Thermoanalysis of Binary Systems

Potassium Perchlorate–Alkali and Alkaline Earth Metal Nitrates

VIRGINIA D. HOGAN and SAUL GORDON[1]
Pyrotechnics Chemical Research Laboratory, Picatinny Arsenal, Dover, N. J.

A THERMOANALYTICAL STUDY of several binary oxidant systems consisting of potassium perchlorate and selected nitrates of alkali and alkaline earth metals was undertaken as a continuation of the work begun with the thermoanalysis of the potassium perchlorate–barium nitrate mixture (*3, 4, 5*). The thermograms of these systems exhibit inflections which indicate phenomena, such as crystalline transitions, fusion, eutectic fusion, and decomposition, that can be attributed to the physico-chemical behavior of the ingredients and their mixtures. The thermal instability of the mixtures precludes the use of cooling techniques; consequently, heating curves obtained via differential thermal analysis (DTA) were used to determine the compositions of the two potassium perchlorate–alkaline earth metal nitrate eutectic mixtures and, in conjunction with thermogravimetry, to account for most of the major thermal phenomena occurring in these systems. A detailed explanation of all of the thermal phenomena indicated by the thermogravimetric and differential thermal analysis heating curves has not been attempted. Temperature discrepancies between the DTA and thermogravimetric curves can usually be accounted for by the fact that in differential thermal analysis the sample temperature is measured, while in thermogravimetric analysis it is the furnace temperature which is measured. Of more fundamental inportance is the fact that DTA indicates a variety of thermal effects which do not have concomitant mass effects—e.g., crystalline transition and fusion.

REAGENTS

The reagents used were: potassium perchlorate, lithium nitrate, analytical reagent (J.T. Baker Chemical Co.); calcium nitrate tetrahydrate, analytical reagent (Mallinckrodt Chemical Works); sodium and strontium nitrates, C.P., potassium chloride and nitrate, analytical reagent (Fisher Scientific Co.); rubidium nitrate, C.P. (A.D. Mackay, Inc.); cesium nitrate, C.P. (Foote Mineral Co.); calcium chloride, anhydrous, reagent, and strontium chloride hexahydrate, C.P. (Merck & Co., Inc.). The calcium nitrate tetrahydrate was dehydrated at 320° C. and the strontium chloride hexahydrate, at 110° C. The binary mixtures were prepared by weighing out sufficient quantities of the ingredients to make 10 to 50 grams of each mixture and blending them with a mortar and pestle. The samples for the individual determinations were taken from the bulk supply.

INSTRUMENTATION AND PROCEDURES

The differential thermal analysis (DTA) apparatus and thermobalance have been described (*2, 3*). Four-gram samples were used for the differential thermal analyses, with the exception of strontium nitrate–potassium perchlorate mixtures, for which 5-gram samples were required. An equal volume of alumina served as the thermally inert reference material. The DTA curves are a record of the temperature difference between the sample and reference materials as a function of the temperature of the sample. The sample and differential temperatures are measured with B & S No. 28 gage Chromel-Alumel thermocouples at sensitivities of 4.0 and 0.5 mv. per inch, respectively. Conventionally, the zero of differential temperature is placed at the center of the record so that endothermal reactions appear as downward deflections; exothermal reactions are deflected upward. The zero of differential temperature—i.e., the baseline—does not always remain constant during a run. It is displaced if the thermal conductivity of the sample changes on heating and if the position of the thermocouple changes as a result of fusion or decomposition of the solid sample. During the decomposition of perchlorate ion in potassium perchlorate and potassium perchlorate-containing mixtures the bubbling and frothing characteristic of the oxygen evolution often displaces the sample from the thermocouple resulting in erratic traces and ill-defined reaction temperatures. The thermogravimetric curves are records of the changes in weight of the 350-mg. samples as a function of furnace temperature, with a full-scale change-in-weight range of 200 mg. In both of these thermoanalytical techniques, the furnace is programmed for a nominal linear heating rate of 15° C. per minute.

As shown in Figures 4 and 7 to 11, both the thermogravimetric and differential thermal analyses of the potassium perchlorate mixtures, with the exception of the 70% calcium nitrate system, were terminated prior to the completion of nitrate decomposition.

RESULTS AND DISCUSSION

Thermoanalytical curves for the ingredients are given in Figures 1 to 3. The thermogravimetric curves shown in these figures confirm the general conclusions reached by Gordon and Campbell in a detailed study of DTA phenomena exhibited by these compounds (*2*). Data from these curves are summarized in Table I. The stoichiometry for the thermogravimetric curves indicates that lithium, sodium, potassium, calcium, and strontium nitrates decompose to their respective oxides at elevated temperatures, while potassium perchlorate decomposes to potassium chloride. However, the magnitude of the weight losses exhibited by rubidium and cesium nitrates cannot be simply accounted for by the stoichiometry of the thermogravimetric curves.

