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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[7] J. Brousquet and M. Dodé, *Compt. rend.*, **230**, 87 (1950).

[8] W. A. Weyl and Tormod Förland, *Ind. Eng. Chem.*, **42**, 257 (1950).

[9] Hedvall, *Chem. Eng. News*, **27**, 1478 (1950).

[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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[1] G. G. Marvin and L. B. Woolaver, *Ind. Eng. Chem., Anal. Ed.*, **17**, 474 (1945).

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

[3] K. A. Hofmann and P. H. Marin, *Sitzber. preuss. Akad. Wiss. phys.-math. Klasse*, 448 (1932).

[4] W. E. Garner, *Trans. Faraday Soc.*, **34**, 940 (1938).

[5] E. G. Prout and F. C. Tompkins, *ibid.*, **40**, 488 (1944).

and found valid earlier by Lewis,[6] was found most useful.

Experimental

For most of our experiments a locally prepared and purified potassium perchlorate (+200 mesh) was used; it contained 0.007% chloride. For some runs J. T. Baker analyzed $KClO_4$ was used. KCl and KI were J. T. Baker analyzed C.P., while the KBr was a Palestine Potash Ltd. product B.P. The apparatus and the analytical methods are described partly in the preceding article.[7]

The kinetic measurements with pure perchlorate showed poor reproducibility. Figure 1 represents a series of decomposition curves obtained at 558 ± 3°; the variations could not be attributed to any one of the factors indicated under Fig. 1. (Concerning the reproducibility of solid reactions see Macdonald.[8])

In the analysis of the products obtained from perchlorate-halogenide mixtures, the chlorate and chloride (plus bromide) were determined by titration and the perchlorate by difference.

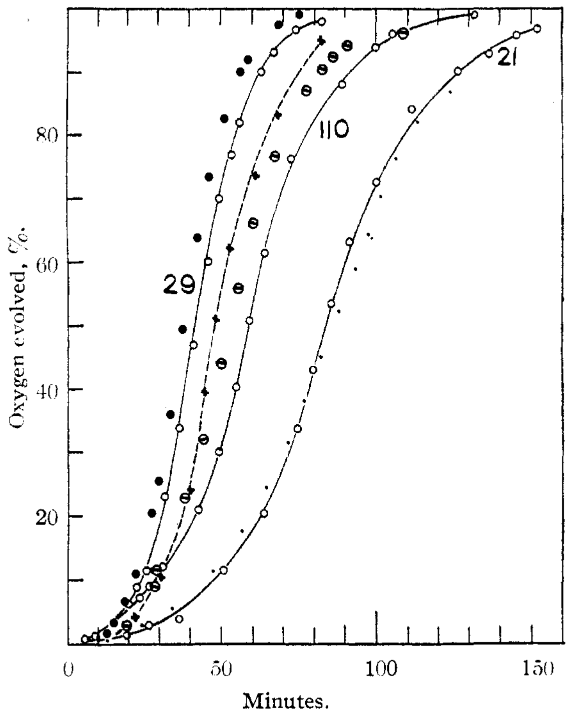

Fig. 1.—Decomposition curves of potassium perchlorate at 558°: all samples were ground to +200 mesh (except 112) and were dried at 110° (except 34). 112 contained chosen crystals of J. T. Baker analyzed. 34 was dried at 350° just before the run. Samples 21, 29, 34, 110, 112 weighed 1.0 g. each; sample 28 weighed 0.1 g.; sample 7 weighed 2.0 g. The i.d. of the reaction tube for samples 7, 28, 29 was 13 mm. for the rest 10 mm.: •, 7; ●, 28; ⊖, 34; +, 112.

