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SURVEY OF THE THERMOCHEMISTRY OF HIGH-ENERGY REACTIONS

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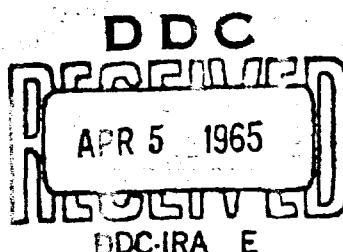
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(Prepared under Contract No. AF 33(616)-7835
by the IIT Research Institute, Chicago, Ill.,
Elliott Raisen, Sidney Katz, and Karl D. Franson, authors)

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FOREWORD

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This report, Technical Report No. IITRI-C191-33, describes the thermodynamic and computational phases of a research program entitled "Study of New Materials Related to the Development of Radiant and Thermal Sources." The report covers the period from April 15, 1962, to August 14, 1963. The investigation was conducted at the IIT Research Institute and its predecessor organization, Armour Research Foundation, Technology Center, Chicago 16, Illinois, under the sponsorship of the Aero-nautical Systems Division, Wright-Patterson Air Force Base, Ohio. Mr. Jason W. Sarnow of the AF Avionics Laboratory served as Project Engineer. The work was performed under Contract AF 33(616)-7835 (IITRI Project C191).

Dr. Sidney Katz, Scientific Advisor, was the Project Leader. Dr. Elliott Raisen served as Group Leader of Thermochemistry and as Task Supervisor. Administrative direction was provided by Dr. J. I. Bregman, Assistant Director of Chemistry Research. Other participants in the work include Paul Ase, Robert H. Boes, Karl Franson, Richard Snow, Betty Isakson, Pat Llewellen, Roberta Patzer, Loretta Lucek, Gertrud Matuschkovitz, and Martha Williams.

ABSTRACT

SURVEY OF THE THERMOCHEMISTRY OF HIGH-ENERGY REACTIONS

This report describes the thermodynamic and computational phases of a survey of exothermic chemical reactions. The purpose of the survey was to ascertain the utility of these chemical reactions as radiation sources for a variety of applications.

All currently available thermochemical data were surveyed. Computer programs were prepared and enthalpies were obtained for all inorganic reactions for which data were adequate. Tabulations included reactions of metals with oxides, fluorides, chlorides, sulfides, phosphides, azides, nitrides, silicides, carbides, nitrates, nitrites, chlorates, perchlorates, chromates, and borides. Data for a total of about 20,000 reactions were obtained. The data for the individual reactions included a balanced chemical equation, and enthalpies and heats of reaction per unit weight and volume. Supplementary tabulations included listings in order of energies of the most energetic reactions in each class, graphical presentations of the reactions of all the metals with various oxidizing agents plotted against enthalpies, similar plots for the reactions of all the oxidants in different classes with various metals, and a total recapitulation of all the reactions in each category in grid form in descending order of energy per unit weight and per unit volume. An extension of this survey to include the detection of the free energies of the reactions is proposed.

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SURVEY OF THE THERMOCHEMISTRY OF HIGH-ENERGY REACTIONS

I. INTRODUCTION

The use of pyrotechnic reactions for the production of radiant and thermal energy has generated an interest in high-energy reactions in this laboratory. As a result, we have been conducting theoretical and experimental studies of high-energy reactions for the past several years. The theoretical studies were concerned with systematic examination of the reactions of metals with different oxidizer systems in order to establish logical criteria for choosing reactions to be studied experimentally. The experimental phases were concerned with the chemical and radiative properties of the reactions and included manipulative studies to establish control over the burning properties of the reactions, calorimetric studies to compare experimental enthalpies with theoretical values, burning-rate studies as a function of the ambient atmosphere, differential thermal analysis and thermogravimetric studies to aid in the interpretation of the kinetics and mechanisms of the reactions, and studies of the spectroradiative properties in the visible and infrared regions of the spectrum.

The most important property of the reaction is its enthalpy, which determines the maximum amount of heat available after the reaction occurs. If the reaction is carried out adiabatically, this heat will raise the temperature of the products to a value which is determined by their specific heats. If the reaction is carried out isothermally, the thermal energy can be used for processes involving energy absorption. The reactions exhibiting high negative enthalpies were therefore of most interest.

Much of the present study was concerned with calculating reaction enthalpies and correlating them with the properties of the reactants and the products and with relationships in the periodic table. The periodic table and the rapidly increasing body of thermochemical data on heat capacities, entropies, and heats and free energies of formation provide a framework for examining and correlating the theoretical behavior of thermochemical reactions. For our practical purposes it was most useful to compare the energy content of the reactions on a volumetric basis, because most of our applications are volume-limited. Since weight limitations are important too, the gravimetric enthalpies were also determined.

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II. SCOPE OF THE STUDY

A. Reactions Surveyed

In earlier work 2600 reactions of metals with binary oxides and 50 reactions of metals with fluorides were examined by using manual computations. On the present program 60,000 high-energy reactions were examined by using a Remington-Rand Univac 1105 computer. Of these, about 20,000 reactions were printed by the computer and 10,000 of them were stored on magnetic tape for further operations. The remaining reactions were discarded either because they had positive enthalpies or because other reactions between the same reactants were found with greater negative enthalpy. In chlorate reactions, for example, each set of reactants may undergo several different stoichiometric reactions to produce different combinations of oxides and chlorides of the constituent metals.

The scope of the theoretical survey is summarized in Table 1. Sixteen classes of oxidizer systems were examined. The data for oxides, fluorides, and chlorides were the most numerous, being represented by 145, 105, and 102 compounds each. The others ranged from 68 for the sulfides to 5 for the chromates. The possible reactions of all these oxidizers with as many as 68 metals were examined.

The data compiled for the oxides were also used in the calculations involving ternary oxidants such as the nitrates, nitrites, chlorates, and perchlorates, in which oxides occur as a product. All the oxide reactions were examined by use of the computer to produce a more complete set of such reactions than those calculated previously; over 20,000 reactions were examined in 6 hours. It is estimated that the same task would take about 1 hour by using an IBM 7090 computer and about 7 man-years by using manual methods.

In general, the perchlorates, chlorates, oxides, and nitrates are the most energetic classes of reactions, followed by the fluorides, nitrites, silicides, nitrides, sulfides, and carbides. The enthalpy of the most energetic reaction in each of these classes is listed in Table 2. The results of this survey were used as a guide in choosing reactions to be studied in the laboratory.

Table 1
SCOPE AND SUMMARY OF THEORETICAL SURVEY
OF THERMOCHEMICAL REACTIONS

Oxidizer Class	Number of Oxidizers	Number of Reactions Examined	Number of Reactions Printed	Enthalpy of the Most Energetic Reactions, cal/cc
Oxides	145*	20,994	9,636	-8279 to -4949
Fluorides	105	n.r.	105	-5586 to -3000
Chlorides	102	10,545	3,061	-3336 to -2593
Sulfides	68	n.r.	2,145	-3169 to -2553
Nitrides	44	n.r.	1,575	-2478 to -1766
Azides	13	n.r.	1,226	-3346 to -1795
Silicides	36	n.r.	302	-5153 to -480
Carbides	30	n.r.	386	-2532 to -1102
Nitrates	18	n.r.	1,226	-7798 to -3468
Nitrites	8	n.r.	800	-4670 to -3476
Phosphides	25	n.r.	500	-1254 to -18
Chlorates	7	16,384	800	-7853 to -6100
Perchlorates	9			-9459 to -6099
Borides	8	n.r.	14	-2994 to -110
Chromates	5	2,920	114	-3845 to -1915
Organic fluorides		Examined on a limited basis manually		

* The data for 71 oxides were used in the nitrate and nitrite computations.

n.r. Not recorded.

Table 2

THE MOST ENERGETIC REACTION IN TERMS
OF VOLUMETRIC ENTHALPY IN EACH CLASS OF OXIDIZERS

Class	Reaction	Enthalpy, cal/cc
Perchlorates	$8\text{Be} + \text{MgClO}_4 = \text{MgCl}_2 + 8\text{BeO}$	-9459
Chlorates	$13\text{Be} + 4 \text{AgClO}_3 = 2\text{Ag}_2\text{Cl} + 12\text{BeO} + \text{BeCl}_2$	-8103
Oxides	$2\text{Be} + \text{RuO}_2 = \text{Ru} + 2\text{BeO}$	-8279
Nitrates	$5\text{Be} + 2\text{LiNO}_3 = \text{LiO} + 5\text{BeO} + \text{N}_2$	-7798
Fluorides	$3\text{Be} + \text{ReF}_6 = \text{Re} + 3\text{BeF}_2$	-5586
Nitrites	$3\text{Be} + 2\text{NaNO}_2 = \text{Na}_2\text{O} + 3\text{BeO} + \text{N}_2$	-4670
Silicides	$3\text{CoSi}_2 + 2\text{Ba} = 3\text{Co} + 2\text{BaSi}_3$	-5153
Chromates	$4\text{Be} + 2\text{PbCrO}_4 = \text{Pb}_2\text{O} + 4\text{BeO} + \text{Cr}_2\text{O}_3$	-3845
Azides	$9\text{Be} + \text{BaN}_6^* = \text{Ba} + 3\text{BeN}_2$	-3346
Nitrides	$2\text{U} + 3\text{Fe}_2\text{N} = 6\text{Fe} + \text{U}_2\text{N}_3$	-2478
Chlorides	$5\text{Ce} + \text{ReCl}_5 = 3\text{Re} + 5\text{CeCl}_3$	-3336
Sulfides	$8\text{Th} + 7\text{FeS}_2 = 7\text{Fe} + 2\text{Th}_4\text{S}_7$	-3169
Carbides	$2\text{Ta} + \text{Li}_2\text{C}_2 = 2\text{Li} + 2\text{TaC}$	-2532

* N_6 represents $(\text{N}_3)_2$

B. Computer Input and Output

All the data used for the computer input were obtained from the sources shown in Table 3 in the order of preference indicated. The National Bureau of Standards Circular 500¹ was used as the primary source whenever possible. In all cases, the heat of formation at 298°K was used.

Table 3
SOURCES OF DATA FOR THERMOCHEMICAL REACTIONS

<u>Property</u>	<u>Source, in Order of Preference</u>
Heat of formation at 298°K (ΔH_{298})	Reference 1, 2, 4, 5
Molecular weight	Reference 5
Density	Reference 5
Melting point	Reference 1, 3, 5
Boiling point	Reference 1, 3, 5

¹Rossini, F. D., Wagman, D. D., Evans, W. H., and Levine, S. Selected Values of Thermodynamic Tables, National Bureau of Standards Circular 500, 1952.

²Glassner, A. The Thermochemical Properties of Oxides, Fluorides and Chlorides to 2500°K, Argonne National Laboratories, No. 5750, 1957.

³Hodgman, C. D., ed., Handbook of Chemistry and Physics, Chemical Rubber Publishing Co., Cleveland, 1954-55.

⁴Quill, L. L., ed., The Chemistry and Metallurgy of Miscellaneous Materials, Thermodynamics, McGraw-Hill Book Co., 1950.

⁵Hodgman, C. D., ed., Handbook of Chemistry and Physics, Chemical Rubber Publishing Co., Cleveland, 1960-61.

The input data consisted of the reactants and products, their heats of formation, and various of their physical properties: molecular weight, melting point, boiling point, and density. Computer programs were designed which combined all the reducing agents (metals) and oxidizers (oxides, chlorides, perchlorates, etc.) into balanced equations and calculated the enthalpy of the stoichiometric reaction. Reactions with positive enthalpies were discarded. Those with negative enthalpies were subjected to further computations to determine the gravimetric and volumetric enthalpies* based on the reactants' weight and volume. Then each reaction was printed together with the data for each component. This output was stored on magnetic tape for the further processing discussed later.

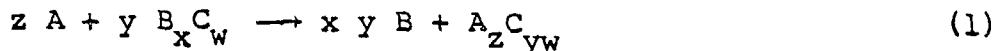
Much of the input data was printed, so that all the properties for each reaction were conveniently assembled in one place. Melting points and boiling points aid in determining practical uses for the reactions. Physical states of the reactants aid in determining the feasibility of formulating and storing the materials. Melting points and boiling points of the products indicate potentially useful properties of the reactions. For example, if the products undergo a phase transition at the temperature of maximum radiative energy, the reaction products will tend to lib rate more of their energy at this temperature and thus increase the efficiency. Also, if gaseous products are desired for radiative or other purposes, reactions that have relatively low-boiling products can be selected. Conversely, if solid products are desired, reactions that have high-melting products can be selected. Assembling the input and calculated data in one place thus increases the versatility of the compilations.

The output consisted of the following input and derived data: a balanced equation, the reaction components, heats of formation at 298°K, the averaged densities of the components, the melting points of the components, the boiling points of the components, heat of the reaction on a molar basis, the reactants' averaged density, the heat of the reaction per unit weight of the reactants (the gravimetric enthalpy), the heat of the reaction per unit volume of reactants (the volumetric enthalpy), and the atomic numbers of the components. Output values were omitted when the data were too limited to allow the required calculation. For example, if the reactant density was unknown, the position for volumetric enthalpy was blank.

* In this work the "volumetric enthalpy" is used to designate the heat of the reaction based on a stoichiometric mixture of reactants occupying a theoretical volume of 1 cc. Similarly, the gravimetric enthalpy is the corresponding heat of reaction based on a gram of reactants.

C. Theory

A generalized equation for the reactions of a metal with a binary compound is:



where A and B are electropositive elements (metals); C is an electronegative element (O, F, Cl, S, C, B, N, H, etc.); and z, y, x, and w are the constants for the stoichiometric reaction after the coefficient of the last term is adjusted to unity. The metal A reduces the compound B_{xw} to form the metal B and the compound of metal A. In order to calculate the energy per unit volume of reactants, the following equation is derived:

$$\Delta H_{cc} = - \frac{\Delta H_{A_z C_{yw}} - y \Delta H_{B_{xw}}} {z V_A + y V_{B_{xw}}} = \frac{\Delta H_{AO_x} - y \Delta H_{BO_x}} {z V_A + y V_{BO_x}} \quad (2)$$

where ΔH_{cc} is the heat of reaction per unit volume of reactants; V is the gram-atomic and gram-molecular volume of the respective reactants, i.e., the atomic or molecular weight divided by the density; and

$$\Delta H_{AO_x} \text{ and } \Delta H_{BO_x}$$

are the molar heats of formation of the products and the reactants, respectively.

To obtain a large energy per unit volume of reactants, it is evident that the heat of formation of the products

$$\Delta H_{A_z C_{yw}}$$

should be large, the heat of formation of reactants

$$\Delta H_{B_{xw}}$$

and the gram-atomic and the gram-molecular volumes of the reactants

$$V_A \text{ and } V_{B_{xw}}$$

should be small, and the coefficients y and z should also be small. According to the usual convention, a negative ΔH is considered as energy output. Thus, in this analysis a "large"

$$\Delta H_{A_z C_y w}$$

in reality signifies a large negative number and a "small"

$$\Delta H_{B_x C_w}$$

signifies a small negative number or even a positive number; hence a large negative value for $\Delta H/CC$ is desired.

The use of Equation 2 can be demonstrated by examples from the oxide systems. In general, the oxide of the reducing agent should have a heat of formation

$$\Delta H_{A_z C_y w}$$

exceeding -250 kcal and the reducing agent itself a gram-atomic volume less than 15 cc, while the oxidizing agent should have a heat of formation

$$\Delta H_{B_x C_w}$$

less than 100 kcal and a gram-molecular volume less than 35 cc. If the components of a reaction satisfy these four conditions, the reaction will be highly energetic, except when the combination of valences produces large values of y and z which nullify the other factors. The y term is especially significant because of its influence on the numerator. The value of y is not a constant for an oxide but is rather a function of the valence of element A in the reaction, and it can only be found by balancing the reaction and adjusting the coefficient of the $A_z C_y w$ term to unity. Various exceptions occur when one of the four factors is outside the specified range, but the extreme value of one or more of the other factors compensates.

The reducing agents Be, Mg, La, and Nd and the oxidizing agents WO_3 , Fe_2O_3 , OsO_4 , and Tl_2O_3 are examples of the various possibilities. For example, the low gram-atomic volumes of Be and Mg (4.96 and 14.0 cc, respectively) compensate for the rather low heats of formation of their oxides (-146.0 and -148.9 kcal, respectively), while the large heats of formation of the oxides of La and Nd (-433 and -436 kcal, respectively) compensate for the high gram-atomic volumes of the metals (50 and 46 cc, respectively). Similarly, the low gram-molecular volumes of WO_3 and Fe_2O_3 compensate for their rather high heats of formation. On the other hand, the low heats of formation of OsO_4 and TlO_3 (-93.6 and -84 kcal, respectively) compensate for their relatively large gram-molecular volumes (51.8 and 44.8 cc, respectively).

D. Presentation of Data

Initially the computer was programmed to take each metal-oxidizer compound in alphabetical order and to treat it as the product of the reaction. When the oxidized metal exists in several valence states, each state was treated as a separate compound. All the other compounds were taken successively in alphabetical order and treated as reactants. A balanced equation was computed by using the appropriate metal from each of the compounds in the reaction. The enthalpy of the reaction was then computed by taking into account the coefficients in the balanced equation. If the enthalpy was negative, the gravimetric and volumetric* enthalpies were calculated and all the data for each reaction were printed. If the enthalpy was positive, the reaction was ignored** and the program went on alphabetically to the next compound. This was done for each metal. Later the order of choosing reactions was based on the reactant oxidizer.

Thus all the reactions of one metal with a series of reactants which yield the same product were printed. When the product exists in a higher valence form, the same process was repeated for the higher valence form. Then the next product was treated in alphabetical order. This type of output, represented by 1 in Table 4, was printed and also stored on magnetic tape. In order to make the data more readily available, the magnetic tape was processed many times with different programs to produce the other types of outputs shown in Table 4. These outputs all contain essentially the same data but arranged in different formats. All the outputs were obtained on volumetric and gravimetric bases.

It would be impractical to reproduce the prodigious amount of material available from the computer. The results are summarized and discussed in this report, and representative data sheets for each type of oxidizer system are included for illustrative purposes.

* The volumetric enthalpies were calculated from the density of condensed phases only.

** Reactions with positive enthalpies are not of interest here. If they were included, twice as many reactions would result.

Table 4
TYPES OF COMPUTER OUTPUTS

Oxidizer Classes Programmed	Type	Description	Purpose
Oxides	1	Compilation of balanced equations together with input and output data for each constituent.	Summarize all the data for each reaction in one place.
Fluorides			
Chlorides			
Sulfides			
Nitrides			
Azides			
Silicides			
Carbides			
Nitrates			
Nitrites			
Phosphides			
Chlorates			
Perchlorates			
Borides			
Chromates			
Oxides	2	A list of all the reactions for each system in order of decreasing negative values of gravimetric enthalpy.	Rapid determination of the most energetic reactions of each oxidizer class on a gravimetric basis. This indicates the maximum energy for a unit weight of reactants.
Chlorides			
Chlorates			
Perchlorates			
Chromates			
Oxides	3	A list of all the reactions for each system in order of decreasing negative values of volumetric enthalpy.	Rapid determination of the most energetic reactions of each oxidizer class on a volumetric basis. This indicates the maximum energy for a unit volume of reactants.
Fluorides			
Chlorides			
Sulfides			
Nitrides			
Azides			
Silicides			
Carbides			
Nitrates			
Nitrites			
Phosphides			
Chlorates			
Perchlorates			
Borides			
Chromates			

Table 4 (cont.)

Oxidizer Classes Programmed	Type	Description	Purpose
Oxides Chlorides Chlorates Perchlorates Chromates	4	A list of all the data used for the graphs. Graphs of the gravimetric enthalpy of one metal versus the oxidizers for each metal.	Helpful in finding the best oxidizer with a particular metal or for examining the periodic behavior of a metal with the different oxidizers, based on a unit weight of reactants.
Oxides Nitrates Chlorides Chlorates Perchlorates Chromates	5	A list of all the data used for the graphs. Graphs of the volumetric enthalpy of one metal versus the oxidizers for each metal.	Helpful in finding the best oxidizer with a particular metal or for examining the periodic behavior of a metal with each oxidizer, based on a unit volume of reactants.
Oxides Chlorides Chlorates Perchlorates Chromates	6	A list of all the data used for the graphs. Graphs of the gravimetric enthalpy of one oxidizer versus the metals for each oxidizer.	Helpful in finding the best metal for a particular oxidizer, or for examining the periodic behavior of an oxidizer with the different metals, based on a unit weight of reactants.
Oxides Chlorides Chlorates Perchlorates Chromates	7	A list of all the data used for the graphs. Graphs of the volumetric enthalpy of one oxidizer versus the metals for each oxidizer.	Helpful in finding the best metal for a particular oxidizer, or for examining the periodic behavior of an oxidizer with the different metals, based on a unit volume of reactants.
Oxides Chlorides Chlorates Perchlorates Chromates	8	A chart of the gravimetric enthalpies of all the reactions for each system listed in general descending order from left to right, and from top to bottom.	The most concise summary of the enthalpies of all the reactions of each class. This table indicates the most energetic metals and oxidizers at a glance, based on a unit weight of reactants.
Oxides Chlorides Chlorates Perchlorates Chromates	9	A chart of the volumetric enthalpies of all the reactions for each system listed in general descending order from left to right, and from top to bottom.	The most concise summary of the enthalpies of all the reactions of each class. This table indicates the most energetic metals and oxidizers at a glance, based on a unit volume of reactants.

III. DISCUSSION OF THERMOCHEMICAL DATA

A. Fluoride Reactions

The molecular, gravimetric, and volumetric enthalpies of about 5000 reactions resulting from the combination of 50 metals with 105 fluorides were calculated and compiled on the computer. The reactions of beryllium with cobalt trifluoride, ferric fluoride, and stannic fluoride are particularly energetic; beryllium fluoride is formed in these reactions.

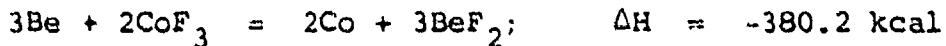
Table 5 is a list of fluoride reactions with negative enthalpies in excess of -3000 cal. The reactions are all of the form:



where BF and AF are the reactant and product fluorides, respectively, and A and B are the corresponding metals. Each reaction is identified by the reactant and product fluoride and their molecular coefficient; the metal reactants and products are omitted from the tabulation.

As a group, the fluorides are a highly energetic series of reactions. Experimental study of many of these reactions should prove interesting, especially those with very high enthalpies and those with products that have low melting or low boiling points. The reactions with the following products merit further study: mercury, cobalt, tin, iron, silver, bismuth, antimony, manganese, nickel, gallium, cadmium, chromium, beryllium fluoride, germanium fluoride, neodymium fluoride, praseodymium fluoride, and lithium fluoride.

Figure 1 illustrates the periodic behavior of the enthalpies of the fluoride reactions. The metals are plotted by atomic number along the abscissa, and the volumetric enthalpies of their reactions with cobalt trifluoride are shown on the ordinate. Cobalt fluoride was chosen as the reactant because most of its reactions are highly energetic. A representative reaction is:



Here, ΔH is the molar enthalpy. The enthalpy in Table 5 is the heat of the reaction on a volumetric basis in terms of calories per cubic centimeter of reacting material, in this case -5111 cal/cc.

All the available data are plotted in Figure 1, and the various points are connected by solid, dotted, or dashed lines to indicate their relationships within the periodic table. The solid lines connect metals with adjacent atomic numbers, the dotted lines connect members of the same group, and the dashed

lines connect the members of a B group (transition metals). The three subfigures 1A, B, and C emphasize each of these relationships.

Figure 1A, in which the adjacent atomic numbers are connected, illustrates the overall periodic behavior of the enthalpies. In general, the Group II elements (beryllium, magnesium, calcium, strontium, and barium) establish the peaks in the energy outputs (i.e., the largest negative enthalpies) and the Group I elements (lithium, sodium, potassium, rubidium, and cesium) establish the minima. The curve is irregular in the neighborhood of strontium and barium because the Group IIIB metals (yttrium, lanthanum, and the rare earths) and the Group IVB metals (titanium, zirconium, and hafnium) have unusually small atomic volumes and their fluorides have relatively high heats of formation.

The elements establishing the peaks in the energy curve are characterized by one or more of the following:

The electronic configuration of their valence orbitals. Their outermost orbital has two electrons, and the next-to-outermost orbital has either one or two electrons.

Their electronic configuration in the fluorides. They all have the rare gas configuration, s^2 or s^2p^6 .

The high heat of formation of the fluoride relative to the fluoride of their nearest neighbors.

Their low gram-atomic volumes.

Groups IIIB and IVB tend to react more energetically than Group II. The fluoride curve is similar to the analogous oxide and nitrate curves, with a few exceptions. Aluminum, for instance, is less energetic than magnesium in the fluoride system and more energetic in the oxygen system, because of the unusually high heat of formation of the oxide.

The relationship of the elements within Groups IA, IIA, IIIA, and IVA is shown in Figure 1B. Except for boron in Group IIIA, the energies of the reactions of cobalt trifluoride within the elements of a group diminish with increasing atomic number. A group relationship is also apparent. In decreasing order of energy, they follow the sequence Group IIA, IIIA, IVA, and IA.

Figure 1C shows the relationship of the elements within the transition metal groups. Groups IIB (zinc and cadmium), VB (vanadium, niobium, and tantalum), and VIB (chromium, molybdenum and tungsten) are similar to Groups IA, IIA, IIIA, and IVA in that the energy tends to decrease with increasing

Table 5
FLUORIDE REACTIONS* WITH HIGHEST NEGATIVE ENTHALPIES

Enthalpy, cal/cc	Reactant	Product	Metal		Fluoride	
			m.p., °C	b.p., °C	m.p., °C	b.p., °C
-5586	ReF ₆	3 BeF ₂	3147		800	
-5206	CF ₄	2 BeF ₂	4400			
-5112	2 CoF ₃	3 BeF ₂	1493	3100		
-5015	ReF ₆	3 YF ₃				
-4960	HgF ₂	BeF ₂	-39	357		
-4926	ReF ₆	2 CeF ₃			1460	
-4870	ReF ₆	2 LaF ₃				
-4830	SnF ₄	2 BeF ₂	232	2337		
-4820	ReF ₆	2 NdF ₃			1410	
-4809	ReF ₆	2 PrF ₃			1370	
-4765	NbF ₅	5 BeF ₂				
-4683	3 CF ₄	4 YF ₃				
-4648	FeF ₂	BeF ₂	1535	2800		
-4603	AgF ₂	BeF ₂	961	2193		
-4563	CoF ₃	YF ₃				
-4534	3 HgF ₂	2 YF ₃				
-4527	3 CF ₄	4 LaF ₃				
-4460	CoF ₃	LaF ₃				
-4450	3 HgF ₂	2 LaF ₃				
-4342	3 SnF ₄	4 YF ₃				
-4272	3 NbF ₃	5 YF ₃	2478	3700		
-4268	3 AgF ₂	2 YF ₃				
-4267	3 SnF ₄	4 LaF ₃				
-4216	3 AgF ₂	2 LaF ₂				
-4213	3 FeF ₂	2 YF ₃				
-4202	3 NbF ₅	5 LaF ₃				
-4156	3 FeF ₂	2 LaF ₃				
-3889	BiF ₃	YF ₃	271	1420		
-3869	BiF ₃	LaF ₃				
-3821	2 SbF ₅	5 BeF ₂	630	1440		
-3707	2 TaF ₅	5 BeF ₂				

Table 5 (cont.)

<u>Enthalpy, cal/cc</u>	<u>Reactant</u>	<u>Product</u>	<u>Metal</u>		<u>Fluoride</u>	
			<u>m.p., °C</u>	<u>b.p., °C</u>	<u>m.p., °C</u>	<u>b.p., °C</u>
-3704	2 VF ₅	5 BeF ₂	1730	3000		
-3611	AgF ₂	2 LiF			845	1681
-3601	3 SbF ₅	5 LaF ₃				
-3601	MoF ₆	3 BeF ₂	2610	4800		
-3589	3 SbF ₅	5 BeF ₂				
-3573	2 MnF ₃	3 BeF ₂	1244	2087		
-3568	NiF ₂	BeF ₂	1455	2800		
-3564	3 TaF ₅	5 LaF ₃				
-3544	3 TaF ₅	5 BeF ₂				
-3502	3 VF ₅	5 LaF ₃				
-3478	3 VF ₅	5 YF ₃				
-3427	MoF ₆	2 LaF ₃				
-3424	2 GaF ₃	3 BeF ₃	30	937		
-3394	MoF ₆	2 BeF ₂				
-3392	VF ₄	2 BeF ₂				
-3376	MnF ₃	LaF ₃				
-3323	3 NiF ₂	2 YF ₃				
-3329	MnF ₃	YF ₃				
-3322	2 SbF ₃	3 BeF ₂				
-3320	2 FeF ₃	3 BeF ₂				
-3259	GaF ₃	LaF ₃				
-3214	SbF ₃	LaF ₃				
-3202	FeF ₃	LaF ₃				
-3192	GaF ₃	YF ₃				
-3183	3 VF ₄	4 BeF ₂				
-3157	SbF ₃	YF ₃				
-3144	3 AgF	LaF ₃				
-3143	CdF ₂	BeF ₂	321	767		
-3109	3 CrF ₃	3 BeF ₂	1900	2480		
-3098	3 AgF	YF ₃				
-3070	3 CdF ₂	2 LaF ₃				
-3038	3 CrF ₃	LaF ₃				

* The first reaction, for example, is: 3 Be + ReF₆ = Re + 3 BeF₂.

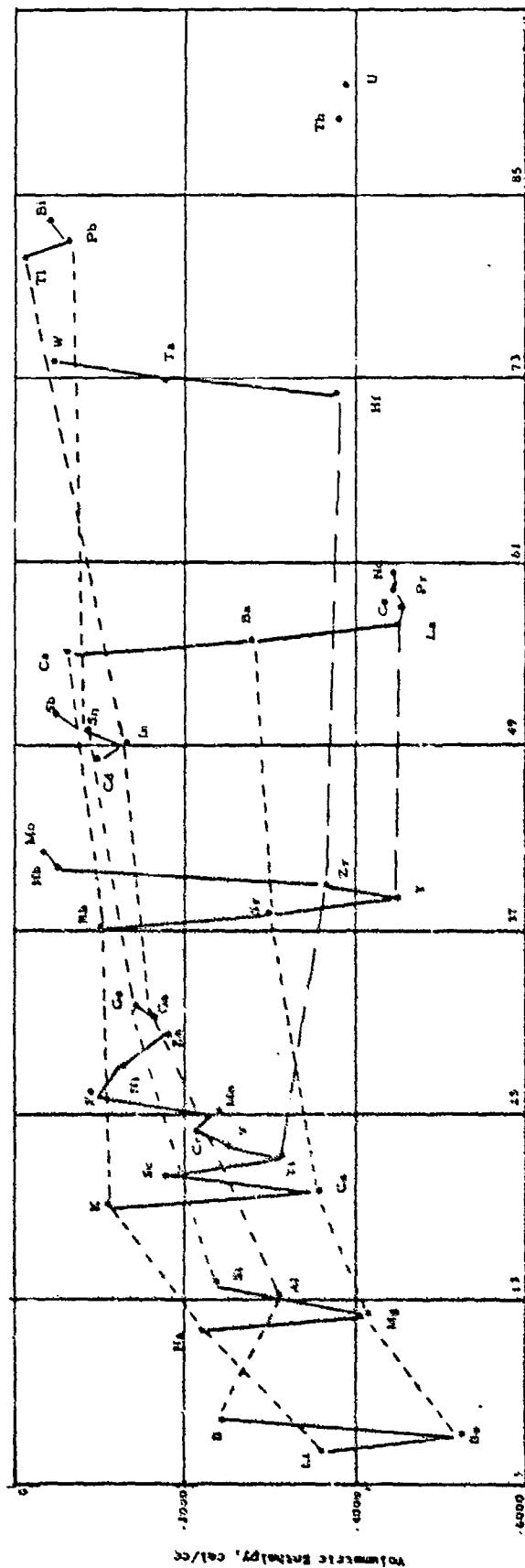


Figure 1
VOLUMETRIC ENTHALPIES OF REACTIONS OF METALS WITH CoF_3

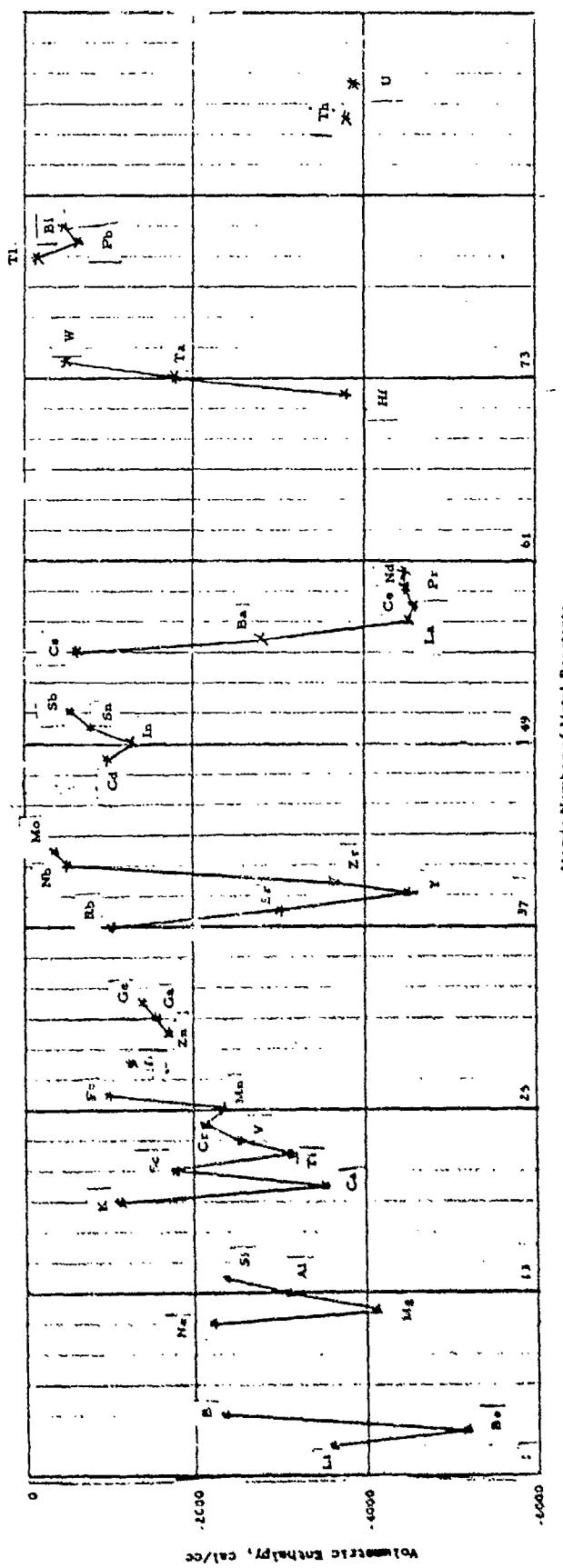


Figure 1A
VOLUMETRIC ENTHALPIES OF REACTIONS OF METALS WITH CoF_3

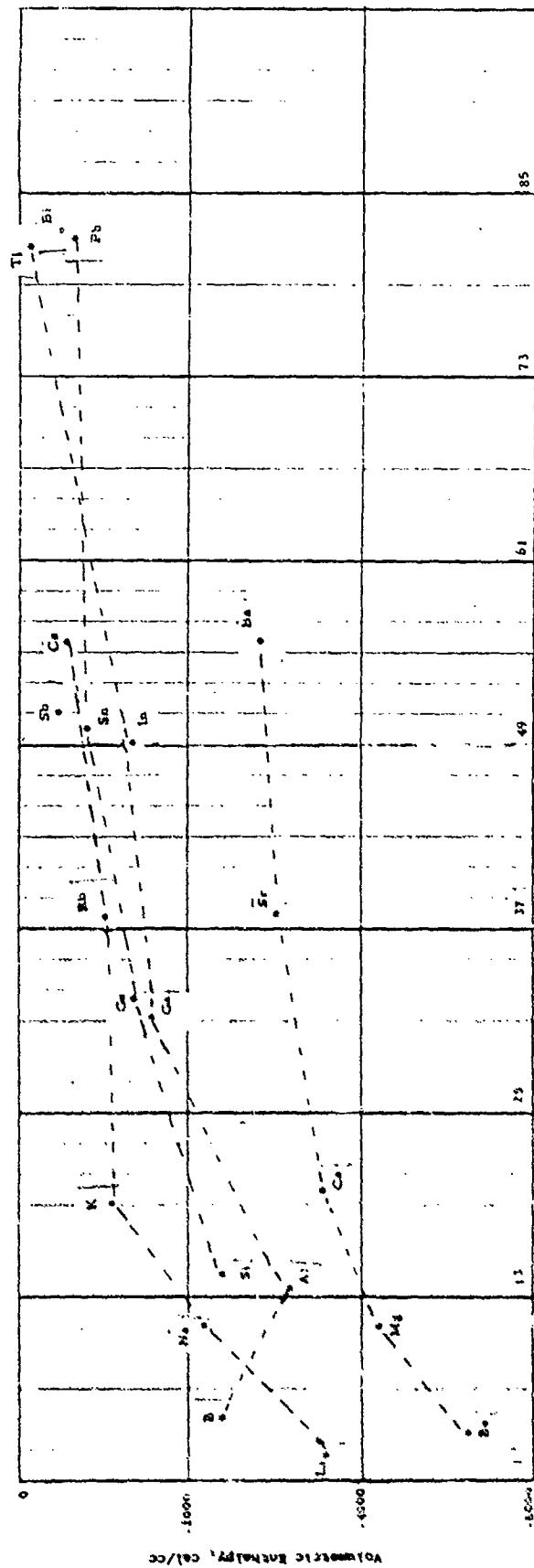
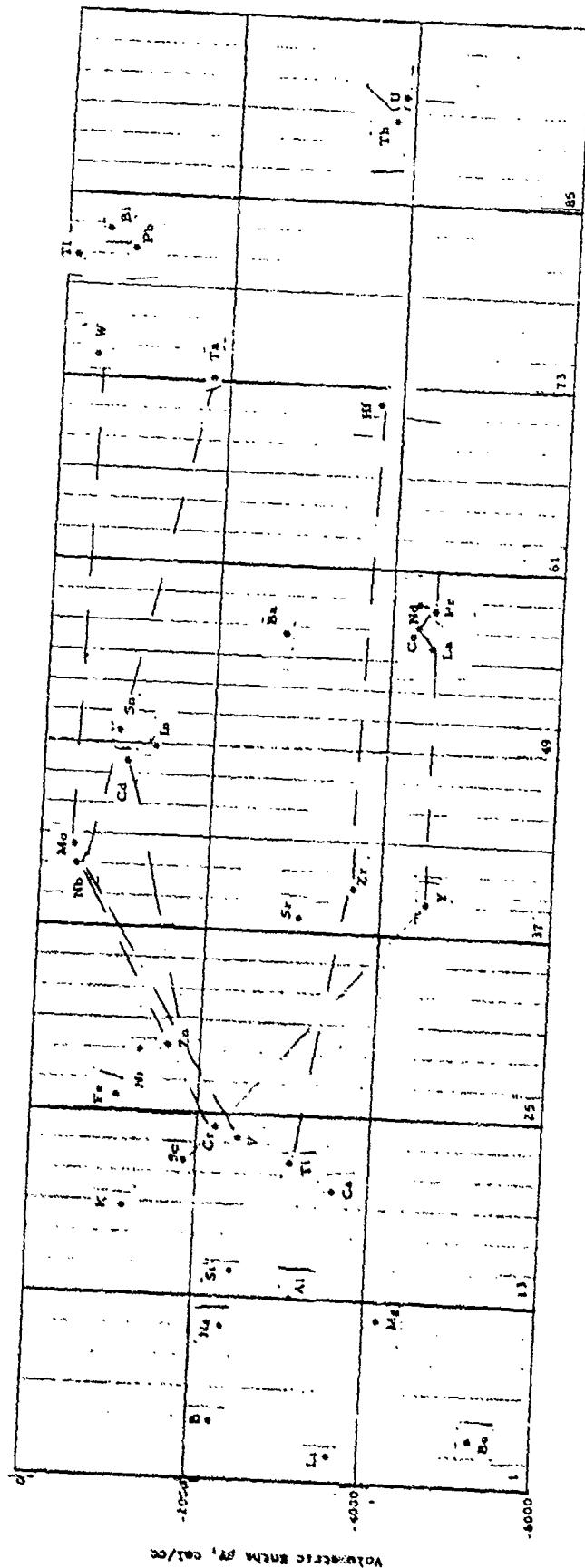


Figure 1a
VOLUMETRIC ENTHALPIES OF REACTIONS OF METALS WITH CoF₃



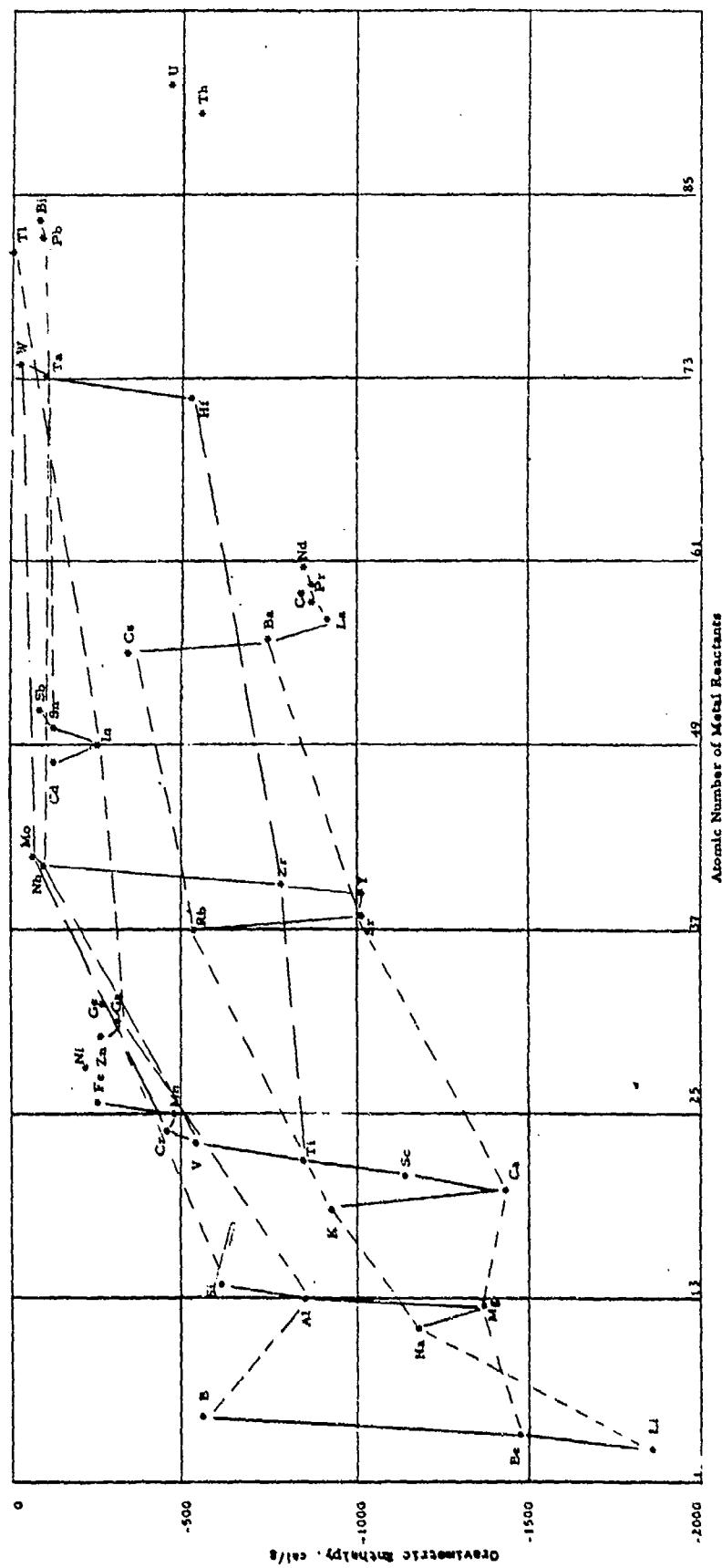
VOLUMETRIC ENTHALPIES OF REACTIONS OF METALS WITH CoF₃
Figure 1C*i*

atomic number. Groups IIIB (scandium, yttrium, and lanthanum, and the rare earth elements) and IVB (titanium, zirconium, and hafnium) exhibit the opposite behavior and increase in energy with increasing atomic number. This behavior is due primarily to the small increase, or even decrease in the atomic volume of the elements in these groups with increasing atomic number, caused by the lanthanide contraction. Groups IIIB and IVB are the most energetic, and Groups IIB, VB, and VIB are the least energetic.

