The Differential Thermal Analysis of Perchlorates. VII. Catalytic Decompositions of the Alkali Metal Perchlorates by Manganese Dioxide

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The thermal stabilities of the pure alkali metal perchlorates ($MClO_4$) and of admixtures with 10 mole % MnO_2 catalyst follow the order Li < Na < K, Rb, Cs. For both pure and catalyst-containing materials, rapid decomposition is preceded by liquid phase formation. Analyses of molten perchlorates near their fusion temperatures show that fusion is coincident with decomposition except for $LiClO_4$ which has a congruent melting point; the simultaneous occurrence of fusion and decomposition is in contrast to the behavior manifested by $MClO_3$ salts, each of which possesses a congruent melting point and a significant range of liquid phase stability. Catalysis of $MClO_4$ pyrolysis by basic substances yielding O^{2-} ion, in conjunction with other evidence, suggests the presence of O atoms in decomposing perchlorates. A proposed mechanism for Cl_2 evolution from $MClO_4$ melts (order of extent of Cl_2 release: $Li \gg Na > K > Rb, Cs = 0$) stipulates an autoionization equilibrium of the type $ClO_4^- \rightarrow ClO_3^+ + O^{2-}$, so that Cl_2 release occurs through the reaction $ClO_4^- + ClO_3^+ \rightarrow [Cl_2O_7] \rightarrow Cl_2 + {}^7/_2O_2$. Such a scheme removes acidic oxides (*e.g.*, P_2O_5, B_2O_3, WO_3, MoO_3, etc.) from consideration as true catalysts inasmuch as they function by removal of oxide ions and hence undergo specific, irreversible reactions with $MClO_4$ salts. In this regard, MnO_2 is primarily a true catalytic agent for $MClO_4$ decomposition, but it also does appear to undergo a small amount of chemical reaction with $LiClO_4$, in particular, to foster Cl_2 evolution, *viz.*, $LiClO_4 + MnO_2 \rightarrow LiMnO_2 + {}^1/_2Cl_2 + 2O_2$.

Introduction

Though the catalytic decomposition of $KClO_3$ by MnO_2 has been extensively studied in the past,[1] relatively little care had been taken to ensure the purity and structural properties of the materials used and to secure comparable data for the other $MClO_3$ salts.[2] The $MClO_4$ compounds in these regards have suffered even greater neglect. Accordingly, in the present study, previously well-characterized reactants were employed to ascertain the course of changes during the pyrolyses of the pure $MClO_4$ salts and of $MClO_4$ samples containing 10 mole % MnO_2.

Experimental

Differential thermal analysis (d.t.a.), thermogravimetric analysis (t.g.a.), and Cl_2 evolution experiments were performed as previously described.[2] Vycor (96% SiO_2) or quartz was used as the sample container because of the high temperatures encountered in this study and because these materials tend to undergo less interaction with molten $MClO_3$ and $MClO_4$ salts to produce Cl_2 than does soft or borosilicate glass.[3,4]

Materials. The preparation and handling of the five $MClO_4$ salts have been detailed elsewhere.[5] All samples were ground to pass a 325 mesh sieve. Each of these materials and subsequently produced reaction residues was analyzed for Cl^- content titrimetrically by the Mohr method and for ClO_3^- content as additional Cl^- after reduction with aqueous SO_2. ClO_4^- was determined gravimetrically as nitron perchlorate after

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(1) "Gmelins Handbuch der anorganischen Chemie," 8 Auflage, System No. 6, "Chlor," Verlag Chemie, G.m.b.h., Berlin, 1926, pp. 340-346.

(2) M. M. Markowitz, D. A. Boryta, and H. Stewart, Jr., *J. Phys. Chem.*, **68**, 2282 (1964).

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

(4) W. H. Sodeau, *ibid.*, **77**, 137 (1900).

(5) M. M. Markowitz, D. A. Boryta, and R. F. Harris, *J. Phys. Chem.*, **65**, 261 (1961).

removal of ClO_3^-. No Cl^- or ClO_3^- was found in any of the $MClO_4$ compounds. Analyses of products: $LiClO_4$: ClO_4^-, 93.8 (calcd. 93.5); $NaClO_4$: ClO_4^-, 81.4 (calcd. 81.2); $KClO_4$: ClO_4^-, 71.7 (calcd. 71.9); $RbClO_4$: ClO_4^-, 19.14 (calcd. 19.18); $CsClO_4$: ClO_4^-, 15.20 (calcd. 15.27). Because of the possible susceptibility of these salts to catalysis of thermal decomposition by trace impurities,[6,7] the compounds were also analyzed spectrographically; B, Co, Cr, Mo, Pb, Sn, Ti, V, and Zn were uniformly found to be absent, whereas Al, Ca, Cu, Fe, Mg, Mn, Ni, and Si were generally present to the extent of 1–10 p.p.m.

Chemically analyzed MnO_2 as tetragonal pyrolusite was available from an earlier study.[2] The screen analysis was 100% through 200 mesh, 43.7% through 325 mesh, and 56.3% on 325 mesh. In order to avoid promotion of catalysis and other effects due to trace impurities,[8,9] the material was analyzed spectrographically and was found free of Pb, Ti, and V with less than 50–100 p.p.m. of Al, Ca, Cu, Ni, and Si, and 300 p.p.m. of Fe. It should be noted that despite the many studies performed concerning the catalytic effects of MnO_2 on the pyrolysis of $KClO_3$, systematic characterization of the catalyst appears to have been consistently omitted.[10,11]

Thermal Profiles of Pure Perchlorate Salts. The pertinent data obtained from the d.t.a. (Figure 1) and t.g.a. (Figure 2) curves for the pure $MClO_4$ compounds are summarized in Tables I and II, respectively.

