High Temperature Properties and Decomposition of Inorganic Salts

Part 4. Oxy-Salts of the Halogens

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The literature dealing with the high-temperature behavior of inorganic oxygen-containing salts of chlorine, bromine and iodine has been critically reviewed. Values of $(G_T^\circ - H_{298}^\circ)/T$ of the reactants and products of the decomposition reactions were calculated and have been tabulated from 298 K up to as high a temperature as possible. Equilibrium constants and partial pressures were tabulated. Auxiliary data on phase transitions and densities have also been included. Qualitative information about the thermal decomposition of the salts is reviewed.

Key words: Bromates; bromites; chlorates; chlorites; critically evaluated data; iodates; iodites; perbromates; perchlorates; periodates; thermal decomposition; thermodynamic functions.

Contents

1. Introduction

During the past decade or two, inorganic salts, particularly in the liquid state, have assumed increasing importance in a variety of applications. They are useful as reaction media, in metallurgical processes, and in electrochemical power sources such as fuel cells and thermal batteries.

Experimentalists and theoreticians have found molten salts an interesting subject for study since these ionic fluids offer an unusual opportunity for the study of short-range ionic interactions in the liquid state. The high-temperature applications of solid salts are also increasing. They are being used, for example, in thermal batteries and as propellants.

So far, attention in this field has largely been focused on the alkali and alkaline earth halides since their stability at high temperatures is well known. The most important decomposition which they can undergo is dissociation to the elements. The extent of this dissociation can be easily calculated from existing thermodynamic compilations.

For most inorganic salts the situation is more complicated. In many cases the decomposition reactions are not well defined and high-temperature thermodynamic and kinetic data are either lacking or scattered through the literature. Thus, although many of these salts might have useful properties, they have received little atten-

tion because in many cases not even the range of thermal stability is known.

The purpose of the present publication is to alleviate this situation by publishing in concise form thermodynamic and kinetic data relevant to the high-temperature behavior of important classes of inorganic salts. For the present, data in this work are restricted to anhydrous compounds with monotomic cations and oxyanions containing one element besides oxygen.

The present work deals with oxygen-containing salts of the halogens. Since the electronegativities of chlorine, bromine, and iodine are less than that of oxygen, they form oxyanions in which the halogen has a formal positive valence. Fluorine is more electronegative than oxygen and therefore forms no compounds of this type.

Some of the compounds which have been widely used in pyrotechnics and explosives, e.g. $KClO_4$, have been well studied for a long time. However, in many cases the literature, particularly with respect to quantitative data, is very meager and the only available information is qualitative.

Since there is relatively little connection between the salts of the three halogens (except from the similarities arising from their position in the periodic table) this work has been divided into three separate sections, each with its own bibliography. In this Introduction only the general features are discussed.

1.1. Thermodynamic Data and Calculations

At the time of writing, values of $\Delta H f^\circ_{298.15}$ and $S^\circ_{298.15}$ have been published in a revision of [1a][1] by the National Bureau of Standards [1b] for all the elements except the alkali metals. Some of the latter were obtained on an informal basis [2]. For some salts not listed in [1a, b] data were obtained from other sources. In general, all values at 298.15 K are given to the number of significant figures justified by the accuracy of the data on which they are based. In converting the original calories to joules an occasional extra significant figure had to be added to allow recovery of the original calories. These extra figures are subscripted. Occasional references are taken from [3].

High-temperature enthalpy and entropy increments, or heat capacities were used whenever possible to construct gibbs energy functions (gef):

$$gef = \frac{G^\circ_T - H^\circ_{298.15}}{T} = \frac{H_T - H^\circ_{298.15}}{T} - (S^\circ_T - S^\circ_{298.15}) - S^\circ_{298.15}.$$

In several cases the calculations could not be carried out because $S^\circ_{298.15}$ values were not available.

When experimentally determined enthalpy increments had been measured they were computer-fitted to a power series in T, usually up to T^4, and the entropy increments constructed from them:

$$H_T - H_{298.15} = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4,$$

$$C_p = \frac{d(H_T - H_{298.15})}{dT},$$

$$S_T - S_{298.15} = \int_{298.15}^T \frac{C_p dT}{T},$$

In these calculations and subsequent ones $(gef, \Delta G^\circ,$ etc.) more significant figures were retained than justified by the original data in order to retain enough figures in the equilibrium calculations. This is similar to the practice employed by [3].

The equilibrium constants and equilibrium partial pressures cannot be more accurate than the data from which they are calculated: $\Delta H f^\circ_{298.15}$, $S^\circ_{298.15}$ and heat capacities. The accuracy with which the first two can be calculated is evident from the tables in each individual case. Heat capacities are generally derived from calorimetric enthalpy increments and are less well known than values at 298 K. However, the contribution they make to the experimental ΔG° increases with temperature. Thus an overall assessment of accuracy is not possible. As a guideline it is worth remembering that at 1000 K an uncertainty of 1 kcal corresponds to an uncertainty factor of two in the equilibrium constant.

Even such crude estimates cannot yet be made for kinetic parameters, such as activation energies. Except for some well-studied salts such as $KClO_4$, for which

several studies agree fairly well, reported values are no more than rough guides as to what may be expected in repeating the experiments.

It is well known that some substances which are thermodynamically unstable nevertheless are quite stable because their thermal decomposition requires a step with a high activation energy. This is the case with the perchlorates. For example, the reaction $KClO_4 = KCl + 2 O_2$ at 298 K has a $\Delta H^\circ = -6.58$ kJ and $\Delta S^\circ = 29.55$ J deg^{-1}. Hence $\Delta G = -15.39$ kJ. Nevertheless, the salt can be heated to several hundred °C before decomposition becomes appreciable. The reason is that the rate-determining step is probably the breaking of a Cl-O bond requiring an activation energy of ~ 290 kJ. Thus, even if data existed for the calculation of high-temperature equilibria it would be pointless to carry them out since they do not predict the actual behavior of the salt. By contrast, iodates and periodates are thermodynamically quite stable, and equilibrium calculations can be used to predict the behavior of the compounds.

In order for the equilibrium pressures of gases to be unique functions of temperature it is necessary that the system be univariant in the sense of the phase rule. This and related questions have been discussed in detail by Bousquet and Remy [4]. Here the conclusions are only briefly summarized.

An equilibrium system represented by

$$A \rightleftarrows B + Gas,$$
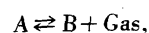
such as $NaIO_3 \rightleftarrows NaI + 3/2 O_2$, is univariant in the phase rule sense below the eutectic (2 components, 3 phases) and the equilibrium constant $K_p = f(p)$ is a unique function of temperature if A and B are solids not forming solid solutions. When the entire condensed phase is liquid, only two phases are present and the gas pressure depends on the liquid composition:

$$K_p = \frac{a_B}{a_A} \cdot f(P).$$

If there are two condensed phases (1 liquid + 1 solid) the system is monovariant and the pressure is independent of composition. Thus the proper application of thermodynamic calculations requires a knowledge of the physical characteristics of the system. The systems for which thermodynamic calculations are given in this work are generally monovariant.

Since the four gases O_2, Cl_2, Br_2, and I_2 frequently appear as decomposition products of the salts, they have been collected in this Introduction for convenience. Values are taken from [3].

TABLE 1.1. $\Delta H f^\circ_{298.15}$ and $S^\circ_{298.15}$ of the halogen gases and O_2 [3]

	$\Delta H F^\circ_{298.15}$ (kJ mol^{-1})	$S^\circ_{298.15}$ (J deg^{-1} mol^{-1})
O_2	0	205.03
Cl_2	0	222.9$_7 \pm 0.04$
Br_2	30.907	245.379
I_2	62.442	260.584

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[1] Numbers in brackets indicate literature references at the end of each main section. All references in the Introduction used in other parts of this work are prefixed with I.

TABLE 1.2. Gibbs energy functions of the halogen gases and O_2
$(G_T^\circ - H_{298.15}^\circ)/T$ (J mol^{-1} deg^{-1}) [3]

T(K)	O_2	Cl_2	Br_2	I_2
298.15	205.033	222.961	245.379	260.584
400	206.196	224.313	246.802	262.036
500	208.413	226.903	249.509	264.789
600	210.932	229.840	252.559	267.881
700	213.501	232.810	255.626	270.985
800	216.061	235.702	258.596	273.989
900	218.442	238.467	261.433	276.855
1000	220.769	241.095	264.119	279.567
1100	222.986	243.584	266.659	282.127
1200	225.103	245.944	269.061	284.554

In addition to the results derived from calorimetry and thermodynamic calculations, our knowledge of high-temperature behavior depends very heavily on non-isothermal studies, such as DTA. Since in these studies the temperature of the samples is increased continuously, substances may appear stable to higher temperatures than would be expected if equilibrium were achieved at each temperature. This is particularly true for substances which decompose very slowly. Another source of discrepancies frequently reported in the literature arises from differences in experimental techniques which produce different vapor phase compositions. For example, whether the sample is tightly packed into a long and narrow tube or loosely poured into an open crucible will affect the vapor retained above the sample, and hence the observed decomposition temperatures. Hence values reported for a given substance by competent investigators may differ and there may in fact be no such unique temperature, independent of the method by which it is obtained. For this reason much of the material in this monograph serves more as a guide to expected behavior rather than listing precise properties to be observed under all experimental conditions.

A dual system of listing temperatures has been used which corresponds to the two types of information listed. "Hard" quantitative data (thermodynamic parameters, densities) are given on the absolute (Kelvin) scale; "soft" semi-quantitative information of the kind described above is given in °C because chemists usually think with this scale.

1.2. Phase Transitions

Since many oxy-halogen salts decompose in the solid state-melting points are available for relatively few compounds. In some cases the decomposition is slow so that the melting point of a nearly pure salt can be measured. Values have been listed whenever possible, even when they are not very precise.

1.3. Density

Except for $LiClO_4$, which is stable for some distance above its melting point, no molten salt densities seem to

have been measured. There are only very few high-temperature solid data. Most ambient-temperature measurements are of fairly low accuracy. The most reasonable values have been listed for convenience. These are obtained either experimentally (usually pycnometrically, by displacement of a liquid such as CCl_4) or calculated from X-ray data. Solids frequently exhibit voids and/or occlude solvent so that reported values may scatter considerably. X-ray values are those for a perfect lattice and thus are only an approximate guide to densities for "real" crystals. Whenever more recent data are not available the evaluation by [5] has been accepted.

1.4. Chemistry of the Halogen-Oxy-Salts

The chemistry of specific classes of salts, e.g. perchlorates, is discussed in the introduction to the particular halogens. Further information is available in textbooks of inorganic chemistry. Sidgwick's work [6], although somewhat out of date, is particularly useful. The stereochemistry of the halogens has been discussed by Wells [7]. Here we note only some generalizations and comparisons of the three halogens.

Apparently the halogen-oxysalts are predominantly ionic, i.e. the anion constitutes a definite charged entity with covalent bonds between the halogen and oxygen atoms, but only electrostatic interactions between cations and anions. This is in contrast to the nitrates where some are ionic and some covalent. Because the outer electronic structure of the halogens is so similar it is not surprising that the structures of corresponding ions are also similar, e.g. ClO_3^-, BrO_3^-, and IO_3^- are pyramidal. Below is a listing of halogen oxyanions as given by Wells [7].

Number of σ-electron pairs	Type of hybrid	Number of lone pairs	Bond arrangement	Examples
4	sp^3	0	tetrahedral	ClO_4^-, IO_4^-
		1	trigonal bi-pyramidal	ClO_3^-, BrO_3^-, IO_3^-
5	$sp^3d_{z^2}$	0	trigonal bi-pyramidal	IO_5^{3-} (?)
6	$sp^3d_\gamma^2$	0	octahedral	IO_6^{5-}

One of the most striking differences between the halogens is the large number of anhydrous iodine compounds, compared to those of chlorine and bromine. However, this difference may only be due to the lack of interest exhibited by chemists in preparing these compounds. Thus, although chlorites have been known for a long time, anhydrous iodites and bromites have been synthesized only recently. Similarly, perbromates were said to be too unstable to exist, but recently several of

these salts have been prepared and the BrO_4^- ion seems to be about as stable as ClO_4^- and IO_4^-. This topic has recently been discussed in detail by Cox and Moore [8]. In nearly all respects the paralellism is complete: hypohalites (XO^-) are not known as pure anhydrous salts; the halites ClO_2^-, BrO_2^-, and IO_2^- are known, although few bromites and iodites have been prepared; the halates ClO_3^-, BrO_3^-, and IO_3^- exist; the (meta)-perhalates ClO_4^-, BrO_4^-, and IO_4^- are known. In each of these groups the structures are quite similar. Only the tendency of iodine in its $+7$ oxidation state to polymerize leads to a variety of iodates, a phenomenon apparently quite absent from chlorine and bromine.

In general, the stabilities of the anions for each oxidation state increase in the order $Cl < Br < I$. How great this difference is may depend on the property used to measure it. For example, both perchlorates and metaperiodates may be heated to several hundred degrees before decomposing, but this similarity is probably due to the kinetics of the decomposition, since perchlorates are thermodynamically unstable even at ambient temperature.

1.5. Units, Symbols, and Abbreviations

J = Joule

cal = Thermochemical calorie = 4.184 J

P = Pressure; 1 atm = 101325 N m^{-2} = 1013250 dyn cm^{-2}

$T(K)$ = Temperature in kelvin, defined on the thermodynamic scale by assigning 273.16 K to the triple point of water (freezing point, 273.15 K = 0 °C)

R = Gas constant = 8.3143 J mol^{-1} deg^{-1} = 1.98717 cal mol^{-1} deg^{-1}

$H°$ = Standard enthalpy

$\Delta H f°$ = Standard enthalpy of formation

$S°$ = Standard entropy

$G°$ = Standard Gibbs energy

gef = Gibbs energy function = $\dfrac{G_T° - H_{298.15}°}{T}$

TCA = Thermogravimetric analysis

DTA = Differential thermal analysis

1.6. References

[1a] Rossini, F. D., Wagman, D. D., Evans, W. H., Levine, S., and Jaffe, L., "Selected Values of Chemical Thermodynamic Properties", NBS Circ. 500, 1952.

[1b] Wagman, D. D., Evans, W. H., Halow, I., Parker, V. B., Bailey, S. M., and Schumm, R. H., "Selected Values of Chemical Thermodynamic Properties", NBS Tech. Note 270-3 (1968); 270-4 (1969); 270-6 (1971).

[1b] is the ongoing revision of [1a]. Values for $\Delta H f°$ and $S°$ at 298.15 K for all salts and oxides in the present monograph are taken from [1b], whenever available. In some instances data not yet published by the authors are also included.

[2] Private Communication, D. D. Wagman, W. H. Evans, and V. B. Parker.

[3] Stull, D. R., and Prophet, H., JANAF Thermochemical Tables. 2nd Ed., NSRDS-NBS 37, 1971.

[4] Bousquet, J., and Remy, J. C., Bull. Soc. Chim. France 705 (1963).

[5] International Critical Tables, Vol. I., McGraw-Hill Book Co., New York, N.Y., 1926.

[6] Sidgwick, N. V., "The Chemical Elements and Their Compounds", Oxford University Press, 1950.

[7] Wells, A. F., "Structural Inorganic Chemistry", 3rd Ed., Clarendon Press, 1962.

[8] Cox, M. M., and Moore, J. W., J. Phys. Chem. 74, 627 (1970).

Other General References

[9] "Gmelin's Handbuch der Anorganischen Chemie", 8th Ed. Verlag Chemie, Weinheim, Germany.

[10] Latimer, W. M., "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions", 2nd Ed., Prentice-Hall, Inc., New York, 1952.

[11] Mellor, J. W., "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Longmans, Green and Co., New York, N.Y.

2. Chlorine

There are only three oxyanions which form anhydrous salts: chlorites (ClO_2^-), chlorates (ClO_3^-), and perchlorates (ClO_4^-). The stability increases with the increasing oxidation state of the halogen. There is no clear evidence for the existence of stoichiometric, anhydrous hypochlorites (ClO^-). Even for the few reported salts $(NaClO, Ca(ClO)_2)$ one finds reports of "smell of chlorine", indicating continuous decomposition at ambient temperature.

The known and doubtful salts are shown in figures 2.1–2.3. Although more elements form perchlorates than chlorites and chlorates, the chlorates seem underrepresented. Any metal that forms a chlorite should also form a chlorate. One would also expect the lanthanides to form all three classes of salts.

The quantitative high-temperature chemistry of chlorine oxy-salts is rather underdeveloped. There are very few thermodynamic data for these compounds above 298 K. Even when they exist, they must be applied cautiously since it may be kinetic rather than thermodynamic factors that determine decomposition behavior. Although the thermal decomposition of a few compounds has been studied very carefully (e.g. the KClO$_4$ literature extends back for more than a hundred years) the bulk of the available information is qualitative. Many of the reactions are complex with mechanisms frequently controversial and not completely worked out. Decomposition products may depend on experimental conditions, if the salt is not quite dry it may hydrolyze.

As pointed out in the introduction, perchlorates are unstable even at ambient temperatures so that thermodynamic calculations are not useful in predicting the actual behavior of the salts (except in predicting the products formed).

Chlorites

The best-studied chlorite, AgClO$_2$, is probably not typical of chlorites generally, since the short Ag-Cl distance is suggestive of AgClO$_2$ molecules. The O-Cl-O in the ClO$_2^-$ ion angle is 110° with a Cl-O interatomic

																H	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

Lanthanides   Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

Actinides   Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lw

FIGURE 2.1. The known chlorites. Shaded, existence known. Half-shaded, existence uncertain. No shading, existence unknown.

																H	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

Lanthanides   Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

Actinides   Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lw

FIGURE 2.2. The known chlorates. Shaded, existence known. Half-shaded, existence uncertain. No shading, existence unknown.

																H	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

Lanthanides   Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

Actinides   Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lw
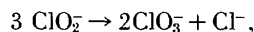
FIGURE 2.3. The known perchlorates. Shaded, existence known. Half-shaded, existence uncertain. No shading, existence unknown.

distance of ∼ 1.5Å. When heated most chlorites disproportionate according to

$$3\ ClO_2^- \rightarrow 2ClO_3^- + Cl^-,$$

although under very rapid heating only O_2 and chlorides may form explosively, probably because the chlorate then decomposes simultaneously.
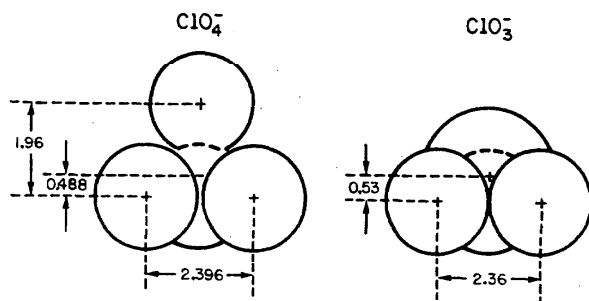
FIGURE 2.4.　The ClO_3^- and ClO_4^- ions. [95]

Chlorates

The chlorate ion is a rather flat pyramid with Cl at the apex and the O-Cl-O bond angle ∼ 110°. The Cl-O distance is near 1.46 Å. A picture of the ion, constructed by [95] from known data is shown in figure 2.4.

Most chlorates undergo two decomposition reactions which usually occur simultaneously:

$$4ClO_3^- \rightarrow 3ClO_4^- + Cl^- \qquad \text{(a)}$$

$$ClO_3^- \rightarrow Cl^- + 3/2\ O_2. \qquad \text{(b)}$$
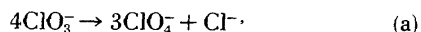
The subsequent fate of the perchlorate depends on the temperature. At relatively low temperatures it is stable and thus remains. At temperatures high enough for it to decompose the final products are the chloride and oxygen. When the metal exists in more than one oxidation state (e.g. Pb, Tl) the oxide may form. The chlorates of the rare earths, scandium, and yttrium form oxychlorides.

Perchlorates

The perchlorate ion (ClO_4^-) is tetrahedral with a Cl-O distance near 1.4 Å (fig. 2.4). The perchlorates decompose by one of two reactions: Salts of the more electropositive metals go to the chloride:

$$MClO_4 \rightarrow MCl + 2O_2.$$
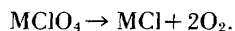
The others (e.g. Cd, Zn) go to the oxide:

$$MClO_4 \rightarrow 1/2\ M_2O + 1/2\ Cl_2 + 7/4\ O_2.$$
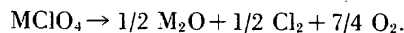
Only $Mg(ClO_4)_2$ simultaneously decomposes by both reactions.

Markowitz [53] has discussed perchlorate decomposition in terms of the thermodynamics of the above two reactions. Since ΔS° for both reactions is highly positive (because gaseous products are formed) the determining factor is ΔH°. Since ΔH° is not very temperature dependent, values at 298 K can be used to predict

the reaction. In effect, when the difference per equivalent in $\Delta H f^\circ$ (chloride-oxide) is negative the product will be the chloride. Most perchlorates form either the chloride or the oxide. $Mg(ClO_4)_2$ and some transition metal perchlorates form both because the enthalpy difference of the products is not very large. However, for both kinds of reaction ΔH is negative, so that it is only a question of which reaction is more spontaneous.

2.1. Aluminum

$Al(ClO_4)_3$

The anhydrous salt decomposes according to the stoichiometry

$$2Al\ (ClO_4)_3 \rightarrow Al_2O_3 + 3Cl_2O + 9O_2.$$
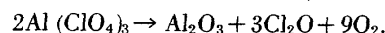
Between 240 and 290 °C the decomposition kinetics fit the Erofeev equation, according to which the fraction decomposed is given by

$$\alpha = 1 - \exp\ (-kt^n),$$

where the value of n depends on the shape of the nuclei. From the temperature dependence of k an Arrhenius activation energy of 82.8 kJ (19.8 kcal) was calculated [6].

