Ammonium hydroxide forms very small colorless crystals which suggest those of sodium and potassium hydroxides; those of $2NH_3,H_2O$, which may be called ammonia semi-hydrate, or may possibly be written $(NH_4)_2O$, ammonium oxide, are much larger, transparent and needle-shaped. Solutions containing from about 25 to 60 per cent. ammonia are very viscous at temperatures below about —60°. At —100° the 33 per cent. solution can hardly be stirred.

The weighings are subject to some small error from accumulated moisture and other causes. Another series of freezing points will be found, with more accurate weighings and with points nearer together, and possibly other properties of the system will be investigated.

UNIVERSITY OF KANSAS, LAWRENCE, KANS.,
April 17, 1909.

THE VELOCITY OF HYDROLYSIS OF AN INORGANIC SALT, POTASSIUM RUTHENIUM CHLORIDE.

BY S. C. LIND AND F. W. BLISS.

Received June 16, 1909.

1. Introduction.—The kinetics of the hydrolysis of inorganic salts has been relatively little studied for two reasons. Most inorganic salts which hydrolyze in aqueous solution do so instantaneously, and in those cases where the rate is measurable, the difficulties of measurement and the number of factors influencing the velocity have rendered the kinetics so complex that, as far as we are aware, a satisfactory kinetic equation has not been established for the hydrolysis of a single purely inorganic salt. On the other hand, the equilibria of salt hydrolyses have been extensively studied and shown by the investigations of Arrhenius,[1] Walker,[2] Shields,[3] and others, to be in accord with the Guldberg-Waage Law of Mass action.

Among the inorganic salts composed of a weak base and a strong acid and which hence liberate acid on hydrolyzing, several cases of time reaction have been observed and studied by means of the rise in electrical conductivity. Among others should be mentioned $FeCl_3$ (H. M. Goodwin, *Z. physik. Chem.*, **21**, 1); $AuCl_3$, $SnCl_4$, $PtCl_4.H_2O$ (F. Kohlrausch, *Ibid.*, **33**, 257, and *Wied. Ann.*, **64**, 423); $AuCl_3$ (Hittorf and Salkowski, *Ibid.*, **28**, 546). There is, however, in general, one marked difference between organic and inorganic hydrolyses aside from their extreme differences in rate, namely that, while the presence of acid accelerates the velocity of the former it retards that of the latter. Also in the former, the equilibrium is unaffected, but in the latter is shifted by the presence

---

[1] Arrhenius. *Z. physik. Chem.*, **5**, 16; **13**, 407.

[2] Walker, *Ibid.*, **4**, 333.

[3] Shields. *Ibid.*, **12**, 167.

of acid. The recent important researches of Stieglitz[1] and his co-workers have rendered it very probable that the theory of "salt formation" is the correct explanation of the catalysis of organic hydrolyses. As to the retarding effect of acid on inorganic hydrolyses, it has been generally regarded as concommitant with and corresponding to the known repression of the equilibrium by acid. This of course assumes a reversible reaction. It will be part of the purpose of this paper to show that also in a reaction found to be irreversible, acid exerts a retarding influence which is approximately proportional to the hydrogen ion concentration. Hence the assumption that it is the water molecule which is the direct hydrolyzing agent does not seem probable but rather that it is the hydroxyl ion. As one may easily convince himself, either assumption gives the same equilibrium equation, but the conditions would be entirely changed for the velocity equations.

2. *The Hydrolysis of Potassium Rutheno-chloride.*—Incidental to a study, suggested by Prof. J. L. Howe, of the structure of a few double salts of ruthenium, one[2] of us found that the above salt (K_2RuCl_5) undergoes, in aqueous solution, a large rise in electrical conductivity accompanying hydrolysis. The reaction sets in at once even in the most concentrated solutions of the salt which can be prepared (about 1/140 m.) and as it proceeds the original orange red color of the solution darkens to an inky black. The completely hydrolyzed solution has the general appearance of a colloid. Traces of precipitation appear on standing a few days, but the dark color is not perceptibly diminished even after filtering a solution which had stood for two years. Centrifugation and the addition of the common colloidal precipitants usually fail to produce precipitation though in one or two instances partial precipitation has resulted. Addition of alkali to the black hydrolyzed solution produces immediate and complete precipitation of the ruthenium as $Ru(OH)_3$, thus indicating that most of the ruthenium was, in some form, still in the field of action. The residue from a portion of the black solution taken to dryness *in vacuo* over sulphuric acid, after standing several months in the desiccator, was treated with water. The black color was immediately restored, a considerable portion of the residue going back into solution. The filtrate from this residue still possessed some conductivity.

The final state reached by the reaction does not, as will be later shown, represent a reversible equilibrium. Migration experiments in agar jelly, such as were described for K_2RuCl_5NO, (*loc. cit.*) showed the dark color migrating only to a limited extent and that in both directions. This may

---

[1] J. Stieglitz, *Amer. Chem. J.*, **39**, 29–63, 166–183, 402–431. I. H. Derby, Wm. McCracken, I. Schlesinger, Dissertations, Chicago, 1908.

[2] Lind, THIS JOURNAL, **25**, 928 (1903).

have been wholly colloidal or suspended, or became so, for the color could not be removed later from the jelly plug by immersion in water. The evidence then as to the final state of the hydrolysis indicates that the hydrolyzed product remains partly in a true state of solution possessing some conductivity, while a smaller part passes into the colloidal state and may gradually be precipitated.

The reaction may be provisionally written:

$$K_2RuCl_5 + 2H_2O = 2KCl + 2HCl + Ru(OH)_2Cl.$$

The conductivity reached at the end of the reaction corresponds well with the demands of this equation, if one allows a small amount of conductivity for the ruthenium compound (in whatever state it may be) after hydrolysis, which has been experimentally justified, as mentioned above.

