log c' - q' \log c'' \tag{12a}$$

This can also be obtained directly by applying the law of mass action to (11), setting $-\log_{[}e^-] = pE$ (15) and $\log K = pE_o$ for (10)

Equations (12) and (12a) do not contain the absolute values for x' and x'', but only the difference D. The material balance of ruthenium atoms and oxidation number gives, for the total concentration B of ruthenium, and the average oxidation number X:

$$B = q'c' + q''c'' \tag{13}$$

$$BX = x'q'c' + x''q''c'' \tag{14}$$

In an actual experiment, X may not be exactly known. What is measured is y, the number of reducing equivalents added per Ru, either by electrolysis or by chemical means. We must have (provide there are no unknown side reactions) $X + y = $ constant; denoting by y' and y'' the values y at the points corresponding to x' and x'', we have

$$X + y = x' + y' = x'' + y'' \tag{15}$$

It follows directly from (9) and (15) that

$$y'' - y' = D \tag{15a}$$

From equations (13-15) we can derive

$$Dq'c' = B(y''-y) \; ; \; Dq''c'' = B(y-y') \tag{16}$$

We may now use (16) to eliminate c' and c'' from (12) and obtain

$$pE = (q'D)^{-1} \log (y''-y) - (q''D)^{-1} \log (y-y') + \text{constant} \tag{17}$$

$$\text{constant} = pE_0 + ((q'D)^{-1} -(q''D)^{-1}) (\log B - \log D) - (q'D)^{-1} \log q'' + (q''D)^{-1} \log q'' \tag{17a}$$

The constant in (17a) is of course, really constant only when B is constant.

Equation (17) is a suitable starting point for the analysis of the redox curves.

Generalized Gran diagram

The exact values for y' and y'' can be derived using a diagram analogous to the Gran diagram for acid-base titrations. (Gran 1952) , by using the points in the neighborhood of the two ends of the shelf.

For $y \lesssim y''$ we may transform (17) to

$$10^{(q''D \cdot pE)} (y-y')^{q''/q'} + (y''-y) \cdot \text{constant} \tag{18}$$

We may plot versus y the left hand term in (18), or only its first factor since the second factor is practically constant, (multiplied by a practical scale factor); the intercept with the y axis of the linear plot will then give y''.

Similarly, close to $y \approx y'$ one may use the expression, also derived from (17)

$$10^{-(q'D \cdot pE)} (y''-y)^{q'/q''} = (y-y') \cdot \text{constant} \tag{19}$$

A plot of the left hand member or only its left factor, will be linear and the intercept will give y'.

Application to irreversible curves

In several of the redox titrations to be described below, it was possible to describe quantitatively the course of the $e(j)$ curve between two "jumps" by equations derived from (12 a) or (17), which are founded on the assumption of a reversible equilibrium (10). Nevertheless, in only two of these cases was something like a reversible reaction observed. In the others, a very different curve was obtained on back-titration. One may then ask, if the quantitative agreement in those latter cases is a sheer coincidence, or if it corresponds to a real reaction.

Let us for example consider the two very different curves obtained on electrolytic reduction of $R_1 = Ru(IV)$, and on titrating partly reduced Ru with Ru(IV). The course of the curve between $X = 4$ and $X = 3.5$ can be explained by assuming in the latter case a mononuclear Ru(IV) species, in the former case a polynuclear one, perhaps tri- or tetranuclear, which looks like a perfect contradiction.

One explanation may be the following. R_1 contains two different Ru(IV) species, say A and A', and it takes some time (of the order of several hours or days) for A

and A′ to come to equilibrium with each other. Of the two species, A′ is present only in a small amount, but it undergoes redox reactions more readily than A. If A and A′ are not at equilibrium, the redox potential $\underline{e}$ measured with an inert electrode is a mixed potential which is in between the two potentials that would correspond to electron exchange equilibrium 1) between the prevalent concentration [A] and some lower oxidation state present, and 2) between [A′] and the same or another lower oxidation state. If A′ reacts more readily with electrons there would be a tendency for the mixed $\underline{e}$ to be mainly determined by the second equilibrium, as long as there is any A′ left.

If these assumptions are true, in the electrolytic or chemical reduction of R_1, A′ is then used up before A, so $\underline{e}$ will be primarily determined by A. On the other hand, when R_1 is added to the solution, A′ (like A) is left unchanged after the equivalence point at X = 3.5, and $\underline{e}$ will be determined by A′.

It is very likely that the reduced state in the $\underline{e}$-determining reaction is different in the two cases. The important point, however, is that there is a possibility that the equilibrium law (Nernst equation) can be applied so that the formulas deduced for A (tri- or tetranuclear) and A′ (monomer) may be correct, although the system as a whole is not at true equilibrium.

A similar explanation may be true in other cases, too, so that the formulas derived may have some sence.

A complication is that the reactive species sometimes may have another oxidation number than the one present in large amounts. We may remind of the $U^{4+} + UO_2^{2+}$ system where a low concentration of UO_2^+ is built up by a slow equilibrium reaction of U^{4+} and UO_2^{2+} whereas the electrode potential is mainly determined by the momentary ratio UO_2^{2+}/UO_2^+.

Reduction of ruthenium (IV), R_1

Reduction with Ti(III)

The R_1 solutions used in these experiments were prepared by dilution with 1 M H_2SO_4 of two stock solutions, a) 18.48 mM^x Ru (IV), 1113 mM^x Na_2SO_4, 44 mM^x H^+; b) 1.43 mM^x Ru(IV), saturated Na_2SO_4, pH = 2-3.

One of the e(y) curves obtained are given in Fig 2. The e of the R_1 solutions was arround 900 mV, which may correspond to some equilibrium with minor Ru species, determined by earlier contacts with air. On adding Ti^{3+}, e(y) had a plateau at ≈ 725 ± 10 mV and decreased steeply at y ≈ 0.5 (reddish-brown solution). In this interval, the $\underline{e}$ with both electrodes seemed to be constant and reproducible. However, as soon as this jump had started, and after the jump, the $\underline{e}$ with both electrodes, still equal, crept slowly toward higher values. In such cases, $\underline{e}$ was read after exactly 5 minutes from the addition of the solution from the buret.

On further increase of y, a second plateau was met at e ≈ 450 mV on which the emf with both electrodes seem to be more stable. Finally, there was a jump around y = 1.0 ± 0.05 (green solution): in this region the emf crept a little to lower values.

Fig 2

Titration of R. 0.62 mM with Ti(III)
71.45 mM in 1N H₂SO₄ : 25°C
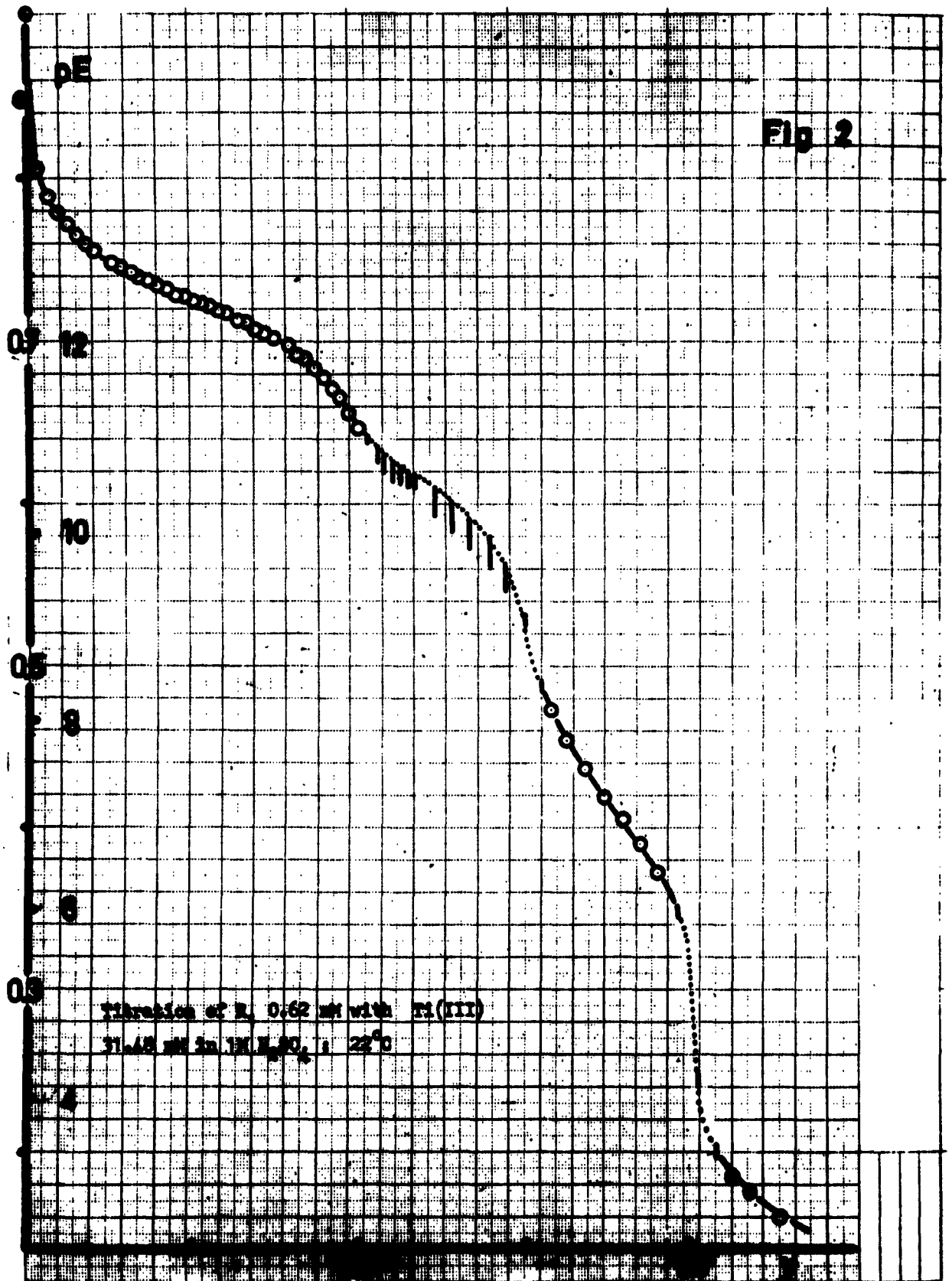
Even if it is difficult to make exact measurements because of the instability of $\underline{e}$, it seems that between y = 0.5 and the plateau at e $\approx$ 450 mV there is a second jump, corresponding to y $\approx$ 0.75 $\overset{+}{-}$ 0.10 (brown solution).

We can thus conclude that there are equivalence points, presumably corresponding to definite states, at y = 0.5, 0.75 and 1.0, corresponding to X = 3.5, 3.25 and 3.0. The latter probably corresponds to the solution G_2, which we think is ruthenium (III). The contradiction with the results on cathodic reduction with controlled potential has been pointed out.

The part of the curve between y = 0 and 0.5 was treated in the same way as for the other reduction curves in this region (Fig 3a).

Cathodic reduction, controlled current

The R_1 solution used in these experiments was prepared by diluting weighed amounts of R_1 stock solution (15.77 mM[*] Ru(IV), 102 mM[*] H^{+}, 1 M[*] SO_4^{2-}) with 1 M H_2SO_4.

For y values lower than 0.5, both the Au and Pt electrodes seem to give constant potentials. For y $>$0.5, $\underline{e}$ increased slowly, and reproducible values could not be obtained. For this reason, only the data for y $\lesssim$ 0.5 will be treated here.

On the e(y) curve, there is a well-defined "shelf" between X = 4 and $\approx$ 3.5. We shall apply to this part the treatment, equations (9-19). Since the jump is at y $\approx$ 0.5, we may set y' = 0, y" = 0.5, and D = 0.5, Let q' = q_1, q" = q_2. We may then write equation (17) in the form:

$$0.5 \text{ pE} = q_1^{-1} \log (0.5 - y) - q_2^{-1} \log y + \text{constant} \qquad (20)$$

By plotting 0.5 pE against log y we could obtain an approximate value for q_2, since at least for small values for y, one may neglect the term log (0.5 - y). Indeed, the plot seems to indicate $q_2 \approx 1.5 \approx 2$. Assuming q_2 = 2, (0.5 pE - q_1^{-1} log (0.5 -y))was plotted versus log y for q_1 = 1,2,3, and 4. For the last three values, the plot seems to give a straight line of slope 0.5 (q_2 = 2); the fit is especially good for q_1 = 3.

Accordingly, a plot pE versus (2/3) log (0.5 - y) - log y gives a straight line of slope 1.

In Fig 3b (to the right) the experimental values e(y) are plotted versus curves calculated for D = 0.5 and q_2 = 2, and q_1 = 2,3 and 4. The best fit obviously is for q_1 = 3.

As shown by Fig 3, the measurements with controlled potential (Fig 3b to the left) reduction and with chemical reduction (Ti^{3+} (Fig 3a) of R_1 also gave e(y) curves that agreed very well with those for controlled current: in our cases, the agreement is best with q_1 = 3 and q_2 = 2 whereas the agreement with q_1 = 4 is acceptable.

The conclusion is that the predominating complexes in the solutions would be Ru_2^{7+} (X = 3 5) and Ru_3^{12+} or Ru_4^{16+} (X = 4), omitting OH and SO_4 groups.

Cathodic reduction, controlled potential

The R_1 solution to be reduced was prepared from the stock solution as above and 1 M H_2SO_4.

The redox potential, e of the R_1 solutions so prepared was found to increase slowly for some time, even if the H_2SO_4 had been thoroughly degassed. In one experiment, for instance, with B = 0.385 mM, e increased by 40 mV during the first 5 h after the preparation, and after 20 h it had reached a stable value, 60mV higher than the initial one. With B = 2 mM, the increase was only about 20 mV during the first 20 h. For this reason, the reduction experiments were not started until about 20 h from the preparation of the solutions.

The controlled-potential circuit was closedfor a suitable period, during which the current was measured at equidistant times. Immediately after the circuit was opened, e was found to increase or decrease until after 3-5 minutes it reached a maximum or minimum value, which was noted. The process was repeated until the cathode potential attained about 200 mV; this limit was set to avoid the reduction of H^+ to H_2.

Fig 2a gives e as a function of y (the number of faradays passed per mole of Ru) at 25°C for experiments with B = 2.13, 1.0 and 0.1 mM Ru. These graphs, like all others obtained in these experiments, show three breaks between y = 0 and y ≈ 1.2.

In the region before the first break at y = 0.50 $\pm$ 0.05, the curves for the three concentrations coincide; e is relatively stable, and changes by no more than about 1 mV per hour. From y ≈ 0.5 on, e becomes markedly unstable and drifts toward higher values. The rate of drift appears to increase with y and decrease with B. For example, for y = 0.5, e changes little if at all after the first 20 h, whilst for y = 1.0, e first changes rapidly for several hours but then increase slowly for at least several days. Fig 2a shows also two curves obtained on interrupting the electrolysis at e = 0.5 for 17 h and 44 h, and then continuing.

These observations indicate several simultaneous reactions, with half-lives from very short values (of the order of seconds) to perhaps many days. For this reason, attempts were made to work at 40°C or 0.5°C, in the hope either speeding up or freezing in some of the slow reactions. This was not too successful: at 40°C, e became unstable even for y < 0.5, and even at 0.5°C a drift was observed in the range y > 0.5. In spite of the drift, the shape of the curve e(y) was the same in all the experiments at 25°C and at 0.5°C.

A second break was found for y = 0.80 $\pm$ 0.05, after which e decreased more rapidly with y than in the earlier two ranges. A third break appears to lie at y ≈ 1.10 $\pm$ 0.05.

In the range 0 < y < 0.8, the solutions remain reddish-brown, but for y > 0.8 the color rapidly changes to a golden-yellow (y ≈ 1.0) and then to a green color(apparently the same as G_2) which coincides with the third break in the e(y) curve.

