4. The titration of iron salts which have been reduced by stannous chloride is rapid and very accurate, the method being preferable to the Zimmermann-Reinhardt method.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

THE DECOMPOSITION OF POTASSIUM CHLORATE AND ITS CATALYSIS BY POTASSIUM CHLORIDE

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Introduction

Two well-known reactions take place independently and simultaneously when potassium chlorate is heated: (1) $4KClO_3 = 3KClO_4 + KCl$; (2) $2KClO_3 = 2KCl + 3O_2$. A third reaction, (3) $KClO_4 = KCl + 2O_2$, ensues at higher temperatures. A recent paper of the authors[2] presented the kinetics of Reaction 3 and its catalysis by ferric oxide. The present paper is concerned with the kinetics of Reactions 1 and 2 and the autocatalysis of Reaction 1 by potassium chloride, a product common to both reactions.

A review of the previous investigations,[3] which have purposed to derive mathematical expressions for the experimental results, presents a maze of complications due to the fact that different temperatures and various concentrations of catalysts affect in a widely different manner the speed of the simultaneous and independent reactions 1, 2 and 3.

The repeated statement that chlorine is a by-product in the decomposition by heat of potassium chlorate and of potassium perchlorate[4] is refuted by the work of Wagner[5] and the present authors who, using pure compounds, could detect no free chlorine.

A further difference in results was reported by Marignac[6] who, working with open tubes and no temperature regulation, found that the presence of potassium chloride and potassium perchlorate occasioned a decrease

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[1] Abstract of the second part of the thesis presented by Carl E. Otto to the Faculty of the Graduate School, University of Cincinnati, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Otto and Fry, THIS JOURNAL, **45**, 1134 (1923).

[3] Teed, *J. Chem. Soc.*, **51**, 283 (1887); Abstr. of *Proc. Chem. Soc.*, **1**, 141 (1885). Potilitzin, *J. Chem. Soc.*, **54**, 219 (1888). Franklin and Dingwall, *ibid.*, **51**, 274 (1887). Mills, *Phil. Mag.*, **23**, 375 (1887); *J. Chem. Soc.*, **52**, 767 (1887). Sodeau, *ibid.*, **81**, 1067 (1902).

[4] Sodeau, *J. Chem. Soc.*, **77**, 137 (1900). Spring and Prost, *Bull. soc. chim.*, **1**, 340 (1889); *J. Chem. Soc.*, **56**, 1105 (1889). Sodeau, *Chem. News*, **80**, 8 (1899). Fowler and Grant, *J. Chem. Soc.*, **57**, 272 (1890).

[5] Wagner, *Z. anal. Chem.*, **21**, 508 (1882).

[6] Marignac, *Bib. Univ. Geneva*, **45**, 346 (1843).

in the yield of perchlorate from chlorate; that is, Reaction 1 was inhibited. Later Scobai[7] repeated the work of Marignac and reported that potassium chloride but not perchlorate influenced Reaction 1. However, the exact nature of the effect he obtained from the potassium chloride is indefinite.

Scobai appears to have been the only investigator to have studied the kinetics of Reactions 1 and 2 but his method of interpreting his experimental data is needlessly inaccurate and open to question. For instance, the formula he employs for Reaction 1 takes no account of the concomitant Reaction 2, which he maintains is negligibly small notwithstanding the fact that it involves about 20% of the total amount of potassium chlorate undergoing transformation. His definition of C_m and $\Delta z/\Delta t$ in the formula, $K = (1/C_m^n) \times (\Delta z/\Delta t)$ is also open to question. Furthermore, a pronounced error is met in the latter part of his article when, using potassium nitrate as solvent, he states that in Reaction 1, K is most consistent when n equals +4 in the formula $K = (1/C_m^n) \times (\Delta y/\Delta t)$. In fact, K, according to Scobai's own data, is most nearly constant when n equals —1. Scobai's experimental observations are in accord with those of the present research. His conclusion that potassium chloride was a catalyst for Reaction 1 which he based upon insufficient evidence has been confirmed.

Theoretical Part

If we let a represent the initial concentration of chlorate, y and z the decrease in concentration due to Reactions 1 and 2, respectively, K_1 and K_2 the velocity coefficients of the respective reactions, and m and n the numbers of molecules taking part in the reactions, the following differential equations are obtained: $\mathrm{d}y/\mathrm{d}t = K_1(a-x)^m$; $\mathrm{d}z/\mathrm{d}t = K_2(a-x)^n$, in which $x = y + z$. Except for Table V, concentrations of substances in this article have been expressed in equivalents of potassium chlorate.

