5. The mobility of the sodium ion at a total concentration of 0.2 *N* and a ratio of 3KCl: 1NaCl has been shown to be practically zero.

6. The deviations between the calculated values and the experimental values of the transference ratios are not due to hydration of ions alone but must be due also to complex formations in solution.

7. The results agree with the work of Smith and Ball[4] and Smith and Wells[5] in which they found that the sodium ion fraction increases with increase in total concentration above 0.2 *N*. Below this concentration the sodium decreases with respect to the potassium.

URBANA, ILLINOIS

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

THE DECOMPOSITION OF POTASSIUM PERCHLORATE AND ITS CATALYSIS BY FERRIC OXIDE

BY CARL E. OTTO[1] WITH H. SHIPLEY FRY

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Introduction

Previous investigations of the decomposition of potassium perchlorate have been made but only incidentally to the study of the decomposition of potassium chlorate. The meagerness of the available data regarding perchlorate decomposition is the occasion for the present study.

Scobai[2] has found that the loss in weight of potassium perchlorate heated to 395° was negligible. Likewise, McLeod[3] noted that even in the presence of manganese dioxide as catalyst potassium perchlorate did not decompose at the boiling point of mercury, but Frankland and Dingwald[4] reported a loss of 3% by weight on heating it for 56 hours in sulfur vapor.

The presence of chlorate in residues of moderately heated perchlorate was observed by Millon,[5] Teed,[6] and Frankland and Dingwald.[4] The latter claimed to have effected its separation by fractional crystallization. Scobai also occasionally found traces of chlorate. It is noteworthy that none of these investigators has found chlorate in perchlorate residues when manganese dioxide or other catalysts were used.

In the present study, the speed of the decomposition of potassium perchlorate by heat has been investigated both without and with a catalyst, *ferric oxide*, which is preferable to the more commonly employed manganese dioxide because it is stable and can be obtained in a state of standard purity as ferric oxide.

[1] Abstract of one section of a thesis submitted to the Graduate Faculty of the University of Cincinnati by Carl E. Otto, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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

[3] McLeod, *J. Chem. Soc.*, **57**, 272 (1890).

[4] Frankland and Dingwald, *ibid.*, **51**, 274 (1887).

[5] Millon, *Ann. chim. phys.*, [3] **7**, 298 (1843).

[6] Teed, *J. Chem. Soc.*, **51**, 283 (1887); *Abst. Proc. Chem. Soc.*, **1**, 141 (1885).

Apparatus

The apparatus of previous investigators has varied from open test-tubes to the self-regulating air-bath of Scobai and the metal-bath of Sodeau.[7] In case chlorine was found to be given off, adsorption towers were used. When the volume of oxygen evolved was desired, a gas buret was incorporated.

The details of the apparatus used in the present work are shown in Fig. 1.

The electrical resistance furnace contained a bath of Wood's metal covered with charcoal to prevent oxidation. The contents were stirred by a centrally placed rotating iron wire connected to an electric motor through a universal joint and pulley. The lid of the furnace contained openings for 4 reaction test-tubes, two of which were connected by means of thick-walled capillary tubing to gas burets with mercury leveling bulbs. All joints were sealed with shellac and tested for leaks before each operation. A sixth hole in the furnace lid was for the insertion of an iron-constantan thermocouple encased in a small iron tube sealed at the lower end and covered with layers of asbestos paper outside the furnace in order that the tube itself might be maintained at the furnace temperature. The latter was regulated by hand with an external resistance. The insulated thermocouple was previously calibrated for lower temperatures by immersion in the Wood's metal bath with a checked mercury thermometer and for higher temperatures by the boiling point of sulfur and the freezing points of lead, aluminum and antimony. The thermocouple wires were run to an ice-bath in a Dewar flask whence copper leads were connected to a sensitive potentiometer.