Fig 2a

Fig 3

a

Ti³⁺ reduction

22° C

Cathodic reduction
(1M H₂SO₄, 25° C)

R₁
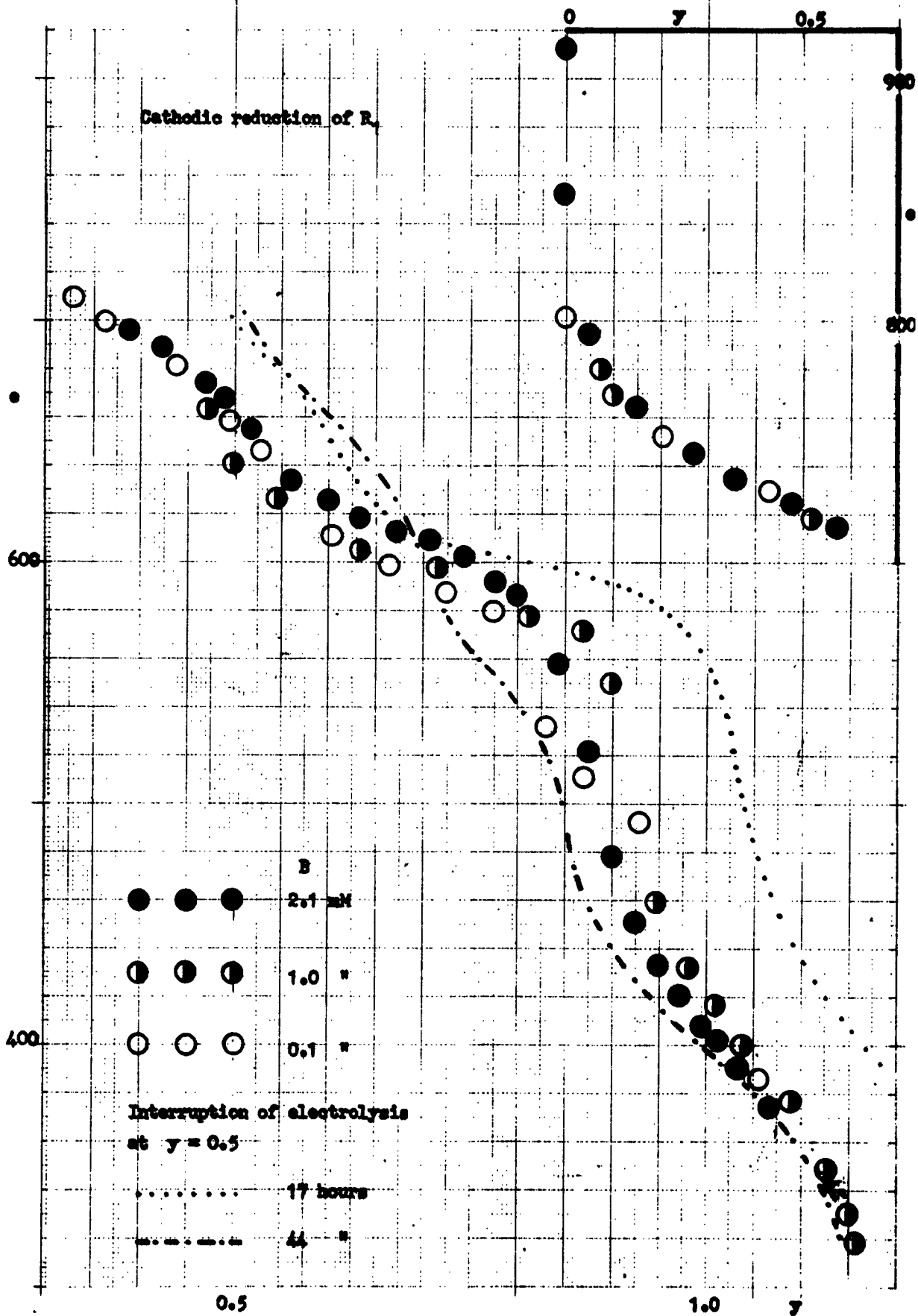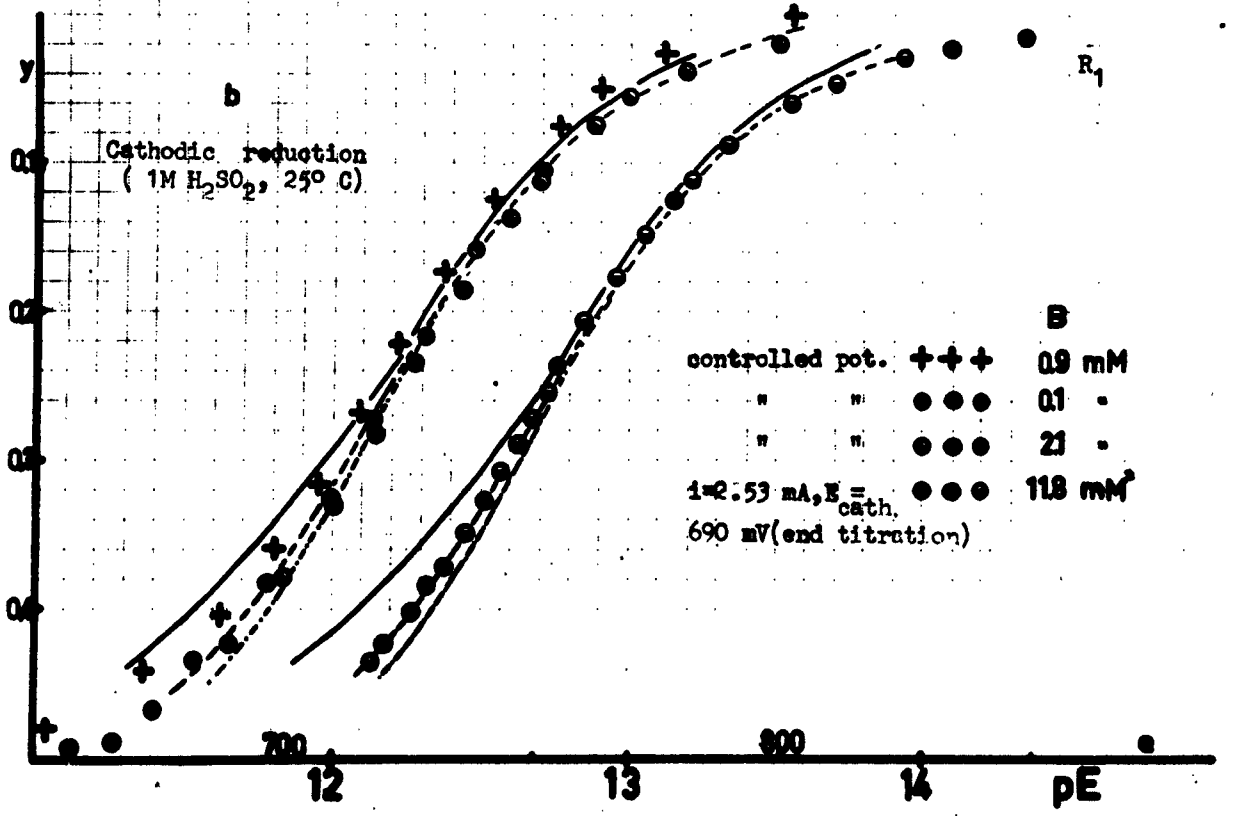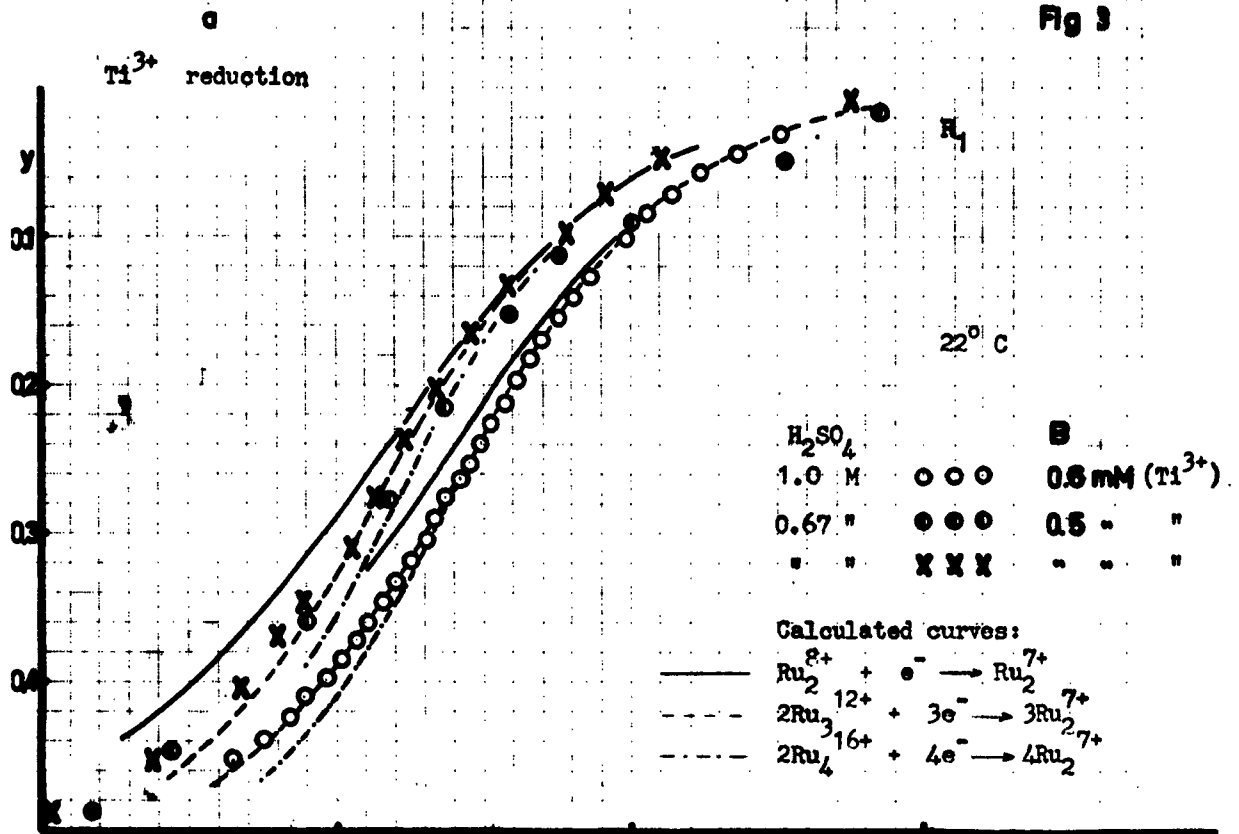
One would thus guess that, at the last break, the solution would correspond to G_2. The fact that the break comes at 1.10 rather than the expected $y = 1.0$ is discussed in the survey above.

Redox titration of reduced Ru(X=3) with R₁

A special experiment was carried out, in which a certain amount of the amber-red Ru(IV)solution R_1 was first reduced to an oxidation state in the neighborhood of X=3, and then Ru(IV) was added from a buret.

The variation of $\underline{e}$ with the volume v of Ru(IV) solution added has been analyzed in order to get information on the species involved. It has been assumed (as is corroborated by our earlier analysis, Brito 1959) that X=4 in the red solution, R_1.

Experimental

The amber-red Ru(IV)solution R_1 was prepared by the elution, with 1 M H_2SO_4, of a Dowex-50 resin saturated with Ru(IV). It was then reduced with H_2, using a small platinized Pt net as a catalyst. During the reduction, the mixed potential e_R, in the presence of H_2 was measured with at least two of the inert electrodes. At first e_R changed slowly, while the color changed from red to dark brown. After a certain time, e_R decreased rapidly, and the solution turned dark green. The electrodes (Au and Pt) had the same potential. When e_R had become close to 165 mV, N_2 was bubbled through the solution for one hour to remove H_2. After this, e_R was ≈ 170 mV, and the color was still green. We then started to add, from the buret, Ru(IV)solution of the same total Ru concentration, efter taking out the small platinized Pt net.

The e(v̇) curve is given in Fig 4. Up to the jump, around 9 ml, $\underline{e}$ was stable, and the electrodes (Pt and Au) gave identical emf within $\pm$ 0.5 mV. In the jump itself (green)-brown solution and up to $\underline{e} \approx 700$ mV, the two electrodes gave identical potentials which, however, increased slowly for a considerable time. For the subsequent part of the titration, the emfs were very stable.
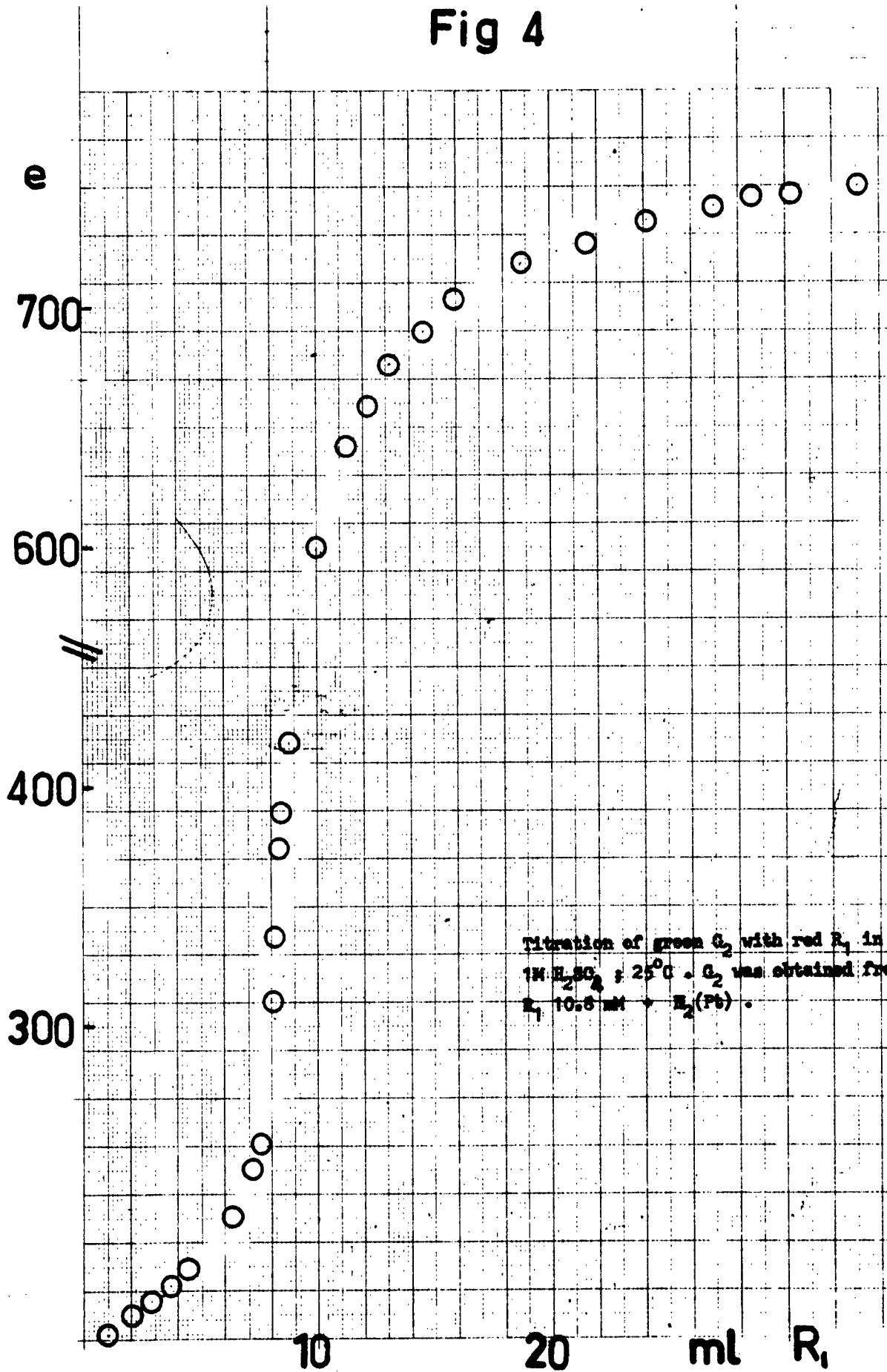
The emfs were measured using the cell

Hg, Hg_2SO_4/ 1 M H_2SO_4// 1 M (Ru(IV), H^+) SO_4/Pt or Au).
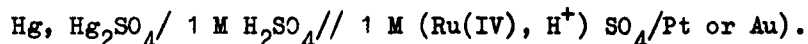
The reference electrode (to the left above) was kept in a "Wilhelm" bridge. Its electrode potential was measured by connecting it with a 1 M H_2SO_4/H_2(Pt) electrode. For measuring the redox potential in the Ru solution we used bright Pt, massive Au, or Au prepared by electrolysis. H_2 and N_2 were purified as described above, and saturated with water vapor by bubbling through 1 M H_2SO_4.

Attempt at interpretation

The red solution R_1 in all probability contains Ru(IV) thus $X_1 = 4$; let us assume that each complex contains q_1Ru. The jump indicates an intermediate species, say, characterized by $X_2=4-D_2$ and $q=q_2$. The shape of the curve indicates that after the jump, the Ru(IV) added does not react but remains unchanged in the solution.

Fig 4

Titration of green Q_2 with red R_1 in 1M H_2SO_4 : $25°C$. Q_2 was obtained from R_1 10.5 mM + $H_2(Pb)$.

Since the two parts of the curve, before and after the jump, are separated by around 5 pE units (300mV), they will be treated independently in the following.

If B is the total concentration of Ru, V_0 is the initial volume of the reduced solution, v is the volume of Ru(IV) solution added, and v_e is the value of v at the jump where $X = X_2 = X_1 - D_2$, then the conservation of valency would require

$$BX(V_0 + v) = BX_2(V_0 + v_e) + BX_1(v - v_e) = B(V_0 + v)(X_1 - D_2) + BD_2(v-v_e) \quad (21)$$

<u>After the jump</u> ($v > v_e$ pE >9). Let us apply the general formulas (9) and following with $q'=q_1$, $c'=c_1$ etc and $D=D_2$. The main equilibrium is then omitting OH complexing:

$$q_2 Ru_{q_1}^{X_1 q_1 +}(c_1) + q_1 q_2 D_2 e^- \rightleftharpoons q_1 Ru_{q_2}^{(X_1 - D_2)q 2+}(c_2) \quad (22)$$
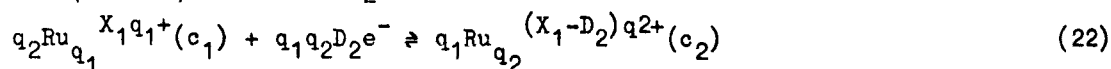
We have (eqn 13) $B = q_1 c_1 + q_2 c_2$;

$$BX = X_1 q_1 c_1 + (X_1 - D_2)q_2 c_2 = B(X_1 - D_2) + D_2 q_1 c_1 \quad (23)$$

Hence with (9) for the concentration of the (unchanged) Ru(IV) and of the intermediate species: (compare eqn (16))

$$q_1 c_1 = B(v - v_e)/(V_0 + v) = B(y_2 - y)/D_2 \quad (24)$$

$$q_2 c_2 = B(V_0 + v_e)/(V_0 + v) = B(y - y_1)/D_2 \quad (25)$$

Introducing (24) and (25) into (12) and rearranging we find

$$\varphi = \text{constant} + \, /q_1 D_2 \quad (26)$$

where

$$\varphi = pE - (q_2 D_2)^{-1} \log(V_0 + v) \quad (27)$$

$$\psi = \log(v - v_e) - \log(V_0 + v) \quad (28)$$

We assumed various values for $q_2 D_2$, between 1 and 10, and for each value calculated and plotted φ versus ψ. From the slope we obtained values for $q_1 D_2$ from 0.42 to 0.49. This indicates that, at least under these conditions, for $q_2 > 10$, $q_1 D_2 \approx 0.5$. On the assumption that q_2 is so large that the second term in (15) is negligible we plotted pE versus ψ and found a straight line of slope $(1/q_1 D_2) \approx 2$. On the same assumption, we plotted $(V_0 + v) 10^{pE/2}$ versus v (eqn (18) Fig 5) which gave a straight line, intercepting the v axis at v_e.