2.2. Barium

$Ba(ClO_2)_2$
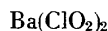
The salt is rather unstable, but its precise mode of decomposition depends on the rate at which it is heated [51, 84]. If it is heated slowly or at a constant temperature in the range 130–180 °C it disproportionates according to

$$3\ Ba(ClO_2)_2 \rightarrow 2\ Ba(ClO_3)_2 + BaCl_2.$$
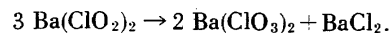
In this temperature range $Ba(ClO_3)_2$ is stable. If the salt is heated so rapidly that this reaction has not gone to completion $Ba(ClO_2)_2$ decomposes explosively near 200 °C according to

$$Ba(ClO_2)_2 = BaCl_2 + 2\ O_2.$$

$Ba(ClO_3)_2$
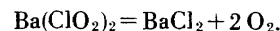
Two studies of the decomposition [53, 85] differ somewhat. There is agreement that both the perchlorate and the chloride are formed:

$$4\ Ba(ClO_3)_2 = 3\ Ba(ClO_4)_2 + BaCl_2, \qquad (1)$$

$$Ba(ClO_3)_2 = BaCl_2 + 3\ O_2. \qquad (2)$$
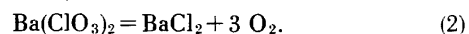
Both agree that the decomposition does not become appreciable until ∼ 380 °C. (The disproportionation does not lead to a weight loss and can only be detected by analysis). At 396° the salt melts and the decomposition becomes rapid since it occurs in the liquid. In this temperature range reaction (2) predominates, whereas the slow decomposition is the major one below 396° [85]. $Ba(ClO_2)_2$ may be an intermediate in the decomposition, but it is too unstable to detect [85].

Ba(ClO₄)₂

The salt exhibits two solid-state phase transitions [I 1a, 94]. The structure of the high temperature γ-form has not yet been determined.

Above 435 °C the salt decomposes according to the overall reaction [1, 81, 101]

$$Ba(ClO_4)_2 = BaCl_2 + 4\ O_2.$$
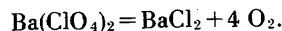
However, the decomposition mechanism appears to be quite complex. Acheson and Jacobs [1] found that $\alpha =$ fraction decomposed versus time plots showed a distinct break at $\alpha = 0.52$ corresponding to the formation of Ba(ClO₂)₂. At the temperature of the experiment this salt is completely dissociated so that the first part of the reaction is

$$3\ Ba(ClO_4)_2 = 2\ Ba(ClO_3)_2 + BaCl_2 + 6\ O_2.$$
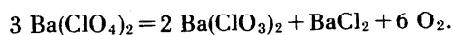
For $\alpha > 0.52$ the decomposition is that of Ba(ClO₃)₂. A chain sequence, involving O atoms as carriers is proposed as a mechanism.

TABLE 2.1.   Properties of Ba-Cl salts

Density

	T(K)	ρ(g cm⁻³)	Ref.
Ba(ClO₄)₂	298	3.681	79

Transitions

Ba(ClO₄)₂	T(K)	Ref.
rhombic → cubic	557	I 1a
cubic → γ	633	101

Thermodynamic data (298.15 K)

$S°$

	J deg⁻¹ mol⁻¹	cal deg⁻¹ mol⁻¹	Ref.
Ba(ClO₂)₂	197.	47	I 1b
Ba(ClO₃)₂	—	—	
Ba(ClO)₂	—	—	
BaCl₂	123.68	29.56	I 1b

$\Delta Hf°$

	kJ mol⁻¹	k cal mol⁻¹	Ref.
Ba(ClO₂)₂	−680.3	−162.6	I 1b
Ba(ClO₃)₂	−762.7	−182.3	I 1b
Ba(ClO₄)₂	−800.0	−191.2	I 1b
BaCl₂	−858.6	−205.2	I 1b

2.3. Bismuth

There seems to be no firm evidence for the existence of anhydrous Bi(ClO₃)₃ and Bi(ClO₄)₃.

2.4. Cadmium

Cd(ClO₃)₂

The anhydrous salt has been prepared [71], but its high-temperature properties have not yet been determined.

Cd(ClO₄)₂

The decomposition of the anhydrous salt has been studied in the range 377–403 °C [82]. At the lower end of the range the decomposition is quite slow, approximately 10 percent of the material decomposing in 2 hours. In contrast, Hering and Leray [36] report decomposition in the range 150–200 °C. This would be expected in the presence of traces of water. Most of the decomposition goes according to

$$Cd(ClO_4)_2 = CdCl_2 + 4\ O_2$$
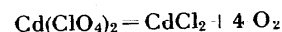
and about 3 percent to the oxide:

$$Cd(ClO_4)_2 = CdO + Cl_2 + 7/2\ O_2.$$
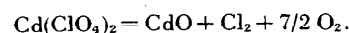
Rosolovskii and Krivstov [72] have used their measurements of the enthalpy of solution of Cd(ClO₄)₂ in water to determine ΔHf°_{298} for this salt. Using older literature values they obtain -49.24 ± 0.42 kcal mol⁻¹. Recalculating with newer values in [I 1b] gives -222.75 ± 1.76 kJ mole⁻¹ (-53.24 ± 0.42 kcal mol⁻¹).

TABLE 2.2.   Properties of Cd-Cl salts

Thermodynamic Data (298.15 K)

$S°$

	J deg⁻¹ mol⁻¹	cal deg⁻¹ mol⁻¹	Ref.
Cd(ClO₃)₂	—	—	
Cd(ClO₄)₂	—	—	
CdCl₂	115.2₇	27.55	I 1b
CdO	54.8	13.1	I 1b

$\Delta Hf°$

	kJ mol⁻¹	kcal mol⁻¹	Ref.
Cd(ClO₃)₂	—	—	
Cd(ClO₄)₂	−222.7₅ ± 1.76	−53.24 ± 0.42	I 1b, 72
CdCl₂	−391.5	93.57	I 1b
CdO	−258.₂	−61.7	I 1b

2.5. Calcium

Ca(ClO)₂

Although several authors have described various materials containing this compound [I 9], these have usually been commercial bleaching powders containing various amounts of CaCl₂, Ca(ClO₃)₂, CaCO₃, and H₂O. The most nearly pure anhydrous salt seems to have been prepared by Urano [90]. The compound is quite stable at 45 °C, losing weight only very slightly (< 5%) over several hundred hours. Above 150 °C it decomposes violently with the evolution of O₂, and leaving CaCl₂.

$Ca(ClO_2)_2$

This salt is a white, crystalline powder, probably pseudocubic in structure [51]. A nearly (93%) pure preparation has .been decomposed at 180–200 °C. At this temperature the salt decomposes according to $3Ca(ClO_2)_2 = 2Ca(ClO_3)_2 + CaCl_2$ [50]. The compound has been reported to explode due to mechanical shock.

$Ca(ClO_3)_2$

The high-temperature properties of this salt appears not to have been studied since about 1900. According to the older literature [I 9], the salt is very hygroscopic.

$Ca(ClO_4)_2$

The anhydrous salt is quite stable up to 270 °C [97a]. At 340° it appears to undergo a polymorphic phase change [100a]. The temperature at which decomposition begins is somewhat uncertain. The DTA peak appears at 470°. The major part of the decomposition, about 98%, is $Ca(ClO_4)_2 = CaCl_2 + 4\ O_2$, only traces of Cl_2 appearing in the gaseous product. The low melting point of 123° reported by Gordon and Campbell [32] is undoubtedly due to retained water.

TABLE 2.3.   Properties of Ca-Cl salts

	Density		
	$T(K)$	$\rho(g\ cm^{-3})$	Ref.
$Ca(ClO_2)_2$	298	2.71	52
	293	2.65	30
$Ca(ClO_4)_2$	298	2.651	79

Thermodynamic data (298.15 K)

	$S°$		
	J deg^{-1} mol^{-1}	cal deg^{-1} mol^{-1}	Ref.
$Ca(ClO_2)_2$	—	—	
$Ca(ClO_3)_2$	—	—	
$Ca(ClO_4)_2$	—	—	
$CaCl_2$	104.6	25.0	11b

	$\Delta Hf°$		
	kJ mol^{-1}	kcal mol^{-1}	Ref.
$Ca(ClO_2)_2$	−678.2	−162.1	11b
$Ca(ClO_3)_2$	—	—	
$Ca(ClO_4)_2$	−736.76	−176.09	11b
$CaCl_2$	−795.8	−190.2	11b

2.6. Cesium

$CsClO_2$

In the temperature range 190–210 °C the salt disproportionates according to the reaction [50].

$$3CsClO_2 \rightarrow 2CsClO_3 + CsCl.$$
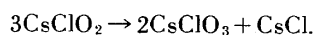
In this temperature range the chlorate is stable.

$CsClO_3$

The salt is stable to its melting point and at least a little beyond. [57] As expected from the large cationic size, $CsClO_3$ is the most stable of the chlorates. Similar to the other alkali metal chlorates, the salt decomposes by the parallel paths

$$CsClO_3 \rightarrow CsCl + 3/2\ O_2, \qquad (a)$$

$$4CsClO_3 \rightarrow 3CsClO_4 + CsCl. \qquad (b)$$
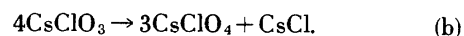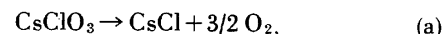
Since the perchlorate is stable near the melting point of the chlorate, both $CsCl$ and $CsClO_4$ accumulate. No detailed study of the relative rates of the two reactions seems to have been carried out, but indications are [57] that the rate of reaction (b) is about three times as fast as that of (a) at 400°. At higher temperatures $CsClO_4$ also decomposes.

$CsClO_4$

The temperature of the orthorhombic ↔ cubic transformation is somewhat dependent on the heating rate. Cabané and Bénard [14] think the transformation occurs reversibly at 489 K. The melting point is estimated because the salt already begins to decompose in the solid state. As is usual for the perchlorates, the overall decomposition leads to the chloride and O_2, with $CsClO_3$ as an unstable intermediate:

$$CsClO_4 = CsClO_3 + 1/2O_2$$
$$CsClO_3 = CsCl + 3/2O_2$$

$$CsClO_4 = CsCl + 2\ O_2$$
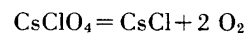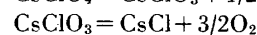
The decomposition kinetics has been studied by Cabané and Bénard [14] in the range 385–467 °C and by Solymosi [80] between 528 and 558 °C, both using weight loss measurements. In addition, Cordes and Smith [25] studied the first 3 percent of the solid decomposition mass-spectrometrically between 330 and 500 °C. This study has the advantage of avoiding melting which occurs as the melting point is lowered by the accumulation of reaction products. $CsClO_4$, in contrast to the other alkali metal perchlorates, is quite volatile, approximately 50 percent of the sample subliming above 500° in 1–2 hours [25]. The solid residue contains approximately ten times as much ClO_3^- as Cl^-. Cabané and Bénard found an Arrhenius activation energy of 117 kJ (35 kcal), approximately equal to the activation energy for diffusion and argued that the rate-determining step involved the diffusion of ClO_4^-. Cordes and Smith [25] obtained 187 ± 8.8 (44.6 ± 2.0 kcal) over the same temperature range. Their mechanism, which is virtually the same for all the alkali metal perchlorates is discussed under $KClO_4$. At the

higher temperature, Solymosi found the activation energy to be near 233 kJ (70 kcal), so that there may be a change in the mechanism as the temperature increases.

TABLE 2.4   Properties of Cs−Cl salts

Density

	ρ(g cm^{-3})	T(K)	Ref.
CsClO$_3$	3.626	ambient	58
CsClO$_4$ (orthorhombic)	3.327	289	4, 38
CsClO$_4$ (cubic)	3.01 ± 0.01 (calc)	> 492	11

Transitions

		T(K)	ΔH(kJ)	Ref.
CsClO$_3$	$\alpha \rightarrow \beta$	578		58
	$\beta \rightarrow 1$	615		58
CsClO$_4$ orthorhombic $\rightarrow$ cubic		498	8.4 ± 0.8	55
cubic $\rightarrow 1$		850 (est.)		55

Thermodynamic data (298.15 K)

$S°$

	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	Ref.
CsClO$_2$	—	—	
CsClO$_3$	16$_7$.	40.	est.
CsClO$_4$	175.2$_7$	41.89	11a
CsCl	101.182 ± 0.021	24.183 ± 0.005	3

$\Delta Hf°$

	kJ mol^{-1}	kcal mol^{-1}	Ref.
CsClO$_2$	—	—	
CsClO$_3$	− 396.	− 94.6	93
CsClO$_4$	− 442.73	− 105.81	11b
CsCl	− 442.83	− 105.84	3

2.7. Cobalt

Co(ClO$_4$)$_2$

The preparation of the purple anhydrous salt has been reported [28]. Its density is ~ 3.2 g cm^{-3} and it is stable in vacuum to ~ 90°C. The decomposition kinetics has recently been studied [92] between 150 and 185°C. The major reaction is

$$Co(ClO_4)_2 \rightarrow CoCl_2 + 2O_2,$$
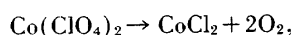
with a lesser contribution from

$$Co(ClO_4)_2 \rightarrow CoO + Cl_2 + 3.5 O_2 \cdot$$
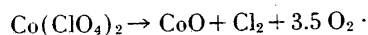
2.8. Copper

Cu(ClO$_2$)$_2$

The nearly pure anhydrous salt, but with a slightly low chlorine content, has been prepared [50]. It is very unstable, transforming into a green powder even in a closed vessel and exploding on being heated.

CuClO$_4$

The preparation of this salt was first described by Gomberg [31], but no further work seems to have been reported since then.

Cu(ClO$_4$)$_2$

Recent studies of this salt are in serious disagreement. Hathaway [35] reports the preparation of the anhydrous salt by fractional vacuum sublimation of Cu(ClO$_4$)$_{2-x}$ (NO$_3$)$_x$. An approximate melting point of 230–240°C was found. On the other hand, Vilcu and Georgescu [92] report that melting of the (supposedly) anhydrous salt begins near 75 °C, simultaneously with decomposition which they studied in the range 80°–110°. It involves the simultaneous reactions

$$Cu(ClO_4)_2 \rightarrow CuCl_2 + 4 O_2,$$

$$Cu(ClO_4)_2 \rightarrow CuO + Cl_2 + 3.5 O_2.$$
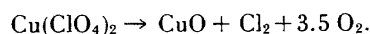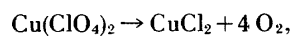
The proportion of the two reactions is determined by the gas phase composition through the equilibrium

$$CuO + Cl_2 = CuCl_2 + 1/2 O_2.$$
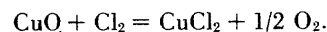
Particularly above 110° the oxide is favored. It is possible that some water was present (the starting material was a hydrate) and the salt melted in its hydration water, but not enough information is given in the paper to know whether this is the case. In contrast, Hathaway [35] reports that Cu(ClO$_4$)$_2$ decomposes at 130° to a basic perchlorate (not further identified.)

2.9. Iron

Fe(ClO$_4$)$_3$

The thermal decomposition of a "dried" (at 110°) hydrate in the range 90–135 °C proceeded entirely to the oxide [92].

$$2Fe(ClO_4)_3 \rightarrow Fe_2O_3 + 3Cl_2 + 10.5 O_2.$$
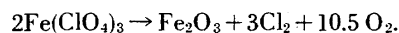
2.10 Lead

Pb(ClO$_2$)$_2$

The salt is pseudo-tetragonal [48]. It disproportionates in the range 70–95 °C according to the reaction

$$3Pb(ClO_2)_2 = 2Pb(ClO_3)_2 + PbCl_2.$$
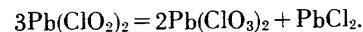
If the compound is heated rapidly, this conversion is apparently not complete and the chlorite decomposes

explosively between 100 and 125 °C [84]. A complete analysis of the products is not available, but apparently both Cl_2 and O_2 are evolved.

$Pb(ClO_3)_2$

The decomposition is complex [85]. Decomposition rates were measured, in terms of the gas evolved, between 194° and 216 °C. Four stages could be distinguished: (1) initial rapid decomposition, (2) slow reaction, (3) extremely rapid decomposition in which approximatly two thirds of the material reacts, (4) a short, slow decay period. The major part of the residue is PbO_2, with some $PbCl_2$. No perchlorate is formed. The reactions therefore probably are

$$Pb(ClO_3)_2 = PbCl_2 + 3O_2,$$

$$Pb(ClO_3)_2 = PbO_2 + 2ClO_2(Cl_2 + 2O_2),$$
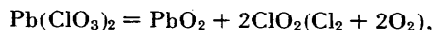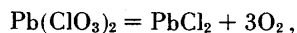
with the second reaction about seven times faster than the first.

$Pb(ClO_4)_2$

Rossolovskii and Krivtsov [72] have used their measurement of the enthalpy of solution of $Pb(ClO_4)_2$ in H_2O to calculate ΔHf°_{298} for this salt. They obtain, using older literature data, $- 49.16 \pm 0.50$ kcal mol^{-1}. Using newer values [I 1b] gives $- 218.40 \pm 2.1$ kJmol^{-1} ($- 52.20 \pm 0.50$ kcal mol^{-1}).

The salt is very hygroscopic, but can be prepared by vacuum treatment of its pyridine adduct [21]. At the melting point decomposition is slow, but becomes more rapid above 300 °C. The decomposition goes both to the chloride and the oxide [97].

$$Pb(ClO_4)_2 = PbCl_2 + 4 O_2,$$

$$Pb(ClO_4)_2 = PbO + Cl_2 + 7/2O_2.$$
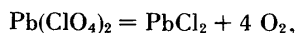
The first of these reactions is the major one [82]. Kinetics were studied in the range 320–355 °C [82].

TABLE 2.5. Properties of Pb-Cl salts

Density			
	ρ(g cm^{-3})	T(K)	Ref.
$Pb(ClO_3)_2$	3.89	393	5
$Pb(ClO_4)_2$	3.86	ambient	21

Transitions			
		T(K)	
$Pb(ClO_4)_2$	c→ l	546 est.	21

Thermodynamic data (298.15 K)

S°			
	J deg^{-1} mol^{-1}	cal deg^{-1} mol^{-1}	Ref.
$Pb(ClO_2)_2$	—	—	
$Pb(ClO_3)_2$	—	—	
$Pb(ClO_4)_2$	—	—	
$PbCl_2$	136.	32.5	I 1b
PbO(red)	66.5	15.9	I 1b
PbO_2	68.6	16.4	I 1b

ΔHf°			
	kJ mol^{-1}	kcal mol^{-1}	Ref.
$Pb(ClO_2)_2$	—	—	
$Pb(ClO_3)_2$	—	—	
$Pb(ClO_4)_2$	$- 218.4 \pm 2.1$	$- 52.0 \pm 0.50$	72, I 1b
$PbCl_2$	$- 359.4$	$- 85.90$	I 1b
PbO(red)	$- 219.0$	$- 52.34$	I 1b
PbO_2	$- 277._4$	$- 66.3$	I 1b

2.11. Lithium

LiClO

The preparation of the anhydrous salt has been described in numerous patents, e.g. [69, 86], because of its importance as a bleaching agent, but not even the range of its thermal stability seems to be known.

$LiClO_2$

When heated in the range 200–210 °C the salt disproportionates in a rather violent manner [51].

$$3LiClO_2 \rightarrow 2LiClO_3 + LiCl.$$
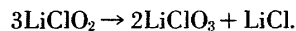
$LiClO_3$

The phase transitions of this salt are in some doubt. Based on the measurements of Brühl [11a], three crystalline forms (two transitions) have been listed in a critical compilation [11a]. A careful reexamination by DTA [57] has yielded only a single solid-state transition. It was found that the high-temperature form supercools easily by as much as 50°, which may account for the earlier results. Liquid $LiClO_3$ is stable over a longer temperature range than other chlorates. Up to ~300 °C no weight loss is detected. At 339° [58] the salt decomposes slowly. The major reactions are

$$LiClO_3 \rightarrow 3/4\ LiClO_4 + 1/4\ LiCl, \tag{1}$$

$$LiClO_3 \rightarrow LiCl + 3/2\ O_2. \tag{2}$$
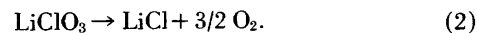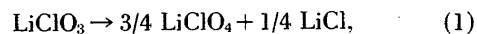
Both of these reactions, occurring in the ratio Rate 1: Rate 2= 5:3, are catalyzed by LiCl. At the temperature of the experiment $LiClO_4$ decomposes quite slowly. Approximately 4 percent of the $LiClO_3$ disappears through oxide formation

$$LiClO_3 \rightarrow 1/2\ Li_2O + 1/2\ Cl_2 + 5/4\ O_2. \tag{3}$$
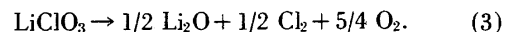
At 370° the rate of decomposition becomes quite rapid. At this and at higher temperature the decomposition of $LiClO_4$ is appreciable, so that the kinetics becomes quite complicated.

$LiClO_4$

The decomposition of this salt has been subject of several studies [56, 80], which agree on the major features. In contrast to the other alkali metal perchlorates, $LiClO_4$ is stable in the solid state and also in the liquid up to ~390 °C. The overall reaction is

$$LiClO_4 \rightarrow LiCl + 2\ O_2.$$

Very small quantities of $LiClO_3$ form as an intermediate, but this salt is very unstable at temperatures where $LiClO_4$ decomposes. Very small quantities of Cl_2 and Li_2O have also been detected. Markowitz and Boryta [56] studied by TGA the decomposition kinetics of both pure $LiClO_4$ and $LiClO_4$-LiCl mixtures below 420°, the highest temperature at which the reaction mixture was not heated appreciably by the heat released in this exothermic reaction. The α vs time curve of pure $LiClO_4$ exhibits an induction period and is sigmoid, indicating that it is autocatalytic. For that range of the decomposition corresponding to the attainment of a saturated solution of LiCl in $LiClO_4$ the kinetics fit the Prout-Tompkins equation

$$\ln \frac{\alpha}{1-\alpha} = kt,$$

originally derived for branching reaction nuclei in solids. When the decomposition is studied for $LiClO_4$ initially saturated with LiCl, the autocatalytic behavior is absent and kinetics are first order. Evidently LiCl functions as a catalyst. Solymosi [80] studied the kinetics of pure $LiClO_4$ by measuring gas evolution between 411 and 430 °C and reached similar conclusions. For the autocatalytic phase both studies obtained 222 kJ (53 kcal) for the activation energy, consistent with $LiClO_4 \rightarrow LiClO_3 + O$, i.e., with the breaking of a Cl-O bond, as the rate-determining step. For the first-order kinetics, however, there is no agreement. Solymosi finds 172 kJ (41 kcal), and Markowitz gives 259 kJ (62 kcal). There is no obvious reason for this discrepancy. High-temperature thermodynamic functions for this salt are given in the JANAF tables.