When the differential formula $K_2 = \dfrac{\mathrm{d}z/\mathrm{d}t}{(a-x)^n}$ is applied to Reaction 2, it is found that K_2 is more nearly a constant when n equals +1. Thus, the decomposition is monomolecular. The derivation of an integrated formula which involves Reactions 1 and 2 is possible only after the order of Reaction 1 is assumed. When this is taken as 4, the following differential equation results, $\mathrm{d}x/\mathrm{d}t = K_1(a-x)^4 + K_2(a-x)$. This, when integrated, gives $K_1 = K_2\left[\dfrac{1-\left(\dfrac{a-x}{a}\,e^{K_2t}\right)^3}{(a-x)^3\,(e^{3K_2t}-1)}\right]$. K_2 must still be determined by the differential formula, that is, by reading the tangents $\mathrm{d}z/\mathrm{d}t$ from the z,t curve and substituting in the formula given above.[8]

The values of z used in constructing the z,t curves were the concentrations of potassium chlorate equivalent to the evolved oxygen minus the oxygen

[7] Scobai, *Z. physik. Chem.*, 44, 319 (1903).

[8] Bray, *J. Phys. Chem.*, 9, 573 (1905).

which arose from the decomposition of potassium perchlorate subsequent to its formation. These subtrahends (w) were small and consequently influenced only the numerical value without altering the character of the results. They were calculated by the formula $w = \frac{y_n + y_{n+1}}{2}(1 - 10^{-K(t_{n+1} - t_n)})$, in which K is the decomposition-velocity coefficient of potassium perchlorate, y_n is the concentration of potassium chlorate converted to perchlorate at the time t_n, and y_{n+1} is the concentration at the time t_{n+1}.

When K_1 was calculated by the above method it was discovered to have a rapidly increasing value. This indicated autocatalysis and confirmation was found experimentally by initial additions of potassium chloride. This discovery necessitates a change in the kinetic equations, for if the speed of Reaction 1 depends upon the concentration of potassium chloride, then the differential equation for this reaction must be changed to $dy/dt = K_1(a-x)^mC^p$, in which C represents the concentration of potassium chloride and p the number of its molecules taking part in the reaction. By examination of the chemical equations it is seen that when no addition of chloride is made $C = z + (y/4)$. The integration of the combined formula, $dx/dt = K_1(a-x)^m(z + (y/4))^p + K_2(a-x)$, has not been found possible, and hence K_1 was calculated in the same manner as K_2.

The following assumptions, similar to those stated in the earlier article on potassium perchlorate, have been made in the present derivations and applications, namely, that the mass law applies in concentrated solutions; that the volume of the solid and liquid phases does not change during decomposition; that the decomposition of potassium perchlorate (temperature correction applied) is the same when dissolved in fused potassium chlorate as when it is in the fused state.

Experimental Part

Pure qualities of imported potassium chlorate and potassium chloride, recrystallized, finely pulverized and dried at 110°, were found upon analysis to be 100% pure.

The apparatus employed has been illustrated and described in the earlier paper.[2]

Portions of potassium chlorate were weighed as in the previous perchlorate investigation, and requisite additions of potassium chloride as catalyst were made to the individual samples.

Since potassium chlorate decomposes on heating according to Reactions 1 and 2, it was necessary to determine both the oxygen evolved and the perchlorate formed at various stages of the reaction. The latter value was obtained by subtracting from the amount of potassium chlorate originally present both the amount decomposed to oxygen and the amount remaining at any particular time. Seven samples were weighed and heated, respectively, for the noted intervals of time in arithmetic sequence. Obviously, the difference between these intervals was smaller, the higher the temperature. Four of these samples were placed in the furnace at the beginning of the experiment and one was heated throughout the experiment. When the other three tubes had been heated for the second, third and sixth intervals, they were removed and replaced, respectively, by the remaining three which by the end of the seventh interval had been heated for the fifth, fourth and first intervals. Thus, the four holes of the furnace were