Table I: Thermal Behavior of $MClO_4$ Salts and of 90 Mole % $MClO_4$–10 mole % MnO_2 Mixtures from D.t.a. Experiments

Sample	Crystallographic transition, °C.	$MClO_4$ fusion, °C.	Onset of rapid dec., °C.	MCl fusion, °C.
$LiClO_4$	. . .	247	438	611
$LiClO_4$–MnO_2	. . .	247	402	612
$NaClO_4$	309	468	525	800
$NaClO_4$–MnO_2	311	450	485	801
$KClO_4$	303	580	580	773
$KClO_4$–MnO_2	300	529	529	769
$RbClO_4$	284	597	597	726
$RbClO_4$–MnO_2	285	545	545	722
$CsClO_4$	225	577	577	650
$CsClO_4$–MnO_2	228	522	522	642

The initial endotherm for each $MClO_4$ salt but $LiClO_4$ denotes a reversible crystallographic transition from the rhombic to the cubic form. The initial endotherm for $LiClO_4$ corresponds to its congruent melting point (247°). By using accurately weighed

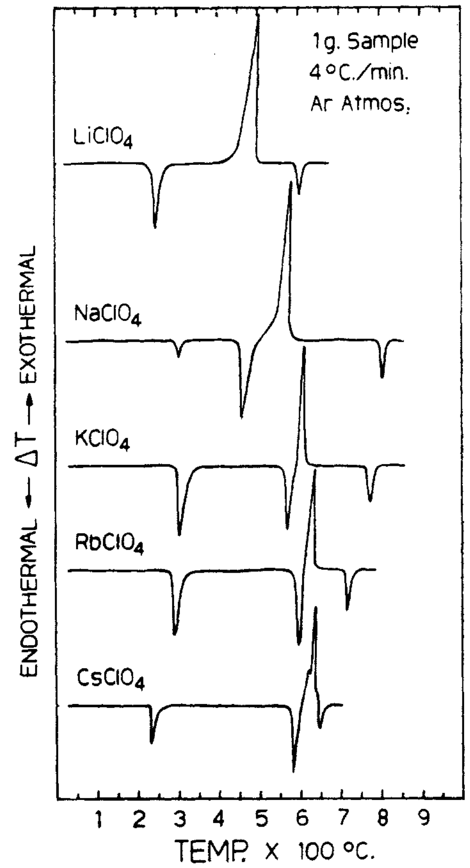

Figure 1. D.t.a. curves for pure alkali metal perchlorates.

Table II: Thermal Behavior of $MClO_4$ Salts and of 90 Mole % $MClO_4$–10 Mole % MnO_2 Mixtures from T.g.a. Experiments

Sample	2% dec. temp., °C.	% wt. loss of $MClO_4$ based on conversion to MCl	Cl_2 evolution, % of total available Cl
$LiClO_4$	470	103.0	1.22
$LiClO_4$–MnO_2	402	102.2	3.81
$NaClO_4$	522	102.4	0.20
$NaClO_4$–MnO_2	440	101.5	Trace
$KClO_4$	583	101.5	Variable: none or a faint trace
$KClO_4$–MnO_2	477	100.6	Trace
$RbClO_4$	611	101.9	None
$RbClO_4$–MnO_2	485	100.6	Trace
$CsClO_4$	601	101.6	None
$CsClO_4$–MnO_2	466	100.7	None

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(6) A. Glasner and A. E. Simchen, *Bull. soc. chim. France*, 233 (1951).

(7) A. E. Simchen, *J. Phys. Chem.*, **65**, 1093 (1961).

(8) J. A. Burrows and F. E. Brown, *J. Am. Chem. Soc.*, **48**, 1790 (1926).

(9) H. A. Neville, *ibid.*, **45**, 2330 (1923).

(10) F. E. Brown, J. A. Burrows, and H. M. McLaughlin, *ibid.*, **45**, 1343 (1923).

(11) H. M. McLaughlin and F. E. Brown, *ibid.*, **50**, 782 (1928).

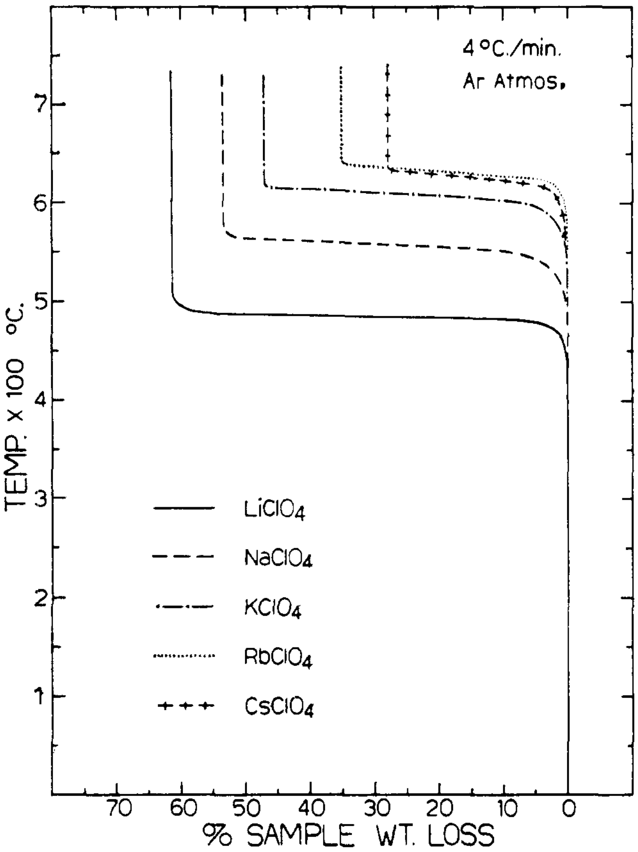

Figure 2. T.g.a. curves for pure alkali metal perchlorates.

Table III: Compositions of Fused, Quenched $MClO_4$ and of 90 Mole % $MClO_4$–10 Mole % MnO_2 Residues near Fusion Temperatures

$MClO_4$	Temp., °C.	Mole fraction $MClO_4$	Mole fraction $MClO_3$	Mole fraction MCl
$NaClO_4$	469	0.9929	0.0000	0.0071
90% $NaClO_4$–10% MnO_2	458	0.9698	0.0001	0.0301
$KClO_4$	584	0.8623	0.0558	0.0819
90% $KClO_4$–10% MnO_2	539	0.8082	0.0187	0.1731
$RbClO_4$	595	0.8877	0.0335	0.0788
90% $RbClO_4$–10% MnO_2	564	0.7837	0.0542	0.1621
$CsClO_4$	573	0.9550	0.0232	0.0218
90% $CsClO_4$–10% MnO_2	535	0.8394	0.0056	0.1550