The analysis of the products from perchlorate–iodide mixtures was carried out as follows: (1) **Iodate**: The iodine liberated after the addition of an excess of iodide and acid was titrated with *a* ml. of 0.1 *N* thiosulfate. (2) **Iodate + chlorate**: The solution was boiled with acid ferrous sulfate and the excess ferrous sulfate titrated with 0.1 *N* permanganate. The difference between this titration and the volume corresponding to the original amount of ferrous salt was *b* ml. (3) **Sum of chloride and iodide**: Titration with 0.1 *N* silver nitrate required *c* ml. (4) **Iodide**: The solution was made slightly acid and the iodine liberated was boiled off. After cooling an excess of potassium iodide was added followed by the titration of the liberated iodine by *d* ml. of 0.1 *N* thiosulfate.[9]

Therefore, the amounts of the respective salts present in the mixture, expressed in millimoles, were

$$KIO_3 = \frac{a}{10 \times 6};\ KI = \frac{5(a-d)}{10 \times 6};\ KCl = \frac{6c - 5(a-d)}{10 \times 6}$$

$$\text{and } KClO_3 = \frac{6b - 5a + 5(a-d)}{10 \times 6} = \frac{6b - 5d}{60}$$

Analytical results are expressed in mole % of perchlorate so that they may be related to the oxygen collected in the gasometer by the equation

$$\%\ KCl + {}^1/_4\%\ KClO_3 = \%O_2 \text{ evolved}$$

or, in the case of perchlorate–iodide mixtures

$$\%\ KCl + {}^1/_4\%KClO_3 - {}^3/_4\%KIO_3 = \%O_2 \text{ evolved}$$

Results

I. Kinetic Measurements. A. Pure Perchlorate.—In Fig. 2 are shown the decomposition curves of pure potassium perchlorate at temperatures between 537 and 600°. The induction period is shortened as the temperature rises, yet the autocatalytic effects is well defined even at 600°. Though the salt fuses after 15–20% of it has decomposed and again solidifies no breaks on the curves are observed. On plotting log $(x/1 - x)$ *versus* time (x being the fraction of oxygen evolved), curves composed of two straight lines are obtained giving two constants of reaction designated by Prout and Tompkins by k_a (acceleration) and k_d (decay). Similar plots were obtained for various solids by other investigators.[10]

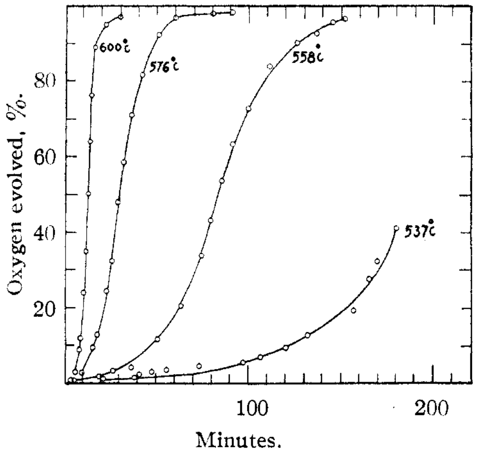

Fig. 2.—The decomposition of pure potassium perchlorate at various temperatures.

The half times ($t_{0.5}$) and the reaction rate constants (k), are summarized in Table I.[11] From these figures the activation energy E = 65,800 cal./mole and the probability factor $A = 1.15 \times 10^{16}$ were calculated.

B. Perchlorate–Chloride Mixtures.—The rate of oxygen evolution from mixtures 10:1 and 1:1 by wt. is shown in Figs. 3 and 4, respectively.

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[6] G. N. Lewis, *Z. physik. Chem.*, **52**, 310 (1905).

[7] A. Glasner and L. Weidenfeld, This Journal, **74**, 2464 (1952).

[8] J. Y. Macdonald, *J. Chem. Soc.*, 832 (1936).

[9] These methods were tested by analyzing mixtures of known composition and proved to give good results.

[10] L. L. Bircumshaw and I. Harris, *J. Chem. Soc.*, 1898 (1948); L. L. Bircumshaw and J. Edwards, *ibid.*, 1800 (1950); J. Vaughan and L. Phillips, *ibid.*, 1560 (1947).