Stable salt pairs in the respective reciprocal systems were established experimentally. A binary mixture of potassium perchlorate with sodium nitrate was heated to a clear melt, cooled, and analyzed by x-ray diffraction. This analysis showed that only the original salts were present after the heat treatment indicating that this is the stable salt pair. Repeated differential thermal analysis was used to identify the stable salt pairs in the potassium perchlorate–alkaline earth metal nitrate systems and the remaining potassium perchlorate–alkali metal nitrate systems. DTA heating curves for mixture samples of the following per cent ratios, 55 to 45 potassium perchlorate–calcium nitrate, 60 to 40 potassium perchlorate–strontium nitrate, and 70 to 30 potassium perchlorate–lithium nitrate and similar curves for the same samples after they have been melted and cooled to room temperature are unchanged, indicating that these

[1] Present address Chemistry Department, Fairleigh Dickinson University, Madison, N. J.

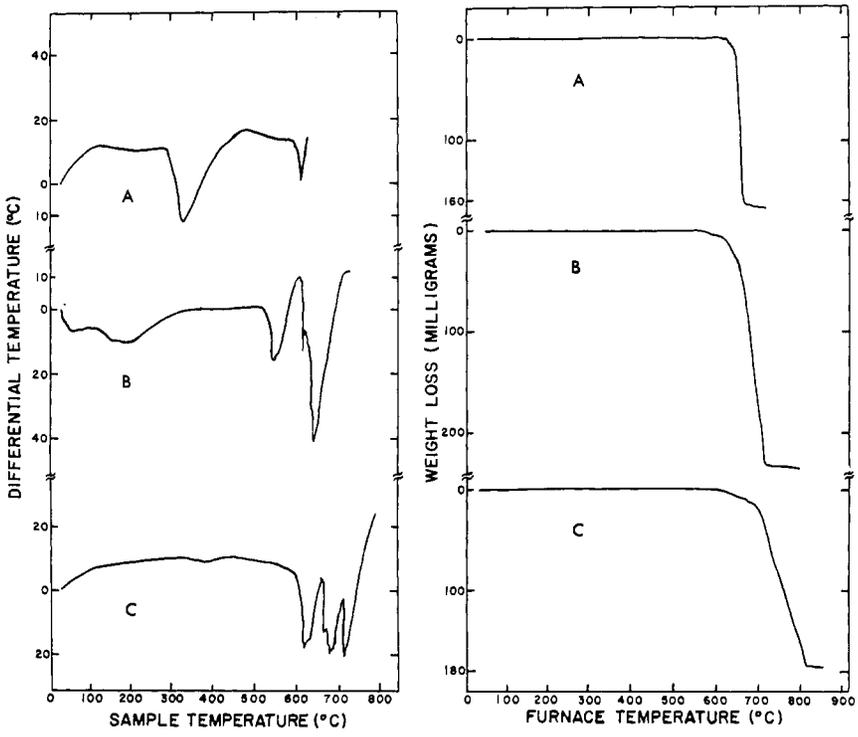


Figure 1. Differential thermal analysis and thermogravimetric curves for potassium perchlorate and the alkaline earth metal nitrates

A. Potassium perchlorate
B. Calcium nitrate
C. Strontium nitrate

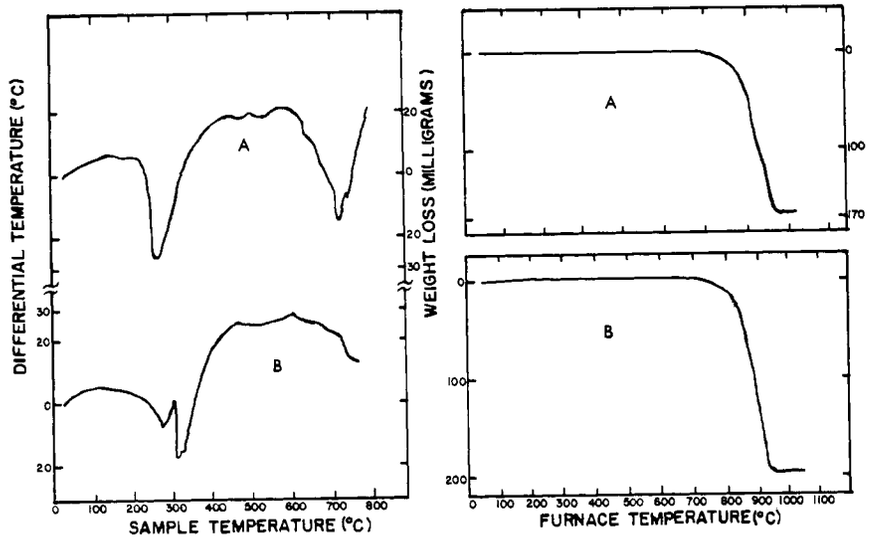


Figure 2. Differential thermal analysis and thermogravimetric curves for the alkali metal nitrates