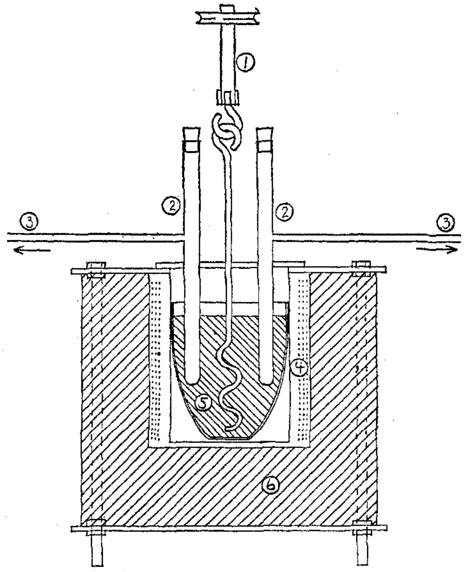

Fig. 1.—Apparatus.

1. Electrically driven stirrer. 2. Reaction test-tubes. 3. To gas burets. 4. Heating coils in alundum cement. 5. Wood's metal bath. 6. Magnesia packing.

Materials.—The catalyst, ferric oxide, was prepared from Mohr's salt by oxidation with nitric acid and repeated precipitations of ferric hydroxide followed by ignition. Samples of the product, on analysis, gave 99.94% and 100.09% of ferric oxide. This was pulverized and 99.15% was found to pass through an 80-mesh sieve. Microscopic examination revealed that the particles had an average diameter before use of 0.011 mm. and afterward of 0.055 mm.

Portions of a commercial "analyzed" potassium perchlorate, dried at 105–110° and free from chloride and chlorate,[8] were heated alone or in the presence of chloride-free

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[7] Sodeau, *J. Chem. Soc.*, **81**, 1074 (1902).

[8] Treadwell-Hall, "Analytical Chemistry," John Wiley and Sons, **1916**, vol. II, p. 669.

sodium carbonate and potassium nitrate and thus were found on complete decomposition to give the calculated amounts of potassium chloride.[9] The potassium perchlorate was pulverized by grinding until 68% passed an 80-mesh sieve 28% was held by a 60-mesh and 4% was between 60 and 80 mesh. The material used in the experiments was not sifted.

Preliminary Experiments

In several preliminary experiments a Liebig absorption bulb containing potassium iodide solution was inserted between the reaction test-tube and the gas buret. Since no free iodine was discovered after the gas evolved from potassium perchlorate had been passed through, its use was discontinued in the remaining part of the investigation. This observation is parallel to that of Wagner[10] who stated that no chlorine is evolved from pure potassium chlorate.

A portion of potassium perchlorate was heated in an open test-tube until fused and the evolution of oxygen was well under way. After sudden cooling, the residue was found free from chlorate. Another portion of pure potassium perchlorate and one containing 10% of potassium chloride were heated for 3 weeks at an average temperature of 357° and also found to be free from chlorate. These experiments were taken to prove that *potassium chlorate is not formed on heating potassium perchlorate either strongly or moderately.*

Theoretical

The significant fact that no chlorate was found in the residues from the decomposition of potassium perchlorate simplified very greatly the study of its decomposition. It proved that only one reaction was taking place, namely, $KClO_4 = KCl + 2O_2$. The order of this reaction and the velocity coefficients can, therefore, be determined by the method of integration.[11]

Since velocity coefficients are a function of the temperature, their evaluation according to the method of integration must be based upon data obtained at constant temperatures if consistent results are to be expected. A relation between the velocity coefficient of reversible reactions at different temperatures has been deduced by van't Hoff and a similar relation has been found by Arrhenius[12] to hold good for irreversible reactions: $d \log K/dT = Q/RT^2$, or $\log K = -Q/RT + B$ (van't Hoff); $\log K = A/T + B$ (Arrhenius).

Another phase of the present investigation was to ascertain what relation the velocity coefficient bore to the amount of catalyst present. Since the method of approach to this problem was that of "cut and try," the

[9] Ref. 8, p. 708.

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

[11] Mellor, "Chemical Statics and Dynamics," Longmans, Green and Co., **1904**, p. 58.

[12] Arrhenius, *Z. physik. Chem.*, **4**, 226 (1889).

discussion of the algebraic equations involved will be postponed until after the experimental data and related calculations have been given.