$MClO_4$ samples during each d.t.a. run in combination with the known value of the heat of transition of $KClO_4$ (3.29 kcal./mole),[12] it was possible to estimate the heats of transition of $NaClO_4$ (0.6 ± 0.1 kcal./mole), $RbClO_4$ (3.0 ± 0.1 kcal./mole), and $CsClO_4$ (2.0 ± 0.2 kcal./mole). For $NaClO_4$, $KClO_4$, $RbClO_4$, and $CsClO_4$ the succeeding endotherm refers to fusion of the $MClO_4$ salt together with any of the decomposition products which have accumulated up to that temperature. The t.g.a. data indicate some small weight losses for these materials within the range of the fusion temperatures. To confirm the concordance of fusion and decomposition phenomena for these substances, they were heated as in a d.t.a. experiment close to their fusion temperatures, and the clear melts were then removed from the furnace, quenched, and analyzed; the results obtained are presented in Table III. As seen, $KClO_4$, $RbClO_4$, and $CsClO_4$ have undergone appreciable decomposition coincident with fusion; $NaClO_4$ is but slightly decomposed. That $NaClO_4$ decomposes at a slow but significant rate upon fusion was further demonstrated in the present study by maintaining a sample for 48 hr. at 470°, after which period the compound had decomposed to NaCl to the extent of 98.8%. The considerable thermal stability of molten $LiClO_4$ near its melting point has been abundantly proven.[13] The presence of chlorate in the residues of Table III is consistent with the known thermal decomposition behavior of $MClO_4$ compounds. Indeed, it can be considered virtually axiomatic in the chemistry of pure $MClO_3$ and $MClO_4$ compounds that at decomposition temperatures the presence of one also betokens the presence of the other.[2,12,14,15]

It is significant to note that the observed fusion temperatures of $NaClO_4$, $KClO_4$, $RbClO_4$, and $CsClO_4$ are functions of the heating rate used. This dependency would, in part, account for the diversity of values given in the literature for the liquefaction of many thermally unstable materials. Thus, in the present investigation, 1-g. samples of $KClO_4$ heated over the range of 10°/min. to 1°/min. gave a spread of 20° for the fusion temperature, this temperature decreasing with decreasing heating rate. Clearly then, the heating rate determines the average residence time at any temperature and thereby the extent of decomposition occurring up to the liquidus temperature of the reaction residue formed. Accordingly, for thermally unstable materials of this type, neglecting heat-transfer effects, a rapid heating rate would approach the fusion temperature more closely than a slow heating rate.

Each of the d.t.a. curves of Figure 1 manifests an exotherm in the higher temperature regions which is associated with the major portions of the thermal decomposition processes of the perchlorate salt to produce ultimately the corresponding metal chloride (MCl).

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(13) M. M. Markowitz, *J. Phys. Chem.*, **62**, 827 (1958).

(14) A. E. Harvey, C. J. Wassink, T. A. Rodgers, and K. H. Stern, *Ann. N. Y. Acad. Sci.*, **78**, 971 (1960).

(15) M. M. Markowitz, D. A. Boryta, and H. Stewart, Jr., *J. Chem. Eng. Data*, **9**, 573 (1964).

The temperature intervals ($T_r - T_f$) between fusion (T_f) and the onset of rapid decomposition (T_r) follow the order Li (191°) > Na (57°) > K, Rb, Cs = 0° and the sequence of thermal stabilities from Table I is found to be Li < Na < Cs < K < Rb. This order follows the order of fusion temperatures under the prevailing thermal treatment rather than the anticipated order of stabilities based solely on considerations of polarizing power[5] as occasioned by the steadily decreasing ionic potential in passing from Li^+ to Cs^+.

The reactions observed for each of the $MClO_4$ salts but $LiClO_4$ during fusion can be represented by the over-all equations

$$\text{major: } MClO_4(s) \longrightarrow MClO_4(l) \quad (1)$$

$$\text{minor: } MClO_4(s,l) \longrightarrow MClO_3(l) + {}^1/_2O_2(g) \quad (2)$$

$$\text{minor: } MClO_4(s,l) \longrightarrow MCl(l) + 2O_2(g) \quad (3)$$

$$\text{minor: } MClO_3(l) \longrightarrow MCl(l) + {}^3/_2O_2(g) \quad (4)$$

These equations are followed with rising temperature by the processes giving rise to the succeeding exotherm which encompasses the reactions

$$MClO_4(l) \longrightarrow MCl(l) + 2O_2(g) \quad (5)$$

followed by

$$MClO_4(l) \longrightarrow MCl(s) + 2O_2(g) \quad (6)$$

each concomitant with

$$MClO_4(l) \longrightarrow MClO_3(l) + {}^1/_2O_2(g) \quad (7)$$

and

$$MClO_3(l) \longrightarrow MCl(l,s) + {}^3/_2O_2(g) \quad (8)$$

and simultaneously with reaction 6

$$MCl(l) \longrightarrow MCl(s) \quad (9)$$

At decomposition temperatures, molten $LiClO_4$ would exhibit substantially the same series of events, *i.e.*, reactions 5–9; $LiClO_3$ is known to be an intermediate in the thermal decomposition of $LiClO_4$. Reaction 1 is, of course, endothermic as is reaction 2 for all the $MClO_4$ compounds, a conclusion reached from estimates of their heats of reaction.[15] Thus, the fusion endotherms for $NaClO_4$, $KClO_4$, $RbClO_4$, and $CsClO_4$ represent the resultant of two endothermic processes (reactions 1 and 2) and two exothermic processes (reactions 3 and 4). The composite decomposition exotherms encompassing eq. 5–9 are consistent with the exothermic natures of reactions 5, 6, 8, and 9 as moderated by the occurrence of endothermic reaction 7 to but a slight degree. Calculations based on available high-temperature heat of formation data for $LiClO_4$, $NaClO_4$, and $KClO_4$ permit verification of this latter statement.[15,16] It would be anticipated that reaction 6 is more exothermic than reaction 5 by approximately the magnitude of the heat of fusion of the respective chloride (*viz.*, LiCl (4.74 kcal./mole), NaCl (6.85 kcal./mole), KCl (6.28 kcal./mole), RbCl (4.40 kcal./mole), and CsCl (3.60 kcal./mole)). However, the d.t.a. exotherms would appear to indicate no discontinuities at any point which could be attributed to augmented heat release due to reaction product crystallization (eq. 6, 8, and 9). Generalizing from the phase diagram for the system $KClO_4$–KCl ($KClO_3$) constructed from the compositions of decomposed $KClO_4$ samples at different temperatures,[17] it would seem that the onset of KCl precipitation occurs quite close to the virtual completion of $KClO_4$ decomposition by reaction 5. This is due to the increasing solubility with rising temperature of the KCl in the decomposing liquid $KClO_4$–KCl ($KClO_3$) solution. Furthermore, thermodynamic considerations show that the exothermicity of reaction 5 is, at reaction temperatures, about the same magnitude as for process 9. Reaction 6 is expected to occur to only a small extent and therefore its high level of heat release would make but a small contribution to the over-all enthalpy change. Accordingly, the heat evolution during the latter part of perchlorate decomposition attributable to reactions 6, 8, and 9 stems primarily from reaction 9, *i.e.*, reaction product crystallization. Thus, the observed exotherm is smooth and indicates no significantly different levels of heat release.