A. Lithium nitrate
B. Sodium nitrate

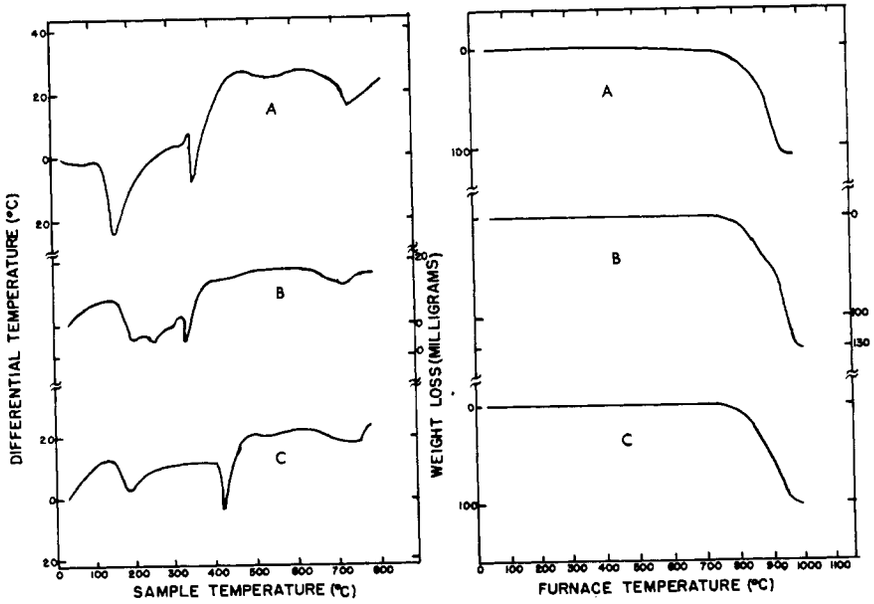
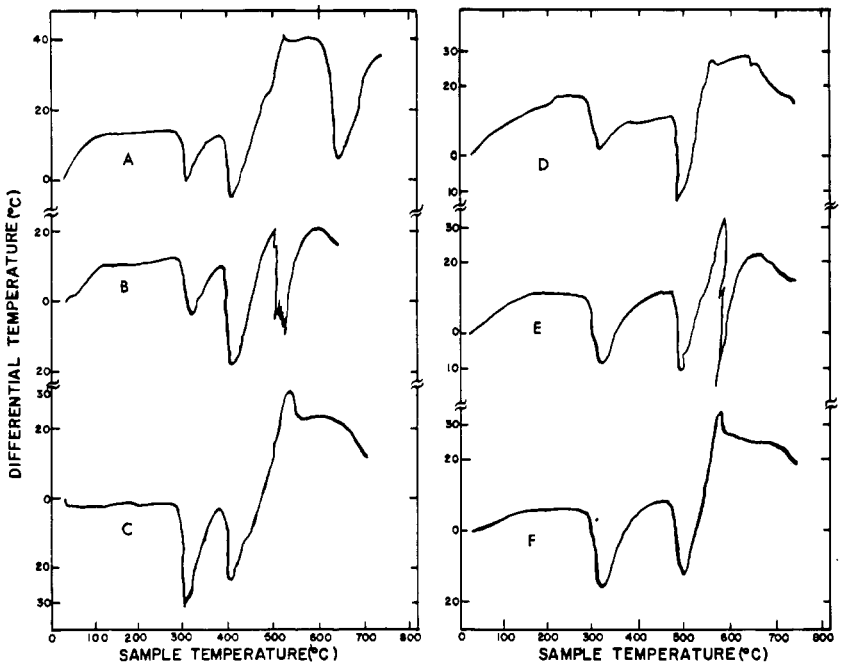


Figure 3. Differential thermal analysis and thermogravimetric curves for the alkali nitrates

A. Potassium nitrate
B. Rubidium nitrate
C. Cesium nitrate

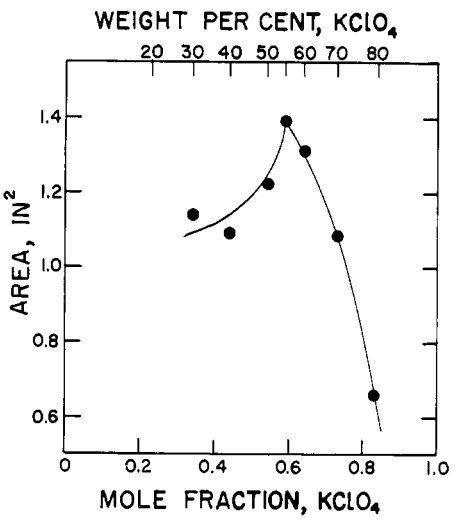


←

Figure 4. Representative differential thermal analysis curves for the binary potassium perchlorate-alkaline earth metal nitrate systems

Curve	%	Mole fraction	$M(NO_3)_2$[a], %
Binary $KClO_4$-$Ca(NO_3)_2$ Compositions			
A	30	0.34	70
B	55	0.59	45
C	70	0.73	30
Binary $KClO_4$-$Sr(NO_3)_2$ Campositions			
D	30	0.40	70
E	60	0.70	40
F	70	0.78	30

[a] M = metal.