TABLE 2.6. Properties of Li-Cl salts

Density

$T(K)$	$\rho(g\ cm^{-3})$	Ref.
LiClO_3		
ambient	2.631	57
410	2.0832	40a
421	2.0756	40a
430	2.0681	40a
440	2.0605	40a
450	2.0529	40a
LiClO_4		
530	2.013	40a
540	2.007	40a

TABLE 2.6. Properties of Li-Cl salts

Density

$T(K)$	$\rho(g\ cm^{-3})$	Ref.
550	2.000	40a
560	1.994	40a
570	1.988	40a
580	1.982	40a
590	1.976	40a
600	1.970	40a
610	1.964	40a
620	1.958	40a
630	1.951	40a
640	1.945	40a
650	1.939	40a

Transitions

	Transition	$T(K)$	ΔH (kJ mol⁻¹)	ΔS (J deg⁻¹)	Ref.
$LiClO_3$	c,II → c,I	384			57
	c,I → l	402			57
$LiClO_4$	c → l	520	20.9	40	55, 56

Thermodynamic data (298.15 K)

$S°$

	J mol⁻¹ deg⁻¹	cal mol⁻¹ deg⁻¹	Ref.
LiClO	–	–	
$LiClO_2$	–	–	
$LiClO_3$	$11_7 \pm 4$	18 ± 1 est	KHS
$LiClO_4$	$12_6 \pm 4$	30 ± 1 est	3
LiCl	59.300 ± 0.063	14.173 ± 0.015	3
Li_2O	37.89	9.056	3

$\Delta Hf°$

	kJ mol⁻¹	kcal mol⁻¹	Ref.
LiClO			
$LiClO_2$			
$LiClO_3$	–293.	–70.0 est.	57
$LiClO_4$	$-380._7 \pm 2._9$	-91.0 ± 0.7	3
LiCl	$-408.26_6 \pm 1.142$	-97.578 ± 0.273	3
Li_2O	–598.7	–143.1	3

2.12. Magnesium

$Mg(ClO_2)_2$

The preparation of this salt has been reported [67], but no evidence was presented to show that the compound was completely anhydrous.

$Mg(ClO_3)_2$

Although the infrared spectrum of this salt has been described [70] there exists no evidence that the anhydrous salt has yet been prepared.

Mg(ClO₄)₂

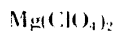The stability range of the anhydrous salt is somewhat in doubt, primarily because it is very hygroscopic and tends to dissolve and/or decompose as a result of hydrate formation. Thus the melting point of 246 °C reported by Gordon and Campbell [32] is clearly too low, in view of the observation that the solid salt is stable up to 320° when carefully vacuum-dried [1]. Decomposition starts near 330°. The decomposition proceeds by the parallel reactions

$$Mg(ClO_4)_2(s) = MgCl_2(s) + 4O_2(g), \qquad (1)$$

$$Mg(ClO_4)_2(s) = MgO(s) + Cl_2(g) + 1/2O_2(g). \qquad (2)$$
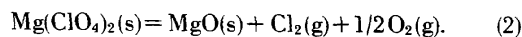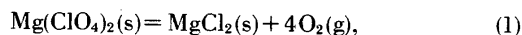
As pointed out by Markowitz [54], $\Delta Gf°$ of $MgCl_2$ and MgO are comparable (they are equal at 427°) so that they may interconvert through the equilibrium

$$MgCl_2 + 1/2O_2 = MgO + Cl_2. \qquad (3)$$
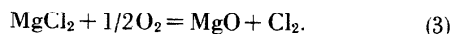
for which $\Delta G° = -RTn(P_{Cl_2}/P_{O_2}^{1/2})$. This equilibrium is achievable in practice and thus the product distribution will be determined by the composition of the gas at the reaction interface and the rate of equilibration of reaction (3). These predictions are borne out by a number of experimental studies. For example, Chudinova [18] found reaction (1) to be dominant at the lower end of the temperature range 360–420°, and (2) at the higher end in a system in which the condensed phase remained in contact with the gas. Very similar results were obtained by Solymosi [82] in the same temperature range. In contrast, Acheson and Jacobs [1] found MgO to be the predominant product when the salt was heated under vacuum in the range 390–440°. This suggests that reaction (2) occurs directly since reaction (3) could not occur in vacuum. Above 600° the product distribution appears to depend only on the internal gaseous environment and to be independent of the gaseous atmosphere above the solid phase. The major product then is MgO.

The $\alpha = f(t)$ curves have been interpreted [1] in terms of a stepwise abstraction of oxygen atoms,

$$ClO_4^- \rightarrow ClO_3^- + O,$$

$$ClO_3^- \rightarrow ClO_2^- + O,$$

$$ClO_2^- \rightarrow ClO^- + O.$$
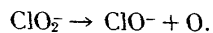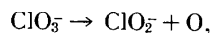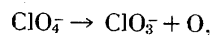
A distinct slowing of the rate above $\alpha = 0.575$ is interpreted in terms of the bimolecular decomposition

$$2ClO^- \rightarrow Cl_2 + O^{2-} + O.$$
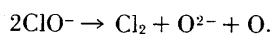
If Cl_2 escapes only by slow diffusion then a back-reaction may occur and the final stage will be slow.

TABLE 2.7.   Properties of Mg-Cl salts

Density			
	$\rho(g\ cm^{-3})$	T	Ref.
Mg(ClO₄)₂	2.21	ambient	59

Thermodynamic data (298.15 K)

$S°$			
	J mol⁻¹ deg⁻¹	cal mol⁻¹ deg⁻¹	Ref.
MgCl₂	89.62	21.42	1 1b
MgO (periclase)	26.9₅	6.44	1 1b

$\Delta Hf°$			
	kJ mol⁻¹	kcal mol⁻¹	Ref.
Mg(ClO₄)₂	− 568.90	− 135.97	1 1b
MgCl₂	− 641.32	− 153.28	1 1b
MgO (periclase)	− 601.70	− 143.81	1 1b

2.13. Manganese

Mn(ClO₄)₂
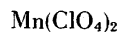
The decomposition of a sample of unknown water content (vacuum-dried at 150 °C) was studied in the range 125–155 °C [92]. The main reaction is

$$Mn(ClO_4)_2 \rightarrow MnCl_2 + 4O_2$$
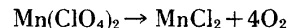
with a smaller fraction decomposing to the oxide:

$$Mn(ClO_4)_2 \rightarrow MnO + Cl_2 + 3.5O_2.$$

2.14. Mercury

Hg₂(ClO₂)₂
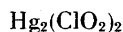
The salt is so unstable that its existence must be regarded as marginal. Several attempts to prepare it [13, 49] have resulted in the preparation of somewhat basic, yellow crystals which turned red in air and decompose explosively on slight heating.

Hg(ClO₂)₂
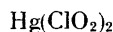
The salt has been prepared [3, 48]. It consists of red crystals whose composition indicates some contamination by HgO. It is fairly unstable, tending to decomposition even at ambient temperature.

Hg(ClO₃)₂
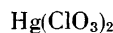
A salt of approximately this composition was prepared and studied by several investigators in the 19th century. This work is summarized by Gmelin [19]. However, it is questionable whether the pure salt has ever been prepared. No work seems to have been done since 1910.

$Hg_2(ClO_4)_2$

A salt of nearly this composition was obtained by dehydration of the 6-hydrate [29]. It melts at 210 °C with the evolution of chlorine oxides.

2.15. Nickel

$Ni(ClO_2)_2$

The anhydrous salt has been prepared [9]. It is very unstable and decomposes at 45 °C according to

$$3Ni(ClO_2)_2 \rightarrow 2Ni(ClO_3)_2 + NiCl_2.$$

$Ni(ClO_3)_2$

There is no detailed description of the anhydrous salt, although spectral measurements of a vacuum-dried salt were reported by Rocchiccioli [70].

$Ni(ClO_4)_2$

Attempts to prepare the salt by vacuum-dehydration of the 2-hydrate were unsuccessful [102]. A light-green, not quite pure anhydrous salt was prepared by the incomplete reaction of $HClO_4$ with $Ni(CF_3COO)_2$ in trifluoroacetic acid [29]. Recently Borgne and Weigel [9] reported the preparation of the anhydrous salt by slow, stepwise dehydration of the hexahydrate. Final heating was carried out at 180 °C. Its structure was determined by X-ray diffraction and a density of 2.985 g cm^{-3} calculated. This result conflicts with an even more recently reported preparation [28] in which the density is given (probably determined pyknometrically) as ~ 3.4 g cm^{-3}. The salt was said to be stable up to 130 °C in vacuum.

The decomposition of a salt of unknown water content was studied by Vilcu and Georgescu [92] between 130 and 170°. They find the major reaction to be

$$Ni(ClO_4)_2 \rightarrow NiCl_2 + 4O_2,$$
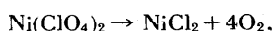
with a minor simultaneous reaction forming the oxide:

$$Ni(ClO_4)_2 \rightarrow NiO + Cl_2 + 3.5O_2.$$

2.26. Potassium

$KClO_2$

The salt is quite hygroscopic. When sealed into glass tubes and heated at 180°–200 °C 98 percent of it disproportionates, as do the other alkali metal chlorites, according to [51]

$$3KClO_2 \rightarrow 2KClO_3 + KCl.$$

$KClO_3$

Although the molten salt is stable for some distance above its melting point [58] no density data of the liquid are yet available. The thermal decomposition of the salt has been studied by many investigators, frequently as part of the decomposition of $KClO_4$ in which it occurs as an intermediate product (see below). The earlier literature has been summarized by Rudloff and Freeman

[73] who studied the kinetics in detail. At temperatures below 500 °C, where $KClO_4$ is stable, the decomposition products are KCl, O_2, and $KClO_4$, consistent with the frequently cited overall stoichiometry [58] in terms of two reactions

$$KClO_3 \rightarrow KCl + 3/2O_2, \tag{1}$$

$$4KClO_3 \rightarrow 3KClO_4 + KCl. \tag{2}$$
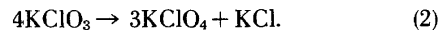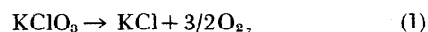
Clearly, reaction (2) cannot correspond to a simple mechanism. However, Rudloff and Freeman [73] found that below 500 °C $KClO_3$ loses only one-third of the weight to be expected from $KClO_3 \rightarrow KCl + 3/2O_2$ and that equivalent amounts of $KClO_4$ and KCl are formed. In this range the kinetics are second-order. On this basis they propose the reaction sequence

$$2KClO_3 \xrightarrow{slow} KClO_4 + (KClO_2) \tag{3}$$

$$\frac{(KClO_2) \xrightarrow{fast} (KClO) + 1/2O_2 \xrightarrow{fast} KCl + O_2}{2KClO_3 \longrightarrow KClO_4 + KCl + O_2} \tag{4}$$
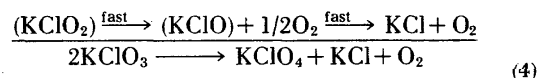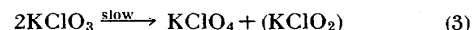
$KClO_2$ is unstable above 200 °C and cannot be detected [58]. It can therefore only be present as an unstable intermediate. The rate-determining step is thus an oxygen atom transfer between two chlorate ions:

$$2ClO_3^- \rightarrow ClO_4^- + ClO_2^-,$$

The frequently observed deceleration of the reaction by KCl is attributed to dilution. Above 500° the decomposition becomes more complicated because $KClO_4$ then also decomposes and $KClO_3$ appears as an intermediate reaction product. Moreover, KCl now catalyzes the reaction. Explanations for this phenomenon, e.g. in terms of polarization centers, are quite speculative.

$KClO_4$

Because of its use in pyrotechnics and propellants the thermal decomposition of this salt has been studied for a long time. Simchen [76] has given references back to 1816. High-temperature thermodynamic functions are listed in the JANAF tables.

The course of the decomposition is complicated by simultaneously occurring phase changes resulting from a lowering of the melting point by the accumulating reaction products (KCl and $KClO_3$), and a subsequent freezing of the melt as the material becomes predominantly KCl. For this reason it is also impossible to determine a precise melting point although it appears to be near 580 °C [55].

Tracer experiments have established that O_2 [88] and Cl$^-$ [91] are formed irreversibly, but that ClO_3^- is transformed to ClO_4^-. Harvey et al. [33, 34] established that in the range 556–580 °C the decomposition of $KClO_4$ is first-order. As reaction products accumulate the solid melts and the rate increases ~ 50-fold.

The kinetics of the liquid-state reaction are also first-order. For both the solid and the liquid the activational

enthalpies and entropies are the same, $\Delta S^{\pm} \approx 8$ J deg^{-1}(2 cal deg^{-1}), indicating that the rate-determining step is the breaking of a Cl-O bond, with the formation of atomic oxygen,

$$KClO_4 \rightarrow KClO_3 + O \quad \Delta H^{\circ} = 290\,kJ\ (69.3\ kcal).$$

The activated complex does not differ much from the ClO_4^- ion. These kinetic results have recently been confirmed by Solymosi [80]. Reactions subsequent to the rate determining one are presumably those described for $KClO_3$ above. Since KCl and O_2 are formed irreversibly, the final result is consistent with the stoichiometry of the overall reaction.

$$KClO_4 \rightarrow KCl + 2O_2.$$

Recently, two studies at lower temperatures have obtained much lower activation energies. Cabané and Bènard [14] measured both decomposition rates and ClO_4^- diffusion between 375 and 480 °C. Since for both of these processes the activation energy was the same for several alkali metal perchlorates, 126 kJ (30 kcal) for $KClO_4$, they argued that the rate-determining step must be the same, i.e. diffusion of ClO_4^-.

A much more detailed experimental and theoretical study of the decomposition kinetics over approximately the same temperature range was carried out by Cordes and Smith [25], using only the first 3 percent of the solid-state decomposition in their analysis. For $KClO_4$, an extrapolation of their data on an Arrhenius plot fits smoothly into the high temperature data of Harvey et al. [33, 34]; i.e. at lower temperatures the plot is linear but exhibits a curvature corresponding to a higher apparent activation energy at higher temperatures. For $KClO_4$ the low temperature data are represented by

$$k_s = Ae^{-E_a/RT},$$

where $A \approx 10^7$ s^{-1} and $E_a = 210 \pm 10$ kJ (50.2 ± 2.5) kcal. They argue from this, that, at least at low temperatures, the rate-determining step cannot be $ClO_4^- \rightarrow ClO_3^- + O$. Instead, they carry out a detailed analysis in terms of Cordes' theory [24] of pre-exponential factors and a molecular model in which internal motions are specified, which leads to a pre-exponential factor in good agreement with experiment. In this model the activated complex is assumed to consist of two neighboring, freely rotating ClO_4^- ions joined by a peroxide linkage (ClO_3)-O-O-(ClO_3). The rate-determining step then consists in the formation of O_2 and two ClO_3^- ions.

To account for the higher E_a values at higher temperatures it is necessary to postulate either increased freedom of motion for the ClO_3^- ions in the lattice or a change in mechanism to that proposed by Harvey et al. [33, 34]. A similar rise of E_a with temperature is observed for $NaClO_4$.

At any rate, it is clear that a theory which predicts pre-exponential factors from a model provides a more stringent test for model building than one which predicts only activation energies.

TABLE 2.8. Properties of K-Cl salts

Phase transitions

	Transition	T(K)	ΔH(kJ)	ΔS(J deg)	Ref.
KClO$_3$	c → l	357			16
KClO$_4$	c, rhombic → c, cubic	572.7	13.8	24.0	11a
	c, cubic → l	853 (est.)			33

Density

	T(K)	ρ(g cm^{-3})	Ref.
KClO$_3$	293	2.338	22
KClO$_4$	284	2.524	61
	291	2.527	39
	298	2.530	99
	613	2.181	37

Thermodynamic data (298.15 K)

S°

	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	Ref.
KClO	82.55	—	
KClO$_2$	—	—	
KClO$_3$	142.9$_7$	34.17	13
KClO$_4$	151.$\pm$1	36.1$\pm$0.2	13
KCl	82.55	19.73	13

ΔHf°

	kJ mol^{-1}	kcal mol^{-1}	Ref.
KClO	—	—	
KClO$_2$	—	—	
KClO$_3$	−391.2$_7$	−93.66	11b
KClO$_4$	−430.1 $\pm$4.2	−102.8 $\pm$1.0	13
KCl	436.68$\pm$0.25	104.37$\pm$0.06	13

2.17. Rare Earths

Chlorites

Nearly anhydrous $Tb(ClO_2)_3$ and $Er(ClO_2)_3$ have been prepared, but none of their properties have been reported as yet. Chlorites of several other rare earths (La, Ce, Pr, Nd, Sm) have been prepared as hydrates only by [8].

Perchlorates

The preparation of the anhydrous salts (by vacuum-drying in the presence of P_2O_5 with the temperature gradually rising to 155°) has been reported [77], but the original paper was not available for study. Whether or not the anhydrous salts can be prepared from their hydrates under TGA may depend on experimental conditions such as heating rate. For example Bel'kova and Aleksenko [5, 6] reported brief plateaus in the TGA curves of the hydrated perchlorates of La, Ce,

Pr, and Sn at weights corresponding to the anhydrous salts, whereas Steinberg and Shidlovsky [87] report finding only inflections for these salts and $Nd(ClO_4)_3$. Except for Nd, these findings are consistent since the latter authors used a faster heating rate.

Belkova, Alekseenko, and Screbrennikov [6] have reported an isothermal decomposition study of several rare earth perchlorates in which the rate of weight loss was measured under flowing nitrogen. The stoichiometry for all the salts could be represented by

$$2M(ClO_4)_3 \rightarrow MOCl + MCl_3 + Cl_2O + 11\ O_2.$$
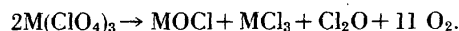
Between 240 and 370 °C the kinetics followed the Erofeev equation in which the fraction decomposed is represented by

$$\alpha = 1 - \exp(-kt^n).$$

The value of n is determined by the properties of the nucleus. The Arrhenius activation energy was determined from the temperature dependence of the rate constant k. The results are shown below:

TABLE 2.9. Activation energies for decomposition of rare earth perchlorates

Salt	E_a	
	kJ	kcal
$La(ClO_4)_3$	142.7	34.1
$Sm(ClO_4)_3$	120.5	28.8
$Gd(ClO_4)_3$	119.2	28.5
$Ho(ClO_4)_3$	108.8	26.0
$Yb(ClO_4)_3$	105.9	25.3
$Lu(ClO_4)_3$	105.0	25.1

2.18. Rubidium

$RbClO_2$

When heated in a closed container at 200–210 °C the salt disproportionates according to [51]

$$3RbClO_2 \rightarrow 2RbClO_3 + RbCl.$$
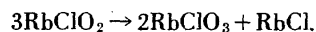
$RbClO_3$

Our knowledge of the high-temperature properties is largely based on a study by Markowitz and Boryta [58]. In contrast to the perchlorate (see below), the salt is quite stable for 20–30° above its melting point (342 °C). Decomposition becomes rapid at 480 °C. The salt disappears by two paths:

$$RbClO_3 \rightarrow RbCl + 3/2\ O_2 \qquad (1)$$

$$4RbClO_3 \rightarrow 3RbClO_4 + RbCl. \qquad (2)$$
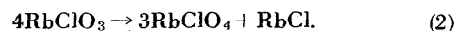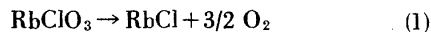
Reaction 2 is the major one by a factor of ~ 8. Only near 600° does the reaction proceed further with the decomposition of the perchlorate. Chlorites and hypochlorites seem to be absent as intermediates.

$RbClO_4$

The salt decomposes during fusion [54] and therefore

the melting point can only be determined approximately. The decomposition is exothermic and yields only RbCl and O_2 as final product. The high-temperature kinetic data can be fitted by various rate equations, all of which yield an Arrhenius activation energy of ~ 293 kJ (70 kcal) [80], consistent with loss of one oxygen atom as the rate-determining step.

$$RbClO_3 \rightarrow RbClO_3 + O.$$

Since $RbClO_3$ is quite unstable in the decomposition range of the perchlorate, the decomposition proceeds to the chloride. In addition to the decomposition reactions

$$RbClO_4 \rightarrow RbClO_3 + 1/2 O_2,$$

$$RbClO_3 \rightarrow RbCl + 3/2 O_2,$$
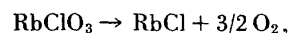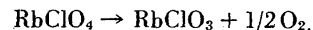
the salts also undergo fusion or solution in the reaction melt so that the physical state of the system depends both on the temperature and the extent of the decomposition.

At lower temperatures (330–480 °C) a much lower activation energy, 192 ± 8 kJ (46.0 ± 1.9 kcal), was observed for the initial 3 percent of the solid-state decomposition [25]. This, and the low observed pre-exponential factor, were interpreted in terms of the abstraction of O_2 from two neighboring ClO_4^- ions, $(ClO_3) = O = O = (ClO_3)$ to form $2ClO_3^-$. The higher activation energy observed at higher temperatures then requires either a change in mechanism or allowance for increased motion by ClO_3^-. The theory is discussed in more detail under $KClO_4$.