A resolution of the decomposition exotherm for $KClO_4$ has been claimed through the use of small sample sizes (0.086 g.) and bare thermocouples.[18] However, the possible catalytic effects of oxide-coated surfaces of the chromel–alumel sensors on the course of $KClO_4$ decomposition were not determined.[15] In addition, during the present investigation sample sizes from 3 to 0.1 g. of $KClO_4$ in d.t.a. experiments with shielded thermocouples yielded substantially identical thermograms without further resolution of the decomposition exotherm.

Both the final endotherms from the d.t.a. data (Table I) and the aggregate weight losses from the t.g.a. results (Table II) show that the final decomposition products of the $MClO_4$ salts are preponderantly the corresponding MCl compounds. The somewhat higher

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(16) Dow Chemical Co., "Joint Army-Navy-Air Force Thermochemical Tables," Supplements of Dec. 31, 1960, Dec. 31, 1961, June 30, 1962, and June 30, 1963, Midland, Mich.

(17) A. E. Harvey, Jr., M. T. Edmison, E. D. Jones, R. A. Seybert, and K. A. Catto, *J. Am. Chem. Soc.*, **76**, 3270 (1954).

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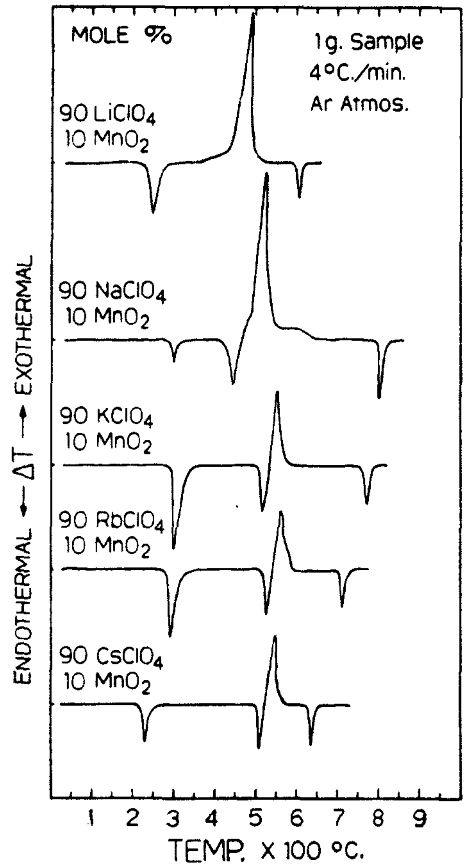

Figure 3. D.t.a. curves for 90 mole % $MClO_4$–10 mole % MnO_2 mixtures.

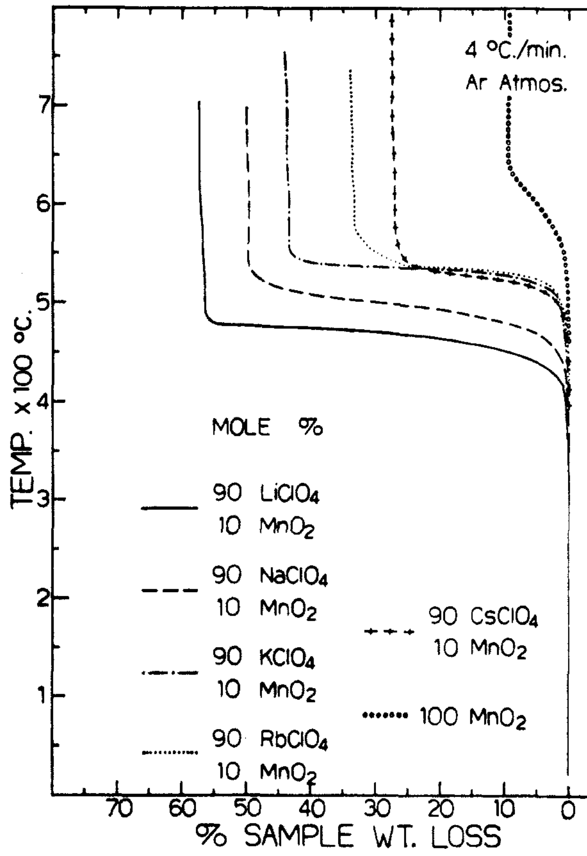

Figure 4. T.g.a. curves for 90 mole % $MClO_4$–10 mole % MnO_2 mixtures.

than theoretical weight losses for the $MClO_4$ compounds are due in part to loss of sample by carryover during the turbulent decomposition reactions.

Thermal Profiles of 90 Mole % $MClO_4$–10 Mole % MnO_2 Mixtures. The pertinent data obtained from the d.t.a. (Figure 3) and t.g.a. (Figure 4) curves for these mixtures are summarized in Tables I and II, respectively.

The d.t.a. curves for the mixtures with catalyst (Figure 3) show a number of pronounced differences upon comparison with the corresponding curves for the pure $MClO_4$ compounds. The liquidus temperatures for $NaClO_4$–MnO_2, $KClO_4$–MnO_2, $RbClO_4$–MnO_2, and $CsClO_4$–MnO_2 are considerably lower than for the pure perchlorate salts, thereby indicating that up to fusion, considerably greater perchlorate decomposition has occurred in the mixtures. Furthermore, the fusion endotherms are smaller than would be expected merely on the basis of sample dilution by an inert, infusible substance. Thus, it appears that the fusion endotherms are composites of the endothermic phase transition from the solid to the liquid state (reaction 1) but decreased in magnitude by an augmented extent to occurrence of the exothermic reaction 3. In the same vein the successive decomposition exotherms are smaller in both peak temperature achieved and in over-all heat release, thereby also substantiating the greater degree of decomposition during fusion. These interpretations are reflected in the data of Table III where at appreciably lower temperatures the $MClO_4$–MnO_2 samples have decomposed to a greater extent than have the pure $MClO_4$ salts.