[11] Zero time is taken at 3 minutes after the fall of the sample into the reaction vessel, this being the time required by the samples to attain the temperature of the oven.

TABLE I

THE DECOMPOSITION CONSTANTS OF PURE $KClO_4$

Temp., °C.	$t_{0.5}$ min.	$k_a \times 10^2$	$k_d \times 10^2$
537	185	2.98	..
558	80.6	6.73	4.70
576	27.0	17.0	4.90
600	9.7	52.3	6.40

The induction period is greatly reduced in the former and practically eliminated in the latter mixtures. The results with the 1:1 mixture, were plotted using the first order equation (constants k_F) and Prout and Tompkins' equation (constant k_S). Straight lines were obtained in both cases but in the latter the agreement is better (Fig. 5). The reaction constants thus obtained are given in Table II, together with the calculated constants of the Arrhenius equation.

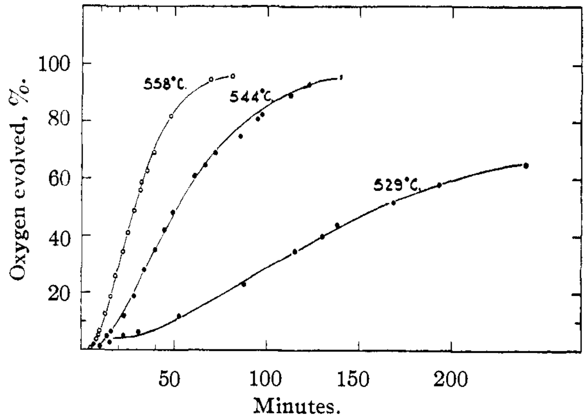

Fig. 3.—The decomposition of potassium perchlorate–chloride mixtures 10:1 by wt.

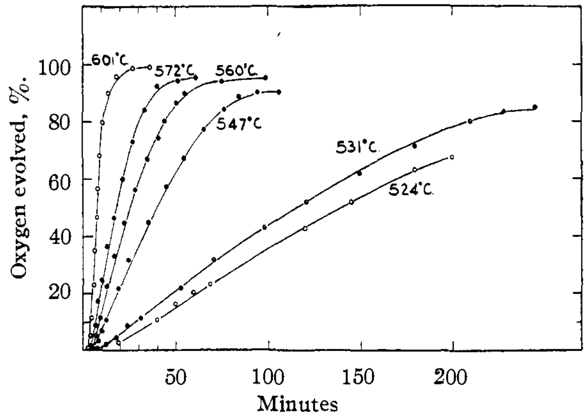

Fig. 4.—The decomposition of potassium perchlorate–chloride mixtures 1:1 by wt.

TABLE II

REACTION CONSTANTS, k_F (FIRST ORDER EQUATION) AND k_S (PROUT AND TOMPKINS' EQUATION), FOR THE DECOMPOSITION OF PERCHLORATE–CHLORIDE MIXTURES

Temp., °C.	524	531	547	560	572	601	$A \times 10^{-15}$	E
$k_F \times 10^2$	0.71	0.94	2.76	4.90	7.25	27.9	6.67	65,400
$k_S \times 10^2$	1.46	1.59	4.69	8.00	10.24	46.7	6.38	64,500

At the same temperatures k_S is approximately equal to k_a for pure perchlorate; also the differences in A and E are not greater than the probable experimental error.