The samples used in the first experiments with this and other ruthenium salts were kindly furnished one of us by Prof. Howe. The rate measurements made at that time by following the rise in conductivity were not published, as it was discovered too late for correction that they had been subject to a large catalytic influence through remaining the whole time in contact with the platinum electrodes. (The acceleration amounts to about 50 per cent. in the Ostwald form of cell.)

However, it may be stated that the primary object of those experiments was to find the initial value of molecular conductivity of 0.005 molar K_2RuCl_5 at 22°, by extrapolating the velocity curves. For this purpose the results were satisfactory, showing for μ a value of about 100 recip. ohms, from which one is justified in assuming that K_2RuCl_5, like K_2RuCl_5NO, is dissociated into 2 K ions and one $RuCl''_5$ ion.

It seemed of interest to devote further study to this reaction in the hopes of giving it kinetic significance. A completely new set of velocity measurements has been made and directed to the investigation of the following factors: temperature, dilution, acid concentration, auto-catalysis, foreign salts, and sunlight.

3. *Preparation and Analysis of the Salt.*—Ruthenium residues from previous experiments were fused with sodium peroxide and the resulting melt containing sodium ruthenate (Na_2RuO_4) was dissolved in water. A stream of chlorine was passed through this solution heated almost to boiling, and ruthenium tetroxide was distilled off and collected in the cold. The liquid tetroxide, which must be used without delay on account of its rapid decomposition into lower oxides, was poured into strong hydrochloric acid and digested on the steam-bath until evolution of chlorine ceased (required about two days). To the resulting strongly acid solution of ruthenium trichloride was added potassium chloride in small quantities, and a precipitate of K_2RuCl_5 crystals formed which

were filtered and washed acid-free with alcohol and dried by evacuation over sulphuric acid.

The analysis of the salt was carried out by heating a sample gently in a porcelain boat contained in a glass tube through which a stream of pure hydrogen was passing. This results in the removal of the three chlorines associated with the ruthenium, leaving behind a residue of metallic ruthenium and potassium chloride from which the latter is dissolved, and later precipitated with silver nitrate, while the ruthenium is dried in an atmosphere of hydrogen and weighed. The results of the analysis were as follows:

		Found.		
	Theory.	I.	II.	III.
3Cl	29.77	29.98	29.77	31.10
2KCl	41.76	41.60	41.92	41.47
Ru	28.47	28.47	28.36	27.33

4. *Method and Apparatus.*—On account of the contact influence of both platinized and bright platinum electrodes (the effect of the former being greater than that of the latter), it was necessary to have the solutions in contact with the electrodes only during the actual time of measurement. The Ostwald type of cell was used and the cell and electrodes were rinsed with conductivity water and dried with the purest filter paper after each measurement.

The Kohlrausch method was used, the bridge being of the rotary type with a carefully calibrated manganine wire nearly three meters in length. The thermostats were of the usual Ostwald type and were kept constant within a few hundredths of a degree.

All solutions were prepared by adding a weighed amount of salt to a weighed amount of the solvent at the desired temperature, correction, of course, being made for temperature and air displacement, and the specific gravity of the solutions of acid or salt used as solvents being taken into account. The assumption was made that for the concentrations employed, 0.005 to 0.00125 molar, the volume of solution would be sensibly equal to that of the solvent.

The time was in all cases counted in minutes beginning with the addition of the finely ground salt to the solvent. The time for the salt to go into solution is thus included with that for the reaction. Since the former depends upon several factors not easy to control with accuracy, it was found in reproducing experiments that small time shifts in the velocity might be produced, the actual rate, however, or slope of the curve remained the same, and the two could be made to coincide by a slight transposition along the time axis. But as will be seen later, our method of obtaining the velocity constant is independent of the time of starting the reaction.

5. *The Velocity Constant.*—In this hydrolysis one meets with the unusual case of a reaction apparently in homogeneous solution, which has a constant rate over a considerable part of its course. This enables one to obtain a velocity constant (k) simply by dividing the increase in conductivity during the constant portion by the time and multiplying by the dilution. The justification for this empirical procedure is to be seen in the extent of the constant portion of the rate, and in the fact that this portion falls in about the same part of the course under all conditions, and is furthermore just that portion in which one is usually most interested in velocity measurements, the first two-thirds. The significance of this constant will be discussed after the experimental results have been presented.

Of course the rise in conductivity does not correspond exactly with the rate of the hydrolysis, because for the same amount of acid set free the rise in conductivity produced will depend upon the temperature and the amount of acid or other substances already in solution. As far as possible, corrections have been made for these influences.

In finding the rate, the values found for specific conductivity by actual experiment are first plotted, the unmistakable straight line portion is then noted, and the rate computed between the two observations nearest the ends of the straight line. The corrections above mentioned are then made on this rate furnishing a corrected rate; and finally, the velocity constant is obtained by multiplying by the dilution. The reproduction of many of the plots has been omitted for the sake of brevity.

6. *The Autocatalytic Influence.*—In his studies of the hydrolysis of ferric chloride, Goodwin (*loc. cit.*) found a pronounced induction period during which little or no conductivity increase occurred, followed by an accelerated rate leading to a maximum. In a later paper he and Grover[1] showed that this is due to the *autocatalytic action* of the colloidal ferric chloride formed in the reaction. Their proof was furnished by diluting ferric chloride solutions with some of the hydrolyzed solution from which other substances had been removed by dialysis, and comparing this rate with that of a solution similarly diluted with water.

In the case of K_2RuCl_5, although the reaction begins apparently at its maximum rate, it was suspected that it might also be autocatalytic. Instead of removing the acid from the completely hydrolyzed solution the opposite course was followed, namely, a solution (*b*) was prepared having the same concentration of HCl and KCl as a portion (*a*) of the completely hydrolyzed solution. Solutions (*a*) and (*b*) were then identical except (*a*) contained 0.005 molar $Ru(OH)_2Cl$. Two 25 cc. portions of a 0.005 molar K_2RuCl_5 solution which had been in action for about ten minutes were simultaneously diluted with 25 cc. each of (*a*)

---

[1] Goodwin and Grover, *Phys. Review*, 11, 193 (1901).

and (*b*), and from this point on the rates were compared. As will be seen from Table I and the corresponding curves 1 and 2, Plot 1, the former showed a rate about double that of the latter. The reaction was thus proved to be autocatalytic, and this conclusion was later confirmed by the results from the hydrolyses begun in acid solution which showed a distinct *induction period* (cf. curves 4, 5 and 6, plot 2).

