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EXPERIMENTAL

Materials

can be used to find the overall equilibrium constant for the

 $GeF_{*}^{2^{-}} + 2H_{2}O \rightleftharpoons GeO_{2}(hex.) + 4H^{+} + 6F^{-},$

 $\frac{[\text{H}^+]^{4}[\text{F}^-]^{6}}{[\text{GeF}_{6}^{2-}]} = \frac{K_1}{[\text{K}_2\text{GeF}_6]}$

To remove the traces of hydrogen carbonate ion from

was heated with a slight excess of "chemically pure" grade

KHF2, after which the cooled solution was neutralised ex-

actly with carbonate-free KOH solution; the solution was

evaporated until KF.2H2O crystallised on cooling, the crys-

tals were washed with a small quantity of ice water, com-

pressed, and dried between sheets of filter paper. K2GeF6

was purified by recrystallisation¹. GeO₂ containing 0.25% Cl, 1.2×10^{-4} % Si, and less than 10^{-5} % Al, As, Mg, and

by prolonged pyrohydrolysis². The X-ray powder diagram

PbF, was prepared by precipitation with NH, F solution

Fe impurities was purified completely from traces of Cl-

from a solution of "analytical reagent" grade lead acetate

which had been further purified by recrystallisation from

1% acetic acid solution; the PbF, precipitate was washed

KF.2H₂O and PbF₂ were prepared only in polyethylene or

tained detectable quantities of Cl⁻, whose presence might

Nitrogen, obtained by the reaction of sodium nitrite

alkaline dithionite solution; the solution in the funnel of

the gas holder and in the storage vessels was protected

from atmospheric oxidation by a layer of oil.

remelting in a high vacuum at 500°).

relatively slow⁴.

and ammonium sulphate solutions, was washed with acidic

Lead amalgam was prepared by the published method³

cury and lead which had been purified from traces of active

pared by electrolysis at a mercury cathode with subsequent

In the first series the equilibrium position was reached

from the direction corresponding to hydrolysis of K2GeF6.

diluting (by weight) the original ~1.562 m solution. An

excess of $K_2 GeF_6$, PbF₂, and GeO₂ was added to the solu-

tions in polyethylene vessels, and the mixtures were kept

at constant temperature in a water thermostat with periodic agitation for 3.5 months at $25^{\circ} \pm 0.1^{\circ}$. This time in-

terval ensured that the equilibrium state was reached,

although the hydrolysis of GeF_6^{2-} in alkaline medium is

metals and then redistilled in a vacuum (the lead was pre-

Preparation of Specimens and Measurement Procedure

KF solutions with molality 0.08-0.5 were prepared by

in an atmosphere of nitrogen from very highly pure mer-

have interfered in the action of the lead fluoride electrode.

platinum vessels. None of the reagents prepared con-

with water acidified with HF, and dried in air. The

showed that the GeO, had the hexagonal structure.

"chemically pure" grade KF, a 15% solution of the latter

hydrolysis of GeF²₆ according to the equation

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(4)

(5)

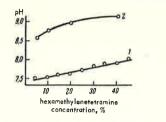


Fig. 5. pH of solutions in the GeO₂aqueous hexamethylenetetramine solution system (1) and in the hexamethylenetetramine-H₂O system (2).

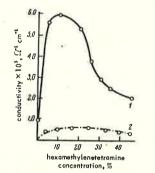


Fig. 6. Electrical conductivity of solutions in the GeO2-aqueous hexamethylenetetramine solutions system at 25° (1) and in the hexamethylenetetramine-H2O system (2).

The pH (Fig. 5) of pure hexamethylenetetramine solutions is much higher than that for solutions of germanium dioxide in hexamethylenetetramine, from which it follows that in this system, as in that containing ammonia, chemical reaction takes place between germanium dioxide and hydroxide ions, as a result of which the activity of the latter decreases considerably.