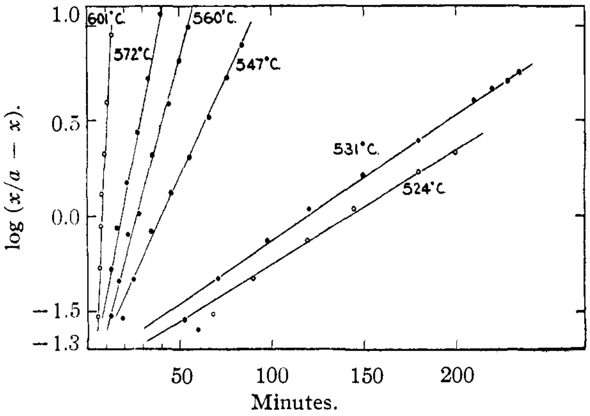

Fig. 5.—Prout and Tompkins' equation applied to the decomposition of perchlorate–chloride mixtures 1:1 by wt.

C. Perchlorate–Bromide Mixtures.—In perchlorate–bromide mixtures, 1:1 by wt. (see Fig. 6), the induction periods are reduced to a minimum at higher temperatures while at the lower temperatures the mixtures appear to approach an equilibrium, retaining 18–25% of the initial amount of oxygen.

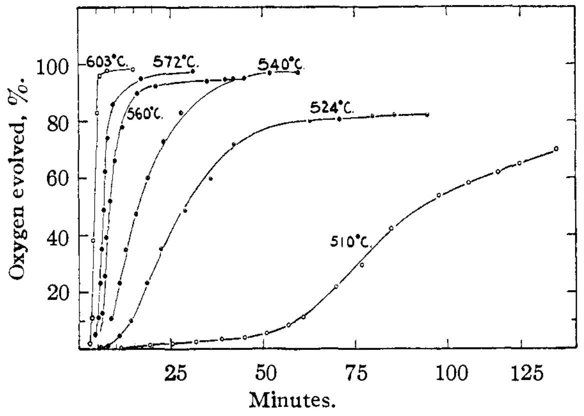

Fig. 6.—The decomposition of potassium perchlorate–bromide mixtures 1:1 by wt.

The mixtures with bromide melted at lower temperature than those with chloride, and Prout and Tompkins' equation does not fit the experiments. On plotting log $(a/a - x)$ *versus* time, however (Fig. 7), a straight line is obtained for each temperature. Taking into account the incomplete decomposition of the perchlorate at the lower temperatures (510 and 524°), a was assumed to be, in these cases, 85% of the amount of perchlorate used.

Table III shows that the rate of decomposition of the perchlorate–bromide mixture is about six times faster than the perchlorate–chloride

TABLE III

FIRST ORDER REACTION CONSTANTS FOR THE DECOMPOSITION OF PERCHLORATE–BROMIDE MIXTURES

Temp., °C.	510	524	540	560	572	603	$A \times 10^{-15}$	E
$k_F \times 10^2$	2.12	5.41	8.63	30.4	46.0	69.0	9.60	63,100

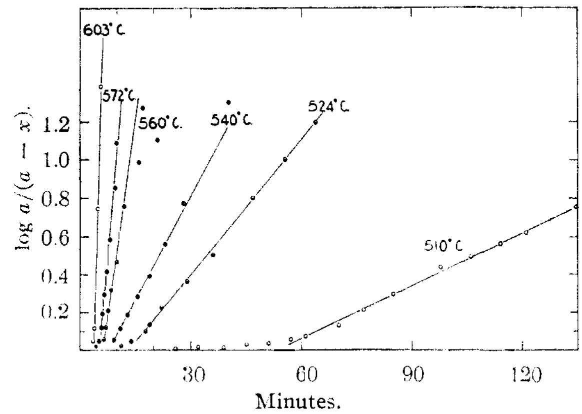

Fig. 7.—The first order equation applied to the decomposition of perchlorate–bromide mixtures.

mixture. This is due to a lower energy of activation (E), A being approximately the same as for pure perchlorate.

D. Perchlorate–Iodide Mixtures.—The catalytic action of potassium iodide on the decomposition of potassium perchlorate was violent, so measurements could be made only at temperatures below 500°. In mixtures 10:1 by wt. (Fig. 8) an induction period was observed, especially at lower temperatures, and the evolution of oxygen ceased before complete decomposition. In order to evaluate the temperature coefficient and the apparent energy of activation (E), the tangents at the steepest parts of the curves (tan α) were compared (Table IV).