<u>Before the jump</u> (pE < 7). Let us assume that, before the jump, the solution contains besides the intermediate complex ($q'=q_2$, $x'=X_1-D_2$), also a complex characterized by $(q''=q_3$, $x''=X_1-D_2-D_3)$. The equilibrium reaction is then

$$q_2 Ru_{q_3}^{(X_1-D_2-D_3)q_3} \rightleftharpoons q_3 Ru_{q_2}^{(X_1-D_2)q 2+} + q_2 q_3 D_3 e^- \quad (29)$$
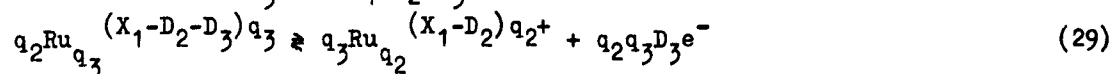
and we have $B = q_2 c_q + q_3 c_3$; $BX = q_2 c_2(X_1-D_2) + q_3 c_3(X_1-D_2-D_3) = B(X_1-D_2) - q_3 c_3 D_3 \quad (30)$

Fig 5
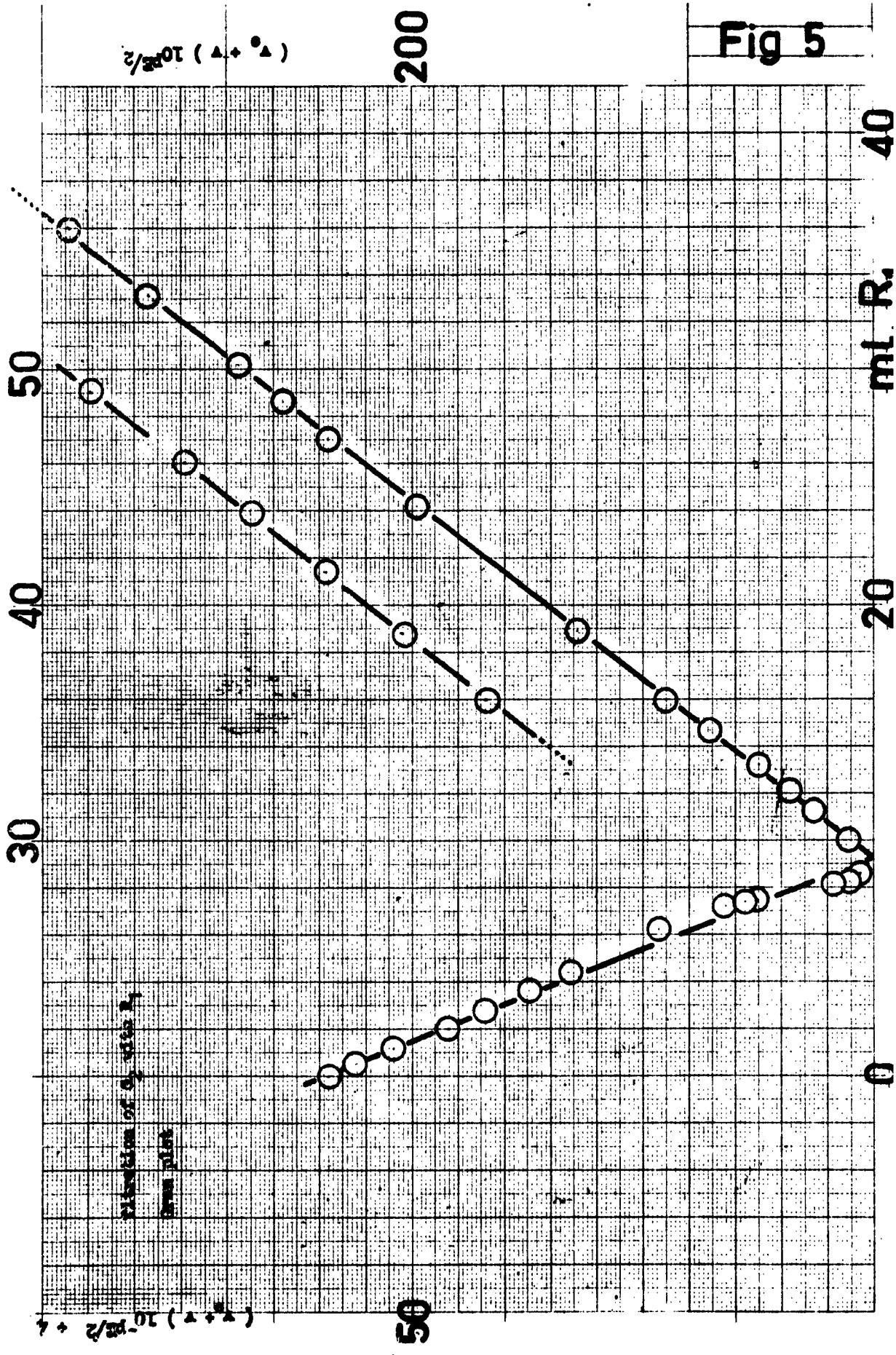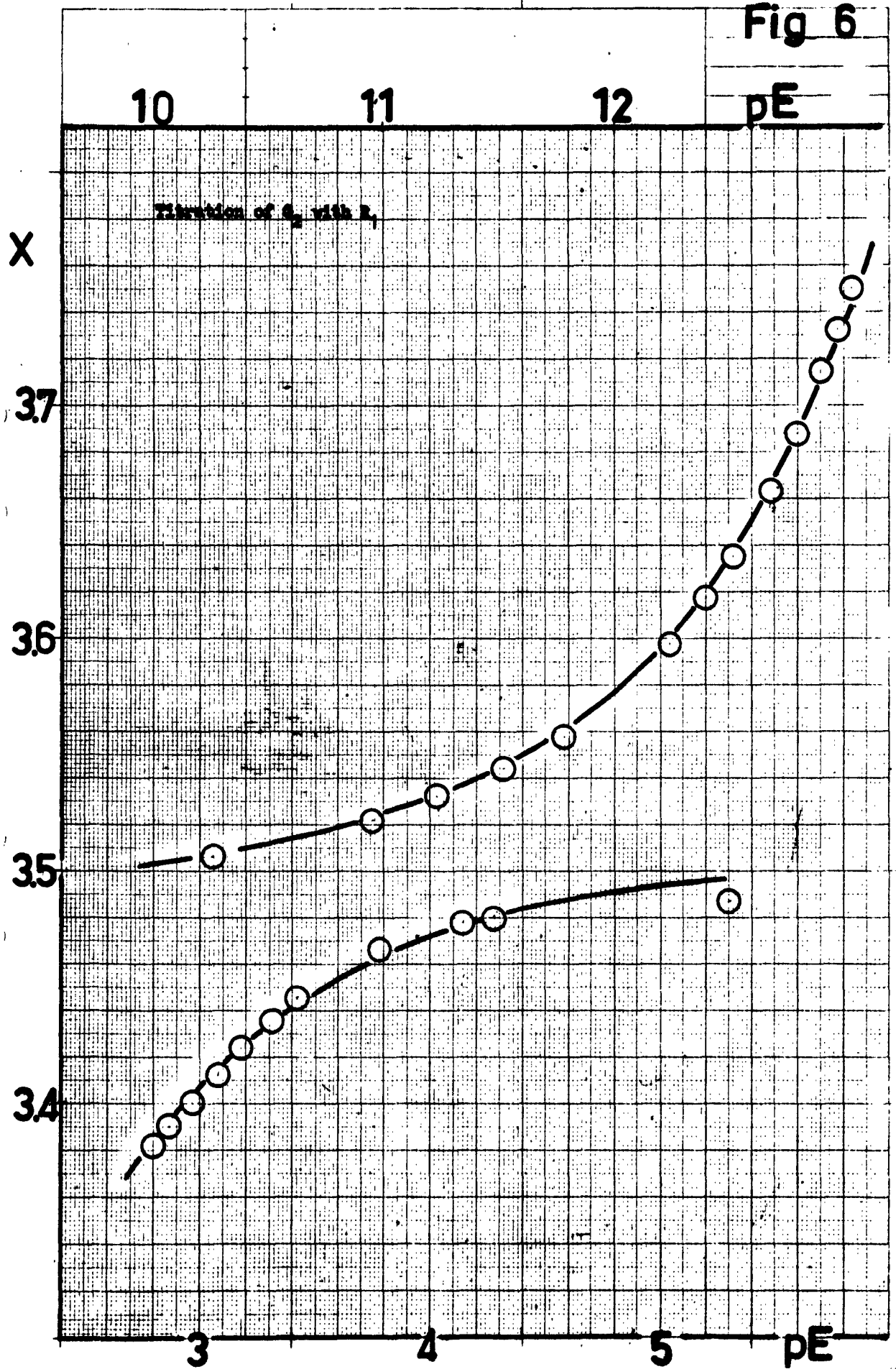
Fig. 6

From (30) and (21) we find, after rearrangement

$$q_2 c_2 = B(1-wD_2/D_3); \quad q_3 c_3 = (BD_2/D_3)(v_e-v)/(V_0 + v) = BD_2 w/D_3 \tag{31}$$

where :

$$u = v_e/(V_0+v_e) - v/(V_0+v); \quad w = (v_e-v)/(V_0+v) = u(V_0+v_e)/V_0 \tag{32}$$

Eqn (12a) for the redox potential would then give

$$pE = (q_2 D_3)^{-1} \log(1-wD_2/D_3) - (q_3 D_3)^{-1} \log w + \text{constant} \tag{33}$$

The second term to the right in (31) seems to be negligible, and a graph of pE versus log w gives a straight line with slope $(1/q_3 D_3) \approx 2$. Again, $(V_0+v)10^{-pE/2}$ versus v gives a straight line with the same intercept, v_e as for the second part of the titration, Fig 5.

Conclusion. Because of the way of preparing the solution, it was not possible to know exactly the value for X in the original solution. However, from experience with redox titrations it seems very likely that the solution at the starting point contains green ruthenium(III), chiefly. Then, $D_2 + D_3 = 1$, and the most likely explanation of the curves would be that two extreme complexes are, mononuclear Ru^{3+} and mononuclear Ru^{4+}, omitting OH and SO_4 complexing. $(q_1 = q_2 = 1)$. We conclude that the intermediate complex has average oxidation number ≈ 3.5, and that it is very large. The accuracy does not allow a very accurate determination of q_2. Fig 6 gives, for one titration, the measured points e (X), and the calculated for $qRu^{3+} + 0.5 q \rightleftharpoons Ru_q^{3.5q+}$, $Ru_q^{3.5q} + 0.5q\ e^- \rightleftharpoons qRu^{3+}$, assuming q=20. The agreement would be equally satisfactory with any large value for q.

Redox reactions of ruthenium B_3

Reduction with titanium (III)

A solution B_3 of apparently the same color as B_4 was obtained from a solution of RuO_4, in 0.2 M H_2SO_4 by electrolytic reduction to red R_1, with platinized Pt-cathode and separate Pt-anode, catalytic reduction with H_2 (Pt) to green G_2, and filtering. The solution was kept in contact with air, and a color change from green to dark brown set in, which was complete after two or three weeks; the redox potential was then e = 840 mV.

Fig 1 gives - schematically - e(y) for a titration of B_3 with Ti(III). There are indications of jumps around y ≈ 0.25 (light brown solution) and around y ≈ 0.5 (light green solution). The apparent oxidation number X of B_3 was determined by oxidation with Ce(IV) to RuO_4 as described in the previous report (Brito 1960). The result for B_3 was X = 3.38 ± 0.05, which agrees with the jump of y ≈ 0.5 to green ruthenium (III), if B_3 has X = 3.4 ± 0.1.

Electrochemical reduction

About one month after the experiment with Ti(III) reduction, several experiments with cathodic reduction were made, with constant current, either with a coulometer, or with the simplified apparatus. With the coulometer, the current was kept at 6.43 mA. In all cases, Ti(IV) was added as an auxiliary system.

Up to y = 0.3, e_{Au} and e_{Pt} were the same and fairly stable. For y >0.3, e was found to creep slowly toward higher values. For y ≈ 0.87, there was a jump and the potential fell to ≈ 300 mV (this was in 2.5 M H_2SO_4). One month more later, the experiment was repeated, and the jump then came at y ≈ 0.98 (this time 1 M H_2SO_4).
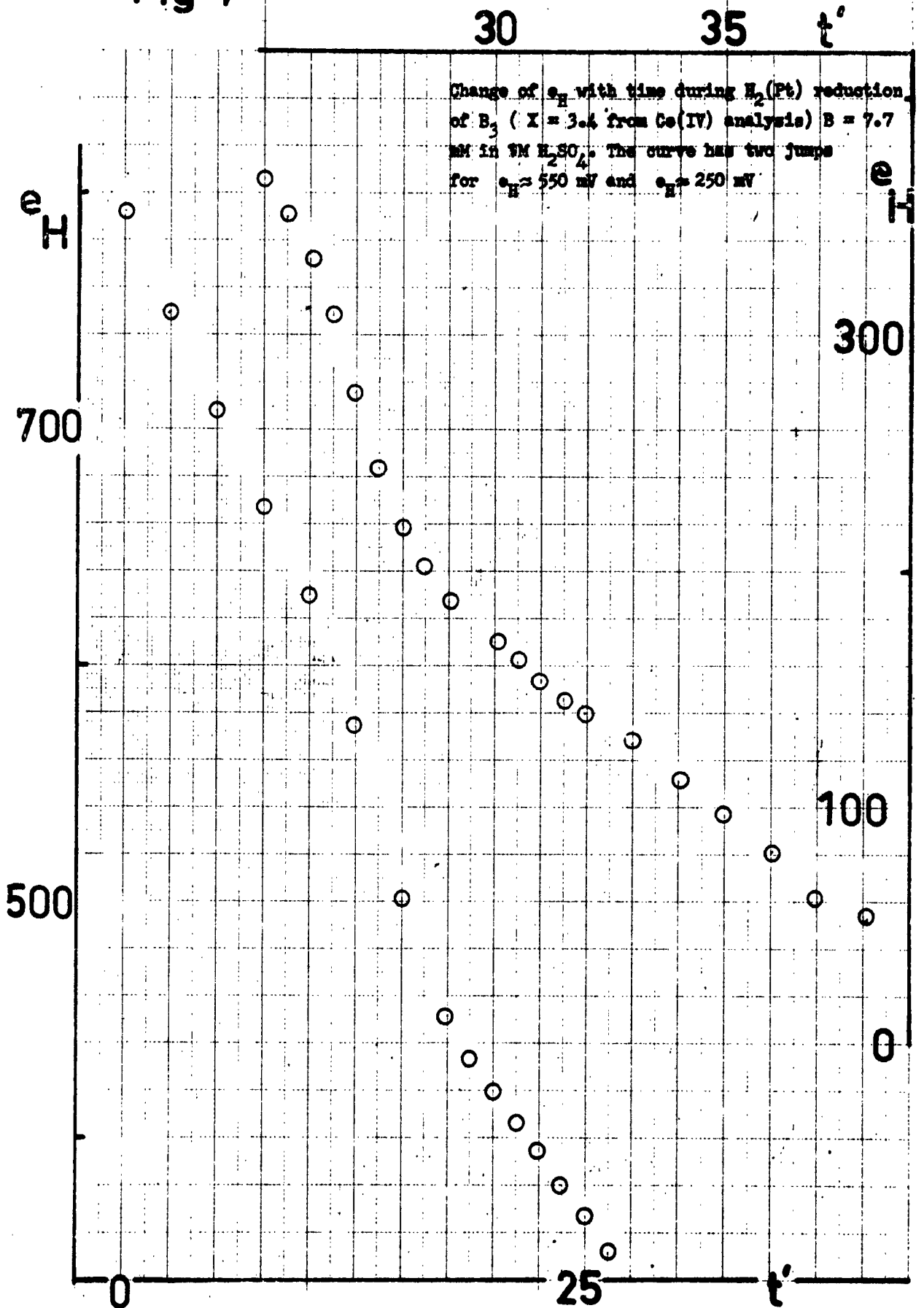
The latter solution was oxidized anodically on platinized Pt: the $e(n_{ox})$ curve was very different and already for n_{ox} ≈ 0.48, e had increased to ≈ 900 mV.

Oxidation number X of B_3

An average of three determinations on fairly fresh ruthenium B_3 gave X = 3.38 ± 0.05.

In this connection the following experiment may be described. A B_3 solution was reduced with H_2 (Pt) and the plot e versus time (Fig 7) gave a jump around 550 mV, a shelf around 380 mV, a new jump around 250 mV, and then the beginning of a shelf around 150 mV. From the resulting green solution, of e ≈ 50 mV, H_2 was immediately expelled with N_2; the solution was slowly oxidized by O_2 diluted with N_2, and the apparent X determined for various points, by cerium(IV) oxidation. The resulting points are given in Fig 1 as single dots: the X values covered were between 2.9 and 3.34. The color again, became dark brown.

Fig 7

Change of e_H with time during $H_2(Pt)$ reduction of B_3 ($X = 3.4$ from $Ce(IV)$ analysis) $B = 7.7$ mM in 9M H_2SO_4. The curve has two jumps for $e_H \approx 550$ mV and $e_H \approx 250$ mV

Redox reactions of ruthenium B_4

A stock solution of B_4 was prepared by distilling RuO_4 into a known amount of ≈ 0.5 M H_2SO_4 containing an excess of H_2O_2, treating the solution with H_2 for about 24 h in the presence of a platinised Pt catalyst, removing the catalyst and then treating the grey-green solution, thus obtained, with O_2 for several hours. Between the preparation and the reduction-oxidation treatments to be described, several months elapsed.

Cathodic reduction

The solutions were made up to contain 1 M H_2SO_4 and electrolyzed with controlled potential. The initial e did not change significantly with time, once thermal equili-librium has been reached, and e was also much more stable during the whole course of the reduction than in the reduction of R_1. Fig 1 gives e(y) for those B values that have hitherto been studied namely 0.30 and 1.43 mM. The curves differ somewhat bet-ween y=0 and y=0.6 but then coincide up to y 0.8. From y = 0.8 on a relatively steep decrease of e begins, which is accompanied by a change in color to an intense green. In the earlier part of the titration, the solutions absorb light so strongly that it is difficult to observe any distinct color change.