Similar relationships for the gravimetric enthalpies (heat output per gram of reactants) are illustrated in Figure 2. A few differences are observed because densities of the reactants vary. Since the volume is not considered, the effect of the lanthanide contraction is not evident, and Groups IIIB and IVB exhibit a normal behavior, with their energy decreasing with increasing atomic number. On the gravimetric basis, lithium is more energetic than beryllium, scandium more energetic than titanium, and Group I more energetic than Group III. The gravimetric enthalpies are lower than the volumetric ones because the densities of the reactants are more than unity in all cases.

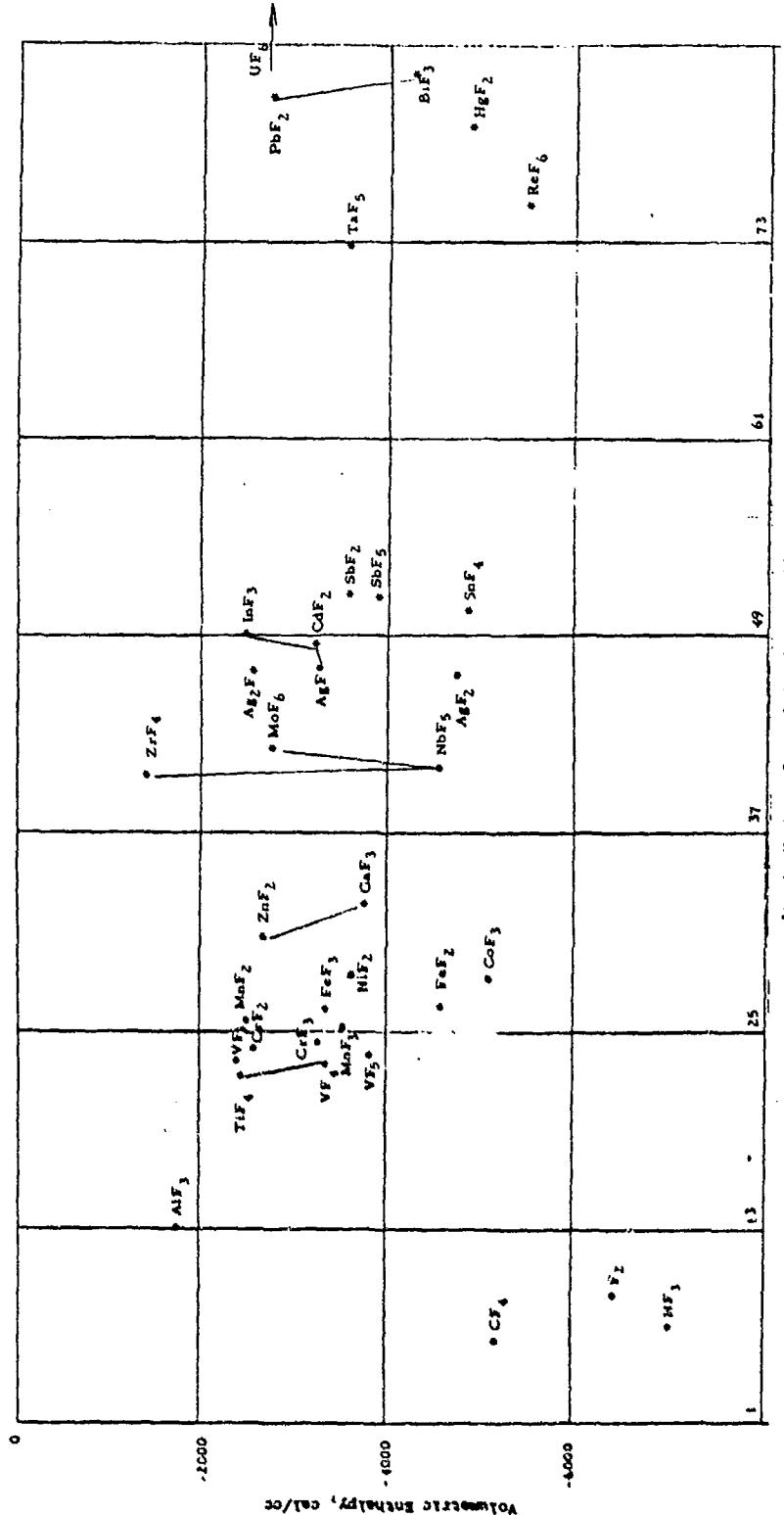
Although the volumetric enthalpies were considered more significant for the present studies, because the establishment of a maximum energy in a fixed volume is usually desired, the gravimetric enthalpies were also considered in choosing the reactions to be studied experimentally. Less information is available on volumetric enthalpies because the densities of the reactants are often not known.

Figures 1 and 2 emphasized the effect of the metal on the enthalpy of the reactions. Figures 3 and 4 emphasize the effect of the fluoride. The volumetric and gravimetric enthalpies of the reactions of the fluorides with beryllium are plotted in Figures 3 and 4 on the ordinate, with the atomic number of the metal in the fluoride shown on the abscissa. A periodic behavior is apparent but is difficult to specify because, fluorides of each metal can exist in different valence states. In general, within a group the energy decreases with increasing atomic number; since the metals are in the oxidized form, the order of the groups is reversed. Thus Groups IIIB and IVB are the least energetic when the metal fluoride, rather than the metal, is used as the reactant. Groups V, VI, VII, and VIIIB, represented by vanadium, chromium, manganese, iron, cobalt, molybdenum, tungsten, rhenium, and osmium fluorides, are the most energetic. When a metal forms more than one fluoride, the one with the greatest number of fluorine atoms is usually the most energetic. The iron fluorides are exceptions, FeF_2 being more energetic than FeF_3 . The trends illustrated in the figures are similar for the other fluorides and metals, except for displacement of the vertical scale.



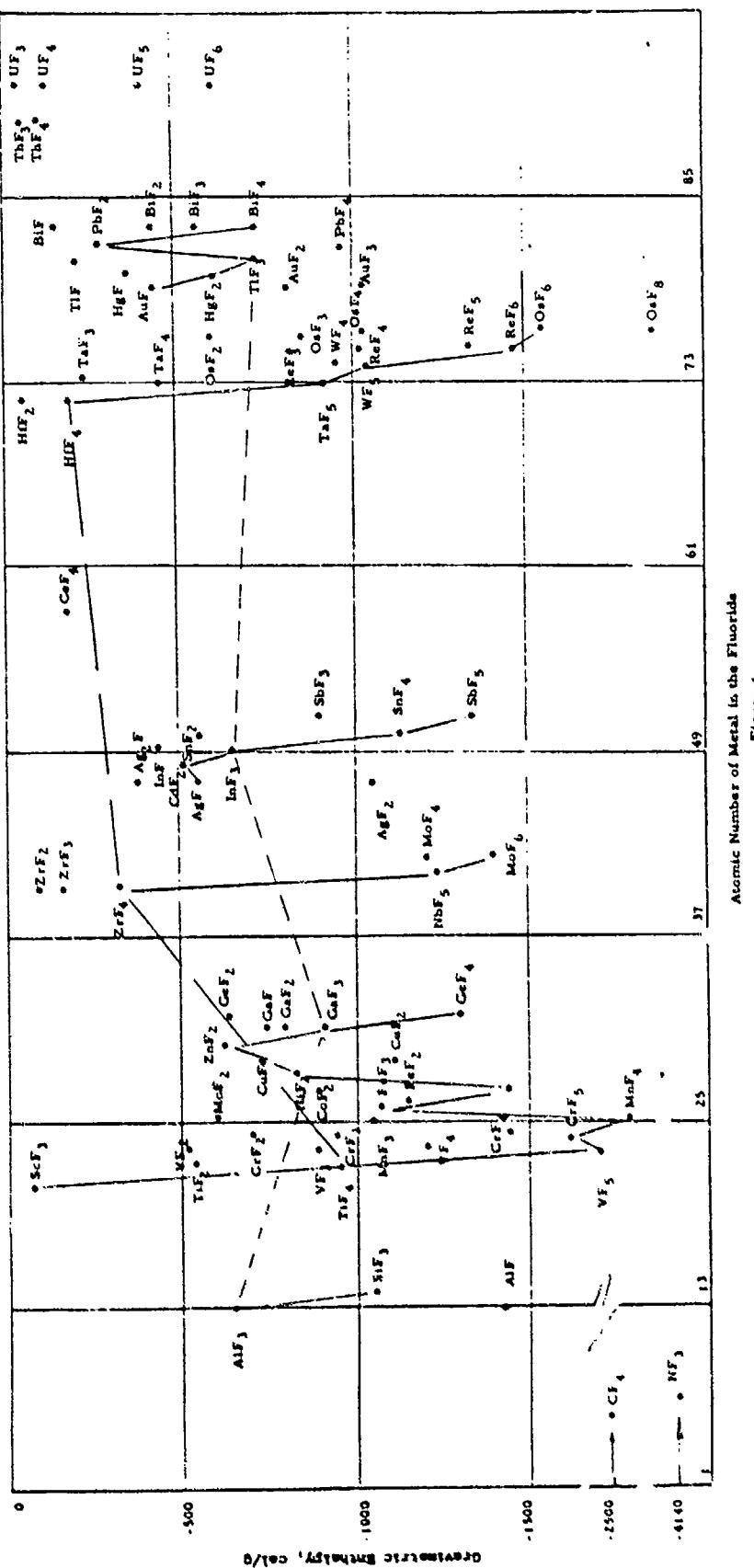
GRAVIMETRIC ENTHALPIES OF REACTIONS OF METALS WITH CoF_3

Figure 2



VOLUMETRIC ENTHALPIES OF REACTIONS OF FLUORIDES WITH B_2

Figure 3



Gravimetric Enthalpies of Reactions of Fluorides with Be

Figure 4

B. Oxide Reactions

A total of 20,994 reactions involving 145 oxides was examined, and the data for 9636 reactions were printed. Of the 9636 reactions, about half were pertinent to the present study; reactions with positive and negative enthalpies were inadvertently included in the output. The oxides form a highly energetic class of reactions, with volumetric enthalpies up to -8279 cal/cc. The oxide systems, including the perchlorates, chlorates, and nitrates, are the most energetic of all the classes of reactions examined. The oxide parameters tend to dominate and, as a result, the trends in perchlorate, chlorate, and nitrate reactions are similar to those in the oxide reactions.

Representative computer outputs, including some of the more energetic reactions, are shown in Table 6. In this format all the data for each reaction are assembled in one place. Several reactions with positive enthalpies are shown. On a molar or gravimetric basis, they are the same as the reverse reaction with a negative enthalpy. On a volumetric basis, the results for the reverse reaction are slightly different, since the reactants and products have different densities. This is illustrated by the reaction of silver with cobalt monoxide and the reverse reaction of cobalt with silver oxide. It is also demonstrated by the fact that the reaction between cobalt and silver oxide is more energetic when the cobalt monoxide, rather than the dicobalt trioxide, is produced. This is not obvious from Table 6 because only the reaction with the greatest thermal output is printed when more than one reaction is possible between any two reactants.

The most energetic oxide reactions are shown in Tables 7 and 8 on volumetric and gravimetric bases, respectively. On the volumetric basis, the best reducing metals are the lower members of Groups IIA and IIIA (beryllium, magnesium, aluminum, and boron), the Group IVB elements (titanium, zirconium, and hafnium), and the IVF and VF elements (lanthanum, cerium, praseodymium, neodymium, promethium, samarium, gadolinium, etc., and thorium and uranium). On the gravimetric basis, the same elements are the best reducing metals, with a few notable exceptions. Lithium is one of the best metals on a gravimetric basis but is very poor on a volumetric basis because of its extremely low density. On the other hand, the extremely high densities of thorium and uranium cause them to be much more effective on a volumetric than on a gravimetric basis.

The most effective oxidizers on a volumetric basis are the oxides of ruthenium, nitrogen, rhenium, sulfur, silver, osmium, selenium, manganese, carbon, cobalt, arsenic, lead, and copper. The most effective oxidizers on a gravimetric basis are the oxides of nitrogen, carbon, sodium, sulfur, ruthenium, molybdenum, indium, potassium, and chromium.

Table 6
DATA ON REACTIONS OF VARIOUS METALS WITH OXIDES

	Cd	+ Ag ₂ O	= 2 Ag	+ CdO
Heat of formation		-7.31	107.87	-60.86
Molecular weight	112.41	231.76	10.50	128.41
Density	8.64	7.14	960.80	8.15
Melting point, °C	320.90	300.00	2193.00	900.00
Boiling point, °C	767.00			900.00
Heat of reaction, kcal	-53.55			
Reactants' density	7.57			
Gravimetric enthalpy, cal/g	-155.60			
Volumetric enthalpy, cal/cc	-1178.15			
	2 Ce	+ 3 Ag ₂ O	= 8 Ag	+ Ce ₂ O ₃
Heat of formation		-7.31	107.87	-435.00
Molecular weight	140.13	231.76	10.50	328.26
Density	6.70	7.14	960.80	6.90
Melting point, °C	775.00	300.00	2193.00	1692.00
Boiling point, °C	2900.00			
Heat of reaction, kcal	-413.08			
Reactants' density	7.01			
Gravimetric enthalpy, cal/g	-423.44			
Volumetric enthalpy, cal/cc	-2968.24			
	Co	+ Ag ₂ O	= 2 Ag	+ CoO
Heat of formation		-7.31	107.87	-57.20
Molecular weight	58.94	231.76	10.50	74.94
Density	8.90	7.14	960.80	5.70
Melting point, °C	1493.00	300.00	2193.00	1800.00
Boiling point, °C	3100.00			
Heat of reaction, kcal	-49.89			
Reactants' density	7.44			
Gravimetric enthalpy, cal/g	-171.63			
Volumetric enthalpy, cal/cc	-1277.10			

Table 6 (cont.)

	2 Ag	+	CoO	=	Co	+	Ag ₂ O
Heat of formation			-57.20		58.94		-7.31
Molecular weight	107.87		74.94		8.90		231.76
Density	10.50		5.70				7.14
Melting point, °C	960.80		1800.00		1493.00		300.00
Boiling point, °C	2193.00				3100.00		
Boiling point, kcal	49.89						
Heat of reaction, kcal							
Reactants' density	8.63						
Gravimetric enthalpy, cal/g	171.64						
Volumetric enthalpy, cal/cc	1480.77						
	2 Al	+	3 CoO	=	3 Co	+	Al ₂ O ₃
Heat of formation			-57.20		58.94		-399.09
Molecular weight	26.98		74.94		8.90		101.94
Density	2.70		5.70				3.97
Melting point, °C	660.00		1800.00		1493.00		2015.00
Boiling point, °C	2327.00				3100.00		3500.00
Heat of reaction, kcal							
Reactants' density	4.69						
Gravimetric enthalpy, cal/g	-816.02						
Volumetric enthalpy, cal/cc	-3828.99						
	2 As	+	3 CoO	=	3 Co	+	As ₂ O ₃
Heat of formation			-57.20		58.94		-156.15
Molecular weight	74.92		74.94		8.90		197.82
Density	5.73		5.70				4.13
Melting point, °C	817.00		1800.00		1493.00		313.00
Boiling point, °C					3100.00		460.00
Heat of reaction, kcal							
Reactants' density	5.71						
Gravimetric enthalpy, cal/g	41.24						
Volumetric enthalpy, cal/cc	235.50						

Table 6 (cont.)

	6 Ag	+	Co_2O_3	=	2 Co	+	$3 \text{Ag}_2\text{O}$
Heat of formation			-140.00				-7.31
Molecular weight	107.87		165.88		58.94		231.76
Density	10.50		5.18		8.90		7.14
Melting point, °C	960.80		895.00		1493.00		300.00
Boiling point, °C	2193.00				3100.00		
Heat of reaction, kcal	118.08						
Reactants' density	8.68						
Gravimetric enthalpy, cal/g	145.22						
Volumetric enthalpy, cal/cc	1260.69						
	2 Al	+	Co_2O_3	=	2 Co	+	Al_2O_3
Heat of formation			-140.00				-399.09
Molecular weight	26.98		165.88		58.94		101.94
Density	2.70		5.18		8.90		3.97
Melting point, °C	660.00		895.00		1493.00		2015.00
Boiling point, °C	2327.00				3100.00		3500.00
Heat of reaction, kcal	-259.09						
Reactants' density	4.23						
Gravimetric enthalpy, cal/g	-1178.54						
Volumetric enthalpy, cal/cc	-4983.12						
	2 As	+	Co_2O_3	=	2 Co	+	As_2O_3
Heat of formation			-140.00				-156.15
Molecular weight	74.92		165.88		58.94		197.82
Density	5.73		5.18		8.90		4.15
Melting point, °C	817.00		895.00		1493.00		313.00
Boiling point, °C	817.00				3100.00		460.00
Heat of reaction, kcal	-16.15						
Reactants' density	5.43						
Gravimetric enthalpy, cal/g	-51.15						
Volumetric enthalpy, cal/cc	-277.55						

Table 6 (cont.)

	6 Li	+	Co_2O_3	=	2 Co	+	3 Li_2O
Heat of formation			-140.00		58.94		-142.40
Molecular weight	6.94		165.88		8.90		29.88
Density	1.52		5.18		1493.00		2.01
Melting point, °C	180.00		895.00		3100.00		1700.00
Boiling point, °C	1326.00						
Heat of reaction, kcal	-287.20						
Reactants' density	1.89						
Gravimetric enthalpy, cal/g	-1383.96						
Volumetric enthalpy, cal/cc	-2610.89						
	3 Mg	+	Co_2O_3	=	2 Co	+	3 MgO
Heat of formation			-140.00		58.94		-143.84
Molecular weight	24.32		165.88		8.90		40.32
Density	1.74		5.18		1493.00		3.58
Melting point, °C	650.00		895.00		3100.00		2800.00
Boiling point, °C	1120.00						
Heat of reaction, kcal	-291.52						
Reactants' density	3.23						
Gravimetric enthalpy, cal/g	-1220.57						
Volumetric enthalpy, cal/cc	-3941.90						
	3 Mn	+	Co_2O_3	=	2 Co	+	3 MnO
Heat of formation			-140.00		58.94		-92.00
Molecular weight	54.94		165.88		8.90		70.93
Density	7.20		5.18		1493.00		5.43
Melting point, °C	1244.00		895.00		3100.00		1650.00
Boiling point, °C	2087.00						
Heat of reaction, kcal	-136.00						
Reactants' density	6.02						
Gravimetric enthalpy, cal/g	-411.25						
Volumetric enthalpy, cal/cc	-2476.56						

Table 6 (cont.)

	4 Ag	+	MnO ₂	=	Mn	+	2 Ag ₂ O
Heat of formation		-124.50					-7.31
Molecular weight	107.87	86.93	54.94				231.76
Density	10.50	5.03	7.20				7.14
Melting point, °C	960.80	535.00	1244.00				300.00
Boiling point, °C	2193.00						
Heat of reaction, kcal	109.89						
Reactants' density		8.88					
Gravimetric enthalpy, cal/g	211.97						
Volumetric enthalpy, cal/cc	1881.95						
	4 Al	+	3 MnO ₂	=	3 Mn	+	2 Al ₂ O ₃
Heat of formation		-124.50					-399.09
Molecular weight	26.98	86.93	54.94				101.94
Density	2.70	5.03	7.20				3.97
Melting point, °C	660.00	535.00	1244.00				2015.00
Boiling point, °C	2327.00						3500.00
Heat of reaction, kcal							
Reactants' density	-424.68						
Gravimetric enthalpy, cal/g	4.02						
Volumetric enthalpy, cal/cc	-1151.80						
	-4624.68						
	4 As	+	3 MnO ₂	=	3 Mn	+	2 As ₂ O ₃
Heat of formation		-124.50					-156.15
Molecular weight	74.92	86.93	54.94				197.82
Density	5.73	5.03	7.20				4.15
Melting point, °C	817.00	535.00	1244.00				313.00
Boiling point, °C	817.00						460.00
Heat of reaction, kcal	61.20						
Reactants' density		5.38					
Gravimetric enthalpy, cal/g	109.19						
Volumetric enthalpy, cal/cc	587.24						

Table 6 (cont.)

	2 Be	+	MnO ₂	=	Mn	+	2 BeO
Heat of formation			-124.50				-146.00
Molecular weight	9.01		86.93	54.94			25.01
Density	1.85		5.03	7.20			3.01
Melting point, °C	1283.00		535.00	1244.00			2530.00
Boiling point, °C	2970.00			2087.00			3900.00
Heat of reaction, kcal	-167.50						
Reactants' density	3.88						
Gravimetric enthalpy, cal/g	-1595.91						
Volumetric enthalpy, cal/cc	-6194.56						
	4 Bi	+	3 MnO ₂	=	3 Mn	+	2 Bi ₂ O ₃
Heat of formation			-124.50				-137.90
Molecular weight	208.99		86.93	54.94			466.00
Density	9.80		5.03	7.20			8.90
Melting point, °C	271.00		535.00	1244.00			820.00
Boiling point, °C	1420.00			2087.00			1890.00
Heat of reaction, kcal	97.70						
Reactants' density	7.99						
Gravimetric enthalpy, cal/g	89.08						
Volumetric enthalpy, cal/cc	712.15						
	C	+	MnO ₂	=	Mn	+	CO ₂
Heat of formation			-124.50				-94.05
Molecular weight	12.01		86.93	54.94			44.01
Density	2.25		5.03	7.20			1.98
Melting point, °C	25.00		535.00	1244.00			-56.20
Boiling point, °C	4347.00			2087.00			-78.50
Heat of reaction, kcal	30.45						
Reactants' density	4.37						
Gravimetric enthalpy, cal/g	307.76						
Volumetric enthalpy, cal/cc	1345.30						

Table 6 (cont.)

	8 Ag	+	N ₂ O ₄	=	2 N	+	4 Ag ₂ O
Heat of formation			2.31				-7.31
Molecular weight			92.00				231.76
Density			1.49				7.14
Melting point, °C	107.87			14.01			
Boiling point, °C	10.50			.81			
Boiling point, °C	960.80						300.00
Heat of reaction, kcal	2193.00						
Reactants' density	-31.53						
Heat of reaction, kcal	6.64						
Gravimetric enthalpy, cal/g	-33.02						
Volumetric enthalpy, cal/cc	-219.14						
	8 Al	+	3 N ₂ O ₄	=	6 N	+	4 Al ₂ O ₃
Heat of formation			2.31				-399.09
Molecular weight	26.98		92.00				101.94
Density	2.70		1.49				3.97
Melting point, °C	660.00						2015.00
Boiling point, °C	2327.00						3500.00
Heat of reaction, kcal	-1603.29						
Reactants' density	1.86						
Gravimetric enthalpy, cal/g	-3259.77						
Volumetric enthalpy, cal/cc	-6050.32						
	8 As	+	3 N ₂ O ₄	=	6 N	+	4 As ₂ O ₃
Heat of formation			2.31				-156.15
Molecular weight	74.92		92.00				197.82
Density	5.73		1.49				4.15
Melting point, °C	817.00						313.00
Boiling point, °C	817.00						460.00
Heat of reaction, kcal	-631.53						
Reactants' density	3.02						
Gravimetric enthalpy, cal/g	-721.45						
Volumetric enthalpy, cal/cc	-2179.44						

Table 6 (cont.)

	4 Be	+	N ₂ O ₄	=	2 N	+	4 BeO
Heat of formation			2.31		14.01		-146.00
Molecular weight	9.01		92.00		.81		25.01
Density	1.05		1.49				3.01
Melting point, °C	1283.00		61.60				2530.00
Boiling point, °C	2970.00						3900.00
Boiling point, °C							
Heat of reaction, kcal	-585.31						
Reactants' density	1.58						
Gravimetric enthalpy, cal/g	-4578.68						
Volumetric enthalpy, cal/cc	-7221.34						
	8 Bi	+	3 N ₂ O ₄	=	6 N	+	4 Bi ₂ O ₃
Heat of formation			2.31		14.01		-137.90
Molecular weight	208.99		92.00		.81		466.00
Density	9.80		1.49				8.90
Melting point, °C	271.00		61.60				280.00
Boiling point, °C	1420.00						1890.00
Boiling point, °C							
Heat of reaction, kcal	-558.53						
Reactants' density	5.48						
Gravimetric enthalpy, cal/g	-286.73						
Volumetric enthalpy, cal/cc	-1570.15						
	2 C	+	N ₂ O ₄	=	2 N	+	2 CO ₂
Heat of formation			2.31		14.01		-94.05
Molecular weight	12.01		92.00		.81		44.01
Density	2.25		1.49				1.98
Melting point, °C	25.00		61.60				-56.20
Boiling point, °C	4347.00						-78.50
Boiling point, °C							
Heat of reaction, kcal	-190.41						
Reactants' density	1.60						
Gravimetric enthalpy, cal/g	-1641.15						
Volumetric enthalpy, cal/cc	-2630.69						

Table 6 (cont.)

	4 Ag	+	PbO ₂	=	Pb	+	2 Ag ₂ O
Heat of formation			-66.12				-7.31
Molecular weight	107.87		239.21		207.21		231.76
Density	10.50		9.38		11.34		7.14
Melting point, °C	960.80		290.00		327.40		300.00
Boiling point, °C	2193.00				1750.00		
Heat of reaction, kcal	51.51						
Reactants' density	10.07						
Gravimetric enthalpy, cal/g	76.80						
Volumetric enthalpy, cal/cc	773.27						
	4 Al	+	3 PbO ₂	=	3 Pb	+	2 Al ₂ O ₃
Heat of formation			-66.12				-399.09
Molecular weight	26.98		239.21		207.21		101.94
Density	2.70		9.38		11.34		3.97
Melting point, °C	660.00		290.00		327.40		2015.00
Boiling point, °C	2327.00				1750.00		3500.00
Heat of reaction, kcal	-599.82						
Reactants' density	7.09						
Gravimetric enthalpy, cal/g	-726.57						
Volumetric enthalpy, cal/cc	-5149.20						
	4 As	+	3 PbO ₂	=	3 Pb	+	2 As ₂ O ₃
Heat of formation			-66.12				-156.15
Molecular weight	74.92		239.21		207.21		197.82
Density	5.73		9.38		11.34		4.15
Melting point, °C	817.00		290.00		327.40		313.00
Boiling point, °C	817.00				1750.00		460.00
Heat of reaction, kcal							
Reactants' density							
Gravimetric enthalpy, cal/g							
Volumetric enthalpy, cal/cc							

Table 6 (cont.)

	2 Be	+	PbO ₂	=	Pb	+	2 BeO
Heat of formation			-65.12		207.21		-146.00
Molecular weight	9.01		239.21		11.34		25.01
Density	1.85		9.38		3.01		3.01
Melting point, °C	1283.00		290.00		327.40		2530.00
Boiling point, °C	2970.00				1750.00		3900.00
Heat of reaction, kcal	-225.88						
Reactants' density			7.30				
Gravimetric enthalpy, cal/g	-878.10						
Volumetric enthalpy, cal/cc	-6406.21						
	2 Bi	+	PbO ₂	=	Pb	+	2 BiO
Heat of formation			-66.12		207.21		-49.95
Molecular weight	208.99		239.21		11.34		224.99
Density	9.80		9.38		3.27		3.27
Melting point, °C	271.00		290.00		40.00		1750.00
Boiling point, °C	1420.00						
Heat of reaction, kcal	-33.78						
Reactants' density			9.64				
Gravimetric enthalpy, cal/g	-51.40						
Volumetric enthalpy, cal/cc	-495.55						
	C	+	PbO ₂	=	Pb	+	CO ₂
Heat of formation			-66.12		207.21		-94.05
Molecular weight	12.01		239.21		11.34		44.01
Density	2.25		9.38		3.27		1.98
Melting point, °C	25.00		290.00		40.00		-56.20
Boiling point, °C	4347.00						-78.50
Heat of reaction, kcal	-27.93						
Reactants' density			8.14				
Gravimetric enthalpy, cal/g	-111.18						
Volumetric enthalpy, cal/cc	-905.23						

Table 6 (cont.)

	4 La	+	3 PbO ₂	=	3 Pb	+	2 La ₂ O ₃
Heat of formation			-66.12				-458.00
Molecular weight	138.92		239.21		207.21		325.84
Density	6.15		9.38		11.34		6.51
Melting point, °C	880.00		290.00		327.40		2315.00
Boiling point, °C	1800.00				1750.00		4200.00
Heat of reaction, kcal	-717.64						
Reactants' density			7.63				
Gravimetric enthalpy, cal/g	-563.60						
Volumetric enthalpy, cal/cc	-4299.78						
	4 Li	+	PbO ₂	=	Pb	+	2 Li ₂ O
Heat of formation			-66.12				-142.40
Molecular weight	6.94		239.21		207.21		29.88
Density	.53		9.38		11.34		2.01
Melting point, °C	180.00		290.00		327.40		1700.00
Boiling point, °C	1326.00				1750.00		
Heat of reaction, kcal	-218.68						
Reactants' density			3.44				
Gravimetric enthalpy, cal/g	-819.12						
Volumetric enthalpy, cal/cc	-2821.65						
	2 Mg	+	PbO ₂	=	Pb	+	2 MgO
Heat of formation			-66.12				-143.84
Molecular weight	24.32		239.21		207.21		40.32
Density	1.74		9.38		11.34		3.58
Melting point, °C	650.00		290.00		327.40		2800.00
Boiling point, °C	1120.00						
Heat of reaction, kcal	-221.56						
Reactants' density			5.38				
Gravimetric enthalpy, cal/g	-769.71						
Volumetric enthalpy, cal/cc	-4143.65						

Table 7
MOST ENERGETIC REACTIONS OF METALS WITH OXIDES,
IN TERMS OF VOLUMETRIC ENTHALPY

Reaction						Enthalpy, cal/cc	
2 Be	+	RuO ₂	=	Ru	+	2 BeO	-8279
5 Be	+	N ₂ O ₅	=	2 N*	+	5 BeO	-7987
7 Be	+	Re ₂ O ₇	=	2 Re	+	7 BeO	-7773
4 Be	+	RuO ₄	=	Ru	+	4 BeO	-7616
2 Be	+	NO ₂	=	N	+	2 BeO	-7390
4 Be	+	N ₂ O ₄	=	2 N	+	4 BeO	-7221
2 Be	+	SO ₂	=	S	+	2 BeO	-6987
4 Be	+	10 SO ₄	=	10 S	+	4 BeO	-6880
3 Be	+	N ₂ O ₃	=	2 N	+	3 BeO	-6820
U	+	RuO ₂	=	Ru	+	UO ₂	-6815
5 U	+	2 N ₂ O ₅	=	4 N	+	5 UO ₂	-6812
5 Hf	+	2 N ₂ O ₅	=	4 N	+	5 HfO ₂	-6732
Hf	+	RuO ₂	=	Ru	+	HfO ₂	-6717
2 Be	+	Ag ₂ O ₂	=	2 Ag	+	2 BeO	-6637
10 Al	+	3 N ₂ O ₅	=	6 N	+	5 Al ₂ O ₃	-6613
4 Al	+	3 RuO ₂	=	3 Ru	+	2 Al ₂ O ₃	-6571
Hf	+	NO ₂	=	N	+	HfO ₂	-6314
5 Zr	+	2 N ₂ O ₅	=	4 N	+	5 ZrO ₂	-6266
7 U	+	2 Re ₂ O ₇	=	4 Re	+	7 UO ₂	-6246
8 Al	+	3 RuO ₄	=	3 Ru	+	4 Al ₂ O ₃	-6235
2 Be	+	SeO ₂	=	Se	+	2 BeO	-6227
2 U	+	N ₂ O ₄	=	2 N	+	2 UO ₂	-6221
4 Al	+	3 NO ₂	=	3 N	+	2 Al ₂ O ₃	-6206
2 Be	+	MnO ₂	=	Mn	+	2 BeO	-6194
2 Be	+	CO ₂	=	C	+	2 BeO	-6185
2 Hf	+	N ₂ O ₄	=	2 N	+	2 HfO ₂	-6158
7 Hf	+	2 Re ₂ O ₇	=	4 Re	+	7 HfO ₂	-6153
Zr	+	RuO ₂	=	Ru	+	ZrO ₂	-6152
Be	+	NO	=	N	+	BeO	-6147
2 U	+	RuO ₄	=	Ru	+	2 RuO ₂	-6435

Table 7 (cont.)

Reaction							Enthalpy, cal/cc
2 Be	+	PbO ₂	=	Pb	+	2 BeO	-6406
3 Be	+	CO ₂ O ₃	=	2 CO	+	3 BeO	-6389
U	+	NO ₂	=	N	+	UO ₂	-6379
2 Hf	+	RuO ₄	=	Ru	+	2 HfO ₂	-6359
5 Be	+	As ₂ O ₅	=	2 As	+	5 BeO	-6345
Be	+	CuO	=	Cu	+	BeO	-6330
4 Be	+	Co ₃ O ₄	=	3 Co	+	4 BeO	-6321
Hf	+	NO ₂	=	N	+	HfO ₂	-6314
5 Zr	+	2 N ₂ O ₅	=	4 N	+	5 ZrO ₂	-6266
7 U	+	2 Re ₂ O ₇	=	4 Re	+	7 UO ₂	-6246
8 Al	+	3 RuO ₄	=	3 Ru	+	4 Al ₂ O ₃	-6235
2 Be	+	SeO ₂	=	Se	+	2 BeO	-6227
2 U	+	N ₂ O ₄	=	2 N	+	2 UO ₂	-6221
4 Al	+	3 NO ₂	=	3 N	+	2 Al ₂ O ₃	-6206
2 Be	+	MnO ₂	=	Mn	+	2 BeO	-6194
2 Be	+	CO ₂	=	C	+	2 BeO	-6185
2 Hf	+	N ₂ O ₄	=	2 N	+	2 HfO ₂	-6158
Be	+	NO	=	N	+	BeO	-6147
5 Th	+	2 N ₂ O ₅	=	4 N	+	5 ThO ₂	-6123
Be	+	N ₂ O	=	2 N	+	BeO	-6098
5 Np	+	2 N ₂ O ₅	=	4 N	+	5 NpO ₂	-6083
8 Al	+	3 N ₂ O ₄	=	6 N	+	4 Al ₂ O ₃	-6050
Th	+	RuO ₄	=	Ru	+	ThO ₂	-6003
14 Al	+	3 Re ₂ O ₇	=	6 Re	+	7 Al ₂ O ₃	-5995
10 Ti	+	3 N ₂ O ₅	=	6 N	+	5 Ti ₂ O ₃	-5941
3 U	+	2 N ₂ O ₃	=	4 N	+	3 UO ₂	-5933
Np	+	RuO ₂	=	Ru	+	NpO ₂	-5926
Zr	+	NO ₂	=	N	+	ZrO ₂	-5902
4 B	+	3 RuO ₂	=	3 Ru	+	2 B ₂ O ₃	-5889
2 Zr	+	RuO ₄	=	Ru	+	2 ZrO ₂	-5888
Be	+	NiO	=	Ni	+	BeO	-5880
3 Hf	+	2 N ₂ O ₃	=	4 N	+	3 HfO ₂	-5879

Table 7 (cont.)

Reaction						Enthalpy, cal/cc	
2 Be	+	TeO ₂	=	Te	+	2 BeO	-5831
Th	+	NO ₂	=	N	+	ThO ₂	-5818
3 Be	+	CrO ₃	=	Cr	+	3 BeO	-5799
2 Th	+	RuO ₄	=	Ru	+	2 ThO ₂	-5795
2 Al	+	N ₂ O ₃	=	2 N	+	Al ₂ O ₃	-5780
2 U	+	10 SO ₄	=	10 S	+	2 UO ₂	-5779
4 Ti	+	3 RuO ₂	=	3 Ru	+	2 Ti ₂ O ₃	-5757
10 Ho	+	3 N ₂ O ₅	=	6 N	+	5 Ho ₂ O ₃	-5751
2 Zr	+	N ₂ O ₄	=	2 N	+	2 ZrO ₂	-5750
U	+	SO ₂	=	S	+	UO ₂	-5749
Np	+	NO ₂	=	N	+	NpO ₂	-5732
U	+	Ag ₂ O ₂	=	2 Ag	+	UO ₂	-5728
2 Hf	+	10 SO ₄	=	10 S	+	2 HfO ₂	-5716
2 Np	+	RuO ₄	=	Ru	+	2 NpO ₂	-5692
2 Th	+	N ₂ O ₄	=	2 N	+	2 ThO ₂	-5685
Hf	+	SO ₂	=	S	+	HfO ₂	-5679
Hf	+	Ag ₂ O ₂	=	2 Ag	+	HfO ₂	-5676
4 B	+	3 NO ₂	=	3 N	+	2 B ₂ O ₃	-5668
2 Be	+	WO ₂	=	W	+	2 BeO	-5646
4 Ti	+	3 NO ₂	=	3 N	+	2 Ti ₂ O ₃	-5610
8 B	+	3 RuO ₄	=	3 Ru	+	4 B ₂ O ₃	-5607
2 Ta	+	N ₂ O ₅	=	2 N	+	Ta ₂ O ₅	-5593
8 Al	+	3 OsO ₄	=	3 Os	+	4 Al ₂ O ₃	-5592
4 Ho	+	3 RuO ₂	=	3 Ru	+	2 Ho ₂ O ₃	-5582
2 Np	+	N ₂ O ₄	=	2 N	+	2 NpO ₂	-5576
4 Al	+	3 Ag ₂ O ₂	=	6 Ag	+	2 Al ₂ O ₃	-5572
7 Zr	+	2 Re ₂ O ₇	=	4 Re	+	7 ZrO ₂	-5562
8 Ti	+	3 RuO ₄	=	3 Ru	+	4 Ti ₂ O ₃	-5553
10 Tb	+	3 N ₂ O ₅	=	6 N	+	5 Tb ₂ O ₃	-5549
4 Al	+	3 SO ₂	=	3 S	+	2 Al ₂ O ₃	-5542
3 Be	+	MoO ₃	=	Mo	+	3 BeO	-5528

Table 7 (cont.)

Reaction							Enthalpy, cal/cc
3 Zr	+	2 N ₂ O ₃	=	4 N	+	3 ZrO ₂	-5510
7 Th	+	2 Re ₂ O ₇	=	4 Re	+	7 ThO ₂	-5505
4 Ho	+	3 NO ₂	=	3 N	+	2 Ho ₂ O ₃	-5500
2 Be	+	MoO ₂	=	Mo	+	2 BeO	-5487
8 B	+	3 N ₂ O ₄	=	6 N	+	4 B ₂ O ₃	-5481
3 Th	+	2 N ₂ O ₃	=	4 N	+	3 ThO ₂	-5477
8 Ti	+	3 N ₂ O ₄	=	6 N	+	4 Ti ₂ O ₃	-5457
10 Sm	+	3 N ₂ O ₅	=	6 N	+	5 Sm ₂ O ₃	-5449
U	+	2 NO	=	2 N	+	UO ₂	-5445
8 Ho	+	3 RuO ₄	=	3 Ru	+	4 Ho ₂ O ₃	-5443
10 Gd	+	3 N ₂ O ₅	=	6 N	+	5 Gd ₂ O ₃	-5412
Hf	+	2 NO	=	2 N	+	HfO ₂	-5406
U	+	2 N ₂ O	=	4 N	+	UO ₂	-5395
8 Ho	+	3 N ₂ O ₄	=	6 N	+	4 Ho ₂ O ₃	-5377
10 Sc	+	3 N ₂ O ₅	=	6 N	+	5 Sc ₂ O ₃	-5368
10 Nd	+	3 N ₂ O ₅	=	6 N	+	5 Nd ₂ O ₃	-5363
Hf	+	2 N ₂ O	=	4 N	+	HfO ₂	-5357
3 Be	+	Fe ₂ O ₃	=	2 Fe	+	3 BeO	-5355
4 Tb	+	3 RuO ₂	=	3 Ru	+	2 Tb ₂ O ₃	-5349
3 Np	+	2 N ₂ O ₃	=	4 N	+	3 NpO ₂	-5348
10 La	+	3 N ₂ O ₅	=	6 N	+	5 La ₂ O ₃	-5339
U	+	PbO ₂	=	Pb	+	UO ₂	-5330
2 Al	+	3 NO	=	3 N	+	Al ₂ O ₃	-5323
4 Tb	+	3 NO ₂	=	3 N	+	2 Tb ₂ O ₃	-5316
7 Np	+	2 Re ₂ O ₇	=	4 Re	+	7 NpO ₂	-5304
5 Si	+	2 N ₂ O ₅	=	4 N	+	5 SiO ₂	-5297
Zr	+	Ag ₂ O ₂	=	2 Ag	+	ZrO ₂	-5297
10 Pr	+	3 N ₂ O ₅	=	6 N	+	5 Pr ₂ O ₃	-5293
Th	+	Ag ₂ O ₂	=	2 Ag	+	ThO ₂	-5289
4 Ta	+	5 RuO ₂	=	5 Ru	+	2 Ta ₂ O ₅	-5284
10 Ce	+	3 N ₂ O ₅	=	6 N	+	5 Ce ₂ O ₃	-5276

Table 7 (cont.)