TABLE I

DECOMPOSITION OF POTASSIUM CHLORATE AT 408.9°

Time Hrs.	Total $KClO_3$ trans. x	$KClO_3$ equiv. to O_2 evolved	$KClO_3$ equiv. to $KClO_4$ in residue (y^1)	$KClO_3$ forming $KClO_4$ ($y^1 + w$) (y)	$KClO_3$ forming O_2 directly (z)	$\frac{dz}{dt}\times10^3$	$\frac{dz/dt}{a-x}$ $K_2\times10^3$	$\frac{dy}{dt}\times10^3$	Conc. $KClO_3$ equiv. to KCl formed C	$\frac{dy/dt}{(a-x)\ C}$ K_1
1		0.0057			0.0057	4.48	4.509			
2		.0100			.0100	3.97	4.015			
3		.0140			.0140	3.75	3.818			
4	0.0232	.0175	0.0057	0.0057	.0175	3.55	3.634	2.016	0.0189	0.1092
5		.0196			.0196	3.38	3.483			
6		.0237			.0237	3.31	3.432			
7		.0271			.0271	3.19	3.334			
8	.0467	.0306	.0161	.0161	.0306	3.08	3.236	2.844	.0346	.0862
9		.0340			.0340	3.00	3.175			
10		.0370			.0370	2.96	3.146			
11		.0396			.0396	2.90	3.112			
12	.0729	.0420	.0309	.0309	.0420	2.88	3.101	3.992	.0497	.0866
13		.0453			.0453	2.84	3.092			
14		.0485			.0484	2.78	3.050			
15		.0518			.0516	2.74	3.024			
16	.1026	.0544	.0482	.0483	.0543	2.66	2.958	6.235	.0664	.1046
17		.0566			.0565	2.52	2.770			
18		.0591			.0591	2.40	2.742			
20	.1540	.0628	.0912	.0913	.0627	2.28	2.689	16.46	.0856	.2273
21		.0660			.0658	2.20	2.666			
22		.0678			.0676	2.16	2.683			
23		.0698			.0696	2.14	2.744			
24	.2536	.0722	.1814	.1816	.0720	2.12	2.834	29.55	.1176	.3367
						Av.	3.062		Av.	0.1584
							± 0.259			± 0.0824
							(8.5%)			(52.0%)

TABLE II

DECOMPOSITION OF POTASSIUM CHLORATE AT 460.1°

Min.										
30		0.0107			0.0107					
45		.0145			.0145					
60	0.0181	.0184			.0184	32.27	32.308	0.2719	0.0181	0.01530
75		.0217			.0217	32.13	32.197			
90		.0244			.0243	32.05	32.138			
105		.0283			.0282	32.02	32.130			
120	.0674	.0315	0.0359	0.0361	.0313	31.99	32.133	0.622	.0405	.01647
135		.0336			.0333	31.96	32.132			
150		.0369			.0364	31.94	32.143			
165		.0395			.0388	31.93	32.172			
180	.1322	.0422	.0900	.0910	.0412	31.90	32.190	1.310	.0647	.02333
195		.0450			.0436	31.86	32.207			
210		.0484			.0466	31.82	32.220			
225		.0523			.0500	31.73	32.178			

240	.2437	.0555	.1882	.1911	.0526	31.69	32.230	1.763	.0125	.02274
255		.0588			.0553	31.59	32.150			
270		.0621			.0579	31.41	31.993			
285		.0653			.0603	31.27	31.887			
300	.3593	.0672	.2921	.2980	.0613	31.19	31.858	2.044	.1402	.02276
315		.0694			.0625	31.11	31.842			
330		.0723			.0641	31.04	31.850			
345		.0752			.0660					
360	.5180	.0775	.4405	.4511	.0669			3.062	.1876	.03465
							Av. 32.103			Av. 0.02254
							± 0.0118			± .00444
							(5.25%)			(19.7%)

TABLE III

DECOMPOSITION OF POTASSIUM CHLORATE AT 492.4°

3		0.0048			0.0048	1.568	1.587			
6		.0101			.0100	1.488	1.529			
9		.0146			.0144	1.290	1.351			
12		.0192			.0188	1.188	1.269			
15	0.0879	.0230	0.0649	0.0655	.0224	1.110	1.217	5.67	0.0388	0.1602
18		.0270			.0262	1.030	1.161			
21		.0296			.0284	0.964	1.121			
24		.0326			.0310	.868	1.046			
27		.0350			.0328	.820	1.021			
30	.2250	.0379	.1871	.1900	.0350	.784	1.019	7.37	.0825	.1148
33		.0398			.0362	.748	0.993			
36		.0422			.0378	.718	.986			
39		.0454			.0402	.670	.953			
42		.0485			.0424	.657	.965			
45	.3217	.0534	.2683	.2755	.0462	.640	.973	8.54	.1151	.1128
60	.4792	.0685	.4107	.4242				8.14	.1610	.0923
75	.5363	.0798	.4565	.4784				7.69	.1775	.0978
90	.6560	.0926	.5634	.5954				7.10	.2094	.0986
105	.7554	.1015	.6539	.6970				6.18	.2326	.1084
							Av. 1.153			Av. 0.1121
							± 0.167			± .0148
							(14.4%)			(13.2%)