Reduction with titanium(III) and chromium(II)

The B_4 solution was one of those used for determining Z and X. The Ce (IV)method gave X = 3.53 $\pm$ 0.05. The stock solution contained 15 mM Ru, and was diluted with 1 M H_2SO_4.

The e(y) curve is given in fig 1 (part of it in more detail in fig 8); the re-sults with Ti(III) and Cr(II) agree reasonably well. The B_4 solution is originally ve-ry dark brown but on titration with Ti(III) or Cr(II) it gradually clears up and at the end of the jump around y $\approx$ 0.5 it is clear brown. Around y $\approx$ 0.8 and e $\approx$ 360 mV there is another potential jump; the solution is then light green.
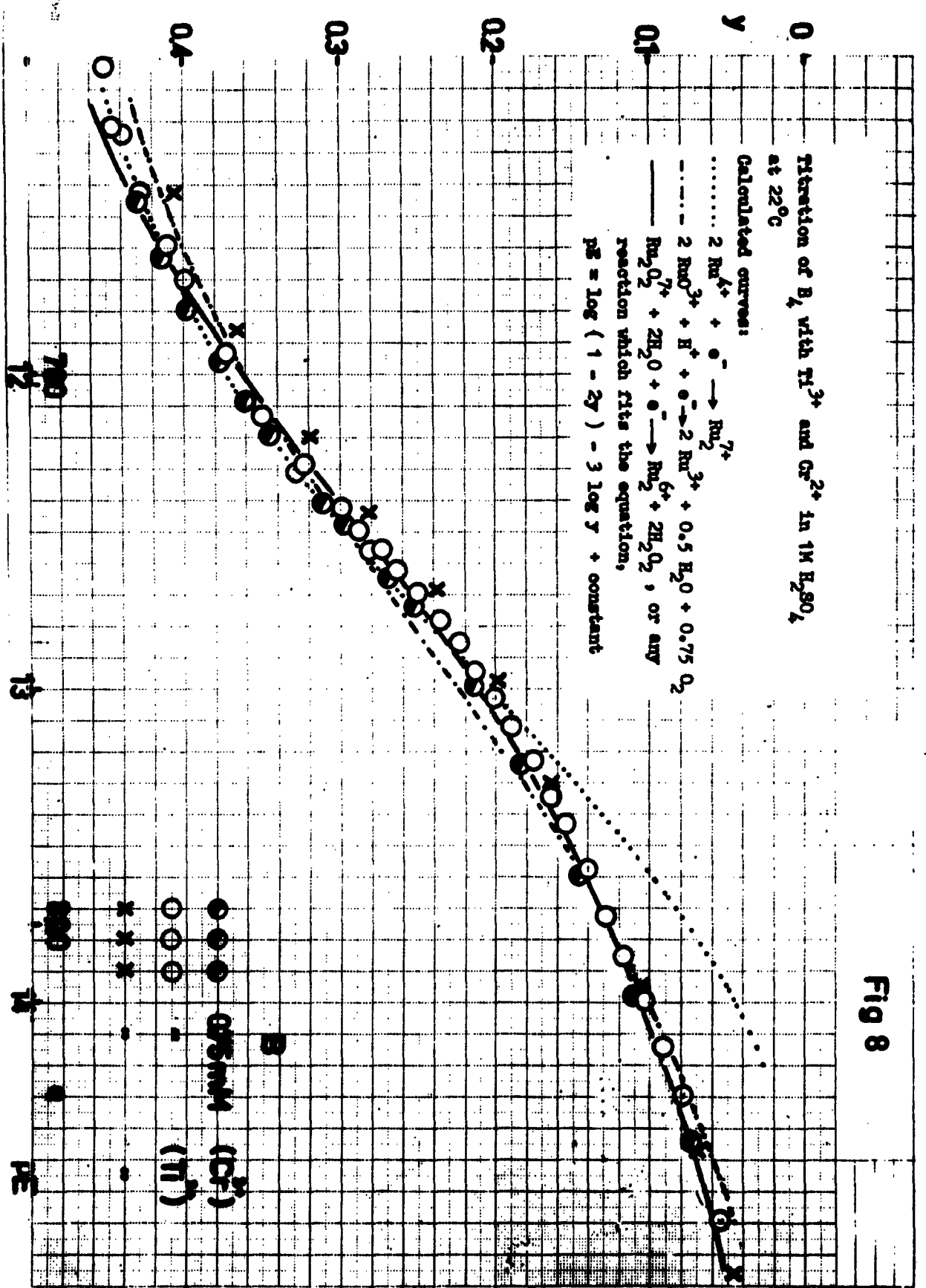
After the titration with Cr(II) a great excess of Cr(II) was added, about 10 times the concentration of Ru, and the solution was kept standing for one night. Next morning the e had increased from negative values up to + 670 mV at which value it seemed to be stabilized. Once more, a large excess of Cr(II) was added until e be-came negative, and again, e increased slowly up to an apparently stable value around 670 mV. Meanwhile one could observe gas bubbles in the bulk of the solution.

Attempts were made to apply the treatment of eqns (9 -19) to the region $0 \ y \ 0.5$. We set $y' = 0$ $(x' \approx 3.8)$, $q' = q_1$; $y'' = 0.5$ $(x'' \approx 3.3)$, $q'' = q_2$, $D = 0.5$ and find from (17):

$$pE = 2q_1^{-1} \log(0.5-y) - 2q_2^{-1} \log y + \text{const}$$

We attempted to fit the data by plotting log (0.5-y) versus $(pE + 2q_2^{-1} \log y)$ for various q_2 values. Plausible linear plots were obtained. For $q_2 = 1$, the slope

Fig 8

y

0

0.1

0.2

0.3

0.4

Titration of B_4 with Ti^{3+} and Cr^{2+} in $1M\ H_2SO_4$ at 22°C

Calculated curves:

.... $2\ Ru^{4+} + e^- \longrightarrow Ru_2^{7+}$

—·—·— $2\ RuO^{3+} + H^+ + e^- \longrightarrow 2\ Ru^{3+} + 0.5\ H_2O + 0.75\ O_2$

———— $Ru_2O_2^{7+} + 2H_2O + e^- \longrightarrow Ru_2^{6+} + 2H_2O_2$, or any reaction which fits the equation,

$pE = \log(1 - 2y) - 3\log y + \text{constant}$

pE

12 13 14

700

B

0.075mM (Cr^{2+})

(Ti^{3+})

was $2q_1^{-1} \approx 1.5$, thus $q_1 \approx 1.33$. For $q_2 = 2$, the slope $2q_1^{-1} = 2$, thus $q_1 = 1$. On the face value this would indicate $q_1 \approx 1$, and q_2 possibly $= 2$ or higher. This, however, is hard to accept. The oxidation numbers for both states have fractional values which indicates either that each consists of species with more than 3 Ru atoms or that each "state" is a mixture of several species, some perhaps with peroxo complexing. The "best" empirical equation $pE = \log (0.5 - y) - 3 \log y$ (Fig 8, full-drawn curve) might be explained formally if it were assumed that also some third species, say, H_2O_2, takes part in the e-determining reaction. However, we think it wise to leave this question open.

Oxidation of B_4

$$e(\Delta X) \text{ for one anodic oxidation of } B_4$$

The curve shews *no* marked features, after an initial rapid change in e of about 400 mV, which is nearly completed at $\Delta X \approx 0.5$.

The value for X in B_4

Immediately after the preparation of a B_4 solution ($e \approx 550$ mV) X was determined with cerium(IV) sulfate by the method described by Brito (1960) which gave $X = 3.1 \pm 0.1$. A new batch of freshly prepared B_4 gave $X = 3.2 \pm 0.2$, whereas after six months we found $X = 3.53 \pm 0.05$. On the other hand, the redox titration curves for this aged B_4 indicate an oxidation number $X \approx 3.8$.

Redox reactions of ruthenium(III), G_2

Redox reactions $G_2 \rightleftharpoons P_1$

Pink solutions of ruthenium (P_1) were prepared by reduction either of R_1 or of B_3 with H_2(Pt) for a night. In the presence of H_2, e = 0 as expected; when H_2 was swept away by a stream of N_2, $\underline{e}$ increased but reached a stable value lower than 100 mV.

This solution P_1 was then oxidized anodically at constant current, sometimes after the addition of Tl^+ or Ce^{3+}.

The measured values for $\underline{e}$ with Au or Pt electrodes (the anode itself, after breaking the current) were the same and very stable. The data agree well, as will be seen, with what can be calculated assuming the process $Ru^{2+} = Ru^{3+} + e^-$. After this reaction was complete, there was a jump at around 300 mV; the solutions were then green. Potentials higher than about 400 mV were not stable in these experiments and will not be discussed here.

If $c_2 = [Ru^{2+}]$ and $c_3 = [Ru^{3+}]$ we have (compare equation 12, $q' = q'' = 1, D = 1$):

$$pE = pE_0 + \log c_3 - \log c_2$$

Let V be the volume of the solution, n the number of faradays added, and n_e the value of n at the equivalence point around 300 mV. B is the present concentration of Ru, which need not be the same as the one added, because some Ru may have been reduced to metal. If the concentrations are c_{20} and c_{30} when the oxidation starts (n = 0), then we have

$$Vc_2 = Vc_{20} - n = n_e - n \; ; \; Vc_3 = Vc_{30} + n$$

Hence

$$10^{pE} = \text{constant} \, (Vc_{30} + n) \, (n_e - n)^{-1} = \text{constant} \, ((Vc_{30} + n_e) \, (n_e - n)^{-1} - 1)$$

The best value for n_e was found by plotting $(n_e - n)^{-1}$ versus 10^{pE} for various values for n_e and choosing the value that gives a straight line. Extrapolation of this line to $10^{pE} = 0$ gave $VB = Vc_{30} + n_3$ which always came out smaller than the amount of Ru added.

It could easily be shown that some Ru had been reduced: the Pt net used for the H_2 reduction was washed and then used as anode in 2 M H_2SO_4, with a current of 1-2 A. After some time, the solution was yellow and smelled strongly from RuO_4; if boiled with H_2O_2, reddish-brown B_1 formed.

On the other hand, n_e was found to be smaller than $(Vc_{30} + n_e)$ by 10-20 μF, which would correspond to an initial "negative" impurity of Ru(III). We guess that this is rather due to incomplete removal of H_2 from the platinized Pt than to a lower oxidation state of Ru.