It was also found that the electrical conductivity of aqueous solutions containing GeO₂ and hexamethylenetetramine is many times greater than that of pure hexamethylenetetramine solutions with the same concentration (Fig. 6). This can be the case only if a compound which is more extensively dissociated than the original components is hexamethylenetetramine- H_2O systems shows that in the first system, where the ammonium hydroxide is a stronger base than hexamethylenetetramine, the ammonium germanate formed is more stable. The increased solubility of germanium dioxide in the presence of hexamethylenetetramine, the decrease in pH, and the increase in the conductivity of aqueous hexamethylenetetramine solutions in the presence of germanium dioxide definitely indicate the formation of a chemical compound, although this could not be isolated in the solid state.

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SUMMARY

- 1. The germanium dioxide-aqueous ammonia solution system has been studied by solubility, electrical conductivity, and potentiometric methods at 25°. The high solubility of germanium dioxide in aqueous solutions (158.6 g GeO₂ litre⁻¹ at 1.2% NH₃) is due to the formation of ammonium germanate with composition $(NH_4)_3HGe_7O_{16}$. With increase in the ammonia concentration, the solubility of ammonium germanate decreases sharply and fine crystals with composition (NH₄)₃HGe₇O₁₆.4H₂O are precipitated.
- 2. The solubility and electrical conductivity in the germanium dioxide-hexamethylenetetramine-water system have been studied. The solubility of germanium dioxide is increased, again due to the formation of germanate, but the compound formed with hexamethylenetetramine is less stable than ammonium germanate.
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Institute of General and Inorganic Chemistry, Academy of Sciences of the Ukrainian SSR

Received 8th October 1964

U.D.C. 546.289.4'161

OVERALL EQUILIBRIUM CONSTANT FOR HYDROLYSIS OF THE HEXAFLUOROGER-MANATE ION GeF2- AT 25°

I. G. Ryss and N. F. Kulish

We determined the equilibrium constant of the process

 $K_2GeF_6(cryst.) + 2H_2O \Rightarrow GeO_2(hex.) + 4H^+ + 6F^- + 2K^+,$

at 25° by potentiometric determination of the activities of the H^+ and F^- ions and measurement of the K^+ ion concentration in KF solutions of various concentrations, saturated with K. GeF, and hexagonal (α -quartz type) GeO₂. It can be seen that the equilibrium constant K_1 for process (1) is

> $K_1 = [H^+]^4 [F^-]^6 [K^+]^2 = [H^+]^4 [F^-]^6 (K^+)^2 \gamma_K^2$ (2)

Here and subsequently the square brackets denote the activities and the parentheses the concentrations of the given ions; γ is the activity coefficient.

The expression for the activity of saturated K GeF. solution:

$$[K_2GeF_6] = [K^+]^2[GeF_6^{2-}], \qquad (3)$$

In the specimens of the second series the equilibrium
position was reached from the direction corresponding to
the formation of
$$K_2GeF_6$$
. ~0.3 g of HF solution containing
the specimens of the second series the equilibrium
nected by ground joints] to ensure
rated with all three solid phases.

The presence of K2GeF6 and GeO2 residues in the specimens before the measurement of the potentials was checked using a microscope. The solubility of GeO₂ in 1.5 m and saturated KF solution at 20° is lower than that in water (~0.03 m and ~0.026 m).

Measurements

Stable and reproducible results could not be obtained with a hydrogen electrode, so that the pH was measured with a quinhydrone electrode. It was established that GeO, does not influence the quinhydrone electrode in the pH range in which we were interested. The activity of the F⁻ ions was measured with a lead fluoride electrode^{3,5} containing a two-phase mixture of lead and PbF, precipitate. The reference electrode was a saturated calomel electrode connected to the circuit through an intermediate vessel containing saturated NH₄NO₃ solution, isolated by means of a No. 4 glass filter.

permanganate solution and stored in a gas holder filled with

In the calculation of $pF = -\log[F^-]$ we used the published values of the standard potential of the lead fluoride electrode⁵ and the mean results obtained in the measurement of the e.m.f. values for both lead fluoride electrodes.

an equimolar quantity of KHF₂ was added to KF solutions saturated with GeO₂, K₂GeF₆, and PbF₂, and containing an excess of the precipitates, in polyethylene vessels. The following reaction took place

$G_0O_2 + 2HF + 2KHF_2 = K_2G_0F_6 + 2H_2O.$

These specimens were then brought to constant temperature under the conditions described above.