In all of these derivations and their applications, the assumptions are that the mass law applies in concentrated solutions, the volume of the solid and liquid phases does not change during decomposition, and the particles of solid catalyst remain uniformly distributed during the experiment.

Method of Operation

Portions of potassium perchlorate and ferric oxide were weighed in approximately simple molecular ratios, intimately mixed and reserved for use in glass-stoppered bottles.

In the following table, the first column indicates the approximate molecular ratio; the second and third, the amounts of potassium perchlorate and ferric oxide; the fourth, the actual molecular ratio; and the fifth the percentage of potassium perchlorate in the mixture.

Table I

Initial Compositions

Nominal molecular ratio $KClO_4$:Fe_2O_3	$KClO_4$ G.	Fe_2O_3 G.	Actual molecular ratio $KClO_4$:Fe_2O_3	$KClO_4$ in mixture %
6:1	2.0436	0.3923	6:0.9995	83.90
3:2	2.4660	1.8944	3:1.9998	44.93
3:4	2.0460	3.1440	3:4.0002	39.42
1:2	2.5274	5.8253	1:2.0000	30.26
1:4	2.0519	9.4589	1:4.0011	17.83

Approximately the desired amount of material, either pure potassium perchlorate or a mixture of this with ferric oxide, was placed in weighed tubes of Pyrex glass. A second weighing gave the amount of the material used. The tubes were then fitted tightly with corks and connected securely with the gas burets. When the furnace had attained equilibrium at or slightly above the desired temperature, the tubes were suddenly plunged into the Wood's metal bath. The interval between attempted simultaneous readings of the gas burets, furnace temperature, room temperature and barometric pressure depended upon the speed of decomposition.

After final readings had been taken the tube was removed from the furnace and cooled to room temperature. The contraction in gas volume was equal to the expansion of the air sealed in the apparatus when raised from room temperature to that of the furnace.

Calculations Based on the Decomposition Data

Forty-five distinct decompositions of potassium perchlorate with various proportions of catalyst were made at temperatures ranging from 450° to 600°. For the sake of brevity, only one table of data, typical of each of the 45, is here presented.

TABLE II

DECOMPOSITION OF POTASSIUM PERCHLORATE

Catalyst ratio = $3KClO_4:4Fe_2O_3$. Wt. of sample = 0.5009 × 0.39422 = 0.1975 g.
Room temp. = 25°. Barometer = 735.1 mm.

Time Min.	Temp. °C.	Oxygen evolved Cc.	x	$a - x$
0	508.0	...	....	....
15	503.3	3.85	0.0535	0.9465
70	501.9	23.70	.3291	.6709
75	501.9	26.95	.3656	.6344
80	506.3	29.85	.4145	.5855
85	506.3	32.70	.4541	.5459
90	506.3	35.20	.4888	.5112
135	507.3	52.77	.7328	.2672
140	507.1	54.33	.7544	.2456
145	507.1	55.90	.7762	.2238
150	506.7	57.52	.7987	.2013
155	506.7	58.40	.8109	.1891
Av.	507			

Time $t = 65$	$a - x_1$	$a - x_2$	K
70–135	0.6709	0.2672	6.151 × 10^{-3}
75–140	.6344	.2456	6.340
80–145	.5855	.2238	6.425
85–150	.5459	.2013	6.665
90–155	.5112	.1891	6.644
		Av.	6.445 × 10^{-3} ± 0.168 × 10^{-3} (2.6%)

Preceding the tabulations of data there are noted the ratio of potassium perchlorate to ferric oxide used; the weight of sample, which multiplied by the percentage of perchlorate in the mixture gives the weight of potassium perchlorate used; the room temperature and the barometric pressure corrected to 0°. The tabulations embody the time of each observation beginning the instant the reaction tube was thrust into the furnace; the temperature of the furnace as shown by the thermocouple readings; the volume of oxygen evolved under the temperature and pressure conditions mentioned, the values being the buret readings minus the contraction when the tube was withdrawn from the furnace; the amount of potassium perchlorate (x) which if completely decomposed would generate this volume of oxygen expressed in fractions of the original amount present; and $a - x$, the fraction of potassium perchlorate which remained undecomposed.