Fig 9

Anodic oxidation of P_1

Gran plot

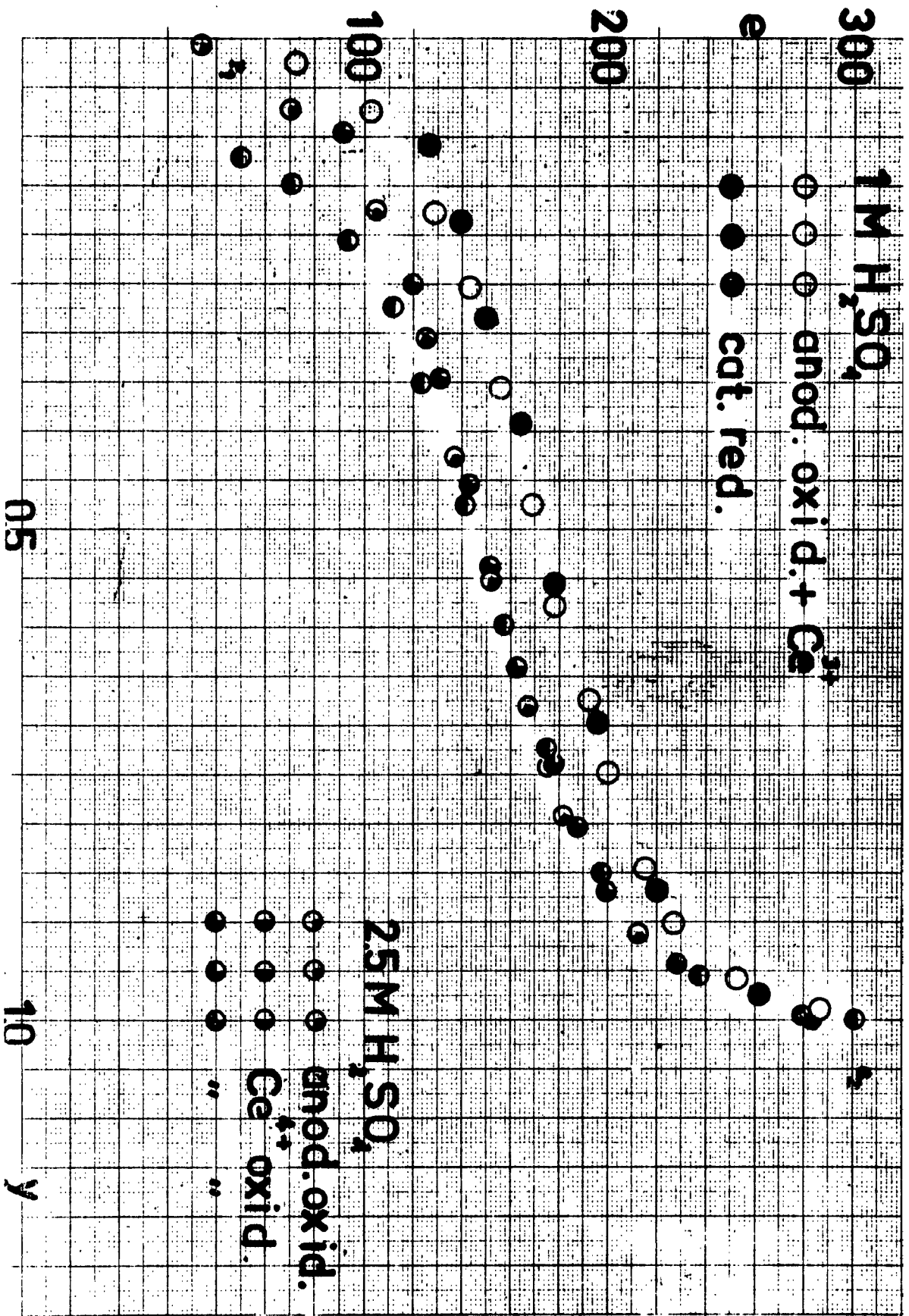$(\pi - x)^{-1} \, 10^{-3}$

20

$10^p E - 3$

2

4
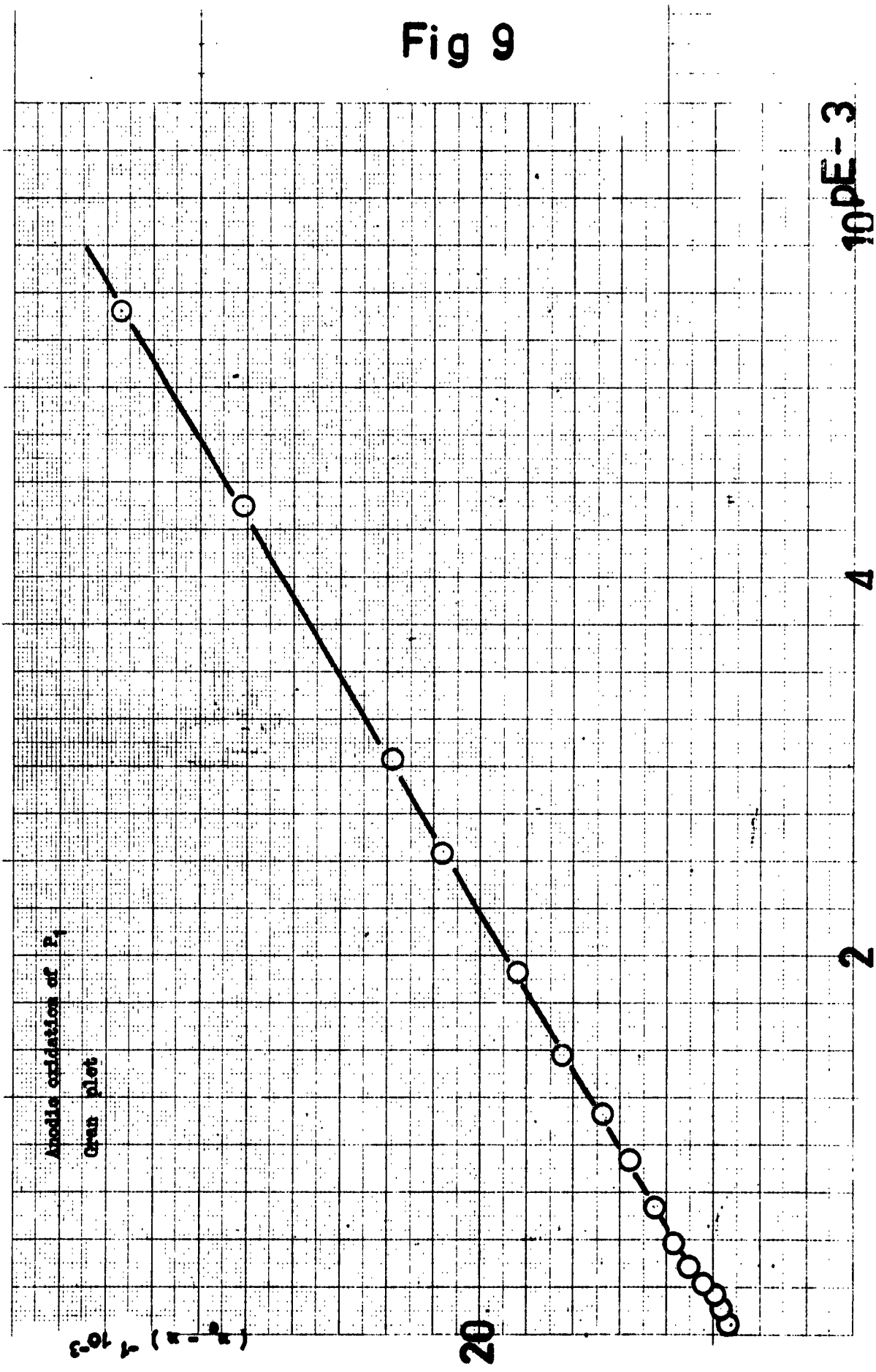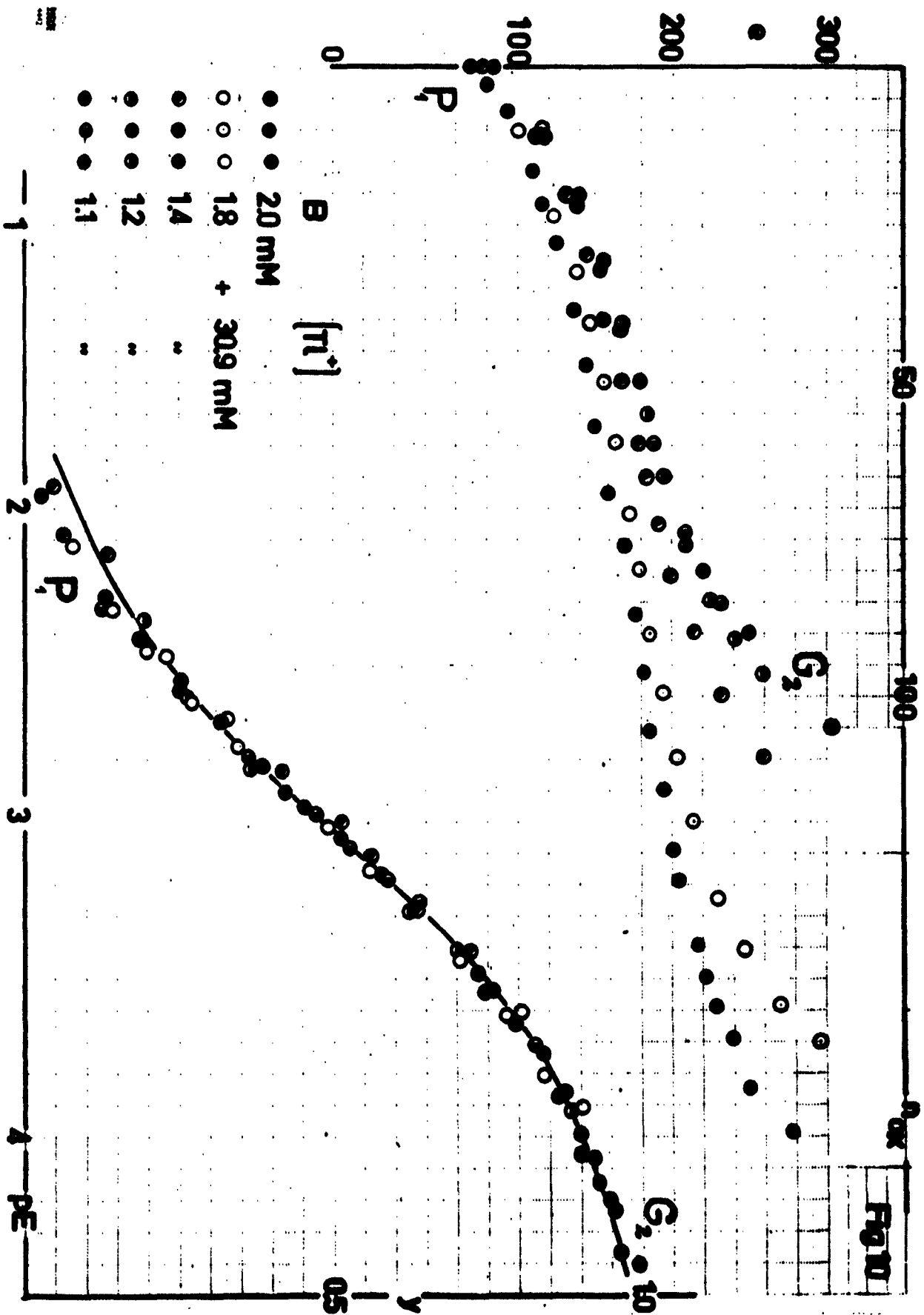
Fig 10

Fig 11

Fig 10' shows data from one experiment, in which a series of alternating reductions and oxidations was made: n_e and thus B obviously decreased for each cycle (upper part). Inserting the appropriate values for n_e and Vc_{30} we could calculate X:

$$X = 2 + c_3/(c_2 + c_3) = 2 + (n + Vc_{30})/(n_e + Vc_{30})$$

In a plot of pE versus X, all points seem to fall practically on the same curve (Fig 10, lower part). The full-drawn curve was calculated from the equation

$$pE = 3.03 + \log (x - 2) - \log (3 - X)$$

which corresponds to $pE_0 = 3.03$, $e_0 \approx 180$ mV for Ru^{2+}, Ru^{3+}/Pt in 1 M H_2SO_4.

Fig 11 gives points from another experiment, in which the current was kept constant (6.43 mA), after two reductions with H_2(Pt) and oxidations with cerium(IV) sulfate ; the medium was 2.5 M H_2SO_4. The highest set of points - shifted parallel upwards - are from an experiment in which the resulting solution was diluted with water to 1 M H_2SO_4, the solution was reduced with H_2(Pt) and again oxidized with a current of 6.43 mA in the presence of Ce^{3+}. At last, it was reduced with 6.43 mA (black dots).

It was observed that the shade and intensity of the pink color was not always the same in a series of repeated oxidation-reduction cycles. One reason may be the decrease of B. At any rate, the measured $\underline{e}$ was very stable.

Redox reactions $G_2 \rightleftarrows Y_3$

Fig 12 gives e(y) curves from a series of experiments, consisting of successive oxidations and reductions starting with green Ru(III), G_2, prepared from R_1. The reactions were carried out by electrolysis at controlled potential and B was 1 mM throughout.

The open circles are from the first experiment, "A", in which a freshly prepared G_2 solution was oxidized. There are two breaks in $\underline{e}$, the second one about 0.45 ± 0.05 X units higher than the first. Between these breaks e(X) has a sloping plateau, with midpoint ≈ 590 mV. At the end of the second break, $\underline{e} \approx 900$ mV, but $\underline{e}$ was unstable and decreased slowly; after 65 hours, $\underline{e}$ had decreased by ≈ 65 mV. The color of the solution remained green throughout the course of the oxidation, but the final drift in $\underline{e}$ was accompanied by a change to an intense golden-yellow color. The solution so obtained, for which $e \approx 790$ mV, will be denoted by Y_3.

The half-filled circles describe the cathodic reduction of this golden-yellow solution Y_3 in the next experiment, "B". The points have been shifted along the X axis so as to coincide with the first curve around $e \approx 300$ mV; the curves then lie close to each other up to $e \approx 600$-900 mV. The final solution from this experiment was again green. This solution was oxidized (full circles) in the final experiment "C". Obviously, the two last curves lie close to each other over the whole of their lengths, and the breaks in $\underline{e}$ occur after the same change in X, namely 0.65 ± 0.05.

Fig 12
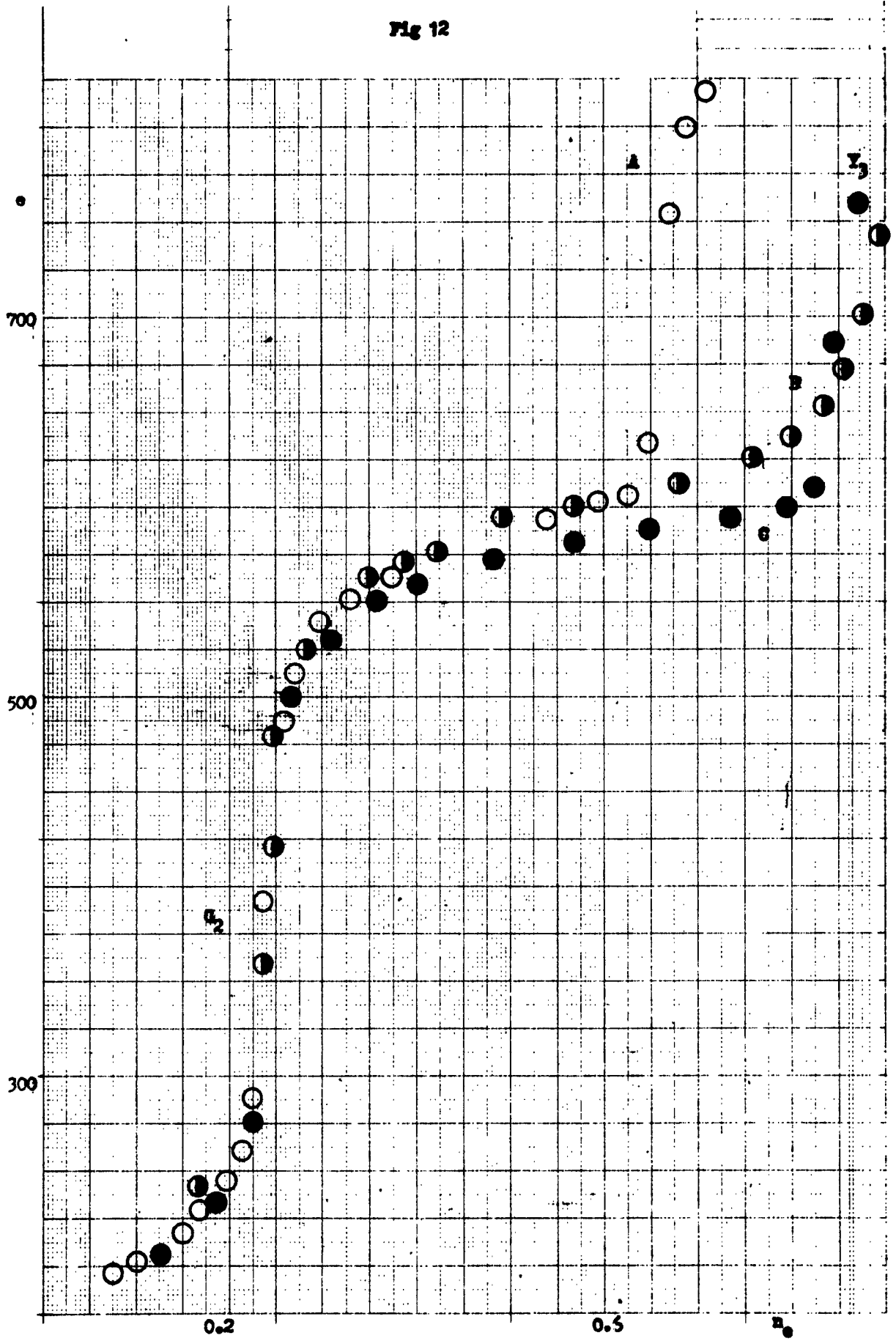
$\theta_2 \rightleftharpoons Y_3$
Same symbols as Fig 12
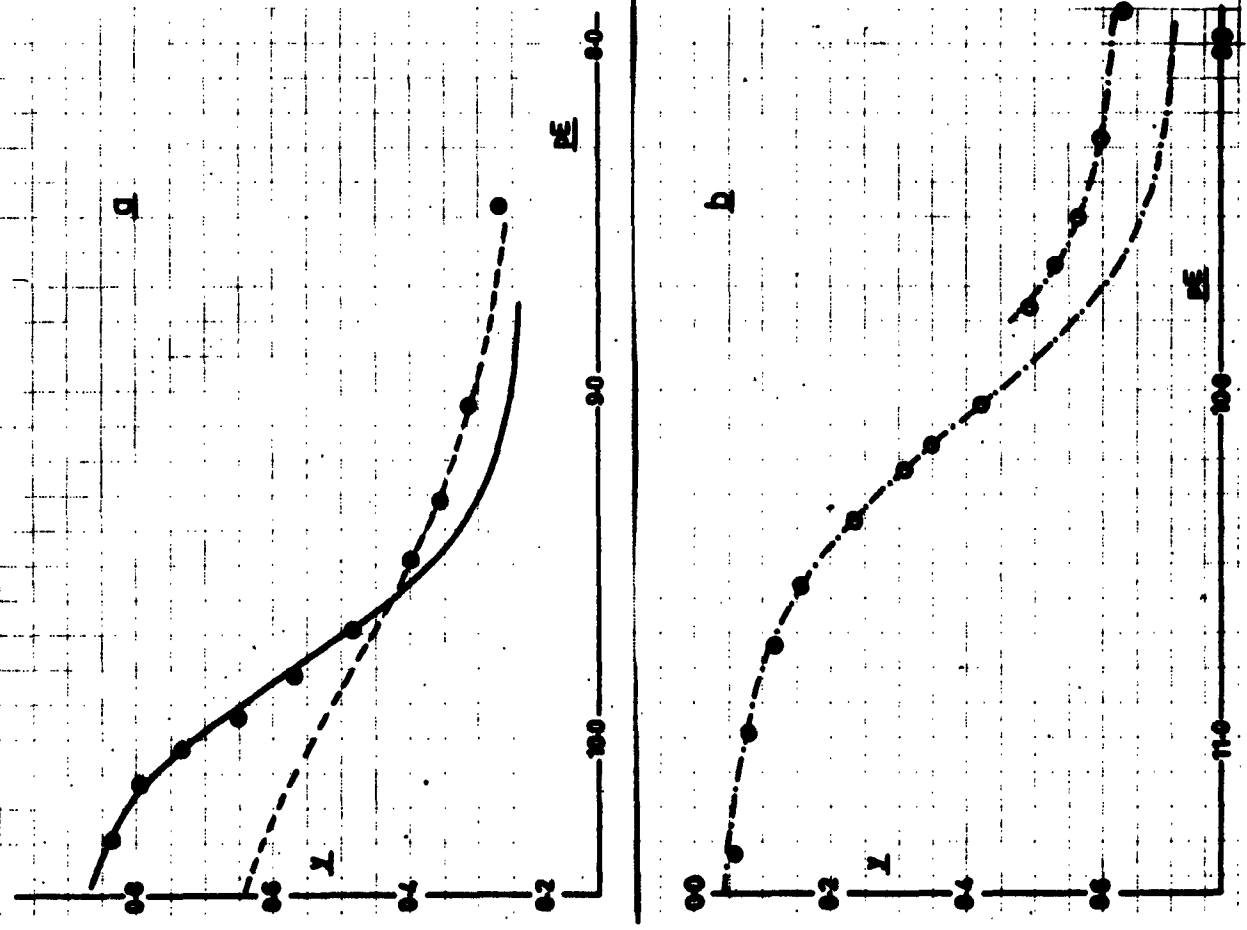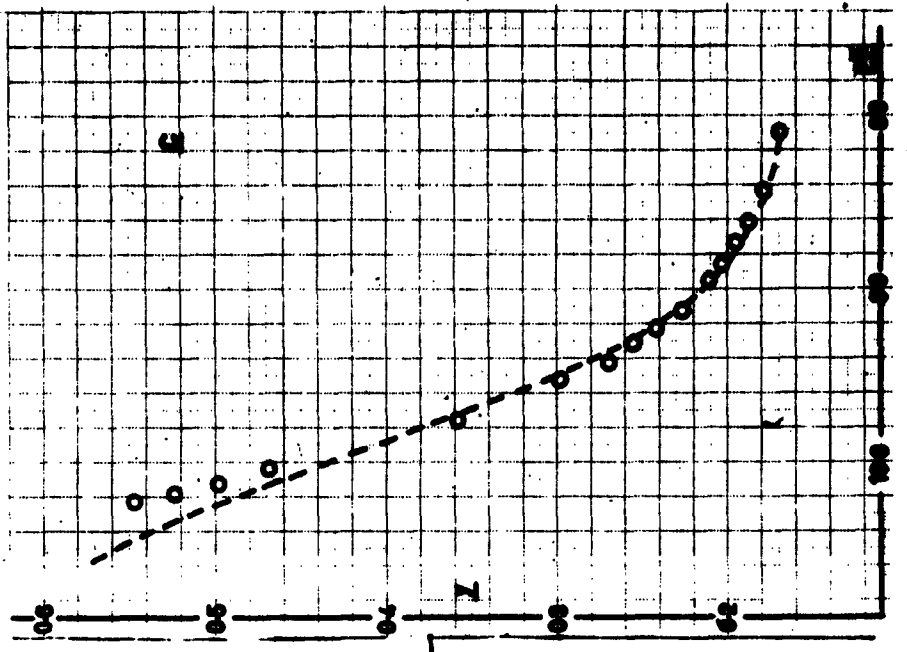Calculated curves, see text

Fig 13

The solution Y_3 seems to be stable: one such solution has remained apparently unchanged for several months although no special precautions have been taken to exclude air from it. Its spectrum is reported in a later section.

Attempts have been made to analyse the data obtained in these experiments using the method outlined earlier. The analysis shows that the greater part of the data is consistent with the successive occurence of the reactions A) $Ru_2^{6+} \rightleftharpoons Ru_2^{7+} + e^-$, B) $2Ru_3^{11+} + 4e^- \rightleftharpoons 3Ru_2^{6+}$ and, in part C) $Ru_3^{9+} \rightleftharpoons Ru_3^{11+} + 2e^-$. More data are needed before any conclusions can be drawn with certainty.

Determinations of hydroxide number Z

Red Ru(IV) R_1

The R_1 solution was obtained by elution, with 1 M Na_2SO_4, of a resin saturated with Ru(IV), prepared as described earlier (Brito 1960). The eluate was concentrated by evaporation in vacuum at room-temperature, adding anhydrous Na_2SO_4 and filtering. In a number of experiments, a R_1 solution with B between 1 mM* and 16 mM* and 1 M* (Na^+ H^+)SO_4^{2-} was neutralized by adding weighed amounts of $NaHCO_3$ solution, while measuring h with a glass electrode as described earlier. Fig 14 shows two typical diagrams for determining E_0 and j.