TABLE 2.10. Properties of Rb-Cl salts

Density			
	ρ (g cm^{-3})	T(K)	Ref.
$RbClO_2$	—		
$RbClO_3$	3.184	ambient	54
$RbClO_4$	3.04	ambient	80

Transitions				
		T(K)	ΔH(kJ)	Ref.
$RbClO_3$	$\alpha \rightarrow \beta$	596		58
	$\beta \rightarrow l$	615		58
$RbClO_4$	rhombohedral $\rightarrow$ cubic	557	12.6 ± 0.4	54
	cubic $\rightarrow l$	597		54

Thermodynamic data (298.15 K)

$S°$			
	J mol^{-1} deg^{-1}	cal. mol^{-1} deg^{-1}	Ref.
RbClO	—	—	
$RbClO_2$	—	—	
$RbClO_3$	151.9	36.3	1 1a
$RbClO_4$	160.7	38.4	1 1a
RbCl	94.6	22.6 est	1 10

ΔH°

	kJ mol^{-1}	kcal mol^{-1}	Ref.
RbClO	—	—	
RbClO$_2$	—	—	
RbClO$_3$	− 397.2	− 94.93	1 1b
RbClO$_4$	− 437.18	− 104.49	1 1b
RbCl	− 435.05	− 103.98	1 1b

2.19. Silver

AgClO$_2$

The anhydrous salt exists as flat, shiny yellow laminae, orthorhombic in structure [23, 26]. The compound is rather unstable. Beginning at 85 °C it disproportionates according to

$$3AgClO_2 = 2AgClO_3 + AgCl.$$

The reaction is first-order with an activation energy of 109 kJ (26.0 kcal). Above 100 °C the thermal decomposition of the salt becomes increasingly important. The precise nature of the decomposition is not quite clear, but the major gaseous product is ClO$_2$ and the solid residue contains both silver and silver oxide. Above 145 °C the reaction becomes explosive. A detailed kinetic analysis of the disproportionation and decomposition reactions has been published [83].

AgClO$_3$

The anhydrous crystal are tetragonal [19]. No solid-state transitions have been reported. The decomposition has been measured in the range 316–339 °C [83], i.e. of the liquid salt. However, the accumulation of reaction products increases the melting point, so that the mass solidifies in this temperature range after about 80 percent of it has decomposed. The gaseous product in mainly O$_2$, with 2–3 percent Cl$_2$. The reaction is therefore

$$2AgClO_3 = 2AgCl + 3O_2.$$
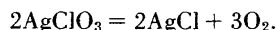
The activation energy is 239 kJ (57. kcal), consistent with the rupture of a Cl-O bond as the rate-determining step

$$AgClO_3 = AgClO_2 + O.$$

Approximately 10 percent of the chlorate disproportionates:

$$4AgClO_3 = 3AgClO_4 + AgCl.$$

AgClO$_4$

There are some contradictions in the literature concerning the high-temperature behavior of this salt. Several authors agree that AgClO$_4$ undergoes a transition from rhombic to cubic in the range 155–159 °C [32, 37, 94], but there is some confusion concerning the melting point and thermal decomposition. For example, Gordon and Campbell [33] report a slight decomposition in the solid state at 277 °C, with violent bubbling of the melt at 473 °C. However, Carnelly and

O'Shea [15] report a melting point of 486 °C. Markowitz has suggested that in Gordon and Cambell's experiment the AgCl, which is formed as decomposition product, lowers the melting point. This explanation was confirmed experimentally by Solymosi [83] who reports a melting point of 476°. This author also studied the decomposition kinetics between 414° and 445°. Virtually the only reaction is

$$AgClO_4 = AgCl + 2 O_2.$$
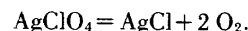
The absence of AgClO$_3$ is not surprising since this compound decomposes at a much lower temperature. The reaction is probably autocatalytic.

TABLE 2.11.   Properties of Ag-Cl compounds

Density			
	T(K)	ρ(gcm^{-3})	Refs.
AgClO$_2$	493	4.67	26
AgClO$_3$	493–496	4.43–4.46	19
AgClO$_4$	433	3.96 (cubic, calc.)	10

Transitions			
		T(K)	Refs.
AgClO$_3$	c → 1	504	1 1a
AgClO$_4$	rhombic → cubic	430	32
	cubic → 1	759	15

Thermodynamic data (298.15 K)

S°			
	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	Ref.
AgClO$_2$	134.6	32.16	1 1b
AgClO$_3$	146.	34.8	42
AgClO$_4$	162.	38.8 (est.)	1 10
AgCl	96.2	23.0	1 1b

$\Delta H f^{\circ}$			
	kJ mol^{-1}	kcal mol^{-1}	Ref.
AgClO$_2$	8.79	2.10	1 1b
AgClO$_3$	−25.5	−6.1	1 1b
AgClO$_4$	−31.1	−7.44	1 1b
AgCl	−127.07	−30.370	1 1b

2.20. Scandium

Sc(ClO$_4$)$_3$

The thermal decomposition of the anhydrous salt proceeds according to the reaction
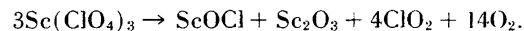
$$3Sc(ClO_4)_3 \rightarrow ScOCl + Sc_2O_3 + 4ClO_2 + 14O_2.$$

In the range 240–370 °C the kinetics follows the Erofeev equation (see under Rare Earths) with an Arrhenius activation energy of 87.4 kJ (20.9 kcal) [6].

2.21. Sodium

NaClO$_2$

The thermal decomposition has been studied by several workers who agree on the main features of the reaction [40, 51, 68, 84]. In an open container reaction begins as low as 140 °C and is certainly rapid above 160°. The major reaction is disproportionation:

$$3NaClO_2 = 2NaClO_3 + NaCl. \qquad (1)$$
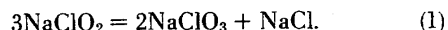
The fraction of NaClO$_2$ which disappears by this path as compared with the direct decomposition

$$NaClO_2 = NaCl + O_2, \qquad (2)$$
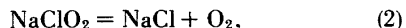
varies from 75 percent to 99 percent, depending on the experimental details. The lower value was reported for rapid heating [68]. All others report 97–99 percent for reaction (1). The kinetics are first-order, with an Arrhenius activation energy of 227 kJ (54.3 kcal), which is less than the Cl-O bond energy [84].

NaClO$_3$

The thermal expansion coefficient of the solid has been measured by Sharma [75] using an interferometric method, and by Deshpande and Mudholker [27] using X-ray diffraction data. At ambient temperature both sets of data agree within 5 percent, but near 500 K Sharma's values are much higher. Deshpande and Mudholker have suggested that the macroscopic expansion coefficient is made up of a sum of terms:

$$\alpha_{macro.} = \alpha_{lattice} + \alpha_{Schottky} - \alpha_{readjustment},$$

so that $\alpha_{macro.}$ determined by the two methods may differ, depending on the relative contributions of the defects and the readjustment of the small single crystals packed together in a mosiac structure with a slight amount of misorientation. Both sets of data have been listed. Sharma has used Grüneisen's law to calculate C_p. His results over the entire temperature range are within 3 percent of those given by Kelley [43] so that the interferometric measurements may reflect the behavior to be expected from "real" NaClO$_3$, whereas the X-ray results refer to an ideal lattice.

NaClO$_3$ is stable well above its melting point. Three thermal decomposition studies of liquid NaClO$_3$ have been published [58, 62, 85] which agree in their main features. Decomposition starts near 400 °C. No Cl$_2$ and ClO$_2$ are formed. The major reaction is

$$NaClO_3 = NaCl + 3/2 \ O_2. \qquad (1)$$
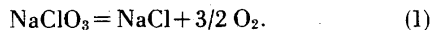
However, NaClO$_4$ is also found to be a product. The amount of this salt formed probably depends on reaction conditions. The overall stoichiometry can be written as

$$4NaClO_3 = 3NaClO_4 + NaCl. \qquad (2)$$
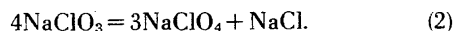
but this is not a likely mechanism. Osada et al. [62] suggest that the atomic oxygen formed as the initial product in reation (1) oxidizes unreacted NaClO$_3$

$$NaClO_3 + O = NaClO_4. \qquad (3)$$

Proper stoichiometric combination of (1) and (3), and allowing for $O + O = O_2$ yields reaction (2). Perchlorate formation becomes increasingly important with increasing temperature, from a few percent at the lower end to perhaps equal amounts with NaCl above 450 °C. NaClO$_4$ is stable up to ~530°. The activation energy of 285 kJ (68 kcal) [85] is consistent with the breaking of a Cl-O bond as the rate-determining step of reaction (1).

NaClO$_4$

In contrast to NaClO$_3$, the perchlorate begins to decompose well below its melting point. Hence the melting point can only be determined approximately. However, since the temperature at which this decomposition becomes appreciable is higher than the stability region of the chlorate, very little NaClO$_3$ is found in the decomposition of NaClO$_4$, even though the initial reaction is probably

$$NaClO_4 = NaClO_3 + 1/2 \ O_2.$$
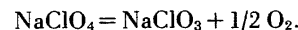
The initial stages of the solid-state decomposition have been studied by Cordes and Smith [25] between 330 and 440 °C. An Arrhenius plot was linear up to ~390°, with an activation energy of ~188 kJ (45 kcal). Above this temperature the slope of the plot increased. This result, as well as the low preexponential factor, was accounted for by a detailed molecular model (discussed under KClO$_4$) in which O$_2$ is abstracted from two neighboring ClO$_4^-$ ions.

$$(ClO_3^-)\text{-}O\text{-}O\text{-}(ClO_3^-) \rightarrow 2ClO_3^- + O_2.$$
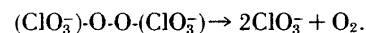
The increase in E_a with rising temperature is accounted for by increased rotational freedom of the ClO$_3^-$ ions.

In contrast, Cabané and Bénard [14] observed an activation energy of only 117 kJ (28 kcal) between 390° and 428 °C, equal to that for diffusion of ClO$_4^-$ through the lattice. They argue that this implies ClO$_4^-$ diffusion to be the rate-determining step.

In the liquid state (490–515) the reaction is catalyzed by NaCl, but the activation energy is near 250 kJ (60 kcal) [80] which is more consistent with the breaking of a Cl-O bond as the rate-determining step:

$$NaClO_4 = NaClO_3 + O.$$

NaClO$_3$ decomposes to NaCl as rapidly as it is formed . The overall decomposition is therefore

$$NaClO_4 = NaCl + 2 \ O_2.$$

although a small part (~0.2%) of the NaClO$_4$ disappears by the reaction [54]

$$2NaClO_4 = Na_2O + Cl_2 + 1/2 \ O_2.$$

Above 525° the decomposition becomes quite rapid [54].

TABLE 2.12. Properties of Na-Cl salts

Density

	T(K)	ρ(gcm^{-3})	Ref.
NaClO$_3$	288	2.489	27

$\alpha_t = 4.029 \times 10^{-5} + 1.459 \times 10^{-8}t + 5.959 \times 10^{-10}t^2$ t in °C 40–220°	27
$\alpha_t = 4.279 \times 10^{-5} + 5.973 \times 10^{-8}t + 7.201 \times 10^{-11}t^2$ t in °C 34–226°	75

NaClO$_4$	653	2.11	37

Transitions

		I	ΔH(kJ mol^{-1})	ΔS(J deg^{-1})	Ref.
NaClO$_3$	c → l	528	22.6	42.7	11a
NaClO$_4$	c, rhombic → c, cubic	582	2.5 ± 0.4		54
	c → l	741			54

Thermodynamic data (298.15 K)

S°

	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	Ref.
NaCl	72.13 ± 0.21	17.24 ± 0.05	13
NaClO	—	—	
NaClO$_2$	111.$_7$	27.7 est	110
NaClO$_3$	126.$_4$	30.2 ± 1.0	13
NaClO$_4$	14$_2$.	34 est	13

$\Delta H f°$

	kJ mol^{-1}	kcal mol^{-1}	Ref.
NaCl	−411.1 ± 0.3	−98.26 ± 0.08	13
NaClO	—	—	
NaClO$_2$	−309.0	−73.85	11b
NaClO$_3$	−360.3	−86.12	11b
NaClO$_4$	−382.7$_5$ ± 0.92	−91.48 ± 0.22	13

2.22. Strontium

Sr(ClO$_2$)$_2$

The preparation of the salt has been described [65, 67]. Heating in the range 180–200 °C leads to virtually complete disproportionation according to [51]

$$3Sr(ClO_2)_2 \rightarrow 2Sr(ClO_3)_2 + SrCl_2.$$
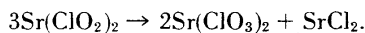
Sr(ClO$_3$)$_2$

The salt is of orthorhombic-bipyramidal structure [89]. It can be heated to at least 120 °C without decomposing [64].

Sr(ClO$_4$)$_2$

Only a brief study of decomposition has been carried

out [19]. Oxygen evolution begins at ~ 415 °C. During the decomposition the salt appears to melt at 450°, but the salt is then no longer pure. The product is virtually entirely SrCl$_2$.

TABLE 2.13. Properties of Sr-Cl salts

Density

	ρ (g cm^3)	T(K)	Ref.
Sr(ClO$_2$)$_2$	3.23	ambient	30
Sr(ClO$_3$)$_2$	3.152	ambient	5
Sr(ClO$_4$)$_2$	3.00 ± 0.03	298	19, 79

Thermodynamic data (298.15 K)

S°

	J deg^{-1} mol^{-1}	cal deg^{-1} mol^{-1}	Ref.
Sr(ClO$_4$)$_2$	—	—	
SrCl$_2$	114.8$_5$	27.45	11b

$\Delta H f°$

	kJ mol^{-1}	kcal mol^{-1}	Ref.
Sr(ClO$_4$)$_2$	− 762.79	− 182.31	11b
SrCl$_2$	− 828.8$_5$	− 198.1	11b

2.23. Thallium

TlClO$_2$

Little is known about this salt. It explodes from mechanical shock and thermally decomposes above 70 °C [47].

TlClO$_3$

The decomposition becomes noticeable near 150 °C. The kinetics have been studied from this temperature up to 170° [85]. The overall reaction can be represented by

$$7TlClO_3 = 3Tl_2O_3 + TlCl + 6ClO_2,$$
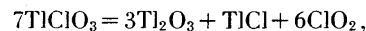
but the mechanism is obviously more complex. Possible reactions by which Tl$_2$O$_3$ and TlCl are produced are:

$$TlClO_3 = TlCl + 3/2O_2,$$

$$2TlClO_3 = Tl_2O_3 + ClO_2 + 1/2Cl_2 + 1/2O_2.$$
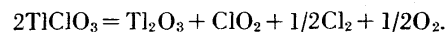
Tl$_2$O may also be formed and oxidized to Tl$_2$O$_3$

$$2TlClO_3 = Tl_2O + 2ClO_2 + 1/2O_2,$$

$$Tl_2O + O_2 = Tl_2O_3.$$
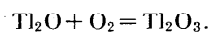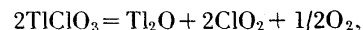
TlClO$_4$

The phase transitions are well established, but little work has been done on the decomposition. DTA measurements [63] indicate that decomposition occurs near 400 °C. Both TlCl and Tl$_2$O$_3$ are formed.

TABLE 2.14. Properties of Tl-Cl salts

Density

	T(K)	d (g cm^{-3})	Ref.
TlClO$_3$	ambient	4.58	15
TlClO$_4$	ambient (rhombic)	4.959 ± .010	100
	553 (cubic)	4.58	37

Transitions

		T(K)	Ref.
TlClO$_4$	c, rhombic → c, cubic	539	41, 63
	c, cubic → l	778	41

Thermodynamic data (298.15 K)

$S°$

	J deg^{-1} mol^{-1}	cal deg^{-1} mol^{-1}	Ref.
TlClO$_3$	169. ± 2	40.4 ± 0.6	44
TlClO$_4$	—	—	
Tl$_2$O	126.	30.	11b
Tl$_2$O$_3$	—	—	
TlCl	111.2$_5$	26.59	11b

$\Delta Hf°$

	kJ mol^{-1}	kcal mol^{-1}	Ref.
TlClO$_3$	—	—	
TlClO$_4$	—	—	
Tl$_2$O	−178.$_7$	−42.7	11b
Tl$_2$O$_3$	—	—	
TlCl	−204.1$_4$	−48.79	11b

2.24. Thorium

Th(ClO$_4$)$_4$

The evidence for the existence of the anhydrous salt is not conclusive. Some crystals were reported to have formed in the reaction between thoria and perchloric acid [17], but no analysis was carried out. The salt would certainly be very hygroscopic. Attempts to dehydrate the hydrate Th(ClO$_4$)$_4$ · 4H$_2$O resulted in the formation of the anhydrous oxy-salt ThO(ClO$_4$)$_2$ [60].

2.25. Tin

Perchlorates

Neither the stannous nor the stannic salts seem to have been prepared in the pure anhydrous state although there are indications that they could be. Thus Gomberg [31] reports the preparation of several anhydrous perchlorates, including stannous and stannic perchlorate, by reacting the metal with an ethereal solution of chlorine tetroxide, but the products were not characterized. Schmidt [74] reported the preparation of the acetonitrile adduct Sn(ClO$_4$)$_2$ · 2CH$_3$CN, but did not attempt to remove the acetonitrile.

2.26. Yttrium

Y(ClO$_4$)$_3$

The thermal decomposition of the anhydrous salt follows the overall stoichiometry
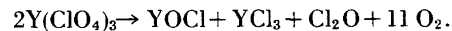
$$2Y(ClO_4)_3 \rightarrow YOCl + YCl_3 + Cl_2O + 11\ O_2.$$

In the range 240–370 °C the kinetics follows the Erofeev equation (see under Rare Earths) with an Arrhenius activation energy of 116.3 kJ (27.8 kcal) [6].

2.27. Zinc

Zn(ClO$_3$)$_2$

The preparation of several chlorates of bivalent chlorates, including Zn(ClO$_3$)$_2$, was reported by Amiel [2], but the salts were not characterized or analyzed. It is therefore doubtful that the anhydrous salt has been prepared.

Zn(ClO$_4$)$_2$

The anhydrous salt has been prepared in a two-stage process whereby the water of hydration is first replaced with dioxane which can then be removed under vacuum without decomposing the salt [20]. The salt is quite stable up to 130 °C. Chudinova has reported the decomposition to occur above 190° [20]. The kinetics of the decomposition were studied by Solymosi in the range 280–310° [82]. The salt decomposes by two parallel reactions

$$Zn(ClO_4)_2 = ZnCl_2 + 4O_2$$

$$Zn(ClO_4)_2 = ZnO + Cl_2 + 7/2\,O_2,$$
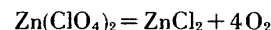
which take place to nearly the same extent. Both reactions appear to be first-order.

Rosolovskii and Krivtsov [72] have used their measurement of the enthalpy of solution of Zn(ClO$_4$)$_2$ in 0.9 M HClO$_4$ to calculate $\Delta Hf°_{298}$ for this salt. They obtain −56.44 ± 0.52 kcal mol^{-1}. Recalculating this value with newer data gives −247.86 ± 2.18 kJ mol^{-1} (−59.29 ± 0.52 kcal mol^{-1}).

2.28. References

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3. Bromine

Less is known about the anhydrous bromine-containing oxy-salts than about the corresponding compounds of chlorine and iodine. This is true with respect to the total number of such salts, as well as the information available concening salts of a given metal. For example, it was generally believed until very recently that only the +5 oxidation state existed for anhydrous salts, i.e., bromates were the only oxyanions of bromine, but very recently the synthesis of $KBrO_4$, $RbBrO_4$, and $CsBrO_4$ has been accomplished [1], and there is no reason to believe that other perbromates could not be prepared. Contrast this situation with the large number of well known perchlorates, and the even larger number of periodates! Similarly, the syntheses of two anhydrous bromites, $LiBrO_2$ and $Ba(BrO_2)_2$, have only recently been reported [17].

Even bromates which are well known have not been extensively studied. Thermodynamic data at 298 K are not plentiful, and above this temperature they are non-existent. Consequently this section is rather brief, includes no high temperature equilibrium calculation, and is based on such qualitative and semiquantitative studies as the author has been able to uncover. Figures 3.1–3.3 show the known anhydrous bromites, bromates, and perbromates

																	H	He
Li	Be												B	C	N	O	F	Ne
Na	Mg												Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn		Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd		In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg		Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac																

Lanthanides   Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

Actinides   Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lw

FIGURE 3.1. The known bromites.

|																	H	He
Li	Be												B	C	N	O	F	Ne
Na	Mg												Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn		Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd		In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg		Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac																

Lanthanides   Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

Actinides   Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lw

FIGURE 3.2. The known bromates. Shaded, existence known. Half-shaded, existence uncertain. No shading, existence unknown.

FIGURE 3.3. The known perbromates.

Bromites

So far only the bromites of barium and lithium have been prepared [17] by heating the corresponding bromate and bromide together. The method should be applicable to other bromites as well. So far very little is known of these salts except that heating produces the bromide:

$$BrO_2^- \rightarrow Br^- + O_2.$$
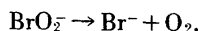
Bromates

These constitute the largest group of bromine oxysalts. The BrO_3^- ion is a flattened pyramid similar to ClO_3^- and IO_3^-. A model derived by [37] from literature data is shown in figure 3.4. The quadrupole spectra of bromates [31] show that the electronic structure of bromine is affected by the metal cation of the salt. The cation is nearer to one of the oxygen atoms than to the bromine;
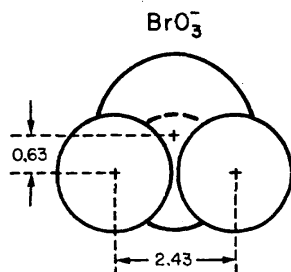
BrO_3^-

FIGURE 3.4. Structure of the BrO_3^- ion. [37].

e.g. in $NaBrO_3$, Na-Br 4.1Å, Na-O 2.38Å. The Br-O distance of 1.78Å is consistent with virtually pure single-bond character.