The cell (Fig. 1) was designed in such a way that there were no temperature differentials and that the solutions and electrodes were kept free from air by blowing nitrogen through all sections of the cell. After the cell had been filled with nitrogen, the solution being studied was introduced into vessel (1) together with the residues saturating it; some of the solution was forced into vessel (2). A stream of nitrogen was then blown through the solution and cell for 30 min [saturation of the N, with water vapour in vessel (2) prevented appreciable evaporation of the solution being studied] and it was forced into the cell, which was rinsed twice with the solution being studied. The solution was then transferred by suction into the lead fluoride electrodest and the quinhydrone electrode, and the e.m.f. measurements were made. . The temperature of the cell was kept constant at 25.00° ± 0.10°. The e.m.f. of the circuits was measured with a PPTV-1 potentiometer with LU-2 attachment. The e.m.f. values for the circuits of the quinhydrone and calomel electrodes were constant to within 0.2 mV; the difference in the potentials of the two lead fluoride electrodes changed with time by not more than several tenths of a millivolt, but the values in different measurements varied from several tenths of a millivolt to 8 mV; this was apparently due to the penetration of traces of oxygen into the electrodes while the latter were being filled. The e.m.f. of the lead fluoride electrodecalomel electrode circuits remained unchanged with time.

[†] After the solution had been transferred by suction into the lead fluoride electrodes, a mixture of solid K_2GeF_6 , GeO_2 , and PbF_2 was introduced into the electrodes [by rotating the vessels (6) connected by ground joints] to ensure that the solution remained satu-

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1) vessel for solution being studied; 2) vessel for bringing the concentration of water vapour in the nitrogen to the equilibrium value above the solution being studied; 3) saturated calomel electrode; 4) lead fluoride electrodes; 5) quinhydrone electrode; 6) vessel containing a mixture of solid K_2 GeF₆, GeO₂, and

August 1965

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The method used by Benoit and Place did not make it possible to detect $\operatorname{GeF}_{\theta}^{2^-}$ in the solution. We obtained reliable evidence for the existence of GeF2- in the solutions by studying not only the equilibria but also the kinetics of the processes 2,4; thus Fig. 5 in the paper by Benoit and Place, showing the ratio of the quantities of the different forms of fluorogermanate, is not correct.

which is only slightly greater than the overall constant for the hydrolysis of SiF2-. 13

Fig. 2. Dependence of $\log c_{K}^{+} - 2pH$

The standard free energy of reaction (4) is $\Delta F_{290}^{\circ} = -RT \ln K = 35.2_0 \pm 0.4_2$ kcal.

log cK+ - 2pH

on 3pF.

+ 2

Using the published value of ΔF_{298}° for hexagonal GeO₂¹⁴ and the tabulated data for ΔF_{298}° for the other substances taking part in the reaction ¹⁵, we calculated the standard free energy of formation of dissolved GeF2- at 25°:

$\Delta F_{f}^{\circ} = -438.0 \pm 1.5$ kcal.

We previously determined the equilibrium constants for the hydrolysis of GeF_6^2 to $[GeF_5(H_2O)]^{-1}$ and to $[Ge(OH)F_4(H_2O)]^{-11}$ The determination of ΔF_f° for GeF_6^{2-1} makes it possible to calculate ΔF_f° for these complexes; the values found (accuracy ±2 kcal) are respectively -424 kcal and -408 kcal.