TABLE I.—AUTOCATALYSIS. (Cf. curves 1 and 2, plot 1.)

Catalyzed with $Ru(OH)_2Cl$.		Not catalyzed.	
Time in minutes.	Sp. cond. in 1/ohms.	Time in minutes.	Sp. cond. in 1/ohms.
5	0.003915	6	0.003882
23	0.004073	23 3/4	0.003975
44	0.004314	46 3/4	0.004069
76 1/2	0.004753	67 1/2	0.004237
108	0.005132	109	0.004430
133	0.005367	134	0.004606
165	0.005642	164	0.004824
229	0.005815	226	0.005215
292	0.005849	290	0.005506
30 days	0.006070	30 days	0.006093
Const. rate =	0.0_4125	*Const. rate* =	0.0_5649
k =	**0.00500**	**k** =	**0.00260**

7. *Influence of Temperature.*—To determine the temperature coefficient of the reaction, measurements were made at 22°, 25°, and 30° of solutions 0.005, 0.0025 and 0.00125 molar, the results of which are given in Tables II, III and IV and a summary in Table V (cf. curves 3, 4 and 5, plot 1).

TABLE II.—INFLUENCE OF TEMPERATURE AT CONCENTRATION 0.005 MOLAR.

Temp. 22°.		Temp. 25°.		Temp. 30°.	
Time in minutes.	Spec. cond. in 1/ohm.	Time in minutes.	Spec. cond. in 1/ohm.	Time in minutes.	Spec. cond. in 1/ohm.
7	0.001287	9	0.001586	9	0.002106
25	0.001722	20	0.001978	18	0.002652
50	0.002134	30	0.002293	24	0.003013
81	0.002605	50	0.002812	33	0.003532
110	0.003037	75	0.003441	43	0.004056
140	0.003466	95	0.003910	53	0.004529
165	0.003804	122	0.004444	63	0.004949
247	0.004670	150	0.004907	88	0.005695
327	0.005218	267	0.005883	213	0.006284
2 days	0.005614	23 days	0.006103	393	0.006366
Rate =	0.0_4152	*Rate* =	0.0_4249	*Rate* =	0.0_4565
Corr. rate =	0.0_4159	*Corr. rate* =	0.0_4249	*Corr. rate* =	0.0_4520
k =	**0.00318**	**k** =	**0.00498**	**k** =	**0.01040**

It will be observed that the value of about *3.0* for a temperature interval of only 8° is considerably higher than the classical *2.0* to *2.2* for

TABLE III.—INFLUENCE OF TEMPERATURE AT CONCENTRATION 0.0025 MOLAR.

Temp. 22°.		Temp. 25°.		Temp. 30°.	
Time in minutes.	Sp. cond. in 1/ohm.	Time in minutes.	Sp. cond. in 1/ohm.	Time in minutes.	Sp. cond. in 1/ohm.
10	0.000923	5	0.000736	6	0.001037
25	0.001054	13	0.000938	10	0.001208
45	0.001309	19	0.001074	15	0.001415
70	0.001670	24	0.001157	20	0.001626
105	0.002043	29	0.001244	30	0.002063
120	0.002252	46	0.001571	40	0.002462
179	0.002667	76	0.002125	55	0.002956
219	0.002805	155	0.002935	75	0.003222
378	0.002899	424	0.003037	95	0.003279
36 hrs.	0.002942	3 days	0.001399	2 days	0.003311
Rate =	0.0_4126	*Rate* =	0.0_4184	*Rate* =	0.0_4428
Corr. rate =	0.0_4130	*Corr. rate* =	0.0_4180	*Corr. rate* =	0.0_4385
k =	**0.00520**	**k** =	**0.00720**	**k** =	**0.01540**

TABLE IV.—INFLUENCE OF TEMPERATURE AT CONCENTRATION 0.00125 MOLAR.