As pointed out by Bancroft and Gesser [4, 5], bromates may decompose by two competing reactions:

$$MBrO_3 \rightarrow MBr + 3/2O_2, \tag{1}$$

$$MBrO_3 \rightarrow 1/2M_2O + 1/2Br_2 + 5/4O_2. \tag{2}$$
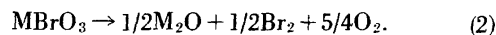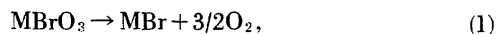
If thermodynamics were the sole determinant as to which reaction occurs the argument developed by

Markowitz [25] for predicting the decomposition products of the perchlorates could be used, i.e., if $[\Delta Gf°(MBr) - \Delta Gf°(MO)]_0$ the oxide should form. Bancroft and Gesser [5] applied this method to the results of their TGA experiments on several bromates. Their results are shown in table 3.1.

TABLE 3.1. Gibbs energy differences

$[\Delta Gf°(Br^-) - \Delta Gf°(O^{2-})]_{equiv.}(kJ)$

Salt	Percent Br⁻	T (K)			F^* (kJ mol⁻¹)
		300	500	1000	
LiBrO₃	90	−57.7	−54.0	−47.3	1159
NaBrO₃	100	−151.	−147.	−137.	352
KBrO₃	100	−217.	−210.	−196.	494
RbBrO₃	100	−233.	−233.		205−226
CsBrO₃	100	−247.			109−138
Mg(BrO₃)₂	5	+70.7	+77.0	+94.6	84
Ca(BrO₃)₂	100	−50.2	−41.4	−21.	1205
Sr(BrO₃)₂	100	−143.	−128.	−110.	278
Ba(BrO₃)₂	100	−205.	−180.	−162.	218
Zn(BrO₃)₂	1	+12.	+22.	+21.	193
Cd(BrO₃)₂	2	−70.7	−59.0	−36.	159
AgBrO₃	100	−80.3			188
Ni(BrO₃)₂	7	+3.	+11.	+35.	193

The rule works reasonably well, particularly when the Gibbs energy difference is large, the most notable exception being $Cd(BrO_3)_2$. However, it cannot be expected to be exact in predicting the composition of product mixtures since this is frequently affected by kinetic factors which are particularly difficult to analyze for reactions involving solids. In this connection it is of interest to examine the activation energies for the decomposition reactions, as calculated by Bancroft and Gesser [5] from their TGA measurements. They applied a method developed by Horowitz and Metzger [19] which requires that the rate constant obeys an Arrhenius

equation. If the reaction is first-order the resulting expression is

$$\ln\left[\ln\frac{W_0 - W_f}{W - W_f}\right] = \frac{E^*\Theta}{RT_s^2}.$$

where W_0 and W_f are the initial and final weights, respectively, T_s is the temperature at which $[(W - W_f) - (W_0 - W_f)] = 1/e$ and $\Theta = T - T_s$. Most of the bromates obeyed this equation over at least the first half of the decomposition.

For $RbBrO_3$ and $CsBrO_3$ the higher value was obtained with a higher heating rate. In addition, differences in constitutional factors, such as particle size and defects in the crystal structure, may affect E^* in some unknown way [34a]. However, large anomalies are quite apparent for $LiBrO_3$ and $Ca(BrO_3)_2$. It is not known whether this is because the reaction is not first-order, or for some other reason. It is also noticeable that E^* values differ considerably even when salts which decompose only to the bromide are considered. This is true even within the same group in the periodic table, such as alkali metal and alkaline earth bromates, where great differences in mechanism and or bond energies within the BrO_3^- group would not be expected. Clearly, the above table is only an argument for further kinetic studies, particularly isothermal ones.

Perbromates

In contrast to the well-known + 7 oxidation state of chlorine and iodine exhibited by the perchlorates and periodates, attempts to prepare perbromates were, until quite recently, unsuccessful. References to the earlier work are given by Bancroft and Gesser [5].

The synthesis of $HBrO_4$ and of its rubidium and potassium salts has now been accomplished, using the oxidation of bromate by XeF_2 or (preferably) molecular fluorine in aqueous solution [2]. Spectral studies show [3] that the BrO_4^- ion is tetrahedral in both the solid state and in aqueous solution. The thermodynamic properties and thermal decomposition of $KBrO_4$ have been studied and will be discussed in the section on potassium.

A more general article on various properties of the perbromates was recently published by Herrell and Gayer [18].
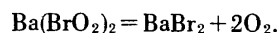
3.1. Barium

$Ba(BrO_2)_2$

This salt has recently been prepared [35] by the thermal decomposition of $Ba(BrO_3)_2$ at 250 °C under an O_2 atmosphere. Decomposition probably proceeds according to

$$Ba(BrO_3)_2 = BaBr_2 + 3O_2,$$

$$2Ba(BrO_3)_2 + BaBr_2 = 3Ba(BrO_2)_2.$$
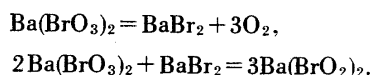
$BaBr_2$ is separated by extraction with anhydrous ethanol.

Above 795° the bromite decomposes rapidly

$$Ba(BrO_2)_2 = BaBr_2 + 2O_2.$$

$Ba(BrO_3)_2$

Two crystalline forms of $Ba(BrO_3)_2$ have been reported [11]. The low temperature form was produced by rapid heating of the monohydrate, whereas isothermal heating of this hydrate between 105 and 120 °C produced the high-temperature form. The transformation I→II was detected by DTA at 160 °C.

Several groups have studied the decomposition of the salt [11, 16]. They all agree that the final product is $BaBr_2$, i.e. the overall reaction is

$$Ba(BrO_3)_2 = BaBr_2 + 3O_2.$$
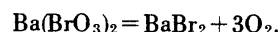
but both $Ba(BrO_2)_2$ (see above) and $Ba(BrO_4)_2$ [16] have been suggested as intermediates, the latter on the basis of a great increase in the rate after one third of the oxygen had disappeared. However, no such inflection was noted by Bancroft and Gesser [5]. Dupuis and Rocchiccioli [11] observed differences in the spectra of $Ba(BrO_3)_2$ heated below and above 159 °C. They argued against the formation of bromite at the higher temperature and hypothesized the existence of two crystalline forms of the bromite. It seems, however, that the work of Tanguy et al. [35] provides firmer evidence for the formation of the bromite as intermediate. The kinetics of the overall decomposition have also recently been measured by Lumme and Lumme [24], using TGA. They find the decomposition occurring in the range 290–380 °C in air, and 265–315 °C in vacuum. The Arrhenius activation energy of 209kJ calculated from these data agrees well with the 218kJ given by Bancroft and Gesser [5].

TABLE 3.2. Properties of Ba-Br salts

Thermodynamic data (298.15K)

	$S°$		
	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	Ref.
$Ba(BrO_2)_2$	—	—	
$Ba(BrO_3)_2$	243.	58.	11b
$BaBr_2$	146.	35.	11b

	$\Delta Hf°$		
	kJ mol^{-1}	kcal mol^{-1}	Ref.
$Ba(BrO_2)_2$	—	—	
$Ba(BrO_3)_2$	−752.66	−179.89	11b
$BaBr_2$	−757.3	−181.0	11b

3.2. Cadmium

$Cd(BrO_3)_2$

The salt can be prepared by step-wise dehydration of the dihydrate. The anhydrous salt is then stable up

to ~ 250 °C, above which it decomposes, largely to the oxide [4, 5].

3.3. Calcium

Ca(BrO₃)₂

$Ca(BrO_3)_2$

Very little work has been done on this salt. It decomposes in the solid state according to

$$Ca(BrO_3)_2 = CaBr_2 + 3O_2,$$

in the temperature range 260–340 °C [5]. As pointed out previously, the high Arrhenius activation energy obtained from TGA seems to be ano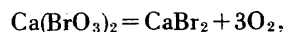malous. A recently reported value of $\Delta Hf^\circ_{238} = -150.7$ kcal [30] is much lower than the NBS-adopted enthalpy.

TABLE 3.3. Properties of Ca-Br salts

Thermodynamic data (298.15 K)

	S°		
	J mol⁻¹ deg⁻¹	cal mol⁻¹	Ref.
Ca(BrO₃)₂	—	—	
CaBr₂	130.	31.	1 lb

	ΔHf°		
	kJ mol⁻¹	kcal mol⁻¹	Ref.
Ca(BrO₃)₂	−718.8	−171.8	1 lb
CaBr₂	−682.8	−163.2	1 lb

3.3. Cesium

CsBrO₃

A specific gravity at 16 °C (d^{16}_{16}) of 4.109 has been reported [7]. Thermal decomposition proceeds to the bromide:

$$CsBrO_3 = CsBr + 3/2O_2.$$

As in the case of RbBrO₃, there is a large discrepancy between the melting point of 420 °C reported by Buell and McCroskey [8] and the beginning temperature for thermal decomposition, 275 °C, reported by Bancroft and Gesser [5]. However, these latter workers worked at very low pressures which favors the decomposition.

3.4. Cobalt

Co(BrO₃)₂

Anhydrous Co(BrO₃)₂ can be prepared by dehydration of the hexahydrate over P₂O₅ at ambient temperature [27]. Heating results in the simultaneous loss of H₂O, Br₂, and O₂, the chief solid product being CoO. No thermodynamic data for the anhydrous salt are available and its thermal decomposition has not yet been studied.

TABLE 3.4. Properties of Cs-Br salts

	Density		
	T (K)	(g cm⁻³)	Ref.
CsBrO₃	293	4.10	15

Thermodynamic data (298.15 K)

	S°		
	J mol⁻¹ deg⁻¹	cal mol⁻¹ deg⁻¹	Ref.
CsBrO₃	162.3	38.8	6
CsBr	121.	29.	1 la

	ΔHf°		
	kJ mol⁻¹	kcal mol⁻¹	Ref.
CsBrO₃	−348.65	−83.33	1 lb
CsBr	−405.7	−96.96	1 lb

3.5. Copper

Cu(BrO₃)₂
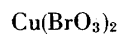
The anhydrous salt has not yet definitely been prepared. The hydrate decomposes at ~ 180 K with the loss of oxygen and possibly bromine, and the formation of Cu₂O and a basic bromate or oxybromide [27].

3.6. Lead

Pb(BrO₃)₂

Very little work has been done on this salt since two people were killed [36] while grinding the material which had been prepared from KBrO₃ and lead acetate—although it was later established that the compound thus formed is diacetatoplumbo · bromate [15]. Pb(BrO₂)₃ · H₂O is reported [I 11] to decompose at ~ 100 °C into PbO₂, PbBr₂, and Br₂. A $\Delta Gf^\circ_{298.15}$ value of − 50.00 kJ is listed by [I 1b].

3.7. Lithium

LiBrO₂

[17]. Preparation of this salt was carried out by heating LiBrO₃ and LiBr between 190 and 220 °C.

$$2LiBrO_3 + LiBr = 3LiBrO_2.$$

The salt is very hygroscopic. At ~ 225 °C it decomposes while melting:

$$LiBrO_2 = LiBr + O_2.$$

LiBrO₃
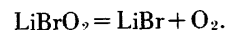
The salt decomposes by two competing reactions [4, 4].

$$LiBrO_3 = LiBr + 3/2O_2. \qquad (1)$$

$$LiBrO_3 = 1/2Li_2O + 1/2Br_2 + 5/4O_2. \qquad (2)$$
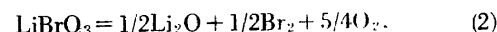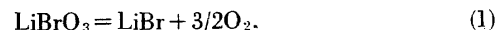
95 percent of the decomposition proceeds by reaction (1). Curiously, the oxide is formed predominantly in the initial stages; it then stops and the major part of the decomposition then goes to LiBr. The products of (2) do net react further so that LiBr cannot be formed by the reaction $1/2Li_2O + 1/2Br_2 = LiBr + 1/4O_2$. The temperature at which decomposition occurs is in doubt. Bancroft and Gesser [4, 5] report it to occur as low as 214 °C, whereas Simmons and Waldeck [32] report the melting point to lie between 248° and 260 °C. The Bancroft and Gesser results were obtained at very low pressures and this may account for the difference.

TABLE 3.5.   Properties of Li-Br salts

	Density		
	$T(K)$	ρ (g cm^{-3})	Ref.
LiBrO$_3$	ambient	3.62 (pyk) 3.76 (X-ray)	9

Thermodynamic data (298.15 K)

	$S°$		
	J deg^{-1} mol^{-1}	cal deg^{-1} mol^{-1}	Ref.
LiBrO$_3$	—	—	
LiBr	74.1	17.7	13
Li$_2$O	37.89	9.056	13

	$\Delta Hf°$		
	kJ mol^{-1}	kcal mol^{-1}	Ref.
LiBrO$_3$	−320.0	−76.49	11b
LiBr	−350.9 ± 0.4	−83.87 ± 0.1	13
Li$_2$O	−598.7	−143.1	13

3.8. Magnesium

Mg(BrO$_3$)$_2$

No thermodynamic data are available. The only thermal decomposition study is that of Bancroft and Gesser [5] who found that the decomposition, beginning near 250 °C, is almost entirely to the oxide,

$$Mg(BrO_3)_2 = MgO + Br_2 + 5/2O_2,$$

with only 5 percent MgBr$_2$ being formed.

3.9. Mercury

HgBrO$_3$

The preparation of this salt is mentioned by Mellor [I 11] and Gmelin [I 9]. Its thermal decomposition apparently leads to formation of metallic mercury, but the decomposition does not seem to have been studied in detail.

Hg(BrO$_3$)$_2$

The anhydrous salt decomposes slightly when heated

to ~ 125 °C and then deflagrates at ~ 155 °C, with HgBr$_2$ as the major product [34].

3.10. Nickel

Ni(BrO$_3$)$_2$

The salt begins to decompose near 160 °C, the product being largely NiO, with some NiBr$_2$ formed as a secondary product [5].

3.11. Potassium

KBrO$_3$

There is some disagreement as to the lowest temperature at which weight loss is observable. Duval [12] and Bancroft and Gesser [5] give this as ~ 370 °C, whereas Jach [20] studied the decomposition kinetics from 342 °C up. The overall decomposition is entirely

$$KBrO_3 = KBr + 3/2O_2$$

Jach found somewhat different kinetics over the ranges 342–367 °C and 379–412 °C, with a transition region in between. Over both ranges the reaction appeared to be first-order, but the Arrhenius activation energies in the low and high regions were 260 kJ (62.2 kcal) and 221 kJ (52.9 kcal), respectively. Over the higher range melting evidently occurred, with the formation of a eutectic at the interface between KBr and KBrO$_3$, and bulk melting near the top end of the range. Over both ranges the reaction begins with rapid nucleation over the entire surface followed by a contracting reaction zone. However, the first-order kinetics do not fit this mechanism and Jach suggests that the extensive cracking of crystals, which is observed during decomposition, is responsible for this. The chemical mechanism of the decomposition has not yet been studied.

KBrO$_4$

The salt was recently prepared by the oxidation of aqueous NaBrO$_3$ with F$_2$ to give HBrO$_4$ and neutralization of the acid with KOH [1, 2]. When heated, it decomposes exothermically at 275–280° to KBrO$_3$ which is stable at this temperature. Thermodynamic properties of the salt and its ions in aqueous solution have been measured [23].

TABLE 3.6.   Properties of K-Br salts

	Density		
	T (K)	ρ (g cm^{-3})	Ref.
KBrO$_3$	290	3.27	15

Thermodynamic data (298.15 K)

	$S°$		
	J deg^{-1} mol^{-1}	cal deg^{-1} mol^{-1}	Ref.
KBrO$_4$	157.3 ± 4.4	37.6 ± 2.0	23
KBrO$_3$	149.1$_6$	35.65	6
KBr	95.94 ± 0.04	22.93 ± 0.01	13

ΔHf°

	kJ mol^{-1}	kcal mol^{-1}	Ref.
KBrO$_4$	-287.6 ± 0.6	-68.74 ± 0.14	23
KBrO$_3$	-333.4	-79.70	11b
KBr	-393.8 ± 0.4	-94.12 ± 0.1	13

3.12. Rare Earths

No work on the anhydrous rare earth bromates seems to have been reported since 1909, when James and Langelier [22] reported their preparation by dehydration of the hydrated salts. Listed below is what little relevant information is provided by these authors.

Nd(BrO$_3$)$_3$

Decomposes with evolution of light and heat above 150 °C.

Pr(BrO$_3$)$_3$

Stable up to 130 °C; decomposes with evolution of light and heat above 150 °C.

Sm(BrO$_3$)$_3$

Decomposes above 150 °C.

La(BrO$_3$)$_3$

Decomposes with evolution of light and heat above 150 °C.

3.13. Rubidium

RbBrO$_3$

A specific gravity value at 16 °C (d_{16}^{16}) of 3.680 has been reported [7]. The salt decomposes entirely to the bromide,

$$RbBrO_3 = RbBr + 3/2O_2,$$

beginning at 360 °C [5]. This value is clearly inconsistent with the melting point of 430 °C reported by Buell and McCroskey [8] for a carefully purified sample. The very low pressures in Bancroft and Gesser's apparatus would favor the decomposition.

TABLE 3.7. Properties of Rb-Br salts

Density			
	T	ρ (g cm^{-3})	Ref.
RbBrO$_3$	ambient	3.68	15

Thermodynamic data (298.15 K)

S°			
	J deg^{-1} mol^{-1}	cal deg^{-1} mol^{-1}	Ref.
RbBrO$_3$	158.6	37.9	6
RbBr	108.3	25.88	6

ΔHf°

	kJ mol^{-1}	kcal mol^{-1}	Ref.
RbBrO$_3$	-340.2_4	-81.32	11b
RbBr	-394.2	-94.22	11b

RbBrO$_4$

The solid salt was briefly isolated in the course of preparing aqueous solutions of it [2]. It seems to have been the first perbromate synthesized chemically.

3.14. Silver

AgBrO$_3$

The salt decomposes according to the reaction

$$AgBrO_3 = AgBr + 3/2O_2.$$
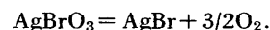
Decomposition starts near 200 °C and is complete near 300° [5]. No high-temperature thermodynamic data are available.

TABLE 3.8. Properties of Ag-Br salts

Density			
	T(K)	ρ (g cm^{-3})	Ref.
AgBrO$_3$	293	5.206	15

Thermodynamic data (298.15 K)

S°			
	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	Ref.
AgBrO$_3$	153.	36.5	11b
AgBr	107.	25.6	11b

ΔHf°

	kJ mol^{-1}	kcal mol^{-1}	Ref.
AgBrO$_3$	$-27.$	-6.5	11b
AgBr	-100.4	-23.99	18b

3.15. Sodium

NaBrO$_3$

The linear thermal expansion coefficient α_l has been measured by Sharma [29] between 36.5 and 285.1 °C, and by Ganesan [84] between $-149°$ and $+171.5$ °C. Although both authors agree well in their results for NaClO$_3$, they disagree considerably on NaBrO$_3$. Near 50 °C both sets of data agree fairly well, but Sharma obtained a much smaller temperature coefficient of α_l. There is no obvious reason for the difference. A comparison is shown graphically in figure 3.5.
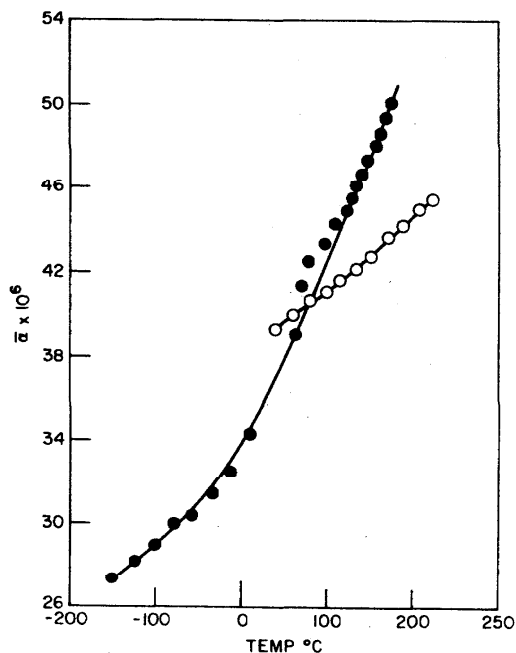
FIGURE 3.5. Linear thermal expansion coefficient of NaBrO₃.
• [14], o [29].

NaBrO₃ decomposes entirely to the bromide

$$NaBrO_3 = NaBr + 3/2O_2.$$

At low pressures the decomposition begins near 320 °C [5]. The decomposition kinetics has been studied by Jach [21] in the range 323–430 °C. Surface nucleation by NaBr is very rapid after which a contracting envelope

TABLE 3.9. Properties of Na-Br salts

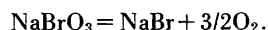| Phase transition			
	Transition	$T(K)$	Ref.
NaBrO₃	c→1	~ 653	13

Density			
	$T(K)$	$\rho(g\ cm^{-3})$	Ref.
NaBrO₃	290	3.339	15

Thermodynamic data (298.15 K)

$S°$			
	J deg⁻¹ mol⁻¹	cal deg⁻¹	Ref.
NaBrO₃	130.5	31.2	6
NaBr	86.82 ± 0.25	20.75 ± 0.06	13

$\Delta H f°$			
	kJ mol⁻¹	kcal mol⁻¹	Ref.
NaBrO₃	− 307.3₆	− 73.46	6
NaBr	− 361.4 ± 0.4	− 86.38 ± 0.10	13

mechanism is followed. An Arrhenius plot exhibits a marked discontinuity at 330 °C. Above this temperature the plot is linear, below it the rate drops abruptly to values much lower than expected from the extrapolation of the high-temperature plot. In the high-temperature region Jach postulates a liquid eutectic region at the NaBr-NaBrO₃ interface. The effect of particle size and dislocations is discussed, but no deatiled mechanism is presented.

3.16. Strontium

Sr(BrO₃)₂

Very little information is available for this salt. No thermodynamic data are listed by [I 1b]. According to the older literature [I 11] decomposition begins near 240 °C and results mainly in the formation of SrBr₂ as well as some SrO. However, the more recent work of Bancroft and Gesser [5] shows that the decomposition is entirely to the bromide,

$$Sr(BrO_3)_2 \rightarrow SrBr_2 + 3O_2,$$
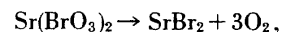
beginning near 265 °C. Similar results were also obtained earlier by Hackspill and Winterer [16].