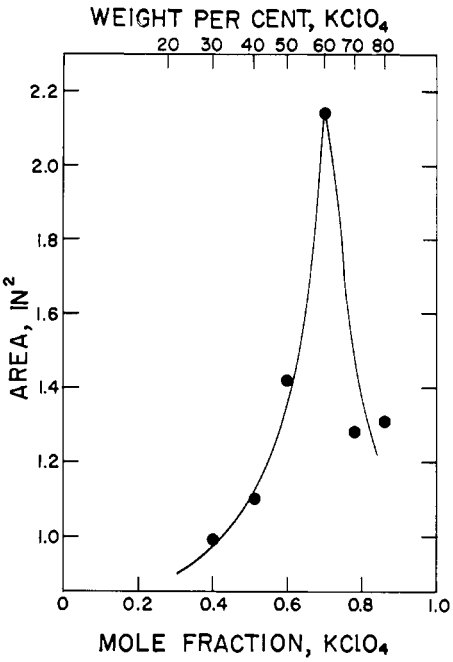


←

Figure 5. Determination of the eutectic composition in the potassium perchlorate/calcium nitrate system from the area of the fusion endotherms at 400° C. on a series of differential thermal analysis curves

→

Figure 6. Determination of the eutectic composition in the potassium perchlorate/strontium nitrate system from the area of the fusion endotherms at 490° C. on a series of differential thermal analysis curves

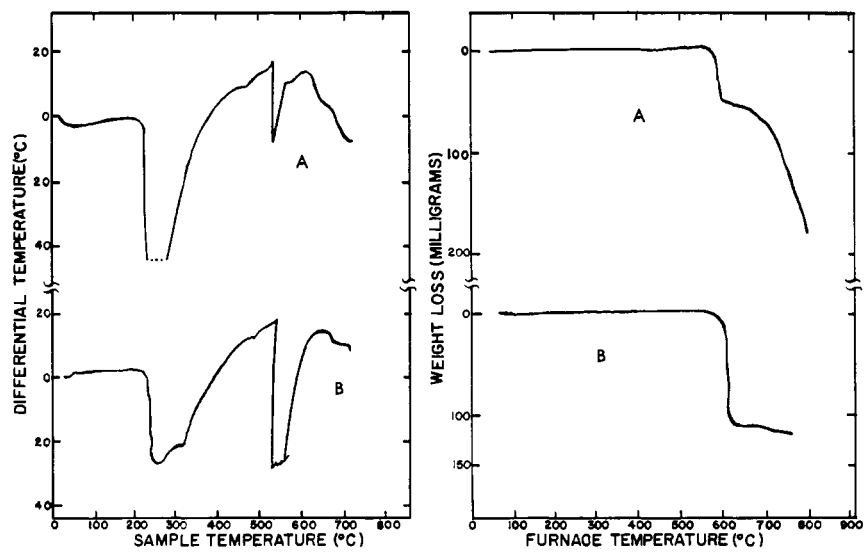


→

Figure 7. Representative differential thermal analysis and thermogravimetric curves for the binary system potassium perchlorate/lithium nitrate

A. 30% (0.18 mole fraction) potassium perchlorate/70% lithium nitrate

B. 70% (0.54 mole fraction) potassium perchlorate/30% lithium nitrate



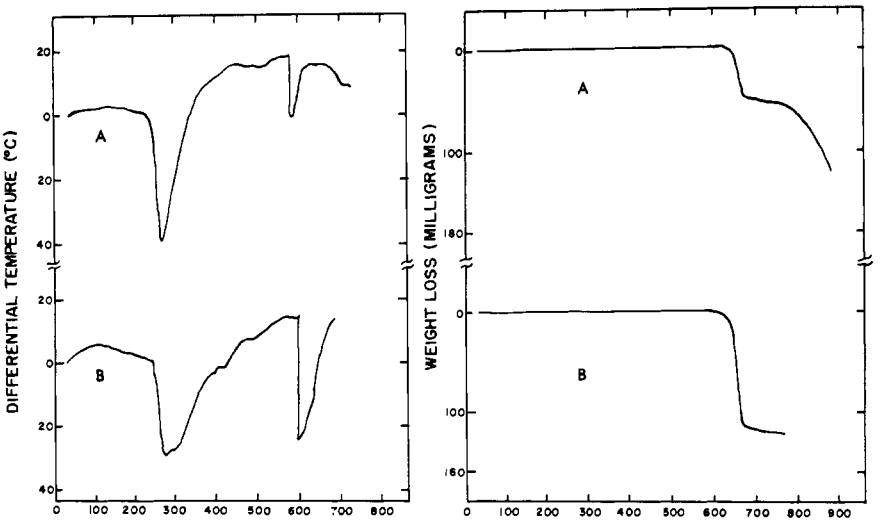


Figure 8. Representative differential thermal analysis and thermogravimetric curves for the binary system potassium perchlorate/sodium nitrate