Since initially the fraction of potassium perchlorate undecomposed is unity, the values of $a - x$ or concentration of reacting substance are found by subtracting x from 1.

This method of obtaining the concentration during the experiment would not give comparable results when different amounts of foreign material are present if the reaction were bi- or polymolecular. But, since it was found that when pure potassium perchlorate was heated the observations gave almost constant values for the velocity coefficient when calculated according to the equation for the first order reaction, the velocity coefficients in the presence of ferric oxide would be calculated in the same way, taking for convenience the initial concentration of potassium perchlorate as one.

The lower part of the table shows the "times" and the values of $a-x$ used to calculate K by the equation, $K = \frac{1}{t_2 - t_1} \log_{10} \frac{a - x_1}{a - x_2}$, where $a-x_1$ is the value of $a-x$ at the time t_1 and $a-x_2$ at the time t_2. Thus values of K of equal weight were obtained and averaged. The average deviation of the values of K and its percentage of the average value of K have been computed in each case to show the uniformity of the observations.

In the abridged tables, III to VIII inclusive, which follow, the velocity coefficients and the average temperatures of the individual experiments have been assembled for each mixture of potassium perchlorate and ferric oxide. The constants A and B in Arrhenius' equation have been evaluated by the method of least squares for each set of data. In order to compare the velocity coefficients for the various mixtures of catalyst with the molecular concentration of catalyst present, constants K were calculated from the latter for various temperatures. Since these should be the most accurate within the range of experimental temperatures, those chosen were 500°, 525°, 550° and 575°. It was found (see Table IX and Fig. 2) that the increase in the velocity coefficient was proportional to the concentration of catalyst; that is, $K_c - K_0 \propto C$, where K_c is the velocity coefficient of the catalyzed reaction; K_0, the velocity coefficient of the uncatalyzed reaction at the same temperature; and C is the molecular concentration of the catalyst; or, at constant temperature, the expression $(K_c - K_0)/C$ is a constant.

To find the relation between these constants and the temperature, their logarithms were plotted against $1/T$ as suggested by Arrhenius and were found to give a straight line; thus, $\log[(K_c - K_0)/C] = A/T + B$. The values of A and B were determined by the method of least squares (see Table IX).

Since K_0 is also a function of the temperature by the relation, $\log K_0 = A_0/T + B_0$, it follows that $K = C.10^{A/T + B} + 10^{A_0/T + B_0}$ in which K combines the meanings formerly given to both K_c and K_0. The constants have the following numerical values: $A = -10{,}587$; $A_0 = -13{,}246$; $B = 11.5679$; $B_0 = 14.0348$.

Velocity coefficients have been calculated by this equation for a few of the experimental conditions, and in Table X are compared with those calculated directly from the data.

The following Table III indicates the decomposition velocity coefficients of pure potassium perchlorate when fused.

TABLE III

PURE POTASSIUM PERCHLORATE WITH NO CATALYST

$t°$	536	551	577	617
K	0.004696	0.007734	0.02676	0.1720

$$\log K + 13245.5/T = 14.0348$$

Tables IV to VIII inclusive give decomposition velocity coefficients of the potassium perchlorate in various molecular ratios with ferric oxide.

TABLE IV

THE RATIO, $6KClO_4:1Fe_2O_3$

$t°$	518	546	556	585	605
K	0.004647	0.01283	0.01458	0.05794	0.1341

$$\log K + 11595/T = 12.2730$$

TABLE V

THE RATIO, $3KClO_4:2Fe_2O_3$

$t°$	508	541	559	587	601
K	0.005429	0.01736	0.04094	0.1273	0.2034

$$\log K + 12072/T = 13.1300$$

TABLE VI

THE RATIO, $3KClO_4:4Fe_2O_3$

$t°$	507	516	538	562	607
K	0.006445	0.01110	0.02284	0.05703	0.2932

$$\log K + 11143/T = 12.1184$$

TABLE VII

THE RATIO, $1KClO_4:2Fe_2O_3$

$t°$	516	534	555	559	582
K	0.01178	0.02110	0.05514	0.07643	0.1594

$$\log K + 11839/T = 13.0541$$

TABLE VIII

THE RATIO, $1KClO_4:4Fe_2O_3$

$t°$	512.0	533.5	543.0	552.6	558.8	562.5
K	0.01304	0.02797	0.03439	0.04668	0.05609	0.06085
$t°$	559.0	573.0	578.4	589.3	606.3	608.7
K	0.07393	0.1465	0.1112	0.1891	0.2733	0.2992