3.17. Thallium

TlBrO₃

The decomposition kinetics have been studied in considerable detail [33]. The decomposition becomes appreciable near 125 °C and results largely in the formation of black thallic oxide:

$$4TlBrO_3 = 2Tl_2O_3 + 2Br_2 + 3O_2.$$
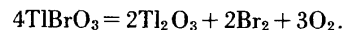
A small amount of TlBr seems to be formed also.

Kinetically, the reaction appears to occur in three stages: (a) an initial phase up to 3–4 percent decomposition which is fitted by the first-order equation

$$\log [p_D/(p_D - p)] = kt,$$

where p_D is the oxygen pressure at the conclusion of the process, followed by a slow constant-area interface reaction ending at ~ 7 percent decomposition. The activation energy for the initial stage is ~ 150 kJ. (b) an acceleration stage fitted by the Prout-Thompkins equation

$$\log [\alpha/(1 - \alpha)] = k_1 t + const.$$

where α is the fraction decomposed at time t. The activation energy for this stage, terminating near 35 percent decomposition, is ~ 209 kJ. (c) the decay stage is well fitted by the contracting sphere model

$$1 - (1 - \alpha)^{1/3} = k_3 t,$$

with an activation energy of ~ 150 kJ. A tentative mechanism proposed to account for these observations identifies the initial phase with rapid decomposition at the subgrain boundaries, followed by progression of the reaction interface into the subgrains.

TABLE 3.10. Properties of Tl-Br Salts

Thermodynamic data (298.15 K)

| | $S°$ | | |
	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	Ref.
TlBrO$_3$	169.	40.3	11b
TlBr	120.	28.8	11b
Tl$_2$O	12$_6$.	30.	11b
Tl$_2$O$_3$	—	—	

| | $\Delta Hf°$ | | |
	kJ mol^{-1}	kcal mol^{-1}	Ref.
TlBrO$_0$	−136.	−32.6	11b
TlBr	−173.	−41.4	11b
Tl$_2$O	−179.	−42.7	11b
Tl$_2$O$_3$	—	—	

3.18. Zinc
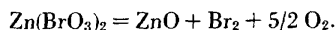
Zn(BrO$_3$)$_2$

No thermodynamic data are available for this salt. Its thermal decomposition was studied by Bancroft and Gesser [5]. Decomposition begins near 150 °C and proceeds nearly entirely to the oxide:

$$Zn(BrO_3)_2 = ZnO + Br_2 + 5/2\ O_2.$$

3.19. References

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4. Iodine

The chief difference between the oxy-anions of iodine and those of chlorine and bromine is the large number of periodates (see below). Otherwise, differences between the respective anions are largely accounted for by the larger size of iodine and its more metallic character.

Iodites

Until recently no anhydrous iodites were known. In 1965 Harmelin and Duval [53] reported a general method for the preparation of iodites: the solid state reduction of iodates by metallic lead. Since the reaction occurred without loss of weight it was postulated to occur according to

$$MIO_3 + Pb = MIO_2 + PbO.$$
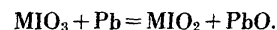
The iodites of Na, K, Ca, Ba, and Pb were prepared in this way at 420–425 °C and the existence of IO_2^- determined from its infrared spectrum. However, the pure compounds were not isolated and no further synthetic work seems to have been done since 1965. Since no further information is available, these compounds are not described under the respective elements.

Iodates

The iodates all contain the pyramidal IO_3^- ion in which the iodine atom is bonded covalently to the three oxygens (fig. 4.1). As shown in figure 4.2 all the alkali metals (except Fr) and alkaline earths (except Be) form anhydrous iodates. Beryllium salts are frequently difficult to obtain in the anhydrous state because of the high charge density of Be^{2+}. Dasent and Waddington [29] have studied the infrared spectra of several iodates. They distinguish between ionic iodates in which the crystals contain discrete, pyramidal IO_3^- groups, e.g. NaIO$_3$, and iodate compounds (-O-IO$_2^-$) in which the metal ion is bonded covalently to oxygen. Examples of the latter type are Pb(IO$_3$)$_2$, and both mercuric and mercurous iodate.

IO_3^-
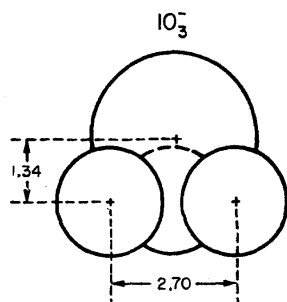
FIGURE 4.1.   Structure of the Io-
date (IO_5^-) ion. [104]

In general, iodates are thermally rather stable. Many of them can be heated to several hundred °C without appreciable decomposition. When they do decompose it is frequently in the solid state or on melting. Thus there are virtually no properties of liquid iodates known. The decomposition reactions fall into three groups:

(a) Iodates of the alkali metals (except lithium), Ag, Co, and probably both Hg(I) and Hg(II) decompose according to

$$IO_3^- \rightarrow I^- + 3/2O_2.$$
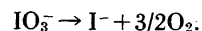
(b) Iodates of Cd, Cu, Zn, Ni, and probably Mg, Tl(I) and Pb go to the oxide

$$4IO_3^- \rightarrow 2O^{2-} + I_2 + 5O_2.$$

Lanthanides   Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

Actinides   Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lw

FIGURE 4.2.   The known iodates. Shaded, existence known. Half-shaded, existence uncertain. No shading, existence unknown.

In addition, iodates of Na and K appear to go partly by this route.

(c) Iodates of Li, Ca, Ba, Sr, and the rare earths form the orthoperiodate:

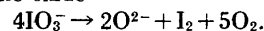$$5IO_3^- \rightarrow IO_6^{5-} + 9/2O_2 + 2I_2.$$
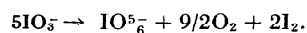
Reactions of type (a) for Na, K, Rb, and Cs can attain equilibrium and equilibrium constants were calculated. Calculations are in good agreement with experimentally determined values. No calculations could be carried out for type (b) reactions. Only for Mg ($IO_3)_2$ have enthalpy increments above 298 K been measured, but in this case S°_{298} is not known. There are no experimental equilibrium studies. For reactions of type (c) only the calculation for Ca could be done. Those for Li, Ba, and Sr lack S°_{298} values for the periodates.

Periodates

The number of iodine-containing acids and salts in which the formal valence of iodine is + 7 is far greater than that for the corresponding chlorine and bromine compounds. This behavior is generally consistent with the increasing metallic character of the heavier elements in a particular group.

Although various authors do not agree in all details on the number of periodic acids and periodates which

exist, and on their nomenclature, we list for the conveni-

TABLE 4.1.   Classification of the periodates

Periodic Acids			
As hydrates of I_2O_7	Acid	As hydrates of HIO_4	Prefix
$I_2O_7 \cdot H_2O$	HIO_4	HIO_4	meta-
$I_2O_7 \cdot 2H_2O$	$H_4I_2O_9$	$2HIO_4 \cdot H_2O$	di-, meso-
$3I_2O_7 \cdot 7H_2O$	$H_7I_3O_{14}$	—	tri-
$I_2O_7 \cdot 4H_2O$	$H_6I_2O_{11}$	$2HIO_4 \cdot 3H_2O$	diortho-
$I_2O_7 \cdot 5H_2O$	H_5IO_6	$HIO_4 \cdot 2H_2O$	ortho-

Periodates		
Salts[a]	As $M_2O \cdot I_2O_7$	Prefix
$MIO_4(M_2I_2O_8)$	$M_2O \cdot I_2O_7$	meta-
$M_4I_2O_9$	$2M_2O \cdot I_2O_7$	dimeso-, pyro-
M_3IO_5	$3M_2O \cdot I_2O_7$	meso-
M_2HIO_5		
$M_6I_2O_{11}$	$4M_2O \cdot I_2O_7$	diortho-
M_5IO_6	$5M_2O \cdot I_2O_7$	ortho-
$M_3H_2IO_6$		
$M_2H_3IO_6$		

[a] Formulas written for a monovalent cation.

ence of the reader the acids and salts which are generally recognized. In this monograph only those salts with a single cation are discussed, those in which one or more metal cations are replaced by hydrogen are omitted.

Structural information on the solid periodates is rather scarce. The IO_4^- ion is known to be tetrahedral [24, 95] and IO_6^{5-} is octahedral [54, 95]. The I-O bonding in these ions has been described [95], but the cation-anion bonding has not been studied. Of the other periodates, only the structure of $K_4I_2O_9$ has been studied. The oxygen-bridged structure of the anion is described under "potassium".

																	H	He
Li	Be												B	C	N	O	F	Ne
Na	Mg												Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

Lanthanides   Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

Actinides   Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lw

FIGURE 4.3. The known meta-periodates. Shaded, existence known. Half-shaded, existence uncertain. No shading, existence unknown.

																	H	He
Li	Be												B	C	N	O	F	Ne
Na	Mg												Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

Lanthanides   Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

Actinides   Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lw

FIGURE 4.4. The known meso-periodates. Shaded, existence known. Half-shaded, existence uncertain. No shading, existence unknown.

																	H	He
Li	Be												B	C	N	O	F	Ne
Na	Mg												Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

Lanthanides   Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

Actinides   Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lw

FIGURE 4.5. The known ortho-periodates. Shaded, existence known. Half-shaded, existence uncertain. No shading, existence unknown.

																	H	He
Li	Be												B	C	N	O	F	Ne
Na	Mg												Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

Lanthanides   Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

Actinides   Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lw

FIGURE 4.6. The known pyro-periodates. Shaded, existence known. Half-shaded, existence uncertain. No shading, existence unknown.

In figures 4.3–4.6 the known anhydrous periodates have been listed. It is obvious that the orthoperiodates are the most common, if the rare earths are excluded, otherwise meso-periodates are. It is likely, however, that the figures merely reflect work that has been done, rather than some limitations on the periodates that could exist. There are undoubtedly many more periodates that could be synthesized.

The various periodates decompose according to several different schemes, generally in the solid state; only the meta-periodates seem to have a melting point.
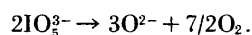
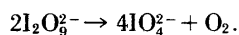(a) The meta-periodates of Na, K, Rb, and Mg decompose to the iodate:

$$IO_4^- \rightarrow IO_3^- + 1/2O_2.$$
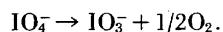
(b) The ortho-periodates of Li, Na, Ca, Sr, and Ba go to the oxide:

$$2IO_6^{5-} = 5O^{2-} + I_2 + 7/2O_2.$$
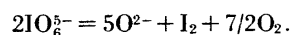
(c) Decomposition of the meso-periodates has not been studied except for the rare earths and Y:

$$2IO_5^{3-} \rightarrow 3O^{2-} + 7/2O_2.$$

(d) Of the pyro-periodates only the cadmium salt has been studied:
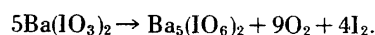
$$2I_2O_9^{2-} \rightarrow 4IO_4^{2-} + O_2.$$

In this reaction a salt of hexavalent iodine is formed. Very little work on salts containing the IO_4^{2-} ion has been reported yet. The decomposition of the diorthosalt has not yet been studied.

4.1. Barium

$Ba(IO_3)_2$

The salt is stable up to ~ 580 °C [40, 81, 102]. Above this temperature it undergoes the Rammelsberg reaction

$$5Ba(IO_3)_2 \rightarrow Ba_5(IO_6)_2 + 9O_2 + 4I_2.$$

The gef for the iodate was calculated from the 298.15 K values in [17b] and the enthalpy increments determined calorimetrically by [30]. Unfortunately, equi-

librium constants for the above reaction cannot be calculated because no $S^\circ_{298.15}$ value is available for the barium paraperiodate.

$Ba_5(IO_6)_2$

This salt is stable to ~ 950 °C [40, 48, 102]. Above this temperature it decomposes according to

$$Ba_5(IO_6)_2 = 5BaO + I_2 + 7/2O_2.$$
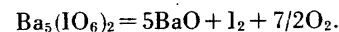
This reaction is reversible [48]. The temperature at which decomposition occurs therefore depends on the gas phase. For example, under vacuum, decomposition becomes noticeable as low as ~ 500°. The lack of $S^\circ_{298.15}$ values for this salt prevents any equilibrium calculations for the above reaction, as well as the gef calculation for the paraperiodate. The $H_T - H_{298.15}$ and $S_T - H_{298.15}$ values are based on the calorimetric enthalpy increments of David, Mathurin, and Thevenot [30].

TABLE 4.2. Properties of Ba-I salts

Density			
	T (K)	ρ (g cm^{-3})	Ref.
$Ba(IO_3)_2$	293	5.2$_3$	15

Thermodynamic data (298.15 K)

S°			
	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	Ref.
$Ba(IO_3)_2$	249.$_4$	59.6	11b
$Ba_5(IO_6)_2$	—	—	
BaO	70.42	16.83	11b

ΔHf°			
	kJ mol^{-1}	kcal mol^{-1}	Ref.
$Ba(IO_3)_2$	− 1027.	− 245.5	11b
$Ba_5(IO_6)_2$	− 3952.	− 944.7	11
BaO	− 553.5	− 132.3	11b

High-temperature thermodynamic data

T(K)	Ba(IO₃)₂ gef J deg⁻¹	BaO gef J deg⁻¹	Ba₅(IO₆)₂ $H_T - H_{298}$ J	Ba₅(IO₆)₂ $S_T - S_{298}$ J deg⁻¹
298	− 249.4	− 70.3	0	0
400	− 256.7	− 72.1	42873	123.38
500	− 271.8	− 75.8	90523	229.56
600	− 289.4	− 79.9	140746	321.11
700		− 84.2	190615	398.05
800		− 88.4	237212	460.37

4.2. Bismuth

Although the existence of Bi(IO₃)₃ has been reported [56, 75], the preparation of the pure anhydrous compound has probably not yet been accomplished.

4.3. Cadmium

Cd(IO₃)₂

The salt is stable up to ~ 560 °C. Above this temperature it decomposes according to [102]

$$2Cd(IO_3)_2 = 2CdO + I_2 + 5O_2.$$

A $\Delta Gf°$ value of 90.13 kcal (377.1 kJ) value has been reported [I 1b].

Cd₃(IO₅)₂

Varhely and Kekedy [103] report this salt to form when its monohydrate loses water at ~ 210°. It is then stable to near 525°. Above this temperature it decomposes to the oxide.

Cd₅(IO₆)₂

Preparation of this compound has been reported [75], but its properties have not yet been determined.

Cd₂I₂O₉

The anhydrous compound has been prepared and its thermal decomposition studied [77]. At temperatures as low at 110° the decomposition leads to the formation of hexavalent cadmium iodate

$$2Cd_2I_2O_9 = 4CdIO_4 + O_2.$$
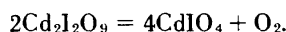
At a higher temperature the latter decomposes to the oxide.

TABLE 4.3. Properties of Cd-I salts

|	Density		
	T(K)	ρ(g cm⁻³)	Ref.
Cd(IO₃)₂	293	6.48	I 5

4.4. Calcium

Ca(IO₃)₂, Ca₅(IO₆)₂

Thermodynamic data: $\Delta Hf°_{298.15}$ values of Ca(IO₃)₂ and Ca₅(IO₆)₂ are taken from [1 1b]. The value for the latter salt differs considerably from others reported

−954.9 [11] and −928 kcal [8]. The recently published $S°_{298}$ value of 55 cal mol⁻¹ deg⁻¹ for Ca(IO₃)₂ [1 1b] is more in line with those for other alkaline earth salts and differs enormously from a previously calculated value of 34.79 [20], gef values for the two salts were calculated from published heat capacity values [7].

Decomposition: It is generally agreed [19, 82] that the decomposition of Ca(IO₃)₂ occurs in two successive steps:

$$5Ca(IO_3)_2 \rightarrow Ca_5(IO_6)_2 + 4I_2 + 9O_2 \qquad (a)$$

$$Ca_5(IO_6)_2 \rightarrow 5CaO + I_2 + 7/2O_2. \qquad (b)$$
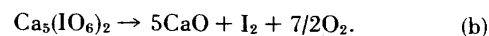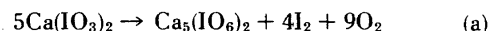
Since both reactions produce gaseous products the stability range would be expected to vary with gas phase pressure and composition. Reaction (a) appears to begin at about 550 °C and to be complete near 770° [82]. However, the reaction seems to be reversible and, according to [19] is the sum of the reactions

$$5Ca(IO_3)_2 = 5CaI_2 + 15O_2,$$

$$5CaI_2 + 5/2O_2 = 5CaO + 5I_2,$$

$$5CaO = I_2 + 7/2O_2 + Ca_5(IO_6)_2.$$
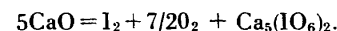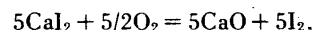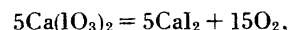
Thus, in vacuum, heating of Ca(IO₃)₂ would produce CaI₂. In air the first reaction is not displaced appreciably to the right below 510° [8]. For this reason the calculation of the equilibrium constant for reaction (a) is somewhat misleading since it suggests appreciable decomposition of Ca(IO₃)₂ in air above 325°. However, the equilibrium can probably not be established unless some CaI₂ is formed. Similarly, Ca₅(IO₆)₂ seems to be stable to a somewhat higher temperature, probably at least 725°, than indicated by the calculation for reaction (b), but the reasons for this are not clear.

CaI₂O₉

This salt has been reported [102] as an intermediate in the dehydration of its 9-hydrate and to be stable to ~ 550 °C. Above this temperature it decomposes according to

$$5CaI_2O_9 = 2Ca_5(IO_6)_2 + 3I_2 + 2\tfrac{1}{2}O_2.$$
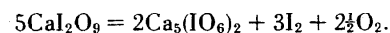
However, the pure anhydrous salt seems not to have been isolated yet.

TABLE 4.4. Properties of Ca-I salts
Thermodynamic data (298.15 K)

	S° J mol⁻¹ deg⁻¹	S° cal mol⁻¹ deg⁻¹	Ref.
Ca(IO₃)₂	230.	55.	1 1b
Ca₅(IO₆)₂	453.6	108.4	20
CaO	39.7	9.50	1 1b
CaI₂	142.	34.	1 1b

$\Delta Hf°$

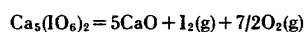|	kJ mol⁻¹	kcal mol⁻¹	Ref.
Ca(IO₃)₂	−1002.₅	−239.6	11b
Ca₅(IO₆)₂	−3826.	−915.	11b
CaO	−635.09	−151.79	11b
CaI₂	−433.5	−127.5	11b

4.5. Cesium

CsIO₃

The ambient temperature density of $CsIO_3$ is uncertain. Pyknometrically determined values listed by [9] vary from 4.83 to 4.94 g cm⁻³, compared to 4.99 calculated from x-ray data. This suggests crystals with varying void content were used. Decomposition occurs on melting with oxygen evolution [23, 105].

$$CsIO_3 \rightarrow CsI + 3/2O_2.$$

Decomposition of Ca₅(IO₆)₂

$$Ca_5(IO_6)_2 = 5CaO + I_2(g) + 7/2O_2(g)$$

$$\Delta H°_{298.15} = 156.05 \text{ kcal, } 652.91 \text{ kJ}$$

T K	Δgef J deg⁻¹	ΔG°/T J deg⁻¹	log K	K	P_O₂ atm	P_I₂ atm	P_TOT atm
298.15	−723.2	1466.7	−76.611	2.450×10⁻⁷⁷	1.25×10⁻¹⁷	3.57×10⁻¹⁸	1.61×10⁻¹⁷
400	−721.7	910.6	47.564	2.732×10⁻⁴⁸	3.56×10⁻¹¹	1.02×10⁻¹¹	4.58×10⁻¹¹
500	−716.9₅	588.9	−30.759	1.740×10⁻³¹	1.93×10⁻⁷	5.51×10⁻⁸	2.48×10⁻⁷
600	−711.2₅	376.9	−19.689	2.047×10⁻²⁰	5.57×10⁻⁵	1.59×10⁻⁵	7.16×10⁻⁵
700	−706.4₅	226.3	−11.820	1.515×10⁻¹²	3.12×10⁻³	8.91×10⁻⁴	4.01×10⁻³
800	−702.0₅	114.1	−5.959	1.098×10⁻⁶	6.26×10⁻²	1.79×10⁻²	8.05×10⁻²
900	−696.9	28.6	−1.492	3.224×10⁻²	0.616	0.176	0.792
1000	−692.7₅	−39.8	+2.081	120.5	3.83	1.09	4.92

Decomposition of Ca(IO₃)₂

$$5Ca(IO_3)_2 = Ca_5(IO_6)_2 + 4I_2(g) + 9O_2(g)$$
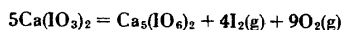
$$\Delta H°_{298.15} = 342.69 \text{ kcal, } 1433.82 \text{ kJ}$$

T K	Ca(IO₃)₂ gef J mol⁻¹ deg⁻¹	Ca₅(IO₆)₂ gef J mol⁻¹ deg⁻¹	CaO gef J mol⁻¹ deg⁻¹	Δgef J deg⁻¹	ΔG°/T	log K	K	P_O₂ atm	P_I₂ atm	P_TOT atm
298.15	−230.1	−453.4	−39.7	−2190	2619	−136.808	1.56×10⁻¹³⁷	4.84×10⁻¹¹	2.15×10⁻¹¹	6.99×10⁻¹¹
400	−237.3₅	−469.5	−41.5	−2187	1398	−73.027	9.40×10⁻⁷⁴	3.10×10⁻⁶	1.38×10⁻⁶	4.48×10⁻⁶
500	−251.3	−501.7₅	−44.9	−2180	687.₆	−35.918	1.21×10⁻³⁶	2.21×10⁻³	0.98×10⁻³	3.19×10⁻³
600	−267.0	−538.3	−48.7	−2173	216.₇	−11.320	4.79×10⁻¹²	1.73×10⁻¹	7.69×10⁻²	2.50×10⁻¹
700	−282.7	−575.3	−52.7	−2167	−118.₇	6.200	1.59×10⁶	3.85	1.71	5.56
800	−297.9	−611.3	−56.6	−2162	−369.₇	19.312	2.05×10¹⁹	39.3	17.5	56.8
900		−645.9	−60.3							
1000		−678.9	−63.8₅							

In order to calculate the equilibrium constant for this reaction, $S°_{298.15}$ of $CsIO_3$ was estimated and enthalpy and entropy increments were calculated from the calorimetric data of [15]. The corresponding increments for CsI were obtained from the estimated Cp values of Kelley [55a]. The resulting equilibrium constants indicate decomposition well below the melting point, but the rate in the solid state may be too slow to be detectable. Bousquet and Remy [17] have calculated the equilibrium pressure of O_2 using thermodynamic values which differ only a little from those used here. They also measured P_{O_2} by both a static and a dynamic method between 533 and 740 K and obtained good agreement with their own calculation. In the static method 45 to 320 days were required to reach equilibrium. Their values of log K are approximately 0.5 more negative than those listed here over the entire temperature range. Most of this difference is accounted for by the slightly different $S°_{298.15}$ values for $CsIO_3$ and CsI (40.5 and 30 cal deg⁻¹, respectively) selected by Bousquet and Remy. In view of

the agreement between their values and experiment these entropies may be preferable.