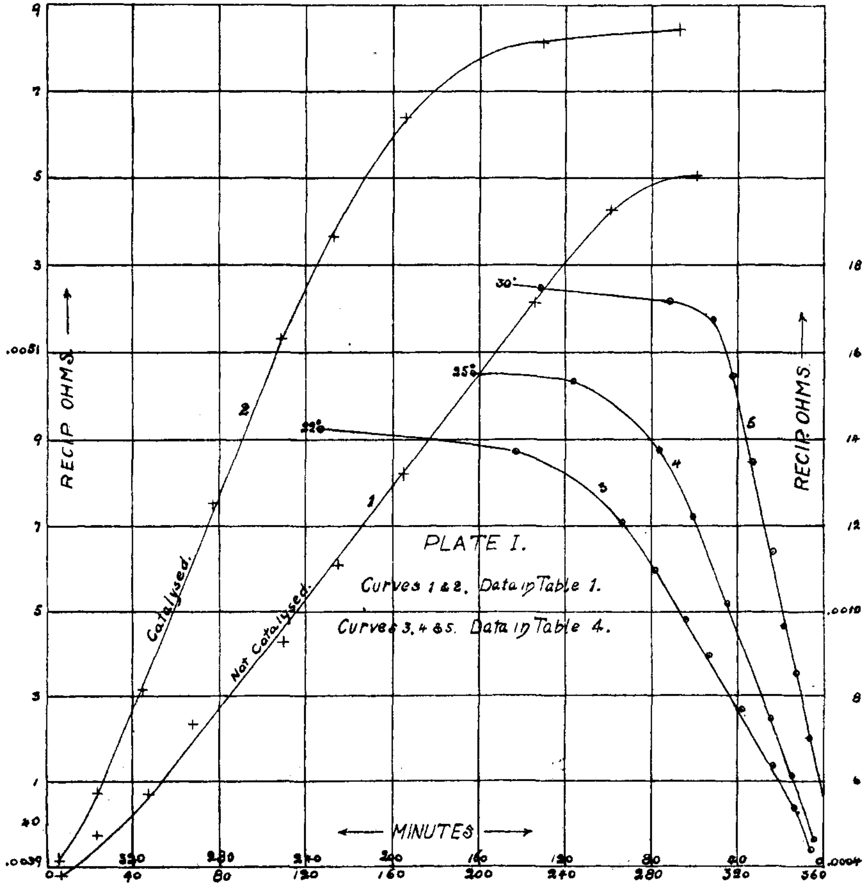
Temp. 22°.		Temp. 25°.		Temp. 30°.	
Time in minutes.	Sp. cond. in 1/ohm.	Time in minutes.	Sp. cond. in 1/ohm.	Time in minutes.	Sp. cond. in 1/ohm.
6	0.0004411	5	0.0004641	7	0.0007013
14	0.0005399	15	0.0006117	9	0.0007352
24	0.0006361	25	0.0007499	13	0.0008578
39	0.0007678	45	0.001022	18	0.0009682
54	0.0008964	61	0.001225	23	0.001141
79	0.001099	77	0.001378	32	0.001363
94	0.001209	160	0.001554	52	0.001678
434	0.001449	283	0.001569	72	0.001715
3 days	0.001466	17 days	0.001633	2 days	0.001772
Rate =	0.0_5880	*Rate* =	0.0_4140	*Rate* =	0.0_4266
Corr. rate =	0.0_5888	*Corr. rate* =	0.0_4134	*Corr. rate* =	0.0_4234
k =	**0.00710**	**k** =	**0.01072**	**k** =	**0.01872**

TABLE V.—SUMMARY ON THE INFLUENCE OF THE TEMPERATURE.

K_2RuCl_5 conc.	Solvent.	Temp.	*k*.	Temp. coefficients.	
0.005	H_2O	22°	0.00318	1.57	3.27
		25°	0.00498	2.09	
		30°	0.01040		
0.0025	H_2O	22°	0.00520	1.39	2.96
		25°	0.00720	2.14	
		30°	0.01540		
0.00125	H_2O	22°	0.00710	1.51	2.64
		25°	0.01072	1.75	
		30°	0.01872		
0.0025	HCl 0.01 N	22°	0.00108	1.89	4.67
		25°	0.00204	2.47	
		30°	0.00504		

a 10° interval, but is not higher, however, than has been found in several other instances (cf. Trautz and Volkmann, *Z. physik. Chem.*, **64**, 63 (1908)). It is also to be noted that the temperature coefficients show a tendency to decrease with decreasing salt concentration. Since the less concentrated solution is the faster, as will be seen later in Table VI, we may say that the faster reaction receives the less acceleration by a rise in temperature. The reactions in acid solution show full accord with this statement, for, being much slower, they show a much higher temperature coefficient (cf. Table V).

8. *Influence of Dilution.*—It is well known that dilution increases the tendency for hydrolysis to take place. The data in Tables II, III and IV will serve in giving a quantitative measure of the effect of dilution at three different temperatures. In Table V a summary is given including the velocities of reactions begun in acid solution for which one may have dilutions of two kinds. Either the dilution of the salt



may be changed while the acid remains constant, or both may be diluted so that their ratio remains constant. The latter represents a condition most nearly parallel to dilution of the salt in aqueous solution where there will always be some acid resulting from hydrolysis, which is, of course, diluted with the salt. On the other hand, dilution of the salt in constant acid appears to have no accelerating effect upon the rate, but rather to produce in most cases a small retardation.

TABLE VI.—SUMMARY ON THE INFLUENCE OF DILUTION.

K_2RuCl_5.	Solvent.	Temp.	*k*.	Dilution coefficient.	
				2 fold.	4-fold.
0.005	H_2O	22°	0.00318	1.63	2.24
0.0025	H_2O	22°	0.00520	1.37	
0.00125	H_2O	22°	0.00710		
0.005	H_2O	25°	0.00498	1.45	2.15
0.0025	H_2O	25°	0.00720	1.49	
0.00125	H_2O	25°	0.01072		
0.005	H_2O	30°	0.01040	1.48	1.80
0.0025	H_2O	30°	0.01540	1.22	
0.00125	H_2O	30°	0.01872		

(*a*) *Salt and acid diluted correspondingly.*

K_2RuCl_5.	In acid, HCl.	Temp.	*k*.	2 fold.	4-fold.
0.005	0.04	25°	0.00041	2.22	4.93
0.0025	0.02	25°	0.00091	2.22	
0.00125	0.01	25°	0.00202		
0.005	0.02	25°	0.00098	2.08	....
0.0025	0.01	25°	0.00204		

(*b*) *Salt diluted. Acid constant.*

K_2RuCl_5.	In acid, HCl.	Temp.	*k*.	2 fold.	4-fold.
0.005	0.01	25°	0.00173	1.18	1.17
0.0025	0.01	25°	0.00204	0.99	
0.00125	0.01	25°	0.00202		
0.005	0.02	25°	0.00098	0.93	0.86
0.0025	0.02	25°	0.00091	0.92	
0.00125	0.02	25°	0.00084		
0.005	0.04	25°	0.00041	0.89	0.94
0.0025	0.04	25°	0.00037	1.05	
0.00125	0.04	25°	0.00039		

One finds that the dilution coefficient is not exactly the same at different temperatures, which is similar to the observation made in regard to the temperature coefficients at different dilutions. The tendency is for the reaction at the lower temperature, and hence the slower reaction to receive the greater impulse by dilution; the solutions in acid of class (*a*) (cf. Table VI) show agreement in exhibiting higher coefficients than the aqueous solutions.

