TABLE IV

SOME PROTON RELAXATION TIMES FOR SUPPORTED MANGANESE OXIDES

Manganese, %	Relaxation times, millisecs.
0.79/0.79	1.83
.79/0.97	3.66
.79/1.2	6.33

ganese oxide remains on the surface, and dispersion increases out to the lowest concentrations used in these studies.

The decrease in activity at very low concentrations is probably caused by a dispersion of the catalyst oxide in particles so small that they can no longer take part in the reaction. Mechanisms for the carbon monoxide oxidation on various oxides used in hopcalite mixtures have been discussed by Benton,[8] Bray,[9] Frazer[10] and Schwab.[11] The mechanism indicated by all of this work is simultaneous reduction of the surface by carbon monoxide and reoxidation by molecular oxygen. For example, the manganese dioxide catalyst can be reduced to manganese sesquioxide with carbon monoxide and sesquioxide reoxidized with oxygen. For the reaction $2Mn_2O_3 + O_2 \rightarrow 4MnO_2$ to proceed, it is difficult to see how atomically dispersed manganese ions could be effective. Patches containing less than perhaps four manganese ions would remain reduced and be inactive as catalysts.

The constant activation energies for the reaction within each catalyst series seems difficult to reconcile with the above mechanism. Previously published work[1] on the hydrogen peroxide decomposition on manganese oxide catalysts similar to those used in this study showed that the activation energy of the reaction can be changed by 3 or 4 kcal. by the stabilization of one valence state by the support. It would seem that a change of that magnitude should be easily detected in these experiments, and should be expected if the above mechanism is involved. It is possible that this difference in activation energy between members of each series is not found because the rate controlling step in the reaction is not the oxidation or the reduction of the active oxide. But if the measured activation energy actually relates to the oxidation or reduction of the manganese (or other ion), we can only conclude that valence stabilization is less important for the oxidation of carbon monoxide than it seems to be for the catalytic decomposition of hydrogen peroxide.

It should be pointed out that work in this Laboratory and elsewhere has now accumulated a substantial group of reactions and catalyst systems for which a minimum catalytic particle size, or "domain," is necessary. The maximum of specific activity found at low promoter concentrations is reminiscent and confirmatory of Griffith's[12] results on promoted molybdena and similar systems.

Acknowledgment.—It is a pleasure to acknowledge receipt of the Sinclair Refining Company Fellowship, which was held by the junior author. Part of the work was done under contract with the Signal Corps Engineering Laboratories.

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[10] W. A. Whitsell and J. C. W. Frazer, *ibid.*, **45**, 2841 (1923); E. C. Pitzer and J. C. W. Frazer, *J. Phys. Chem.*, **45**, 761 (1941).

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EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF INORGANIC AND ANALYTICAL CHEMISTRY OF THE HEBREW UNIVERSITY AND THE LABORATORIES OF THE SCIENTIFIC DEPARTMENT, MINISTRY OF DEFENCE]

Thermal Decomposition of Potassium Chlorate and Chlorate–Chloride Mixtures[1]

BY A. GLASNER AND L. WEIDENFELD

The continuous evolution of oxygen from pure potassium chlorate and from potassium chlorate–chloride mixtures was measured gasometrically, at temperatures ranging from 400 to 575°, and in each case the composition of the residue was determined. The activity of potassium chloride depends on the history of each specimen; certain specimens accelerate the evolution of oxygen, while others, due to their assumed ability to absorb "active" oxygen, favor the formation of perchlorate. Also in ternary mixtures of chlorate–chloride–perchlorate an induced formation of perchlorate has been observed. These phenomena explain the establishment of an equilibrium made evident by almost complete cessation of the evolution of oxygen, especially at lower temperatures. The conflicting results reported by previous workers were compared with our results and were found to conform with the use of different specimens of potassium chloride.