$CsIO_3$ and CsI form a eutectic at 781 K. Above this temperature decomposition leads to the formation of a liquid phase but P_{O_2} will remain independent of composition as long as solid phase is present.

$CsIO_4$

The salt exists in three crystalline modifications [2]. The forms II and III probably are tetragonal and orthorhombic, respectively. The structure of I is less certain. The transformation I→ II exhibits a large hysteresis. The transformation listed was obtained with rising temperature. On decreasing the temperature it occurs ~ 30° lower. The density of what is probably II is ~ 4.25 g cm^{-3} [19]. Decomposition is reported [23] to go to the iodate near 500°

$$CsIO_4 \rightarrow CsIO_3 + 1/2O_2$$
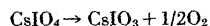
but no quantitative data on the reaction are available.

$Cs_4I_2O_9$

Preparation of this salt was recently reported [59], but its properties have not yet been measured.

$Cs_2I_4O_{11}$

The preparation of this salt was reported a long time ago [106]. When heated in a closed tube it first evolves I_2 and then melts with the evolution of I_2 and O_2. The residue is CsI.

TABLE 4.5.   Properties of Cs-I salts

Density			
	$T(K)$	ρ (g cm^{-3})	Ref.
$CsIO_3$	293	4.937	87
$CsIO_4$	288	4.259	4

Phase transitions					
		$T(K)$	ΔH(kJ)	ΔS(J deg^{-1})	Ref.
$CsIO_3$	$c \rightarrow l$	838	13	15.5	18
$CsIO_4$	I→ II	288±3	1.6±0.1		2
	II→ III	423	0.7±0.1		2

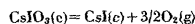| Thermodynamic data (298.15 K)			
$S°$			
	J deg^{-1} mol^{-1}	cal mol^{-1} deg^{-1}	Ref.
$CsIO_3$	16$_7$.	40.	est.
$CsIO_4$	—	—	
CsI	13$_0$.	31.	IIa

$\Delta Hf°$			
	kJ mol^{-1}	cal mol^{-1}	Ref.
$CsIO_3$	−525.946	−125.704	15
$CsIO_4$	—	—	
CsI	−348.1$_5$	−83.21	IIb

Decomposition of $CsIO_3$

$$CsIO_3(c) = CsI(c) + 3/2O_2(g)$$

$$\Delta H°_{298.15} = 177.796 \text{ kJ, } 42.494 \text{ kcal}$$

T K	$CsIO_3$ gef J deg^{-1}	CsI gef J deg^{-1}	Δgef J deg^{-1}	$\Delta G°/T$	$\log K$	K	P_{O_2} atm
298.15	−167.0	−130.0	−270.55	325.78	−17.017	9.62×10^{-18}	4.52×10^{-12}
400	−168.0	−130.5	−271.80	172.69	−9.021	9.53×10^{-10}	9.68×10^{-7}
500	−170.0	−131.4	−274.02	81.57	−4.261	5.49×10^{-5}	1.44×10^{-3}
600	−172.3	−132.5	−276.60	19.73	−1.031	9.32×10^{-2}	2.05×10^{-1}
700	−174.5	−133.5	−279.25	−25.26	+1.319	20.8	7.57

4.6. Cobalt

$Co(IO_3)_2$

The blue-violet salt appears to be stable at least to 220 °C [39a] but decomposes in the range 415–425° to give Co_3O_4 [81, 102] according to the reaction

$$3Co(IO_3)_2 \rightarrow Co_3O_4 + 3I_2 + 7O_2.$$
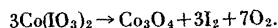
A $\Delta Hf°_{298.15}$ value of −124.3 kcal (−520.1 kJ) is listed in [I Ia], but this has been dropped from the revision [I Ib].

TABLE 4.6.   Properties of Co-I salts

Density			
	$T(K)$	ρ (g cm^{-3})	Ref.
$Co(IO_3)_2$	298	4.931	66

4.7. Copper

$Cu(IO_3)_2$

This salt appears to be stable up to ~ 440 °C [39a]

but above that temperature decomposes to the oxide [65, 81]

$$Cu(IO_3)_2 \rightarrow CuO + I_2 + 5/2O_2.$$

An activation energy of 325 kJ has been reported for this reaction in air from TGA data [65]. $\Delta Hf^\circ_{298.15}$ has been calculated, using heats of solution data [49]. When the newer data in [I 1b] are used this value shifts from -92.7 to -93.1 kcal mol^{-1}.

TABLE 4.7. Properties of Cu-I salts

Density			
	$T(K)$	$\rho(g\ cm^{-3})$	Ref.
Cu(IO$_3$)$_2$	298	4.89	67

Thermodynamic data (298.15 K)

S°			
	J deg^{-1} mol^1	cal deg^{-1} Mol^{-1}	Ref.
Cu(IO$_3$)$_2$	21$_8$.	52 est	49
CuO	42.64	10.19	I 1b

ΔHf°			
	kJ mol^{-1}	kcal mol^{-1}	Ref.
Cu(IO$_3$)$_2$	$-389._5$	-93.1	49
CuO	$-157._{32}$	-37.6	I 1b

4.8. Indium

In(IO$_3$)$_3$

The anhydrous crystalline white salt was first prepared by Mathers and Schluederberg [69], and the existence of the compound confirmed [44]. On heating, the crystals turn brown and give off iodine vapor [69]. No other properties of this salt seem to have been reported.

InIO$_5$

The preparation of the yellowish crystalline compound was reported by Ensslin [44], but none of its properties have been examined.

4.9. Iron

Fe(IO$_3$)$_3$

Preparation of the anhydrous salt was reported by Endredy [43]. It is stable in air up to 130 °C. Above that temperature it decomposes with the evolution of molecular iodine. The final product is Fe$_2$O$_3$.

Unambiguous preparations of anhydrous periodates are very scarce. The following have been reported. In each case the chemical analysis fits the stoichiometry quite well.

Fe$_5$(IO$_6$)$_2$

Reported by Kimmins [57] to be a brick-red crystalline salt, the iron content was slightly below the theoretical value.

Fe(IO$_4$)$_3$

Preparation is reported both by Kimmins [57] and Von Endredy [43]. The yellow salt can be heated in dry air up to 125 °C. Above this temperature it turns first brown and then black, while I$_2$ is evolved. The residue is Fe$_2$O$_3$.

Fe$_5$(IO$_6$)$_3$

The preparation of the salt has been reported [93], but its properties have not yet been studied.

4.10. Lead

Pb(IO$_3$)$_2$

The salt is stable up to 400 °C. Above this temperature it decomposes with the evolution of I$_2$ and O$_2$ [39].

Pb(IO$_3$)$_4$

The anhydrous salt was prepared by dehydration of its dihydrate between 100 and 120 °C [87] but no further work seems to have been reported.

Pb(IO$_4$)$_2$

The preparation of the salt in a slightly impure state has been described by Kimmins [57].

Pb$_3$(IO$_5$)$_2$

The preparation of this salt was described by Willard and Thompson [108]. Decomposition begins in the range 430–450 °C. Näsänen and Uggla [74] report an intermediate 8PbO · PbI$_2$, whereas Varhely and Kekedy [102] show only a plateau on their TGA curve corresponding to PbO.

TABLE 4.7. Properties of Pb-I salts

Thermodynamic data (298.15 K)

S°			
	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	Ref.
Pb(IO$_3$)$_2$	313.	74.8	I 1b

ΔHf°			
	kJ mol^{-1}	kcal mol^{-1}	Ref.
Pb(IO$_3$)$_2$	-495.4	-118.4	I 1b

Density			
	$\rho(g\ cm^{-3})$	$T(K)$	Ref.
Pb(IO$_3$)$_2$	6.50	ambient	101

4.11. Lithium

LiIO₃

The salt exists in two crystalline modifications [62, 91, 103]. Vaporization of an aqueous solution below ~ 60 °C yields hexagonal crystals, above 90° it yields the tetragonal form; in between it yields both. At 260 °C the hexagonal form transforms to the tetragonal with a volume change of 3.2 cm³ mol⁻¹. The latter decomposes on melting. The decomposition has been studied by Bousquet and David [9]. The overall process is the formation of the paraperiodate

$$5LiIO_3 \rightarrow Li_5IO_6 \pm 2I_2 + 9/2O_2, \qquad (1)$$
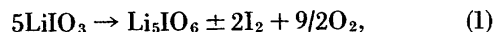
analogous to the reactions of the alkaline earth iodates. The reaction proceeds a little faster in O_2 than in N_2 atmosphere. The authors, on the basis of numerous subsidiary experiment propose the following mechanism to account for the overall reaction (1):

$$LiIO_3 \rightleftarrows LiI + 3/2O_2 \qquad (I)$$

$$2LiI + 1/2O_2 \rightarrow Li_2O + I_2 \qquad (II)$$

$$6Li_2O + 4I_2 \rightarrow Li_5IO_6 + 7LiI \qquad (IIIa)$$

$$5Li_2O + I_2 + 7/2O_2 \rightarrow 2Li_5IO_6 \qquad (IIIb)$$

$$2LiIO_3 + 3LiI \rightarrow Li_5IO_6 + 2I_2 \qquad (IV)$$

with I and IV constituting the major steps.

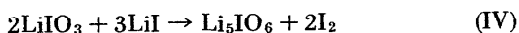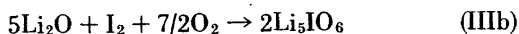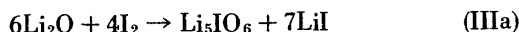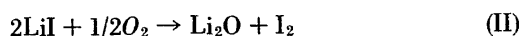Enthalpy increments of $LiIO_3$ and Li_5IO_6 have been measured [10] up to 623 and 867 K, respectively. The experimental values were used to generate $H_T - H_{298.15}$ and $S_T - S_{298.15}$ values for the two salts. Since entropy data are lacking it was not possible to calculate equilibrium constants for the decomposition reactions.

Li₂IO₄

This unusual compound, in which the valence state of iodine is +6, between iodate (+5) and periodate (+7) results from the thermal decomposition of $Li_2H_3IO_6$ [33]. Detailed X-ray, infrared, and magnetic susceptibility measurements were used to establish the chemical individuality of the salt. The salt is stable to ~ 450 °C.

Li₅IO₆

The salt sublimes at 730 °C. At 850° it decomposes by the reaction [91, 51]

$$2Li_5IO_6 = 5Li_2O + I_2 + 7/2O_2.$$

TABLE 4.8. Properties of Li-I salts

	Density		
	T(K)	ρ(g cm⁻³)	Ref.
LiIO₃	305	4.502	87

Phase transitions

		T (K)	ΔH (kJ)	ΔS (J deg⁻¹)	Ref.
LiIO₃	(hexagonal→ tetragonal)	533±5	2.2	4.2	62
LiIO₃	(tetragonal)→ l	723			9

Thermodynamic data (298.15 K)

$S°$

	J deg⁻¹ mol⁻¹	cal deg⁻¹ mol⁻¹	Ref.
LiIO₃	—	—	
Li₂IO₄	—	—	
Li₅IO₆	—	—	
Li₂O	37.89	9.056	I 3
LiI	—	—	

$\Delta Hf°$

	kJ mol⁻¹	kcal mol⁻¹	Ref.
LiIO₃	−511.91	−122.35	94
Li₂IO₄	—	—	
Li₅IO₆	−2044. ±6	−488.5 ± 1.5	11
Li₂O	−598.7	−143.1	I 3
LiI	−272.1	−65.03	I 1b

Enthalpy and entropy increments of LiIO₃ and Li₅IO₆

T (K)	LiIO₃		Li₅IO₆	
	$H_T - H_{298.15}$ J mol⁻¹	$S_T - S_{298.15}$ J deg⁻¹ mol⁻¹	$H_T - H_{298.15}$ J mol⁻¹	$S_T - S_{298.15}$ J deg⁻¹ mol⁻¹
400	10,982	31.541	25,761	74.077
500	22,943	58.182	51,016	130.430
600	36,086	82.112	76,270	176.475
700			105,709	215.405
800			126,779	249.128

4.12. Magnesium

Mg(IO₃)₂

The value of $\Delta Hf°_{298.15} = - 905.0 \pm 6.7$ kJ mol⁻¹ (−216.3 ± 1.6 kcal mol⁻¹) calculated by [11] seems somewhat low, but no other value has been reported. $S°_{298.15}$ is not available. Enthalpy increments for this salt have been measured calorimetrically up to 827 K [14]. These were used to generate enthalpy and entropy increments at 100° intervals. According to [103], the anhydrous salt, prepared by dehydrating the 4-hydrate, is stable up to ~ 575 °C. Above this temperature it decomposes to the oxide.

Mg(IO₄)₂

This salt is reported as an intermediate in the decomposition of its 8-hydrate [35], stable up to ~ 525 °C. Above this temperature decomposition to $Mg(IO_3)_2$ occurs.

$Mg_2I_2O_9$

This salt is probably not stable in the anhydrous state. Varhely and Kekedy [102] report the dehydration of a 12-hydrate, but their TGA curve is not horizontal and MgO is formed gradually. A more careful examination by Dratovský and Kóslerová [35] indicates the starting material to be the 13-hydrate. Heating leads to the successive formation of the 2.5-hydrate, $MgIO_4 \cdot 1/2H_2O$, and MgO.

TABLE 4.9. Properties of Mg-I salts

Enthalpy and entropy increments of $Mg(IO_3)_2(c)$

T K	$H_T - H_{298.15}$ J mol^{-1}	$S_T - S_{298.15}$ J deg^{-1} mol^{-1}
400	21,840	63.191
500	53,961	110.984
600	64,668	150.033
700	86,082	183.049
800	107,495	211.648

4.13. Manganese

$Mn(IO_3)_2$

Minovici and Kollo [72] report that the salt is stable up to 200 °C, but according to Duval [38a] it increases up to 2 percent in weight on being heated to 340° due to uptake of oxygen. Apparently the iodate is partly transformed to the periodate on heating. Decomposition of both salts is complete at 875°, the only solid phase remaining is Mn_3O_4. However, other oxides (MnO, MnO_2) have also been reported as products in the range 555–835° [102]. The oxide formed is expected to depend on the partial pressure of O_2 in the system.

$Mn_3(IO_5)_2$

Preparation of this material has been reported [89]. The pink crystals decomposed above 12 °C. Since the product was stated to be manganese hydroxide there is some question as to whether the salt was really anhydrous.

4.14. Mercury

Several iodates and periodates of both Hg(I) and Hg(II) have been known for a long time. The older literature is summarized by [I 9] and [I 11]. However, very little work has been done on these compounds during the last fifty years. No thermodynamic data are listed by [I 1b]. A brief summary relating to thermal decomposition is given below.

$Hg_2(IO_3)_2$

The salt is stable up to $\sim 175°$. Above 500 K decomposition results in the formation of HgI_2, which sublimes [102].

$Hg(IO_3)_2$

Heating results in the formation of HgI_2 and O_2 [I 9].

$Hg_2(IO_4)_2$

The salt is stable up to ~ 100 °C. Decomposition begins near 130° and is complete at 200° [I 9].

$Hg_5(IO_6)_2$

The salt can be heated at least to 100 °C without weight loss [107]. There is some disagreement concerning stability above this temperature. Duval [38a] finds continuous weight loss above 200°, whereas Varhely and Kekedy [102], also using TGA, find no weight loss up to 500°. The decomposition reactions have not been studied in detail, but Hg_2I_2, HgI_2, HgO, and Hg have been reported as products [I 9].

Hg_4I_2O

Preparation of this salt has been reported [92, 97]. Its mode of decomposition is not known, but is probably similar to that of the other mercury periodates.

4.15. Nickel

$Ni(IO_3)_2$

This salt may exist in two modifications: green and yellow. The latter appears to be the form reported by Meusser [71]. Martinez-Cros and Le Boucher [67] report distinctly different densities for the two forms. Pechkovskii and Sofronova [81] find from DTA and TGA that the salt is stable up to 487°C and decomposes above this temperature by the reaction

$$Ni(IO_3)_2 = NiO + O_2 + 5/2O_2.$$
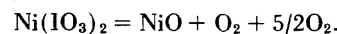
$Ni_3(IO_5)_2$

The preparation of a greenish-yellow amorphous salt of this composition was described by Kimmins [57].

$Ni_2I_2O_4$

The black crystalline salt is stable to at least 100°C [57].

TABLE 4.10. Properties of Ni-I salts

Thermodynamic data (298.15 K)

	$S°$		
	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	Ref.
$Ni(IO_3)_2$	213.	51	I 1b
NiO	38.0	9.08	I 1b

	$\Delta Hf°$		
	kJ mol^{-1}	kcal mol^{-1}	Ref.
$Ni(IO_3)_2$	−489.1	−116.9	I 1b
NiO	−239.7	−57.3	I 1b

Density

	$T(K)$	g cm^{-3}	Ref.
Ni(IO$_3$)$_2$ (yellow)	298	5.02	67
Ni(IO$_3$)$_2$ (green)	298	4.61	67

4.16. Plutonium

Pu(IO$_3$)$_4$
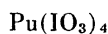
The preparation of submicrogram quantities of the yellow salt was reported more than 20 years ago [27], but its properties were not studied.

4.17. Potassium

KIO$_3$

The decomposition of the salt has been studied experimentally by both a dynamic and a static method [17] between 655 and 736 K. Over this temperature range the reaction

$$KIO_3 \rightarrow KI + 3/2O_2,$$

requires 50–600 days to reach equilibrium. Using the gef values for KI in [I 3] and C_p values for KIO$_3$ determined by [1] equilibrium constants for the reaction were calculated. Calculated values were ∼ 0.3 more negative in log K than experimental values, with the same $\Delta H°$. The KIO$_3$-KI system exhibits a eutectic at 730 K [13]. Above this temperature a liquid phase is present. If the system is one-component, however, P_{O_2} will be a unique function of temperature. This will be true as long as there is a solid phase present (see Introduction).

It is interesting to note that Duval [42] found no weight loss when KIO$_3$ was heated *rapidly* to 500 °C, a temperature at which the equilibrium press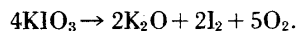ure of O$_2$ exceeds 1 atm. As is also evident from the long equilibration times the decomposition is very sluggish. There is some indication [96] that there is also a secondary reaction to the oxide:

$$4KIO_3 \rightarrow 2K_2O + 2I_2 + 5O_2.$$

Periodates

Several anhydrous periodates of potassium are known. Their description is complicated by the fact that some authors describe these salts in terms of the formula $nK_2O \cdot mI_2O_7$, although (1) I$_2$O$_7$ probably does not exist as a discrete compound, and (2) the I$_2$O$_7$ group apparently does not exist in the crystal structure of periodates (see Introduction). The main reason for the system seems to be that I$_2$O$_7$ can be regarded as the (hypothetical) anhydride of H$_2$I$_2$O$_8$ (HIO$_4$) and hydrates of the salts can then be represented on the ternary I$_2$O$_7$-K$_2$O-H$_2$O diagram (see [6]). In this section the dual nomenclature is retained to facilitate comparison with the original literature.

KIO$_4$ (K$_2$O·I$_2$O$_7$)
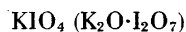
The formula of this salt is frequently given as K$_2$I$_2$O$_8$

although the existence of tetrahedral IO$_4^-$ groups in the solid is well established [22]. The salt is stable up to at least 260–290 °C [6, 42] and perhaps 330 °C [96]. The decomposition reaction is

$$KIO_4 \rightarrow KIO_3 + 1/2O_2.$$

No thermodynamic values have been measured. The kinetics of the reaction has been studied in some detail [83]. Various equations were used to represent different stages of the reaction. The activation energy is 209 kJ (50 kcal), consistent with the breaking of an I-O bond and the formation of atomic oxygen as the rate-determining steps.

K$_4$I$_2$O$_9$ (2K$_2$O · I$_2$O$_7$)
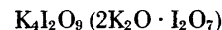
The anhydrous salt is stable to 445 °C [6]. Its crystal structure has been determined [22]. The I$_2$O$_9^{4-}$ ion is a distinct entity which can be represented by
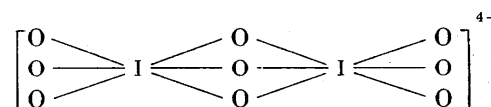
but its decomposition reaction is not known, although (like all potassium periodates) the final product is KI.

K$_3$IO$_5$ (3K$_2$O·I$_2$O$_7$)
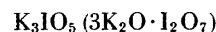
The salt was prepared by dehydration of its hydrates [6]. It is stable up to 440°, but the decomposition reaction has not been studied, nor are its properties known.

K$_5$IO$_6$ (5K$_2$O · I$_2$O$_7$)

The ortho periodate is stable up to 570°, but no further information is available [6].