The data from the t.g.a. experiments (Table II) indicate the occurrence of considerable solid-state decomposition of $NaClO_4$, $KClO_4$, $RbClO_4$, and $CsClO_4$ in admixtures with MnO_2 prior to fusion inasmuch as the 2% decomposition temperatures are appreciably below the observed d.t.a.-determined fusion temperatures. Despite the low melting points[2] for $NaClO_3$ (263°), $KClO_3$ (357°), $RbClO_3$ (342°), and $CsClO_3$ (388°), it is unlikely that any liquid $MClO_3$ will accumulate in the pre-bulk fusion decomposition stage because of the relative ease of catalysis of chlorate decomposition by the MnO_2 present[2]; rather, in this region it is felt that the decomposition of the $MClO_4$ salts follows essentially the reaction

$$MClO_4(s) \longrightarrow MCl(s) + 2O_2(g) \quad (10)$$

It should be noted that the $[MClO_3/MCl]$ ratios at fusion for the MnO_2-containing mixtures of Table III are lower than for the pure salts.

As the final reaction product endotherms (Figure 3, Table I) and t.g.a. weight loss data (Figure 4, Table II) indicate, the corresponding chlorides constitute the final decomposition products of the $MClO_4$ compounds. The total weight losses were corrected to account for the reaction

$$2MnO_2(s) \longrightarrow Mn_2O_3(s) + {}^1/_2O_2(g) \quad (11)$$

which is known to go to completion at about 650° under the conditions employed in the present study (Figure 4). The reaction product (Mn_2O_3) was identified by chemical and X-ray analyses.

The clear, colorless aqueous extracts from the residues of the catalyzed mixtures of Table III were qualitatively tested for water-soluble Mn by treatment with KIO_4 and dilute H_2SO_4, followed by boiling. No water-extractable Mn was found, thereby indicating that manganates and permanganates were not formed in the course of catalysis up to this point and that the catalytic action of the MnO_2 probably proceeded heterogeneously on the catalyst surface with little or no contribution from homogeneous solution catalysis, unlike the effects found for $KClO_3$–MnO_2 mixtures.[19] X-Ray powder patterns from the mixtures of Table III showed that the MnO_2 was unaltered. Similar behavior was found for the aqueous extract and residual catalyst from a $LiClO_4$–MnO_2 sample heated up to 402° and then quenched.

In another series of experiments, each of the five $MClO_4$–MnO_2 mixtures was decomposed at about 600° under flowing Ar, cooled, and then extracted with water. Only the $LiClO_4$–MnO_2 mixture showed the presence of water-soluble Mn. X-Ray powder patterns of the catalyst from this decomposed sample showed the presence of some $Mn(OH)_2$, probably stemming from the hydrolysis of $LiMnO_2$, the formation of which will be discussed in a later section; the X-ray patterns from the other catalyst residues corresponded to unchanged pyrolusite. Thus, for $NaClO_4$, $KClO_4$, $RbClO_4$, and $CsClO_4$, catalytic decomposition by MnO_2 appears to involve primarily heterogeneous effects, while in the case of $LiClO_4$ some catalyst solution effects in the melt also seem probable. It should be noted that some type of specific interaction between $LiClO_4$ and MnO_2 is indicated by the enhanced Cl_2 release during decomposition in the presence of the catalyst (Table II). This aspect will be covered in greater detail subsequently.

Chlorine Evolution from Decomposing Perchlorate Melts. As evidenced from the d.t.a. and t.g.a. studies, the preponderant decomposition reactions of the $MClO_4$ compounds are such as to follow the general equation

$$MClO_4 \longrightarrow + MCl + 2O_2 \quad (12)$$

Indeed this would be anticipated on the basis of the greater thermodynamic stabilities of the product chlorides over the equivalent oxides which would be produced by the alternate mode of decomposition as represented by

$$2MClO_4 \longrightarrow M_2O + Cl_2 + {}^7/_2O_2 \quad (13)$$

Nevertheless, as shown in the last column of Table II, reaction 13 does occur to some small extent for all but pure $RbClO_4$ and $CsClO_4$ and for all the $MClO_4$–MnO_2 mixtures except $CsClO_4$–MnO_2.

The instances of $LiClO_4$ and of the $LiClO_4$–MnO_2 sample were studied most intensively and extensively because the Cl_2 evolution phenomenon appeared greatest here. The entry of 1.22% in Table II for $LiClO_4$ represents the average of 18 determinations with an average deviation of ±0.16%. The extent of Cl_2 release appears to be relatively independent of the average rate of $LiClO_4$ decomposition. This was shown by decomposing samples of $LiClO_4$ in isothermal experiments at 50° intervals over the temperature range from 400 to 700°. In these experiments the average degree of Cl_2 evolution was 1.22 ± 0.22% (average of 11 runs). Interestingly, attempts to secure an alkali balance concordant with the Cl_2 release were unsuccessful. Thus in 12 experiments only 42.8 ± 6.2% of the Li_2O could be titrated with standard 0.1 *N* HCl, thereby suggesting attack of the silica structure of the container surfaces by the base liberated at the high temperatures.

Previous workers had found that BaO_2 was effective in eliminating Cl_2 release from burning halate and perhalate–metal fuel composites.[20,21] Accordingly, it was shown subsequently that Cl_2 release from decomposing $LiClO_4$ could be completely suppressed by the incorporation of 5 wt. % Li_2O_2 or its equivalent of Li_2O, LiOH, Na_2O_2, or Li_2CO_3. However, in silica containers such suppression was usually obtained only after the container had first been pretreated with a

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[19] J. M. Gaidis and E. G. Rochow, *J. Chem. Educ.*, **40**, 78 (1963).

[20] W. H. Schechter, R. R. Miller, R. M. Bovard, C. B. Jackson, and J. R. Pappenheimer, *Ind. Eng. Chem.*, **42**, 2348 (1950).