Reaction						Enthalpy, cal/cc
Hf +	PbO ₂	=	Pb	+	HfO ₂	-5274
2 Al +	3 N ₂ O	=	6 N	+	Al ₂ O ₃	-5273
2 Zr +	10 SO ₄	=	10 S	+	2 ZrO ₂	-5266
2 Th +	10 SO ₄	=	10 S	+	2 ThO ₂	-5261
4 Ta +	5 NO ₂	=	5 N	+	2 Ta ₂ O ₅	-5256
2 Ti +	N ₂ O ₃	=	2 N	+	Ti ₂ O ₃	-5242
8 Tb +	3 RuO ₄	=	3 Ru	+	4 Tb ₂ O ₃	-5238
4 Sm +	3 RuO ₂	=	3 Ru	+	2 Sm ₂ O ₃	-5236
U +	2 CuO	=	2 Cu	+	UO ₂	-5236
U +	SeO ₂	=	Se	+	UO ₂	-5232
5 Mg +	N ₂ O ₅	=	2 N	+	5 MgO	-5227
4 Sm +	3 NO ₂	=	3 N	+	2 Sm ₂ O ₃	-5226
2 B +	N ₂ O ₃	=	2 N	+	B ₂ O ₃	-5221
2 Ho +	N ₂ O ₃	=	2 N	+	Ho ₂ O ₃	-5206
4 Gd +	3 RuO ₂	=	3 Ru	+	2 Gd ₂ O ₃	-5194
4 Gd +	3 NO ₂	=	3 N	+	2 Gd ₂ O ₃	-5193
8 Tb +	3 N ₂ O ₄	=	6 N	+	4 Tb ₂ O ₃	-5193
Th +	SO ₂	=	S	+	ThO ₂	-5188
3 U +	2 Co ₂ O ₃	=	4 Co	+	3 UO ₂	-5183
5 U +	2 As ₂ O ₅	=	4 As	+	5 UO ₂	-5183
Hf +	SeO ₂	=	Se	+	HfO ₂	-5181
Zr +	SO ₂	=	S	+	ZrO ₂	-5180
Hf +	2 CuO	=	2 Cu	+	HfO ₂	-5180
2 Nb +	N ₂ O ₅	=	2 N	+	Nb ₂ O ₅	-5178
4 Nd +	3 NO ₂	=	3 N	+	2 Nd ₂ O ₃	-5154
4 Al +	3 PbO ₂	=	3 Pb	+	2 Al ₂ O ₃	-5149
4 Nd +	3 RuO ₂	=	3 Ru	+	2 Nd ₂ O ₃	-5145
4 Sc +	3 NO ₂	=	3 N	+	2 Sc ₂ O ₃	-5144
8 Sm +	3 RuO ₄	=	3 Ru	+	4 Sm ₂ O ₃	-5140
4 La +	3 NO ₂	=	3 N	+	2 La ₂ O ₃	-5140
14 Ti +	3 Re ₂ O ₇	=	6 Re	+	7 Ti ₂ O ₃	-5137

Table 7 (cont.)

Reaction							Enthalpy, cal/cc
4 Sc	+	3 RuO ₂	=	3 Ru	+	2 Sc ₂ O ₃	-5131
8 Ta	+	5 RuO ₄	=	5 Ru	+	4 Ta ₂ O ₅	-5131
4 La	+	3 RuO ₂	=	3 Ru	+	2 La ₂ O ₃	-5128
Np	+	Ag ₂ O ₂	=	2 Ag	+	NpO ₂	-5125
5 Hf	+	2 As ₂ O ₅	=	4 As	+	5 HfO ₂	-5125
3 Hf	+	2 Co ₂ O ₃	=	4 Co	+	3 HfO ₂	-5124
2 Be	+	GeO ₂	=	Ge	+	2 BeO	-5118
Th	+	2 NO	=	2 N	+	ThO ₂	-5117
14 Ho	+	3 Re ₂ O ₇	=	8 Re	+	⁷ Ho ₂ O ₃	-5113
Be	+	HgO	=	Hg	+	BeO	-5112
Zr	+	2 NO	=	2 N	+	ZrO ₂	-5105
8 Sm	+	3 N ₂ O ₄	=	6 N	+	4 Sm ₂ O ₃	-5105
8 Gd	+	3 RuO ₄	=	3 Ru	+	4 Gd ₂ O ₃	-5104
U	+	10 SO ₂	=	10 S	+	UO ₂	-5095
4 Pr	+	3 NO ₂	=	3 N	+	2 Pr ₂ O ₃	-5093
8 Ta	+	5 N ₂ O ₄	=	10 N	+	4 Ta ₂ O ₅	-5082
4 Ce	+	3 NO ₂	=	3 N	+	2 Ce ₂ O ₃	-5074
8 Gd	+	3 N ₂ O ₄	=	6 N	+	4 Gd ₂ O ₃	-5073
Th	+	2 N ₂ O	=	4 N	+	ThO ₂	-5072
4 Pr	+	3 RuO ₂	=	3 Ru	+	2 Pr ₂ O ₃	-5070
2 U	+	Co ₃ O ₄	=	3 Co	+	2 UO ₂	-5066
8 Nd	+	3 RuO ₄	=	3 Ru	+	4 Nd ₂ O ₃	-5063
14 B	+	3 Re ₂ O ₇	=	6 Re	+	⁷ B ₂ O ₃	-5063
4 Al	+	3 SeO ₂	=	3 Se	+	2 Al ₂ O ₃	-5063
2 Np	+	10 SO ₄	=	10 S	+	2 NpO ₂	-5061
Zr	+	2 N ₂ O	=	4 N	+	ZrO ₂	-5055
8 La	+	3 RuO ₄	=	3 Ru	+	4 La ₂ O ₃	-5051
2 Al	+	3 CuO	=	3 Cu	+	Al ₂ O ₃	-5051
Hf	+	10 SO ₂	=	10 S	+	HfO ₂	-5046
3 Be	+	WO ₃	=	W	+	3 BeO	-5045
4 Ce	+	3 RuO ₂	=	3 Ru	+	2 Ce ₂ O ₃	-5045

Table 7 (cont.)

Reaction							Enthalpy, cal/cc
8 Sc	+	3 RuO ₄	=	3 Ru	+	4 Sc ₂ O ₃	-5044
2 Tb	+	N ₂ O ₃	=	2 N	+	Tb ₂ O ₃	-5036
8 Nd	+	3 N ₂ O ₄	=	6 N	+	4 Nd ₂ O ₃	-5036
2 Mg	+	NO ₂	=	N	+	2 MgO	-5029
U	+	CO ₂	=	C	+	UO ₂	-5028
8 La	+	3 N ₂ O ₄	=	6 N	+	4 La ₂ O ₃	-5026
4 Ho	+	3 Ag ₂ O ₂	=	6 Ag	+	2 Ho ₂ O ₃	-5024
10 V	+	3 N ₂ O ₅	=	6 N	+	5 V ₂ O ₃	-5020
8 Sc	+	3 N ₂ O ₄	=	6 N	+	4 Sc ₂ O ₃	-5018
4 Ti	+	3 Ag ₂ O ₂	=	6 Ag	+	2 Ti ₂ O ₃	-5018
Si	+	NO ₂	=	N	+	SiO ₂	-5015
2 Hf	+	Co ₃ O ₄	=	3 Co	+	2 HfO ₂	-5006
8 Pr	+	3 RuO ₄	=	3 Ru	+	4 Pr ₂ O ₃	-4997
2 Mg	+	RuO ₂	=	Ru	+	2 MgO	-4989
10 Al	+	3 As ₂ O ₅	=	6 As	+	5 Al ₂ O ₃	-4988
2 Al	+	Co ₂ O ₃	=	2 Co	+	Al ₂ O ₃	-4983
8 Pr	+	3 N ₂ O ₄	=	6 N	+	4 Pr ₂ O ₃	-4978
8 Ce	+	3 RuO ₄	=	3 Ru	+	4 Ce ₂ O ₃	-4974
Hf	+	CO ₂	=	C	+	HfO ₂	-4973
Np	+	2 NO	=	2 N	+	NpO ₂	-4964
8 Ho	+	3 OsO ₄	=	3 Os	+	4 Ho ₂ O ₃	-4960
8 Ce	+	3 N ₂ O ₄	=	6 N	+	4 Ce ₂ O ₃	-4956
2 Sm	+	N ₂ O ₃	=	2 N	+	Sm ₂ O ₃	-4955
Np	+	SO ₂	=	S	+	NpO ₂	-4951
4 B	+	3 Ag ₂ O ₂	=	6 Ag	+	2 B ₂ O ₃	-4951
Si	+	RuO ₂	=	Ru	+	SiO ₂	-4950
3 U	+	2 SO ₃	=	2 S	+	3 UO ₂	-4949

*N refers to molecular nitrogen and is thus 1/2 N₂.

Table 8

MOST ENERGETIC REACTIONS OF METALS WITH OXIDES,
IN TERMS OF GRAVIMETRIC ENTHALPY

Reaction						Enthalpy, cal/g
3 Be + NO_3	=	N^*	+	3 BeO		-5064
5 Be + N_2O_5	=	2 N	+	5 BeO		-4703
2 Be + NO_2	=	N	+	2 BeO		-4686
4 Be + N_2O_4	=	2 N	+	4 BeO		-4578
3 Be + N_2O_3	=	2 N	+	3 BeO		-4444
1 Be + NO	=	N	+	BeO		-4294
6 Li + NO_3	=	N	+	3 Li_2O		-4246
4 Li + NO_2	=	N	+	2 Li_2O		-3970
10 Li + N_2O_5	=	2 N	+	5 Li_2O		-3956
8 Li + N_2O_4	=	2 N	+	4 Li_2O		-3876
6 Li + N_2O_3	=	2 N	+	3 Li_2O		-3800
2 B + NO_3	=	N	+	B_2O_3		-3765
2 Li + NO	=	N	+	Li_2O		-3736
2 Al + NO_3	=	N	+	Al_2O_3		-3553
4 B + 3 NO_2	=	3 N	+	2 B_2O_3		-3465
10 B + 3 N_2O_5	=	3 N	+	5 B_2O_3		-3423
8 B + 3 N_2O_4	=	6 N	+	4 B_2O_3		-3350
4 Al + 3 NO_2	=	3 N	+	2 Al_2O_3		-3343
10 Al + 3 N_2O_5	=	6 N	+	5 Al_2O_3		-3309
2 Li + N_2O_3	=	2 N	+	B_2O_3		-3297
3 Mg + NO_3	=	N	+	3 MgO		-3293
2 B + 3 NO	=	3 N	+	B_2O_3		-3284
8 Al + 3 N_2O_4	=	6 N	+	4 Al_2O_3		-3259
Be + CO	=	C	+	BeO		-3230
2 Al + N_2O_3	=	2 N	+	Al_2O_3		-3224
2 Al + 3 NO	=	3 N	+	Al_2O_3		-3221
2 Be + CO_2	=	C	+	2 BeO		-3190
2 Be + Na_2	=	Na	+	2 BeO		-3151
2 Mg + NO_2	=	N	+	2 MgO		-3124

Table 8 (cont.)

Reaction						Enthalpy, cal/g
Be + N_2O	=	2 N	+	BeO	-3120	
3 Si + $2 NO_3$	=	2 N	-	3 SiO_2	-3083	
4 Mg + N_2O_4	=	2 N	+	4 MgO	-3051	
Mg + NO	=	N	+	MgO	-3045	
3 Mg + N_2O_3	=	2 N	+	3 MgO	-3030	
Si + NO_2	=	N	+	SiO_2	-2881	
5 Si + $2 N_2O_5$	=	N	+	5 SiO_2	-2824	
Si + $2 NO$	=	2 N	+	SiO_2	-2821	
2 Li + N_2O	=	2 N	+	Li_2O	-2796	
2 Sc + NO_3	=	N	+	Sc_2O_3	-2790	
2 Si + N_2O_4	=	2 N	+	2 SiO_2	-2787	
3 Si + $2 N_2O_3$	=	2 N	+	3 SiO_2	-2776	
2 Li + CO	=	C	+	Li_2O	-2769	
4 Li + NaO_2	=	Na	+	$2 Li_2O$	-2693	
2 Be + SO_2	=	2 S	+	2 BeO	-2692	
4 Sc + $3 NO_2$	=	3 N	+	$2 Sc_2O_3$	-2662	
4 Li + CO_2	=	C	+	$2 Li_2O$	-2657	
6 Li + SO_3	=	S	+	$3 Li_2O$	-2650	
2 Sc + $3 NO$	=	3 N	+	Sc_2O_3	-2644	
4 Be + RuO_4	=	Ru	+	4 BeO	-2636	
10 Sc + $3 N_2O_5$	=	6 N	+	$5 Sc_2O_3$	-2617	
5 Be + MoO_5	=	Mo	+	5 BeO	-2601	
2 Sc + N_2O_3	=	2 N	+	Sc_2O_3	-2597	
6 Sc + $3 N_2O_4$	=	6 N	+	$4 Sc_2O_3$	-2597	
3 Ca + NO_3	=	N	+	3 CaO	-2571	
4 Be + K_2O_4	=	2 K	+	4 BeO	-2524	
Ca + NO	=	N	+	CaO	-2475	
2 Ca + NO_2	=	N	+	2 CaO	-2471	
2 Al + $3 N_2O$	=	3 N	+	Al_2O_3	-2459	
Be + SO	=	S	+	BeO	-2452	
5 Ca + N_2O_5	=	2 N	+	5 CaO	-2430	

Table 8 (cont.)

Reaction						Enthalpy, cal/g	
3 Ca	+	N ₂ O ₃	=	2 N	+	3 CaO	-2423
4 Ca	+	N ₂ O ₄	=	2 N	+	4 CaO	-2417
Mg	+	N ₂ O	=	2 N	+	MgO	-2389
3 Be	+	CrO ₃	=	Cr	+	3 BeO	-2358
2 B	+	3 N ₂ O	=	6 N	+	1 B ₂ O ₃	-2345
8 Li	+	RuO ₄	=	Ru	+	4 Li ₂ O	-2339
Be	+	SiO	=	Si	+	BeO	-2331
4 Li	+	SO ₂	=	S	+	2 Li ₂ O	-2328
2 Ti	+	3 NO	=	3 N	+	Ti ₂ O ₃	-2323
2 Al	+	3 CO	=	3 C	+	Al ₂ O ₃	-2318
4 Ti	+	3 NO ₂	=	6 N	+	2 Ti ₂ O ₃	-2300
4 Be	+	Nb ₂ O ₄	=	2 Nb	+	4 BeO	-2284
2 P	+	NO ₃	=	N	+	P ₂ O ₃	-2282
10 Li	+	MoO ₅	=	Mo	+	5 Li ₂ O	-2269
2 Ti	+	N ₂ O ₃	=	2 N	+	Ti ₂ O ₃	-2252
10 Ti	+	3 N ₂ O ₅	=	6 N	+	5 Ti ₂ O ₃	-2247
4 Al	+	3 NaO ₂	=	3 Na	+	2 Al ₂ O ₃	-2244
Mg	+	CO	=	C	+	MgO	-2244
8 Ti	+	3 N ₂ O ₄	=	6 N	+	4 Ti ₂ O ₃	-2237
8 Li	+	K ₂ O ₄	=	2 K	+	4 Li ₂ O	-2203
2 P	+	3 NO	=	3 N	+	P ₂ O ₃	-2202
2 Li	+	SO	=	S	+	Li ₂ O	-2201
2 Al	+	SO ₃	=	S	+	Al ₂ O ₃	-2197
2 Be	+	Li ₂ O ₂	=	2 Li	+	2 BeO	-2195
2 Mg	+	NaO ₂	=	Na	+	2 MgO	-2178
4 P	+	3 NO ₂	=	3 N	+	2 P ₂ O ₃	-2154
4 Al	+	3 CO ₂	=	3 C	+	2 Al ₂ O ₃	-2150
3 Mg	+	SO ₃	=	S	+	3 MgO	-2136
2 Sc	+	3 N ₂ O	=	6 N	+	Sc ₂ O ₃	-2114
2 B	+	3 CO	=	3 C	+	B ₂ O ₃	-2108
Si	+	2 N ₂ O	=	4 N	+	SiO ₂	-2104

Table 8 (cont.)

Reaction						Enthalpy, cal/g
2 P	+	N ₂ O ₃	=	2 N	+	P ₂ O ₃
4 Be	+	MoO ₄	=	Mo	+	4 BeO
2 Mg	+	CO ₂	=	C	+	2 MgO
10 P	+	3 N ₂ O ₃	=	6 N	+	5 P ₂ O ₃
8 P	+	3 N ₂ O ₄	=	6 N	+	4 P ₂ O ₃
2 Li	+	SiO	=	Si	+	Li ₂ O
3 Be	+	K ₂ O ₃	=	2 K	+	3 BeO
6 Li	+	CrO ₃	=	Cr	+	3 Li ₂ O
Ca	+	N ₂ O	=	2 N	+	CaO
7 Be	+	Tc ₂ O ₇	=	2 Tc	+	7 BeO
8 Al	+	3 RuO ₄	=	3 Ru	+	4 Al ₂ O ₃
3 Zr	+	2 NO ₃	=	2 N	+	3 ZrO ₂
4 B	+	3 NaO ₂	=	3 Na	+	2 B ₂ O ₃
Zr	+	2 NO	=	2 N	+	ZrO ₂
4 Mg	+	RuO ₄	=	Ru	+	4 MgO
4 Al	+	3 SO ₂	=	3 S	+	2 Al ₂ O ₃
2 B	+	SO ₃	=	S	+	B ₂ O ₃
Zr	+	NO ₂	=	N	+	ZrO ₂
3 C	+	2 NO ₃	=	2 N	+	3 CO ₂
2 Be	+	MgO ₂	=	Mg	+	2 BeO
2 Al	+	3 SO	=	3 S	+	Al ₂ O ₃
2 Mg	+	SO ₂	=	S	+	2 MgO
10 Al	+	3 MoO ₅	=	3 Mo	+	5 Al ₂ O ₃
3 Zr	+	2 N ₂ O ₃	=	4 N	+	3 ZrO ₂
2 Sc	+	3 CO	=	3 C	+	Sc ₂ O ₃
C	+	2 NO	=	2 N	+	CO ₂
Mg	+	SO	=	S	+	MgO
5 Mg	+	MoO ₅	=	Mo	+	5 MgO
2 Zr	+	N ₂ O ₄	=	2 N	+	2 ZrO ₂
5 Zr	+	2 N ₂ O ₅	=	4 N	+	5 ZrO ₂
3 Ti	+	NO ₃	=	N	+	3 TiO
2 Ti	+	3 N ₂ O	=	6 N	+	Ti ₂ O ₃

Table 8 (cont.)

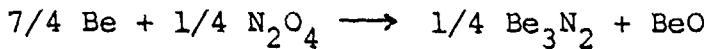
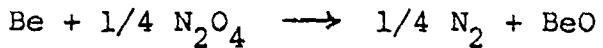
Reaction						Enthalpy, cal/g	
5 Be	+	As ₂ O ₅	=	2 As	+	5 BeO	-1860
8 Al	+	3 K ₂ O ₄	=	6 K	+	4 Al ₂ O ₃	-1859
2 V	+	3 NO	=	3 N	+	V ₂ O ₃	-1848
2 V	+	NO ₃	=	N	+	V ₂ O ₃	-1848
4 Sc	+	3 NaO ₂	=	3 Na	+	2 Sc ₂ O ₃	-1845
Ca	+	CO	=	C	+	CaO	-1843
4 Mg	+	K ₂ O ₄	=	2 K	+	4 MgO	-1842
8 Li	+	MoO ₄	=	Mo	+	4 Li ₂ O	-1838
4 B	+	3 CO ₂	=	3 C	+	2 B ₂ O ₃	-1835
2 Be	+	SeO ₂	=	Se	+	2 BeO	-1826
Si	+	2 CO	=	2 C	+	SiO ₂	-1814
8 B	+	3 RuO ₄	=	3 Ru	+	4 B ₂ O ₃	-1802
2 Sc	+	SO ₃	=	S	+	Sc ₂ O ₃	-1802
6 Li	+	K ₂ O ₃	=	2 K	+	3 Li ₂ O	-1800
14 Li	+	Tc ₂ O ₇	=	Tc	+	7 Li ₂ O	-1794
2 Ca	+	NaO ₂	=	Na	+	2 CaO	-1789
2 Al	+	3 SiO	=	3 Si	+	Al ₂ O ₃	-1785
2 Be	+	Na ₂ O ₂	=	2 Na	+	2 BeO	-1785
8 Be	+	Re ₂ C ₈	=	2 Re	+	8 BeO	-1780
Mg	+	SiO	=	Si	+	MgO	-1778
3 Be	+	TcO ₃	=	Tc	+	3 BeO	-1775
4 V	+	3 NO ₂	=	3 N	+	2 V ₂ O ₃	-1767
C	+	NO ₂	=	N	+	CO ₂	-1760
3 Ca	+	SO ₃	=	S	+	3 CaO	-1752
2 V	+	N ₂ O ₃	=	2 N	+	V ₂ O ₃	-1742
8 Sc	+	3 RuO ₄	=	3 Ru	+	4 Sc ₂ O ₃	-1736
4 Sc	+	3 CO ₂	=	3 C	+	2 Sc ₂ O ₃	-1731
8 Li	+	Nb ₂ O ₄	=	2 Nb	+	4 Li ₂ O	-1725
2 Cr	+	3 NO	=	3 N	+	Cr ₂ O ₃	-1723
2 B	+	3 SO	=	3 S	+	B ₂ O ₃	-1712
3 C	+	2 N ₂ O ₃	=	4 N	+	3 CO ₂	-1712
8 V	+	3 N ₂ O ₄	=	6 N	+	4 V ₂ O ₃	-1707
4 Ca	+	RuO ₄	=	Ru	+	4 CaO	-1704

Table 8 (cont.)

Reaction							Enthalpy, cal/g
10 V	+	3 N ₂ O ₅	=	6 N	+	5 V ₂ O ₃	-1703
2 Cr	+	NO ₃	=	N	+	Cr ₂ O ₃	-1702
2 Nb	+	5 NO	=	5 N	+	Nb ₂ O ₅	-1700
Be	+	InO	=	In	+	BeO	-1695
3 Mg	+	CrO ₃	=	Cr	+	3 MgO	-1694
2 P	+	3 N ₂ O	=	6 N	+	P ₂ O ₃	-1693
2 Al	+	CrO ₃	=	Cr	+	Al ₂ O ₃	-1693
4 Be	+	OsO ₄	=	Os	+	4 BeO	-1690
4 Be	+	Rb ₂ O ₄	=	2 Rb	+	4 BeO	-1689
2 Ca	+	CO ₂	=	C	+	2 CaO	-1689
2 Sc	+	3 SO	=	3 S	+	Sc ₂ O ₃	-1678
6 Nb	+	5 NO ₃	=	5 N	+	3 Nb ₂ O ₅	-1676
3 Si	+	2 SO ₃	=	2 S	+	3 SiO ₂	-1665
4 B	+	3 SO ₂	=	3 S	+	2 B ₂ O ₃	-1661
Zr	+	2 N ₂ O	=	4 N	+	ZrO ₂	-1657
Ca	+	SO	=	S	+	CaO	-1655
10 Li	+	As ₂ O ₅	=	2 As	+	5 Li ₂ O	-1649
4 Li	+	SeO ₂	=	Se	+	2 Li ₂ O	-1646
10 B	+	3 MoO ₅	=	3 Mo	+	5 B ₂ O ₃	-1642
2 C	+	N ₂ O ₄	=	2 N	+	2 CO ₂	-1641
4 Sc	+	3 SO ₂	=	3 S	+	2 Sc ₂ O ₃	-1637
5 C	+	2 N ₂ O ₅	=	4 N	+	5 CO ₂	-1630
4 Cr	+	3 NO ₂	=	3 N	+	2 Cr ₂ O ₃	-1628
10 Sc	+	3 MoO ₅	=	3 Mo	+	5 Sc ₂ O ₃	-1626
16 Li	+	Re ₂ O ₈	=	2 Re	+	8 Li ₂ O	-1620
2 Si	+	RuO ₄	=	Ru	+	2 SiO ₂	-1617
4 Li	+	MgO ₂	=	Mg	+	2 Li ₂ O	-1616
2 Ca	+	SO ₂	=	S	+	2 CaO	-1614
2 Li	+	InO	=	In	+	Li ₂ O	-1613
2 Cr	+	N ₂ O ₃	=	2 N	+	Cr ₂ O ₃	-1609
4 Nb	+	5 NO ₂	=	5 N	+	2 Nb ₂ O ₅	-1606
5 Ca	+	MoO ₅	=	Mo	+	5 CaO	-1605
2 Ti	+	3 CO	=	3 C	+	Ti ₂ O ₃	-1600
2 Be	+	MnO ₂	=	Mn	+	2 BeO	-1595
6 Nb	+	5 N ₂ O ₃	=	10 N	+	3 Nb ₂ O ₅	-1588

* Refers to molecular nitrogen and is thus 1/2 N₂.

The oxides of nitrogen are excellent oxidizers because they uniquely combine the characteristics of a slightly positive heat of formation, a small gram-atomic volume, and small values of z and y in their stoichiometric equations. In addition to the unusually large thermal outputs, their reactions are unique in other respects. For instance, with many metals either gaseous nitrogen or a metal nitride is produced:



Only the reactions producing gaseous nitrogen were considered here.

The periodicity of the enthalpies is illustrated in Figures 5, 6, and 7. The periodic behavior demonstrated by the oxides is somewhat different from that of the fluorides. Energy peaks (actually minima in the curves) occur at every ninth atomic number, forming the series beryllium, aluminum, titanium, gallium, zirconium, indium, and hafnium. Except for beryllium, these elements comprise Groups IIIA and IVB. In this analysis the elements from lanthanum to lutetium are considered as one unit. The rare earth elements, lanthanum to holmium and probably thorium to element 103, also form a broad energy peak within the peaks separated by nine units. The elements at the energy peaks are characterized by the electronic configuration of their valence orbitals. The electronic configuration in the oxides is the rare gas s^2 or $s^2 p^6$ or the pseudo rare gas $s^2 p^6 d^{10}$. Other characterizing features of the energy peaks are the high heats of formation of their oxides relative to the oxides of their immediate neighbors, their low gram-atomic volumes, and their low values of z and y due to the stoichiometry of their oxidation states.

The high volumetric energy outputs exhibited by the reactions with beryllium are due to the extremely low atomic volume of the metal. It also exhibits a high gravimetric energy output because its atomic weight is low. Because of these factors, the heat of formation of the oxide per unit volume and per unit weight is comparatively high. The heat of formation of magnesium oxide is about the same as that of beryllium oxide, but the atomic volume and the atomic weight of the metal are greater. Magnesium reactions are therefore not as energetic as beryllium reactions.

A similar situation exists between boron and aluminum. The smaller atomic volume and atomic weight of boron tend to increase the volumetric and gravimetric energies of its reactions. But aluminum reactions are much more energetic because aluminum oxide has a much higher heat of formation than boric oxide. These factors are discussed more thoroughly under nitrate reactions.

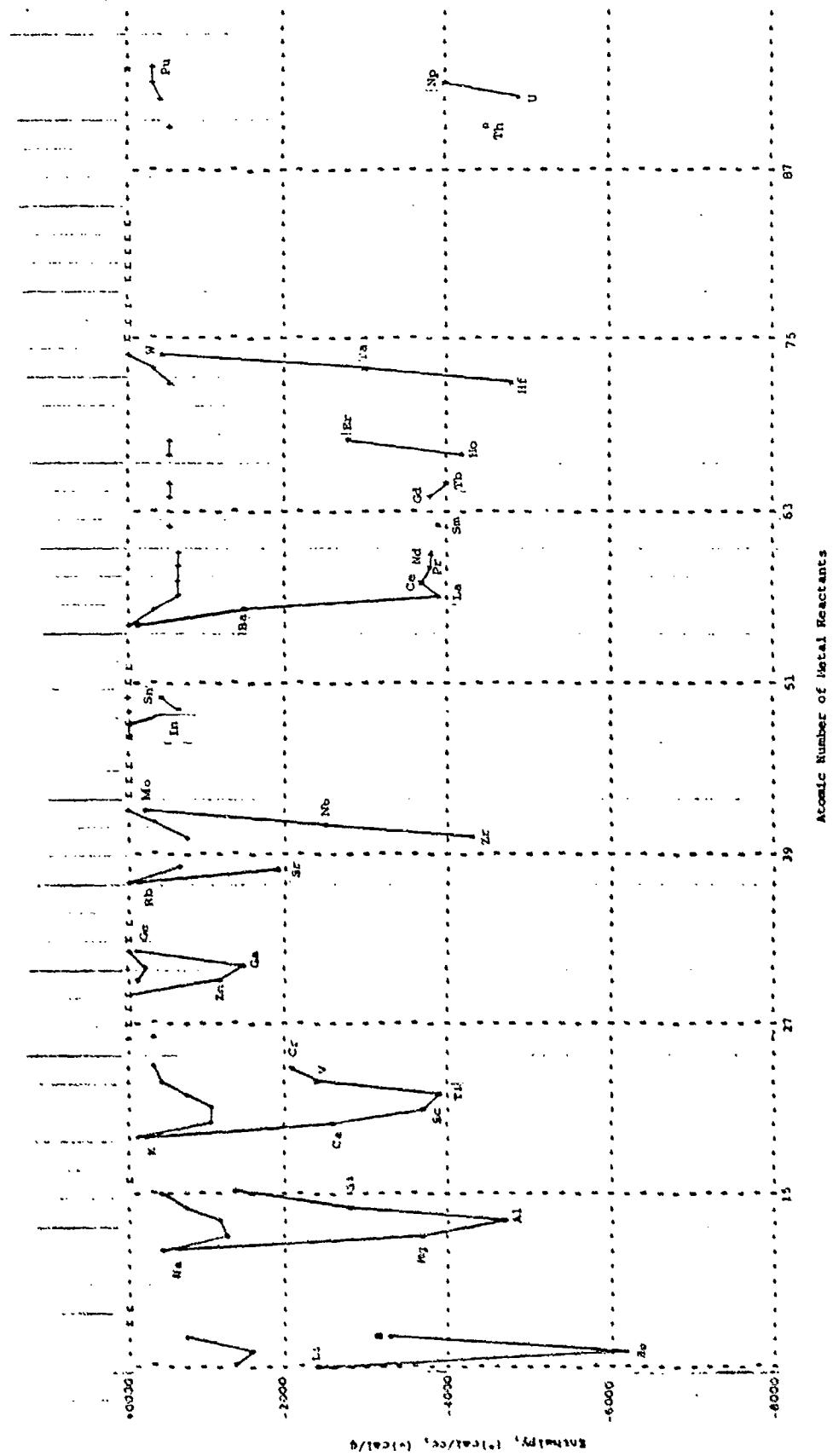


Figure 5
GRAVIMETRIC AND VOLUMETRIC ENTHALPIES OF REACTIONS OF METALS WITH MoO_3

Figure 5
GRAVIMETRIC AND VOLUMETRIC ENTHALPIES OF REACTIONS OF METALS WITH MoO_3

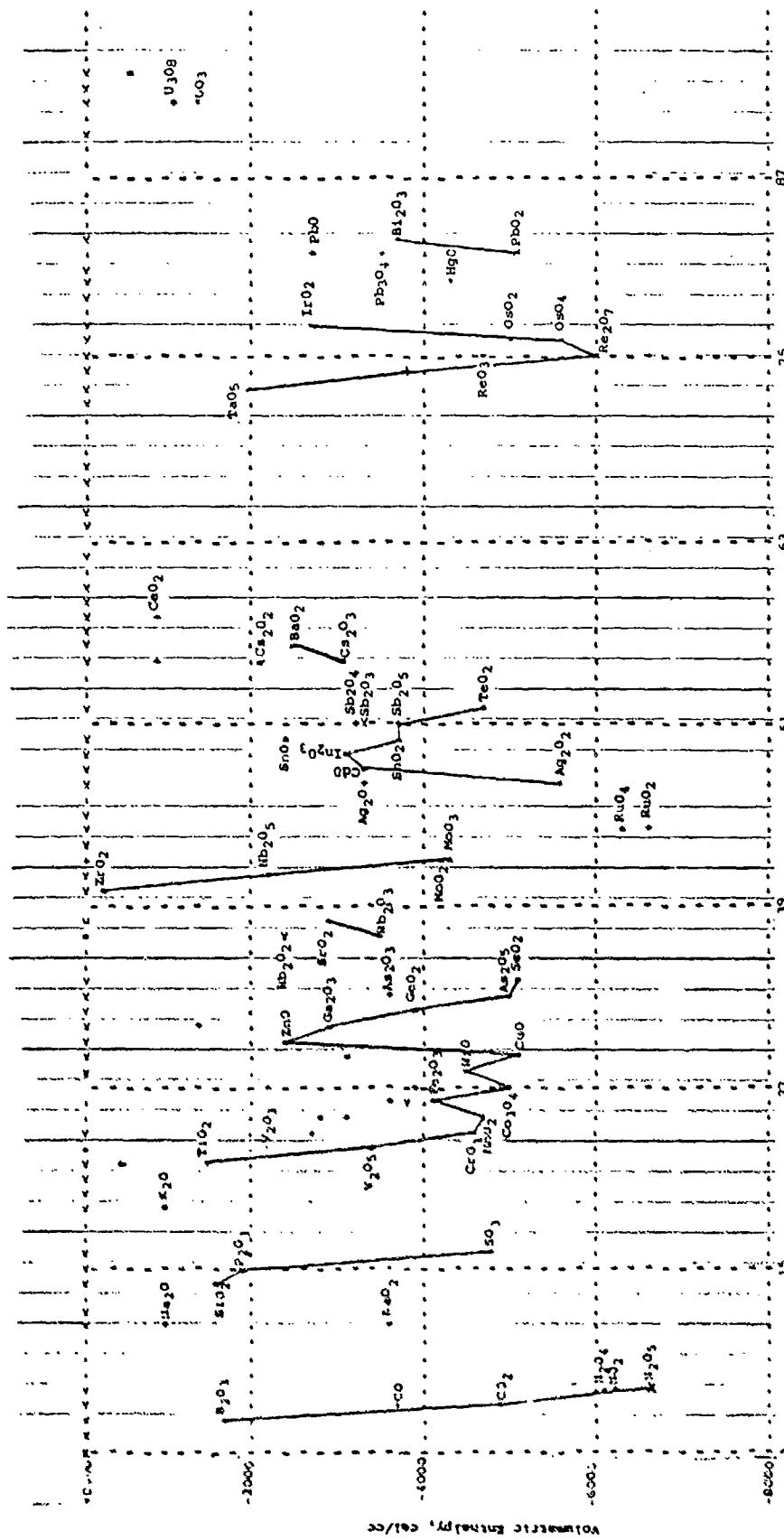


FIGURE 6
VOLUNTARY ENTHALPIES OF REACTIONS OF OXIDES WITH AN

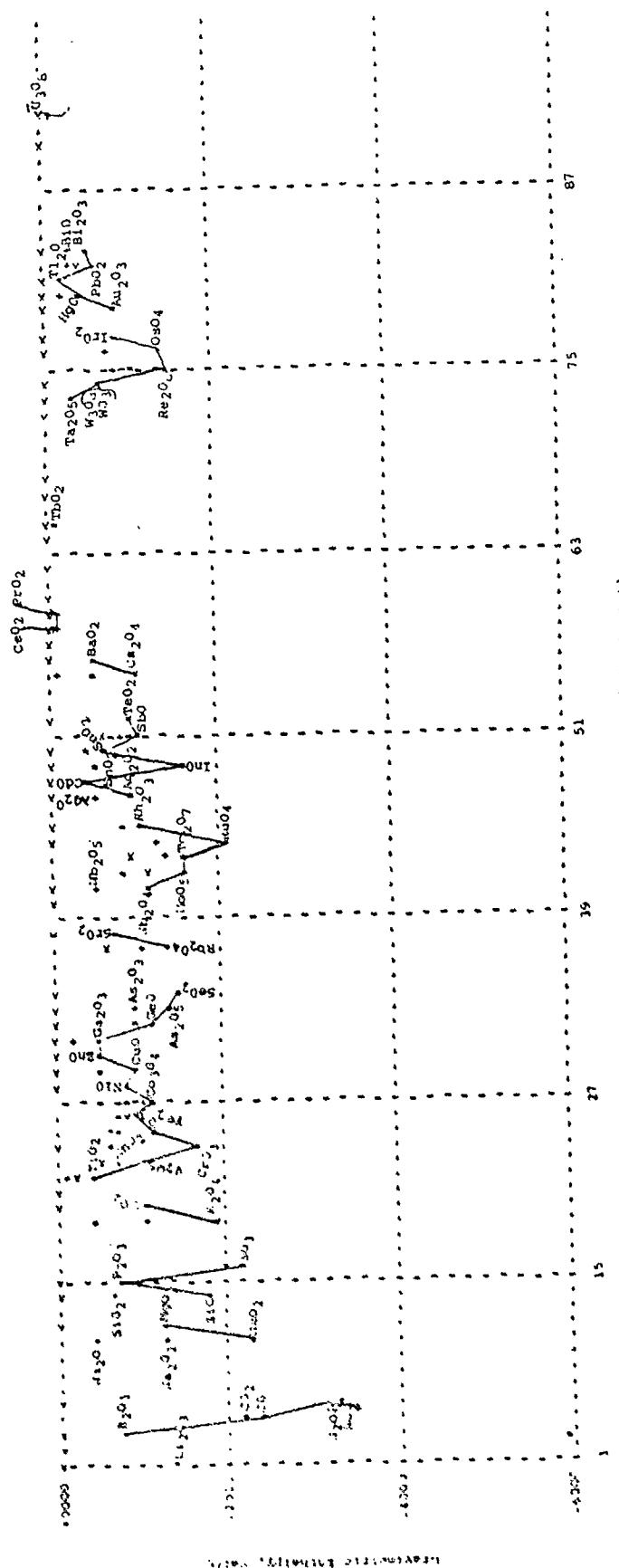


Figure 7
GRAVIMETRIC ENTHALPIES OF REACTIONS OF OXIDES WITH Al

Titanium, zirconium, and hafnium occupy peak positions because their gram-atomic volumes are relatively low and the heats of formation of their oxides are relatively high. Although gallium and indium have very low energy outputs, they are higher than their immediate neighbors because of their lower gram-atomic volumes and because of the higher heats of formation of their oxides relative to those of their neighbors. The extremely low gram-atomic volume of beryllium placed it in a peak position, in spite of the relatively low heat of formation of its oxide.

The peak positions of the rare earths lanthanum to holmium are due to the reverse phenomenon. Their relatively large gram-atomic volumes are compensated by the extremely high heats of formation of their oxides. Although data are not available, it seems that the energy outputs of all the members of the rare earth series should be comparable and therefore they will establish a horizontal position in the curve between lanthanum and lutetium. The volumetric energy for erbium is based on a questionable value for the density of the metal--4.77 g/cc.⁵ The anomalous position it occupies in the volumetric curve indicates that this density is probably in error. The interposition of the rare earth elements between zirconium and hafnium plus the lanthanide contraction cause hafnium to have a gram-atomic value comparable to that of zirconium even though its atomic weight is much greater.

The trend of the enthalpies within the various groups of the periodic table is similar to that of the fluorides (Figure 1B). The energy decreases from lithium to cesium. Group IIA energies also decrease from beryllium to barium. The Group II values are higher than the Group I values because all the factors -- ΔH_{AO_x} , gram-atomic volume, z, and y -- are more favorable. Group III elements exhibit a similar trend, but their outputs are lower, because the less favorable z and y values predominate even though their ΔH_{AO_x} 's and gram-atomic volumes are more favorable. This relationship is best illustrated by comparing calcium and gallium, which have gram-atomic volumes of 25.8 and 11.8 cc and ΔH_{AO_x} 's of 152 and 259 kcal, respectively. In spite of these decided advantages, the thermal release of calcium is superior to that of gallium because of the more favorable z and y values. Because of the unusually high heat of formation of its oxide, aluminum occupies an anomalous position above magnesium.

The trend in enthalpies within the transition metal groups in the periodic table is also similar to that of the fluorides (Figure 1C). The first two groups, copper, silver, gold,* and zinc, cadmium, mercury, exhibit a decrease in enthalpy with

* Copper, silver, and gold are not shown on the plot in Figure 5 because their reactions yield positive enthalpies.

increasing atomic number. Their enthalpies are all very low because of their low ΔH_{AO_x} 's. The energies decrease both because the ΔH_{AO_x} 's decrease and because the gram-atomic volumes increase with increasing atomic number.

Within Group IVB (titanium, zirconium, and hafnium), Group VB (vanadium, niobium, and tantalum,) and Group VIB (chromium, molybdenum, and tungsten) the enthalpies increase with atomic number because their gram-atomic volumes and the heats of formation of their oxides become more favorable. In comparing one group with another, however, the normalized enthalpies decrease with increasing group number. The reasons for this differ between Groups IV and V and between Groups V and VI. Even though the gram-atomic volumes and ΔH_{AO_x} 's of Group V are more favorable than those of Group IV, their energies are lower because of the predominant effect of the unfavorable z and y values. Whereas the gram-atomic volumes and the z and y values of Group VI are more favorable, the unfavorable ΔH_{AO_x} 's cause Group VI energies to be even lower than those of Group V.

Curves of the type shown in Figure 5 were drawn for the other oxides. Similar trends were exhibited, but the curves were displaced vertically because of the differences in the parameters of each oxide.