The following general principle may then be stated with respect to the influence of dilution or change of temperature. *The slower reaction, whether owing to temperature, dilution, or acid influence, receives the greater acceleration either from rise in temperature or increase in dilution.* This principle is purely empirical and we have no theoretical explanation to offer.

It may also be of interest to note that the acceleration produced by doubling the dilution is roughly equal to that upon increasing the temperature three degrees.

9. Attempts to Shift the Equilibrium.—After a solution of K_2RuCl_5 has stood from two or three days to two weeks, depending on the concentration and acid content, the rise has either ceased or become so slow as to be difficult to measure with certainty. The following tests were made on such a solution to ascertain whether the final state reached is a reversible equilibrium.

First, enough hydrochloric acid was added to a hydrolyzed solution of 0.005 molar K_2RuCl_5 to bring the total acid concentration up to about 0.04 *N*. The specific conductivity immediately after the addition of the acid was 0.01317 recip. ohms and after two days' standing was practically identical, 0.01316. This total absence of effect of acid upon the equilibrium becomes more significant when compared with the large effect of 0.04 HCl on the rate, where, as will be later shown, a more than tenfold retardation is produced. This also agrees with the qualitative observation that the reaction cannot be reversed even by strong acid, judging by the color.

Second, the dilution of a completely hydrolyzed solution was doubled by the addition of water. An immediate measurement gave a conductivity of 0.001617 at 25° and after two days it was still 0.001616.

Third, a hydrolyzed solution was heated to about 60° and then rapidly cooled to its original temperature, 25°. No change in conductivity was observed.

Since dilution, change of temperature, and addition of acid produce apparently no shift in the equilibrium, we must conclude that the reaction is irreversible and hence does not reach a homogeneous equilibrium. This conclusion is also in agreement with that reached by Malfitano and Michel in regard to the irreversibility of the hydrolysis of ferric chloride by hydrochloric acid (cf. *C. r.*, **145**, 1275).

10. Retardation by Acid.—Having seen the reaction to be irreversible, there remains no reason to predict that acid should have a retarding effect on the rate if we write the reaction:

$$K_2RuCl_5 + 2H_2O \longrightarrow 2KCl + 2HCl + Ru(OH)_2Cl.$$

It is, however, well known that acid always has a retarding influence on such hydrolyses. Malfitano and Michel[1] have been, as far as we are aware, the only ones to measure the rate of hydrolysis of an inorganic salt ($FeCl_3$) in solutions containing initial acid. Their study was more directed to the complete repression of the hydrolysis by acid as influenced by temperature, concentration of the salt or acid, and the period in which the acid was added. They found complete repression possible if the addition was initial or during the *induction period* (they do not use this term). After the induction period was passed they found that acid can only retard but not prevent hydrolysis. They found the acid concentration necessary to prevent hydrolysis to be much smaller than that produced by the reaction itself on going to completion, but to be greatly increased at a higher temperature. In their third paper (*loc. cit.*) Malfitano and Michel have studied the specific effect of the valence of the anion of the acid, and find that the retardation is more affected by the specific nature of the anion than by the hydrogen ion concentration. This result seems to us not at all unexpected if one consider the strong tendency of some of the acids used by them, to form undissociated ferric salts in solution and thus remove iron from the field of hydrolysis (*e. g.*, phosphoric and oxalic acids).

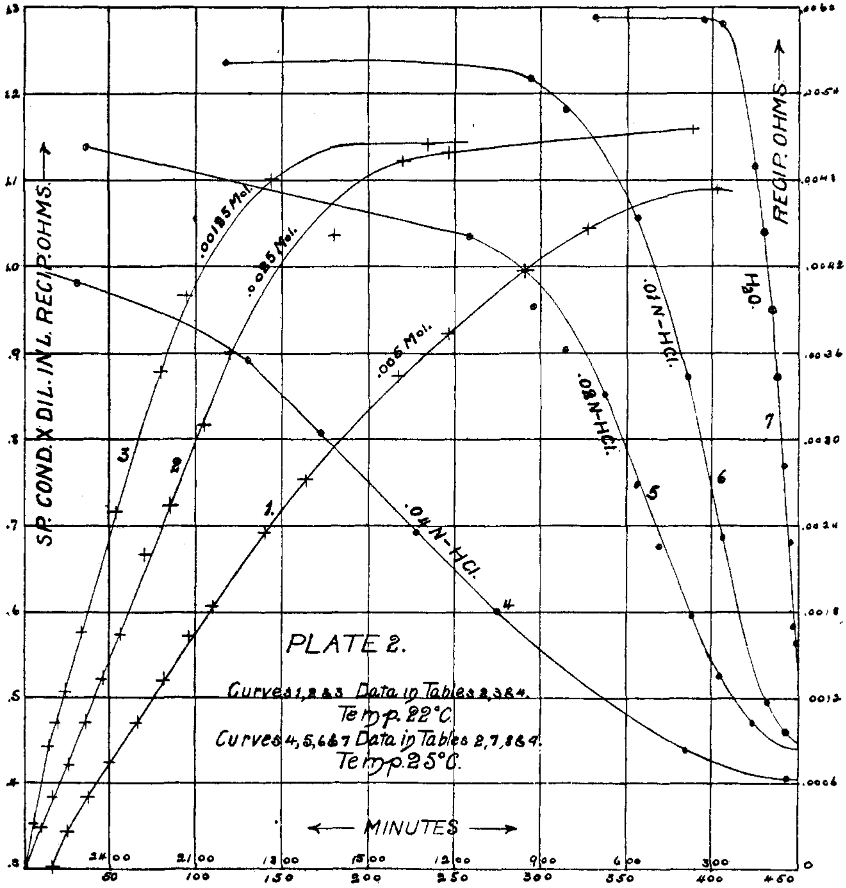
Before knowing of the work of Malfitano and Michel, we had also in the present investigation begun the study of the retarding effect of hydrochloric acid on the hydrolysis of K_2RuCl_5, but from a different point of view. We were not concerned with the specific effect of the anion but solely with the effect of the hydrogen ion concentration and have hence confined ourselves to the use of hydrochloric acid of varying dilutions. We have also made no attempt to study the concentration of acid necessary to prevent hydrolysis, which would be much greater than in the case of ferric chloride since an acid of several times the concentration of that produced by the reaction itself is in this case not sufficient to prevent hydrolysis, and the conductivity method becomes unsuitable to measure small changes in the presence of so much acid. It may be said, however, in passing, that in our opinion the induction period, as interpreted by Goodwin and Grover (*loc. cit.*) and as further developed in this paper for the reactions taking place in initial acid, will explain all the observations of Malfitano and Michel in regard to the ability of hydrochloric acid to stop the reaction in its earlier but not in its later stages, without the assumption of consecutive reactions which they make.