A. 30% (0.21 mole fraction) potassium perchlorate/70% sodium nitrate

B. 70% (0.59 mole fraction) potassium perchlorate/30% sodium nitrate

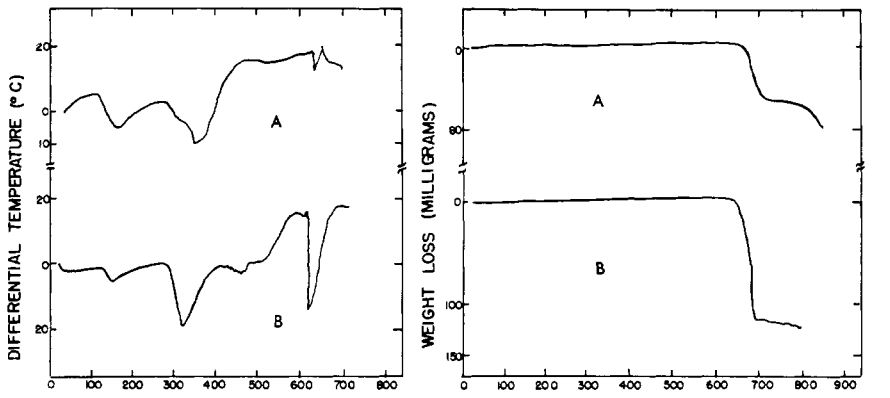


Figure 9. Representative differential thermal analysis and thermogravimetric curves for the binary system potassium perchlorate/potassium nitrate

A. 30% (0.24 mole fraction) potossium perchlorate/70% potassium nitrate

B. 70% (0.63 mole fraction) potassium perchlorate/30% potassium nitrate

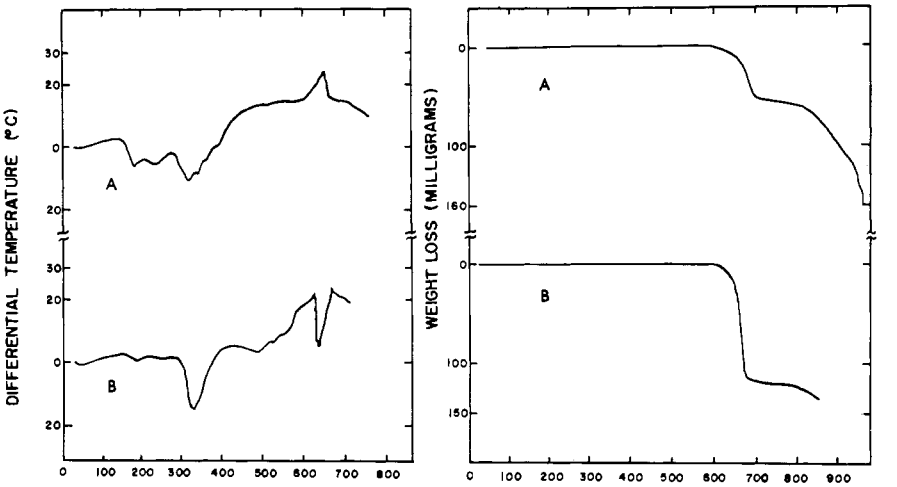


Figure 10. Representative differential thermal analysis and thermogravimetric curves for the binary system potassium perchlorate/rubidium nitrate

A. 30% (0.31 mole froction) potassium perchlorate/70% rubidium nitrate

B. 70% (0.71 mole fraction) potassium perchlorate/30% rubidium nitrate

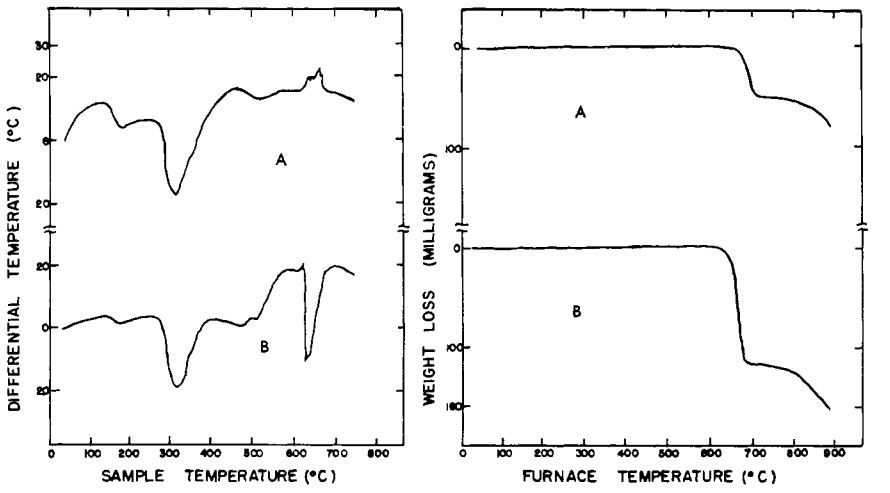


Figure 11. Representative differential thermal analysis and thermogravimetric curves for the binary system potassium perchlorate/cesium nitrate