The thermal decomposition of potassium chlorate has been studied by Serullas[2] and others.[3–5] Farmer and Firth[3] found that potassium chloride accelerated the reaction so that in shorter time intervals, as compared with pure chlorate, equal amounts of perchlorate were produced, but the amount of oxygen evolved increased whereas the data of Otto and Fry[4] indicate the effect of potassium chloride to be just the opposite. When Hofmann and Marin[5] heated pure potassium chlorate, they obtained a 72% by weight conversion to perchlorate.

The object of this work was to clarify the mechanism of these complex reactions and elucidate whether or not an equilibrium exists between oxygen and the oxygenated halogenides. Experimental: $KClO_3$ Kahlbaum p.A. and Baker Analyzed $KClO_3$ and KCl were used.

Experimental

The apparatus consisted of a Pyrex reaction vessel and a gasometer (Fig. 1). The lower part of the apparatus fitted

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[1] For material supplementary to this article order Document 3490 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

[2] Serullas, *Ann. chim. phys.*, [2] **45**, 270 (1830); **46**, 325 (1831).

[3] W. Farmer and J. B. Firth, *J. Chem. Soc.*, **125**, I, 82 (1924).

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slopewise into a tubular electric oven while the upper part was wrapped in asbestos. Two chromel–Alumel thermocouples were used for measuring the temperature: one was placed inside the reaction vessel; the other touched it from the outside. A test-tube (50 mm. × 10 mm.) holding the sample (~ 2 g.) was placed in the side arm A. Water saturated with oxygen was used as the leveling liquid in the gasometer.

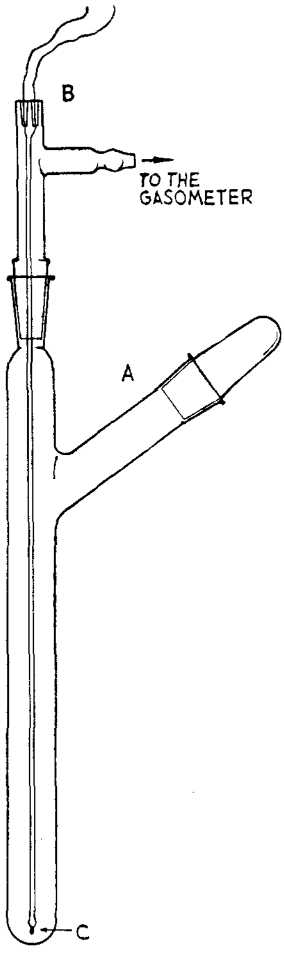

Fig. 1.—Reaction vessel with thermocouple.

The reaction vessel was maintained for 15–20 minutes at the temperature desired for the reaction before the test-tube plus the sample was dropped into the lower part of the apparatus. The amount of oxygen evolved was recorded as a function of time. The ternary mixtures, KClO$_3$-KCl-KClO$_4$, formed during the reaction (or initially prepared) were partly melted at the lower temperatures, but occasionally they became a clear melt at higher temperatures. The residue from each run was analyzed for both chlorate and chloride, and the perchlorate was taken as the difference from 100%. The loss of oxygen could be calculated from the analytical results and checked by the volume of the gas actually observed in the gasometer. The agreement, on the whole, was fairly good (±2%).

(a) **Decomposition of Pure Chlorate.**—Figure 2 shows the evolution of oxygen (in %) as a function of time at various temperatures, from 455 to 575°. On the 527° curve points from two separate runs were plotted in order to show the reproducibility of the experiments. The curves obtained at the various temperatures are not all of the same type: at 455° the evolution of gas is slow, amounting to only 2.5% after 200 minutes, and it is nearly linear. At 506 and 527° the curves are of the S type showing a greatly reduced slope far below 100% of oxygen evolved. At higher temperatures the curves tend to a form typical for a first order reaction.