The volumetric and gravimetric enthalpies of the reactions of the various oxides with aluminum metal are shown in Figures 6 and 7, respectively. These curves appear as an inverted version of the curves in Figure 5 because the metals that act as effective reducing agents form oxides that are poor oxidizing agents and vice versa. Thus the maximum volumetric energy outputs occur with the oxides of nitrogen, arsenic, sulfur, selenium, tellurium, the transition metals (chromium, manganese, iron, cobalt, nickel, copper, molybdenum, ruthenium, silver, rhenium, and osmium), and lead. The gravimetric behavior is similar, with the notable exception of the alkali metals. They exhibit relatively high gravimetric outputs, but their volumetric outputs are relatively low because of their very low densities. These curves enable one to determine the best oxide that can be used with aluminum metal for applications involving different parameters. Similar curves were drawn for all the metals.

The volumetric and gravimetric enthalpies of 9636 reactions of the oxides are summarized in Tables 9 and 10, respectively. The most energetic reactions are in the upper left portion of the tables. The most effective oxidizers are on the left and the most effective reducing agents are on the top. The orders of efficacy mentioned previously are confirmed here.

Table 9
VOLUMETRIC ENTHALPIES OF REACTIONS OF METALS WITH OXIDES
in descending order from top to bottom and left to right)

Table 9 (cont.)

Table 6 (cont.)

CONTINUATION

Table 9 (cont.)

	Cs_2O	Al_2O_3	BfO_2	UO_2	Sc_2O_3	BeO	Li_2O	Al_2O_3	BeO	ThO_2	SrO	MgO	Pr_2O_3	Sm_2O_3	Cd_2O_3	Ce_2O_3	CaO	Er_2O_3	Na_2O_3
SE	-1008	-965	-850	-637	-535	-397	-182	309	0	-152	-133	103	-66	-43	-426	272	264	02	
U	-832	-131	43	109	-48	745	562	214	501	689	437	409	409	730	767	564	521		
HF	-836	-178	-39	67	-70	108	721	186	450	547	397	387	409	688	719	568	521		
AI	-601	125	103	213	11	435	841	856	603	668	520	507	531	807	846	645	645		
Ti	-934	-685	-1482	-483	-403	-338	245	0	-151	-151	-151	-52	-52	-217	207	207	207		
ZR	-741	250	369	302	414	126	405	933	1094	832	411	501	501	1010	1010	806	806		
NP	-659	455	723	627	710	897	1255	1155	628	825	661	665	665	1230	1230	1032	1032		
29	-901	-520	-117	-622	-348	-568	-116	240	19	-129	-73	-73	-73	-34	-32	-32	-32		
T1	-647	475	550	444	590	253	1052	1166	929	526	910	911	758	771	796	870	870		
D0	-950	-707	602	-458	-418	-772	95	-185	-150	-253	-253	-150	-150	-160	-171	48	48		
LA	-562	-621	-52	-643	-550	-400	-143	-785	-785	-216	-211	-235	-235	-241	-241	-149	-149		
SM	-685	-527	-111	-374	-315	-222	-20	270	64	-100	-100	-121	-121	-121	-121	-231	-231		
CD	-532	-534	-276	311	-204	-261	-80	267	61	-104	-104	-115	-115	-115	-115	-233	-233		
TA	-346	234	237	2090	2271	1072	2208	2573	3632	2635	1557	2807	2368	2241	2164	2226	2364		
ND	-1007	-635	-8166	-408	-799	-331	-171	-59	-171	-171	-171	-171	-171	-171	-171	-171	-171		
PR	-613	-657	-790	-454	-423	-357	-196	184	-95	-78	-153	-153	-153	-153	-153	-153	-153		
CE	-517	-511	-72	-574	-257	-244	-90	-257	-257	-136	-136	-136	-136	-136	-136	-136	-136		
S1	-380	2104	1675	1710	1426	1618	2217	1618	2217	3057	2776	136	105	105	215	215	215		
SC	-797	-197	-195	-54	-64	-92	-701	516	413	-57	120	294	399	274	287	510	510		
MG	-464	-470	-125	-725	-263	-225	-49	217	96	-76	144	216	216	216	216	216	216		
B	-62	218	2120	2224	425	2116	2733	2635	3691	176	1611	2017	2496	2276	2345	2639	2639		
B1	-350	5128	2631	2534	2724	1308	2592	2854	4216	3645	1635	1246	2731	2590	2522	2750	2750		
CP	-201	5224	2221	2621	2811	1375	2470	2474	3119	1905	1354	1264	2614	2614	2615	2873	2873		
V	-324	2550	2557	2119	2257	1129	2229	2229	5521	1601	1601	1601	2375	2216	2216	2394	2394		
HI	-4224	2534	2393	2147	2500	1622	2242	2895	3307	2576	1654	2743	2378	2260	2255	2452	2452		
ER	-455	-54	-651	-402	-402	-354	-354	-354	-354	-164	-164	-164	-164	-164	-164	-164	-164		
GA	-1359	2662	2653	2410	2674	1256	2692	2714	3707	2751	1641	1641	1641	1641	1641	1641	1641		
H	132	563	4745	4372	4372	2216	4187	3115	6183	4857	2739	4324	4279	4279	4279	4279	4279		
CA	-634	-544	-2059	4541	3794	-3531	-2531	13	-172	-172	-172	-172	-172	-172	-172	-172	-172		
ZN	-99	-619	-619	-760	4203	2552	1336	2667	2662	2635	2114	1656	1971	2545	2417	2417	2417		
LI	-732	-271	-760	-192	-142	-110	-110	247	104	91	-27	13	13	13	13	13	13		
P	-165	2164	2026	1842	4116	1137	2000	2235	2849	2849	2849	2849	2849	2849	2849	2849	2849		
H2	-234	6215	5297	4624	5102	2477	4576	6143	7504	5298	5215	5815	4665	4665	4665	4665	4665		
F2	176	4425	4706	4727	4727	4727	4727	4727	4727	4727	4727	4727	4727	4727	4727	4727	4727		
SI	82	3067	3082	3193	3165	1850	3174	3255	4653	3593	2374	1934	3263	3187	3187	3187	3187		
CE	656	2923	5110	2692	2692	1026	2493	2493	6179	3626	4357	4464	2171	2171	2171	2171	2171		
IN	412	5052	2652	2652	2652	1526	2652	2652	3201	3037	2037	2037	2795	2856	2856	2856	2856		
RE	416	6116	6116	6116	6116	6055	6055	6055	6055	6055	6055	6055	6055	5913	5913	5913	5913		
SI	421	4925	4626	4261	4151	2929	5446	5454	9715	4049	2867	1784	3874	3874	3874	3874	3874		
C	421	7659	6449	5842	6151	2917	5917	4049	4049	3655	3605	4949	5423	5752	5752	5752	5752		
CO	222	4554	4456	4052	4200	2279	3065	4074	5047	4487	2926	4844	4024	3525	3525	3525	3525		
BA	-552	-7	46	202	714	166	166	214	214	125	125	125	125	202	202	202	202		
SR	-662	-276	723	-238	-214	-216	-143	-115	-105	-99	-99	-99	-99	-120	-120	-118	-118		
HS	-209	600	423	542	633	458	458	458	611	620	620	620	620	767	767	767	767		
CU	451	4C84	3748	3685	3864	1936	3219	3219	4924	3575	2803	3745	3745	3745	3745	3745	3745		
SE	654	6254	3616	3564	4112	2209	3625	3625	3625	4260	3784	3861	3861	3784	3784	3784	3784		
BI	374	3622	2417	3510	3493	2131	2131	2027	3021	3021	2268	1419	3011	2922	2922	2922	2922		
CA	7577	6432	6207	6207	6207	6207	6207	6207	6207	6207	6207	6207	6207	5715	5715	5715	5715		
RI	721	8375	7366	6534	6534	6534	6534	6534	6534	6534	6534	6534	6534	5715	5715	5715	5715		
RI	743	660	5447	5476	5476	5476	5476	5476	5476	5476	5476	5476	5476	5715	5715	5715	5715		
S	672	5261	4627	4716	4716	4716	4716	4716	4716	4716	4716	4716	4716	5493	5493	5493	5493		
K	666	455	866	875	476	396	396	4067	5073	5139	5139	5139	5139	4943	4943	4943	4943		
H3	682	976	8456	4212	4212	4212	4212	4212	4212	4212	4212	4212	4212	4767	4767	4767	4767		
TG	274	291	262	197	197	197	197	197	197	197	197	197	197	4374	4374	4374	4374		
R1	117	850	462	470	393	402	402	402	402	402	402	402	402	5492	5492	5492	5492		
A2	603	4315	4487	3077	3692	2642	3417	3417	3417	3417	3417	3417	3417	4292	4292	4292	4292		
A3	1152	9C77	6C70	7360	7654	4159	4159	5377	5377	4906	4906	4906	4906	3793	3793	3793	3793		

Table 10
GRAVIMETRIC ENTHALPIES OF REACTIONS OF METALS WITH OXIDES

Table 10 (cont.)

Table 10 (cont.)

Table 10 (cont.)

SAMPLE 10 (cont.)

Table 10 (cont.)

C. Nitrate and Nitrite Reactions

The interactions of 18 nitrates and 8 nitrites with metals were examined, and 1226 reactions resulted. The groups of reactions embodying the nitrates and nitrites are highly energetic. In general, the nitrates are more energetic than the nitrites.

The data for a few of the more energetic reactions are shown in Table 11. These data were abstracted from the series of reactions of elements with lead nitrate listed on the computer data sheets. Reactions with lead nitrate can produce several oxides. For aluminum, boron, beryllium, calcium, and cesium, the most energetic reaction produces Pb_2O . For barium, bismuth, carbon, and cadmium, the most energetic reaction produces PbO . The reactions producing Pb_2O are generally more energetic.

Table 12 lists the 199 most energetic nitrate and nitrite reactions. Beryllium, uranium, hafnium, aluminum, zirconium, thorium, boron, titanium, tantalum, neodymium, lanthanum, scandium, praseodymium, cerium, magnesium, silicon, vanadium, chromium, niobium, gallium, and calcium are the best reducing metals, in that order. Lithium nitrate, lead nitrate, calcium nitrate, strontium nitrate, silver nitrate, sodium nitrate, barium nitrate, potassium nitrate, rubidium nitrate, barium nitrite, silver nitrite, sodium nitrite, and cesium nitrate are the best oxidizing agents, in that order. These relationships are depicted graphically in Figures 8, 9, and 10.

The periodicity of the data is apparent in Figure 8. These curves are similar to those depicting the behavior of oxides with metals, and the same rules seem to be applicable. The "rule of nine" that was observed in the oxide reactions is still valid: the minima in the curve, corresponding to maximum thermal outputs, occur at every ninth atomic number starting with beryllium, aluminum, titanium, gallium, zirconium, indium (no data), lanthanum, and hafnium.

The dotted lines connect the members of a periodic group with five or more members. Thus, the members of Groups IA (lithium, sodium, potassium, rubidium, and cesium) and IIA (beryllium, magnesium, calcium, strontium, and barium) are connected. The energy of the reaction decreases with increasing atomic number of the members of a group. This is generally true for the other "long" groups (IIIA and VIA), except for anomalies evident at aluminum and carbon.

These anomalies are related to the volumetric enthalpy, which is highly dependent upon the heats of formation of the products and reactants, on the volume of the reactants, and on the coefficients of the terms in the balanced equation. Aluminum and boron have the same stoichiometric coefficients, and

Table 11
DATA ON REACTIONS OF VARIOUS METALS WITH LEAD NITRATE

	$22 \text{ Al} + 6 \text{ Pb}(\text{NO}_3)_2 = 3 \text{ Pb}_2\text{O} + 11 \text{ Al}_2\text{O}_3 + 6 \text{ N}_2$					
Heat of formation	-107.35	-51.20	-399.09			
Molecular weight	26.98	331.23	430.42	101.94	28.02	
Density	2.70	4.53	8.34	3.97		
Melting point, °C	660.00	470.00	2015.00	-209.86		
Boiling point, °C	2327.00		3500.00	-195.80		
Heat of reaction, kcal	-3899.49					
Reactants' density	3.92					
Gravimetric enthalpy, cal/g	-1501.88					
Volumetric enthalpy, cal/cc	-5922.77					
	$22 \text{ B} + 6 \text{ Pb}(\text{NO}_3)_2 = 3 \text{ Pb}_2\text{O} + 11 \text{ B}_2\text{O}_3 + 6 \text{ N}_2$					
Heat of formation	-107.35	-51.20	-302.00			
Molecular weight	10.82	331.23	430.42	69.64	28.02	
Density	2.37	4.53	8.34	1.84		
Melting point, °C	2040.00	470.00	1500.00	450.00	-209.86	
Boiling point, °C	2550.00				-195.00	
Heat of reaction, kcal	-2831.50					
Reactants' density	4.13					
Gravimetric enthalpy, cal/g	-1272.34					
Volumetric enthalpy, cal/cc	-5251.75					
	$5 \text{ Ba} + \text{ Pb}(\text{NO}_3)_2 = \text{ PbO} + 5 \text{ BaO} + \text{ N}_2$					
Heat of formation	-107.35	-52.40	-133.40			
Molecular weight	331.23	223.21	153.36	28.02		
Density	3.50	4.53	8.00	5.72		
Melting point, °C	704.00	470.00	2000.00	1923.00	-209.86	
Boiling point, °C	1638.00			2000.00	-195.80	
Heat of reaction, kcal	-612.05					
Reactants' density	3.78					
Gravimetric enthalpy, cal/g	-601.21					
Volumetric enthalpy, cal/cc	-2272.34					

Table 11 (cont.)

	11 Be	+ 2 Pb(NO ₃) ₂	=	Pb ₂ O	+ 11 BeO	+ 2 N ₂
Heat of formation		-107.35		-51.20	-146.00	
Molecular weight	9.01	331.23		430.42	25.01	28.02
Density	1.85	4.53		8.34	3.01	
Melting point, °C	1283.00	470.00			2530.00	-209.86
Boiling point, °C	2970.00				3900.00	-195.80
Heat of reaction, kcal	-1442.50					
Reactants' density	3.81					
Gravimetric enthalpy, cal/g	-1894.03					
Volumetric enthalpy, cal/cc	-7218.66					
	10 Bi	+ 3 Pb(NO ₃) ₂	=	3 PbO	+ 5 Bi ₂ O ₃	+ 3 N ₂
Heat of formation		-107.35		-52.40	-137.90	
Molecular weight	208.99	331.23		223.21	466.00	28.02
Density	9.80	4.53		8.00	8.90	
Melting point, °C	271.00	470.00			820.00	-209.86
Boiling point, °C	1420.00				1390.00	-195.80
Heat of reaction, kcal	-524.65					
Reactants' density	7.13					
Gravimetric enthalpy, cal/g	-170.14					
Volumetric enthalpy, cal/cc	-1212.75					
	5 C	+ 2 Pb(NO ₃) ₂	=	2 PbO	+ 5 CO ₂	+ 2 N ₂
Heat of formation		-107.35		-52.40	-94.05	
Molecular weight	12.01	331.23		223.21	44.01	28.02
Density	2.25	4.53		8.00	1.98	
Melting point, °C	25.00	470.00			-56.20	-209.86
Boiling point, °C	4347.00				-78.50	-195.80
Heat of reaction, kcal	-360.35					
Reactants' density	4.18					
Gravimetric enthalpy, cal/g	-498.74					
Volumetric enthalpy, cal/cc	-2083.80					

Table 11 (cont.)

	11 Ca	+ 2 Pb(NO ₃) ₂	=	Pb ₂ O	+ 11 CaO	+ 2 N ₂
Heat of formation		-107.35		-51.20	-151.90	
Molecular weight	40.08	331.23		430.42	56.08	28.02
Density	1.55	4.53		8.34	3.35	
Melting point, °C	850.00	470.00			2580.00	209.86
Boiling point, °C	1240.00				2850.00	-195.80
Heat of reaction, kcal	-1507.40					
Reactants' density						
Gravimetric enthalpy, cal/g						
Volumetric enthalpy, cal/cc	2.56	-1366.22				
		-3500.07				
	5 Cd	+ Pb(NO ₃) ₂	=	PbO	+ 5 CdO	+ N ₂
Heat of formation		-107.35		-52.40	-60.86	
Molecular weight	112.41	331.23		223.21	128.41	28.02
Density	8.64	4.53		8.00	8.15	
Melting point, °C	320.90	470.00			900.00	209.86
Boiling point, °C	767.00					-195.80
Heat of reaction, kcal	-249.35					
Reactants' density						
Gravimetric enthalpy, cal/g	6.47	-279.14				
Volumetric enthalpy, cal/cc	-1804.64	-1804.64				
	22 Ce	+ 6 Pb(NO ₃) ₂	=	3 Pb ₂ O	+ 11 Ce ₂ O ₃	+ 6 N ₂
Heat of formation		-107.35		-51.20	-435.00	
Molecular weight	140.13	331.23		430.42	328.26	28.02
Density	6.70	4.53		8.34	6.90	
Melting point, °C	775.00	470.00			1692.00	209.86
Boiling point, °C	2900.00					-195.80
Heat of reaction, kcal	-4294.50					
Reactants' density						
Gravimetric enthalpy, cal/g	5.64	-847.00				
Volumetric enthalpy, cal/cc	-4777.81	-4777.81				

Table 12

MOST ENERGETIC NITRATE AND NITRITE REACTIONS WITH METALS,
IN TERMS OF VOLUMETRIC ENTHALPY

Reaction							Enthalpy, cal/cc
5 Be + 2 Li(NO ₃) ₂	=	Li ₂ O	+ 5 BeO	+ N ₂			-7798
11 Be + 2 Pb(NO ₃) ₂	=	Pb ₂ O	+ 11 BeO	+ 2 N ₂			-7218
5 Be + Ca(NO ₃) ₂	=	CaO	+ 5 BeO	+ N ₂			-7006
5 Be + Sr(NO ₃) ₂	=	SrO	+ 5 BeO	+ N ₂			-6697
5 Be + 2 Ag(NO ₃)	=	Ag ₂ O	+ 5 BeO	+ N ₂			-6623
5 U + 4 Li(NO ₃)	=	2 Li ₂ O	+ 5 UO ₂	+ 2 N ₂			-6537
5 Hf + 4 Li(NO ₃)	=	2 Li ₂ O	+ 5 HfO ₂	+ 2 N ₂			-6454
10 Al + 6 Li(NO ₃)	=	3 Li ₂ O	+ 5 Al ₂ O ₃	+ 3 N ₂			-6324
11 U + 4 Pb(NO ₃) ₂	=	2 Pb ₂ O	+ 11 UO ₂	+ 4 N ₂			-6110
5 Be + 2 Na(NO ₃)	=	Na ₂ O	+ 5 BeO	+ N ₂			-6090
11 Hf + 4 Pb(NO ₃) ₂	=	2 Pb ₂ O	+ 11 HfO ₂	+ 4 N ₂			-6042
5 Be + Ba(NO ₃) ₂	=	BaO	+ 5 BeO	+ N ₂			-5963
5 Zr + 4 Li(NO ₃)	=	2 Li ₂ O	+ 5 ZrO ₂	+ 2 N ₂			-5956
5 U + 2 Ca(NO ₃) ₂	=	2 CaO	+ 5 UO ₂	+ 2 N ₂			-5948
22 Al + 5 Pb(NO ₃) ₂	=	3 Pb ₂ O	+ 11 Al ₂ O ₃	+ 6 N ₂			-5922
5 Hf + 2 Ca(NO ₃) ₂	=	2 CaO	+ 5 HfO ₂	+ 2 N ₂			-5884
5 Th + 4 Li(NO ₃)	=	2 Li ₂ O	+ 5 ThO ₂	+ 2 N ₂			-5849
10 Al + 3 Ca(NO ₃) ₂	=	3 CaO	+ 5 Al ₂ O ₃	+ 3 N ₂			-5767
10 B + 6 Li(NO ₃)	=	3 Li ₂ O	+ 5 B ₂ O ₃	+ N ₂			-5674
5 U + 2 Sr(NO ₃) ₂	=	2 SrO	+ 5 UO ₂	+ 2 N ₂			-5674
5 U + 4 Ag(NO ₃)	=	2 Ag ₂ O	+ 5 UO ₂	+ 2 N ₂			-5672
5 Hf + 4 Ag(NO ₃)	=	2 Ag ₂ O	+ 5 HfO ₂	+ 2 N ₂			-5618
5 Hf + 2 Sr(NO ₃) ₂	=	2 SrO	+ 5 HfO ₂	+ 2 N ₂			-5616
10 Ti + 6 Li(NO ₃)	=	3 Li ₂ O	+ 5 Ti ₂ O ₃	+ 3 N ₂			-5603
11 Zr + 4 Pb(NO ₃) ₂	=	2 Pb ₂ O	+ 11 ZrO ₂	+ 4 N ₂			-5594
11 Th + 4 Pb(NO ₃) ₂	=	2 Pb ₂ O	+ 11 ThO ₂	+ 4 N ₂			-5544
10 Al + 6 Ag(NO ₃)	=	3 Ag ₂ O	+ 5 Al ₂ O ₃	+ 3 N ₂			-5510
10 Al + 3 Sr(NO ₃) ₂	=	3 SrO	+ 5 Al ₂ O ₃	+ 3 N ₂			-5500
5 Zr + 2 Ca(NO ₃) ₂	=	2 CaO	+ 5 ZrO ₂	+ 2 N ₂			-5452

Table 12 (cont.)

Reaction						Enthalpy, cal/cc
5 Th + 2 Ca(NO ₃) ₂	=	2 CaO	+ 5 ThO ₂	+ 2 N ₂		-5422
22 Ti + 6 Pb(NO ₃) ₂	=	3 Pb ₂ O	+ 11 Ti ₂ O ₃	+ 6 N ₂		-5270
22 B + 6 Pb(NO ₃) ₂	=	3 B ₂ O	+ 11 B ₂ O ₃	+ 5 N ₂		-5251
5 Th + 4 Ag(NO ₃)	=	2 Ag ₂ O	+ 5 ThO ₂	+ 2 N ₂		-5224
5 Zr + 4 Ag(NO ₃)	=	2 Ag ₂ O	+ 5 ZrO ₂	+ 2 N ₂		-5223
5 Th + 2 Sr(NO ₃) ₂	=	2 SrO	+ 5 ThO ₂	+ 2 N ₂		-5199
5 Zr + 2 Sr(NO ₃) ₂	=	2 SrO	+ 5 ZrO ₂	+ 2 N ₂		-5195
5 Ta + 2 Li(NO ₃)	=	Li ₂ O	+ Ta ₂ O ₅	+ N ₂		-5163
5 J + 4 Na(NO ₃)	=	2 Na ₂ O	+ 5 UO ₂	+ 2 N ₂		-5151
10 Ti + 3 Ca(NO ₃) ₂	=	3 CaO	+ 5 Ti ₂ O ₃	+ 3 N ₂		-5137
5 Hf + 4 Na(NO ₃)	=	2 Na ₂ O	+ 5 HfO ₂	+ 2 N ₂		-5104
10 B + 3 Ca(NO ₃) ₂	=	3 CaO	+ 5 B ₂ O ₃	+ 3 N ₂		-5088
10 Nd + 6 Li(NO ₃)	=	3 Li ₂ O	+ 5 Nd ₂ O ₃	+ 3 N ₂		-5080
5 U + 2 Ba(NO ₃) ₂	=	2 BaO	+ 5 UO ₂	+ 2 N ₂		-5078
10 La + 6 Li(NO ₃)	=	3 Li ₂ O	+ 5 La ₂ O ₃	+ 3 N ₂		-5067
3 Be + 2 Ag(NO ₂)	=	Ag ₂ O	+ 3 BeO	+ N ₂		-5064
10 Sc + 6 Li(NO ₃)	=	3 Li ₂ O	+ 5 Sc ₂ O ₃	+ 3 N ₂		-5062
5 Hf + 2 Ba(NO ₃) ₂	=	2 BaO	+ 5 HfO ₂	+ 2 N ₂		-5034
10 Pr + 6 Li(NO ₃)	=	3 Li ₂ O	+ 5 Pr ₂ O ₃	+ 3 N ₂		-5012
10 Al + 6 Na(NO ₃)	=	3 Na ₂ O	+ 5 Al ₂ O ₃	+ 3 N ₂		-4991
10 Ce + 6 Li(NO ₃)	=	3 Li ₂ O	+ 5 Ce ₂ O ₃	+ 3 N ₂		-4988
5 Mg + 2 Li(NO ₃)	=	Li ₂ O	+ 5 MgO	+ N ₂		-4936
10 Ti + 6 Ag(NO ₃)	=	3 Ag ₂ O	+ 5 Ti ₂ O ₃	+ 3 N ₂		-4932
10 Al + 3 Ba(NO ₃) ₂	=	3 BaO	+ 5 Al ₂ O ₃	+ 3 N ₂		-4927
10 Ti + 3 Sr(NO ₃) ₂	=	3 SrO	+ 5 Ti ₂ O ₃	+ 3 N ₂		-4884
5 Si + 4 Li(NO ₃)	=	2 Li ₂ O	+ 5 SiO ₂	+ 2 N ₂		-4877
22 Nd + 6 Pb(NO ₃) ₂	=	3 Pb ₂ O	+ 11 Nd ₂ O ₃	+ 6 N ₂		-4864
22 La + 6 Pb(NO ₃) ₂	=	3 Pb ₂ O	+ 11 La ₂ O ₃	+ 6 N ₂		-4860
10 B + 6 Ag(NO ₃)	=	3 Ag ₂ O	+ 5 B ₂ O ₃	+ 3 N ₂		-4842
5 Be + 2 K(NO ₃)	=	K ₂ O	+ 5 BeO	+ N ₂		-4831

Table 12 (cont.)

Reaction						Enthalpy, cal/cc
22 Sc + 6 Pb(NO ₃) ₂	=	3 Pb ₂ O	+ 11 Sc ₂ O ₃	+ 6 N ₂		-4830
5 Be + 2 Rb(NO ₃) ₂	=	Rb ₂ O	+ 5 BeO	+ N ₂		-4821
22 Ta + 10 Pb(NO ₃) ₂	=	5 Pb ₂ O	+ 11 Ta ₂ O ₅	+ 10 N ₂		-4821
22 Pr + 6 Pb(NO ₃) ₂	=	3 Pb ₂ O	+ 11 Pr ₂ O ₃	+ 6 N ₂		-4804
22 Ce + 6 Pb(NO ₃) ₂	=	3 Pb ₂ O	+ 11 Ce ₂ O ₃	+ 6 N ₂		-4777
10 B + 3 Sr(NO ₃) ₂	=	5 SrO	+ 5 B ₂ O ₃	+ 3 N ₂		-4775
5 Th + 4 Na(NO ₃) ₂	=	2 Na ₂ O	+ 5 ThO ₂	+ 2 N ₂		-4774
10 Nd + 3 Ca(NO ₃) ₂	=	3 CaO	+ 5 Nd ₂ O ₃	+ 3 N ₂		-4773
10 La + 3 Ca(NO ₃) ₂	=	3 CaO	+ 5 La ₂ O ₃	+ 3 N ₂		-4772
10 Sc + 3 Ce(NO ₃) ₂	=	3 CaO	+ 5 Sc ₂ O ₃	+ 3 N ₂		-4733
11 Mg + 2 Pb(NO ₃) ₂	=	Pb ₂ O	+ 11 MgO	+ 2 N ₂		-4729
5 Th + 2 Ba(NO ₃) ₂	=	2 BaO	+ 5 ThO ₂	+ 2 N ₂		-4728
10 Pr + 3 Ca(NO ₃) ₂	=	3 CaO	+ 5 Pr ₂ O ₃	+ 3 N ₂		-4716
5 Zr + 1 Na(NO ₃) ₂	=	2 Na ₂ O	+ 5 ZrO ₂	+ 2 N ₂		-4708
2 Nb + 2 Li(NO ₃) ₂	=	Li ₂ O	+ Nb ₂ O ₅	+ N ₂		-4707
10 Ce + 3 Ca(NO ₃) ₂	=	3 CaO	+ 5 Ce ₂ O ₃	+ 3 N ₂		-4688
2 Ta + Ca(NO ₃) ₂	=	CaO	+ Ta ₂ O ₅	+ N ₂		-4683
3 Be + 2 Na(NO ₂) ₂	=	Na ₂ O	+ 3 BeO	+ N ₂		-4670
5 Zr + 2 Ba(NO ₃) ₂	=	2 BaO	+ 5 ZrO ₂	+ 2 N ₂		-4658
5 Mg + Ca(NO ₃) ₂	=	CaO	+ 5 MgO	+ N ₂		-4641
10 La + 6 Ag(NO ₃) ₂	=	3 Ag ₂ O	+ 5 La ₂ O ₃	+ 3 N ₂		-4640
3 Be + Ba(NO ₂) ₂	=	BaO	+ 3 BeO	+ N ₂		-4640
10 La + 3 Sr(NO ₃) ₂	=	3 SrO	+ 5 La ₂ O ₃	+ 3 N ₂		-4591
10 Sc + 6 Ag(NO ₃) ₂	=	3 Ag ₂ O	+ 5 Sc ₂ O ₃	+ 3 N ₂		-4589
11 Si + 4 Pb(NO ₃) ₂	=	2 Pb ₂ O	+ 11 SiO ₂	+ 4 N ₂		-4587
10 Nd + 3 Sr(NO ₃) ₂	=	3 SrO	+ 5 Nd ₂ O ₃	+ 3 N ₂		-4584
10 Pr + 6 Ag(NO ₃) ₂	=	3 Ag ₂ O	+ 5 Pr ₂ O ₃	+ 3 N ₂		-4584
10 V + 6 Li(NO ₃) ₂	=	3 Li ₂ O	+ 5 V ₂ O ₃	+ 3 N ₂		-4571
10 Ce + 6 Ag(NO ₃) ₂	=	3 Ag ₂ O	+ 5 Ce ₂ O ₃	+ 3 N ₂		-4556
10 Pr + 3 Sr(NO ₃) ₂	=	3 SrO	+ 5 Pr ₂ O ₃	+ 3 N ₂		-4531

Table 12 (cont.)

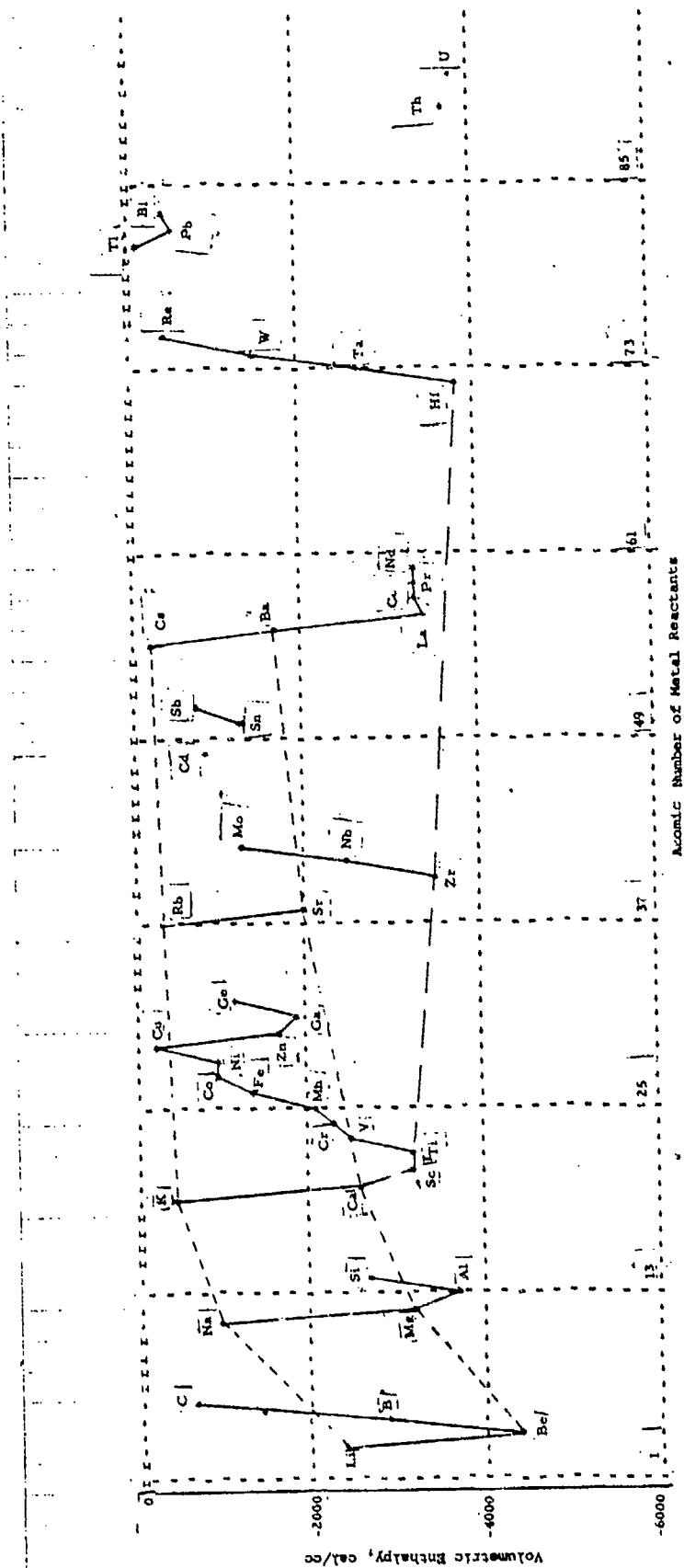
Reaction						Enthalpy, cal/cc
10 Sc + 3 Sr(NO ₃) ₂	=	3SrO	+ 5	Sc ₂ O ₃	+ 3 N ₂	-4531
5 Mg + 2 Ag(NO ₃)	=	Ag ₂ O	+ 5	MgO	+ N ₂	-4512
10 Ce + 3 Sr(NO ₃) ₂	=	3 SrO	+ 5	Ce ₂ O ₃	+ 3 N ₂	-4501
2 Ta + 2 Ag(NO ₃)	=	Ag ₂ O	+ 5	Ta ₂ O ₅	+ N ₂	-4489
5 Si + 2 Ca(NO ₃) ₂	=	2 CaO	+ 5	SiO ₂	+ 2 N ₂	-4467
5 Mg + Sr(NO ₃) ₂	=	SrO	+ 5	MgO	+ N ₂	-4454
3 U + 4 Ag(NO ₂)	=	2 Ag ₂ O	+ 3	UO ₂	+ 2 N ₂	-4433
10 Ti + 6 Na(NO ₃)	=	3 Na ₂ O	+ 5	Ti ₂ O ₃	+ 3 N ₂	-4409
22 Nb + 10 Pb(NO ₃) ₂	=	5 Pb ₂ O	+ 11	Nb ₂ O ₅	+ 10 N ₂	-4408
3 HF + 4 Ag(NO ₂)	=	2 Ag ₂ O	+ 3	HfO ₂	+ 2 N ₂	-4407
10 Cr + 6 Li(NO ₃)	=	· ₂ O	+ 5	Cr ₂ O ₃	+ 3 N ₂	-4405
2 Ta + Sr(NO ₃) ₂	=	SrO	+ 5	Ta ₂ O ₅	+ N ₂	-4399
5 Be + 2 Cs(NO ₃)	=	Cs ₂ O	+ 5	BeO	+ N ₂	-4377
10 Ti + 3 Ba(NO ₃) ₂	=	3 BaO	+ 5	Ti ₂ O ₃	+ 3 N ₂	-4373
2 Al + 2 Ag(NO ₂)	=	Ag ₂ O	+ 5	Al ₂ O ₃	+ N ₂	-4323
22 V + 6 Pb(NO ₃) ₂	=	3 Pb ₂ O	+ 11	V ₂ O ₃	+ 6 N ₂	-4306
5 Si + 4 Ag(NO ₃)	=	2 Ag ₂ O	+ 5	SiO ₂	+ 2 N ₂	-4303
2 Nb + Ca(NO ₃) ₂	=	CaO	+ 5	Nb ₂ O ₃	+ N ₂	-4285
10 La + 6 Na(NO ₃)	=	3 Na ₂ O	+ 5	La ₂ O ₃	+ 3 N ₂	-4250
3 Th + 4 Ag(NO ₂)	=	2 Ag ₂ O	+ 3	ThO ₂	+ 2 N ₂	-4232
10 Nd + 6 Na(NO ₃)	=	3 Na ₂ O	+ 5	Nd ₂ O ₃	+ 3 N ₂	-4230
10 La + 3 Ba(NO ₃) ₂	=	3 BaO	+ 5	La ₂ O ₃	+ 3 N ₂	-4229
10 Nd + 3 Ba(NO ₃) ₂	=	3 BaO	+ 5	Nd ₂ O ₃	+ 3 N ₂	-4209
5 Si + 2 Sr(NO ₃) ₂	=	2 SrO	+ 5	SiO ₂	+ 2 N ₂	-4207
10 B + 6 Na(NO ₃)	=	3 Na ₂ O	+ 5	B ₂ O ₃	+ 3 N ₂	-4199
10 V + 3 Ca(NO ₃) ₂	=	3 CaO	+ 5	V ₂ O ₃	+ 3 N ₂	-4195
10 Pr + 6 Na(NO ₃)	=	3 Na ₂ O	+ 5	Pr ₂ O ₄	+ 3 N ₂	-4185
10 B + 3 Ba(NO ₃) ₂	=	3 BaO	+ 5	B ₂ O ₃	+ 3 N ₂	-4168
10 Pr + 3 Ba(NO ₃) ₂	=	3 BaO	+ 5	Pr ₂ O ₃	+ 3 N ₂	-4166
10 Sc + 6 Na(NO ₃)	=	3 Na ₂ O	+ 5	Sc ₂ O ₃	+ 3 N ₂	-4153

Table 12 (cont..)

Reaction						Enthalpy, cal/cc
10 Ce + 6 Na(NO ₃)	=	3 Na ₂ O	+ 5 Ce ₂ O ₃	+ 3 N ₂		-4149
22 Cr + 6 Pb(NO ₃) ₂	=	3 Pb ₂ O	+ 11 Cr ₂ O ₃	+ 6 N ₂		-4143
10 Sc + 3 Ba(NO ₃) ₂	=	3 BaO	+ 5 Sc ₂ O ₃	+ 3 N ₂		-4143
10 Ce + 3 Ba(NO ₃) ₂	=	3 BaO	+ 5 Ce ₂ O ₃	+ 3 N ₂		-4131
3 Zr + 4 Ag(NO ₂)	=	2 Ag ₂ O	+ 3 ZrO ₂	+ 2 N ₂		-4126
2 Nb + 2 Ag(NO ₃)	=	Ag ₂ O	+ Nb ₂ O ₃	+ N ₂		-4124
5 U + 4 K(NO ₃)	=	2 K ₂ O	+ 5 UO ₂	+ 2 N ₂		-4118
5 Mg + 2 Na(NO ₃)	=	Na ₂ O	+ 5 MgO	+ N ₂		-4104
5 U + 4 Rb(NO ₃)	=	2 Rb ₂ O	+ 5 UO ₂	+ 2 N ₂		-4103
5 Hf + 4 K(NO ₃)	=	2 K ₂ O	+ 5 HfO ₂	+ 2 N ₂		-4092
5 Mg + Ba(NO ₃) ₂	=	BaO	+ 5 MgO	+ N ₂		-4088
5 Hf + 4 Rb(NO ₃)	=	2 Rb ₂ O	+ 5 HfO ₂	+ 2 N ₂		-4077
10 V + 6 Ag(NO ₃)	=	3 Ag ₂ O	+ 5 V ₂ O ₃	+ 3 N ₂		-4051
3 U + 2 Ba(NO ₂) ₂	=	2 BaO	+ 3 UO ₂	+ 2 N ₂		-4043
10 Cr + 3 Ca(NO ₃) ₂	=	3 CaO	+ 5 Cr ₂ O ₃	+ 3 N ₂		-4031
3 Hf + 2 Ba(NO ₂) ₂	=	2 BaO	+ 3 HfO ₂	+ 2 N ₂		-4022
3 U + 4 Na(NO ₂)	=	2 Na ₂ O	+ 3 UO ₂	+ 2 N ₂		-4018
2 Nb + Sr(NO ₃) ₂	=	SrO	+ Nb ₂ O ₅	+ N ₂		-4006
3 Hf + 4 Na(NO ₂)	=	2 Na ₂ O	+ 3 HfO ₂	+ 2 N ₂		-3996
10 Al + 6 K(NO ₃)	=	3 K ₂ O	+ 5 Al ₂ O ₃	+ 3 N ₂		-3995
10 Al + 6 Rb(NO ₃)	=	3 Rb ₂ O	+ 5 Al ₂ O ₃	+ 3 N ₂		-3980
2 Al + Ba(NO ₂) ₂	=	BaO	+ Al ₂ O ₃	+ N ₂		-3940
10 V + 3 Sr(NO ₃) ₂	=	3 SrO	+ 5 V ₂ O ₃	+ 3 N ₂		-3936
5 Th + 4 K(NO ₃)	=	2 K ₂ O	+ 5 ThO ₂	+ 2 N ₂		-3933
5 Th + 4 Rb(NO ₃)	=	2 Rb ₂ O	+ 5 ThO ₂	+ 2 N ₂		-3920
2 Al + 2 Na(NO ₂)	=	Na ₂ O	+ Al ₂ O ₃	+ N ₂		-3906
2 Ti + 2 Ag(NO ₂)	=	Ag ₂ O	+ Ti ₂ O ₃	+ N ₂		-3905
10 Cr + 6 Ag(NO ₃)	=	3 Ag ₂ O	+ 5 Cr ₂ O ₃	+ 3 N ₂		-3895
3 Th + 2 Ba(NO ₂) ₂	=	2 BaO	+ 3 ThO ₂	+ 2 N ₂		-3892
2 La + 2 Ag(NO ₂)	=	Ag ₂ O	+ La ₂ O ₃	+ N ₂		-3885

Table 12 (cont.)