The value of ΔF_f° for undissociated aqueous HF, which is required for the calculations and is not given in reference books ¹⁵, can be calculated from $\Delta H^{\circ} = -3.18$ kcal ¹⁶ and the dissociation constant $K = 6.7_1 \times 10^{-4}$ ¹⁷ for the dissociation of aqueous HF to form ions at 25°. The free energy of formation of undissociated aqueous HF at 25° is -70.41 kcal.

A recent paper by Benoit and Place¹⁸ described a study of the formation of fluorogermanates by methods involving the extraction of germanium with carbon tetrachloride and determination of the activity of F- with an iron(II)-iron(III) electrode. Benoit and Place did not make allowance for the existence of fluoroaquogermanates in the solutions but it can be shown that this has no influence on the determination of the mean ratio $\overline{i} = F/Ge$ in the complexes. The mean value which they found for \overline{i} in the complexes does not exceed 5. In the extraction experiments they used 8.12-11.12 m HCl, and HF concentrations not exceeding ~0.5 m. Since the acidity h_0 of 6 m HCl is 132, and that of 10 m HCl is 4800, 19 and the equilibrium constant for the process

$$GeF_6^{2^-} + H_3O^+ \rightleftharpoons [GeF_g(H_3O]^- + HF,$$
 (6)

is 0.29,¹ it can readily be seen that the equilibrium ratio of the concentrations of GeF_6^2 and $[GeF_5(H_2O)]^-$ in these conditions must be negligible. In the potentiometric determination of \overline{i} , Benoit and Place used solutions with (H⁺) = = 0.50 M and an HF concentration not exceeding 0.04 M; our data indicate that in these conditions the ratio of the concentrations of $\operatorname{GeF}_6^{2^-}$ and $[\operatorname{GeF}_5(\operatorname{H}_2O)]^-$ may reach ~0.275, which corresponds to $\overline{i} = 5.2$. Under these conditions, however, considerable hydrolysis of $[GeF_5(H_2O)]^$ to [Ge(OH)F4(H2O)] and possibly to [GeF4(H2O)2] may occur, leading to a significant decrease in \overline{i} .

The numerical values of β_5' and β_4' relate to $[H^+] = 0.5$ M. The numerators of these ratios contain the sums of the

concentrations of all forms of fluorogermanate containing respectively five or four F atoms per Ge atom. If it is assumed that the predominant forms are [GeF₅(H₂O)]⁻ and [Ge(OH)F₄(H₂O)]⁻, the ratio β'_4/β'_5 should be close the constant for equilibrium (7). In actual fact, $\beta'_4/\beta'_5 \simeq 2.3 \times 10^{-2}$. The agreement with the above value is better than might have been expected.

With the same assumption, we can calculate the value of β'_5 from the values which we have obtained for the constants for equilibria (4) and (6), the dissociation constant of HF, and the solubility of GeO₂. Using for the latter the published value $s = 4.33 \times 10^{-2}$ M, ²⁰ we obtain $\beta'_5 = 0.80 \times$ $\times 10^8$, which differs from that found by Benoit and Place by less than one order of magnitude; the same discrepancy is observed in the case of the values of β'_{4} .

for the process

2. The standard free energies of formation of the ions GeF_6^{2-} , $[GeF_5(H_2O)]^-$, and $[Ge(OH)F_4(H_2O)]^-$ have been calculated. The equilibria in fluorogermanate solutions have been discussed. It has been shown that Benoit and Place 18. could not detect the existence of $\operatorname{GeF}_6^{2^-}$ in solution with the procedure and conditions which they used. The

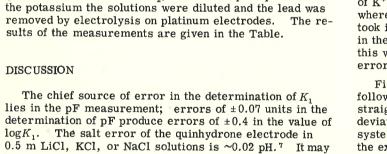


Fig. 1. Cell used to measure pH and pF:

0.5 m LiCl, KCl, or NaCl solutions is ~0.02 pH.⁷ It may be assumed that in ~0.5 m KF it has approximately the same value, which corresponds to an error of 0.08 in $\log K_1$. This error decreases with dilution of the KF solutions.