For the results of our experiments in acid solution see Tables VII,

---

[1] Malfitano and Michel, *C. r.*, **145**, 185, 1275; **146**, 338 (1908).

VIII, IX, and Plot 2. Table X contains a summary of results, from which it will be seen in the last column that the product of velocity constant times acid concentration is approximately constant, or to be more exact, the retardation by acid is a little greater than would correspond to exact inverse proportionality between velocity and hydrogen ion concentration. The best explanation of this seems to be the assumption that it is the concentration of the *OH ion* that determines the rate of hydrolysis, since the OH ion concentration is, of course, inversely proportional to the H ion concentration. To account for the slight additional retardation it seems probable that it is the anion $RuCl''_5$ which undergoes direct hydrolysis, and that its concentration is somewhat reduced by combination with H ion to form undissociated H_2RuCl_5 or $HRuCl'_5$. This view is supported by the fact that the conductivities of K_2RuCl_5 and HCl when mixed are only slightly additive, as may be



seen from the initial conductivity values of any such solution. Accordingly, one should write for the hydrolytic reaction:

$$RuCl''_5 + 2OH' = Ru(OH)_2Cl + 4Cl'.$$

Two questions arise in connection with this formulation. First, why is the reaction proportional to the first instead of the second power of the hydroxyl ion concentration when two hydroxyl ions enter into the reaction; and second, why is the reaction, being ionic, not instantaneous? In answer to the first we cite the cases of the saponification of the polybasic esters which have been investigated by Löwenberg,[1] Geitel,[2] Abel,[3] Meyer,[4] Kremann,[5] and others, who have uniformly found that whether the ester be di- or tribasic, the saponification is of the second order as

TABLE VII.—RETARDATION BY ACID. 0.01 *N* HCl.

Temp. 25°.

$K_2RuCl_5 = 0.005$.		$K_2RuCl_5 = 0.0025$.		$K_2RuCl_5 = 0.00125$.	
Minutes.	1/ohm.	Minutes.	1/ohm.	Minutes.	1/ohm.
40	0.005057	8	0.004644	23	0.004278
111	0.005283	50	0.004677	85	0.004325
266	0.006433	110	0.004797	145	0.004390
382	0.007417	143	0.004865	208	0.004432
560	0.008649	171	0.004939	274	0.004547
680	0.009106	200	0.005040	332	0.004648
800	0.009407	329	0.005668	518	0.005082
2516	0.009720	477	0.006395	758	0.005418
33 days	0.009948	1447	0.006957	1833	0.005512
Rate =	0.0_5858	*Rate* =	0.0_5500	*Rate* =	0.0_5253
Corr. =	0.0_5866	*Corr.* =	0.0_5510	*Corr.* =	0.0_5253
k =	0.00173	**k** =	0.00204	**k** =	0.00202

Temp. 30°. $K_2RuCl_5 = 0.0025$.		Temp. 1/0.0025. $K_2RuCl_5 = 0.0025$.	
Min.	1/ohm.	Min.	1/ohm.
6	0.004908	73	0.004415
10	0.004926	114	0.004435
20	0.004942	272	0.004574
50	0.005070	394	0.004783
110	0.005469	508	0.005001
170	0.006275	714	0.005461
262	0.007014	836	0.005756
292	0.007172	2 days	0.006382
412	0.007374		
Rate =	0.0_4135	*Rate* =	0.0_525
Corr. =	0.0_4126	*Corr.* =	0.0_527
k =	0.00504	**k** =	0.00108

---

[1] Löwenberg, *Z. physik. Chem.*, 15, 389 (1894).

[2] Geitel, *J. pr. Chem.*, **55**, 429 (1897).

[3] Abel, *Z. physik. Chem.*, **56**, 558 (1906).

[4] Meyer, *Z. Elektrochem.*, 13, 186 (1907).

[5] Kreman, *Monatsh.*, **28**, 607 (1908). *Z. Elektrochem.*, **13**, 307.

TABLE VIII.—RETARDATION OF ACID. 0.02 *N* HCl. TEMPERATURE 25°.

$K_2RuCl_5 = 0.005$.		$K_2RuCl_5 = 0.0025$.		$K_2RuCl_5 = 0.0025$.	
Minutes.	1/ohm.	Minutes.	1 ohm.	Minutes.	1/ohm.
34	0.008950	17	0.008552	36	0.008292
163	0.009131	136	0.008621	136	0.008326
277	0.009434	194	0.008663	266	0.008410
382	0.009878	327	0.008781	406	0.008461
485	0.01036	377	0.008827	569	0.008569
567	0.01079	487	0.009011	725	0.008742
678	0.01132	592	0.009211	893	0.008919
810	0.01173	702	0.009438	1091	0.009111
921	0.01203	846	0.009776	1463	0.009258
1147	0.01271	1512	0.01057	2201	0.009333
		Duplicate (with time shift) from which rate was taken.			
2484	0.01328	537	0.009124	79 hrs.	0.009353
7 days	0.01364	662	0.009396	*Rate* =	0.0_5104
Rate =	0.0_5485	763	0.009636	*Corr.* =	0.0_5105
Corr. =	0.0_5490	879	0.009893	**k** =	**0.00084**
k =	**0.00098**	1100	0.01024		
		4 days	0.01071		
		Rate =	0.0_5225		
		Corr. =	0.0_5227		
		k =	**0.00091**		

TABLE IX.—RETARDATION BY ACID. 0.04 *N* HCl. TEMPERATURE 25°.