Reaction						Enthalpy, cal/cc
2 Ta + 2 Na(NO ₃)	=	Na ₂ O	+ Ta ₂ O ₅	+ N ₂		-3873
5 Mn + 2 Li(NO ₃)	=	Li ₂ O	+ 5 MnO	+ N ₂		-3869
2 Ta + Ba(NO ₃) ₂	=	BaO	+ Ta ₂ O ₅	+ N ₂		-3866
3 Th + 4 Na(NO ₂)	=	2 Na ₂ O	+ 3 ThO ₂	+ 2 N ₂		-3859
2 Nd + 2 Ag(NO ₂)	=	Ag ₂ O	+ Nd ₂ O ₃	+ N ₂		-3853
2 Pr + 2 Ag(NO ₂)	=	Ag ₂ O	+ Pr ₂ O ₃	+ N ₂		-3823
2 Ce + 2 Ag(NO ₂)	=	Ag ₂ O	+ Ce ₂ O ₃	+ N ₂		-3793
2 Sc + 2 Ag(NO ₂)	=	Ag ₂ O	+ Sc ₂ O ₃	+ N ₂		-3778
5 Zr + 4 K(NO ₃)	=	2 K ₂ O	+ 5 ZrO ₂	+ 2 N ₂		-3774
10 Cr + 3 Sr(NO ₃) ₂	=	3 SrO	+ 5 Cr ₂ O ₃	+ 3 N ₂		-3763
3 Mg + 2 Ag(NO ₂)	=	Ag ₂ O	+ 3 MgO	+ N ₂		-3760
5 Zr + 4 Rb(NO ₃)	=	2 Rb ₂ O	+ 5 ZrO ₂	+ 2 N ₂		-3757
3 Zr + 2 Ba(NO ₂) ₂	=	2 BaO	+ 3 ZrO ₂	+ 2 N ₂		-3752
5 U + 4 Cs(NO ₃)	=	2 Cs ₂ O	+ 5 UO ₂	+ 2 N ₂		-3739
5 Si + 4 Na(NO ₃)	=	2 Na ₂ O	+ 5 SiO ₂	+ 2 N ₂		-3731
5 Si + 2 Ba(NO ₃) ₂	=	2 BaO	+ 5 SiO ₂	+ 2 N ₂		-3728
5 Hf + 4 Cs(NO ₃)	=	2 Cs ₂ O	+ 5 HfO ₂	+ 2 N ₂		-3720
3 Zr + 4 Na(NO ₂)	=	2 Na ₂ O	+ 3 ZrO ₂	+ 2 N ₂		-3702
11 Mn + 2 Pb(NO ₃) ₂	=	Pb ₂ O	+ 11 MnO	+ 2 N ₂		-3686
2 B + 2 Ag(NO ₂)	=	Ag ₂ O	+ B ₂ O ₃	+ N ₂		-3681
10 Al + 6 Cs(NO ₃)	=	3 Cs ₂ O	+ 5 Al ₂ O ₃	+ 3 N ₂		-3629
5 Th + 4 Cs(NO ₃)	=	2 Cs ₂ O	+ 5 ThO ₂	+ 2 N ₂		-3615
5 Mn + Ca(NO ₃) ₂	=	CaO	+ 5 MnO	+ N ₂		-3602
2 La + Ba(NO ₂) ₂	=	BaO	+ La ₂ O ₃	+ N ₂		-3592
10 La + 6 K(NO ₃)	=	3 K ₂ O	+ 5 La ₂ O ₃	+ 3 N ₂		-3588
5 Ca + 2 Li(NO ₃)	=	Li ₂ O	+ 5 CaO	+ N ₂		-3585
10 La + 6 Rb(NO ₃)	=	3 Rb ₂ O	+ 5 La ₂ O ₃	+ 3 N ₂		-3574
2 Nd + Ba(NO ₂) ₂	=	BaO	+ Nd ₂ O ₃	+ N ₂		-3557
10 Nd + 6 K(NO ₃)	=	3 K ₂ O	+ 5 Nd ₂ O ₃	+ 3 N ₂		-3548
2 La + 2 Na(NO ₂)	=	Na ₂ O	+ La ₂ O ₃	+ N ₂		-3542



VOLUMETRIC ENTHALPIES OF REACTIONS OF METALS WITH CaNO_3

Figure 8

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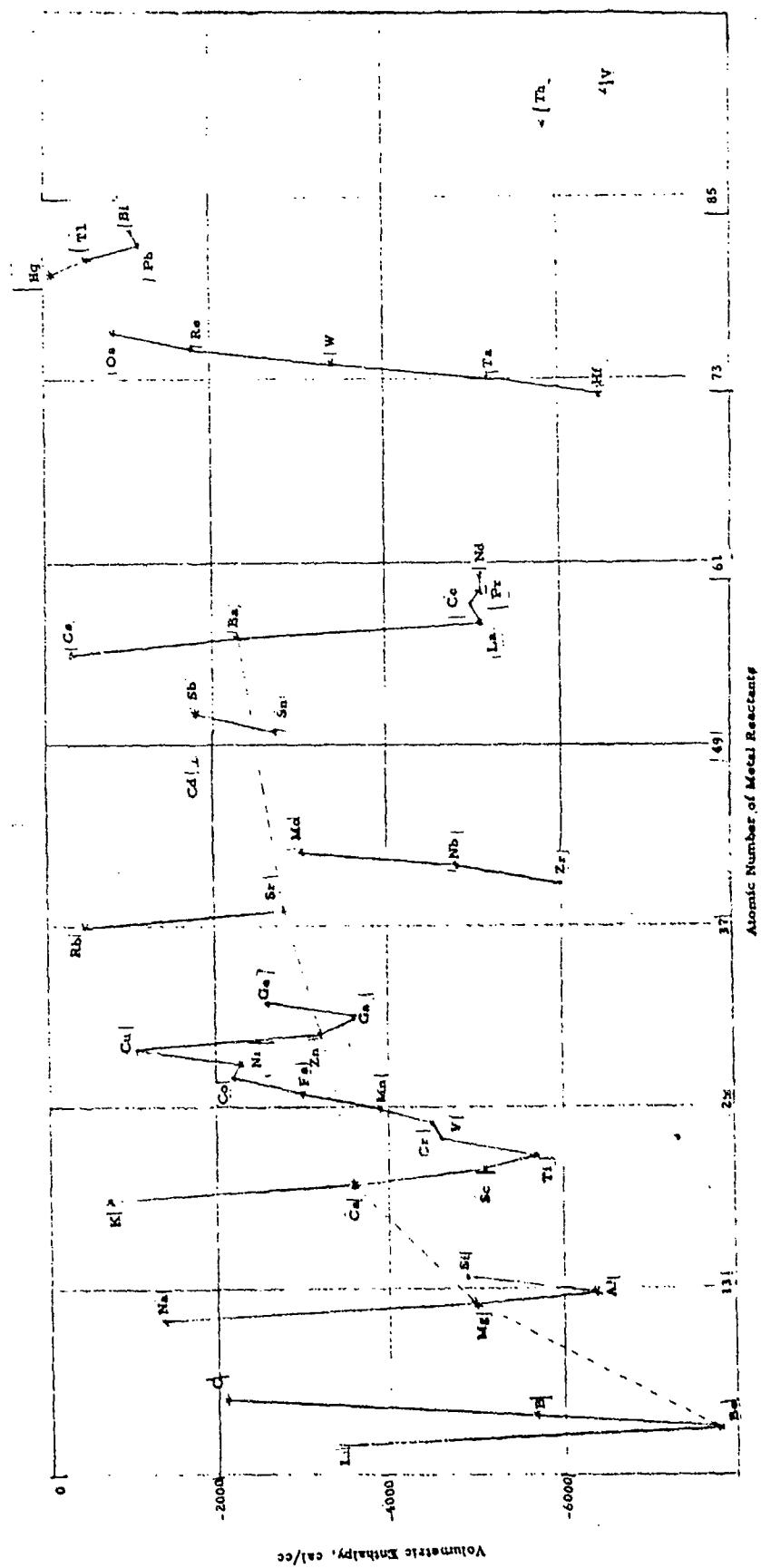


Figure 9
VOLUMETRIC ENTHALPIES OF REACTIONS OF METALS WITH LaNO_3

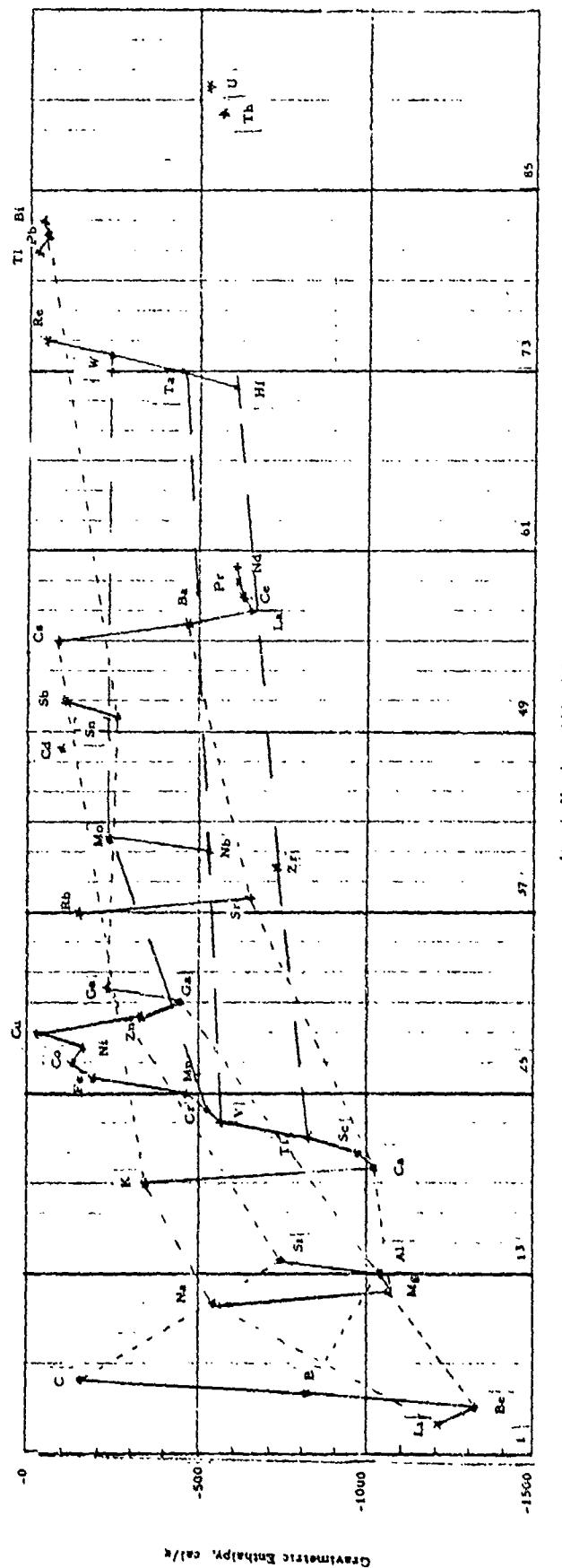


Figure 10
GRAVIMETRIC ENTHALPIES OF REACTIONS OF METALS WITH CaNO_3

the products and reactants are the same except for boric oxide and aluminum oxide. Thus the coefficients of the reaction, the heat of formation, the volume of the nitrate, and the volume of the resultant oxide are not involved in the fact that aluminum reactions are more energetic than boron reactions. The remaining factors contributing to the reaction enthalpy are the atomic volumes of boron and aluminum and the heats of formation of boric oxide and aluminum oxide. Since boron's atomic volume, 4.57 cc, is much less than that of aluminum, 9.99 cc, its reactions would be expected to be more energetic. However, the unusually high heat of formation of aluminum oxide compared with that of boric oxide, -399 and -302 kcal, respectively, causes the aluminum reactions to be especially energetic. The effect of the heat of formation is enhanced by the stoichiometric coefficient of these oxides in the balanced equation because these factors multiply the difference between the heats of formation.

Comparison of beryllium and magnesium illustrates this further. Beryllium has a much lower atomic volume than magnesium, 4.94 compared with 13.95 cc. But unlike aluminum and boron, the heat of formation of magnesium oxide is slightly less than that of beryllium oxide, -144 compared with -146 kcal, so that beryllium reactions are more energetic than magnesium reactions. A similar situation in reverse exists with carbon. Its reaction energies are low compared with those of silicon because of the low heat of formation of carbon dioxide compared with that of silicon dioxide, -94 compared with -205 kcal.

Except for these anomalies, the reactions in a group become less energetic with increasing atomic number of the metal reactant. Group I has the least energetic reactions and Group II the most energetic. Group I reactions are not energetic because of the large atomic volumes of the metals and the low heats of formation of the oxides. The Group II and VI reactions are intermediate between the Group I and II extremes.

The dashed lines in Figure 8 connect members of the "short" groups in the periodic table. These groups also have an interesting behavior. In the first three groups in the series, Group IIIB (scandium, yttrium, and lanthanum), Group IVB (titanium, zirconium, and hafnium), and Group VB (vanadium, niobium, and tantalum), the reaction energy increases with increasing atomic number. The remaining groups, Group VIB (chromium, molybdenum, and tungsten), Group VIIIB (manganese, technetium, and rhenium), Group VIII (iron, ruthenium, dysprosium, cobalt, rhodium, iridium, nickel, palladium, and platinum), Group IB (copper, silver, and gold), and Group IIB (zinc, cadmium, and mercury), exhibit a decrease in energy with increasing atomic number. The members of Group VIII are not

evident because their reactions in general have a positive enthalpy and are not recorded. As drawn in Figure 8, the dashed lines (only one is drawn in for reference) connecting the members in Groups IIB, IVB, VB, VIB, VIIIB, and IIB start with a negative slope for Group IIB and become more positive for each group in the above order. Some of the reasons for this behavior have been discussed previously with respect to the lanthanide contraction.

Figures 9, 10, and 11 illustrate that the reactions of metals with other nitrates or nitrites exhibit the same behavior except for vertical displacement of the ordinate scale. The two nitrates chosen represent the extremes of reaction energy with any particular metal, lithium nitrate (Figure 9) being the most energetic and cesium nitrate (Figure 10) the least energetic of those included in this study.

The gravimetric relationships are essentially the same as the volumetric ones (Figures 9 and 11 versus Figure 10) except for reversal of the magnesium and aluminum energies. Magnesium is more energetic on the gravimetric basis because the small atomic volume of aluminum is not involved. The energy decreases with increasing atomic number of the Group IIB and IVB elements. These elements behave normally on a gravimetric basis because the lanthanide contraction is not involved.

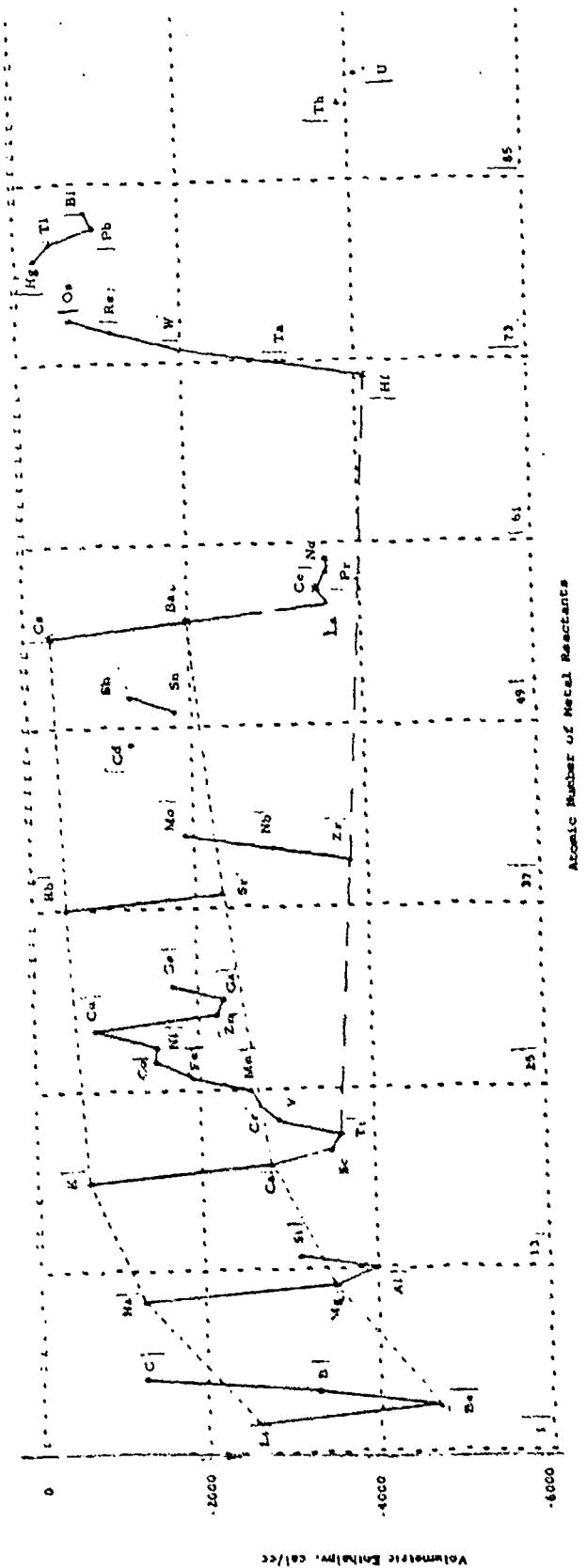


Figure 11
VOLUMETRIC ENTHALPIES OF REACTIONS OF METALS WITH $\text{Ba}(\text{NO}_2)_2$

D. Silicide Reactions

The reactions of various metals with 36 silicides are represented by 302 reactions in the present study. Six typical reactions are shown in Table 13 and the 50 most energetic reactions are shown in Table 14. Table 14 shows that the silicide reactions with barium metal are the most energetic. This is because BaSi_3 has an unusually high heat of formation, -407 kcal. When barium is the reactant, Ba_2Si_2 may also form and result in a less energetic reaction. Strontium also produces moderately energetic reactions because the heats of formation of SrSi_2 and SrSi_1 are -150 and -113 kcal respectively. With the exception of these four silicides, the heats of formation of the silicides for which data are available are very low. In fact, the remainder serve preferentially as reactants because of their low heats of formation.

The periodic behavior of enthalpies of these reactions as typified by the cobalt disilicide reactions is shown in Figure 12. Because of the paucity of data, only the Group II metal reactions are available for comparative purposes. The behavior of the Group II silicides is the reverse of that exhibited by the nitrates and oxides; i.e., magnesium is least energetic and barium is most energetic. This occurs because barium silicide has a much higher heat of formation than magnesium silicide, whereas barium oxide has a lower heat of formation and a larger molecular volume than magnesium oxide.

The gravimetric behavior is shown in Figure 13. It is essentially the same as the volumetric behavior. The energy of the Group II elements increases with increasing atomic number.

Although experimental studies of silicide reactions are of great interest, they would be time-consuming because very few of the reactants are available and would have to be synthesized individually.

Table 13
DATA ON REACTIONS OF VARIOUS METALS WITH SILICIDES

	Sr	+	Co_2Si	=	2 Co	+	SrSi
Heat of formation			-27.60				-113.00
Molecular weight	87.63		145.94		58.94		115.72
Density	2.60		7.28		8.90		
Melting point, °C	770.00		1325.00		1493.00		
Boiling point, °C	1384.00				3100.00		
Heat of reaction, kcal	-85.40						
Reactants' density	4.35						
Gravimetric enthalpy, cal/g	-365.63						
Volumetric enthalpy, cal/cc	-1588.82						
	Sr	+	CoSi	=	Co	+	SrSi
Heat of formation			-24.00				-113.00
Molecular weight	87.63		87.00		58.94		115.72
Density	2.60		6.30		8.90		
Melting point, °C	770.00		1390.00		1493.00		
Boiling point, °C	1384.00				3100.00		
Heat of reaction, kcal	-89.00						
Reactants' density	3.68						
Gravimetric enthalpy, cal/g	-509.65						
Volumetric enthalpy, cal/cc	-1873.16						
	2 Sr	+	CoSi_2	=	Co	+	2 SrSi
Heat of formation			-24.60				-113.00
Molecular weight	87.63		115.06		58.94		115.72
Density	2.60		5.30		8.90		
Melting point, °C	770.00		1275.00		1493.00		
Boiling point, °C	1384.00				3100.00		
Heat of reaction, kcal	-201.40						
Reactants' density	3.26						
Gravimetric enthalpy, cal/g	-693.72						
Volumetric enthalpy, cal/cc	-2259.95						

Table 13 (cont.)

	2 Ba	+	3 CoSi ₂	=	3 Co	+	2 BaSi ₃
Heat of formation			-24.60		58.94		-407.00
Molecular weight	137.36		115.06		8.90		221.63
Density	3.50		5.30				
Melting point, °C	704.00		1275.00		1493.00		
Boiling point, °C	1638.00				3100.00		
Heat of reaction, kcal	-740.20						
Reactants' density	4.32						
Gravimetric enthalpy, cal/g	-1194.06						
Volumetric enthalpy, cal/cc	-5153.89						
	Ba	+	CoSi ₃	=	Co	+	BaSi ₃
Heat of formation			-25.60		58.94		-407.00
Molecular weight	137.36		143.21		8.90		221.63
Density	3.50						
Melting Point, °C	704.00		1305.00		1493.00		
Boiling Point, °C	1638.00				3100.00		
Heat of reaction, kcal	-381.40						
Reactants' density							
Gravimetric enthalpy, cal/g	-1359.38						
Volumetric enthalpy, cal/cc							
	Ba	+	3 FeSi	=	3 Fe	+	BaSi ₃
Heat of formation			-19.20		55.85		-407.00
Molecular weight	137.36		83.91		7.86		221.63
Density	3.50		6.10				
Melting Point, °C	704.00		1430.00		1535.00		
Boiling Point, °C	1638.00				2800.00		
Heat of reaction, kcal	-349.40						
Reactants' density	4.83						
Gravimetric enthalpy, cal/g	-897.99						
Volumetric enthalpy, cal/cc	-4339.68						

Table 14
 MOST ENERGETIC SILICIDE REACTIONS* WITH METALS,
 IN TERMS OF VOLUMETRIC ENTHALPY

<u>Reactant</u>	<u>Product</u>	Enthalpy, cal/cc
3 CoSi ₂	2 BaSi ₃	-5153
3 FeSi	BaSi ₃	-4339
3 ZrSi ₂	2 BaSi ₃	-4174
3 CoSi	BaSi ₃	-4152
3 CaSi ₂	2 BaSi ₃	-3639
CoSi ₂	Ba ₂ Si ₂	-3417
3 Co ₂ Si	BaSi ₃	-3262
2 FeSi	Ba ₂ Si ₂	-3099
3 Ni ₂ Si	BaSi ₃	-3065
ZrSi ₂	Ba ₂ Si ₂	-3045
2 CoSi	Ba ₂ Si ₂	-3006
CaSi ₂	Ba ₂ Si ₂	-2829
2 Cu ₂ Si	Ba ₂ Si ₂	-2629
2 Ni ₂ Si	Ba ₂ Si ₂	-2521
CoSi ₂	SrSi ₂	-2263
CoSi ₂	2 SrSi	-2259
FeSi	SrSi	-1976
ZrSi ₂	2 SrSi	-1946
CoSi	SrSi	-1873
2 FeSi	SrSi ₂	-1823
CaSi ₂	2 SrSi	-1793
ZrSi ₂	SrSi ₂	-1783
2 CoSi	SrSi ₂	-1663
Co ₂ Si	SrSi	-1588
CaSi ₂	SrSi ₂	-1578
Ni ₂ Si	SrSi	-1472

Table 14 (cont.)

<u>Reactant</u>	<u>Product</u>	Enthalpy, cal/cc
2 Co ₂ Si	SrSi ₂	-1284
2 Ni ₂ Si	SrSi ₂	-1117
3 CoSi ₂	2 Zr ₅ Si ₃	-1055
CoSi ₂	2 Zr ₂ Si	- 957
CoSi ₂	2 ZrSi	- 916
CoSi ₂	2 Ni ₂ Si	- 885
3 FeSi	Zr ₅ Si ₃	- 789
CoSi ₂	2 Ni ₃ Si	- 757
FeSi	Zr ₂ Si	- 728
3 CaSi ₂	2 Zr ₅ Si ₃	- 716
CaSi ₂	2 Zr ₂ Si	- 670
3 CoSi	Zr ₅ Si ₃	- 661
CoSi ₂	Ca ₂ Si ₂	- 645
CoSi ₂	2 CaSi	- 645
CoSi	Zr ₂ Si	- 614
CoSi ₂	2 Ca ₂ Si	- 602
FeSi	ZrSi	- 574
ZrSi ₂	2 Ni ₂ Si	- 551
FeSi	Ni ₂ Si	- 534
CaSi ₂	2 ZrSi	- 516
ZrSi ₂	2 Ni ₃ Si	- 501
FeSi	Ni ₃ Si	- 485
3 Co ₂ Si	Zr ₅ Si ₃	- 484
CaSi ₂	2 Ni ₂ Si	- 480

*The first reaction, for example, is:
 $2 \text{Ba} + 3 \text{CoSi}_2 = 3 \text{Co} + 2 \text{BaSi}_3$.

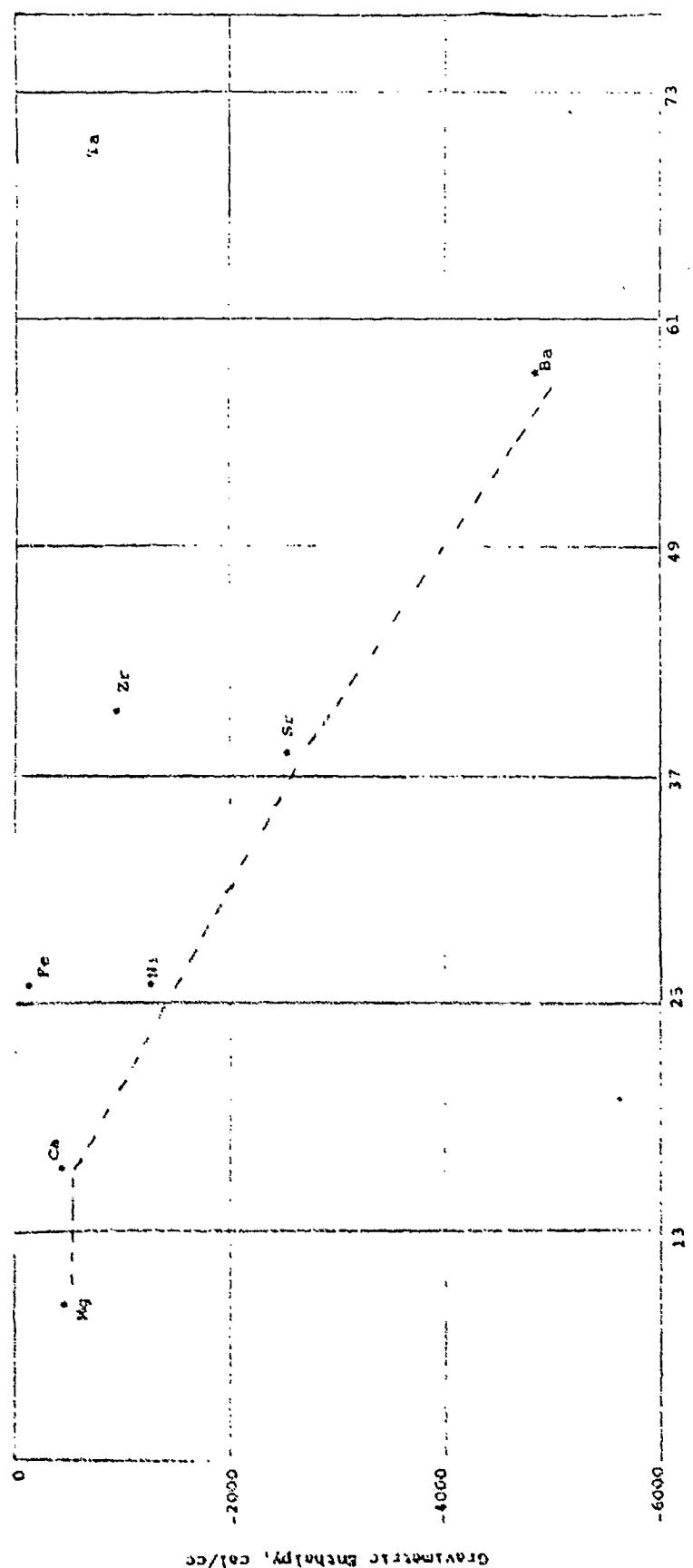


Figure 12
VOLUMETRIC ENTHALPIES OF REACTIONS OF METALS WITH CoSi_2

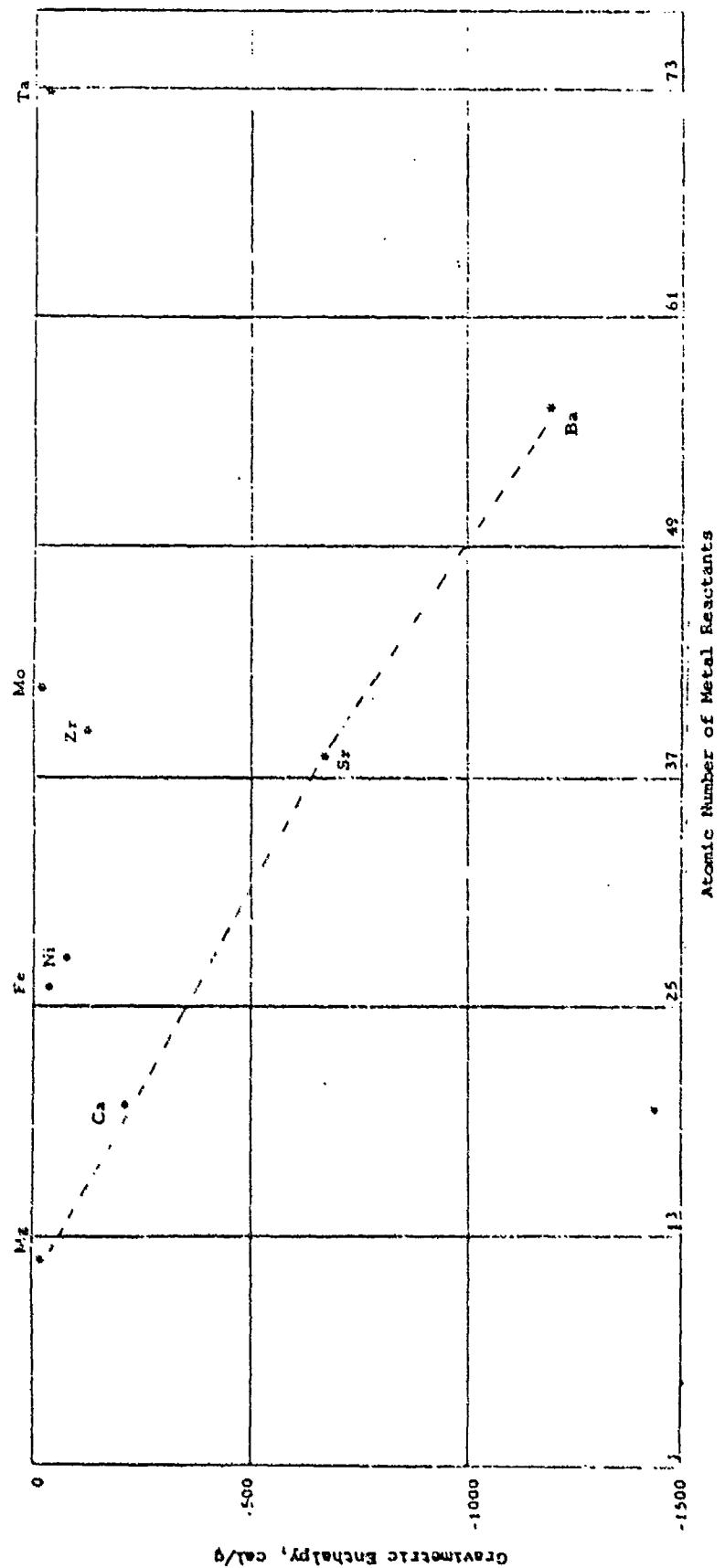


Figure U3
GRAVIMETRIC ENTHALPIES OF REACTIONS OF METALS WITH CoSi_2

E. Carbide Reactions

Based on the data available for 30 carbides, 386 reactions were analyzed. The carbide reactions are not a very energetic class. The most energetic reactions are listed in Table 15. Tantalum, titanium, and zirconium are the most energetic metal reactants, forming tantalum carbide, titanium carbide, and zirconium carbide, respectively. Many different carbides, e.g., lithium carbide, vanadium carbide, tungsten carbide, calcium carbide, and trichromium dicarbide, perform as useful reactants. Three representative reactions are shown in Table 16.

The reactions of a few of the metals with lithium carbide are shown in Figure 14. Although no useful correlations can be made because of the lack of data, Figure 14 does show that tantalum, titanium, and zirconium are the most energetic metals in these systems.

Table 15

MOST ENERGETIC CARBIDE REACTIONS* WITH METALS,
IN TERMS OF VOLUMETRIC ENTHALPY

<u>Reactant</u>	<u>Product</u>	<u>Enthalpy, cal/cc</u>
Li_2C_2	2 TaC	-2532
VC	TaC	-2351
WC	TaC	-2334
CaC_2	2 TaC	-2222
Cr_3C_2	2 TaC	-2186
Ni_3C	TaC	-2165
Li_2C_2	2 TiC	-2119
Mo_2C	TaC	-2056
Na_2C_2	2 TaC	-1987
Fe_3C	TaC	-1956
WC	TiC	-1937
VC	TiC	-1925
UC_2	2 TaC	-1900
Ni_3C	TiC	-1896
CaC_2	2 TiC	-1853
Cr_3C_2	2 TiC	-1803
Mo_2C	TiC	-1774
Mn_3C	TaC	-1717
Al_4C_3	3 TaC	-1713
Na_2C_2	2 TiC	-1705
Fe_3C	TiC	-1690
ThC_2	2 TaC	-1639
SiC	TaC	-1588

Table 15 (cont.)

<u>Reactant</u>	<u>Product</u>	<u>Enthalpy, cal/cc</u>
B ₄ C	TaC	-1508
UC ₂	2 TiC	-1482
Ni ₃ C	ZrC	-1477
Li ₂ C ₂	2 ZrC	-1472
Mn ₃ C	TiC	-1459
Al ₄ C ₃	3 TiC	-1411
Ni ₃ C	UC	-1402
Li ₂ C ₂	2 UC	-1358
Mo ₂ C	ZrC	-1351
WC	ZrC	-1340
CaC ₂	2 ZrC	-1307
Fe ₃ C	ZrC	-1298
VC	ZrC	-1291
Na ₂ C ₂	2 ZrC	-1289
Mo ₂ C	UC	-1267
ThC ₂	2 TiC	-1263
Cr ₃ C ₂	2 ZrC	-1244
NbC	TaC	-1237
WC	UC	-1223
B ₄ C	TiC	-1220
Fe ₃ C	UC	-1216
Na ₂ C ₂	2 UC	-1202
CaC ₂	2 UC	-1196
SiC	TiC	-1181
VC	UC	-1163
Cr ₃ C ₂	2 UC	-1125
Mn ₃ C	ZrC	-1102

* The first reaction, for example, is:
 $2 \text{ Ta} + \text{Li}_2\text{C}_2 = 2 \text{ Li} + 2 \text{ TaC}$.

Table 16
DATA ON REACTIONS OF VARIOUS METALS WITH CARBIDES

	2 Ta	+	Li_2C_2	=	2 Li	+	2 TaC
Heat of formation			-14.20				-63.80
Molecular weight	180.95		37.90		6.94		192.87
Density	16.60		1.65		0.53		14.65
Melting point, °C	2977.00				180.00		3827.00
Boiling point, °C	4100.00				1326.00		5500.00
Heat of reaction, kcal	-113.40						
Reactants' density	8.93						
Gravimetric enthalpy, cal/g	-283.64						
Volumetric enthalpy, cal/cc	-2532.90						
	3 Ta	+	Mg_2C_3	=	2 Mg	+	3 TaC
Heat of formation			19.00				-63.80
Molecular weight	180.95		84.67		24.32		192.87
Density	16.60				1.74		14.65
Melting point, °C	2977.00				650.00		3827.00
Boiling point, °C	4100.00				1120.00		5500.00
Heat of reaction, kcal	-210.40						
Reactants' density							
Gravimetric enthalpy, cal/g	-335.29						
Volumetric enthalpy, cal/cc							
	2 Ta	+	MgC_2	=	Mg	+	2 TaC
Heat of formation			21.00				-63.80
Molecular weight	180.95		48.34		24.32		192.87
Density	16.60				1.74		14.65
Melting point, °C	2977.00				650.00		3827.00
Boiling point, °C	4100.00				1120.00		5500.00
Heat of reaction, kcal	-148.60						
Reactants' density							
Gravimetric enthalpy, cal/g	-362.23						
Volumetric enthalpy							

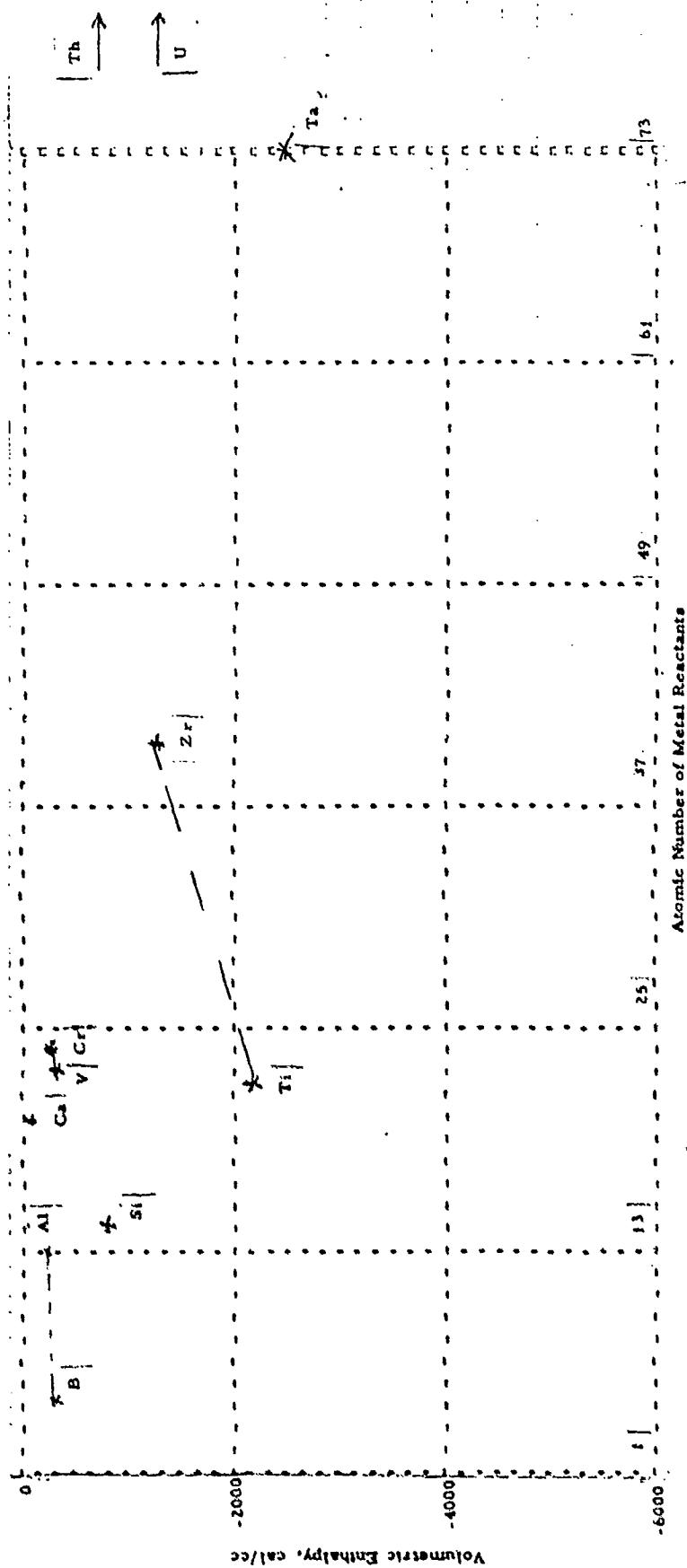


Figure 14
VOLUMETRIC ENTHALPIES OF REACTIONS OF METALS WITH LiC_2

F. Sulfide Reactions

The data for 68 sulfides were used to calculate the enthalpies of 2145 reactions of sulfides with metals. These reactions are, in general, only moderately energetic. The 50 most energetic reactions are shown in Table 17. The reactions of iron disulfide with thorium, cesium, and lanthanum are the most energetic. The energies of these reactions are not considered high for pyrotechnic materials but are high enough to warrant a modest experimental study. In most cases several sulfide products, involving different valences of the metals, form from the same two reactants. It would be interesting to determine which reactions predominate, since this will define the experimental reaction energy. This energy is a function of the kinetics of the reaction and the thermodynamic equilibrium based on free energies. A few representative reactions are shown in Table 18.

Figure 15 illustrates the periodic relationships between the reactions of metals with iron disulfide. The relationship is essentially the same as that among the nitrate reactions except for some differences with the low-atomic number metals. For instance, in the sulfide systems the Group II metals exhibit a maximum energy output at calcium, whereas in the nitrate systems beryllium and magnesium are more energetic than calcium. In the nitrate systems, the energy output based on the volume of reactants decreases in going from beryllium to barium because the product oxides all have approximately the same heats of formation, -133 to -152 kcal, and the reactant metals increase in atomic volume, 4.74 to 39.2 cc. In the sulfide systems, the effect of the reactant volumes is the same, but the heats of formation vary widely, with a pronounced maximum (-115 kcal) at calcium sulfide and a minimum (-56 kcal) at beryllium sulfide. In this case, the effect of the heats of formation predominates and the energy outputs also have a maximum at calcium. Another interesting difference between the sulfide and nitrate systems is that in the former aluminum is less energetic than magnesium and in the latter the reverse is true. This phenomenon results from the unusually high heat of formation of aluminum oxide, -399 kcal.

Table 17
MOST ENERGETIC SULFIDE REACTIONS* WITH METALS,
IN TERMS OF VOLUMETRIC ENTHALPY

<u>Reactant</u>	<u>Product</u>	<u>Enthalpy, cal/cc</u>
7 FeS ₂	2 Th ₄ S ₇	-3169
2 FeS ₂	Ce ₃ S ₄	-3104
7 FeS ₂	2 Th ₄ S ₇	-3093
3 FeS ₂	2 Ce ₂ S ₃	-3089
FeS ₂	2 ThS	-3074
3 FeS ₂	2 La ₂ S ₃	-3061
2 FeS ₂	Ce ₃ S ₄	-3038
3 FeS ₂	2 Ce ₂ S ₃	-3018
FeS ₂	2 ThS	-3018
FeS ₂	2 CeS	-2995
3 FeS ₂	2 La ₂ S ₃	-2993
FeS ₂	2 CeS	-2939
FeS ₂	ThS ₂	-2935
7 Co ₂ S ₃	3 Th ₄ S ₇	-2920
Co ₂ S ₃	3 ThS	-2894
4 Ce ₂ S ₃	3 Ce ₃ S ₄	-2892
Co ₂ S ₃	Ce ₂ S ₃	-2865
FeS ₂	ThS ₂	-2851
Ce ₂ S ₃	La ₂ S ₃	-2849
Co ₂ S ₃	3 CeS	-2822
Co ₃ S ₄	4 ThS	-2781
7 Co ₃ S ₄	4 Th ₄ S ₇	-2769
Co ₃ S ₄	Ce ₃ S ₄	-2760
3 Co ₃ S ₄	4 Ce ₂ S ₃	-2726
3 Co ₃ S ₄	4 La ₂ S ₃	-2715
Co ₃ S ₄	4 CeS	-2711

Table 17 (cont.)