PbF.

Potassium in the equilibrium solutions was determined

gravimetrically as KBF₄⁶ after evaporation with HBF₄ and

HCl; repeated addition of HCl was necessary for the com-

plete removal of germanium. Solutions with lower initial

KF concentration (less than 0.03 m) contained appreciable

quantities of dissolved PbF_2 ; before the precipitation of

Initial KE	Results of measurements				Initial KF	Results of measurements			
concentra- tion, m	рF	pH	°K+	$-\log K_1$	concentra- tion, m	pF	рН	с ^{к+}	— log K _l
E	xperim	ents of :	lirst series		Ex	perimen	its of s	second ser	les
0.4996 0.2495 0.1248 0.0625 0.0313 0.0157 0.0078	0.614 0.875 1.37 1.70 1.94 2.18 2.36	$\begin{array}{c} 6.71 \\ 6.17 \\ 5.33 \\ 4.69 \\ 4.19 \\ 3.70 \\ 3.48 \end{array}$	$\begin{array}{c} 0.4734\\ 0.2506\\ 0.1329\\ 0.07546\\ 0.05701\\ 0.05066\\ 0.04620\\ \end{array}$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.2500 0.1249 0.0623 0.0312 0.0154	0.486 0.880 1.27 1.67 1.91 2.14 2.38	$\begin{array}{c} 6.66 \\ 6.10 \\ 5.38 \\ 4.73 \\ 4.25 \\ 3.79 \\ 3.47 \end{array}$	$\begin{array}{c} 0.4945\\ 0.2530\\ 0.1337\\ 0.07714\\ 0.05873\\ 0.05078\\ 0.04632 \end{array}$	30 J7 30 87 30 89 31 17 30 92 30 59 30 83
			Mean	30.99	1	10 II		Mean	30.78

The diffusion potentials, obtained by means of Henderson's equation⁸, were nearly zero in the most concentrated KF solutions; in the most dilute solutions they may exceed the pH or pF by ~ 0.02 .

Since it is difficult to estimate the activity coefficient of K⁺ (particularly in solutions with low KF concentration, where the concentration of K_2GeF_6 and PbF_2 is higher), we took its value as equal to unity. Since the power of γ_{K^+} in the expression for K_1 is low, the error introduced in this way is small compared with that produced by the errors in the pF measurement.

Fig. 2 shows a plot of $(\log c_{K^+} - 2pH)$ against 3 pF. It follows from Eqn. (2) that in the equilibrium systems a straight line should be obtained, with slope of unity. The deviations from linearity in Fig. 2 are random, and not systematic, confirming that equilibrium was reached in the experiments of both series and that the results of the measurements contain no systematic errors. The mean value of $-\log K$, found from the experiments of the first series is 30.99 ± 0.30 (standard deviation); the experiments of the second series gave $-\log K_1 = 30.78 \pm 0.32$. The mean value from the two series is $\log K_1 = -30.8_{\rm B} \pm$ ± 0.3 , or $K_1 = (0.65-2.7) \times 10^{-31}$. The straight line in Fig. $\hat{2}$ is drawn through the ordinate corresponding to the mean value of $\log K_{11}$

The solubility of K₂GeF₆ at 25° is c = 0.0221 m;⁹ this value shows good agreement with the value c = 0.0223 m.¹⁰

The degree of hydrolysis of GeF_{4}^{2-} in this solution is $z = 0.20.^{11}$ Assuming that the mean activity coefficients of K_2GEF_6 and K_2SO_4 are equal (at the same molality), we find $\gamma_{+} = 0.629$.¹² Thus the activity of saturated K, GeF₆ solution at 25° is