$$\log K + 10020/T = 10.8540$$

For the following table the velocity coefficients have been calculated and assembled for each concentration of catalyst at 500°, 525°, 550°

and 575°. This table shows that at constant temperature the increase in the velocity coefficient due to the introduction of a catalyst is proportional to the concentration of the catalyst.

TABLE IX

INTERPOLATED VELOCITY-COEFFICIENTS

Temp. °C.	$KClO_4$	$\frac{6KClO_4}{1Fe_2O_3}$	$\frac{3KClO_4}{2Fe_2O_3}$	$\frac{3KClO_4}{4Fe_2O_3}$	$\frac{1KClO_4}{2Fe_2O_3}$	$\frac{1KClO_4}{4Fe_2O_3}$	
	0	0.14286	0.40000	0.57142	0.66667	0.80000	Conc. catalyst (C)
500	0.0_37936	$.0_21875$	$.0_23257$	$.0_25050$	$.0_25481$	$.0_27789$	
525	$.0_22654$	$.0_25532$	.01005	.01429	.01654	.01984	K_c
550	$.0_28702$	.01528	.02894	.03793	.04670	.04775	
575	.02601	.03978	.07835	.09496	.1240	.1091	
500	.....	$.0_27567$	$.0_26157$	$.0_27448$	$.0_27030$	$.0_28744$	
525	.....	.02015	.01849	.02037	.02132	.02149	$\frac{K_c-K_0}{C}$
550	.....	.04605	.05060	.05115	.05700	.04881	
575	.....	.09639	.1308	.1207	.1470	.1039	

Temp. °C.	Av. $\frac{K_c-K_0}{C}$	$\frac{K_c-K_0}{C}$ (calc. from eq.)
500	0.007389 ± 8.6%	0.007446
525	0.02036 ± 4.1%	0.02000
550	0.05072 ± 5.3%	0.05058
575	0.1198 ± 11.4%	0.1211

$$\log [(K_c-K_0)/C] + 10587/T = 11.5679.$$

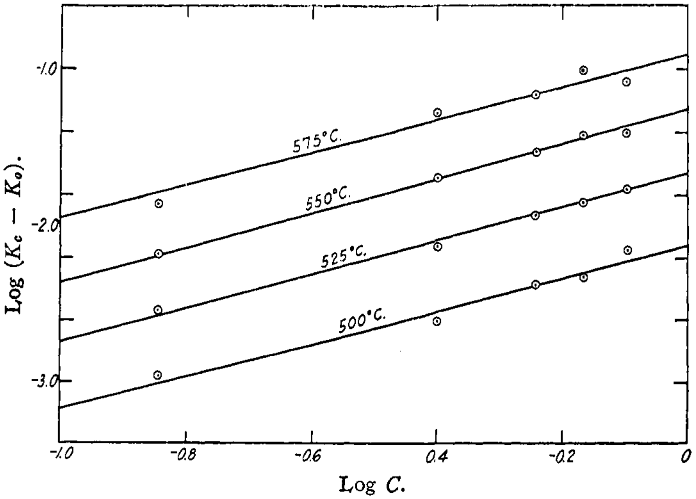

Fig. 2.—Log vel. const. *vs.* log conc. catalyst showing a straight line relation between log $(K_c - K_0)$ and log C.