TABLE IV

DECOMPOSITION OF POTASSIUM CHLORATE AT 505.7°

3		0.0042			0.0040	1.418	1.455			
6		.0089			.0086	1.400	1.472			
9		.0132			.0126	1.388	1.495			
12		.0174			.0164	1.350	1.519			
15	0.1209	.0223	0.0984	0.1000	.0207	1.335	1.523	7.07	0.0457	0.1760
18		.0272			.0249	1.300	1.538			
21		.0324			.0292	1.274	1.560			
24		.0370			.0326	1.250	1.563			
27		.0424			.0368	1.208	1.443			
30	.2552	.0480	.2072	.2143	.0409	1.074	1.315	8.94	.0945	.1270
33		.0517			.0430	0.936	1.183			
36		.0559			.0454	.802	1.083			
45	.4296	.0684	.3612	.3782				11.90	.1460	.1429
60	.5732	.0839	.4893	.5220				8.03	.1817	.1036
75	.6812	.0997	.5815	.6340				7.34	.2057	.1119
90	.7805	.1157	.6648	.7408				6.86	.2249	.1390
							Av. 1.434			Av. 0.1334
							± 0.111			± .0192
							(7.7%)			(14.4%)

occupied continuously and the chlorate remaining after heating for the seven different intervals could be determined. Determinations of the amounts of potassium chlorate decomposing to oxygen were made only on the samples heated for the sixth and seventh intervals.

The entire reaction residue was dissolved in water, the solution divided into aliquot portions and the chlorate content in each was determined, by boiling with an excess of 0.1 N ferrous sulfate solution.[9]

The decomposition data of potassium chlorate at four temperatures are shown in Tables I, II, III and IV, the columns of which are self-explanatory. All of the observations taken were not used in the calculations of the constants K_1 and K_2, since unavoidable experimental errors caused the values to become obviously very far from constant. A very few omissions and slight discrepancies are apparent. The marked general trend of the data nevertheless warrants the subsequent conclusions.

In order to evaluate the constants in the equation $\mathrm{d}y/\mathrm{d}t = K_1(a-x)^m C^p$, it was changed to the form $\log \frac{\mathrm{d}y/\mathrm{d}t}{(a-x)^m} = p \log C + \log K_1$. With m taken as 1, 2, 3 and 4, the values calculated for $\log \frac{\mathrm{d}y/\mathrm{d}t}{(a-x)^m}$ were plotted against the corresponding log C's. It was discovered that the best straight lines were obtained when $m = 1$. At three of the four temperatures used the slope (p) of the line was also 1. In the other case it was somewhat greater. Since m and p must be integers, the constant K_1 was calculated as shown in the last column of the preceding tables by the formula $K_1 = \frac{\mathrm{d}y/\mathrm{d}t}{(a-x)C}$.

The values of K_1 and K_2 were found to be dependent upon the absolute temperature according to the equation of Arrhenius: $\log K = (A/T) + B$.

In Table V, as previously mentioned, are the results of experiments on the heating of potassium chlorate to which initial additions of potassium chloride had been made. All of the tubes of one group were placed in and taken out of the furnace at the same time. They were then analyzed for chlorate and it was noticed (Column 6) that more chlorate had suffered change in the tubes containing the greater amount of potassium chloride. In the first group, determinations of the fraction of chlorate, decomposing to oxygen directly, were made for each sample and, subtracted from the total fraction changed, gave the fraction transformed to potassium perchlorate. Since the fraction yielding oxygen varied slightly while the potassium chloride increased from 0 to 12%, determination of the amount of chlorate participating in this side reaction was made in the later groups only with the initially pure potassium chlorate. This decision was somewhat unfortunate since in the last experiment, due to the lower temperature and the additions of potassium chloride, the mixtures were unfused

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[9] Treadwell-Hall, "Analytical Chemistry," John Wiley and Sons, **1919, Vol.** 2, p. 669.

at the end, and probably throughout the experiment. However, even when solid, the disappearance of potassium chlorate paralleled the concentration of potassium chloride. Thus, it is evident that *the transformation of potassium chlorate to potassium perchlorate is catalyzed by potassium chloride.*