 $[K_{a}GeF_{6}]_{sat} = 4c^{3}(1-z)\gamma^{3} = 4 \times (0.0221)^{3} \times 0.8 \times (0.629)^{3} = 8.6 \times 10^{-6}.$ Substituting this value in Eqn. (5), we find that at 25°

 $\log K = -25.8, \pm 0.3,;$ $K = (0.76 - 3.2) \times 10^{-26},$



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The equilibrium constant for the process

$$[GeF_{\mathfrak{g}}(H_{2}O)]^{-} + H_{2}O \rightleftharpoons [Ge(OH)F_{\mathfrak{q}}(H_{2}O)]^{-} + HF,$$

calculated from our data ^{1,11}, is $\sim 2 \times 10^{-2}$. At [HF] = 0.04 M, the ratio of the concentrations of [Ge(OH)F₄(H₂O)]⁻ and $[GeF_5(H_2O)]^-$ is ~0.5 and the corresponding value of i is ~4.67. For the formation of $[GeF_4(H_2O)_2]$, which is possible in strongly acidic solutions, i undergoes a further decrease.

Benoit and Place calculated the ratios

$$\begin{split} \beta_{5}^{\prime} &= \frac{\sum\limits_{j=N-1}^{j=N-1} (Ge(OH)_{j}F_{\bullet})}{(GeO_{2}) (HF)^{5}} = (8.8 \pm 0.2) \times 10^{8} \, , \\ \beta_{5}^{\prime} &= \frac{\sum\limits_{j=N-1}^{j=N-1} (Ge(OH)_{j}F_{\bullet})}{(GeO_{2}) (HF)^{4}} = (2.0 \pm 0.3) \times 10^{7} \, . \end{split}$$

SUMMARY

1. Measurements of the pH, pF, and K⁺ ion concentrations in solutions saturated with K_2GeF_6 and GeO_2 at 25° have been used to obtain the following equilibrium constants:

for the process

 $K_{a}GeF_{6}(cryst.) + 2II_{2}C \iff GeO_{2}(hex.) + 4II^{+} + 6F^{-} + 2K^{+},$ $\log K_{_{298}}=-30.8_{_{8}}\pm0.3_{_{1}};$

> $\operatorname{GeF}_6^{2^*} + 2\operatorname{Il}_2 O \rightleftharpoons \operatorname{GeO}_2(\operatorname{hex.}) + 4\operatorname{Il}^+ + 6\operatorname{F}_6^*$ $\log K_{398} = -25.8_1 \pm 0.3_1.$

> > 999

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"constants" β'_4 and β'_5 found by Benoit and Place show satisfactory agreement with the values calculated from the results of our studies.

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Dnepropetrovsk Institute of Railway Transport Engineers

Dnepropetrovsk Chemical Technology Institute

U.D.C. 546.719.5-386

Received 20th June 1964

ETHYLENEDIAMINE COMPLEXES OF RHENIUM(V)

L. I. Evteev

Ethylenediamine complexes of rhenium(V) were first prepared by Lebedinskii and Ivanov-Emin¹, who observed the interconversion of these compounds and noted the

formation of a sparingly soluble green precipitate. It was suggested that the green salt is formed by two complex ions with a structure analogous to that of Magnus' green salt[†].² Tronev and Babeshkina³ prepared a monoethylenediamine complex of rhenium ReO, Ent. Our experiments established the structure of the complexes of rhenium(V) with ethylenediamine.