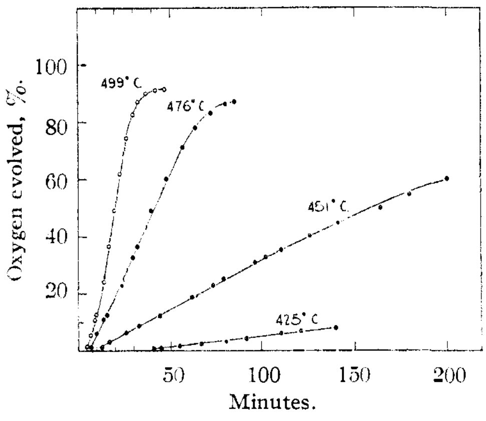

Fig. 8.—The decomposition of potassium perchlorate–iodide mixtures 10:1 by wt.

TABLE IV

COMPARATIVE RATE OF EVOLUTION OF OXYGEN FROM PERCHLORATE–IODIDE MIXTURES

Temp., °C.	425	451	476	499	E
tan α	0.094	0.353	1.5	4.8	57,200

On plotting log tan α *versus* $1/T$, where T is the temperature on the absolute scale, points lying on a straight line were obtained. The energy of activation E = 57,200 cal./mole was calculated.

Perchlorate–iodide mixtures 1:1 by wt. decomposed at a measurable rate even at 375°. The gasometric curves were discontinuous; at 410° for example, there was an induction period of nearly one hour, after which a sudden burst (*ca.* 6%) of oxygen occurred, followed by a continuous slow decomposition. It will be shown later that during the induction period more than 90% of the iodide was converted into iodate.

II. Analytical Results.—Some analytical results of partly decomposed samples of pure perchlorate and of mixtures with chloride or with bromide are given in Table V. All values are given in mole % of the initial amount of perchlorate. Chlorate is formed as an intermediate in all cases: its quantity decreases with rising temperature, and is somewhat larger for mixtures with halogenides than for pure perchlorate. The last perchlorate–bromide mixture (524°) was analyzed some time after the evolution of oxygen had stopped. This sample did not contain any chlorate, but the retained oxygen could be released on increasing the temperature.

TABLE V

ANALYSIS OF PARTIALLY DECOMPOSED POTASSIUM PERCHLORATE

Halogenide added[a]	Temp., °C.	O_2 evolved, %	KCl formed, %	$KClO_3$ formed, %	$KClO_4$ residual, %
	535	53.7	51.0	7.3	41.7
	561	26.6	23.9	6.3	69.8
	558	31.4	29.0	6.9	64.1
None	562	69.0	67.0	5.8	27.2
	575	6.3	4.75	1.52	93.7
	575	23.5	19.8	3.71	76.5
	575	66.15	63.2	2.95	33.85
	549	42.5	41.5	4.7	53.8
KCl 188	558	66.3	65.0	8.3	26.7
	573	...	48.4	5.0	46.6
	517	21.7	16.6	9.4	74.0
	510	32.0	33.4	7.8	58.8
KBr 116	516	53.0	47.0	5.3	47.7
	510	84.0	83.7	0.83	15.5
	524	85.0	84.0	0.0	16.0

[a] Numbers indicate moles per 100 moles of perchlorate.

The analytical results for the perchlorate–iodide mixtures are given in Table VI. Since the solutions of the samples were neutral and no iodine was ever liberated, it is concluded that no periodate was formed.