<u>Reactant</u>	<u>Product</u>	<u>Enthalpy, cal/cc</u>
NiS	ThS	-2708
2 Co ₂ S ₃	3 Th ₂ S ₂	-2695
4 NiS	Ce ₃ S ₄	-2678
7 NiS	Th ₄ S ₇	-2675
CoS	ThS	-2667
NiS	CeS	-2641
3 NiS	Ce ₂ S ₃	-2641
3 FeS ₂	2 Th ₂ S ₃	-2636
3 NiS	La ₂ S ₃	-2633
4 CoS	Ce ₃ S ₄	-2630
7 CoS	Th ₄ S ₇	-2621
ReS ₂	2 ThS	-2615
CuS	ThS	-2612
CoS	CeS	-2600
WS ₂	2 ThS	-2599
3 CoS	Ce ₂ S ₃	-2590
3 CoS	La ₂ S ₃	-2584
4 CuS	Ce ₃ S ₄	-2571
2 ReS ₂	Ce ₃ S ₄	-2570
FeS ₂	CeS ₂	-2568
CS ₂	2 ThS	-2563
3 FeS ₂	2 Th ₂ S ₃	-2560
7 CuS	Th ₄ S ₇	-2556
7 ReS ₂	2 Th ₄ S ₇	-2553

*The first reaction, for example, is:
 $8 \text{ Th} + 7 \text{ FeS}_2 = 7 \text{ Fe} + 2 \text{ Th}_4\text{S}_7$.

Table 18

DATA ON REACTIONS OF VARIOUS METALS WITH SULFIDES

	3 Ce	+	2 FeS ₂	=	2 Fe	+	Ce ₃ S ₄
Heat of formation			-36.88		55.85		-421.50
Molecular weight	140.13		119.98		7.86		548.65
Density	6.70		4.87				
Melting point, °C	775.00		450.00		1535.00		2050.00
Boiling point, °C	2900.00				2800.00		
Boiling point, °C							
Heat of reaction, kcal	-347.74						
Reactants' density	5.90						
Gravimetric enthalpy, cal/g	-526.60						
Volumetric enthalpy, cal/cc	-3104.33						
	3 Ce	+	2 FeS ₂	=	2 Fe	+	Ce ₃ S ₄
Heat of formation			-42.52		55.85		-421.50
Molecular weight	140.13		119.98		7.86		548.65
Density	6.70		5.00				
Melting point, °C	775.00		1171.00		1535.00		2050.00
Boiling point, °C	2900.00				2800.00		
Boiling point, °C							
Heat of reaction, kcal	-336.46						
Reactants' density	5.96						
Gravimetric enthalpy, cal/g	-509.52						
Volumetric enthalpy, cal/cc	-3038.38						
	3 Ce	+	4 GaS	=	4 Ga	+	Ce ₃ S ₄
Heat of formation			-46.40		69.72		-421.50
Molecular weight	140.13		101.79		5.90		548.65
Density	6.70		3.86				
Melting point, °C	775.00		965.00		29.78		2050.00
Boiling point, °C	2900.00				937.00		
Boiling point, °C							
Heat of reaction, kcal	-235.90						
Reactants' density	4.92						
Gravimetric enthalpy, cal/g	-285.06						
Volumetric enthalpy, cal/cc	-1402.27						

Table 18 (cont.)

	8 Th	+ 7 FeS ₂	= 7 Fe	+ 2 Th ₄ S ₇
Heat of formation		-36.88	55.85	-665.00
Molecular weight	232.00	119.98	7.86	1152.46
Density	11.20	4.87		
Melting point, °C	1640.00	450.00	1535.00	2027.00
Boiling point, °C	4500.00		2800.00	
Heat of reaction, kcal	-1071.84			
Reactants' density				
Gravimetric enthalpy, cal/g	7.97			
Volumetric enthalpy, cal/cc	-397.59			
	-3169.53			
	8 Th	+ 7 FeS ₂	= 7 Fe	+ 2 Th ₄ S ₇
Heat of formation		-42.52	55.85	-665.00
Molecular weight	232.00	119.98	7.86	1152.46
Density	11.20	5.00		
Melting point, °C	1640.00	1171.00	1535.00	2027.00
Boiling point, °C	4500.00		2800.00	
Heat of reaction, kcal	-1032.36			
Reactants' density				
Gravimetric enthalpy, cal/g	8.08			
Volumetric enthalpy, cal/cc	-382.94			
	-3093.80			
	4 Th	+ 7 GaS	= 7 Ga	+ Th ₄ S ₇
Heat of formation		-46.40	69.72	-665.00
Molecular weight	232.00	101.79	5.90	1152.46
Density	11.20	3.86	29.78	
Melting point, °C	1840.00	965.00	937.00	2027.00
Boiling point, °C	4500.00			
Heat of reaction, kcal	-340.20			
Reactants' density				
Gravimetric enthalpy, cal/g	6.13			
Volumetric enthalpy, cal/cc	-207.37			
	-1272.01			

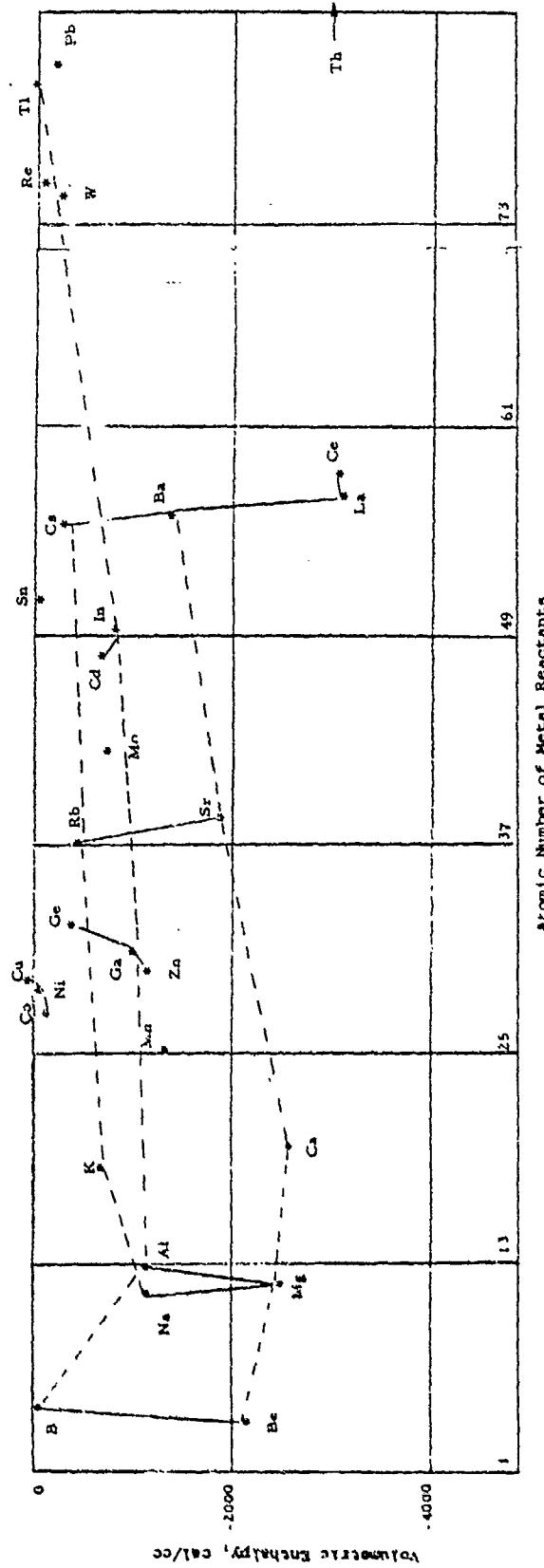


Figure 15
VOLUMETRIC ENTHALPIES OF REACTIONS OF METALS WITH FeS_2

G. Nitride and Azide Reactions

The data for 44 nitrides and 13 azides were used to compute the enthalpies of 1575 reactions. These reactions, like the sulfides, are only moderately energetic and appear to warrant only a modest experimental study. Caution must be exercised in experimental work because many of the azide compounds are very reactive. The 50 most energetic reactions are listed in Table 19. The reactions of barium azide (BaN_6 or $\text{Ba}(\text{N}_3)_2$) with beryllium, yttrium, titanium, zirconium, hafnium, thorium, and aluminum metal are the most energetic. The reactions of iron nitride with these metals are also fairly energetic.

Several representative reactions are shown in Table 20. Certain interesting relationships are apparent. For instance, the azide or nitride of barium can be used as the reactant. The azide is more energetic because it has a lower heat of formation. Copper can also be used as a nitride or azide, but not enough data are available to calculate the volumetric enthalpies. On a gravimetric basis, the reaction of copper azide with titanium is highly energetic. In some cases more than one nitride can be used as a reactant or is formed as a product from the same reactant metal. This is illustrated by the iron nitrides, Fe_2N and Fe_4N .

The periodic relationships of the reactions with barium azide and with the iron nitride Fe_2N are shown in Figures 16 and 17. Although all the possible lines have not been drawn, it is evident that except for minor deviations the behavior of these systems closely resembles that of the oxide and nitrate systems. This is especially apparent in Groups II and III: aluminum is more energetic than magnesium.

Table 19

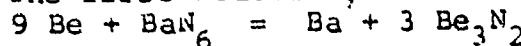
MOST ENERGETIC NITRIDE AND AZIDE REACTIONS* WITH METALS,
IN TERMS OF VOLUMETRIC ENTHALPY

<u>Reactant</u>	<u>Product</u>	<u>Enthalpy, cal/cc</u>
BaN ₆	3 Be ₃ N ₂	-3346
BaN ₆	2 U ₂ N ₃	-3308
BaN ₆	6 UN	-3109
BaN ₆	6 TiN	-3087
BaN ₆	6 ZrN	-3014
BaN ₆	6 HfN	-2961
2 BaN ₆	3 Th ₃ N ₄	-2692
BaN ₆	6 AlN	-2499
3 Fe ₂ N	U ₂ N ₃	-2478
2 Fe ₂ N	Be ₃ N ₂	-2470
BaN ₆	NbN ₆	-2460
BaN ₆	6 YN	-2444
Fe ₂ N	UN	-2431
BaN ₆	6 TaN	-2423
Fe ₂ N	ZrN	-2387
Fe ₂ N	TiN	-2368
Fe ₂ N	HfN	-2330
BaN ₆	6 CeN	-2298
BaN ₆	6 ScN	-2182
4 Fe ₂ N	Th ₃ N ₄	-2153
CrN	UN	-2098
3 CrN	U ₂ N ₃	-2093
GaN	UN	-2078
3 GaN	U ₂ N ₃	-2070
CrN	ZrN	-2059

Table 19 (cont.)

<u>Reactant</u>	<u>Product</u>	<u>Enthalpy, cal/cc</u>
2 CrN	Be ₃ N ₂	-2057
GaN	ZrN	-2044
2 BaN ₆	3 Si ₃ N ₄	-2037
2 GaN	Be ₃ N ₂	-2037
BaN ₆	6 LaN	-2012
BN	UN	-1994
CrN	TiN	-1978
CrN	HfN	-1970
GaN	TiN	-1969
3 BN	U ₂ N ₃	-1967
Fe ₂ N	YN	-1964
GaN	HfN	-1963
BN	ZrN	-1961
2 BN	Be ₃ N ₂	-1922
Fe ₂ N	AlN	-1907
Fe ₂ Ni	CeN	-1901
Fe ₂ N	NbN	-1894
BaN ₆	6 YN	-1878
BN	HfN	-1869
Fe ₂ N	TaN	-1866
BN	TiN	-1864
BaN ₆	6 BN	-1795
4 GaN	Th ₃ N ₄	-1777
Fe ₂ N	ScN	-1776
4 CrN	Th ₃ N ₄	-1766

*The first reaction, for example, is:



N₆ represents the azide (N₃)₂

Table 20
DATA ON REACTIONS OF VARIOUS METALS WITH NITRIDES AND AZIDES

	3 Be	+	2 AlN	=	2 Al	+	Be ₃ N ₂
Heat of formation			-57.70				-135.70
Molecular weight	9.01		40.98		26.98		55.06
Density	1.85		3.26		2.70		
Melting point, °C	1283.00		220.00		660.00		2200.00
Boiling point, °C	2970.00				2327.00		2240.00
Heat of reaction, kcal	-20.30						
Reactants' density	2.74						
Gravimetric enthalpy, cal/g	-186.24						
Volumetric enthalpy, cal/cc	-510.60						
	3 Be	+	2 BN	=	2 B	+	Be ₃ N ₂
Heat of formation			32.10				-135.70
Molecular weight	9.01		24.83		10.82		55.06
Density	1.85		2.20		2.37		
Melting point, °C	1283.00				2040.00		2200.00
Boiling point, °C	2970.00				2550.00		2240.00
Heat of reaction, kcal	-71.50						
Reactants' density	2.06						
Gravimetric enthalpy, cal/g	-932.22						
Volumetric enthalpy, cal/cc	-1922.64						
	9 Ba	+	BaN ₆	=	Ba	+	3 Be ₃ N ₂
Heat of formation			8.00				-135.70
Molecular weight	9.01		221.41		137.36		55.06
Density	1.85		2.94		3.50		
Melting point, °C	1283.00				704.00		2200.00
Boiling point, °C	2970.00						2240.00
Heat of reaction, kcal	-399.10						
Reactants' density	2.54						
Gravimetric enthalpy, cal/g	-1319.22						
Volumetric enthalpy, cal/cc	-3346.49						

Table 20 (cont.)

	$3\ Be$	$+$	$2\ Fe_2N$	$=$	$4\ Fe$	$+$	Be_3N_2
Heat of formation			-90				-135.70
Molecular weight			125.71				55.06
Density	9.01			55.85			
Melting point, °C	1.85		6.35	7.86			
Boiling point, °C	1283.00			1535.00			2200.00
Heat of reaction, kcal	2970.00			2800.00			2240.00
Reactants' density	-133.90						
Gravimetric enthalpy, cal/g	5.14						
Volumetric enthalpy, cal/cc	-480.86						
	-2470.05						
	$3\ Be$	$+$	$2\ Fe_4N$	$=$	$8\ Fe$	$+$	Be_3N_2
Heat of formation			-2.55				-135.70
Molecular weight	9.01		237.41				55.06
Density	1.85		6.57	55.85			
Melting point, °C	1283.00			7.86			
Boiling point, °C	2970.00			1535.00			2200.00
Heat of reaction, kcal	-130.60			2800.00			2240.00
Reactants' density	5.78						
Gravimetric enthalpy, cal/g	-260.23						
Volumetric enthalpy, cal/cc	-1503.11						
	$3\ Be$	$+$	$2\ GaN$	$=$	$2\ Ga$	$+$	Be_3N_2
Heat of formation			-25.00				-135.70
Molecular weight	9.01		83.73				55.06
Density	1.85		6.10	69.72			
Melting point, °C	1283.00			5.90			
Boiling point, °C	2970.00			29.78			2200.00
Heat of reaction, kcal	-85.70			937.00			2240.00
Reactants' density	4.62						
Gravimetric enthalpy, cal/g	-440.62						
Volumetric enthalpy, cal/cc	-2037.17						

Table 20 (cont.)

	6 Ti	+	BaN ₆	=	Ba	+	6 TiN
Heat of formation			-8.00				-73.00
Molecular weight	47.90		221.41		137.36		61.91
Density	4.50		2.94		3.50		5.43
Melting point, °C	1812.00				704.00		2927.00
Boiling point, °C	3000.00						
Heat of reaction, kcal	-430.00						
Reactants' density	3.65						
Gravimetric enthalpy, cal/g	-845.11						
Volumetric enthalpy, cal/cc	-3087.33						
	2 Ti	+	Ba ₃ N ₂	=	3 Ba	+	2 TiN
Heat of formation			-86.90				-73.00
Molecular weight	47.90		440.10		137.36		61.91
Density	4.50				3.50		5.43
Melting point, °C	1812.00				704.00		2927.00
Boiling point, °C	3000.00		1000.00				
Heat of reaction, kcal	-59.10						
Reactants' density							
Gravimetric enthalpy, cal/g							
Volumetric enthalpy, cal/cc	-110.28						
	2 Ti	+	Be ₃ N ₂	=	3 Be	+	2 TiN
Heat of formation			-135.70				-73.00
Molecular weight	47.90		55.06		9.01		61.91
Density	4.50				1.85		5.43
Melting point, °C	1812.00				1283.00		2927.00
Boiling point, °C	3000.00		200.00				
Heat of reaction, kcal	-10.30		2240.00		2970.00		
Reactants' density							
Gravimetric enthalpy, cal/g							
Volumetric enthalpy, cal/cc	-68.28						

Table 20 (cont.)

	Ti	+	Cu ₃ N	=	3 Cu	+	TiN
Heat of formation			17.80				-73.00
Molecular weight	47.90		204.63		63.54		61.91
Density	4.50				8.92		5.43
Melting point, °C	1812.00				1083.00		2927.00
Boiling point, °C	3000.00				2582.00		
Heat of reaction, kcal	-90.80						
Reactants' density							
Gravimetric enthalpy, cal/g							
Volumetric enthalpy, cal/cc			-359.56				
	3 Ti	+	CuN ₃	=	Cu	+	3 TiN
Heat of formation			60.50				-73.00
Molecular weight	47.90		105.56		63.54		61.91
Density	4.50				8.92		5.43
Melting point, °C	1812.00				1083.00		2927.00
Boiling point, °C	3000.00				2582.00		
Heat of reaction, kcal	-279.50						
Reactants' density							
Gravimetric enthalpy, cal/g							
Volumetric enthalpy, cal/cc			-1121.30				
	Ti	+	Fe ₂ N	=	2 Fe	+	TiN
Heat of Formation			~90				-73.00
Molecular weight	47.90		125.71		55.85		61.91
Density	4.50		6.35		7.86		5.43
Melting point, °C	1812.00				1535.00		2927.00
Boiling point, °C	3000.00				2800.00		
Heat of reaction, kcal	-72.10						
Reactants' density							
Gravimetric enthalpy, cal/g							
Volumetric enthalpy, cal/cc			-415.30		-2368.49		

Table 20 (cont.)

	Zr	+	AlN	=	Al	+	ZrN
Heat of formation			-57.70				-82.20
Molecular weight	91.22		40.98		26.98		105.23
Density	6.40		3.26		2.70		7.09
Melting point, °C	1852.00		220.00		660.00		2952.00
Boiling point, °C	2900.00				2327.00		
Heat of reaction, kcal	-24.50						
Reactants' density	4.93						
Gravimetric enthalpy, cal/g	-185.22						
Volumetric enthalpy, cal/cc	-913.37						
	Zr	+	BN	=	B	+	ZrN
Heat of formation			-32.10				-82.20
Molecular weight	91.22		24.83		10.82		105.23
Density	6.40		2.20		2.38		7.09
Melting point, °C	1852.00				2040.00		2952.00
Boiling point, °C	2900.00				2550.00		
Heat of reaction, kcal	-50.10						
Reactants' density	4.54						
Gravimetric enthalpy, cal/g	-431.71						
Volumetric enthalpy, cal/cc	-1961.67						
	6 Zr	+	BaN ₆	=	Ba	+	6 ZrN
Heat of formation			-8.00				-82.20
Molecular weight	91.22		221.41		137.36		105.23
Density	6.40		2.94		3.50		7.09
Melting point, °C	1852.00				704.00		2952.00
Boiling point, °C	2900.00				1638.00		
Heat of reaction, kcal	-4.85						
Reactants' density	4.78						
Gravimetric enthalpy, cal/g	-631.17						
Volumetric enthalpy, cal/cc	-3014.96						

Table 20 (cont.)

	Zr	+	Cu ₃ N	=	3 Cu	+	ZrN
Heat of formation			17.80				-82.20
Molecular weight	91.22		204.63		63.54		105.23
Density	6.40				8.92		7.09
Melting point, °C	1852.00				1083.00		2952.00
Boiling point, °C	2900.00				2582.00		
Heat of reaction, kcal	-100.00						
Reactants' density							
Gravimetric enthalpy, cal/g			-338.01				
Volumetric enthalpy, cal/cc							
	3 Zr	+	CuN ₃	=	Cu	+	3 ZrN
Heat of formation			60.50				-82.20
Molecular weight	91.22		105.56		63.54		105.23
Density	6.40				8.92		7.09
Melting point, °C	1852.00				1083.00		2952.00
Boiling point, °C	2900.00				2582.00		
Heat of reaction, kcal	-307.10						
Reactants' density							
Gravimetric enthalpy, cal/g			-809.81				
Volumetric enthalpy, cal/cc							
	Zr	+	Fe ₂ N	=	2 Fe	+	ZrN
Heat of formation			-°90				-82.20
Molecular weight	91.22		125.71		55.85		105.23
Density	6.40		6.35		7.96		7.09
Melting point, °C	1852.00				1535.00		2952.00
Boiling point, °C	2900.00				2800.00		
Heat of reaction, kcal	-81.30						
Reactants' density							
Gravimetric enthalpy, cal/g			6.37				
Volumetric enthalpy, cal/cc			-374.78				
			-2387.67				

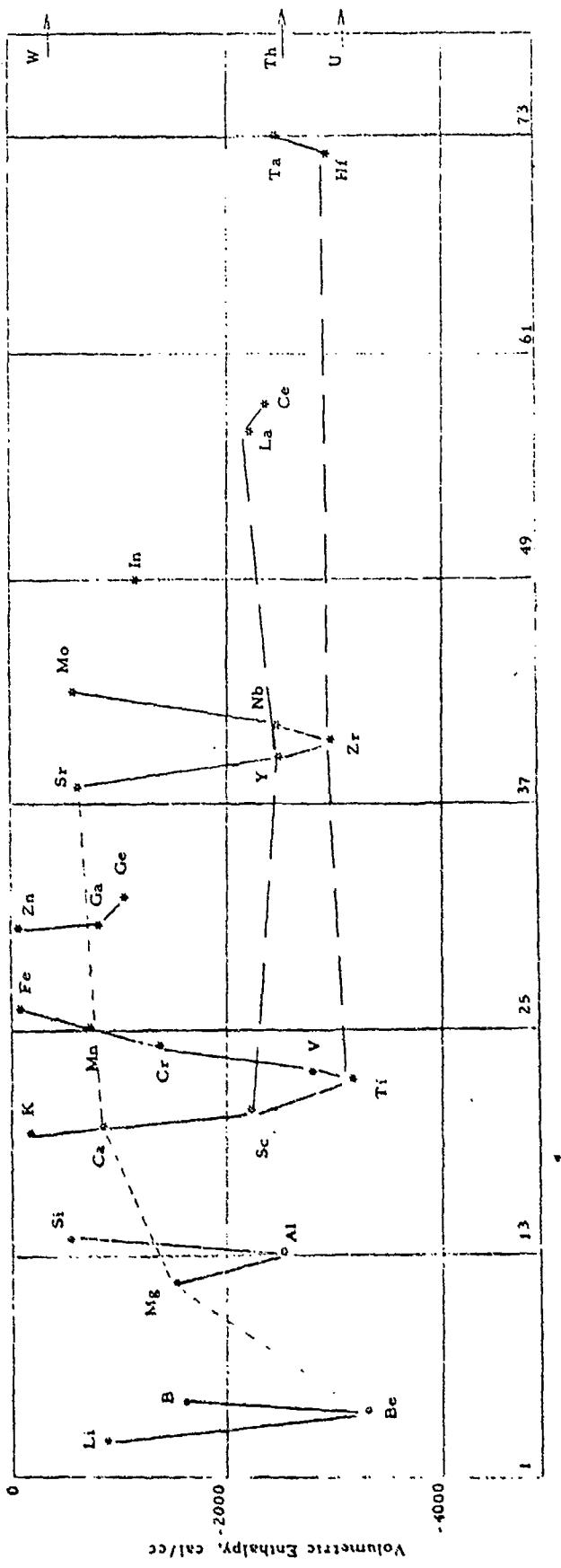
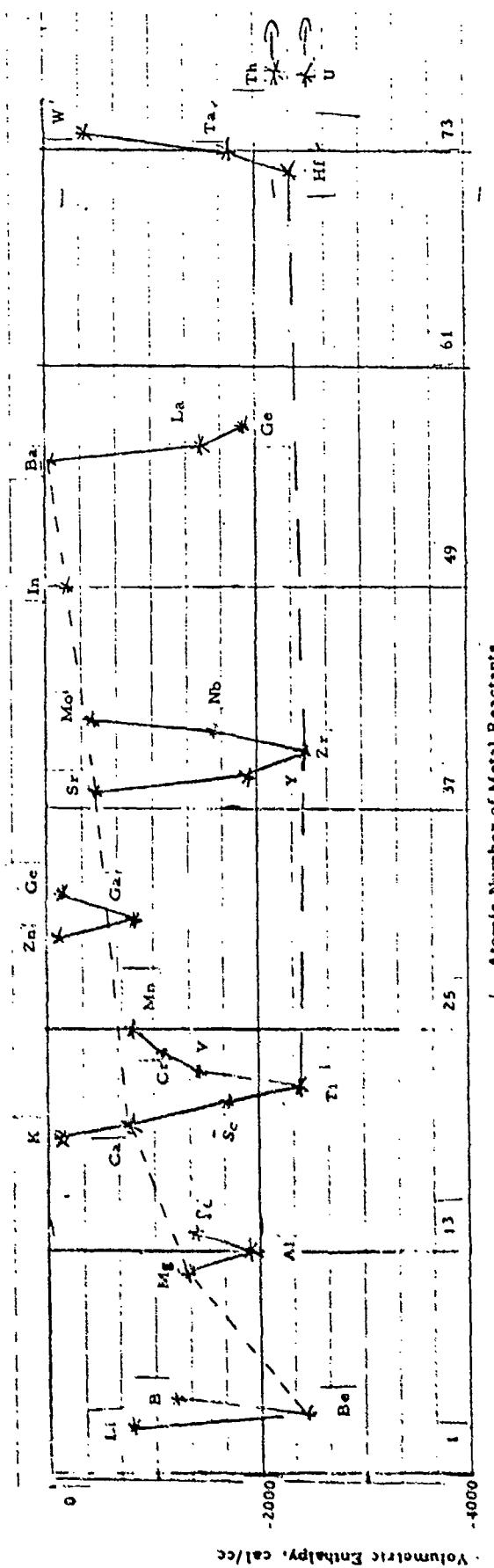


Figure 16
VOLUMETRIC ENTHALPIES OF REACTIONS OF METALS WITH $\text{Ba}(\text{N}_3)_2$



| Atomic Number of Metal Reactants

Figure 17
VOLUMETRIC ENTHALPIES OF REACTIONS OF METALS WITH Fe_2N

H. Chlorate and Perchlorate Reactions

The possible reactions of 50 metals with 7 chlorates and 9 perchlorates resulted in the computation of 16,384 reactions. Only 801 of them were printed, because reactions with positive enthalpies were discarded, as were those with the lowest enthalpy from the possible combinations of each pair of reactants. Examples of the computer output for some of the more energetic reactions are shown in Table 21.

Chlorates and perchlorates are combinations of chlorine and oxygen systems. The chloride of the metal reactant is rarely produced, and when it is produced, it is in a very low ratio compared with its oxide. For example, note the reaction between beryllium and silver chlorate in Table 22. This occurs because the oxides of the highly reactant metals generally have higher negative heats of formation than the chlorides.

The chlorates and perchlorates are much more energetic than the comparable oxide systems. In fact, they are the most energetic systems examined. The 200 most energetic reactions are shown in Tables 22 and 23. The most energetic reaction, between beryllium and magnesium perchlorate, has a volumetric enthalpy of -9459 cal/cc, which is appreciably higher than the most energetic oxide and nitrate reactions: beryllium with ruthenium oxide, -7800 cal/cc; and beryllium with lithium nitrate, -7798 cal/cc. The beryllium-lithium perchlorate reaction, -9088 cal/cc, which is the next most energetic perchlorate reaction, compares with the beryllium-lithium nitrate reaction

The chlorates and perchlorates are listed in order of their effective energies in Table 24. In general, the perchlorate of a metal is more energetic than the chlorate. Silver is an exception because the chlorate has a much higher density than the perchlorate, and thus on a volumetric basis the chlorate is more energetic than the perchlorate.

The periodic trends in the gravimetric and volumetric enthalpies are shown in Figure 18 for reactions of all the metals with magnesium perchlorate. The trends are almost the same as those in the nitrate and oxide systems. The most energetic reactions occur with beryllium, aluminum, titanium, zirconium, hafnium, and the rare earths lanthanum, cerium, praseodymium, and neodymium. The alkali metals tend to have the lowest enthalpies. These trends are essentially the same for all the oxidizers in the oxide, nitrate, and chlorate-perchlorate systems, and for the gravimetric and volumetric bases. Thus, all the curves are similar except for vertical displacement of the ordinates. This type of plot allows one to choose a metal reactant for a particular oxidizer, magnesium perchlorate in this case.

Table 21

DATA ON REACTIONS OF VARIOUS METALS WITH CHLORATES AND PERCHLORATES

	13 Mg + 4 AgClO ₃ = 2 Ag ₂ Cl + 12 MgO + MgCl ₂	13 Mn + 4 AgClO ₃ = 2 Ag ₂ Cl + 12 MnO + MnCl ₂	Mo + AgClO ₃ = AgCl + MoO ₃
Heat of formation	-5.73	-30.90	-30.73
Molecular weight	24.32	191.34	95.32
Density	1.74	4.43	3.58
Melting point, °C	650.00	231.00	2.32
Boiling point, °C	1120.00	279.00	714.00
Heat of reaction, kcal	-1918.36		1418.00
Reactants' density	3.05		
Gravimetric enthalpy, cal/g	-1773.76		
Volumetric enthalpy, cal/cc	-5411.93		
Heat of formation	-5.73	-30.90	-92.00
Molecular weight	54.94	191.34	70.93
Density	7.20	4.43	5.43
Melting point, °C	1244.00	231.00	650.00
Boiling point, °C	2087.00	270.00	1190.00
Heat of reaction, kcat	-1258.18		
Reactants' density	5.44		
Gravimetric enthalpy, cal/g	-850.36		
Volumetric enthalpy, cal/cc	-4626.26		
Heat of formation	95.95	191.34	-30.36
Molecular weight	10.20	4.43	143.95
Density	2610.00	231.00	5.56
Melting point, °C	4800.00	270.00	4.50
Boiling point, °C			795.00
Heat of reaction, kcal	-204.96	1557.00	1155.00
Reactants' density	5.46		
Gravimetric enthalpy, cal/g	-713.43		
Volumetric enthalpy, cal/cc	-3896.71		

Table 21 (cont.)

	13 Zn + 4 AgClO ₃ = 2 Ag ₂ Cl + 12 ZnO + ZnCl ₂	10 Zr + 6 AgClO ₃ = 3 Ag ₂ Cl + 9 ZrO ₂ + ZrCl ₃	16 Ag + 2 AgClO ₄ = 8 Ag ₂ O + 2 AgCl
Heat of formation	-5.73	-30.90	-83.17
Molecular weight	65.38	191.34	251.20
Density	7.14	4.43	5.47
Melting point, °C	419.50	231.00	1800.00
Boiling point, °C	907.00	270.00	1800.00
Heat of reaction, kcal	-1136.32		
Reactants' density	5.54		
Gravimetric enthalpy, cal/g	-703.47		
Volumetric enthalpy, cal/cc	-3894.08		
Heat of formation	-5.73	-30.90	-258.20
Molecular weight	91.22	191.34	251.20
Density	6.40	4.43	5.46
Melting point, °C	185.20	231.00	2700.00
Boiling point, °C	2900.00	270.00	4300.00
Heat of reaction, kcal	-2590.12		
Reactants' density	5.13		
Gravimetric enthalpy, cal/g	-1257.10		
Volumetric enthalpy, cal/cc	-6448.18		
Heat of formation	-7.75		-7.31
Molecular weight	107.87	207.34	231.76
Density	10.50	2.81	7.14
Melting point, °C	960.80	486.00	300.00
Boiling point, °C			455.00
Heat of reaction, kcal	2193.00		1557.00
Reactants' density	-103.67		
Gravimetric enthalpy, cal/g	6.86		
Volumetric enthalpy, cal/cc	-48.43		
	-332.11		

Table 21 (cont.)

	$2 \text{ Zr} + \text{ LiClO}_4 = \text{ LiCl} + 2 \text{ ZrO}_2$	$8 \text{ Ag} + \text{ Mg(ClO}_4)_2 = \text{ MgO}_2 + 3 \text{ Ag}_2\text{O}_2 + 2 \text{ AgCl}$	$16 \text{ Al} + 3 \text{ Mg(ClO}_4)_2 = 3 \text{ MgCl}_2 + 8 \text{ Al}_2\text{O}_3$
Heat of formation	-91.22	-106.10	-140.60
Molecular weight	640	106.50	223.23
Density	1852.00	2.43	56.32
Melting point, °C	2900.00	236.00	2.60
Boiling point, °C		440.00	251.00
Heat of reaction, kcal			
Reactants' density	3.99	-508.00	2193.00
Gravimetric enthalpy, cal/g	-1758.15	-1758.15	-87.92
Volumetric enthalpy, cal/cc	-7021.28	-7021.28	6.46
			-80.95
			-523.21
Heat of formation	107.87	-148.90	-153.40
Molecular weight	10.50	123.23	95.23
Density	960.80	251.00	2.60
Melting point, °C			251.00
Boiling point, °C			
Heat of reaction, kcal			
Reactants' density	3.99		
Gravimetric enthalpy, cal/g	-1758.15		
Volumetric enthalpy, cal/cc	-7021.28		
Heat of formation	26.98	-140.60	-153.40
Molecular weight	2.70	223.23	95.23
Density	660.00	251.00	2.60
Melting point, °C			251.00
Boiling point, °C			
Heat of reaction, kcal			
Reactants' density	2.64	-3231.12	714.00
Gravimetric enthalpy, cal/g	-2933.73	2.64	2015.00
Volumetric enthalpy, cal/cc	-7742.25	-3231.12	3500.00

Table 21 (cont.)

	4 Ge	+	Mg(ClO ₄) ₂	=	MgCl ₂	+	4 GeO ₂
Heat of formation			-140.60		-153.40		-128.30
Molecular weight	72.60		223.23		95.23		104.60
Density	5.35		2.60		2.32		4.70
Melting point, °C	960.00		251.00		714.00		1000.00
Boiling point, °C	2700.00				1418.00		
Heat of reaction, kcal	-526.00						
Reactants' density	3.67						
Gravimetric enthalpy, cal/g	-1024.08						
Volumetric enthalpy, cal/cc	-3753.44						
	4 Hf	+	Mg(ClO ₄) ₂	=	MgCl ₂	+	4 HF O ₂
Heat of formation			-140.60		-153.40		-271.50
Molecular weight	178.50		223.23		95.23		210.60
Density	13.30		2.60		2.32		9.63
Melting point, °C	2227.00		251.00		714.00		2810.00
Boiling point, °C	3200.00				1418.00		
Heat of reaction, kcal	-1098.80						
Reactants' density	6.72						
Gravimetric enthalpy, cal/g	-1172.39						
Volumetric enthalpy, cal/cc	-7874.34						
	8 Hg	+	Mg(ClO ₄) ₂	=	MgCl ₂	+	8 HgO
Heat of formation			-140.60		-153.40		-21.68
Molecular weight	200.61		223.23		95.23		216.61
Density	13.55		2.60		2.32		11.14
Melting point, °C	-38.87		251.00		714.00		500.00
Boiling point, °C	356.57				1418.00		
Heat of reaction, kcal	186.24						
Reactants' density	8.95						
Gravimetric enthalpy, cal/g	-101.88						
Volumetric enthalpy, cal/cc	-911.45						

Table 22

MOST ENERGETIC CHLORATE AND PERCHLORATE REACTIONS WITH METALS,
IN TERMS OF VOLUMETRIC ENTHALPY

Reaction					Enthalpy, cal/cc
8 Be +	$Mg(ClO_4)_2$	=	$MgCl_2$	+ 8 BeO	-9459
4 Be +	$Li(ClO_4)$	=	LiCl	+ 4 BeO	-9088
13 Be +	4 $Ag(ClO_3)$	=	2 Ag_2Cl	+ 12 BeO + $BeCl_2$	-8103
4 U +	$Mg(ClO_4)_2$	=	$MgCl_2$	+ 4 UO_2	-7989
4 Hf +	$Mg(ClO_4)_2$	=	$MgCl_2$	+ 4 HfO_2	-7874
3 Be +	$Na(ClO_3)$	=	NaCl	+ 3 BeO	-7853
4 Be +	$K(ClO_4)$	=	KCl	+ 4 BeO	-7850
16 Al +	3 $Mg(ClO_4)_2$	=	3 $MgCl_2$	+ 8 Al_2O_3	-7742
2 U +	$Li(ClO_4)$	=	LiCl	+ 2 UO_2	-7670
2 Hf +	$Li(ClO_4)$	=	LiCl	+ 2 HfO_2	-7562
8 Al +	3 $Li(ClO_4)$	=	3 LiCl	+ 4 Al_2O_3	-7431
16 B +	3 $Mg(ClO_4)_2$	=	3 $MgCl_2$	+ 8 B_2O_3	-7423
4 Zr +	$Mg(ClO_4)_2$	=	$MgCl_2$	+ 4 ZrO_2	-7318
8 Be +	$Ba(ClO_4)_2$	=	$BaCl_2$	+ 8 BeO	-7302
8 B +	3 $Li(ClO_4)$	=	3 LiCl	+ 4 B_2O_3	-7038
2 Zr +	$Li(ClO_4)$	=	LiCl	+ 2 ZrO_2	-7021
4 Be +	$Rb(ClO_4)$	=	RbCl	+ 4 BeO	-7002
4 Th +	$Mg(ClO_4)_2$	=	$MgCl_2$	+ 4 ThO_2	-6998
10 U +	6 $Ag(ClO_3)$	=	3 Ag_2Cl	+ 9 UO_2 + UCl_3	-6989
16 Ti +	3 $Mg(ClO_4)_2$	=	3 $MgCl_2$	+ 8 Ti_2O_3	-6951
13 Hf +	8 $Ag(ClO_3)$	=	4 Ag_2Cl	+ 12 HfO_2 + $HfCl_4$	-6905
2 Th +	$Li(ClO_4)$	=	LiCl	+ 2 ThO_2	-6750
3 U +	2 $Na(ClO_3)$	=	2 NaCl	+ 3 UO_2	-6750
13 Al +	6 $Ag(ClO_3)$	=	3 Ag_2Cl	+ 6 Al_2O_3 + $AlCl_3$	-6733
16 Ta +	5 $Mg(ClO_4)_2$	=	5 $MgCl_2$	+ 8 Ta_2O_5	-6730
2 U +	$K(ClO_4)$	=	KCl	+ 2 UO_2	-6720
3 Hf +	2 $Na(ClO_3)$	=	2 NaCl	+ 3 HfO_2	-6675
8 Ti +	3 $Li(ClO_4)$	=	3 LiCl	+ 4 Ti_2O_3	-6658

Table 22 (cont.)

Reaction					Enthalpy, Cal/cc
3 Be +	K(ClO ₃)	=	KCl	+ 3 BeO	-6653
2 Hf +	K(ClO ₄)	=	KCl	+ 2 HfO ₂	-6643
3 Be +	Rb(ClO ₃)	=	RbCl	+ 3 BeO	-6616
17 Be + 4 Ag(ClO ₄)		=	2 Ag ₂ Cl	+ 16 BeO + BeCl ₂	-6573
2 Al +	Na(ClO ₃)	=	NaCl	+ Al ₂ O ₃	-6562
4 Be +	Cs(ClO ₄)	=	CsCl	+ 4 BeO	-6533
8 Al + 3 K(ClO ₄)		=	3 KCl	+ 4 Al ₂ O ₃	-6527
10 Zr + 6 Ag(ClO ₃)		=	3 Ag ₂ Cl	+ 9 ZrO ₂ + ZrCl ₃	-6448
8 Ta + 5 Li(ClO ₄)		=	5 LiCl	+ 4 Ta ₂ O ₅	-6388
4 U +	Ba(ClO ₄) ₂	=	BaCl ₂	+ 4 UO ₂	-6292
4 Si +	Mg(ClO ₄) ₂	=	MgCl ₂	+ 4 SiO ₂	-6289
13 Th + 8 Ag(ClO ₃)		=	4 Ag ₂ Cl	+ 12 ThO ₂ + ThCl ₄	-6289
16 Nb + 5 Mg(ClO ₄) ₂		=	5 MgCl ₂	+ 8 Nb ₂ O ₅	-6249
2 B +	Ag(ClO ₃)	=	AgCl	+ B ₂ O ₃	-6242
3 Zr + 2 Na(ClO ₃)		=	2 NaCl	+ 3 ZrO ₂	-6234
4 Hf +	Ba(ClO ₄) ₂	=	BaCl ₂	+ 4 HfO ₂	-6228
2 Zr +	K(ClO ₄)	=	KCl	+ 2 ZrO ₂	-6192
16 Al + 3 Ba(ClO ₄) ₂		=	3 BaCl ₂	+ 8 Al ₂ O ₃	-6119
3 Th + 2 Na(ClO ₃)		=	2 NaCl	+ 3 ThO ₂	-6102
13 Ti + 6 Ag(ClO ₃)		=	3 Ag ₂ Cl	+ 6 Ti ₂ O ₃ + TiCl ₃	-6100
16 Sc + 3 Mg(ClO ₄) ₂		=	3 MgCl ₂	+ 8 Sc ₂ O ₃	-6099
2 Th +	K(ClO ₄)	=	KCl	+ 2 ThO ₂	-6063
2 B +	Na(ClO ₃)	=	NaCl	+ B ₂ O ₃	-6061
2 U +	Rb(ClO ₄)	=	RbCl	+ 2 UO ₂	-6040
16 Nd + 3 Mg(ClO ₄) ₂		=	3 MgCl ₂	+ 8 Nd ₂ O ₃	-6036
8 B + 3 K(ClO ₄)		=	3 KCl	+ 4 B ₂ O ₃	-6004
2 Si +	Li(ClO ₄)	=	LiCl	+ 2 SiO ₂	-5983
16 La + 3 Mg(ClO ₄) ₂		=	3 MgCl ₂	+ 8 La ₂ O ₃	-5981
2 Hf +	Rb(ClO ₄)	=	RbCl	+ 2 HfO ₂	-5981
16 V + 3 Mg(ClO ₄) ₂		=	3 MgCl ₂	+ 8 V ₂ O ₃	5980

Table 22 (cont.)