EXPERIMENTAL

Preparation of the Yellow Compound [Re(OH)2(En-)2]C1§

20-30 g K₂[ReCl₆] were dissolved in 500 ml water and 40 ml ethylenediamine were added. A black liquid formed immediately and this was poured into a 30×40 cm enamelled photographic dish to give a layer of thickness $\sim 3-5$ cm. The black products of the hydrolysis of rhenium(IV) were oxidised by atmospheric oxygen, partly to Re^V and partly to Re^{VI} . Oxidation was continued for 7–10 d. It was found that the thinner the layer of solution, the more rapid the formation of a transparent yellow-brown liquid. The resulting solution was evaporated in a vacuum to two--thirds of its initial volume and cooled to room temperature, after which the vacuum was released. When the liquid evaporated too rapidly, so that it deposited crystals of a yellow salt, water was added in small portions until the yellow crystals dissolved completely. The liquid was then cooled with ice for 2-3 h. The resulting white crystals of $KReO_4$ were filtered off. The filtrate was again evaporated in a vacuum until the yellow salt $[Re(OH)_2(En^-)_2]Cl$ began to crystallise. The solution was then cooled to room temperature and the vacuum was released. The resulting crystals of [Re(OH)₂(En⁻)₂]Cl were filtered off, washed with 80% alcohol, and dried first in air to remove the alcohol and then to constant weight in a desiccator over CaCl, (crystal fraction 1). Mean analyses are given.

Found, %: Re 49.71; Cl 9.51; N 14.90. Valency 4.88.

Calculated for [Re(OH)₂(En⁻)₂]Cl, %: Re 49.80; Cl 9.48; N 14.98. Valency 5.

Treatment of the mother-liquor with an equal volume of alcohol gave a further quantity of the yellow complex $[\text{Re}(OH)_2(\text{En}^-)_2]$ Cl. The alcoholic mother-liquor remaining after the separation of [Re(OH)₂(En⁻)₂]Cl was dark red (almost black) due to the reaction products of ethylenediamine. The results in Table 1 show that the reaction gave approximately 50% [Re(OH)₂(En⁻)₂]Cl and 50% KReO₄.

In some experiments, when the oxidation was not complete, a small quantity of black product formed at the bottom of the flask. This was filtered off, washed with water, dried, and analysed

- Substance 1. Found, %: Re 61.59; Cl 0; N 6.23. Valency 4.08.
- Substance 2. Found, %: Re 62.32; Cl 0; N 5.35. Valency 4.11.

Calculated for Re(OH)₄.2H₂O, %: Re 64.15; C1 0; N 0. Valency 4.0.

\$ En represents ethylenediamine which has lost a proton. NH₂CH₂CH₂NH⁻.

Material balance for the preparation of the
yellow salt [Re(OH) ₂ (En ⁻) ₂]Cl.

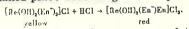
K. ReCl. taken,	(Re(OH))		KReO ₄	obtained	Molar ratio [Re(OH) ₂ (En°) ₂]Cl	
9	g*	%	Ø	%	KReO4	
27.0 32.0 21.0	10.5 11.0 8.7	48.3 43.7 48.0	6.8 9.2 6.2	41.5 47.4 48.7	1.19 0.90 0.99	

* The sum of the crystals of the first fraction and the crystals obtained by precipitation with alcohol.

The results show that the black substance is probably a mixture of $[Re(OH)_{s}(En^{-})]$ and $Re(OH)_{4}$. $nH_{2}O$.

To investigate the structure of the complex, we recorded the infrared spectrum of [Re(OH)2(En-)2]Cl in liquid paraffin on an IKS-14 instrument with LiF prism (Fig. 1a). The spectrum has a broad absorption band at 3470 cm⁻¹, probably due to the hydroxyl group. Measurement of the electrical conductivity of the yellow salt showed that it dissociates in solution to give two ions and is not hydrolysed (Tables 2 and 3). The mobility of the complex cation $[\text{Re}(OH)_2(\text{En}^{-})_2]^{\dagger}$ is 27 Ω^{-1} cm². Direct chromatographic determination of the charge on the complex cation gave the value +1.06. Measurement of the pH of the solutions (Table 4) showed that the yellow complex has weak alkaline properties. At a concentration of the complex of 10-4 M the reaction of the medium is due to acidic impurities, chiefly CO₂ from the atmosphere.