[21] J. F. O'Brien, *Proc. Iowa Acad. Sci.*, **66**, 194 (1959).

reaction mixture at decomposition temperatures when but about 0.2% Cl_2 was released; succeeding experiments with base-containing $LiClO_4$ in the same container always gave Cl_2-free O_2. Clearly then some interaction between the glass surface and the $LiClO_4$ is indicated. No Cl_2 was obtained from reaction of 80 mole % $LiClO_4$ (5 wt. % Li_2O_2)-20 mole % Mn mixtures when held in stainless steel vessels.[22]

D.t.a. and t.g.a. experiments showed that the presence of oxide-producing substances in $LiClO_4$ drastically reduced the thermal stability of the perchlorate. Thus, the 2% decomposition temperature of $LiClO_4$ dropped from 470 to 281° (5.0 wt. % Li_2O_2), 306° (4.35 wt. % Li_2O), 311° (8.11 wt. % Na_2O_2), 410° (5.21 wt. % LiOH), and 431° (7.89 wt. % Li_2CO_3). Except for the inversion of Li_2O_2 and Li_2O, this is the order of ease of formation of O^{2-} ions from the various anions. The decomposition accelerating effects due to the presence of base in $MClO_3$ and $MClO_4$ melts had been previously noted for $KClO_4$,[17,19] $NaClO_4$ and $NaClO_3$,[23] and $KClO_3$.[24] The promotion of $LiClO_4$ pyrolysis by Li_2O was further demonstrated in some isothermal experiments. Thus, samples containing 90 wt. % $LiClO_4$-10 wt. % Li_2O heated for 20-, 30-, and 60-min. periods at 336° under flowing Ar showed, respectively, 13.0, 56.9, and 89.2% losses of $LiClO_4$ content, whereas pure $LiClO_4$ similarly heated for 1 hr. showed no change in $LiClO_4$ assay. In addition, each of the samples containing Li_2O showed the presence of trace amounts of O_2^{2-} ion after heating as determined by the $Ti(SO_4)_2$-H_2SO_4 and $KMnO_4$ tests for H_2O_2. Similarly, a sample of 95 wt. % $LiClO_4$-5 wt. % Li_2O maintained at 275° for 16 hr. under flowing Ar was 13.2% decomposed with respect to $LiClO_4$ content; pure $LiClO_4$ under the same heating conditions is unchanged.[13] The heated $LiClO_4$-Li_2O sample was found to contain O_2^{2-} ion. Li_2O_2 itself starts to decompose rapidly at about 300° as per[25]

$$Li_2O_2(s) \longrightarrow Li_2O(s) + {}^1/_2O_2(g) \qquad (14)$$

It should be noted that the formation of O_2^{2-} ions has been conjectured to account for the catalysis of the thermal decomposition of $KClO_4$ by MgO[17] and of $NaClO_3$ and $NaClO_4$ by NaOH.[23] However, these experiments with $LiClO_4$ appear to be the first to demonstrate the formation of O_2^{2-} ions in a decomposing perchlorate melt.

Of considerable interest is the ability of Li_2O_2 additions to $LiClO_4$-MnO_2 mixtures to counterbalance the tendency for enhanced Cl_2 evolution due to the presence of the MnO_2 (Table II). Thus, but 0.20% Cl_2 was obtained from the $LiClO_4$ in a 90 mole % (5 wt. % Li_2O_2)-10 mole % MnO_2 mixture, whereas the 90 mole % $LiClO_4$-10 mole % MnO_2 mixture alone yielded 3.81% Cl_2 upon decomposition. It is known from the combustion of 80 mole % $LiClO_4$-20 mole % Mn and 80 mole % $LiClO_4$ (5 wt. % Li_2O_2)-20 mole % Mn mixtures that the final combustion product residue contains, in part, lithium manganite, $LiMnO_2$,[22] in addition to MnO and Mn_3O_4. This observation would lead to the conclusion that the promotion of Cl_2 production from $LiClO_4$ by MnO_2 is due to a specific interaction stemming from the amphoteric nature of the Mn compound so that an acid-base reaction of the type below may proceed to some extent at these elevated temperatures.

$$2LiClO_4 \text{ (or } Li_2O\cdot Cl_2O_7) + 2MnO_2 \longrightarrow 2LiMnO_2 + Cl_2 + 4O_2 \qquad (15)$$

Clearly, in the presence of added Li_2O equivalents, the Cl_2 may be removed by virtue of the combination

$$Li_2O + Cl_2 \longrightarrow 2LiCl + {}^1/_2O_2 \qquad (16)$$

or the MnO_2 may react directly with the Li_2O present,[26] *viz.*

$$Li_2O + 2MnO_2 \longrightarrow 2LiMnO_2 + {}^1/_2O_2 \qquad (17)$$

In any case, it is probably the $LiMnO_2$ that leads to the presence of water-soluble Mn in the extracts from $LiClO_4$-MnO_2 residues formed at high temperatures.

Discussion of Results

The d.t.a. curves (Figures 1 and 3) demonstrate that the thermal decompositions of $MClO_4$ compounds are exothermic, as are the decompositions of heavy metal azides and fulminates, rather than endothermic, as characterizes many other pyrolysis reactions which yield both a condensed phase residue and a gas as reaction products (*e.g.*, the decompositions of salt hydrates, hydroxides, peroxides, carbonates, sulfates, etc.). The common characteristics for such exothermic decompositions appear to be both a highly favorable negative free energy change for the reaction path manifested in contrast to the equilibrium type dissociation reactions of the endothermic decompositions (*i.e.*, $\Delta F° \cong 0$) and a change in the oxidation states

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[22] M. M. Markowitz and E. W. Dezmelyk, "A Study of the Application of Lithium Chemicals to Air Regeneration Techniques in Manned, Sealed Environments," Technical Documentary Report No. AMRL-TDR-64-1, Wright-Patterson Air Force Base, Ohio, Feb. 1964.

[23] R. P. Seward and H. W. Otto, *J. Phys. Chem.*, **65**, 2078 (1961).

[24] G. J. Fowler and J. Grant, *J. Chem. Soc.*, **57**, 272 (1890).

[25] T. V. Rode, T. A. Dobrynina, and G. A. Gol'der, *Izv. Akad. Nauk SSSR, Otd. Khim.*, 611 (1955).

[26] W. D. Johnston and R. R. Heikes, *J. Am. Chem. Soc.*, **78**, 3255 (1956).

of the constituent atoms of the disrupted anion (*viz.*, for ClO_4^-, $Cl^{7+} \rightarrow Cl^-$, and $O^{2-} \rightarrow {}^1/_2O_2$.).