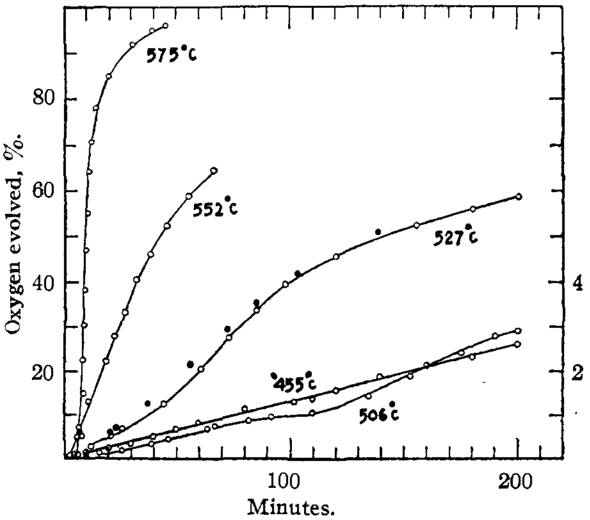

Fig. 2.—The decomposition of pure chlorate at various temperatures for the 455° curve use the right-hand scale).

Comparing the times necessary for the evolution of 20% of oxygen a temperature coefficient of *three*, for 25°, is obtained. This gives an apparent energy of activation equal to 54,000 cal./mole.

(b) **Chlorate–Chloride Mixtures.**—Figure 3 shows the evolution of oxygen (in %) from chlorate–chloride mixtures (1:1.14[A], or 8:1 by wt.) dried at 110° for two hours. The catalytic action of the chloride on the rate of gas evolution is evident; the mixture decomposes at 400° more quickly than the pure chlorate at 500° and the effect increases greatly with the proportion of chloride present. The sudden flattening of the curves at a degree of decomposition far below 100 per cent. is characteristic.[6]

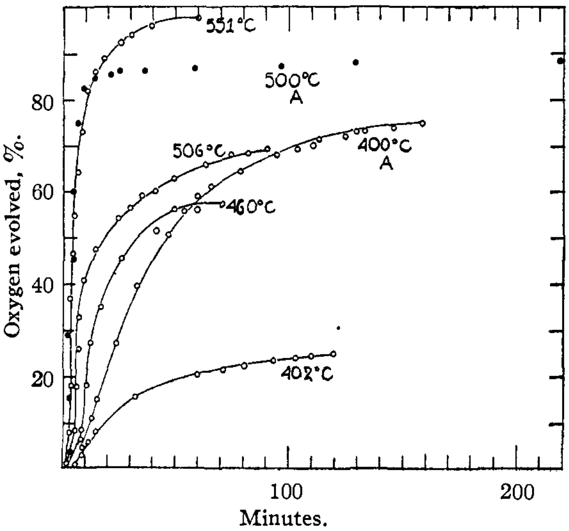

Fig. 3.—The decomposition of chlorate in chlorate–chloride mixtures 8:1 by wt. (dried at 110°). Curves marked by A had the original composition KClO$_3$/KCl = 1:1.14 by wt.

(c) **Chlorate–Chloride and Perchlorate Mixtures.**—The flattening of the decomposition curves and the observation that invariably some perchlorate is produced in the decomposition led to an investigation of the decomposition of the chlorate in ternary mixtures.

The molar composition and the rate of evolution of oxygen from these samples at 455° is shown in Fig. 4.

The catalytic effect of the chloride is inhibited in these mixtures by the presence of the perchlorate, this inhibition becoming more pronounced with the increase in the molar ratio KClO$_4$/KCl. No. 5, containing chloride from a previously decomposed mixture, is an exception; the evolution of oxygen in this case is as slow as for the pure chlorate at the same temperature. All five curves in Fig. 4 demonstrate a sudden decrease in the rate of decomposition; they give the impression that the mixtures are approaching a state of equilibrium.