At the end of this "titration", acid was added until h $\approx$ 5-10 mM*, after which H_2 was passed through, in contact with a Pt electrode of large surface. After 24 h, all Ru had precipitated as metal on the electrode and as a mirror on the bottom of the vessel. The remaining solution was neutralized with $NaHCO_3$ as earlier, the potential was measured with $Ru(H_2)$ and $Pt(H_2)$ electrodes, which agree within $\pm$ 0.05 mV and a plot analogous to a Gran plot (1952) was made. Fig 15 shows a typical diagram: the abscissa is w, the weight of $NaHCO_3$ solution added, and the ordinate is

$$G = (w_0 + w - w(CO_2)) \ 10^{(E-jh)/59.154}.$$

Here w_0 is the weight of the original solution, and $w(CO_2)$ is the weight of CO_2 formed. The plot is linear, and the intercept on the w axis gives $H_+ = H + XB$ for the original solution. This, by the way, came out about 7 % higher than the approximate value obtained by $NaHCO_3$ precipitation of "RuO_2".

From these data, it was now possible to calculate BZ. As seen from fig 16, $Z \approx 3$ in all the range. As a check, corresponding Gran plots were made for all titrations: they all came out linear, as they should for a constant Z, and gave the intercept corresponding to H + BZ. (Fig 17).

We conclude that the main species in R_1 solutions is $(Ru(OH)_3^+)_n$, with n = 3 or 4 (from redox titrations). The same conclusion was drawn by Brito (1960) for the R_1 solution in perchlorate medium.
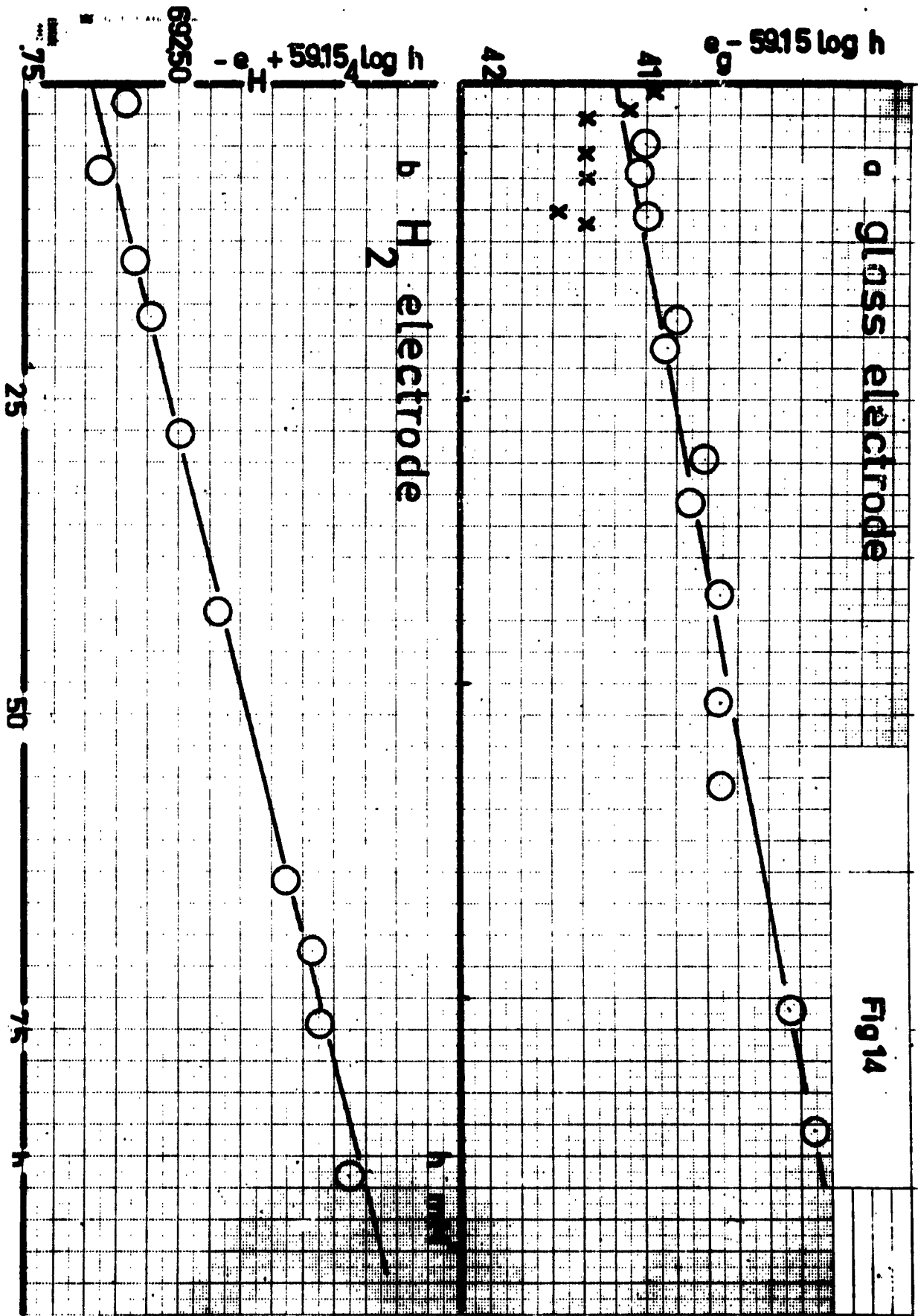
Fig 14

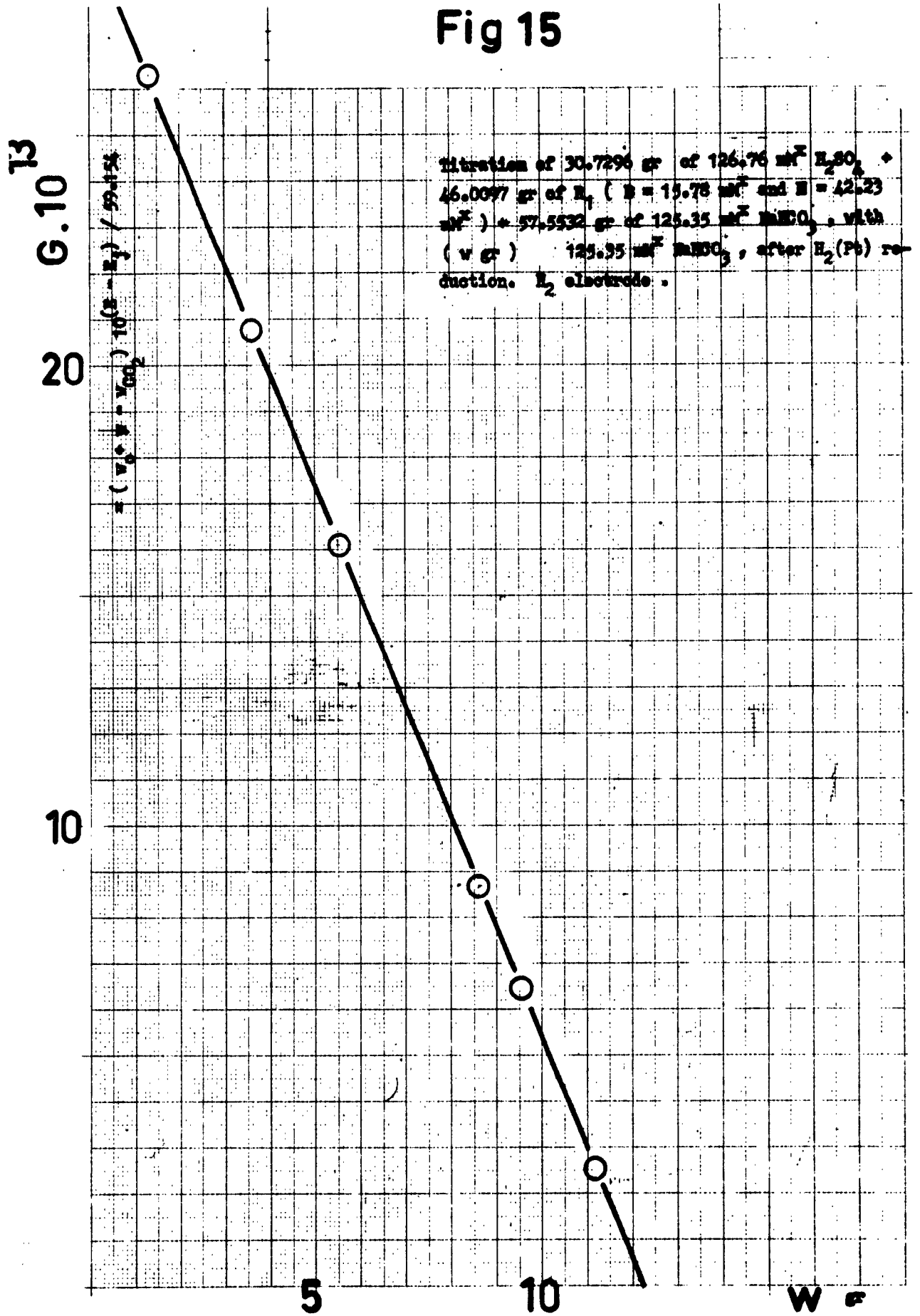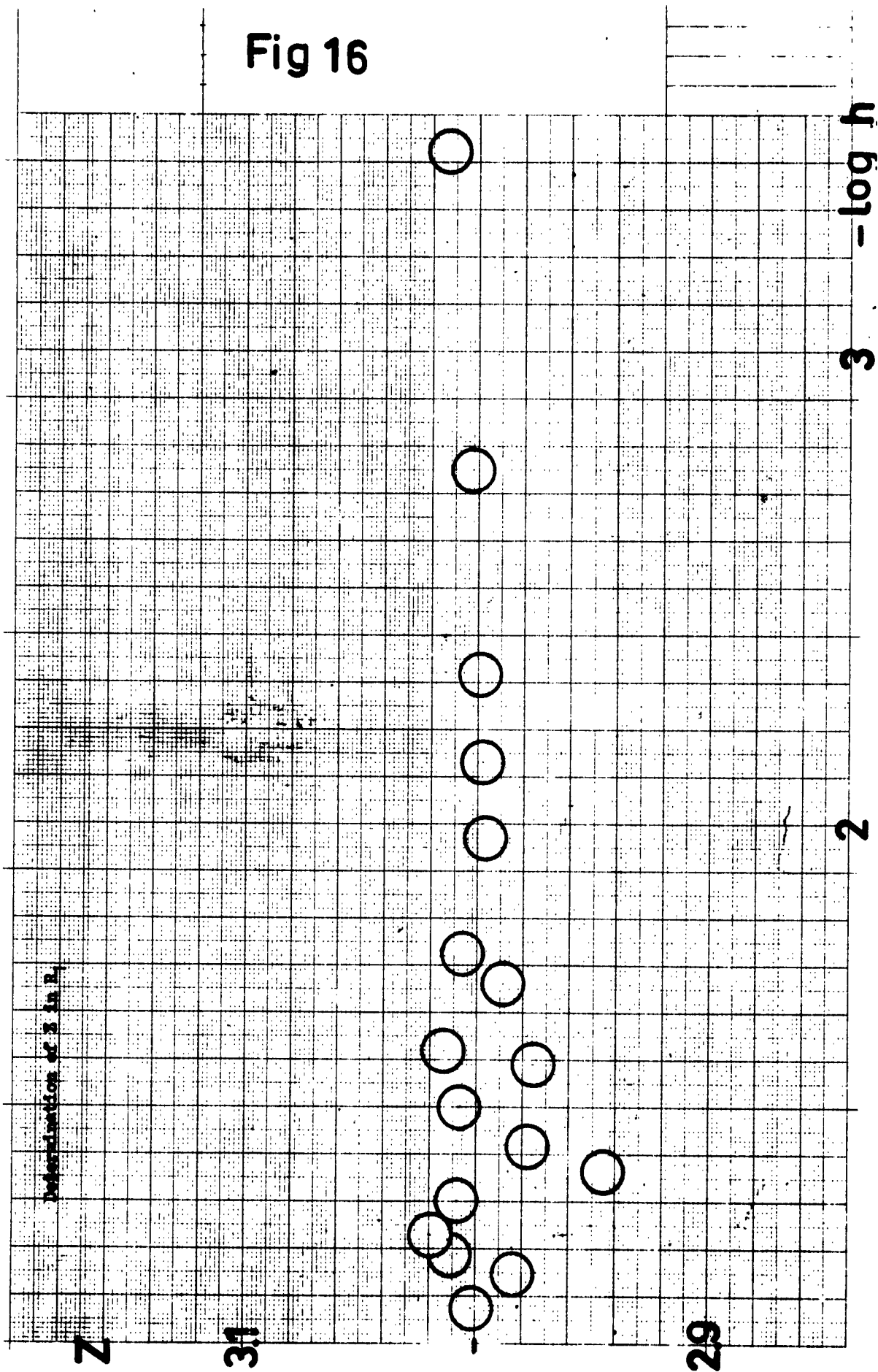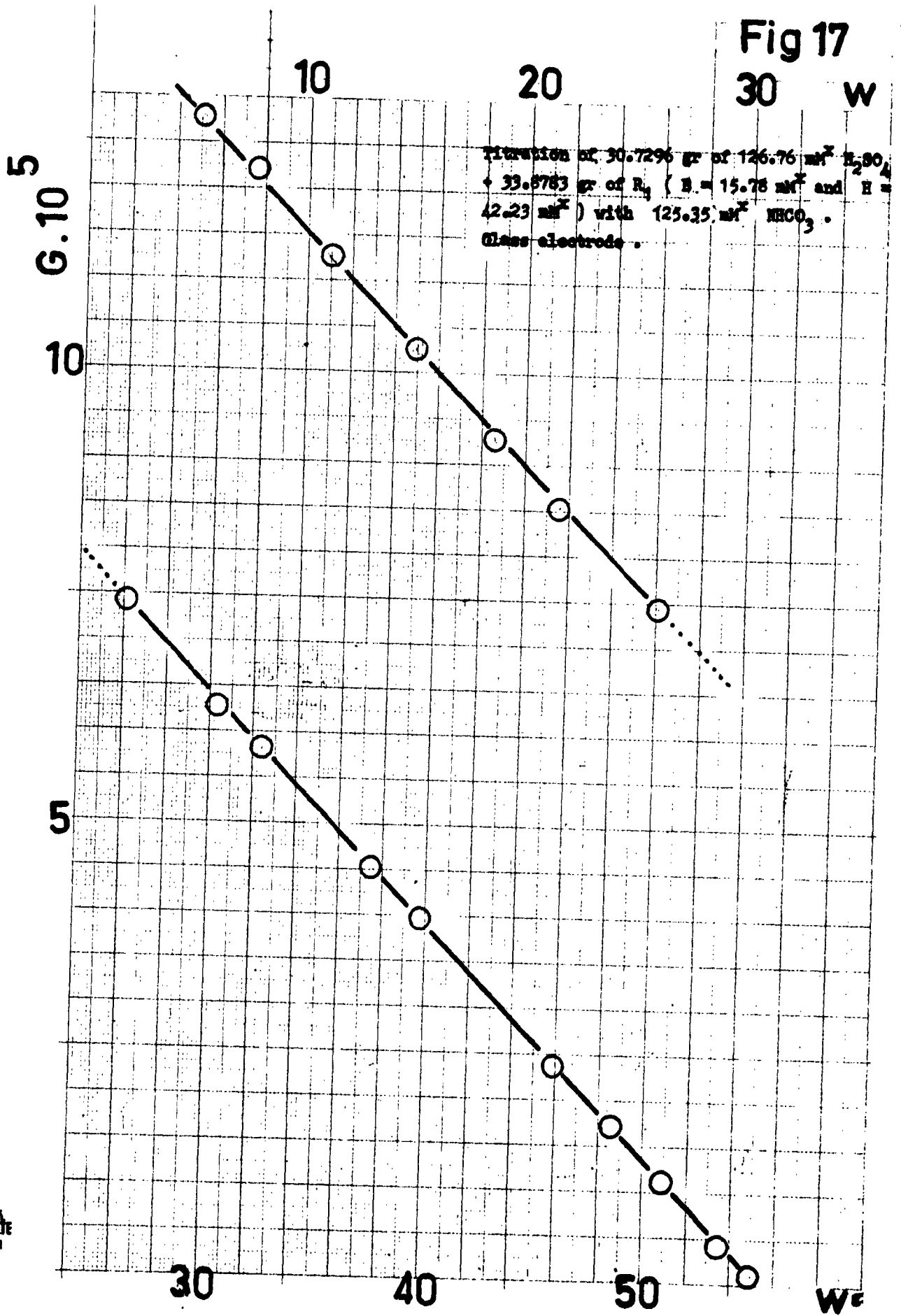a glass electrode

$e_g - 59.15 \log h$

b H_2 electrode

$-e_H + 59.15 \log h$

Fig 15

Titration of 30.7296 gr of 126.76 mN H$_2$SO$_4$ + 46.0097 gr of H$_1$ (H = 15.78 mN and H = 42.23 mN) + 57.5532 gr of 125.35 mN NaHCO$_3$, with (w gr) 125.95 mN NaHCO$_3$, after H$_2$(Pt) reduction. H$_2$ electrode.

Fig 16

Fig 17

Titration of 30.7296 gr of 126.76 mM^x H_2SO_4 + 33.6783 gr of R_4 ($H = 15.76$ mM^x and $H = 42.23$ mM^x) with 125.35 mM^x NH_4CO_3 . Glass electrode .

Z for B$_4$

The B$_4$ solution was prepared as described earlier (see Redox reactions of B$_4$).

In most of the titrations, B was kept constant, but two further titrations were made, in which this was not so. In the first of these, h and B were varied by the addition of 1 M Na$_2$SO$_4$. In the second, they were varied by the addition of more acidic and more concentrated solution of B$_4$, together with enough concentrated Na$_2$SO$_4$ solution to keep $[SO_4^{2-}]$ constant. The latter experiment was completed with a reverse titration in which B and h were varied by the addition of NaOH + Na$_2$SO$_4$.
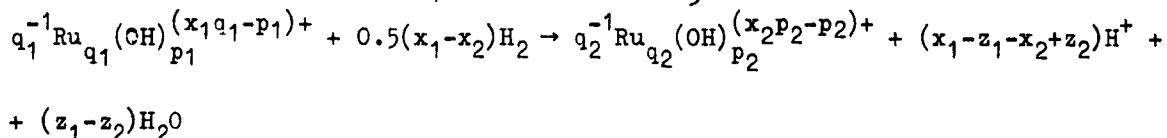
What is known for each solution is really not H, but H_{Br} = H + B(1.2 X - 1.6) since the bromate method was used. If, for each experiment with a constant B value, h was plotted as a function of H_{Br}, a set of parallel straight lines with slope = 1 was obtained (Actually, in Fig 18 we have plotted h versus H_{Br} - 2B in order to distinguish the lines for different B). Since h = H_{Br} - (1.2X - 1.6) + + BZ, this indicates that Z is constant for each B.