TABLE 4.11.   Properties of K-I salts

	Density		
	$T(K)$	ρ (g cm^{-3})	Ref.
KIO$_3$	305	3.93	86
KIO$_4$	288	3.618	4
K$_4$I$_2$O$_9$	ambient	3.7	22

	Phase transitions		
	Transition	$T(K)$	Ref.
KIO$_3$	$c \rightarrow l$	833 ± 4	13, 88

Thermodynamic data (298.15 K)

	$S°$		
	J deg^{-1}	cal deg^{-1} mol^{-1}	Ref.
KIO$_3$	151.4$_6$	36.20	I 1a
KIO$_4$	—	—	
K$_4$I$_2$O$_9$	—	—	
K$_3$IO$_5$	—	—	
K$_5$IO$_6$	—	—	
KI	106.38$_8$	25.427	I 3

4.18. Radium

$Ra(IO_3)_2$
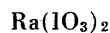
The salt has been reported [84] but no high-temperature properties have been measured.

4.19. Rare Earths

Iodates

The thermal decomposition of the rare earth iodates was studied by two groups [52, 109]. In both cases, the starting materials were the hydrated salts which lost water easily, according to [109] below 100°. The an-

$\Delta H f°$

	kJ mol^{-1}	kcal mol^{-1}	Ref.
KIO_3	− 510.03	− 121.90	J 1b
KIO_4	− 472.0 ± 0.8	− 112.8 ± 0.2	94
$K_4I_2O_9$	—	—	
K_3IO_5	—	—	
K_5IO_6	—	—	
KI	− 327.9 ± 0.4	− 78.37 ± 0.1	J 3

Decomposition of KIO_3

$$KIO_3(c) = KI(c) + 3/2O_2(g)$$

$$\Delta H°_{298.15} = 182.13\ kJ,\ 43.53\ kcal$$

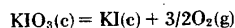| T K	KIO_3 gef J deg^{-1} mol^{-1}	KI gef J deg^{-1} mol^{-1}	Δgef J deg^{-1}	$\Delta G°/T$ J deg^{-1}	log K	P_{O_2} atm
298.15	−151.46	−106.388	−262.478	348.389	−18.1983	7.37×10^{-13}
400	−155.57	−108.470	−262.194	193.131	−10.0883	1.84×10^{-11}
500	−163.53	−112.445	−261.535	102.725	−5.3659	2.65×10^{-6}
600	−172.54	−116.955	−260.813	42.737	−2.2323	5.86×10^{-3}
700	−181.65	−121.541	−260.143	0.0427	−0.0022	1.00
800	−190.52	−126.056	−259.628	−31.966	+1.6697	46.7

hydrous salts then convert to periodates at considerably higher temperature by the Rammelsberg reaction.

$$10M(IO_3)_3 = 2M_5(IO_6)_3 + 12I_2 + 27O_2.$$
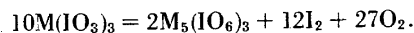
The reported onset of the reaction as given by [110] is listed below. Temperatures listed by [52] are higher.

Salt	Onset of decomposition, °C	Salt	Onset of decomposition, °C
La $(IO_3)_3$	480	Dy $(IO_3)_3$	466
Ce $(IO_3)_3$	400	Ho $(IO_3)_3$	463
Pr $(IO_3)_3$	440	Er $(IO_3)_3$	462
Nd $(IO_3)_3$	474	Tm $(IO_3)_3$	462
Sm $(IO_3)_3$	471	Yb $(IO_3)_3$	458
Eu $(IO_3)_3$	470	Lu $(IO_3)_3$	455
Gd $(IO_3)_3$	464		

It is evident that the thermal stability in the series decreases with increasing cationic charge density, presumably because of increasing anionic polarization. An iodate of Ce(IV) has also been reported [76, 102], but only its crystal structure has been reported. $S_{298.15}$ for all the rare earth iodates were calculated by Bertha and Choppin [5] in the course of calculating hydration entropies for these salts. Although the trend from lanthanum to lutetium is probably correct, the approximations made preclude an absolute accuracy greater than the total range of values, 300 ± 8 J deg^{-1} mol (72 ± 2 cal deg^{-1} mol^{-1}).

Periodates

The ortho periodates, $M_5(IO_6)_3$, which are formed by

the thermal decomposition of iodates (see above) are stable to near 1000 °C, but their decomposition has not been studied in detail. They decompose to the oxides. The mesoperiodates of lanthanum and praesodymium have been reported [64]. $LaIO_5$ is stable to ~ 420 °C, $PrIO_5$ to 400°. Decomposition goes to the oxide:

$$2LaIO_5 \rightarrow La_2O_3 + I_2 + 7/2O_2,$$

$$6PrIO_5 \rightarrow Pr_6O_{11} + 3I_2 + 19/2I_2.$$

4.20. Rubidium

$RbIO_3$

The salt decomposes according to

$$RbIO_3 \rightarrow RbI + 3/2O_2.$$
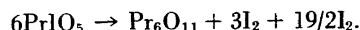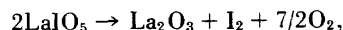
Bousquet and Remy determined the melting point, ΔH_m, and ΔS_m from the phase diagram of the $RbIO_3$-RbI system [17]. The eutectic is at 777 K. Consequently, any decomposition above this temperature will result in the formation of liquid phase but the pressure of O_2 will remain a unique function of temperature, as long as a solid phase is present and the system is one-component.

Enthalpy increments of $RbIO_3$ were measured calorimetrically by Bousquet, Perachon, and Remy [15] up to 707 K. The resultant data were fitted to a power series in T which was then used to generate enthalpy and entropy increments at equal temperature intervals. Since only the lack of a $S°_{298.15}$ value for $RbIO_3$ prevented the calculation of gef values it was estimated by comparison with other alkali metal halates. The estimate agrees with a similar one made by [17].

Cp values of RbI estimated by Kelley [55a] were used to generate enthalpy and entropy increments. In this way equilibrium constants for reaction (1) were calculated that are probably good to within an order of magnitude. These calculations indicate that decomposition in air becomes appreciable between 600 and 700 K, well below the melting point.

Bousquet and Remy [17] have carried out a similar calculation with values that differ only slightly from those used in this work. They also measured the equilibrium pressure of O_2 by both a static and dynamic method between 597 and 740 K. Under static conditions 25 to 200 days (at various temperatures) were required to reach a steady pressure. Agreement between both sets of calculations and experimental values is quite good. Ambient-temperature density values listed by [1 9] vary from 4.34 to 4.56 g cm^{-3}.

RbIO$_4$

Older references are given by [1 9]. No recent work has been reported. By analogy with CsIO$_4$ the decomposition probably proceeds according to

$$RbIO_4 \rightarrow RbIO_3 + 1/2 O_2,$$

but no measurements have been reported.

TABLE 4.12. Properties of Rb-I salts

Density

	$T(K)$	$\rho(g\ cm^{-3})$	Ref.
RbIO$_3$	305	4.471	4
RbIO$_4$	289	3.918	86

Phase transformations

		$T(K)$	$\Delta H(kJ)$	$\Delta S(J\ deg^{-1})$	Ref.
RbIO$_3$	$c \rightarrow l$	863	8.8	10.2	17

Thermodynamic properties (298.15 K)

$S°$

	J deg^{-1} mol^{-1}	cal deg^{-1} mol^{-1}	Ref.
RbIO$_3$	16$_{0.7}$	38.$_4$	est.
RbI	118.0$_3$	28.21	1 1a

$\Delta H f°$

	kJ mol^{-1}	kcal mol^{-1}	Ref.
RbIO$_3$	−515.322	−123.165	15
RbI	−333.1$_3$	−79.62	1 1b

Decomposition of RbIO$_3$

$$RbIO_3(c) = RbI(c) + 3/2 O_2(g)$$
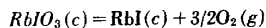
$$\Delta H°_{298.15} = 182.192\ kJ,\ 43.545\ kcal$$

T K	RbIO$_3$ *gef* J deg^{-1}	RbI *gef* J deg^{-1}	Δgef J deg^{-1}	$\Delta G°/T$ J deg^{-1}	log K	K	P_{O_2} atm
298.16	− 160.7	− 118.03	− 264.88	346.195	− 18.0837	8.25×10^{-19}	8.80×10^{-13}
400	− 164.9	− 120.07	− 264.46	191.020	− 9.9780	1.05×10^{-10}	2.23×10^{-11}
500	− 173.0	− 124.03	− 263.65	100.734	− 5.2619	5.47×10^{-6}	3.10×10^{-7}
600	− 182.2	− 128.51	− 262.71	40.943	− 2.1386	2.73×10^{-3}	3.75×10^{-4}
700	− 191.4	− 133.04	− 261.89	− 1.616	+ 0.0844	1.21	1.14

4.21. Silver

AgIO$_3$

Little work has been done on the thermal decomposition of this salt. It is apparently stable to ~ 405 °C. Above this temperature decomposition yields AgI [37, 50, 78].

AgIO$_4$

The salt decomposes near 200 °C, and explosively at a lower temperature in vacuum. The products are AgIO$_3$ and AgI [78].

AgIO$_5$

The thermal decomposition of this salt has been studied by several workers. The decomposition products reported seem to vary with the decomposition temperature. The lowest temperature is reported by Curti and

Coggiola [28] who find formation of AgIO$_3$ near 175 °C. However, both Varhely and Kekedy [103] and Paćesová, Rathanová, and Rosický [78] find the salt to be stable to ~ 425–445°. Since AgIO$_3$ is unstable at this temperature decomposition proceeds directly to the iodide:

$$2Ag_3IO_5 = 2AgI + 4\ Ag + 5O_2.$$

Ag$_5$IO$_6$

The salt has been reported to be stable to at least 60 °C [99]. Both it and Ag$_3$IO$_5$ are black, and give the same X-ray pattern [28]. However, the existence of the salt seems to by beyond question, particularly since the reaction

$$4Ag_3IO_5 \rightarrow 2Ag_5IO_6 + 2AgIO_3 + O_2,$$
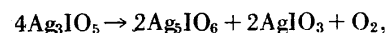
in the presence of base has been studied [28].

Ag$_4$I$_2$O$_9$

There is some question whether the pure, anhydrous

salt has been prepared. The 3-hydrate has been prepared, but attempts to remove H_2O by a variety of procedures always leads to loss of some O_2 along with the water [28, 55, 79].

TABLE 4.13. Properties of Ag-I salts

	Density		
	$T(K)$	$\rho(g\ cm^{-3})$	Ref.
$AgIO_3$	293	5.525	1 5
Ag_5IO_6	ambient	1.884	47a

Thermodynamic data (298.15 K)

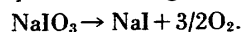|	ΔHf°		
	$kJ\ mol^{-1}$	$k\ cal\ mol^{-1}$	Ref.
$AgIO_3$	−171.1	−40.9	1 1b
Ag_3IO_5	—	—	
AgI	−61.84	−14.78	1 1b

	S°		
	$J\ mol^{-1}\ deg^{-1}$	$cal\ mol^{-1}\ deg^{-1}$	Ref.
$AgIO_3$	149.4	35.7	1 1b
A_3IO_5	—	—	
AgI	115._5	27.6	1 1b

4.22. Sodium

$NaIO_3$

The salt decomposes according to

$$NaIO_3 \rightarrow NaI + 3/2O_2.$$

Equilibrium pressures were measured by Bousquet and Remy [16] by two different methods between 593 and 900 K, but the results exhibit considerable scatter. The same authors have also calculated equilibrium pressures from thermodynamic data [17] up to 593 K. We have calculated equilibrium values up to 700 K since C_p values for $NaIO_3$ are available only up to this temperature [17]. For NaI we have accepted the evaluation by [I 3], although the value of $\Delta Hf^\circ_{298.15}$ differs somewhat from the newer value of −69.2 kcal [I 1b].

Since $NaIO_3$ decomposes only slowly, the melting point obtained by a short extrapolation of the $NaIO_3$-NaI phase diagram is probably accurate to $\pm 1^\circ$.

If the compound is heated fairly rapidly, as in DTA measurements [46], the salt can be melted without appreciable decomposition, perhaps up to $\sim 460\ ^\circ C$. There is some evidence that, at least under nonequilibrium conditions, ~ 28 percent of the $NaIO_3$ decomposes to the oxide:

$$4NaIO_3 \rightarrow 2Na_2O + 2I_2 + 5O_2.$$

Na_2IO_4

This salt, in which iodine is in a +6 oxidation state results from heating $Na_2H_3IO_6$ at 120-180 °C [34]. Using X-ray diffraction, magnetic susceptibility, and infrared absorption, the chemical individuality of the

salt was established, i.e., it is not a mixture of $NaIO_3$ and Na_3IO_5. The compound is stable up to 370 °C, but its decomposition procucts have not yet been identified.

$NaIO_4$

$\Delta Hf^\circ_{298.15}$ has been determined. The value listed is that calculated by Mercer and Farrar [70]. This value would shift slightly if a different value for $\Delta Hf^\circ_{298.15}$ for NaI were adopted.

The thermal expansion of the salt is quite different along the a and c axes. Between 25 and 120 °C the expansion coefficients are represented by [31].

$$\alpha_a = 36.57 \times 10^{-6} + 3.89 \times 10^{-8}t + 14.19 \times 10^{-11}t^2,$$

$$\alpha_c = 49.49 \times 10^{-6} + 18.42 \times 10^{-8}t - 9.22 \times 10^{-11}t^2,$$

with t in °C.

Heating of $NaIO_4$ at 290-300 °C leads to the formation of $NaIO_3$ [36]:

$$NaIO_4 \rightarrow NaIO_3 + 1/2O_2.$$

No $S^\circ_{298.15}$ and high-temperature thermodynamic data for the periodate are available.

Na_5IO_6

As with the alkaline earths, this is the stablest of the periodates. It decomposes above 700° according to [110].

$$2Na_5IO_6 \rightarrow 5Na_2O + I_2.$$
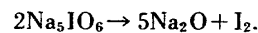
TABLE 4.14. Properties of Na-I salts

	Density		
	$T(K)$	$\rho(g\ cm^{-3})$	Ref.
$NaIO_3$	293	4.277	1 5
$NaIO_4$	289	3.865	105

Phase transitions

	Transition (K)	$\Delta H(kJ)$	ΔS $(J\ deg^{-1})$	Ref.
$NaIO_3$	695 ± 1	$35._1 \pm 0.8$	50.9	15

Thermodynamic data (298.15)

	S°		
	$J\ deg^{-1}\ mol^{-1}$	$cal\ deg\ mol^{-1}$	Ref.
$NaIO_3$	$135. \pm 4.2$	32.3 ± 1.0	58
$NaIO_4$	—	—	
Na_2IO_4	—	—	
NaI	98.3	23.5	1 3
Na_2O	75.27	17.99	1 3

	ΔHf°		
	$kJ\ mol^{-1}$	$kcal\ mol^{-1}$	Ref.
$NaIO_3$	−490.712	−117.283	1 1b
$NaIO_4$	-439.95 ± 1.26	-105.15 ± 0.30	70
NaI	-28.9 ± 0.08	-68.8 ± 0.2	1 3
Na_2O	−415.9	−99.4	1 3

Decomposition of $NaIO_3$

$$NaNO_3(c) = NaI(c) + 3/2O_2(g)$$

$$\Delta H^\circ_{298.15} = 202.853 \text{ kJ, } 48.483 \text{ kcal}$$

T (K)	$NaIO_3$ gef J deg^{-1}	NaI gef J deg^{-1}	Δgef J deg^{-1}	$\Delta G^\circ/T$ J deg^{-1}	$\log K$	K	P_{O_2} atm
298.15	− 135.143	− 98.500	− 270.907	409.465	− 21.3886	4.09×10^{-22}	5.51×10^{-15}
400	− 139.951	− 114.077	− 283.420	223.712	− 11.6857	2.06×10^{-12}	1.62×10^{-8}
500	− 148.582	− 126.219	− 290.257	115.449	− 6.0305	9.32×10^{-7}	9.43×10^{-5}
600	− 159.039	− 136.361	− 293.720	44.368	− 2.3176	4.81×10^{-3}	2.85×10^{-2}
700	− 170.817	− 145.114	− 194.549	− 4.759	+ 0.2485	1.77	1.46

4.23. Strontium

$Sr(IO_3)_2$

The salt is stable at least to 550 °C. Above 600° it undergoes the Rammelsberg reaction [39a, 102]

$$5Sr(IO_3)_2 \rightarrow Sr_5(IO_6)_2 + 4I_2 + 9O_2.$$
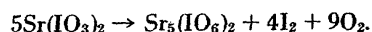
gef values for the iodate were calculated from the $\Delta H f^\circ_{298.15}$ and $S^\circ_{298.15}$ values in [I 1b] and the enthalpy increments determined by [30]. However, a lack of $S^\circ_{298.15}$ for the paraperiodate prevents the calculation of the equilibrium constant for the above reaction.

$Sr_5(IO_6)_2$

The salt is stable to ~ 930 °C. At ~ 1000° it decomposes to the oxide at an appreciable rate [103].

$$2Sr_5(IO_6)_2 = 10SrO + 2I_2 + 7O_2.$$

Enthalpy and entropy increments are based on the calorimetric measurements of [30]. The lack of $S^\circ_{298.15}$ values prevents further calculations.

TABLE 4.15. Properties of Sr-I salts

Density

	T(K)	ρ(g cm^{-3})	Ref.
$Sr(IO_3)_2$	288	5.045	I 5

Thermodynamic data (198.15 K)

S°

	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	Ref.
$Sr(IO_3)_2$	234.	56.	I 1b
$Sr_5(IO_6)_2$	—	—	
SrO	54.3	13.0	I 1b

$\Delta H f^\circ$

	kJ mol^{-1}	kcal mol^{-1}	Ref.
$Sr(IO_3)_2$	−1019.	−243.6	I 1b
$Sr_5(IO_6)_2$	−3975.	−950.1	11
SrO	−592.0	−141.50	I 1b

High temperature thermodynamic properties

T K	$Sr(IO_3)_2$ gef J deg^{-1}	SrO gef J deg^{-1}	$Sr_5(IO_6)_2$ $H_T - H_{298.15}$ J	$Sr_5(IO_6)_2$ $S_T - S_{298.15}$ J deg^{-1}
298	−234.3	−54.3	0	0
400	−242.0	−56.2	42388	121.60
500	−257.2	−59.7	89885	227.32
600	−275.2	−63.7	140476	319.42
700	−294.0	−67.9	191442	397.92
800		−71.9	240062	462.82

4.24. Thallium

$TlIO_3$

The existence of the anhydrous salt is well established and its structure has been studied [90]. However, no work seems to have been reported concerning its high temperature behavior since the 19th century. According to this older work, summarized in [I 9], the salt is stable up to ~ 150 °C, and melts with evolution of O_2 and I_2, the residue consisting of a mixture of oxide and iodide.

$Tl_5(IO_6)_3$

The preparation of this salt of Tl(III) has recently been reported [25]. It is brown and decomposes above 260 °C. The X-ray spectrum of the salt was measured

TABLE 4.16. Properties of Tl-I salts

Thermodynamic data (298.15 K)

S°

	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	Ref.
$TlIO_3$	177.	42.2	I 1b
Tl_2O	126.	30.	I 1b
TlI	128.	30.5	I 1b

$\Delta H f^\circ$

	kJ mol^{-1}	kcal mol^{-1}	Ref.
$TlIO_3$	− 267.	− 63.9	I 1b
Tl_2O	− 179.	− 42.7	I 1b
TlI	− 124.	− 29.6	I 1b

4.25. Thorium

$Th(IO_3)_4$

Probably exists as an anhydrous compound up to ~ 300 °C. However, since it is very hydgroscopic it has not yet been prepared in the anhydrous state at ambient temperature, but only by the thermal dehydration of a hydrate [38].

4.26. Titanium

$Ti(IO_3)_4$

Preparation of the anhydrous salt by dehydration of its dihydrate at' 100 °C has been reported [86]. The density at 305 K (determined pyknometrically) is 4.080 g cm^{-3} [1 5].

4.27. Yttrium

$Y(IO_3)_3$

The anhydrous salt can be prepared by dehydration of its 4-hydrate below 100 °C. It then decomposes, beginning near 470 °C, according to the overall reaction [109]

$$10Y (IO_3)_3 = 2Y_5 (IO_6)_3 + 12I_2 + 27O_2.$$
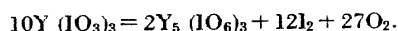
The periodate decomposes to the oxide near 1000 °C, but this reaction has not yet been studied in detail.
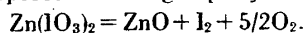
YIO_5

This compound was prepared by the thermal decomposition of $YH_2IO_6 \cdot 3H_2O$ [60]. It is stable up to 250 °C and then decomposes to the oxide:

$$2YIO_5 \rightarrow Y_2O_3 + I_2 + 7/2O_2.$$
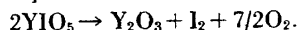
4.28. Zinc

$Zn(IO_3)_2$

The salt is stable up to ~520 °C. Above this temperature it decomposes according to [102]

$$Zn(IO_3)_2 = ZnO + I_2 + 5/2O_2.$$

A $\Delta G f^{\circ}_{298.15}$ value of -433.80 kJ $(-103.68$ kcal) has been reported for the salt [1 1b].

$Zn_5(IO_6)_2$

Preparation of the anhydrous compound has been reported [47, 98] but its properties have not yet been studied.

TABLE 4.17.   Properties of Zn-I salts

	Density		
	$T(K)$	$\rho(g\ cm^{-3})$	Ref.
$Zn(IO_3)_2$	298	5.063	66

Thermodynamic data (298.15 K)

	S°		
	J mol^{-1} deg^{-1}	cal mol^{-1} deg^{-1}	Ref.
$Zn(IO_3)_2$ ZnO	43.64	10.43	1 1b

	ΔHf°		
	kJ mol^{-1}	kcal mol^{-1}	Ref.
$Zn(IO_3)_2$ ZnO	-348.3	-83.24	1 1b

4.29. Zirconium

$Zr(IO_3)_4$

The crystal structure of the anhydrous salt has been determined [61]. The density of the tetragonal prisms is 5.00 ± 0.01 g cm^{-3} at ambient temperature.

4.30. References

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