Reaction				Enthalpy, cal/cc
16 Pr + 3 Mg(ClO ₄) ₂	=	3 MgCl ₂ + 8 Pr ₂ O ₃		-5946
16 Ce + 3 Mg(ClO ₄) ₂	=	3 MgCl ₂ + 8 Ce ₂ O ₃		-5941
2 Ti + Na(ClO ₃)	=	NaCl + Ti ₂ O ₃		-5926
8 Nb + 5 Li(ClO ₄)	=	5 LiCl + 4 Nb ₂ O ₅		-5914
8 Mg + Mg(ClO ₄) ₂	=	MgCl ₂ + 8 MgO		-5886
16 Cr + 3 Mg(ClO ₄) ₂	=	3 MgCl ₂ + 8 Cr ₂ O ₃		-5885
8 Sc + 3 Li(ClO ₄)	=	3 LiCl + 4 Sc ₂ O ₃		-5877
8 Ti + 3 K(ClO ₄)	=	3 KCl + 4 Ti ₂ O ₃		-5876
8 Al + 3 Rb(ClO ₄)	=	3 RbCl + 4 Al ₂ O ₃		-5875
8 Nd + 3 Li(ClO ₄)	=	3 LiCl + 4 Nd ₂ O ₃		-5832
4 Zr + Ba(ClO ₄) ₂	=	BaCl ₂ + 4 ZrO ₂		-5817
8 La + 3 Li(ClO ₄)	=	3 LiCl + 4 La ₂ O ₃		-5786
3 U + 2 K(ClO ₃)	=	2 KCl + 3 UO ₂		-5779
6 Ta + 5 Ag(ClO ₃)	=	5 AgCl + 3 Ta ₂ O ₅		-5767
8 Pr + 3 Li(ClO ₄)	=	3 LiCl + 4 Pr ₂ O ₃		-5747
3 U + 2 Rb(ClO ₃)	=	2 RbCl + 3 UO ₂		-5747
13 U + 6 Ag(ClO ₄)	=	3 Ag ₂ Cl + 12 UO ₂	+ UCl ₃	-5747
4 Th + Ba(ClO ₄) ₂	=	BaCl ₂ + 4 ThO ₂		-5743
8 Ce + 3 Li(ClO ₄)	=	3 LiCl + 4 Ce ₂ O ₃		-5737
3 Hf + 2 K(ClO ₃)	=	2 KCl + 3 HfO ₂		-5728
3 Hf + 2 Rb(ClO ₃)	=	2 RbCl + 3 HfO ₂		-5696
17 Hf + 8 Ag(ClO ₄)	=	4 Ag ₂ Cl + 16 HfO ₂	+ HfCl ₄	-5688
4 Mg + Li(ClO ₄)	=	LiCl + 4 MgO		-5683
8 V + 3 Li(ClO ₄)	=	3 LiCl + 4 V ₂ O ₃		-5676
2 U + Cs(ClO ₄)	=	CsCl + 2 UO ₂		-5662
2 Al + K(ClO ₃)	=	KCl + Al ₂ O ₃		-5629
2 Hf + Cs(ClO ₄)	=	CsCl + 2 HfO ₂		-5612
2 Al + Rb(ClO ₃)	=	RbCl + Al ₂ O ₃		-5597
6 Ta + 5 Na(ClO ₃)	=	5 NaCl + 3 Ta ₂ O ₅		-5596
16 Zr + 8 Rb(ClO ₄)	=	8 RbCl + 16 ZrO ₂		-5585

Table 22 (cont.)

Reaction					Enthalpy, cal/cc
13 Nd + 6 Ag(ClO ₃)	=	3 Ag ₂ Cl + 6 Nd ₂ O ₃	+ NdCl ₃		-5583
13 Sc + 6 Ag(ClO ₃)	=	3 Ag ₂ Cl + 6 Sc ₂ O ₃	+ ScCl ₃		-5568
8 Cr + 3 Li(ClO ₄)	=	3 LiCl + 4 Cr ₂ O ₃			-5565
16 B + 3 Ba(ClO) ₄	=	3 BaCl ₂ + 8 B ₂ O ₃			-5562
13 La + 6 Ag(ClO ₃)	=	3 Ag ₂ Cl + 6 La ₂ O ₃	+ LaCl ₃		-5553
17 Al + 6 Ag(ClO ₄)	=	3 Ag ₂ Cl + 8 Al ₂ O ₃	+ AlCl ₃		-5553
2 Th + Rb(ClO ₄)	=	RbCl + 2 ThO ₂			-5542
8 Ta + 5 K(ClO ₄)	=	5 KCl + 4 Ta ₂ O ₅			-5530
16 Ti + 3 Ba(ClO ₄) ₂	=	3 BaCl ₂ + 8 Ti ₂ O ₃			-5523
13 Ce + 6 Ag(ClO ₃)	=	3 Ag ₂ Cl + 6 Ce ₂ O ₃	+ CeCl ₃		-5514
13 Pr + 6 Ag(ClO ₃)	=	3 Ag ₂ Cl + 6 Pr ₂ O ₃	+ PrCl ₃		-5514
8 Al + 3 Cs(ClO ₄)	=	3 CsCl + 4 Al ₂ O ₃			-5512
3 Si + 2 Ag(ClO ₃)	=	2 AgCl + 3 SiO ₂			-5477
13 Mg + 4 Ag(ClO ₃)	=	2 Ag ₂ Cl + 12 MgO	+ MgCl ₂		-5411
6 Nb + 5 Ag(ClO ₃)	=	5 AgCl + 3 Nb ₂ O ₅			-5380
2 Sc + Na(ClO ₃)	=	NaCl + Sc ₂ O ₃			-5379
2 Nd + Na(ClO ₃)	=	NaCl + Nd ₂ O ₃			-5374
3 Zr + 2 K(ClO ₃)	=	2 KCl + 3 ZrO ₂			-5363
2 La + Na(ClO ₃)	=	NaCl + La ₂ O ₃			-5350
3 Th + 2 K(ClO ₃)	=	2 KCl + 3 ThO ₂			-5348
13 Zr + 6 Ag(ClO ₄)	=	3 Ag ₂ Cl + 12 ZrO ₂	+ ZrCl ₃		-5333
3 Zr + 2 Rb(ClO ₃)	=	2 RbCl + 3 ZrO ₂			-5332
8 Sc + 3 K(ClO ₄)	=	3 KCl + 4 Sc ₂ O ₃			-5329
8 Nd + 3 K(ClO ₄)	=	3 KCl + 4 Nd ₂ O ₃			-5327
3 Th + 2 Rb(ClO ₃)	=	2 RbCl + 3 ThO ₂			-5320
17 Th + 8 Ag(ClO ₄)	=	4 Ag ₂ Cl + 16 ThO ₂	+ ThCl ₄		-5320
3 Si + 2 Na(ClO ₃)	=	2 NaCl + 3 SiO ₂			-5316
2 Pr + Na(ClO ₃)	=	NaCl + Pr ₂ O ₃			-5307
8 La + 3 K(ClO ₄)	=	3 KCl + 4 La ₂ O ₃			-5305
8 Ti + 3 Rb(ClO ₄)	=	3 RbCl + 4 Ti ₂ O ₃			-5299

Table 22 (cont.)

Reaction					Enthalpy, cal/cc
2 Ce +	Na(ClO ₃)	=	NaCl	+ Ce ₂ O ₃	-5290
8 B +	3 Rb(ClO ₄)	=	3 RbCl	+ 4 B ₂ O ₃	-5289
8 Pr +	3 K(ClO ₄)	=	3 KCl	+ 4 Pr ₂ O ₃	-5259
2 Si +	K(ClO ₄)	=	KCl	+ 2 SiO ₂	-5247
2 Zr +	Cs(ClO ₄)	=	CsCl	+ 2 ZrO ₂	-5246
2 Th +	Cs(ClO ₄)	=	CsCl	+ 2 ThO ₂	-5245
3 Mg +	Na(ClO ₃)	=	NaCl	+ 3 MgO	-5243
8 Ce +	3 K(ClO ₄)	=	3 KCl	+ 4 Ce ₂ O ₃	-5242
9 V +	4 Ag(ClO ₃)	=	2 Ag ₂ Cl	+ 4 V ₂ O ₃ + VCl ₂	-5233
6 Nb +	5 Na(ClO ₃)	=	5 NaCl	+ 3 Nb ₂ O ₅	-5205
4 Mg +	K(ClO ₄)	=	KCl	+ 4 MgO	-5193
16 Ta +	5 Ba(ClO ₄) ₂	=	5 BaCl ₂	+ 8 Ta ₂ O ₅	-5155
6 Mn +	Mg(ClO ₄) ₂	=	MgCl ₂	+ 2 Mn ₃ O ₄	-5132
13 Cr +	6 Ag(ClO ₃)	=	3 Ag ₂ Cl	+ 6 Cr ₂ O ₃ + CrCl ₃	-5129
8 Nb +	5 K(ClO ₄)	=	5 KCl	+ 4 Nb ₂ O ₅	-5128
2 Ti +	K(ClO ₃)	=	KCl	+ Ti ₂ O ₃	-5095
16 Nd +	3 Ba(ClO ₄) ₂	=	3 BaCl ₂	+ 8 Nd ₂ O ₃	-5086
16 La +	3 Ba(ClO ₄) ₂	=	3 BaCl ₂	+ 8 La ₂ O ₃	-5074
16 Sc +	3 Ba(ClO ₄) ₂	=	3 BaCl ₂	+ 8 Sc ₂ O ₃	-5071
2 Ti +	Rb(ClO ₃)	=	RbCl	+ Ti ₂ O ₃	-5065
2 V +	Na(ClO ₃)	=	NaCl	+ V ₂ O ₃	-5054
2 B +	K(ClO ₃)	=	KCl	+ B ₂ O ₃	-5046
17 Ti +	6 Ag(ClO ₄)	=	3 Ag ₂ Cl	+ 8 Ti ₂ O ₃ + TiCl ₃	-5041
16 Pr +	3 Ba(ClO ₄) ₂	=	3 BaCl ₂	+ 8 Pr ₂ O ₃	-5026
2 B +	Rb(ClO ₃)	=	RbCl	+ B ₂ O ₃	-5010
16 Ce +	3 Ba(ClO ₄) ₂	=	3 BaCl ₂	+ 8 Ce ₂ O ₃	-5005
8 V +	3 K(ClO ₄)	=	3 KCl	+ 4 V ₂ O ₃	-4978
8 Ti +	3 Cs(ClO ₄)	=	3 CsCl	+ 4 Ti ₂ O ₃	-4977
8 Mg +	Ba(ClO ₄) ₂	=	BaCl ₂	+ 8 MgO	-4960
8 B +	3 Ag(ClO ₄)	=	3 AgCl	+ 4 B ₂ O ₃	-4941

Table 22 (cont.)

Reaction				Enthalpy, cal/cc
2 Cr +	Na(ClO ₄)	=	NaCl + Cr ₂ O ₃	-4933
8 W +	3 Mg(ClO ₄) ₂	=	3 MgCl ₂ + 8 WO ₃	-4923
8 Nd +	3 Rb(ClO ₄)	=	3 RbCl + 4 Nd ₂ O ₃	-4922
4 Si +	Ba(ClO ₄) ₂	=	BaCl ₂ + 4 SiO ₂	-4921
8 La +	3 Rb(ClO ₄)	=	3 RbCl + 4 La ₂ O ₃	-4916
8 Ta +	5 Rb(ClO ₄)	=	5 RbCl + 4 Ta ₂ O ₅	-4912
8 B +	3 Cs(ClO ₄)	=	3 CsCl + 4 B ₂ O ₃	-4905
8 Sc +	3 Rb(ClO ₄)	=	3 RbCl + 4 Sc ₂ O ₃	-4896
8 Pr +	3 Rb(ClO ₄)	=	3 RbCl + 4 Pr ₂ O ₃	-4866
8 Cr +	3 K(ClO ₄)	=	3 KCl + 4 Cr ₂ O ₃	-4851
8 Ce +	3 Rb(ClO ₄)	=	3 RbCl + 4 Ce ₂ O ₃	-4843
3 Mn +	Li(ClO ₄)	=	LiCl + Mn ₃ O ₄	-4839
17 La +	6 Ag(ClO ₄)	=	3 Ag ₂ Cl + 8 La ₂ O ₃ + LaCl ₃	-4803
17 Nd +	6 Ag(ClO ₄)	=	3 Ag ₂ Cl + 3 Nd ₂ O ₃	-4802
4 Mg +	Rb(ClO ₄)	=	RbCl + 4 MgO	-4799
16 Nb +	5 Ba(ClO ₄) ₂	=	5 BaCl ₂ + 8 Nb ₂ O ₅	-4786
2 Nd +	K(ClO ₃)	=	KCl + Nd ₂ O ₃	-4783
2 La +	K(ClO ₃)	=	KCl + La ₂ O ₃	-4782
2 La +	Rb(ClO ₃)	=	RbCl + La ₂ O ₃	-4759
2 Nd +	Rb(ClO ₃)	=	RbCl + Nd ₂ O ₃	-4759
17 Pr +	6 Ag(ClO ₄)	=	3 Ag ₂ Cl + 8 Pr ₂ O ₃ + PrCl ₃	-4854
2 Sc +	K(ClO ₃)	=	KCl + Sc ₂ O ₃	-4749
17 Sc +	6 Ag(ClO ₄)	=	3 Ag ₂ Cl + 8 Sc ₂ O ₃ + ScCl ₃	-4745
17 Ce +	6 Ag(ClO ₄)	=	3 Ag ₂ Cl + 8 Ce ₂ O ₃ + CeCl ₃	-4739
2 Pr +	K(ClO ₃)	=	KCl + Pr ₂ O ₃	-4732
2 Sc +	Rb(ClO ₃)	=	RbCl + Sc ₂ O ₃	-4724
6 Ta +	5 K(ClO ₃)	=	5 KCl + 3 Ta ₂ O ₅	-4713
2 Pr +	Rb(ClO ₃)	=	RbCl + Pr ₂ O ₃	-4709
16 Ga +	3 Mg(ClO ₄) ₂	=	3 MgCl ₂ + 8 Ga ₂ O ₃	-4708
2 Ce +	K(ClO ₃)	=	KCl + Ce ₂ O ₃	-4708
2 Si +	Rb(ClO ₄)	=	RbCl + 2 SiO ₂	-4701

Table 22 (cont.)

Reaction					Enthalpy, cal/cc
8 La + 3 Cs(ClO ₄) ₂	=	3 CsCl	+ 4 La ₂ O ₃		-4691
8 Nd + 3 Cs(ClO ₄) ₂	=	3 CsCl	+ 4 Nd ₂ O ₃		-4689
2 Ce + Rb(ClO ₃)	=	RbCl	+ Ce ₂ O ₃		-4685
6 Ta + 5 Rb(ClO ₃)	=	5 RbCl	+ 3 Ta ₂ O ₅		-4679
16 V + 3 Ba(ClO ₄) ₂	=	3 BaCl ₂	+ 8 V ₂ O ₃		-4670
3 Mg + K(ClO ₃)	=	KCl	+ 3 MgO		-4666
17 Mg + 4 Ag(ClO ₄)	=	2 Ag ₂ Cl	+ 16 MgO	+ MgCl ₂	-4661
8 Sc + 3 Cs(ClO ₄) ₂	=	3 CsCl	+ 4 Sc ₂ O ₃		-4648
3 Mg + Rb(ClO ₃)	=	RbCl	+ 3 MgO		-4643
8 Pr + 3 Cs(ClO ₄) ₂	=	3 CsCl	+ 4 Pr ₂ O ₃		-4639
13 Mn + 4 Ag(ClO ₃)	=	2 Ag ₂ Cl	+ 12 MnO	+ MnCl ₂	-4626
8 Ta + 5 Ag(ClO ₄)	=	5 AgCl	+ 4 Ta ₂ O ₅		-4626
8 Ce + 3 Cs(ClO ₄) ₂	=	3 CsCl	+ 4 Ce ₂ O ₃		-4614
4 W + 3 Li(ClO ₄)	=	3 LiCl	+ 4 WO ₃		-4587
8 Ta + 5 Cs(ClO ₄) ₂	=	5 CsCl	+ 4 Ta ₂ O ₅		-4577
4 Mg + Cs(ClO ₄) ₂	=	CsCl	+ 4 MgO		-4572
8 Nb + 5 Rb(ClO ₃)	=	5 RbCl	+ 4 Nb ₂ O ₅		-4554
16 Cr + 3 Ba(ClO ₄) ₂	=	3 BaCl ₂	+ 8 Cr ₂ O ₃		-4539
3 Si + 2 K(ClO ₃)	=	2 KCl	+ 3 SiO ₂		-4529
3 Si + 2 Rb(ClO ₃)	=	2 RbCl	+ 3 SiO ₂		-4498
8 V + 3 Rb(ClO ₄) ₂	=	3 RbCl	+ 4 V ₂ O ₃		-4455
8 Ga + 3 Li(ClO ₄) ₂	=	3 LiCl	+ 4 Ga ₂ O ₃		-4454
2 Si + Ag(ClO ₄) ₂	=	AgCl	+ 2 SiO ₂		-4454
8 Mo + 3 Mg(ClO ₄) ₂	=	3 MgCl ₂	+ 8 MoO ₃		-4449

Table 23

MOST ENERGETIC CHLORATE AND PERCHLORATE REACTIONS WITH METALS,
IN TERMS OF GRAVIMETRIC ENTHALPY

Reaction					Enthalpy, cal/g
4 Be +	$\text{Li}(\text{ClO}_4)_2$	=	LiCl	+ 4 BeO	-4037
8 Be +	$\text{Mg}(\text{ClO}_4)_2$	=	MgCl_2	+ 8 BeO	-3998
16 Li +	$\text{Mg}(\text{ClO}_4)_2$	=	MgO	+ 7 Li_2O + 2 LiCl	-3576
3 Li +	$\text{Li}(\text{ClO}_4)_2$	=	LiCl	+ 4 Li_2O	-3463
3 Be +	$\text{Na}(\text{ClO}_3)_2$	=	NaCl	+ 3 BeO	-3374
4 Be +	$\text{K}(\text{ClO}_4)_2$	=	KCl	+ 4 BeO	-3348
34 Li +	$2 \text{Cu}(\text{ClO}_4)_2$	=	Cu_2O	+ 15 Li_2O + 4 LiCl	-3323
12 Li +	$2 \text{Li}(\text{ClO}_3)_2$	=	Li_2O	+ 5 Li_2O + 2 LiCl	-3310
16 Li +	$2 \text{Na}(\text{ClO}_4)_2$	=	Na_2O	+ 7 Li_2O + 2 LiCl	-3110
26 Li +	$2 \text{Cu}(\text{ClO}_3)_2$	=	Cu_2O	+ 11 Li_2O + 4 LiCl	-3015
3 Be +	$\text{K}(\text{ClO}_3)_2$	=	KCl	+ 3 BeO	-2999
6 Li +	$\text{Na}(\text{ClO}_3)_2$	=	NaCl	+ 3 Li_2O	-2969
8 Li +	$\text{K}(\text{ClO}_4)_2$	=	KCl	+ 4 Li_2O	-2937
8 Al +	$3 \text{Li}(\text{ClO}_4)_2$	=	3 LiCl	+ 4 Al_2O_3	-2934
16 Al +	$3 \text{Mg}(\text{ClO}_4)_2$	=	3 MgCl_2	+ 8 Al_2O_3	-2933
8 B +	$3 \text{Li}(\text{ClO}_4)_2$	=	3 LiCl	+ 4 B_2O_3	-2912
16 B +	$3 \text{Mg}(\text{ClO}_4)_2$	=	3 MgCl_2	+ 8 B_2O_3	-2912
8 Be +	$\text{Ba}(\text{ClO}_4)_2$	=	BaCl_2	+ 8 BeO	-2891
8 Mg +	$\text{Mg}(\text{ClO}_4)_2$	=	MgCl_2	+ 8 MgO	-2784
4 Mg +	$\text{Li}(\text{ClO}_4)_2$	=	LiCl	+ 4 MgO	-2782
6 Li +	$\text{K}(\text{ClO}_3)_2$	=	KCl	+ 3 Li_2O	-2666
4 Be +	$\text{Rb}(\text{ClO}_4)_2$	=	RbCl	+ 4 BeO	-2638
16 Li +	$2 \text{Ba}(\text{ClO}_4)_2$	=	BaCl_2	+ 8 Li_2O	-2575
2 Al +	$\text{Na}(\text{ClO}_3)_2$	=	NaCl	+ Al_2O_3	-2565
17 Be +	$4 \text{Ag}(\text{ClO}_4)_2$	=	2 Ag_2Cl	+ 16 BeO + BeCl_2	-2533
8 Al +	$3 \text{K}(\text{ClO}_4)_2$	=	3 KCl	+ 4 Al_2O_3	-2530
4 Si +	$2 \text{Mg}(\text{ClO}_4)_2$	=	MgCl_2	+ 4 SiO_2	-2486
3 Mg +	$\text{Na}(\text{ClO}_3)_2$	=	NaCl	+ 3 MgO	-2474
2 Si +	$\text{Li}(\text{ClO}_4)_2$	=	LiCl	+ 2 SiO_2	-2473

Table 23 (cont.)

Reaction					Enthalpy, cal/q
2 B + Na(ClO ₃) =	NaCl + B ₂ O ₃				-2455
4 Mg + K(ClO ₄) =	KCl + 4 MgO				-2442
8 B + 3 K(ClO ₄) =	3 KCl + 4 B ₂ O ₃				-2408
16 Sc + 3 Mg(ClO ₄) ₂ =	3 MgCl ₂ + 8 Sc ₂ O ₃				-2394
8 Sc + 3 Li(ClO ₄) =	3 LiCl + 4 Sc ₂ O ₃				-2383
8 Li + Rb(ClO ₄) =	RbCl + 4 Li ₂ O				-2364
17 Li + 2 Ag(ClO ₄) =	Ag ₂ Cl + 8 Li ₂ O + LiCl				-2351
2 Al + K(ClO ₃) =	KCl + Al ₂ O ₃				-2321
3 Be + Rb(ClO ₃) =	RbCl + 3 BeO				-2281
3 Mg + K(ClO ₃) =	KCl + 3 MgO				-2261
8 Ca + Mg(ClO ₄) ₂ =	MgCl ₂ + 8 CaO				-2257
4 Ca + Li(ClO ₄) =	LiCl + 4 CaO				-2245
16 Al + 3 Ba(ClO ₄) ₂ =	3 BaCl ₂ + 8 Al ₂ O ₃				-2242
14 Al + 2 Cu(ClO ₄) ₂ =	Cu ₂ O + 5 Al ₂ O ₃ + 4 AlCl				-2234
12 Li + Ba(ClO ₃) ₂ =	BaO + 5 Li ₂ O + 2 LiCl				-2217
8 Mg + Ba(ClO ₄) ₂ =	BaCl ₂ + 8 MgO				-2191
4 Be + Cs(ClO ₄) =	CsCl + 4 BeO				-2174
2 B + K(ClO ₃) =	KCl + B ₂ O ₃				-2168
13 Be + 4 Ag(ClO ₃) =	2 Ag ₂ Cl + 12 BeO + BeCl ₂				-2167
3 Si + 2 Na(ClO ₃) =	2 NaCl + 3 SiO ₂				-2157
2 Sc + Na(ClO ₃) =	NaCl + Sc ₂ O ₃				-2156
8 Sc + 3 K(ClO ₄) =	3 KCl + 4 Sc ₂ O ₃				-2122
2 Si + K(ClO ₄) =	KCl + 2 SiO ₂				-2112
14 B + 2 Cu(ClO ₄) ₂ =	Cu ₂ O + 5 B ₂ O ₃				-2083
16 B + 3 Ba(ClO ₄) ₂ =	5 BaCl ₂ + 8 B ₂ O ₃				-2076
16 Ti + 3 Mg(ClO ₄) ₂ =	3 MgCl ₂ + 8 Ti ₂ O ₃				-2071
6 Li + Rb(ClO ₃) =	RbCl + 3 Li ₂ O				-2071
8 Al + 3 Rb(ClO ₄) =	3 RbCl + 4 Al ₂ O ₃				-2067
3 Ca + Na(ClO ₃) =	NaCl + 3 CaO				-2065
13 Li + 2 Ag(ClO ₃) =	Ag ₂ Cl + 6 Li ₂ O + 1 LiCl				-2054
8 Ti + 3 Li(ClO ₄) =	3 LiCl + 4 Ti ₂ O ₃				-2053

Table 23 (cont.)

Reaction					Enthalpy, cal/g
4 Mg +	Rb(ClO ₄)	=	RbCl	+ 4 MgO	-2035
4 Ca +	K(ClO ₄)	=	KCl	+ 4 CaO	-2034
20 Al +	6 Na(ClO ₄)	=	3 Na ₂ O	+ 7 Al ₂ O ₃ + 6 AlCl	-2015
17 Mg +	4 Ag(ClO ₄)	=	2 Ag ₂ Cl	+ 16 MgO + MgCl ₂	-2000
17 Al +	6 Ag(ClO ₄)	=	3 Ag ₂ Cl	+ 8 Al ₂ O ₃ + AlCl ₃	-1999
2 Sc +	K(ClO ₃)	=	KCl	+ Sc ₂ O ₃	-1984
34 Be +	4 Cu(ClO ₄) ₂	=	2 Cu ₂ O	+ 15 BeO + 4 BeCl ₂	-1978
16 Al +	6 Li(ClO ₃)	=	3 Li ₂ O	+ 5 Al ₂ O ₃ + 6 AlCl	-1977
8 Li +	Cs(ClO ₄)	=	CsCl	+ 4 Li ₂ O	-1977
12 Be +	4 Li(ClO ₃)	=	2 Li ₂ O	+ 5 BeO + 2 BeCl ₂	-1935
3 Si +	2 K(ClO ₃)	=	2 KCl	+ 3 SiO ₂	-1935
16 Sc +	3 Ba(ClO ₄) ₂	=	3 BaCl ₂	+ 8 Sc ₂ O ₃	-1924
3 Ca +	K(ClO ₃)	=	KCl	+ 3 CaO	-1920
34 Al +	6 Cu(ClO ₃) ₂	=	3 Cu ₂ O	+ 11 Al ₂ O ₃ + 12 AlCl	-1903
8 B +	3 Rb(ClO ₄)	=	3 RbCl	+ 4 B ₂ O ₃	-1878
2 Ti +	Na(ClO ₃)	=	NaCl	+ Ti ₂ O ₃	-1876
8 Ca +	Ba(ClO ₄) ₂	=	BaCl ₂	+ 8 CaO	-1869
4 Si +	Ba(ClO ₄) ₂	=	BaCl ₂	+ 4 SiO ₂	-1859
8 Ti +	3 K(ClO ₄)	=	3 KCl	+ 4 Ti ₂ O ₃	-1839
2 Al +	Rb(ClO ₃)	=	RbCl	+ Al ₂ O ₃	-1831
3 Mg +	Rb(ClO ₃)	=	RbCl	+ 3 MgO	-1821
8 B +	3 Ag(ClO ₄)	=	3 AgCl	+ 4 B ₂ O ₃	-1800
8 Sc +	3 Rb(ClO ₄)	=	3 RbCl	+ 4 Sc ₂ O ₃	-1794
20 B +	6 Na(ClO ₄)	=	3 Na ₂ O	+ 7 B ₂ O ₃ + 6 BC1	-1793
4 Zr +	Mg(ClO ₄) ₂	=	MgCl ₂	+ 4 ZrO ₂	-1777
13 Mg +	4 Ag(ClO ₃)	=	2 Ag ₂ Cl	+ 12 MgO + MgCl ₂	-1773
26 Be +	4 Cu(ClO ₃) ₂	=	2 Cu ₂ O	+ 11 BeO + 4 BeCl ₂	-1771
17 Sc +	6 Ag(ClO ₄)	=	3 Ag ₂ Cl	+ 8 Sc ₂ O ₃ + Sc ₂ O ₃	-1770
16 B +	6 Li(ClO ₃)	=	3 Li ₂ O	+ 5 B ₂ O ₃ + 6 BC1	-1758
2 Zr +	Li(ClO ₄)	=	LiCl	+ 2 ZrO ₂	-1758
4 Ca +	Rb(ClO ₄)	=	RbCl	+ 4 CaO	-1757

Table 23 (cont.)

Reaction						Enthalpy, cal/g
17 Ca + 4 Ag(ClO ₄)	=	2 Ag ₂ Cl + 16 CaO	+ CaCl ₂			-1754
13 Al + 6 Ag(ClO ₃)	=	3 Ag ₂ Cl + 6 Al ₂ O ₃	+ AlCl ₃			-1747
8 Al + 3 Cs(ClO ₄)	=	3 CsCl + 4 Al ₂ O ₃				-1747
4 Mg + Cs(ClO ₄)	=	CsCl + 4 MgO				-1744
16 Be + 4 Na(ClO ₄)	=	2 Na ₂ O + 7 BeO	+ 2 BeCl ₂			-1729
2 Ti + K(ClO ₃)	=	KCl + Ti ₂ O ₃				-1729
2 Si + Rb(ClO ₄)	=	RbCl + 2 SiO ₂				-1699
34 B + 6 Cu(ClO ₃) ₂	=	3 Cu ₂ O + 11 B ₂ O ₃	+ 12 BC1			-1682
16 Ti + 3 Ba(ClO ₄) ₂	=	3 BaCl ₂ + 8 Ti ₂ O ₃				-1675
2 Si + Ag(ClO ₄)	=	AgCl + 2 SiO ₂				-1644
3 Zr + 2 Na(ClO ₃)	=	2 NaCl + 3 ZrO ₂				-1643
2 B + Rb(ClO ₃)	=	RbCl + B ₂ O ₃				-1632
2 Sc + Rb(ClO ₃)	=	RbCl + Sc ₂ O ₃				-1622
2 Zr + K(ClO ₄)	=	KCl + 2 ZrO ₂				-1610
3 Ca + Rb(ClO ₃)	=	RbCl + 3 CaO				-1607
13 Ca + 4 Ag(ClO ₃)	=	2 Ag ₂ Cl + 12 CaO	+ CaCl ₂			-1594
16 V + 3 Mg(ClO ₄) ₂	=	3 MgCl ₂ + 8 V ₂ O ₃				-1588
13 Sc + 6 Ag(ClO ₃)	=	3 Ag ₂ Cl + 6 Sc ₂ O ₃	+ ScCl ₃			-1584
8 Ti + 3 Rb(ClO ₄)	=	3 RbCl + 4 Ti ₂ O ₃				-1561
8 V + 3 Li(ClO ₄)	=	3 LiCl + 4 V ₂ O ₃				-1560
8 Sc + 3 Cs(ClO ₄)	=	3 CsCl + 4 Sc ₂ O ₃				-1554
4 Ca + Cs(ClO ₄)	=	CsCl + 4 CaO				-1546
8 B + 3 Cs(ClO ₄)	=	3 CsCl + 4 B ₂ O ₃				-1540
3 Zr + 2 K(ClO ₃)	=	2 KCl + 3 ZrO ₂				-1534
2 B + Ag(ClO ₃)	=	AgCl + B ₂ O ₃				-1533
17 Ti + 6 Ag(ClO ₄)	=	3 Ag ₂ Cl + 8 Ti ₂ O ₃	+ TiCl ₃			-1528
3 Si + 2 Rb(ClO ₃)	=	2 RbCl + 3 SiO ₂				-1502
4 Zr + Ba(ClO ₄) ₂	=	BaCl ₂ + 4 ZrO ₂				-1491
34 Mg + 4 Cu(ClO ₄) ₂	=	2 Cu ₂ O + 30 MgO	+ 4 MgCl ₂			-1478
12 Mg + 4 Li(ClO ₃)	=	2 Li ₂ O + 10 MgO	+ 2 MgCl ₂			-1470

Table 23 (cont.)

Reaction					Enthalpy, cal/g
16 Cr + 3 Mg(ClO ₄) ₂	=	3 MgCl ₂ + 8 Cr ₂ O ₃			-1462
2 V + Na(ClO ₃)	=	NaCl + V ₂ O ₃			-1451
16 Nb + 5 Mg(ClO ₄) ₂	=	5 MgCl ₂ + 8 Nb ₂ O ₅			-1448
12 Na + 2 Li(ClO ₃)	=	Li ₂ O + 5 Na ₂ O + 2 NaCl			-1446
18 Na + 2 Mg(ClO ₄) ₂	=	2 MgO + 7 Na ₂ O ₂ + 4 NaCl			-1445
34 Na + 2 Cu(ClO ₄) ₂	=	Cu ₂ O + 15 Na ₂ O + 4 NaCl			-1443
4 C + Mg(ClO ₄) ₂	=	MgCl ₂ + 4 CO ₂			-1433
8 Cr + 3 Li(ClO ₄)	=	3 LiCl + 4 Cr ₂ O ₃			-1432
3 Si + 2 Ag(ClO ₃)	=	2 AgCl + 3 SiO ₂			-1425
2 Si + Cs(ClO ₄)	=	CsCl + 2 SiO ₂			-1422
2 Ti + Rb(ClO ₃)	=	RbCl + Ti ₂ O ₃			-1420
8 Nb + 5 Li(ClO ₄)	=	5 LiCl + 4 Nb ₂ O ₅			-1419
8 V + 3 K(ClO ₄)	=	3 KCl + 4 V ₂ O ₃			-1411
16 Zr + 8 Rb(ClO ₄)	=	8 RbCl + 16 ZrO ₂			-1403
16 Al + 3 Ba(ClO ₃) ₂	=	3 BaO + 5 Al ₂ O ₃ + 6 AlCl			-1398
26 Mg + 4 Cu(ClO ₃) ₂	=	2 Cu ₂ O + 22 MgO + 4 MgCl ₂			-1382
26 Na + 2 Cu(ClO ₃) ₂	=	Cu ₂ O + 11 Na ₂ O + 4 NaCl			-1381
13 Zr + 6 Ag(ClO ₄)	=	3 Ag ₂ Cl + 12 ZrO ₂ + ZrCl ₃			-1379
2 C + Li(ClO ₄)	=	LiCl + 2 CO ₂			-1376
13 Ti + 6 Ag(ClO ₃)	=	3 Ag ₂ Cl + 6 Ti ₂ O ₃ + TiCl ₃			-1369
8 Ti + 3 Cs(ClO ₄)	=	3 CsCl + 4 Ti ₂ O ₃			-1357
2 Cr + Na(ClO ₃)	=	NaCl + Cr ₂ O ₃			-1340
2 V + K(ClO ₃)	=	KCl + V ₂ O ₃			-1339
6 Nb + 5 Na(ClO ₃)	=	5 NaCl + 3 Nb ₂ O ₅			-1332
16 Na + 2 Na(ClO ₄)	=	Na ₂ O + 7 Na ₂ O ₂ + 2 NaCl			-1317
18 Na + 4 Li(ClO ₄)	=	2 Li ₂ O + 7 Na ₂ O ₂ + 4 NaCl			-1306
16 Mg + 4 Na(ClO ₄)	=	2 Na ₂ O + 14 MgO + 2 MgCl ₂			-1301
8 Cr + 3 K(ClO ₄)	=	3 KCl + 4 Cr ₂ O ₃			-1299
3 Zr + 2 Rb(ClO ₃)	=	2 RbCl + 3 ZrO ₂			-1296
8 Nb + 5 K(ClO ₄)	=	5 KCl + 4 Nb ₂ O ₅			-1292

Table 23 (cont.)

Reaction					Enthalpy, cal/g
16 V + 3 Ba(ClO ₄) ₂	=	3 BaCl ₂ + 8 V ₂ O ₃			-1292
16 La + 3 Mg(ClO ₄) ₂	=	3 MgCl ₂ + 8 La ₂ O ₃			-1280
12 Ca + 4 Li(ClO ₃)	=	2 Li ₂ O + 10 CaO + 2 CaCl ₂			-1274
8 La + 3 Li(ClO ₄)	=	3 LiCl + 4 La ₂ O ₃			-1262
34 Ca + 4 Cu(ClO ₄) ₂	=	2 Cu ₂ O + 30 CaO + 4 CaCl ₂			-1260
10 Zr + 6 Ag(ClO ₃)	=	3 Ag ₂ Cl + 9 ZrO ₂ + ZrCl ₃			-1257
2 Zr + Cs(ClO ₄)	=	CsCl + 2 ZrO ₂			-1244
2 Cr + K(ClO ₃)	=	KCl + Cr ₂ O ₃			-1237
8 Sr + Mg(ClO ₄) ₂	=	MgCl ₂ + 8 SrO			-1235
8 Na + K(ClO ₄)	=	KCl + 4 Na ₂ O			-1234
3 C + 2 Na(ClO ₃)	=	2 NaCl + 3 CO ₂			-1233
6 Nb + 5 K(ClO ₃)	=	5 KCl + 3 Nb ₂ O ₅			-1233
16 Pr + 3 Mg(ClO ₄) ₂	=	3 MgCl ₂ + 8 Pr ₂ O ₃			-1229
12 Be + 2 Ba(ClO ₃) ₂	=	2 BaO + 5 BeO + 2 BeCl ₂			-1225
2 La + Na(ClO ₃)	=	NaCl + La ₂ O ₃			-1224
6 Mn + Mg(ClO ₄) ₂	=	MgCl ₂ + 2 Mn ₃ O ₄			-1221
4 Sr + Li(ClO ₄)	=	LiCl + 4 SrO			-1216
26 Ca + 4 Cu(ClO ₃) ₂	=	2 Cu ₂ O + 22 CaO + 4 CaCl ₂			-1214
8 Pr + 3 Li(ClO ₄)	=	3 LiCl + 4 Pr ₂ O ₃			-1211
16 Ce + 3 Mg(ClO ₄) ₂	=	3 MgCl ₂ + 8 Ce ₂ O ₃			-1208
8 V + 3 Rb(ClO ₄)	=	3 RbCl + 4 V ₂ O ₃			-1202
16 Nd + 3 Mg(ClO ₄) ₂	=	3 MgCl ₂ + 8 Nd ₂ O ₃			-1200
8 La + 3 K(ClO ₄)	=	3 KCl + 4 La ₂ O ₃			-1200
16 Cr + 3 Ba(ClO ₄) ₂	=	3 BaCl ₂ + 8 Cr ₂ O ₃			-1192
8 Ce + 3 Li(ClO ₄)	=	3 LiCl + 4 Ce ₂ O ₃			-1190
3 Mn + Li(ClO ₄)	=	LiCl + Mn ₃ O ₄			-1190
16 Nb + 5 Ba(ClO ₄) ₂	=	5 BaCl ₂ + 8 Nb ₂ O ₅			-1189
6 Na + K(ClO ₃)	=	KCl + 3 Na ₂ O			-1185
35 V + 12 Ag(ClO ₄)	=	6 Ag ₂ Cl + 16 V ₂ O ₃ + 3 VCl ₂			-1183
8 Nd + 3 Li(ClO ₄)	=	3 LiCl + 4 Nd ₂ O ₃			-1182
3 Sr + Na(ClO ₃)	=	NaCl + 3 SrO			-1179

Table 23 (cont.)