A. 30% (0.38 mole fraction) potassium perchlorate/70% cesium nitrate

B. 70% (0.77 mole fraction) potossium perchlorate/30% cesium nitrate

Table I. Thermoanalytical Data (DTA and TGA) for Ingredients

Compound	Crystalline Transition, ° C. DTA band width[a]	Crystalline Transition, ° C. Reported value[b]	Fusion, ° C. DTA band width[a]	Fusion, ° C. Reported value[b]	Decomposition, ° C. DTA band width[a]	Decomposition, ° C. TGA[c]
$KClO_4$	290–335	300	600–615	525	...	630–675
$LiNO_3$	...	...	235–270	251.4	625–725	580–775
$NaNO_3$	150–280	250–275	310–315	305.5	625–760	700–955
KNO_3	120–155	128	345–355	333	655–735	670–960
$RbNO_3$	155–200	161	325–330	305	645–705	765–995
	230–250	219				
$CsNO_3$	145–180	161	405–420	407	635–735	740–960
$Ca(NO_3)_2$	...	...	520–550	561	610–645	570–720
$Sr(NO_3)_2$	...	...	570–620	615	630–785	590–820

[a] Temperature range, initial departure from baseline to peak. [b] References (*1, 2, 6, 9*). [c] Temperature range from initial weight loss to nominally constant weight plateau.

are the stable salt pairs. However, the DTA heating curves for samples of 50 to 50 potassium perchlorate–rubidium nitrate and 50 to 50 potassium perchlorate–cesium nitrate and duplicate curves for these same samples after they have been melted and immediately cooled to room temperature are distinctly different. X-ray diffraction analysis of these cooled melts shows the presence of all four metathetically related salts—i.e., the 50 to 50 potassium perchlorate–rubidium nitrate melt contains potassium nitrate and rubidium perchlorate, as well as some potassium perchlorate and rubidium nitrate; and the 50 to 50 potassium perchlorate–cesium nitrate melt contains potassium nitrate and cesium perchlorate, as well as some potassium perchlorate and cesium nitrate. Occurrence of the metathetical reactions indicates that the stable systems, when the melts are quenched, consist of the respective equilibrium mixtures of four metathetically related salts—i.e., these two systems do not have stable salt pairs.

The DTA curves for mixtures of potassium perchlorate with calcium and strontium nitrates, represented by the curves in Figure 4, each show an endothermal peak which cannot be assigned to any of the thermal reactions exhibited by the ingredients. These endotherms occur at approximately 400° C. for calcium nitrate mixtures and approximately 490° C. for strontium nitrate mixtures. Since partial melting is observed while these endotherms are occurring, the heat absorption must be due to the fusion of eutectic mixtures. The DTA and thermogravimetric data for these systems are summarized in Table II.

This thermal behavior, eutectic fusion immediately preceding catalyzed perchlorate decomposition, is like that of the potassium perchlorate–barium nitrate system (*3*). The molar compositions of the eutectic mixtures of potassium perchlorate with calcium nitrate and of potassium perchlorate with strontium nitrate were determined by planimetering the areas of the eutectic fusion endotherms on the DTA curves for series of mixtures. Area *vs.* composition curves are shown in Figures 5 and 6. In the potassium perchlorate–calcium nitrate system, the eutectic composition occurs at approximately 55% potassium perchlorate by weight, corresponding to 0.59 mole fraction of potassium perchlorate. The eutectic composition of the potassium perchlorate–strontium nitrate system occurs at approximately 60% by weight of potassium perchlorate, corresponding to 0.70 mole fraction of potassium perchlorate. The corresponding values for the barium nitrate–

Table II. Differential Thermal Analysis and Thermogravimetric Data

Composition $KClO_4$-$M(NO_3)_2$,[b] %	Mole Fraction of $KClO_4$	Endothermic DTA Bands, Temp., ° C.[a] $KClO_4$ transition	Endothermic DTA Bands, Temp., ° C.[a] Partial melting, eutectic fusion	Perchlorate Decompn., TGA Temp., ° C.[c]	Perchlorate Decompn., TGA Weight Loss, % Calcd.	Perchlorate Decompn., TGA Weight Loss, % Exptl.	NO_3^- Decompn. Temp., ° C., TGA[d]
Binary Potassium Perchlorate–Calcium Nitrate Compositions							
30/70	0.34	290–310	390–405	540–565	13.9	14.0	610
40/60	0.44	290–315	385–400	560–580	18.5	18.5	650
50/50	0.54	285–305	385–415	...	...	...	...
55/45	0.59	290–320	390–410	525–565	25.4	25.2	630
60/40	0.64	285–320	390–420	...	...	...	...
70/30	0.73	290–310	385–410	520–570	32.3	31.5	665
80/20	0.83	285–320	390–410	...	...	...	...
Binary Potassium Perchlorate–Strontium Nitrate Compositions							
30/70	0.40	295–320	475–495	570–590	13.9	13.3	690
40/60	0.51	290–320	470–495	565–595	18.5	18.3	705
50/50	0.60	280–320	470–490	565–595	23.1	23.1	710
55/45	0.65	290–325	475–490	565–595	25.4	24.9	695
60/40	0.70	290–325	470–495	...	...	...	...
65/35	0.74	290–320	470–490	575–615	30.0	29.7	720
70/30	0.78	290–325	470–495	565–600	32.3	32.4	725
80/20	0.86	...	...	575–620	37.0	36.4	650