(d) **Mixtures with Other Specimens of Potassium Chloride.**—The results with mixtures No. 5 in Fig. 4 indicate that there exist differences between different samples of potassium chloride. Two samples of the latter were prepared: (1) by complete thermal decomposition of potassium perchlorate (KCl*); (2) by heating potassium chloride at 600° for one hour (KCl**). Both samples were shown by argentometric titration to contain 100% KCl. These samples

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[6] Mixtures prepared from the same lot of potassium chloride with Kahlbaum or Baker brand of potassium chlorate always gave identical results, irrespective of powder size or the way of mixing. But experiments repeated at a later period with a different lot of potassium chloride gave results analogous to those with the heated specimen described (d). Preliminary results on further experimentation, with chlorate–chloride mixtures, have shown that irradiation of the chloride by weakly radioactive substances, various heat treatments, or the addition of certain impurities, influence greatly the relative amount of oxygen evolved and perchlorate formed, under otherwise identical conditions,

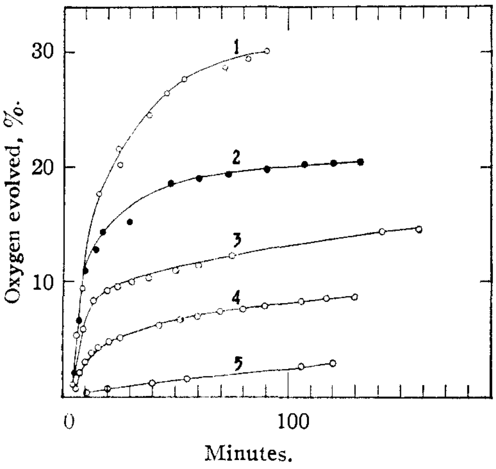

Fig. 4.—The decomposition of chlorate in ternary mixtures at 455° (dried at 110°). For 100 moles $KClO_3$ the samples contained moles of KCl and $KClO_4$ as follows: 1, 25:18.75; 2, 50:75; 3, 25:37.5; 4, 25:75; 5, 92.5:14.5; sample 5 was prepared from a partially decomposed chlorate–chloride mixture to which a further amount of chlorate has been added.

were mixed with chlorate in the molar ratio of 100:20.4, and subjected to thermal decomposition at temperatures between 450 to 550°. The rate of oxygen evolution is shown in Fig. 5. The curves obtained are almost identical with those of pure chlorate at the corresponding temperatures. Thus the potassium chloride obtained by the decomposition of perchlorate behaves differently from the analytical KCl dried at 110°. The analytical KCl heated at 600° has only a slight accelerating effect on the evolution of oxygen from the chlorate.

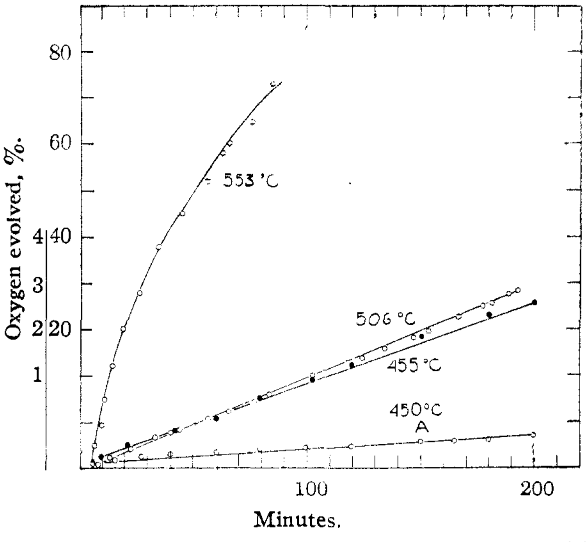

Fig. 5.—The decomposition of chlorate in mixtures with chloride obtained from potassium perchlorate (8:1 by wt.). The sample which contained KCl** is marked with A. For the 455° curve use small scale on left.

Analysis of the Decomposition Residues.—In Table I are summarized the analytical results obtained with pure potassium chlorate, and its mixtures with the various specimens of potassium chloride and perchlorate. All results are expressed in percentages of chlorate, based on the consideration that the $KClO_4$ formed according to the equation: $4KClO_3 \rightarrow 3KClO_4 + KCl$, equals 75 mole % of $KClO_3$. The oxygen evolved and the ratio *R*, obtained by dividing the per cent. of chlorate converted into perchlorate by the per cent. of gas evolved, are given in the last two columns of the table.