The complexity of the mixtures inevitably re-

TABLE VI

ANALYSIS OF PARTIALLY DECOMPOSED POTASSIUM PERCHLORATE–IODIDE MIXTURES

KI[a]	Temp., °C.	O_2 evolved, %	KCl formed, %	$KClO_3$ formed, %	$KClO_4$ residual, %	KI residual	KIO_3 formed
81	380	0.0	10.9	37.0	52.1	54.8	25.6
		.0	16.4	41.0	42.6	52.0	30.0
		.0	39.4	53.6	7.0	9.6	71.0
		3.7	52.8	39.8	7.4	0.0	78.0
		15.25	75.0	20.0	5.0	.0	79.6
	400	14.6	68.8	21.2	10.0	.0	78.0
		25.0	90.0	6.54	3.46	.0	82.0
8.65	425	4.05	7.6	7.6	84.8	0.0	7.9
	425	8.00	15.0	5.3	79.7	.0	7.72
	451	60.0	67.2	2.28	30.52	.0	7.9
	476	87.2	95.0	0.63	4.37	.0	7.6
	499	91.2	100.0	0.53	0.0	1.21	7.0
134	400	25.5	100.0	0.0	0.0	34.0	100
	425	26.5	100.0	0.0	0.0	36.2	97.8

[a] Moles per 100 moles of potassium perchlorate.

duces the accuracy of the analysis, thus not in all cases does the oxygen or the iodine add up to the original amounts.

During the incubation period the perchlorate decomposes without evolution of oxygen since this is absorbed by the iodide to form iodate. The decomposition of the perchlorate is stepwise, producing initially chlorate, so that in mixtures with much iodide over 50% chlorate may accumulate. Generally no gas is evolved until over 90% of the iodide has been converted. An exception was observed in the 100:134 mixtures, in which over 25% of the oxygen was released in a sudden burst (the total reaction time = 16 minutes) though only about 75% of the iodide had been consumed. An analogous burst of oxygen was mentioned earlier with the 100:81 mixtures, whereas in the case of the 100:8.65 mixtures this effect was hardly noticeable.

Both the perchlorate and the chlorate continue to decompose, after the complete conversion of the iodide into iodate, at temperatures at which the pure substances would not decompose. This catalytic effect of the iodate reported by Hofmann and Marin[3] was confirmed by us in experiments not recorded here.

Discussion

Tables V and VI prove that the decomposition of the perchlorate proceeds stepwise and that chlorate is formed invariably as an intermediate. This reaction is accelerated by the halogenides in the order of increasing atomic weights. Thus the temperature at which the decomposition of the perchlorate becomes appreciable is reduced by more than 100° by potassium iodide, which is converted into iodate. It is unlikely that reactions such as

$$\mathrm{KClO_4 + KI \longrightarrow KCl + KIO_3 + O}$$

or

$$\mathrm{KClO_3 + KI \longrightarrow KCl + KIO_3}$$

occur as these would not allow for the large accumulation of chlorate observed. Furthermore, the decomposition of perchlorate as well as chlorate is accelerated by the iodate, yet no oxygen is evolved from these mixtures until the greater part of the original iodide has disappeared. It is, therefore, suggested that by the decomposition of perchlorate or chlorate active, probably atomic, oxygen is produced, which reacts with the iodide

$$\mathrm{KI + 3O \longrightarrow KIO_3}$$

In the preceding paper[7] it has been concluded that the formation of perchlorate from chlorate proceeds by a similar process and the following reactions are postulated

$$\mathrm{KClO_4\,(+KCl) \longrightarrow KClO_3\,(+KCl) + O}$$

$$\mathrm{KClO_3 \longrightarrow KCl + 3O}$$

$$\mathrm{KCl + 4O \rightleftharpoons KClO_4}$$

This leads eventually to an equilibrium, which has been actually observed in a number of cases, *e.g.*, in the perchlorate–bromide mixtures (see also ref. 3).