$K_2RuCl_5 = 0.005$.		$K_2RuCl_5 = 0.0025$.		$K_2RuCl_5 = 0.00125$.	
Minutes.	1/ohm.	Minutes.	1/ohm.	Minutes.	1/ohm.
34	0.01662	221	0.01632	196	0.01608
398	0.01681	781	0.01648	739	0.01613
1046	0.01778	922	0.01658	939	0.01615
1324	0.01834	1021	0.01666	1202	0.01624
1657	0.01902	1407	0.01700	1421	0.01633
1915	0.01953	1672	0.01725	1864	0.01655
2497	0.02008	2208	0.01772	2218	0.01666
5367	0.02083	2490	0.01785	2506	0.01669
7130	0.02105	2980	0.01797	2999	0.01675
Rate =	0.0_5201	4 days	0.01807	12 days	0.01678
Corr. =	0.0_5205	*Rate* =	0.0_6887	*Rate* =	0.0_6468
k =	**0.000410**	*Corr.* =	0.0_6914	*Corr.* =	0.0_6483
		k =	**0.000366**	**k** =	**0.000386**

if it were a monobasic ester. Wegscheider discussed this, enumerated all the ways in which the order may be accounted for and deduced equations. Of course the most patent explanation in our case is that one chlorine reacts with great rapidity as compared with the other. In answer to the second question raised above, as to why the reaction is not instantaneous, one needs only to point out that the reaction is not entirely ionic, since its rate is also dependent upon the concentration of the catalyzing substance $Ru(OH)_2Cl$. And furthermore, it is to be noted that the reaction is assumed to be between negative ions which would be an additional reason for its not taking place with the rapidity characterizing reactions between ions of opposite charges.

Finally, it is desirable to mention that other mechanisms are possible for this reaction which have not been mentioned on account of their uncertainty and lack of data, but the main experimental fact, independent of all theory, is that the rate of the reaction is inversely proportional to the H ion concentration.

TABLE X.—SUMMARY OF RETARDATION BY ACID.

Molar conc. of K_2RuCl_5.	Conc. of HCl.	Temp.	k.	Av. conc. of HCl.	$k \times HCl \times 10^6$.
0.005	0.01	25°	0.00173	0.015	26
0.005	0.02	25°	0.00098	0.025	24
0.005	0.04	25°	0.00041	0.045	18
0.0025	0.01	25°	0.00204	0.0125	25
0.0025	0.02	25°	0.00091	0.0212	19
0.0025	0.04	25°	0.00037	0.042	16
0.00125	0.01	25°	0.00202	0.0112	23
0.00125	0.02	25°	0.00084	0.0212	18
0.00125	0.04	25°	0.00039	0.0412	16

11. Influence of Salts.—To obtain a comparison with the influence of acids, the rate of hydrolysis of 0.00125 molar K_2RuCl_5 has been measured in 0.01 molar KCl, NaCl, KNO_3, and $NaNO_3$ and in 0.02 molar KCl. The data and a summary of results will be found in Table XI. In all cases a retardation was produced. The retardation was relatively small except for 0.02 KCl, which fact may also be regarded as in favor of the hypothesis that it is the $RuCl''_5$ anion which undergoes direct hydrolysis. It is, however, to be remembered that part of this apparent lowering in velocity must be attributed to the repressive effect of the salt on the conductivity of hydrochloric acid and potassium chloride. On account of the uncertainties involved, no corrections for this have been made. However, the corrections could hardly be so great as to account for the total reduction in rate, and we must conclude that the salts have some retarding effect. This is in general agreement with the work of Buchböck,[1] who found the rate of decomposition of carbonyl sulphide in water to be retarded by the presence of salts and still more by acids. His concentrations of salt and acid were much higher (0.5 to 4.0 normal) than we have employed. His acid retardation was less than proportional to the acid concentration. He concluded that the retarding power was a function of the atomic weight of the positive ion, acids falling into place owing to the very low atomic weight of hydrogen. Our results indicate no such periodic relation.

---

[1] Buchböck, *Z. physik. Chem.*, 23, 123 (1897).

TABLE XI.—INFLUENCE OF SALTS. 0.00125 MOLAR K_2RuCl_5. TEMPERATURE 25°.

0.01 KCl.		0.01 NaCl.		0.01 KNO_3.	
Minutes.	**1/ohm.**	**Minutes.**	**1/ohm.**	**Minutes.**	**1/ohm.**
6	0.001783	7	0.001572	6	0.001761
11	0.001883	15	0.001694	15	0.001899
16	0.001963	23	0.001776	23	0.002002
22	0.002045	33	0.001899	39	0.002189
36	0.002200	46	0.002032	53	0.002331
51	0.002355	64	0.002211	68	0.002459
81	0.002582	93	0.002432	99	0.002710
175	0.002894	155	0.002639	114	0.002794
363	0.002925	402	0.002657	353	0.002906
1 day	0.002972	3 days	0.002738	1 day	0.002917
Uncorrected rate.		**Uncorrected rate.**		**Uncorrected rate.**	
$0.0_{4}107$		**$0.0_{4}108$**		**$0.0_{4}105$**	

0.01 $NaNO_3$.		0.02 KNO_3.	
Minutes.	**1/ohm.**	**Minutes.**	**1/ohm.**
5	0.001559	8	0.003088
13	0.001683	18	0.003231
21	0.001787	28	0.003343
29	0.001888	47	0.003478
45	0.002071	62	0.003616
63	0.002259	92	0.003820
78	0.002377	122	0.003958
93	0.002495	163	0.004114
108	0.002576	4 days	0.004269
3 days	0.002737		
Uncorrected rate.		**Uncorrected rate.**	
$0.0_{4}118$		$0.0_{4}80$	

SUMMARY.