TABLE I

ANALYSIS OF VARIOUS DECOMPOSITION RESIDUES, EXPRESSED IN MOLE % OF $KClO_3$

Samples of KCl added[a]	Temp., °C.	Time, min.	$KClO_3$ residual, %	$KClO_4$ formed, %	O_2 evolved, %	*R*
None	455	70	89.9	5.55	2.7	2.0
		130	82.9	10.2	3.5	2.9
		200	82.3	11.15	2.9	3.1
		200	80.7	11.75	3.65	3.2
	510	62	4.6	54.9	22.2	2.5
	506	200	6.8	48.0	29.2	1.64
	552	66	3.66	24.0	64.3	0.37
	575	10	4.46	37.74	45.3	0.83
20.4 KCl	402	120	70.6	3.3	25.0	0.13
	451	71	27.5	11.4	57.3	0.2
	505	70	5.6	25.0	61.1	0.41
	510	62	4.4	28.3	57.9	0.49
	551	60	0.34	1.62	97.5	0.017
188 KCl	406	30	42.3	3.5	53.0	0.06
		166	19.5	4.5	74.5	0.06
20.4 KCl*	455	130	72.7	19.0	2.0	9.5
		200	51.3	34.0	3.5	9.7
	506	70	7.3	58.7	14.4	4.1
		200	6.0	42.0	38.0	1.1
	553	60	1.3	14.3	79.6	0.18
20.4 KCl**	454	70	77.7	14.7	2.7	5.45
	450	200	49.6	32.9	6.54	5.0
	510	62	7.15	47.75	29.2	1.6
KCl; $KClO_4$						
25; 18.75	455	90	57.0	9.75	30.0	0.33
25; 37.5	455	130	42.3	31.5	15.7	2.0
25; 37.5	450	228	35.5	37.3	14.8	2.5
50; 75	452	132	42.5	27.9	20.3	1.37
92.5; 14.5	456	120	78.0	14.3	2.9	4.96

[a] Moles per 100 moles of potassium chlorate.

Discussion

All previous authors have assumed that potassium chlorate decomposes simultaneously in two ways

$$2KClO_3 \longrightarrow 2KCl + 3O_2 \qquad \text{(I)}$$

and

$$4KClO_3 \longrightarrow 3KClO_4 + KCl \qquad \text{(II)}$$

and that potassium chloride catalyzes either one or the other of these reactions. In the present work the rate of evolution of oxygen in accordance with reaction (I) may be judged from Figs. 2–5, which leave no doubt as to the effect of the various specimens of potassium chloride.

The rate of the formation of perchlorate (II) may be judged by the analyses of the partly decomposed residues summarized in Table I: (1) By comparing the percentages of the products formed in a certain time and temperature. (2) By comparing the ratio of the percentages of perchlorate to oxygen produced (*R*).

Comparisons should be made preferably at low temperatures (455°) and with samples in which the decomposition of the chlorate has not gone too far. When this is done, it may be easily seen that KCl*, KCl** and $KClO_4$ increase considerably the rate of formation of perchlorate, producing thereby only a slight increase in the rate of evolution of oxygen.

The experiments of Hofmann and Marin[4] demonstrate that the ratio R varies only slightly for 20 to 90% chlorate decomposed at a given temperature. Some of our pairs of experiments (Table I) confirm this. Thus within certain limits results may be expressed by a single figure. In our experiments with pure chlorate at 455°, R had a value around 3. In mixtures with KCl^* this rose up to 10 while in mixtures with KCl dried at 110°, R was reduced to 0.2 and even to 0.06. The latter results are qualitatively similar to those of Farmer and Firth[3] but more accentuated in the release of oxygen. On the other hand, our results with KCl^{**} were very much like those of Otto and Fry,[4] yielding a value around 5 for R.