The existence of an equilibrium would require at least one of the reactants to be mobile. As in most (though not in all) cases the equilibrium mixtures are solid, it must be assumed that at elevated temperatures atomic oxygen may diffuse through the partially decomposed perchlorate lattice. Glasner and Simchen[12] have calculated that the distance between the periphery of two adjacent chloride ions occupying the original sites of two perchlorate ions is greater than the diameter of an oxygen atom (see also Garner).[13] Incidentally, a collapse of the perchlorate lattice would disturb the postulated equilibrium, a phenomenon which may account for the sudden burst of oxygen observed in the perchlorate–iodine mixtures.

Regarding the kinetics of the decomposition of potassium perchlorate it has been noted that this is analogous to the thermal decomposition of some solids, and on plotting the values of log $(x/1 - x)$, *versus* time, curves similar to those of other solid reactions were obtained. Prout and Tompkins' equation written in the differential form

$$dx/dt = kx(1 - x)$$

demands that the rate of the reaction be proportional to the mass of both the decomposed and the undecomposed salt present. This could only be understood if the reagents mix thoroughly in the solid state.[4,6,14] However if we assume a certain mobility of the liberated gas through the original lattice an explanation for the mechanism of decomposition can be given which is in accordance with the observed kinetics.

Spontaneous decomposition should start on the surface of the perchlorate crystal

$$\mathrm{KClO_4 \longrightarrow KCl + 2O_2}$$

The chloride ion thus formed may attract oxygen atoms from neighboring perchlorate ions thereby producing a new chloride ion on the surface or in the next layer of the lattice. This reaction could advance into the crystal in a zig-zag line, and a stream of oxygen could flow from the inside to the surface. It could be expected that the chloride ions thus surrounded by a stream of oxygen would not catalyze the further decomposition of adjacent perchlorate ions, and of the temperature were sufficiently low, perchlorate ions could be formed again. Occasionally there will be a disruption in the flow of oxygen, the frequency of which will depend on the ratio of the rate of diffusion to that of dislocation of oxygen from perchlorate ions. At points where such discontinuities occur a new line of decomposition may start which would produce a branching chain reaction. The rate of decomposition would be, therefore, proportional to the total length of the line of chloride ions present at any moment in the crystals (x).[15] Also as the number of neighbors of any given ion in a crystal is fixed, and branching on the side of a certain ion could occur only a limited number of times, the decomposition would be proportional to the amount of undecomposed perchlorate ions $(1 - x)$. Including the spontaneous surface de-

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(12) A. Glasner and E. Simchen, *Bull. soc. chim.* [5] **18**, 233 (1951).

(13) W. E. Garner, *J. Chem. Soc.*, 1239 (1947).

(14) D. J. M. Bevan, J. P. Shelton and J. S. Anderson, *ibid.*, 1729 (1948).

(15) Being virtually equivalent to the fraction of oxygen decomposed.

composition, we thus obtain for the rate of evolution of oxygen the equation

$$dx/dt = kx(1 - x) + k_1(1 - x)^{2/3}$$

This equation was integrated numerically for a number of runs and found to coincide with the experimental curves. As the surface decomposition is as a rule much slower than the autocatalytic reaction, the fractional index may be taken equal to one to a good approximation; with $K = k_1/k$ integration gives

$$\frac{1}{K + 1} [\log (K + x/1 - x) - \log K] = kt \quad (1)$$

This equation offers two improvements as compared to that of Prout and Tompkins: (1) the plots of the logarithmic term *versus* time do not start at minus infinity; (2) by a proper choice of K the asymmetry of the sigmoid curve is compensated and a single rate constant is obtained.