The signs of the enthalpy changes accompanying the thermal breakdown of $KClO_4$ have been a matter of some dispute.[18,27] However, recently available high-temperature enthalpy data[16] have permitted more exact calculations which are in substantial agreement with the d.t.a. behavior observed in the present study. At rapid decomposition the bulk of the pyrolysis occurs through the reactions

$$KClO_4(l) \longrightarrow KCl(l) + 2O_2(g) \qquad (18)$$

and

$$KClO_4(l) \longrightarrow KCl(s) + 2O_2(g) \qquad (19)$$

The heat of formation of liquid $KClO_4$ is not known but estimated heat of formation data are available for solid $KClO_4$ up to 1500°K. Thus, the heats of reaction ($\Delta H_r°$) for the changes

$$KClO_4(s) \longrightarrow KCl(l) + 2O_2(g) \qquad (20)$$

and

$$KClO_4(s) \longrightarrow KCl(s) + 2O_2(g) \qquad (21)$$

may be computed. Taking an average reaction temperature of 900°K., $\Delta H_r°(20) = -4.50$ kcal./mole and $\Delta H_r°(21) = -10.51$ kcal./mole. Inasmuch as the change

$$KClO_4(s) \longrightarrow KClO_4(l) \qquad (22)$$

is endothermic, $\Delta H_r°(18)$ and $\Delta H_r°(19)$ will be more exothermic than $\Delta H_r°(20)$ and $\Delta H_r°(21)$ by the heat of fusion of $KClO_4$ at 900°K. Assuming a reasonably low entropy of fusion for $KClO_4$ (2.5 e.u.)[28] because of the crystallographic transition, $\Delta H_r°(22) = 2.3$ kcal./mole; thus, $\Delta H_r°(18) = -6.8$ kcal./mole and $\Delta H_r°(19) = -12.8$ kcal./mole. As noted earlier, $\Delta H_r°(18) \cong -\Delta H°_{\text{fusion}}(KCl) \cong -6$ kcal./mole.

It is of interest to contrast the thermal behavior of $MClO_4$ compounds with that of the corresponding $MClO_3$ salts.[2,15] Thus, the latter possess congruent melting points whereas the former, except for $LiClO_4$, concomitantly fuse and decompose. Both $LiClO_4$ and $LiClO_3$, however, manifest the longest intervals between congruent melting and the onset of rapid decomposition when compared with the other alkali metal derivatives. It seems clear then that the melting points observed for $NaClO_4$, $KClO_4$, $RbClO_4$, and $CsClO_4$ are functions of the extents of decomposition up to the liquidus temperatures observed and as such are dependent on the experimental techniques employed and the thermal history of the samples used.[7]

Rapid decomposition of the heavier $MClO_4$ salts sets in after fusion of the solid perchlorates for both the pure materials (Figure 1, Table I) and for the $MClO_4$–MnO_2 mixtures (Figure 3, Table I). This type of behavior would indicate that increased anion mobility facilitates the pyrolytic processes, as pointed out in an earlier study.[5] The d.t.a. data give the order of thermal stability of the perchlorates as Li < Na < Cs < K < Rb, which conforms to the order of their fusion temperatures rather than to the inverse order of polarizing power or ionic potential of the cation. However, it may be seen that the degree of differentiation of thermal stability among $KClO_4$, $RbClO_4$, and $CsClO_4$ is small, despite the appreciable variation in cation size in proceeding from K^+ (1.33 Å.) to Cs^+ (1.65 Å.), so that the order Li < Na < K, Rb, Cs seems most generally appropriate. This is the conclusion reached from a similar study of the five $MClO_3$ compounds[2,15] and suggests that for both chlorate and perchlorates a leveling effect in polarizing power occurs among the M^+ ions for values of the ionic potential at and below that of K^+.

As would be anticipated, the $MClO_4$ salts are thermally more stable than the corresponding chlorates.[2,15] Consequently, but small quantities of chlorate are formed in the course of $MClO_4$ pyrolysis,[7,12,14,17,29] whereas the converse is true during the thermal decompositions of $MClO_3$ compounds. Indeed, such behavior would tend to substantiate that the equilibrium

$$MClO_4 \longrightarrow MClO_3 + {}^1/_2O_2 \qquad (23)$$

tends to lie to the left as indicated by thermodynamic considerations.[15] Furthermore, the smooth continuous nature of the perchlorate decomposition exotherms tends to rule out any substantial accumulation of $MClO_3$ intermediate.

As with the pure $MClO_4$ compounds, the order of thermal stability of the MnO_2-containing samples is best expressed as Li < Na < K, Rb, Cs. Qualitatively, the catalytic effects of MnO_2 appear to be less pronounced with the $MClO_4$ salts than with the $MClO_3$ compounds. Thus, for example, for $NaClO_4$, $KClO_4$, $RbClO_4$, and $CsClO_4$ the 2% decomposition temperatures are reduced about 100° whereas for the chlorates[2] the reduction is about 150° in the presence of MnO_2. In either instance, however, the mechanisms of the

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(29) A. Glasner and L. Weidenfeld, *J. Am. Chem. Soc.*, **74**, 2462, 2467 (1952).

catalysis appear obscure at present. Thus, it has been suggested that a manganese chlorate or perchlorate is alternately formed and decomposed in the catalytic process.[7] However, the decomposition of a manganese perchlorate ($Mn(ClO_4)_2$ or $Mn(ClO_4)_4$) would be expected to yield MnO_2 as a reaction product and thereby promote abundant evolution of Cl_2 as per reactions 24 and 25,[30] a circumstance which has been shown not to prevail. Currently proposed mechanisms

$$Mn(ClO_4)_2 \longrightarrow MnO_2 + Cl_2 + 3O_2 \qquad (24)$$

$$Mn(ClO_4)_4 \longrightarrow MnO_2 + 2Cl_2 + 7O_2 \qquad (25)$$

for perchlorate decompositions appear to favor the production of O atoms as the primary pyrolytic step, *viz.*[5,14,17,29,31]

$$MClO_4 \longrightarrow MClO_3 + O \qquad (26)$$

Accordingly, it seems possible that the role of MnO_2 as a catalyst is to favor the abstraction of atomic O, perhaps by formation of some transient peroxide derivative as is formed with the more basic oxides such as Li_2O and MgO. These more basic materials seem to function as more efficient catalysts for perchlorate decomposition than does MnO_2 as clearly demonstrated in the present study with $LiClO_4$ through the postulated reaction sequence

$$LiClO_4 + Li_2O \longrightarrow LiClO_3 + Li_2O_2 \qquad (27)$$

$$Li_2O_2 \longrightarrow Li_2O + {}^1/_2O_2 \qquad (28)$$

$$LiClO_3 \longrightarrow LiCl + {}^3/_2O_2 \qquad (29)$$

Virtually no information appears to be available concerning the catalytic activity of MnO_2 as a function of its structural properties (*e.g.*, surface area and crystal form). Furthermore, a clear resolution between heterogeneous and homogeneous catalytic effects remains to be performed, although this investigation indicates homogeneous solution effects to be important only in the $LiClO_4$–MnO_2 system.