Considering the relative constancy of R for a certain mixture and temperature as well as the general accelerating effect of all specimens of potassium chloride on the decomposition of the chlorate (see Table I), we have come to the conclusion that reaction (II) is not a *simultaneous* reaction, but the perchlorate is formed in a *consecutive* reaction with potassium chloride which is capable of absorbing oxygen derived from reaction (I). As KCl^* does not absorb oxygen from the air we assume that atomic oxygen is involved in this reaction. Further, we suggest that in the various mixtures a real equilibrium is obtained[7] in which the perchlorate and chlorate are continuously formed and decomposed. This is evident from the flattened curves in Figs. 3 and 4, where the continued slow evolution of gas probably is due to the occasional formation and escape of oxygen molecules.

It is of interest that the presence of perchlorate in these mixtures "induces" the potassium chloride dried at 110° to increase its power for the absorption of oxygen, so that in a series of mixtures the ratio R increases with the relative amount of perchlorate present.

The maximum values of R attained in KCl^* mixtures suggest a kind of "memory effect."[8]

The activity of the various specimens of chloride may be due to strains, as assumed by Hedvall,[9] or to crystal defects (for example of the Shottky–Wagner type). In this connection the substantial differences observed by Vaino Hovi[10] in the heat of formation of mixed crystals should be mentioned.

The possible influence of the fact that the fused mixture solidifies in the course of a run, has not been dealt with.[11] However a forthcoming paper will show that the state of aggregation of such mixtures is of only secondary importance.

These experiments were carried out under the auspices of the Scientific Department, Israeli Ministry of Defence, and are published with its permission.

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(10) Vaino Hovi, *Ann. Acad. Sci. Fennicae, Ser. A. I. Math.-Phys.*, Nos. 54, 55 (1948).

(11) FIAT Review of German Science 1939–1946, Inorg. Chem. Part V, W. Schroder, "Löslichkeitsgleichgewichte," pp. 149–151.

JERUSALEM, ISRAEL RECEIVED MARCH 19, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF INORGANIC AND ANALYTICAL CHEMISTRY OF THE HEBREW UNIVERSITY AND THE LABORATORIES OF THE SCIENTIFIC DEPARTMENT, MINISTRY OF DEFENCE]

The Thermal Decomposition of Potassium Perchlorate and Perchlorate–Halogenide Mixtures. A Study in the Pyrolysis of Solids

BY A. GLASNER AND L. WEIDENFELD

The kinetics of the thermal decomposition of potassium perchlorate and its mixtures with potassium halogenides were studied at atmospheric pressure. The decomposition curves of the perchlorate are of the sigmoid type characteristic for solid reactions. The halogenides reduce the induction period and accelerate the decomposition. In some cases, at comparatively low temperatures, the reaction mixtures retain a considerable percentage of oxygen. It is suggested that the oxygen may diffuse through the partially decomposed perchlorate and thus establish a state of equilibrium. A probable mechanism for the decomposition of the perchlorate is proposed; the equation arrived at for the rate of decomposition represents the experimental results satisfactorily. The proposed mechanism may be generally applicable to the type of reactions represented by: solid I → solid II + gas.

Potassium perchlorate is reported to melt at 610°, and to decompose appreciably at temperatures above 500°.[1] On partial decomposition the perchlorate fuses at about 536°. Otto and Fry[2] studied the kinetics of the decomposition, beginning at the point of fusion, and concluded that it is a reaction of the first order, corresponding to the simple equation: $KClO_4 \rightarrow KCl + 2O_2$ and that no chlorate is formed as an intermediate. Hofmann and Marin,[3] on the other hand, concluded from the analysis of a large number of partially decomposed perchlorate samples, that up to 14.55% (by weight) chlorate was formed from pure perchlorate and 35.4% from perchlorate–chloride mixtures.

The object of this study was to elucidate the mechanism of the thermal decomposition of potassium perchlorate especially in the solid state (before fusion has set in). The curves representing the oxygen evolution *versus* time are of the sigmoid type characteristic for many reactions of solids.[4] Of the expressions proposed for solid reactions of the type

$$\text{solid I} \longrightarrow \text{solid II} + \text{gas}$$

that formulated by Prout and Tompkins[5]

$$\log (x/1 - x) = kt + c$$

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