So, what we can obtain from the data is Z´= (h - H_{Br})/ B. Fig 19 gives a plot of Z´as a function of h for the various titrations. It seems that Z´comes out as almost a constant Z´= 0.25 ± 0.10 for all experiments.

Now, we have the relationship Z = Z´+ (1.2 X - 1.6). Thus Z depends on the value given to X. From the redox EMF titrations X seems to be ≈ 3.8, even though Ce^{4+} analysis seems to indicate X = 3.2, for a fresh solution and X = 3.5 after six months. The experiments for determining Z have been made during this interval. The value for Z would be Z = 3.2 (X=3.8), Z = 2.85 (X=3.5), Z = 2.5 (X=3.2), always ± 0.1. At any rate, it seems safe to conclude that the OH number for the B$_4$ complex is practically or completely constant, and not far from 3.

Z for B$_5$

Solutions of brown ruthenium B$_5$ were prepared by reduction of R$_1$ with H$_2$(Pt). In a typical experiment R$_1$ with B = 8.64 mM^x and h = 105.41 mM^x, was reduced until e = 332 mV as measured with a Pt electrode after expelling H$_2$ with N$_2$. If we let the index "1" denote R$_1$ and "2" denote B$_5$, the reaction formula is:

$$q_1^{-1}Ru_{q_1}(OH)_{p_1}^{(x_1q_1-p_1)+} + 0.5(x_1-x_2)H_2 \rightarrow q_2^{-1}Ru_{q_2}(OH)_{p_2}^{(x_2p_2-p2)+} + (x_1-z_1-x_2+z_2)H^+ +$$

$$+ (z_1-z_2)H_2O$$

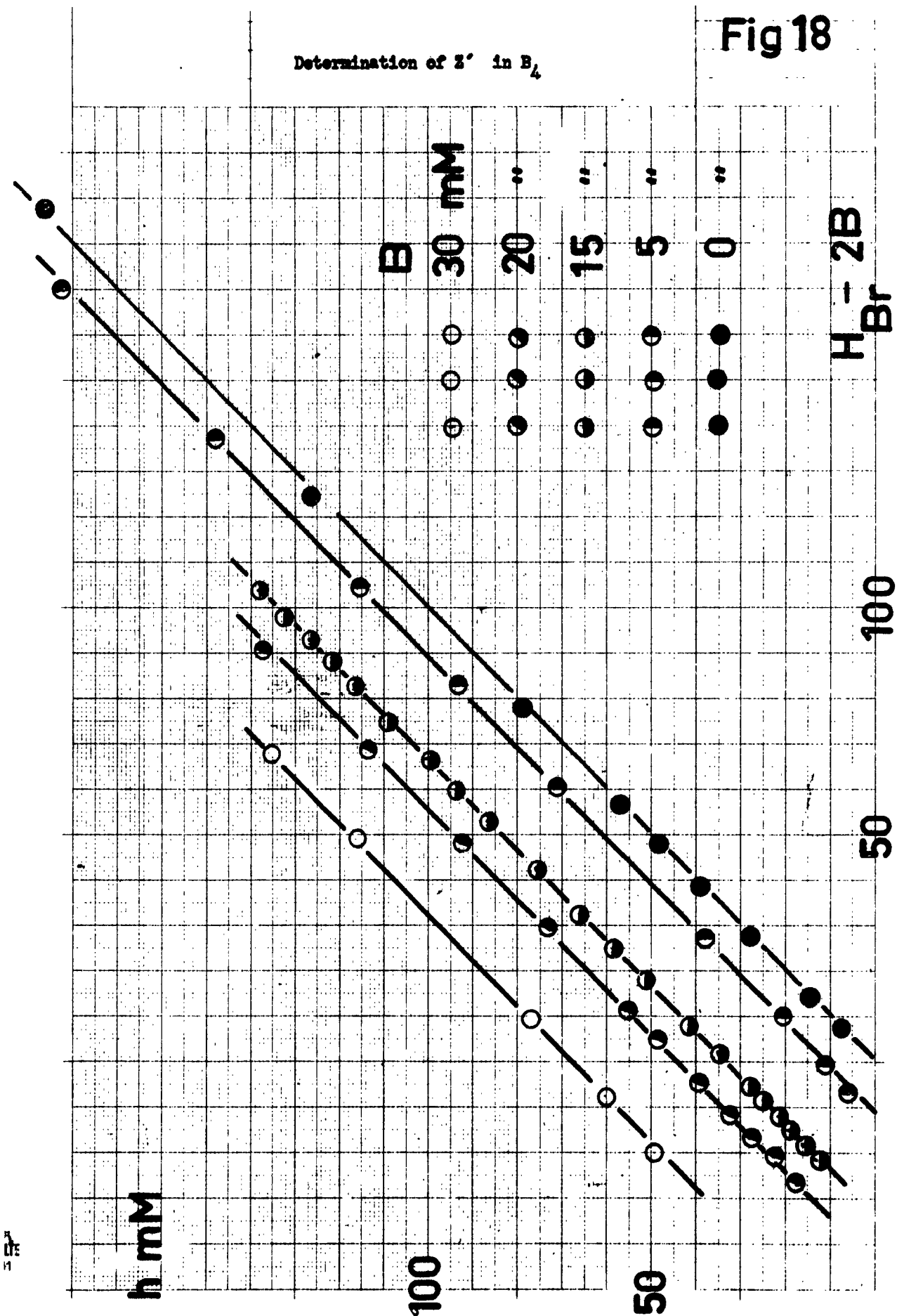where $z_1 = p_1q_1^{-1}$, $z_2 = p_2q_2^{-1}$.

The course of the reduction was also followed with a glass electrode from whose change of potential (0.9 mV) an approximate value for the total change of

Fig 18

Determination of Z′ in B_4

Determination of Z' in B4
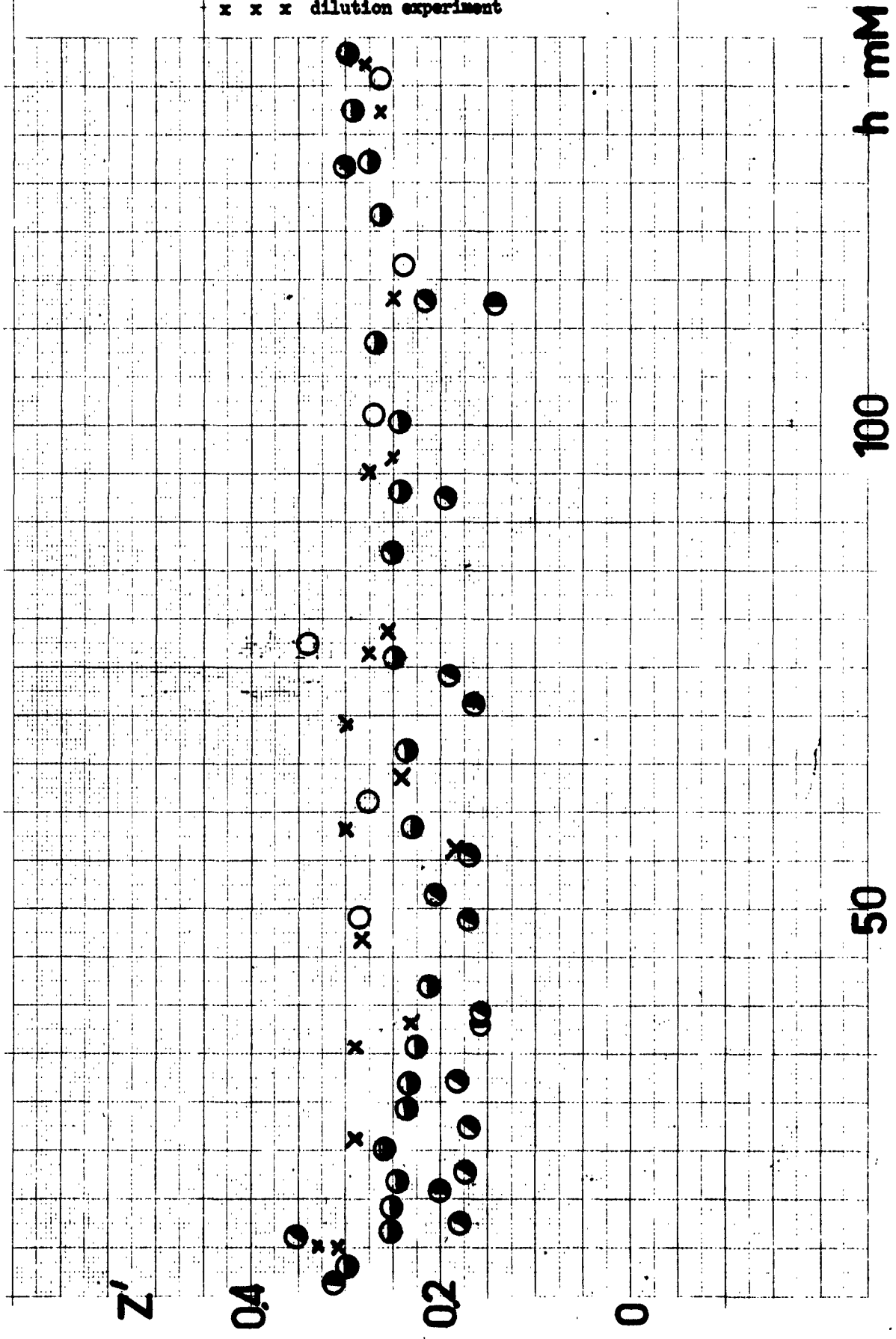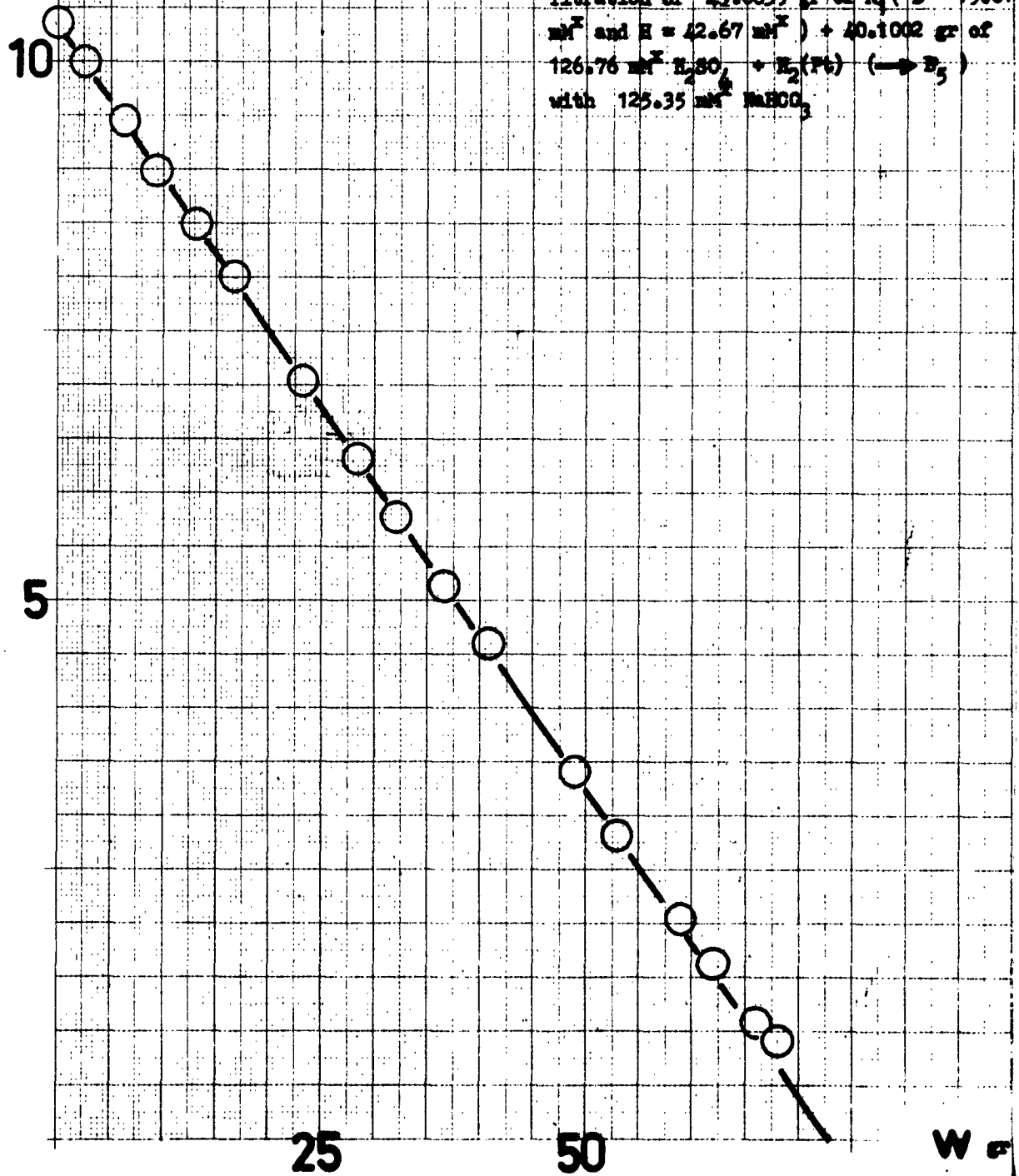Same symbols as Fig 18
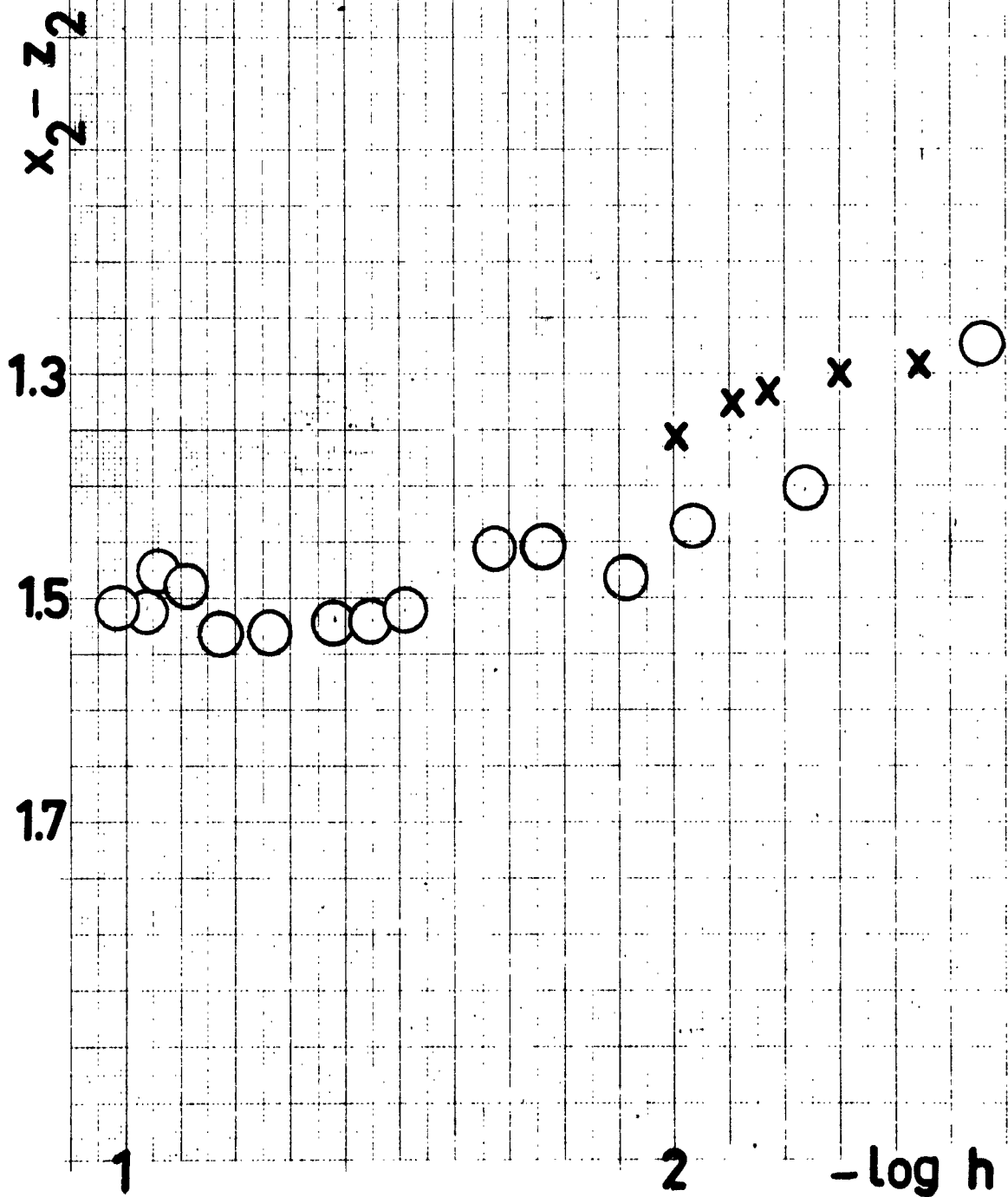x x x   dilution experiment

Fig 19

Fig 20

$$G = (w_s + w - w_{CO_2}) \cdot 10^{(B - B_j)} / 59.154$$

Titration of 49.6839 gr of R_1 (B = 15.61 mM^X and H = 42.67 mM^X) + 40.1002 gr of 126.76 mM^X H_2SO_4 + E_2(Pt) ($\longrightarrow B_5$) with 125.35 mM^X $NaHCO_3$

Fig 21

Determination of $x_2 - z_2$ in B_5
x x x back titration of B_5 with R_1

h per total ruthenium concentration was found to be $\Delta hB = (101.8 - 105.4)/8.64 = -0.42 = x_1 - z_1 - x_2 + z_2$.