TABLE V

DECOMPOSITION OF POTASSIUM CHLORATE CATALYZED BY POTASSIUM CHLORIDE

All were fused except the last four

$KClO_3$ taken G.	KCl taken G.	Initial concn. of KCl by weight %	$KClO_3$ in residue G.	Fraction $KClO_3$ untrans.	Fraction $KClO_3$ trans.	Fraction $KClO_3$ giving O_2	Fraction $KClO_3$ giving $KClO_4$
Time = 1 hr. Temp. = 463°							
0.4795	0.0	0.00	0.4701	0.9804	0.0196	0.0304	0.0
.5035	.0262	4.95	.4238	.8417	.1583	.0300	.1283
.5850	.0473	7.48	.4492	.7678	.2322	.0299	.2023
.5619	.0783	12.23	.3864	.6876	.3124	.0295	.2829
Time = 15 min. Temp. = 487°							
.5682	.0	0.00	.5183	.9121	.0879	.0230	.0649
.7071	.0185	2.55	.6531	.9237	.0763	...	.0533
.7456	.0303	3.90	.6742	.9042	.0958	...	.0728
.6137	.0632	9.34	.5075	.8268	.1731	...	.1501
.6385	.1037	13.97	.5003	.7836	.2164	...	.1934
Time = 4 hrs. Temp. = 408°							
.6721	.0	0.00	.6565	.9768	.0232	.0175	.0057
.6836	.0279	3.92	.6813	.9967	.0033	...	...
.7257	.0461	5.97	.7206	.9929	.0071	...	...
.7474	.0753	9.15	.7324	.9800	.0200	...	...
.7008	.0923	11.64	.6804	.9710	.0290	...	...

It is suggested that it would be an interesting problem to find out if a greater yield of potassium perchlorate from the chlorate than that reported by Blau and Weingand[10] could be effected by this means. However, for commercial operation, the inefficiency of the higher fusion point of the melt and the lower percentage of potassium perchlorate in the residue might counterbalance the efficiency of the increased yield.

Summary

Preliminary experiments showed that no chlorine was evolved with the oxygen in the decomposition of potassium chlorate.

Since the velocity of the transformation of potassium chlorate into potassium perchlorate at constant temperature increased as the reaction proceeded, autocatalysis (previously indicated by the work of Scobai) was evident. This was confirmed by adding various amounts of potassium chloride to the potassium chlorate before heating. These initial additions

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[10] Blau and Weingand, *Z. Elektrochem.*, **27**, 1 (1921).

of potassium chloride as catalyst to the potassium chlorate accelerated the reaction 4 $KClO_3$ = 3 $KClO_4$ + KCl, but did not accelerate the reaction 2 $KClO_3$ = 2 KCl + 3O_2.

These explanations concordant with the experimental data of Scobai substantiate his interpretations.

The velocity coefficient at constant temperature of the reaction, 4 $KClO_3$ = 3 $KClO_4$ + KCl, conforms to the expression $K_1 = \frac{dy/dt}{C(a-x)}$ in which dy/dt is the instantaneous speed of the reaction, C the concentration of potassium chloride and $(a-x)$ the concentration of potassium chlorate.

The reaction, 2 $KClO_3$ = 2 KCl + 3 O_2, has been shown to be monomolecular.

The logs of the velocity coefficients K_1 and K_2 have been plotted against the reciprocals of the absolute temperatures and these points lie approximately on straight lines.

CINCINNATI, OHIO

[CONTRIBUTION FROM KENT CHEMICAL LABORATORY, THE UNIVERSITY OF CHICAGO]

A METHOD FOR THE PREPARATION OF THE DOUBLE FLUORIDES OF THE METALS OF THE PLATINUM GROUP AND THE ABSORPTION SPECTRA OF THE HALOGENO PLATINATES

BY H. I. SCHLESINGER AND MARK W. TAPLEY[1]

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In connection with other work being done in this Laboratory on complex inorganic compounds it was desired to obtain the absorption spectra of the halogeno platinates. Methods for the preparation of the chloro-, bromo- and iodoplatinates are well known but the fluoroplatinate has hitherto not been prepared. In this connection it may be pointed out that very little is known about the fluorides of the platinum group metals; the only ones which have been examined in detail are those of osmium and platinum. Consequently, some preliminary work was done to determine whether the method which we have developed for the preparation of potassium fluoroplatinate can be used for the other corresponding salts of this group in the hope that through them the simple fluorides could be obtained.

Occasional reference to complex fluorides of the group is found in the literature. Berzelius[2] states that he prepared potassium, sodium, and ammonium platinum fluorides as viscous, non-recrystallizable salts, soluble in water; the solution becomes acid and

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[1] The work herein reported constitutes the basis of a dissertation presented to the Graduate Faculty of the University of Chicago by Mark W. Tapley in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Berzelius, "Lehrbuch der Chemie," 1825, vol. 2, p. 953.