[Re(OH)2(En-)2]Cl also exhibits alkaline properties in the solid state (Table 5). When treated with dry HCl in a desiccator, it absorbs one mole of HCl per mole of salt. The reaction takes place according to the equation: (1)



The absorption spectrum of an aqueous solution of [Re(OH), (En⁻), [Cl in the visible range (Fig. 2) shows maxima at 300 nm and 440 nm.

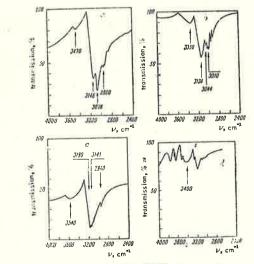


Fig. 1. Infrared spectra of the compounds:

- a) $[\operatorname{Re}(\operatorname{OH})_2(\operatorname{En}^-)_2]Cl;$ b) $[\operatorname{Re}(\operatorname{OH})_2(\operatorname{En}^-)\operatorname{En})]Cl_2;$
- c) $[\operatorname{Re}(OH)\operatorname{Cl}(\operatorname{En}^{-})\operatorname{En}][\operatorname{Re}\operatorname{Cl}_{6}]; d) [\operatorname{Re}(OH)\operatorname{Cl}_{2}(\operatorname{En}^{2-})].$

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TABLE 2. Dependence of the electrical conductivity of a solution of the yellow salt [Re(OH)2(En)2]Cl on dilution at 25°. Dilution, Amcorr

litre mole ^{•1}	Ω ⁻¹ cm ^a
1000	102.9
2000	103.0
4000	104.2
8000	104.1

TABLE 3. Time dependence of the electrical conductivity of [Re(OH)2(En-)2]Cl at a dilution of 1000 litre mole⁻¹.

Time	Λ _{m corr} Ω ^{r1} cm ²	Time	$\Lambda_{m corr}$ $\Omega^{a_{cm}^{a}}$
5 min 10 min 30 min 1 b	102.8 102.9 102.8 102.9	2 h 5 h 24 h	102.9 103.0 103.0

TABLE 4. Change in the pH of [Re(OH)₂(En⁻)₂]Cl solution with

time.

Time

5 min 10 min 20 min 30 min 1 h 2 h 3 h 5 h 24 h

1	[Re(OH),(En"),]CI concentration, M						
	c = 0.1335	c =		$c = 1.7 \times 10^{48}$	$c = 10^{-4}$		
	pH of water 6.11	solution	watar	pH of water 6.20	pH of water 6,02		
	7.59 7.59 7.59 7.61 7.61 7.61 7.61 7.60 7.63	$ \begin{array}{r} 6.13 \\ 6.20 \\ 6.22 \\ 6.26 \\ 0.32 \\ 6.32 \\ 6.32 \\ 6.66 \\ \end{array} $	6,16 6,13 6,02 5,87 5,85 5,80 5,80 5,80 5,80 5,80	6.20 6.22 6.24 6.24 6.28 6.30 5.30 6.35 6.35	6.05 6.01 6.00 5.97 5.96 5.96 5.97 5.99		

TABLE 5. Titration of the yellow salt [Re(OH)2. .(En⁻)₂]Cl with gaseous HCl.

[Ka(OH);(En*);]Cl taken, g	Weight of specimen after absorp- tion of HCL, g	HCI absorbad, 9	Molar ratio HCI salt	
0.2535	0.2783	0.0248	0.977	
0.1733	0.1904	0.0171	1.010	
0.2773	0.3047	0.0274	1.011	

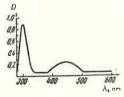


Fig. 2. Absorption spectrum of aqueous [Re(OH)₂(En⁻)₂]Cl solution.

^{1.} I.G.Ryss and N.F.Kulish, Zhur. Neorg. Khim., 9, 1103 (1964) [Russ. J. Inorg. Chem., 603 (1964)].

^{† [}Pt(NH₃)₄][PtCl₄] (Ed. of Translation).

[‡] En represents ethylenediamine.