Since for red R_1, $x_1 = 4$, $z_1 = 3$ (see above) we would have, for the resulting B_5: $z_2 = x_2 - 1.42$.

The solution was then neutralized with $NaHCO_3$ until $h = 2.75$ mM^x($\underline{e} = 276$ mV). A Gran plot, Fig 20, carried out in the same way as for R_1 above, was linear (which indicates a practically constant z_2) and gave a intercept from which we calculated: $z_2 = x_2 - 1.505$ in the brown B_5 solution.

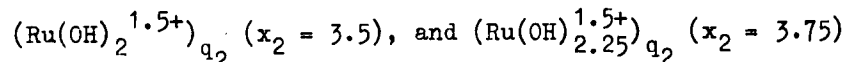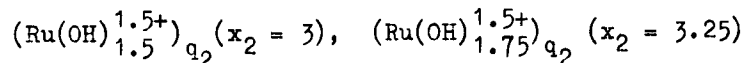In Fig 21 we plotted the data as $(x_2 - z_2)$ versus log h.

Then finally, the solution was backtitrated with the original R_1 until $h = 10$ mM^x($\underline{e} = 540$ mV), and $x_2 - z_2$ was calculated assuming no reaction between R_1 and B_5 (crosses in Fig 21).

Thus the results seem to indicate the approximate formula

$$(Ru(OH)_{z_2}^{1.5+})q_2$$
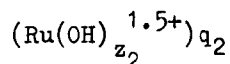
at least for $-\log h \leq 2$.

Now, by assuming different values for x_2, we have for B_5

$$(Ru(OH)_{1.5}^{1.5+})_{q_2}(x_2 = 3), \quad (Ru(OH)_{1.75}^{1.5+})_{q_2} (x_2 = 3.25)$$

$$(Ru(OH)_2^{1.5+})_{q_2} (x_2 = 3.5), \text{ and } (Ru(OH)_{2.25}^{1.5+})_{q_2} (x_2 = 3.75)$$

Absorption spectra

The absorption spectra of various solutions met with during our studies on Ru solutions were measured using a Hilger or a Beckman recording spectrophotometer, and are given in Figs 22, 23 and 24.

Fig 22 gives, in the range 2400 to 3300 Å, the spectrum for green G_2, which was obtained by reduction of R_1 in 1 M H_2SO_4 with H_2(Pt) until $e_H \approx 0$ and kept in O_2-free CO_2 during the measurements ; and also that for the same solution after two days' keeping in air $(G_2 \rightarrow B_3)$. Likewise, it gives the spectrum of red R_1 in 1 M H_2SO_4, and that of B_4 in the same medium measured six months after preparation.

Fig 23 gives the spectrum of B_4 in 0.5 M H_2SO_4, 1) 60 h after preparation, 2) after 1 month and 3) after 7 months. In the visible range the peak around
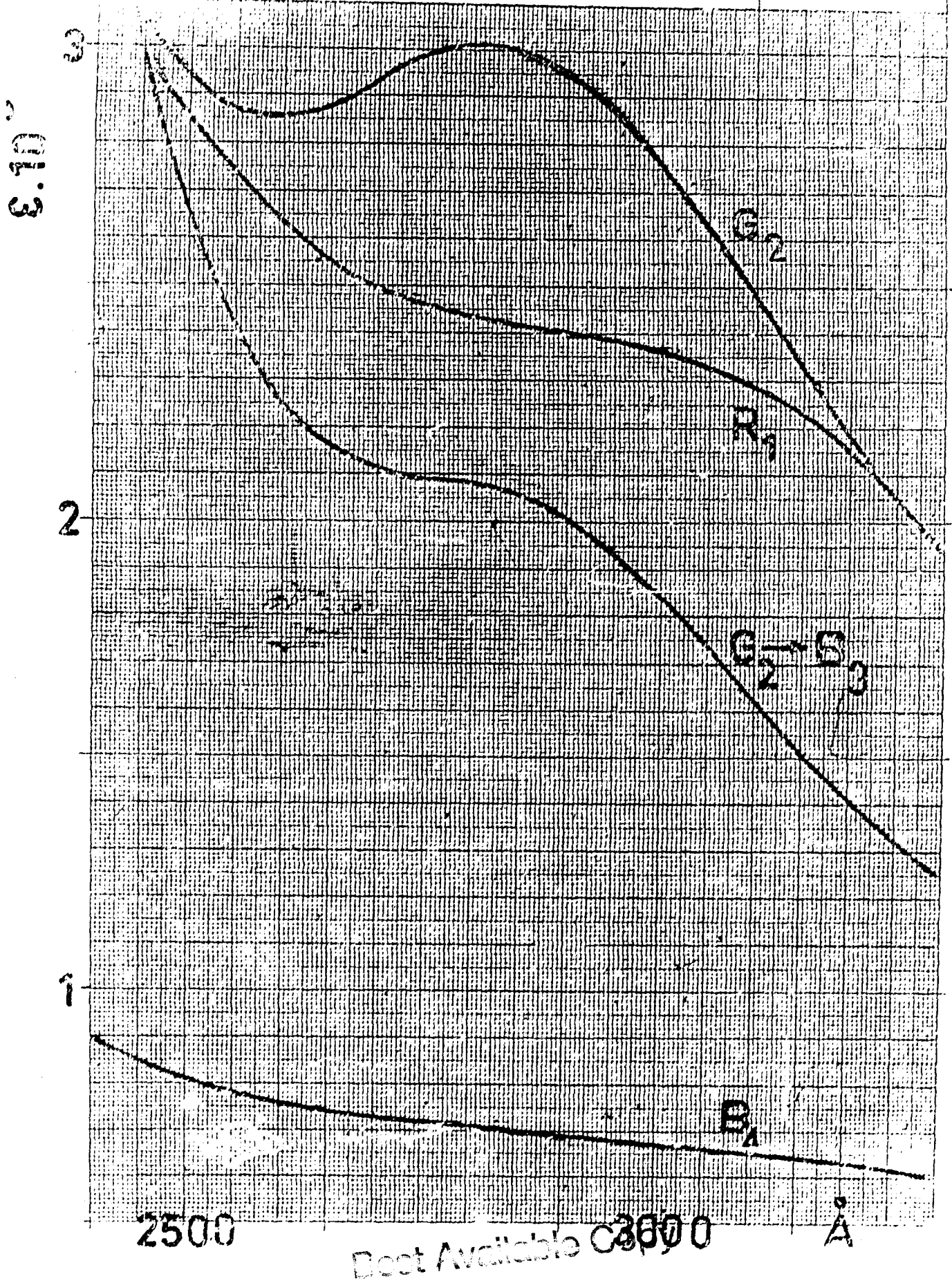
Fig 22

Fig 23

The absorption spectrum of B_4

1.= after 60 hours
2.= " 1 month
3.= " 7 "

E
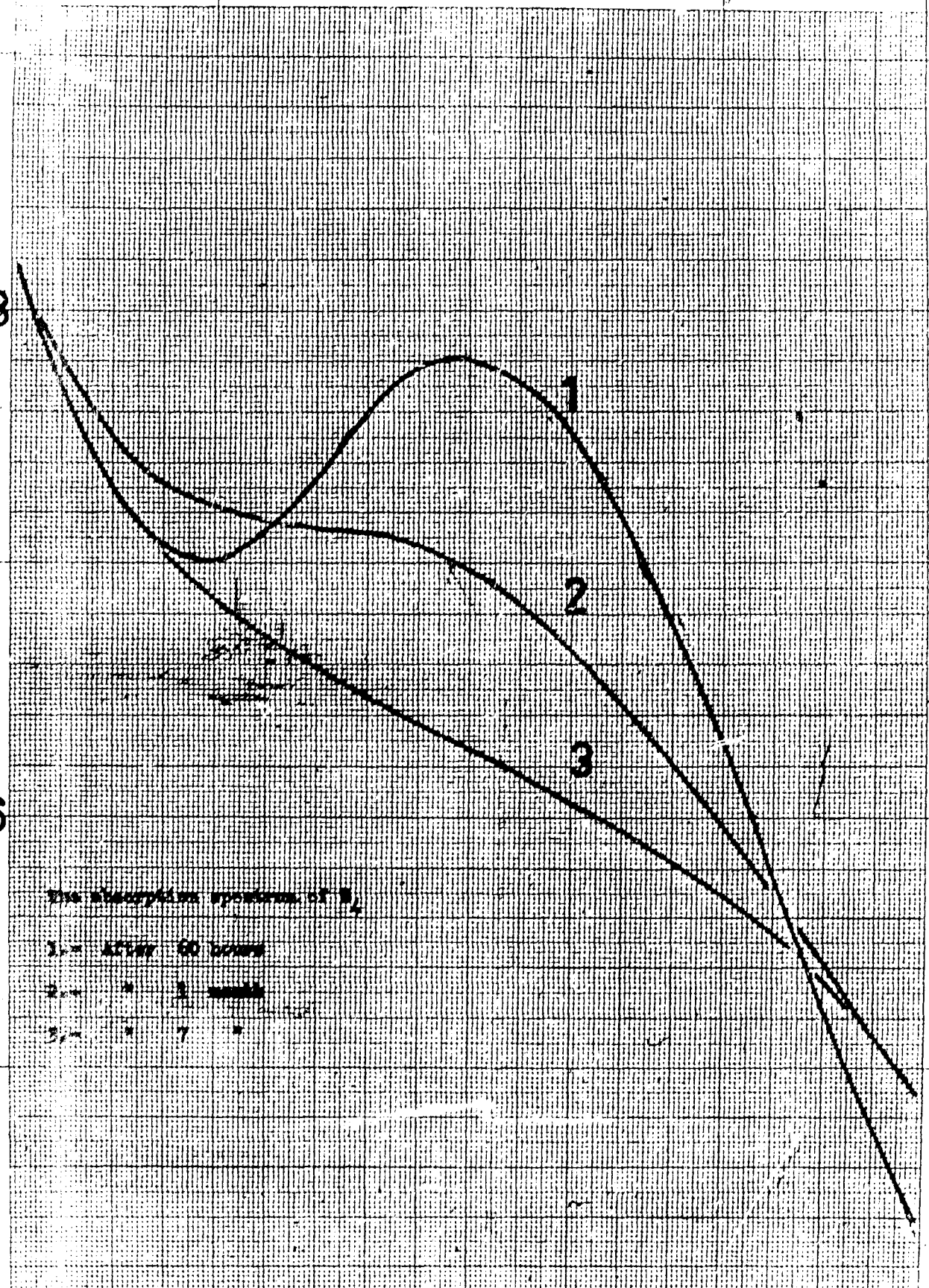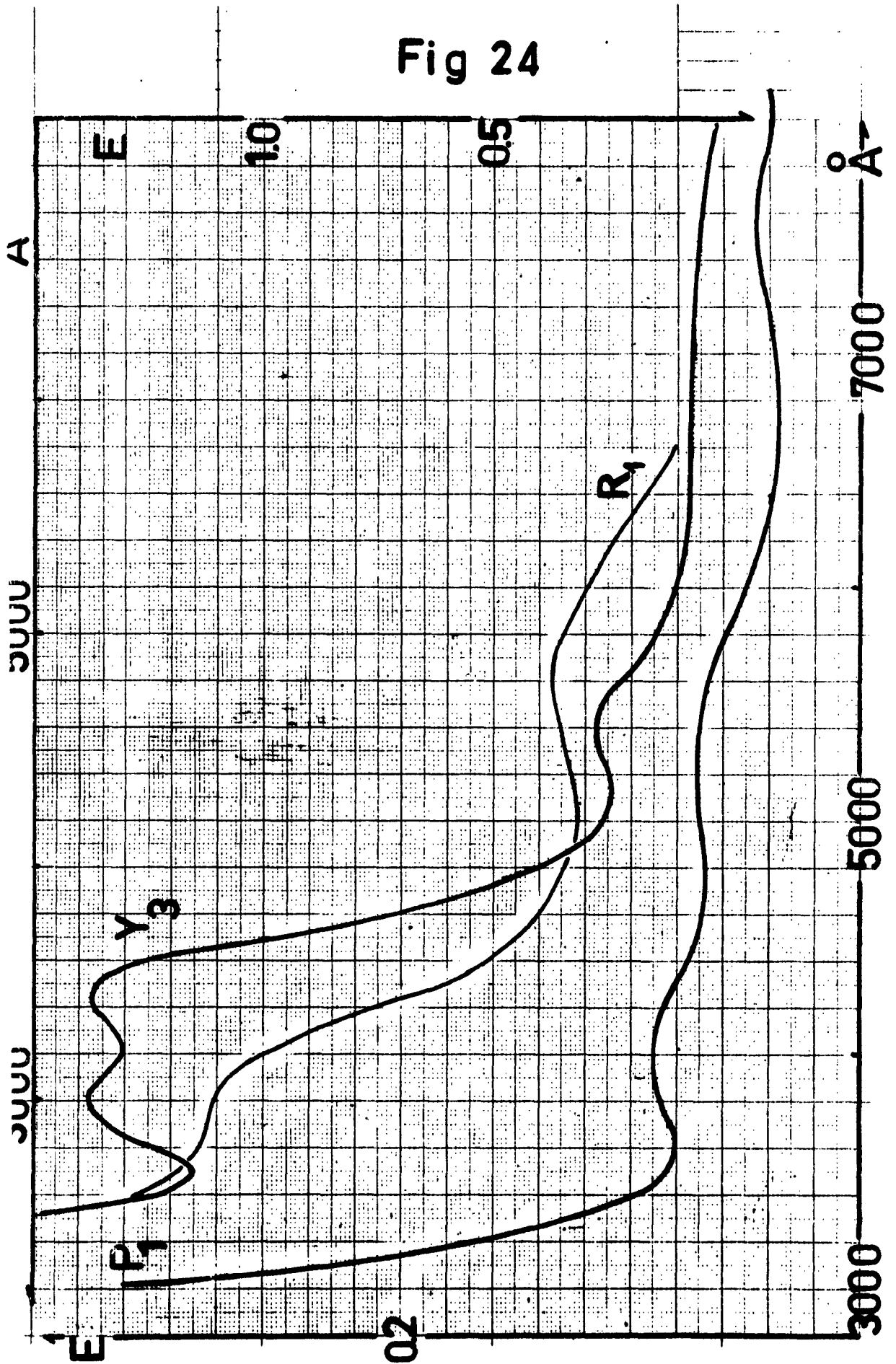0.8
0.6

2500   3000   Å

Fig 24

4800 Å, that has been found for red R_1, (Fig 24), was not encountered. The peak around 2850 Å occurs for freshly prepared solutions and is similar to the peak at 2800 Å for green G_2. However, that peak slowly becomes less marked, and finally disappears , as the solution ages.

Fig 24 contains the spectra of pink P_1 (coordinates to lower left), red R_1 and golden yellow Y_3 (coordinates to upper right), all in 1 M H_2SO_4.

P_1 was obtained by reduction of R_1 with H_2(Pt) and kept in O_2-free CO_2 during the measurements. Since some Ru has precipitated as metal during the H_2(Pt) reduction we do not know B and cannot give $\mathcal{E}$.

The spectrum of golden yellow Y_3 was measured in a 1 mM solution prepared as described, p. 2:29 , and waiting one month, when it had assumed the golden yellow colour. It has some features similar to those of other ruthenium solutions described here as well as some different. The peak centered at 4600 Å is closely similar to that at 4800 Å, obtained with R_1 solutions. On the other hand, the two closely-spaced peaks centered at 3000 and 3450 Å have no very similar counterpart in the spectra of other ruthenium sulfate solutions. There is, however, some resemblance between these features and the spectrum of G_1 (Brito 1960) which has a peak at 3000 Å, a shelf at 3400 Å and a peak at 4800 Å.

Conclusions and outlines for future work

It may be apparent from the report given, and perhaps especially from fig 1, that the ruthenium system is greatly complicated by the formation of polynuclear complexes of mixed valency, and by the slowness of many of the reactions.

Even if we cannot claim to have ended up with a clear picture at least we think we have collected enough information for planning a worth-while larger attack on aqueous ruthenium chemistry.

The choice of sulfate medium seems to be right: in this way one avoids chloro complexing, and the reduction of ClO_4^-. For studies of redox reactions, without bothering about the number of hydroxo groups bound, H_2SO_4 solutions seem suitable: one should in the future also try higher concentrations than 1 M.

For future work it is imperative to search for water-proof equilibrium and structure data. It should not be impossible to work at considerably higher temperatures, say $75^\circ C$, which would speed up the attainment of equilibrium, so that equilibrium analysis could be applied to a large part of the system. Another important task is trying to prepare crystalline phases containing some of the species met with in the solutions, and to find the structure of these species by X-ray structure analysis.

By these two ways, equilibrium analysis and structure analysis, one may hope to find with some certainty the formula of the complexes. Other methods, such as studies of irreversible curves (for instance polarography) and spectra may give good finger-prints for characterizing certain species but cannot be expected to lead to a certain assignment.

The two species that give the best reversible potential in 1 M H_2SO_4 are Ru^{2+} ("P_1") and Ru^{3+} ("G_2"). One should however try to study the behavior of Ru(III) at various pH and also to find out whether some green solutions found in this region - which have in this report been undiscriminatingly denoted as G_2 - may not contain other species.

Another well characterized solution is R_1, which seems to contain $(Ru(OH)_3)_n^{n+}$. The existence of species with X = 3.5 seems well established: however, they may have very different properties depending on the way of preparation, (Ti^{3+} reduction or electrolytic reduction of R_1, addition of R_1 to G_2). The relationship between these species and the species found in B_3, B_4, Y_2 and Y_3 would certainly be interesting to know. It seems uncertain whether the deviations in X for these other complexes, especially B_3 and B_4, may be connected with some peroxo complexing or whether it is only a gradual shift in the ratio between different oxidation states of Ru.

Finally it should be noted that a state with X $\approx$ 3.25 seems to be well defined.

It is our intention to pursue these studies further, even after the sponsorship of USAF has terminated.

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