In addition to O^{2-} ion catalysis of the pyrolyses of $LiClO_4$, $KClO_4$,[17] and $NaClO_4$,[23] there are a number of other pieces of evidence pointing to the existence of O atoms during the decompositions of $MClO_4$ salts. The direct transfer of O atoms to Mn metal is suggested by the formation of Mn_3O_4 in an 80 mole % $LiClO_4$–20 mole % Mn mixture maintained for several hours at 225°. The oxidation of the metal occurs apparently without liquid phase formation and without any loss in system weight.[32] The formation of reactive O atoms would also help to explain the low temperature pre-ignition reactions observed between $KClO_4$ and various carbonaceous fuels where rapid oxidation is found to occur considerably below the normal range of decomposition temperatures of the oxidant.[33] Furthermore, the oxidation of bromides and iodides to the respective halates by $KClO_4$[29,34] without appreciable O_2 evolution points to direct O-transfer reactions. The inability to oxygenate chlorates to perchlorates by high-pressure treatment with molecular O_2[15,35] despite the favorable thermodynamic potential for such reactions would indicate the need for the participation of a kinetically more reactive form of oxygen to achieve the conversion.[31] In this same regard, it should be pointed out that despite the thermodynamic potential for oxygenation of Li_2O by molecular O_2 at moderate pressures, it has not been possible to bring about this reaction by application of even very high pressures of O_2, whereas the peroxygenation of Li_2O can be performed in decomposing $LiClO_4$ melts as demonstrated here. Thus, an appreciable body of chemical evidence exists to support the kinetic view for the presence of O atoms in decomposing perchlorates.[14,17,29,31]

For the pure $MClO_4$ salts the degree of Cl_2 release during decomposition follows the order $Li \gg Na > K > Rb, Cs = 0$ (Table II). Of all the $MClO_4$ compounds, $LiClO_4$ is the only one for which conversion to oxide (reaction 13) is thermodynamically possible as well as the more familiar decomposition to chloride by reaction 12.[36] The preponderant occurrence of reaction 12 over reaction 13 is due to the greater thermodynamic stabilities of the MCl compounds relative to the equivalent oxides.[36] However, the mechanism by which the small amount of Cl_2 is formed from the decomposing $MClO_4$ compounds merits some further consideration. The presence of O atoms may cause a reaction such as

$$2Cl^- + O \longrightarrow Cl_2 + O^{2-} \qquad (30)$$

A more general explanation might be based on the autoionization of perchlorate melts, much as occurs with molten nitrates[37,38]

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$$NO_3^- \rightleftarrows NO_2^+ + O^{2-} \qquad (31)$$

Thus, for the perchlorates the self-ionization equilibrium might be represented as

$$ClO_4^- \rightleftarrows ClO_3^+ + O^{2-} \qquad (32)$$

and Cl_2 evolution would then ensue by the reaction

$$ClO_3^+ + ClO_4^- \longrightarrow [Cl_2O_7] \longrightarrow Cl_2 + {}^7/_2O_2 \qquad (33)$$

Such a mechanism would also be consistent with the oxide-donating or basic properties of perchlorates, so that an O^{2-} ion acceptor or acid would move reaction 32 to the right and thus increase the rate and extent of reaction 33. A number of investigators have noted that catalysts for $MClO_3$ and $MClO_4$ decompositions can generally be divided into two categories: oxide catalysts (*e.g.*, Fe_2O_3, MnO_2, Bi_2O_3, CuO, SnO_2, etc.) which yield substantially Cl_2-free O_2 and oxide catalysts (*e.g.*, P_2O_5, B_2O_3, WO_3, MoO_3, V_2O_5, etc.) which cause much Cl_2 production. It now seems clear that the first group of materials represents true catalytic agents while the second group of substances are polymeric acids, capable of O^{2-} ion capture and thus enter into specific, irreversible chemical reactions with the Cl-containing oxy anions.

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Remarks on Refractive Index Mixture Rules

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The most important refractive index mixture rules used for determining the refractive index of a solute are scrutinized regarding their relative merits and interrelations. The Dale–Gladstone and the Biot–Arago equations are found to follow from either the Lorentz–Lorenz equation or the Wiener equation if the solution is dilute and if, in addition, the refractive indices of solute and solvent are nearly the same. A mixture rule proposed by the writer represents the limiting form of the Wiener equation in case of dilute solutions without restriction as to the value of the refractive indices. The performance of all equations is tested on literature data. The results are in line with expectation on the basis of theoretical analysis. The special case of solutes of colloidal dimensions, where none of the equations applies satisfactorily, is briefly discussed.

It is often desirable to know the refractive index of a solute. This index can be derived from the refractive indices of solution and solvent on using a suitable "mixture rule." There are several available. Little is known about the conditions under which each may usefully be applied nor about their interrelation. The present paper deals with both problems.

I. The Principal Mixture Rules. Omitting mixture rules of minor significance one has the choice among eq. 1–5. Here, n_{12}, n_1, and n_2 are the refrac-

$$\frac{n_{12}^2 - 1}{n_{12}^2 + 2} = \phi\frac{n_1^2 - 1}{n_1^2 + 2} + \phi_2\frac{n_2^2 - 1}{n_2^2 + 2} \qquad (1)$$

$$\frac{n_{12}^2 - n_1^2}{n_{12}^2 + 2n_1^2} = \phi_2\frac{n_2^2 - n_1^2}{n_2^2 + 2n_1^2} \qquad (2)$$

$$\frac{n_{12} - n_1}{n_1} = \frac{3}{2}\phi_2\left(\frac{m^2 - 1}{m^2 + 2}\right) \qquad (3)$$

$$(n_{12} - 1) = \phi_1(n_1 - 1) + \phi_2(n_2 - 1) \qquad (4)$$