[a] Temperature range, initial departure from baseline to endothermic peak. [b] M = metal. [c] Temperature range, initial weight loss to nominally constant weight plateau. [d] Temperature of initial departure from nominally constant weight plateau corresponding to perchlorate decomposition. Experiment terminated before completion of nitrate decomposition.

Table IV. Differential Thermal Analysis and Thermogravimetric Data for Binary Potassium Perchlorate–Alkali Metal Nitrate Compositions

Compn.		Endothermic DTA Bands		Fusion, ° C.[b]		Bubbling Reaction	ClO_4^- Decompn., TGA			
% $KClO_4/LiNO_3$	Mole Fraction of $KClO_4$	Temp., ° C.[a]	Observations	Partial	Complete	° C[b]	Temp., ° C.[c]	Wt. calcd.	Loss, % exptl.	NO_3^- temp., ° C.[d]
30/70	0.18	230–240[e]	Partial melting, eutectic fusion	235	450	520	575–600	13.9	16.1	665
70/30	0.54	225–265	Partial melting, eutectic fusion $LiNO_3$ m.p., 251° C.	380	450	515	580–640	32.3	32.2	720
$KClO_4/NaNO_3$										
30/70	0.21	230–265	Partial melting, eutectic fusion	260	485	545	625–680	13.9	14.3	780
70/30	0.59	240–275	Partial melting, eutectic fusion	265	480	520	620–680	32.3	33.2	750
$KClO_4/KNO_3$										
30/70	0.24	120–160	KNO_3 tr.(transition)	365	450	530	655–710	13.9	15.1	805
		290–350	$KClO_4$ tr. p., 300° C. Partial melting, eutectic fusion. KNO_3 m.p. 333° C.							
70/30	0.63	120–145	KNO_3 tr.	510	540	545	640–695	32.3	34.1	>785
		290–325	$KClO_4$ tr. KNO_3 m.p., 333° C.							
		435–465	...							
$KClO_4/RbNO_3$										
30/70	0.31	145–180	$RbNO_3$ tr.	415	450	510	605–705	13.9	15.1	795
		215–235	$RbNO_3$ tr.							
		290–320	$KClO_4$ tr. $RbNO_3$ m.p., 305° C.							
50/50	0.52	150–185	$RbNO_3$ tr.	...	...	...	...	...	...	...
		220–240	$RbNO_3$ tr.							
		285–320	$KClO_4$ tr. $RbNO_3$ m.p., 305° C.							
70/30	0.71	155–185	$RbNO_3$ tr.	555	565	570	615–685	32.3	33.2	785
		220–245	$RbNO_3$ tr.							
		290–330	$KClO_4$ tr. $RbNO_3$ m.p., 305° C.							
		415–485	...							
		515–530	...							
$KClO_4/CsNO_3$										
30/70	0.38	140–175	$CsNO_3$ tr.	400	485	515	650–710	13.9	13.7	810
		265–320	$KClO_4$ tr. p., 300° C.							
		480–515	Slight bubbling							
50/50	0.59	140–165	$CsNO_3$ tr.	...	...	...	...	...	...	...
		265–300	$KClO_4$ tr. p., 300° C.							
		425–430	$CsNO_3$ m.p., 407° C.							
70/30	0.77	135–170	$CsNO_3$ tr.	525	550	525	630–690	32.3	33.2	795
		265–315	$KClO_4$ tr. p., 300° C.							
		425–475	$CsNO_3$ m.p., 407° C.							
		505–510	...							

[a] Temperature range, initial departure from baseline to peak. [b] Observed in DTA. [c] Temperature range from initial weight loss to nominally constant weight plateau. [d] Temperature of initial departure from nominally constant weight plateau corresponding to perchlorate decomposition. Experiment terminated before completion of nitrate decomposition. [e] This value approximate as peak of curve is off-scale.