From the inflection point of the experimental decomposition curves we have $K = 1 - 2x_{max}$ (x_{max} being the fraction of solid decomposed up to the point of maximum reaction velocity). If K is extremely small, x_{max} is nearly equal to 50%,[6] and $k = k_a = k_d$. For medium values of K we have $k_a > k > k_d$. If K is large, equation (1) approaches the form of a first order kinetics (Fig. 7) and k approaches k_F. Also, when x is not very different from 1 a first order kinetics may be expected as quite frequently observed for the last part of the thermal decomposition of solids.[2]

In conclusion it seems reasonable to assume that in the various halogenide–perchlorate mixtures the governing factor is not the lowered melting point but the large increase in the number of perchlorate ions decomposed on the surface of the crystals because of the close contact with the halogenide ions (which is equivalent to a large increase in K). The values of k_a, A and E given in Tables I to IV are in accord with this hypothesis. For pure perchlorate these values differ only slightly from those of its mixtures with chloride. The main effect of the chloride is the shortening of the induction period. In the bromide mixtures a new ion is introduced which reduces appreciably the energy of activation and thereby produces a corresponding acceleration in the rate of reaction, without changing A significantly.

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

JERUSALEM, ISRAEL RECEIVED APRIL 12, 1951

[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS AND THE KNOLLS ATOMIC POWER LABORATORY]

Heat Capacity of Potassium and Three Potassium–Sodium Alloys between 0° and 800°, the Triple Point and Heat of Fusion of Potassium[1]

BY THOMAS B. DOUGLAS, ANNE F. BALL, DEFOE C. GINNINGS AND WILLIAM D. DAVIS[2]

Measurements were made of the changes in enthalpy of potassium and three potassium–sodium alloys (containing approximately 45, 54 and 78% of potassium) over the range 0 to 800°, using an ice calorimeter as earlier with sodium. The precision for two of the alloys was inferior to that usually obtained with this apparatus, owing to a solid-phase transformation during cooling. From the enthalpy values were derived the heat capacities, as well as the heat of fusion and relative entropy of potassium. The heat capacities of the liquid alloys were found to correspond closely at each temperature between 100 and 800° to those calculated additively from the authors' values for pure liquid potassium and sodium. As with sodium, each liquid shows a minimum in heat capacity between 500 and 650°. The melting curve and triple point of potassium also were determined.

It was the purpose of this investigation to measure accurately the heat capacities of potassium and three potassium–sodium alloys from 0° to approximately their normal boiling points. These measurements provided also an opportunity to study the deviations of the heat capacities of these alloys from those calculated additively from the values for the pure component elements. Because certain of these alloys have lower freezing points than pure sodium, it is sometimes more practical to use them as heat transfer media. Less precise measurements have been made by other observers on potassium up to about 350°, but no measurements seem to have been reported for any potassium–sodium alloy.

Experimental

Preparation of Samples.—Measurements were made on two samples each of 100%- and 78%-potassium and on one sample of each of the other two alloys. The samples were sealed in containers at the Knolls Atomic Power Laboratory. The containers were made from the same stock of stainless steel No. 347 as those used in the earlier investigation of sodium,[3] and had approximately the same size (about 10 cm.^{3}), shape and mass. Some modifications of the earlier procedure were necessary, owing to the greater chemical reactivity of the present materials.

The samples of 100% potassium were prepared by the triple distillation of a nominally pure sample from Baker Chemical Co. The three alloys, likewise having been prepared by distillation, were received in stainless steel cylinders from Mine Safety Appliance Co. One sample each of potassium and the 78% potassium alloy that had been used in the thermal measurements was analyzed spectrochemically at the National Bureau of Standards. Of the 55 chemical elements tested for, only the following were detected as impurities. In the sample of potassium were found between 0.01 and 0.1% of sodium, between 0.001 and 0.01% of calcium, and traces (less than 0.001% of each) of aluminium, chromium, iron, magnesium, rubidium, manganese and silicon. The 78% potassium alloy showed only calcium, magnesium, rubidium, iron and silicon, and these only in trace amounts.

The spectrochemical analysis did not include a search for the common non-metals. However, an analysis made

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[2] Knolls Atomic Power Laboratory, General Electric Company, Schenectady, New York.

[3] D. C. Ginnings, T. B. Douglas and Anne F. Ball, *J. Research Natl. Bur. Standards*, **45**, 23 (1950).