	H_2O.	0.01 *N*. $NaNO_3$.	0.01 *N*. NaCl.	0.01 *N*. KCl.	0.01 *N*. KNO_3.	0.02 *N*. KCl.	0.01 *N*. HCl.	0.02 *N*. HCl.	0.04 *N*. HCl.
Rate.	$0.0_{4}140$	$0.0_{4}118$	$0.0_{4}108$	$0.0_{4}107$	$0.0_{4}105$	$0.0_{4}080$	$0.0_{4}019$	$0.0_{4}010$	$0.0_{4}005$

12. Absence of the Influence of Sunlight.—In measuring the rate of hydrolysis of $PtCl_4.H_2O$, Kohlrausch[1] made the very interesting discovery that the velocity of the reaction is greatly influenced by exposure to direct sunlight, the acceleration being 10- to 12-fold for a 0.001 normal solution. We regarded it of interest to test the influence of sunlight on this somewhat similar reaction. Duplicate experiments at 25° with 0.00125 mol. K_2RuCl_5, the one in total darkness and the other in direct sunlight, showed that there is no difference within a few per cent. Both curves coincided so nearly with each other and with the corresponding curve in Plot (1), Curve 4, obtained under ordinary conditions of diffused light in an open thermostat, that it was deemed unnecessary to reproduce the curve or give the data.

---

[1] Kohlrausch, *Loc. cit.*

13. Conclusion.—It has been shown that the hydrolysis of potassium ruthenochloride is an irreversible reaction where the extent of replacement corresponds to two out of the three possible chlorine atoms. We have seen that all the reactions have constant rates over a considerable part of their courses, which are comparable from reaction to reaction and which may be converted into velocity constants by multiplying by the molar dilutions. The rate, as has been shown, is approximately inversely proportional to the average acid concentration existing during the period of constancy, which we have interpreted as signifying that the hydroxyl ion and not the water molecule, as usually assumed, is the hydrolyzing agent. As has also been pointed out, this new assumption does not affect equations of equilibrium but only those of velocity, which have been little developed for the inorganic hydrolyses. It is evident that if this assumption were true for every hydrolysis *retarded* instead of *accelerated* by acid that a very far-reaching distinction would have been established between the organic hydrolyses of the type of sugar inversion and inorganic ones like bismuth or ferric chlorides. We are not prepared to make this assertion without further evidence, but desire to point out that it appears to be in accord with the results of this research and that further study by means of other salts possibly presenting simpler relations is very desirable.

In regard to the constant rate observed in this reaction it must be admitted that all attempts to find a kinetic equation which should give quantitative expression to all the factors involved have failed. So baffling is the appearance of a constant rate under all conditions that one might be led to suppose that the rise in conductivity is not due to a homogeneous reaction. However, the lack of precipitation, the failure to prove extensive colloidal solution, the positive poof that a large share of ruthenium compound, after hydrolysis, is in a true state of solution, as well as the high value of the temperature coefficient (about 4.0), render this view improbable. We have been forced to be content with the explanation only general in character, that the constant rate is a result of the positive catalytic influence of the hydrolyzed product which balances those factors tending to produce a fall in rate such as diminishing concentrations of salt and hydroxyl ion. This explanation seems plausible if one remember that the decrease of salt and hydroxyl ion concentration and increase of catalyzer are all taking place at the same rate and that it has already been shown that the catalytic effect of the hydrolyzed product is enough to double the rate in a solution in which catalyzer is introduced in quantity equivalent to the salt concentration.

Summary.

The results of this investigation may be summarized as follows:

1. Potassium ruthenochloride (K_2RuCl_5) undergoes, in aqueous solu-

tion, an hydrolysis, the rate of which may be conveniently measured by determining the rise in electrical conductivity produced by the hydrochloric acid liberated.

2. The final state reached does not represent true equilibrium, in that it is not changed by dilution, addition of acid, nor change of temperature.

3. The hydrolyzed product (probably $Ru(OH)_2Cl$) has a positive catalytic influence on the rate, which results in a period of constant rate extending approximately over its first half, which may be used, with slight corrections, to obtain a velocity constant.

4. The rate of reaction in hydrochloric acid solution is roughly proportional to the acid concentration. A possible interpretation of this fact is that the hydroxyl ion concentration determines the rate of hydrolysis, or is the direct hydrolyzing agent.

5. The velocity in aqueous solution is at a maximum at the beginning of the reaction while in acid solution a distinct induction period is exhibited similar to that which Goodwin found for ferric chloride, and which may be similarly attributed to autocatalysis as has been confirmed by direct experiment.

6. The temperature coefficient between 22° and 30° is, for 0.005 molar solution, *3.27*; for 0.0025 is *2.96*; for 0.00125 is *2.63*; for 0.0025 in 0.01 *N* HCl is *5.40*.

7. Dilution also increases the rate. The coefficient for the fourfold dilution from 0.005 to 0.00125 molar is, at 22°, *2.23*; at 25° is *2.17*; at 30° is 1.80. At 25°, in 0.01 *N* HCl, it is *1.08*, or dilution may be said to have practically no influence when the acid concentration remains constant. But when the concentration of both salt and acid are diminished fourfold from 0.005 molar salt in 0.04 *N* HCl to 0.00125 molar salt in 0.01 *N* HCl, the coefficient at 25° is *5.15*.

8. From the results stated in *6* and *7* the general conclusion may be drawn that the accelerating influence of either increase in temperature or dilution has the greater effect on the slower reaction.

9. Sunlight has no influence on the rate of the reaction, contrary to the experience of Kohlrausch with $PtCl_4.H_2O$.

10. Both platinum and platinum black electrodes have a positive catalytic influence on the rate of hydrolysis. For the latter it amounts to 50 per cent. in the Ostwald type of cell.

11. Doubling the dilution produces about the same amount of acceleration as increasing the temperature three degrees.

CHEMICAL LABORATORY, UNIVERSITY OF MICHIGAN.