Table III. Thermogravimetric Evidence for Thermal Stabilization of the Nitrate Ion by the Potassium Ion in the $KClO_4/Ca(NO_3)_2$ and $KClO_4/Sr(NO_3)_2$ Systems

Compounds	% of NO_3^- Compd.	Mole Fraction of NO_3 Compd.	Decompn. Temp. Range, ° C.[a]
KNO_3	...	...	670–960
$Sr(NO_3)_2$	...	...	590–820
$Ca(NO_3)_2$	...	...	570–720
KCl-KNO_3	58	0.5	700–>955
$SrCl_2$-$Sr(NO_3)_2$	57	0.5	560–825
$SrCl_2$-KNO_3	56	0.66	650–>850
KCl-$Sr(NO_3)_2$	59	0.33	640–>945
$CaCl_2$-KNO_3	65	0.66	610–>875
KCl-$Ca(NO_3)_2$	52	0.33	610–>860

[a] From initial weight loss to nominally constant weight plateau. In some cases the experiment was terminated before this plateau was reached.

potassium perchlorate eutectic mixture are 52% potassium perchlorate, a mole fraction of 0.66.

As in the case of the potassium perchlorate–barium nitrate system, the DTA curves of the potassium perchlorate–calcium nitrate and potassium perchlorate–strontium nitrate systems show that the mixtures which most closely approach the eutectic compositions exhibit strongly endothermic perchlorate decomposition in contrast to the marked exothermicity observed with pure potassium perchlorate (Figure 1) and with other mixtures (Figure 4). These phenomena can be accounted for by the solubility considerations that were discussed in connection with the potassium perchlorate–barium nitrate system (*3*), and by the anomalous effects which occur during perchlorate ion decomposition.

A further point of similarity between the barium nitrate system and the systems containing calcium and strontium nitrates is the DTA and thermogravimetric evidence that the temperature range over which the rate of decomposition of the nitrate ion becomes appreciable is raised by the presence of potassium chloride. The thermogravimetric decomposition temperature ranges for potassium nitrate, strontium nitrate, calcium nitrate, and the stoichiometrically related binary compositions of potassium nitrate with potassium chloride, strontium nitrate with strontium chloride, strontium nitrate with potassium chloride, strontium chloride with potassium nitrate, calcium nitrate with potassium chloride, and calcium chloride with potassium nitrate are listed in Table III. These data show that the chloride-nitrate mixtures containing both alkali and alkaline earth metal cations, while thermally less stable than potassium nitrate, are thermally more stable than their respective alkaline earth metal nitrates. Since potassium chloride raises the decomposition temperature range of potassium nitrate, and strontium chloride lowers that of strontium nitrate, the alkali metal cation appears responsible for the thermal stabilization effect observed in these mixtures (*3*).

The thermoanalytical curves for binary mixtures of potassium perchlorate with the alkali metal nitrates are illustrated in Figures 7 through 11. The data are summarized in Table IV. Low temperature endotherms of the lithium and sodium nitrate systems begin below the melting points of the nitrates as well as below the transition temperature of potassium perchlorate. This suggests that, when mixed with potassium perchlorate, these nitrates form eutectic mixtures that melt at approximately 230° and 245° C., respectively.

All of the binary alkali metal nitrate mixtures, with the exception of those containing 70% rubidium and cesium nitrates, exhibit sharply defined endothermal loss of oxygen from perchlorate ion. Weakly exothermal perchlorate decomposition is apparently peculiar to the nitrate-rich binary mixtures of potassium perchlorate with rubidium and cesium nitrates. This indicates that, with these two exceptions, the chlorides formed may be sufficiently soluble in the melts to prevent immediate "freezing out," a phenomenon which cannot be readily distinguished from exothermal decomposition (*7*). The bubbling and frothing effect in perchlorate ion decompositions may account for the lack of smoothness of the decomposition bands.

Unlike the other potassium perchlorate–alkali and alkaline earth metal nitrate mixtures, the potassium perchlorate–rubidium nitrate and potassium perchlorate–cesium nitrate mixtures show no definite endotherms at the reported melting points of the nitrates and, except for the cesium nitrate–rich mixture, partial melting is not observed until temperatures appreciably above these melting points are reached.

LITERATURE CITED

(1) Borchardt, H.J., Daniels, Farrington, *J. Phys. Chem.* **61**, 917–21 (1957).
(2) Gordon, Saul, Campbell, Clement, *Anal. Chem.* **27**, 1102–9 (1955).
(3) Hogan, V.D., Gordon, Saul, *J. Phys. Chem.* **62**, 1433–5 (1958).
(4) *Ibid.*, **63**, 93–6 (1959).
(5) *Ibid.*, **64**, 172–3 (1960).
(6) Hueckel, Walter, "Structural Chemistry of Inorganic Compounds," Vol. II, pp. 667–70, Elsevier, New York, 1951.
(7) Markowitz, M.M., *J. Phys. Chem.* **61**, 505–6 (1957).
(8) Markowitz, M.M., Boryta, D.A., *Ibid.*, **64**, 1711. (1960).
(9) Silverman, Alexander, Insley, Herbert, Morey, G.W., Rossini, F.D., *Bull. Natl. Research Council (U. S.)* No. 118, June (1949).

RECEIVED for review February 5, 1960. Accepted June 27, 1961.