TABLE X

COMPARISON OF VALUES OF K CALCULATED FROM THE GENERAL EQUATION (K) AND DIRECTLY FROM DATA ($K_{obs.}$)

Conc. of catalyst	Temp. ° Abs.	K	$K_{obs.}$
0	809	0.004587	0.004696
0	850	.02827	.02676
0.14286	791	.004125	.004647
.14286	858	.06369	.05794
.40000	781	.005301	.005429
.40000	832	.04087	.04094
.57142	780	.006776	.006445
.57142	835	.05909	.05703
.66667	789	.01121	.01178
.66667	828	.05148	.05514
.80000	785	.01110	.01304
.80000	851	.1367	.1112

Summary

1. The decomposition of potassium perchlorate into potassium chloride and oxygen is unimolecular.
2. The particles of the catalyst, ferric oxide, increased 5-fold in diameter during the reaction.
3. The decomposition of potassium perchlorate either with or without the catalyst is not accompanied by an evolution of chlorine.
4. The velocity coefficient is in conformity with Arrhenius' law within the temperature range studied.
5. With ferric oxide as catalyst, the increase in the velocity coefficient at constant temperature is proportional to the weight concentration of catalyst.
6. The expression $(K_c - K_0)/C$ varies with the temperature according to the law of Arrhenius.

Conclusions 4, 5 and 6 seem to indicate that the addition of the catalyst does not accelerate the reaction already proceeding, but that a concomitant reaction occurs which involves the catalyst, probably in the formation of an intermediate compound, while the original reaction proceeds unchanged. The total velocity is the sum of the velocity of the uncatalyzed reaction and the velocity of the reaction due to the presence of the catalyst. Only the velocity of the latter reaction is influenced by the concentration of the catalyst. This deduction is possible because the decomposition reaction velocities of the catalyzed and the uncatalyzed potassium perchlorate are of the same order of magnitude.

From this point of view, an expression like that of Arrhenius has been developed by which the velocity coefficient under any condition of temperature and concentration of catalyst can be calculated: $K = C.\ 10^{A/T+B} + 10^{A_0/T+B_0}$. Values computed from this expression approximate those experimentally determined.

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[CONTRIBUTION FROM THE HAVEMEYER CHEMICAL LABORATORY, NEW YORK UNIVERSITY]

THE MUTUAL SOLUBILITY OF LIQUIDS. I. THE MUTUAL SOLUBILITY OF ETHYL ETHER AND WATER. II. THE SOLUBILITY OF WATER IN BENZENE

BY ARTHUR E. HILL

Received February 8, 1923

An inspection of the literature shows that measurements of the mutual solubility of liquids are rather surprisingly few, in comparison with the numerous measurements of the solubility of solids in liquids. Such compilations as Landolt's "Tabellen" and Seidell's "Solubilities" contain in all but few pages of results on the liquid-liquid systems. The results themselves are in many instances founded on careful work; in others the results are only approximate, and frequently the temperature ranges are very limited. Lack of completeness and lack of certainty exist for some of the very common pairs of liquids, as for example chloroform and water, of which the composition of the chloroform phase is known at one temperature only, and ether and water, for which the observed values at 0° vary more than 20%. On account of these facts, work has been begun in this Laboratory with a view to extending the number of pairs investigated and to improving the accuracy of our present data when possible.

The solubility of liquids cannot ordinarily be determined by the simple and accurate technique which can be used for solids. No method of really general applicability has been devised. Probably the procedure which has been most often followed is that of Alexejew,[1] according to which weighed quantities of the 2 liquid components are sealed in a glass tube and heated to the temperature at which the 2 phases coalesce, or cooled until the single phase separates into 2 phases, the temperature being marked by the appearance or disappearance of a turbidity. In many cases the point of turbidity can be detected within 0.1° or less, making the method of high accuracy; in some others the tendency to form an emulsion is not present and the method loses in accuracy or fails completely. All in all, however, it appears to be the most generally reliable method which has been devised.

At the time of proposing this excellent method Alexejew, to whom we owe the first complete study of solubilities of liquids, thought well to introduce a general classification of methods. His own procedure, in which the composition of the systems studied was determined by weighing out the com-

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[1] Alexejew, *Wied. Ann.*, **28**, 305 (1886).