Reaction					Enthalpy, cal/g
16 Ga + 3 $Mg(ClO_4)_2$	=	3 $MgCl_2$	+ 8 Ga_2O_3		-1177
2 Pr + $Na(ClO_3)$	=	NaCl	+ Pr_2O_3		-1176
4 Hf + $Mg(ClO_4)_2$	=	$MgCl_2$	+ 4 HfO_2		-1172
2 La + $K(ClO_3)$	=	KCl	+ La_2O_3		-1170
2 C + $K(ClO_4)$	=	KCl	+ 2 CO_2		-1160
2 Ce + $Na(ClO_3)$	=	NaCl	+ Ce_2O_3		-1157
4 Sr + $K(ClO_4)$	=	KCl	+ 4 SrO		-1155
2 Hf + $Li(ClO_4)$	=	LiCl	+ 2 HfO_2		-1153
8 Pr + 3 $K(ClO_4)$	=	3 KCl	+ 4 Pr_2O_3		-1153
2 Nd + $Na(ClO_3)$	=	NaCl	+ Nd_2O_3		-1150
8 Ga + 3 $Li(ClO_4)$	=	3 LiCl	+ 4 Ga_2O_3		-1147
16 La + 3 $Ba(ClO_4)_2$	=	3 $BaCl_2$	+ 8 La_2O_3		-1145
8 Ce + 3 $K(ClO_4)$	=	3 KCl	+ 4 Ce_2O_3		-1133
3 Nd + 3 $K(ClO_4)$	=	3 KCl	+ 4 Nd_2O_3		-1127
16 Ca + 4 $Na(ClO_4)$	=	2 Na_2O	+ 7 CaO + 2 $CaCl_2$		-1125
2 Pr + $K(ClO_3)$	=	KCl	+ Pr_2O_3		-1125
3 Sr + $K(ClO_3)$	=	KCl	+ 3 SrO		-1125
3 Hf + 2 $Na(ClO_3)$	=	2 NaCl	+ 3 HfO_2		-1121
16 B + 3 $Ba(ClO_3)_2$	=	3 BaO	+ 5 B_2O_3 + 6 RCl		-1116
12 Na + $Ba(ClO_3)_2$	=	RaO	+ 5 Na_2O + 2 NaCl		-1112
8 Cr + 3 $Rb(ClO_4)$	=	3 RbCl	+ 4 Cr_2O_3		-1108
8 Nb + 5 $Rb(ClO_4)$	=	5 RbCl	+ 4 Nb_2O_5		-1107

Table 24
CHLORATES AND PERCHLORATES
IN DESCENDING ORDER OF HEAT OF REACTION

<u>Volumetric Heat of Reaction</u>	<u>Gravimetric Heat of Reaction</u>
$Mg(ClO_4)_2$	$Mg(ClO_4)_2$
$LiClO_4$	$LiClO_4$
$AgClO_3$	$NaClO_3$
$NaClO_3$	$KClO_4$
$KClO_4$	$KClO_3$
$Ba(ClO_4)_2$	$Ba(ClO_4)_2$
$RbClO_4$	$RbClO_4$
$KClO_3$	$AgClO_4$
$RbClO_3$	$RbClO_3$
$AgClO_4$	$AgClO_3$
$CsClO_4$	$CsClO_4$
	$Cu(ClO_4)_2$
	$Cu(ClO_3)_2$
	$LiClO_3$
	$Ba(ClO_3)_2$

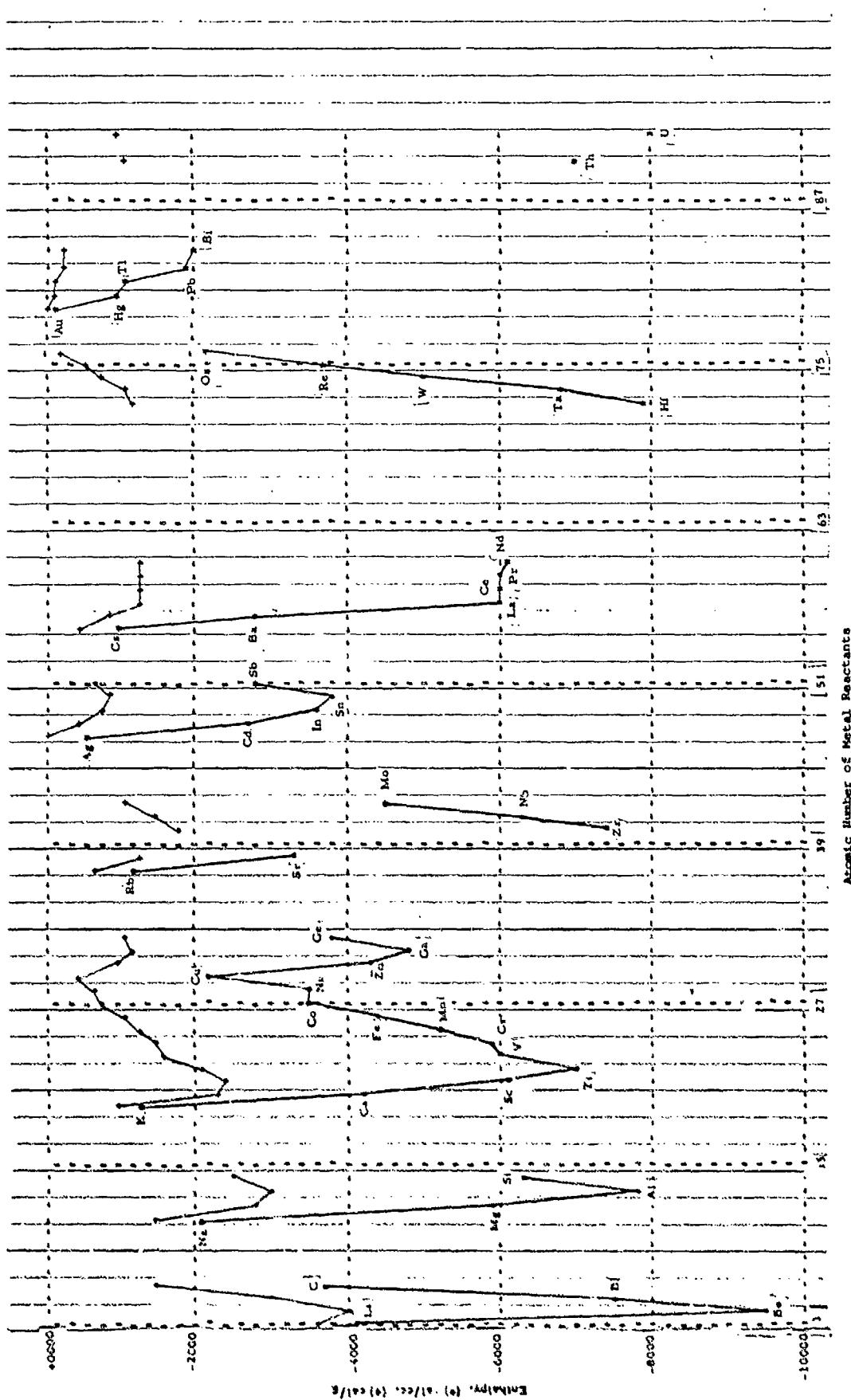


FIGURE 16
GRAVIMETRIC AND VOLUMETRIC EMISSALIES OF REACTIONS OF METALS WITH $Mg(ClO_4)_2$

The plot in Figure 19 presents the data in a different manner. The volumetric enthalpies for the reactions of all the chlorates and perchlorates with beryllium are plotted. This allows one to choose an oxidizer for a particular metal reactant, beryllium in this case. Lithium perchlorate is the best oxidizer, and the alkali metal perchlorates follow a decreasing trend in enthalpy in progressing to cesium perchlorate. The gravimetric enthalpies, shown in Figure 20, exhibit similar trends.

The volumetric and gravimetric enthalpies of all 801 chlorate and perchlorate reactions are summarized in Tables 25 and 26, respectively. The same trends noted previously are apparent here.

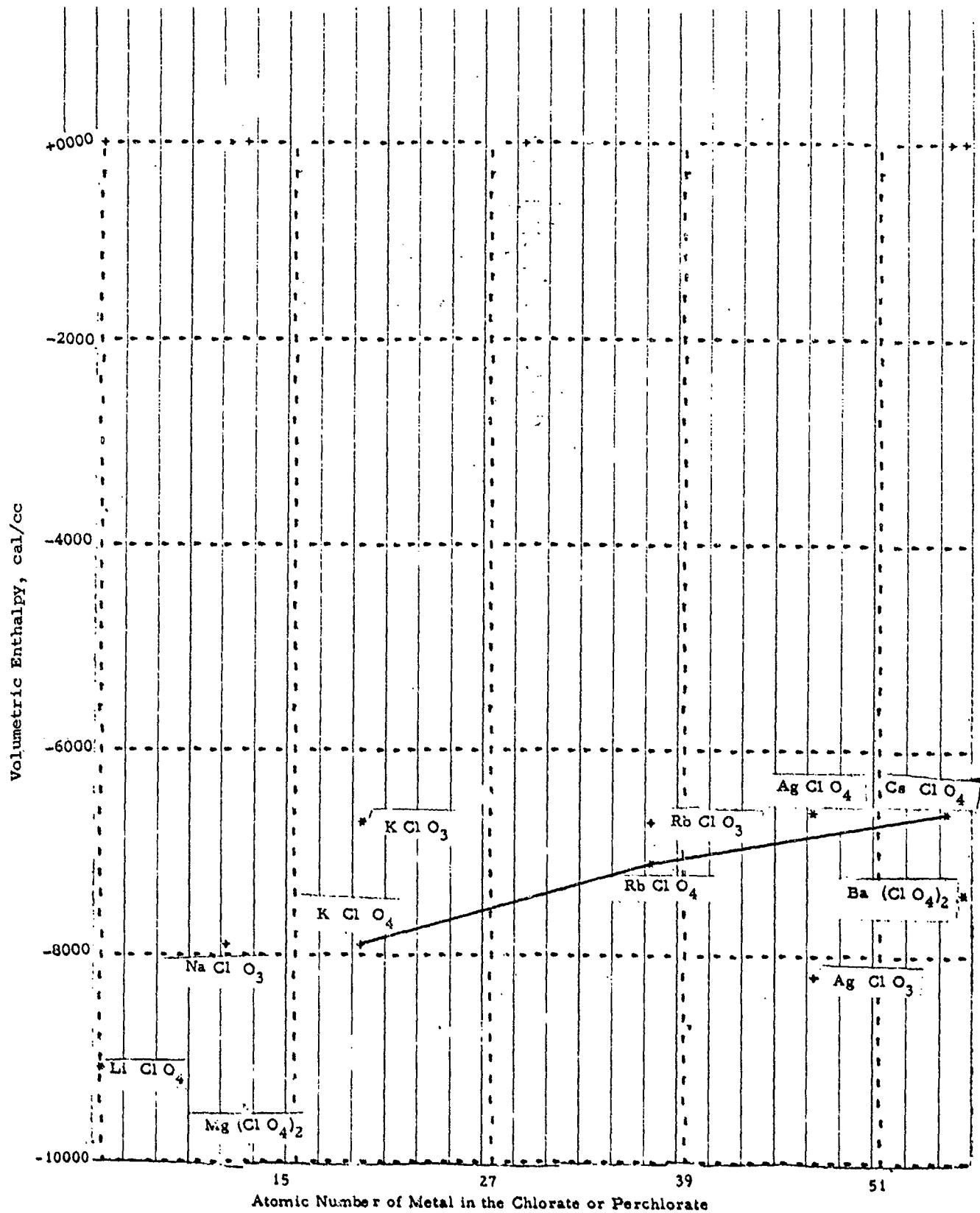


Figure 19

VOLUMETRIC ENTHALPIES OF REACTIONS
OF CHLORATES AND PERCHLORATES WITH Be

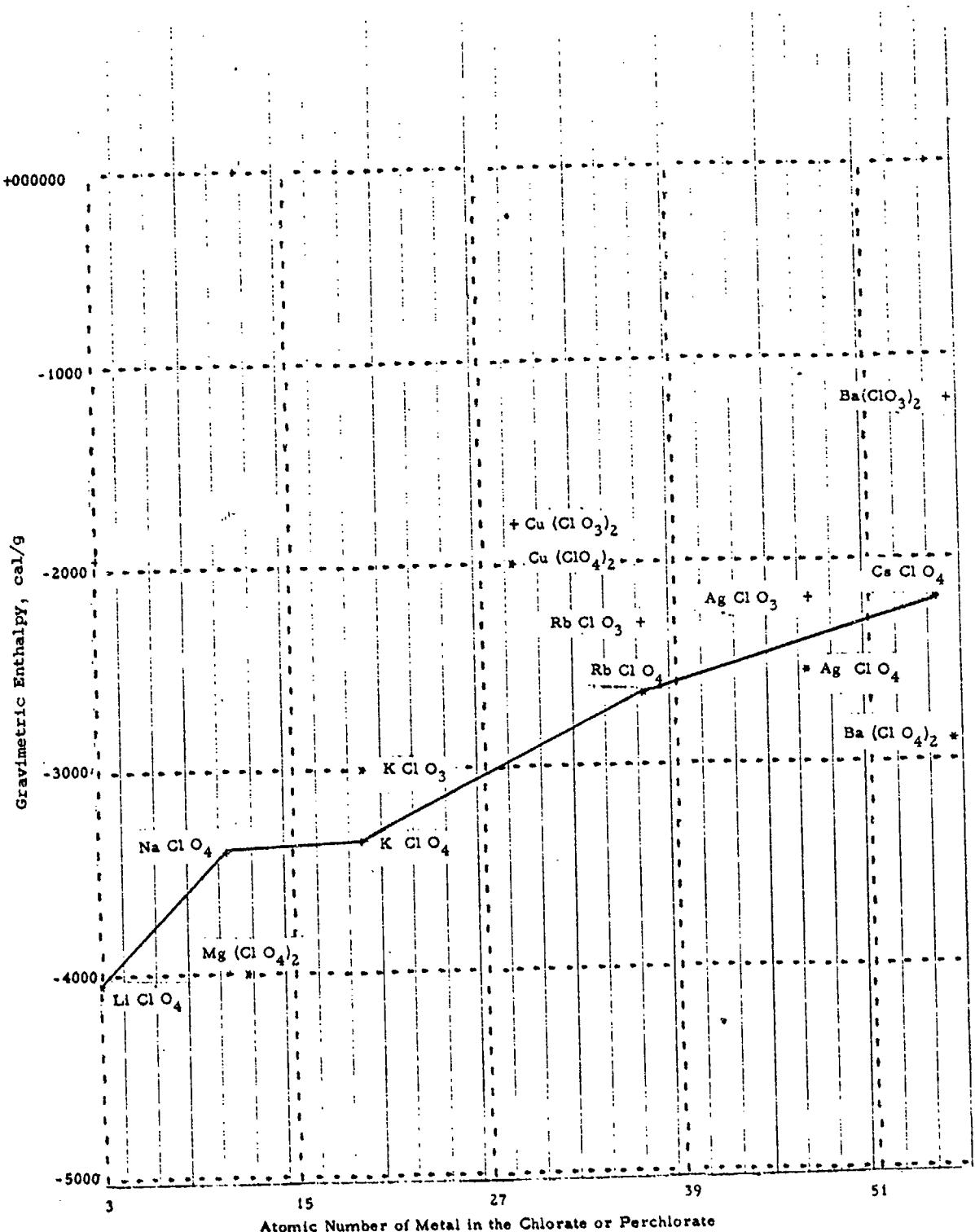


Figure 20

GRAVIMETRIC ENTHALPIES OF REACTIONS
OF CHLORATES AND PERCHLORATES WITH Be

Table 25

VOLUMETRIC ENTHALPIES OF REACTIONS OF METALS WITH CHLORATES AND PERCHLORATES
(In descending order from top to bottom and left to right)

	$Mg(ClO_4)_2$	$LiClO_4$	$AgClO_3$	$NaClO_3$	$KClO_4$	$Ba(ClO_4)_2$	$RbClO_4$	$RbClO_3$	$AgClO_4$	$CsClO_4$
BE	-9459	-9088	-8103	-7853	-7850	-7302	-7002	-6653	-6616	-6578
U	-7989	-7670	-6989	-6750	-6720	-6292	-6040	-5779	-5747	-5847
HF	-7874	-7562	-6905	-6675	-6643	-6228	-5981	-5728	-5696	-5688
AL	-7742	-7431	-6733	-6562	-6527	-6119	-5875	-5629	-5597	-5553
B	-7423	-7038	-6242	-6061	-6004	-5562	-5289	-5046	-5010	-4941
ZR	-7318	-7021	-6448	-6234	-6192	-5817	-5585	-5363	-5332	-5333
TH	-6998	-6750	-6289	-6102	-6063	-5743	-5542	-5348	-5320	-5320
TI	-6951	-6658	-6100	-5926	-5876	-5523	-5299	-5095	-5065	-5041
TA	-6730	-6388	-5767	-5596	-5530	-5155	-4912	-4713	-4679	-4577
SI	-6289	-5983	-5477	-5316	-5247	-4291	-4701	-4529	-4498	-4454
NB	-6249	-5914	-5380	-5205	-5128	-4786	-4554	-4381	-4348	-4307
SC	-6099	-5877	-5568	-5379	-5329	-5071	-4896	-4749	-4724	-4745
ND	-6036	-5832	-5583	-5374	-5327	-5086	-4922	-4783	-4759	-4802
LA	-5981	-5786	-5553	-5350	-5305	-5074	-4916	-4782	-4759	-4803
V	-5980	-5676	-5233	-5054	-4978	-4670	-4455	-4300	-4269	-4263
PR	-5946	-5747	-5514	-5307	-5259	-5026	-4866	-4732	-4709	-4754
CE	-5941	-5737	-5514	-5290	-5242	-5005	-4843	-4708	-4685	-4739
MG	-5886	-5683	-5411	-5243	-5193	-4960	-4799	-4666	-4643	-4661
CR	-5885	-5565	-5129	-4933	-4851	-4539	-4319	-4167	-4136	-4130
MN	-5132	-4839	-4626	-4395	-4310	-4074	-3892	-3786	-3758	-3804
W	-4928	-4587	-4276	-4080	-3965	-3701	-3489	-3392	-3359	-3353
GA	-4708	-4454	-4230	-4075	-3984	-3773	-3600	-3514	-3488	-3478
MO	-4449	-4115	-3896	-3697	-3569	-3339	-3138	-3072	-3043	-3048
FE	-4337	-4038	-3852	-3669	-3551	-3341	-3155	-3090	-3061	-3065
ZN	-4262	-4029	-3894	-3731	-3637	-3460	-3303	-3240	-3215	-3237
CA	-4195	-4068	-4031	-3891	-3839	-3725	-3628	-3576	-3560	-3606
LI	-4068	-3796	-3804	-3642	-3587	-3483	-3389	-3347	-3332	-3396
SN	-3759	-3521	-3441	-3283	-3175	-3021	-2870	-2832	-2807	-2818
GE	-3753	-3496	-3416	-3247	-3131	-2971	-2811	-2775	-2749	-2763
RE	-3654	-3229	-3264	-3058	-2910	-2736	-2553	-2531	-2500	-2526
C	-3628	-3295	-3236	-3025	-2873	-2699	-2513	-2494	-2463	-2491
IN	-3570	-3360	-3310	-3166	-3066	-2933	-2797	-2766	-2743	-2756
NI	-3462	-3206	-3172	-3001	-2878	-2734	-2580	-2559	-2533	-2555
CO	-3446	-3164	-3135	-2948	-2815	-2676	-2524	-2507	-2481	-2508
SR	-3211	-3112	-3159	-3029	-2976	-2909	-2837	-2819	-2806	-2862
SB	-2777	-2561	-2625	-2468	-2347	-2253	-2126	-2135	-2112	-2144
BA	-2701	-2615	-2701	-2571	-2520	-2473	-2412	-2408	-2397	-2462
CD	-2630	-2451	-2521	-2385	-2280	-2202	-2093	-2103	-2083	-2123
CU	-2182	-1935	-2105	-1930	-1784	-1722	-1597	-1644	-1619	-1670
OS	-2178	-1902	-2104	-1902	-1732	-1665	-1524	-1582	-1555	-1614
NA	-2078	-1823	-1957	-1698	-1627	-1663	-1565	-1583	-1574	-1690
BI	-1906	-1742	-1893	-1761	-1649	-1609	-1516	-1556	-1537	-1579
PB	-1862	-1720	-1855	-1739	-1641	-1606	-1524	-1559	-1543	-1580
K	-1299	-1080	-1245	-1068	-971	-1040	-931	-966	-957	-1072
RB	-1105	-912	-1065	-910	-787	-878	-727	-799	-764	-920
TL	-1092	-884	-1033	-945	-871	-872	-825	-872	-861	-906
HG	-911	-759	-1023	-889	-764	-771	-697	-778	-761	-821
CS	-911	-752	-882	-759	-655	-735	-606	-678	-651	-773
AU	-107	629	-83	624	837	459	803	724	773	168
AG	-523	-190	-460	-329	-217	-248	-193	-284	-270	-332
										-189

Table 26

GRAVIMETRIC ENTHALPIES OF REACTIONS OF METALS WITH CHLORATES AND PERCHLORATES
(In descending order from top to bottom and left to right)

Mg(ClO ₄) ₂	NaClO ₃	KClO ₃	RbClO ₄	RbClO ₃	CsClO ₄	Cu(ClO ₃) ₂	LiClO ₃	Ba(ClO ₃) ₂
LiClO ₄	KClO ₄	Ba(ClO ₄) ₂	AgClO ₄	AgClO ₃	Cu(ClO ₄) ₂	LiClO ₃	Ba(ClO ₃) ₂	
-3998 -4037 -3374 -3348 -2999 -2991 -2638 -2533 -2281 -2167 -2174 -1978 -1771 -1935 -1729 -1225								
LI -3576 -3463 -2960 -2977 -2666 -2575 -2364 -2351 -2071 -2054 -1977 -1923 -1915 -1710 -1110 -2217								
AL -2933 -2934 -2564 -2470 -2321 -2242 -2067 -1999 -1831 -1747 -1747 -1747 -1734 -1697 -1677 -2015 -1798								
BR -2912 -2912 -2445 -2408 -2168 -2076 -1878 -1600 -1632 -1533 -1540 -2083 -1692 -1758 -1793 -1116								
MG -2784 -2782 -2471 -2462 -2261 -2191 -2035 -2000 -1821 -1773 -1744 -1748 -1792 -1470 -1501 -1632								
SI -2486 -2473 -2157 -2112 -1935 -1859 -1699 -1644 -1502 -1425 -1422 -1707 -7640 -650 -470 -403								
SC -2394 -2383 -2156 -2122 -1984 -1924 -1794 -1770 -1622 -1594 -1554 -948 -909 -650 -787 -476								
CA -2257 -2245 -2064 -2074 -1920 -1869 -1757 -1754 -1607 -1594 -1546 -1260 -1214 -1274 -1125 -987								
TI -2071 -2053 -1876 -1879 -1729 -1675 -1561 -1420 -1349 -1357 -965 -817 -835 -736 -634								
ZR -1777 -1758 -1647 -1610 -1534 -1491 -1403 -1379 -1296 -1257 -1244 -905 -892 -870 -781 -672								
V -1588 -1560 -1451 -1411 -1359 -1292 -1202 -1183 -1104 -1067 -1049 -920 -773 -789 -677 -574								
CR -1462 -1432 -1340 -1299 -1237 -1192 -1104 -1098 -1021 -992 -968 -752 -697 -706 -600 -511								
NB -1448 -1419 -1339 -1292 -1233 -1189 -1107 -1107 -1023 -999 -971 -821 -729 -262 -167 -171								
NA -1445 -1306 -1102 -1234 -1185 -1029 -1074 -981 -1001 -908 -954 -1443 -1391 -1446 -1317 -1112								
C -1433 -1376 -1233 -1140 -1079 -1012 -895 -910 -803 -791 -732 -283 -197 -125 -3 -34								
LA -1280 -1262 -1224 -1200 -1170 -1145 -1097 -1102 -1045 -1039 -1012 -931 -534 -534 -453 -444								
SP -1235 -1216 -1179 -1155 -1125 -1100 -1052 -1072 -1001 -1013 -967 -722 -717 -733 -641 -605								
PR -1229 -1211 -1174 -1153 -1125 -1101 -1055 -1060 -1006 -1001 -973 -511 -510 -510 -434 -426								
MN -1221 -1190 -1067 -1028 -997 -965 -906 -917 -884 -850 -813 -432 -7605 -612 -514 -468								
CE -1208 -1190 -1157 -1133 -1106 -1082 -1036 -1036 -1044 -988 -986 -946 -808 -510 -510 -430 -424								
ND -1200 -1182 -1150 -1197 -1101 -1077 -1032 -1037 -986 -990 -954 -948 -500 -504 -422 -416								
GA -1177 -1147 -1100 -1061 -1025 -984 -924 -932 -866 -854 -821 -736 -703 -686 -703 -538								
HF -1172 -1153 -1121 -1096 -1070 -1046 -1000 -993 -953 -932 -920 -889 -563 -560 -510 -469								
FE -1030 -992 -958 -913 -884 -846 -781 -783 -752 -729 -686 -435 -412 -403 -317 -301								
NO -1030 -989 -952 -904 -771 -833 -765 -707 -692 -713 -611 -451 -393 -370 -300 -260								
IH -1025 -1008 -991 -970 -953 -933 -898 -895 -861 -850 -838 -734 -336 -333 -266 -276								
GE -1074 -986 -941 -906 -877 -834 -774 -772 -745 -723 -678 -17 -22 -62 -82 -72								
TA -1012 -988 -964 -935 -914 -887 -840 -850 -800 -794 -765 -467 -430 -417 -375 -328								
K -997 -954 -879 -802 -801 -688 -799 -650 -665 -606 -924 -909 -635 -836 -765 -765								
U -929 -912 -900 -879 -866 -848 -815 -806 -787 -765 -761 -365 -361 -357 -300 -301								
ZN -908 -881 -844 -832 -816 -789 -743 -752 -708 -703 -672 -503 -482 -479 -397 -371								
BA -816 -800 -795 -776 -768 -752 -725 -740 -704 -723 -682 -780 -748 -749 -722 -664								
SN -813 -792 -774 -750 -728 -700 -655 -675 -626 -630 -590 -417 -393 -373 -310 -290								
W -768 -737 -734 -709 -690 -663 -620 -641 -595 -600 -460 -720 -249 -257 -218 -197								
CO -750 -711 -711 -612 -608 -582 -541 -559 -522 -492 -487 -744 -364 -352 -260 -262								
IN -725 -698 -669 -668 -662 -638 -602 -621 -581 -587 -550 -406 -550 -438 -517 -449								
NI -692 -659 -644 -627 -622 -495 -534 -579 -534 -493 -499 -787 -366 -754 -272 -263								
SR -620 -587 -589 -541 -560 -535 -497 -524 -482 -495 -446 -210 -193 -181 -117 -132								
RB -620 -522 -506 -443 -448 -432 -374 -472 -570 -468 -337 -465 -443 -417 -615 -615								
RE -558 -525 -541 -504 -507 -482 -447 -476 -436 -451 -404 -480 -155 -127 -65 -82								
CS -452 -376 -376 -334 -335 -350 -280 -363 -281 -745 -248 -308 -312 -312 -275 -283								
CU -411 -388 -414 -379 -389 -366 -335 -370 -334 -355 -304 -271 -247 -245 -204 -201								
CD -445 -422 -439 -414 -420 -404 -382 -400 -378 -397 -356 -304 -259 -248 -193 -201								
SI -264 -286 -245 -274 -264 -264 -246 -270 -256 -232 -187 -155 -135 -131 -112								
OS -265 -237 -269 -210 -254 -237 -217 -249 -244 -246 -201 -127 -111 -91 -50 -63								
PB -248 -215 -237 -217 -223 -216 -205 -224 -210 -223 -197 -130 -134 -124 -95 -108								
TL -115 -92 -107 -94 -101 -96 -91 -102 -96 -106 -39 -110 -109 -104 -87 -94								
HG -101 -86 -109 -92 -104 -93 -86 -100 -96 -113 -93 -67 -41 -53 -26 -43								
AU -12 64 69 95 89 53 93 21 49 90 18 22 38 72 46								
AG -80 -25 -43 -99 -42 -34 -24 -48 -38 -66 -26 -55 -54 -43 -13 -20								

I. Chloride Reactions

The computer was used to examine 10,545 reactions involving 102 chlorides, and 3061 of these reactions were printed. As a class, the chloride reactions are not especially energetic. The highest enthalpy recorded was only -3336 cal/cc, for the reaction of cerium with rhenium pentachloride. The chloride reactions are less energetic than the fluoride, oxide, chlorate, perchlorate, nitrate, nitrite, chromate, and silicide reactions.

The computer output for some of the more energetic reactions is shown in Table 27. Molybdenum and tungsten chlorides behave as some of the better oxidizers in the chloride systems. The reactions of molybdenum pentachloride, tungsten pentachloride, and tungsten hexachloride with various metals are included in the table.

The most energetic reactions are presented in Tables 28 and 29. On a volumetric basis the most effective metal reducing agents are the rare earths (cerium, lanthanum, praseodymium, neodymium, thorium, and uranium), the rare earth predecessors (yttrium and scandium), the alkali metals (lithium), the alkaline earth metals (beryllium, magnesium, and calcium), and hafnium and zirconium. Beryllium is not the most energetic reducing agent in the chloride systems, because the heat of formation of beryllium chloride is comparatively low. The heats of formation of the alkali earth chlorides increase monotonically, while the heats of formation of the alkalis with oxides exhibit a maximum at calcium. The chlorides increase from -122 to -205 kcal/mole from beryllium to barium; and the oxides increase from -146 to -151 kcal/mole from beryllium to calcium and then decrease to -133 kcal/mole at barium. The behavior of beryllium in the chloride systems may be considered normal and its behavior in the oxide systems anomalous. Its effectiveness in the oxide systems compared with the other alkaline earth metals is thus due to the relatively high heat of formation of the oxide. In addition, because of its low atomic volume and weight, it is still an effective reducing agent in the chloride systems, although it is exceeded in efficacy by several other metals including calcium and magnesium. The most effective oxidizers on a volumetric basis are rhenium pentachloride, hexachloroethane, tungsten tetrachloride, tungsten pentachloride, and tungsten hexachloride.

On a gravimetric basis the alkali metals (lithium, sodium, and potassium) are the most effective reducing agents, followed by the alkaline earth metals (calcium, magnesium, and beryllium), the rare earth predecessors (scandium and yttrium), and titanium. The alkali metals are relatively energetic on a gravimetric basis, and are much less energetic on a volumetric basis because of their extremely low densities. The most effective practical oxidizers on a gravimetric basis are the chlorides of carbon

Table 27
DATA ON VARIOUS REACTIONS OF METALS WITH CHLORIDES

	5 Ba	+	2 MoCl ₅	=	2 Mo	+	5 BaCl ₂	
Heat of formation			-90.80				-205.56	
Molecular weight	137.36		273.24		95.95		208.27	
Density	3.50		2.93		10.20			1.90
Melting point, °C	704.00		194.00		2610.00		962.00	
Boiling point, °C	1638.00		268.00		4800.00		1189.00	
Heat of reaction, kcal	-846.20							
Reactants' density	3.22							
Gravimetric enthalpy, cal/g	-686.14							
Volumetric enthalpy, cal/cc	-2210.16							
	5 Be	+	2 MoCl ₅	=	2 Mo	+	5 BeCl ₂	
Heat of formation			-90.80				-122.30	
Molecular weight	9.01		273.24		95.95		79.93	
Density	1.85		2.93		10.20			1.90
Melting point, °C	1283.00		194.00		2610.00		405.00	
Boiling point, °C	2970.00		268.00		4800.00		547.00	
Heat of reaction, kcal	-429.90							
Reactants' density	2.80							
Gravimetric enthalpy, cal/g	-726.74							
Volumetric enthalpy, cal/cc	-2037.45							
	5 Bi	+	4 MoCl ₅	=	4 Mo	+	5 BiCl ₄	
Heat of formation			-90.80				-120.00	
Molecular weight	208.99		273.24		95.95		350.83	
Density	9.80		2.93		10.20			
Melting point, °C	271.00		194.00		2610.00		225.00	
Boiling point, °C	1420.00		263.00		4800.00			
Heat of reaction, kcal	-236.80							
Reactants' density	4.45							
Gravimetric enthalpy, cal/g	-110.76							
Volumetric enthalpy, cal/cc	.493 .43							

Table 27 (cont..)

	5 Mg	+	2 MoCl ₅	=	2 Mo	+	5 MgCl ₂
Heat of formation	-90.80			95.95			-153.40
Molecular weight	24.32		273.24		10.20		95.23
Density	1.74T		2.93		2610.00		2.32
Melting point, °C	650.00P		194.00		4800.00		714.00
Boiling point, °C	2120.00		268.00				1418.00
Heat of reaction, kcal	-585.40						
Reactants' density	2.66						
Gravimetric enthalpy, cal/g	-876.24						
Volumetric enthalpy, cal/cc	-2282.04						
	5 Mn	+	2 MoCl ₅	=	2 Mo	+	5 MnCl ₂
Heat of formation	-90.80			95.95			-115.30
Molecular weight	54.94		273.24		10.20		125.84
Density	7.20		2.93		2610.00		2.98
Melting point, °C	1244.00		194.00		4800.00		650.00
Boiling point, °C	2087.00		268.00				1190.00
Heat of reaction, kcal	-394.90						
Reactants' density	3.65						
Gravimetric enthalpy, cal/g	-480.39						
Volumetric enthalpy, cal/cc	-1756.73						
	5 Na	+	MoCl ₅	=	Mo	+	5 NaCl
Heat of formation	-90.80			95.95			-98.23
Molecular weight	22.99		273.24		10.20		53.45
Density	.97		2.93		2610.00		2.16
Melting point, °C	98.00		194.00		4800.00		808.00
Boiling point, °C	889.00		268.00				1465.00
Heat of reaction, kcal	-400.36						
Reactants' density	1.83						
Gravimetric enthalpy, cal/g	-1031.34						
Volumetric enthalpy, cal/cc	-1890.01						

Table 27 (cont.)

	5 Ba	+	2 WCl ₅	=	2 W	+	5 BaCl ₂
Heat of formation			-84.00		183.86		-205.56
Molecular weight	137.36		361.21		19.30		208.27
Density	3.50		3.88				
Melting point, °C	704.00		248.00		380.00		962.00
Boiling point, °C	1638.00		276.00		5900.00		1189.00
Heat of reaction, kcal	-859.80						
Reactants' density	3.68						
Gravimetric enthalpy, cal/g	-610.12						
Volumetric enthalpy, cal/cc	-2246.91						
	5 Be	+	2 WCl ₅	=	2 W	+	5 BeCl ₂
Heat of formation			-84.00		183.86		-122.30
Molecular weight	9.01		361.21		19.30		79.93
Density	1.85		3.88				1.90
Melting point, °C	1283.00		248.00		380.00		405.00
Boiling point, °C	2970.00		276.00		5900.00		547.00
Heat of reaction, kcal	-443.50						
Reactants' density	3.64						
Gravimetric enthalpy, cal/g	-577.86						
Volumetric enthalpy, cal/cc	-2103.99						
	5 Bi	+	4 WCl ₅	=	4 W	+	5 BiCl ₄
Heat of formation			-84.00		183.86		-120.00
Molecular weight	208.99		361.21		19.30		350.83
Density	9.80		3.88				
Melting point, °C	271.00		248.00		380.00		225.00
Boiling point, °C	1420.00		276.00		5900.00		
Heat of reaction, kcal	-264.00						
Reactants' density	5.19						
Gravimetric enthalpy, cal/g	-106.03						
Volumetric enthalpy, cal/cc	-550.50						

Table 27 (cont.)

	5 Mg	+ 2 WCl ₃	= 2 W	+ 5 MgCl ₂	
Heat of formation		-84.00		-153.40	
Molecular weight	24.32	361.21	183.86	95.23	
Density	1.74	3.88	19.30	2.32	
Melting point, °C	650.00	248.00	380.00	714.00	
Boiling point, °C	1120.00	276.00	5900.00	1418.00	
Heat of reaction, kcal	-599.00				
Reactants' density	3.29				
Gravimetric enthalpy, cal/g	-709.70				
Volumetric enthalpy, cal/cc	-2336.96				
	5 Mn	+ 2 WCl ₅	= 2 W	+ 5 MnCl ₂	
Heat of formation		-84.00		-115.30	
Molecular weight	54.94	361.21	183.86	125.84	
Density	7.20	3.88	19.30	2.98T	
Melting point, °C	1244.00	248.00	380.00	650.00	
Boiling point, °C	2087.00	276.00	5900.00	1190.00	
Heat of reaction, kcal	-408.50				
Reactants' density	4.44				
Gravimetric enthalpy, cal/g	-409.68				
Volumetric enthalpy, cal/cc	-1818.92				
	5 Na	+ WCl ₅	= W	+ 5 NaCl	
Heat of formation		-84.00		-98.23	
Molecular weight	22.99	361.21	183.86	58.45	
Density	0.97	3.88	19.30	2.16	
Melting point, °C	98.00	248.00	380.00	808.00	
Boiling point, °C	889.00	276.00	5900.00	1465.00	
Heat of reaction, kcal	-407.16				
Reactants' density	2.25				
Gravimetric enthalpy, cal/g	-855.08				
Volumetric enthalpy, cal/cc	-1923.05				

Table 27 (cont.)

	2 La	+	WCl ₆	=	W	+	2 LaCl ₃
Heat of formation	-98.70		183.86		-263.60		
Molecular weight	396.66		19.30		245.29		
Density	3.52		380.00		3.84		
Melting point, °C	284.00		5900.00		870.00		
Boiling point, °C	336.50						
Heat of reaction, kcal	-428.50						
Reactants' density	4.27						
Gravimetric enthalpy, cal/g	-635.29						
Volumetric enthalpy, cal/cc	-2714.35						
	6 Li	+	WCl ₆	=	W	+	6 LiCl
Heat of formation	-98.70		183.86		-97.70		
Molecular weight	396.66		19.30		42.40		
Density	3.52		380.00		2.07T		
Melting point, °C	284.00F		5900.00		610.00		
Boiling point, °C	336.50						
Heat of reaction, kcal	-487.50						
Reactants' density	2.30						
Gravimetric enthalpy, cal/g	-1112.25						
Volumetric enthalpy, cal/cc	-2556.84						
	3 Mg	+	WCl ₆	=	W	+	3 MgCl ₂
Heat of formation	-98.70		163.86		-153.40		
Molecular weight	396.66		19.30		95.23		
Density	3.52		380.00		2.32		
Melting point, °C	284.00		5900.00		714.00		
Boiling point, °C	336.50				1418.00		
Heat of reaction, kcal	-361.50						
Reactants' density	3.04						
Gravimetric enthalpy, cal/g	-769.77						
Volumetric enthalpy, cal/cc	-2338.01						

Table 28

MOST ENERGETIC CHLORIDE REACTIONS WITH METALS,
IN TERMS OF VOLUMETRIC ENTHALPY

Reaction					Enthalpy, cal/cc
5 Ce	+	3 ReCl ₅	=	3 Re	+ 5 CeCl ₃ -3336
5 La	+	3 ReCl ₅	=	3 Re	+ 5 LaCl ₃ -3301
5 Pr	+	3 ReCl ₅	=	3 Re	+ 5 PrCl ₃ -3259
5 Nd	+	3 ReCl ₅	=	3 Re	+ 5 NdCl ₃ -3244
5 Y	+	3 ReCl ₅	=	3 Re	+ 5 YCl ₃ -3178
2 Ce	+	C ₂ Cl ₆	=	2 C	+ 2 CeCl ₃ -3047
2 La	+	C ₂ Cl ₆	=	2 C	+ 2 LaCl ₃ -3025
5 Li	+	ReCl ₅	=	Re	+ 5 LiCl -3006
5 U	+	3 ReCl ₅	=	3 Re	+ 5 UC ₃ -2986
2 Pr	+	C ₂ Cl ₆	=	2 C	+ 2 PrCl ₃ -2986
2 Nd	+	C ₂ Cl ₆	=	2 C	+ 2 NdCl ₃ -2970
5 Ca	+	2 ReCl ₅	=	2 Re	+ 5 CaCl ₂ -2916
5 Hf	+	3 ReCl ₅	=	3 Re	+ 5 HfCl ₃ -2899
2 Y	+	C ₂ Cl ₆	=	2 C	+ 2 YCl ₃ -2897
5 Mg	+	2 ReCl ₅	=	2 Re	+ 5 MgCl ₂ -2872
5 Sc	+	3 ReCl ₅	=	3 Re	+ 5 ScCl ₃ -2860
5 Th	+	4 ReCl ₅	=	4 Re	+ 5 ThCl ₄ -2859
5 Zr	+	3 ReCl ₅	=	3 Re	+ 5 ZrCl ₃ -2824
6 Li	+	C ₂ Cl ₆	=	2 C	+ 6 LiCl -2814
4 Ce	+	3 WCl ₄	=	3 W	+ 4 CeCl ₃ -2807
4 La	+	3 WCl ₄	=	3 W	+ 4 LaCl ₃ -2788
4 Pr	+	3 WCl ₄	=	3 W	+ 4 PrCl ₃ -2745
3 Ca	+	C ₂ Cl ₆	=	2 C	+ 3 CaCl ₂ -2735
5 Ce	+	3 WCl ₅	=	3 W	+ 5 CeCl ₃ -2731
2 Ce	+	WCl ₆	=	W	+ 2 CeCl ₃ -2730
5 Be	+	2 ReCl ₅	=	2 Re	+ 5 BeCl ₂ -2729
4 Nd	+	3 WCl ₄	=	3 W	+ 4 NdCl ₃ -2726
2 U	+	C ₂ Cl ₆	=	2 C	+ 2 UC ₃ -2725
5 La	+	3 WCl ₅	=	3 W	+ 5 LaCl ₃ -2715

Table 28 (cont.)

Reaction						Enthalpy, cal/cc	
2 La	+	WCl ₆	=	W	+	2 LaCl ₃	-2714
5 Sr	+	2 ReCl ₅	=	2 Re	+	5 SrCl ₂	-2682
5 Ce	+	3 MoCl ₅	=	3 Mo	+	5 CeCl ₃	-2676
5 Pr	+	3 WCl ₅	=	3 W	+	5 PrCl ₃	-2672
2 Pr	+	WCl ₆	=	W	+	2 PrCl ₃	-2671
5 La	+	3 MoCl ₅	=	3 Mo	+	5 LaCl ₃	-2661
3 Mg	+	C ₂ Cl ₆	=	2 C	+	3 MgCl ₂	-2656
4 Ce	+	3 C ₂ Cl ₄	=	6 C	+	4 CeCl ₃	-2655
2 Hf	+	C ₂ Cl ₆	=	2 C	+	2 HfCl ₃	-2655
5 Nd	+	3 WCl ₅	=	3 W	+	5 NdCl ₃	-2653
2 Nd	+	WCl ₆	=	W	+	2 NdCl ₃	-2652
4 La	+	3 C ₂ Cl ₄	=	6 C	+	4 LaCl ₃	-2643
2 Sc	+	C ₂ Cl ₆	=	2 C	+	2 ScCl ₃	-2638
4 Y	+	3 WCl ₄	=	3 W	+	4 YCl ₃	-2632
3 Th	+	2 C ₂ Cl ₆	=	4 C	+	3 ThCl ₄	-2629
5 Pr	+	3 MoCl ₅	=	3 Mo	+	5 PrCl ₃	-2617
4 Li	+	WCl ₄	=	W	+	4 LiCl	-2612
4 Pr	+	3 C ₂ Cl ₄	=	6 C	+	4 PrCl ₃	-2609
5 Nd	+	3 MoCl ₅	=	3 Mo	+	5 NdCl ₃	-2598
2 Zr	+	C ₂ Cl ₆	=	2 C	+	2 ZrCl ₃	-2596
4 Nd	+	3 C ₂ Cl ₄	=	6 C	+	4 NdCl ₃	-2593
5 Ba	+	2 ReCl ₅	=	2 Re	+	5 BaCl ₂	-2576
5 Y	+	3 WCl ₅	=	3 W	+	5 YCl ₃	-2558
2 Y	+	WCl ₆	=	W	+	2 YCl ₃	-2558
5 Li	+	WCl ₅	=	W	+	5 LiCl	-2556
6 Li	+	WCl ₆	=	W	+	6 LiCl	-2556
3 Sr	+	C ₂ Cl ₆	=	2 C	+	3 SrCl ₂	-2547
2 Ca	+	WCl ₄	=	W	+	2 CaCl ₂	-2529
4 Li	+	C ₂ Cl ₄	=	2 C	+	4 LiCl	-2523
4 Ce	+	3 CCl ₄	=	3 C	+	4 CeCl ₃	-2523
Ce	+	MoCl ₃	=	Mo	+	1 CeCl ₃	-2521

Table 2E (cont.)

Reaction						Enthalpy, cal/cc
4 Y	+	3 C ₂ Cl ₄	=	6 C	+	4 YCl ₃ -2516
4 La	+	3 CCl ₄	=	3 C	+	4 LaCl ₃ -2513
5 Li	+	MoCl ₅	=	Mo	+	5 LiCl -2512
La	+	MoCl ₃	=	Mo	+	LaCl ₃ -2509
5 Y	+	3 MoCl ₅	=	3 Mo	+	5 YCl ₃ -2500
3 Be	+	C ₂ Cl ₆	=	2 C	+	3 BeCl ₂ -2494
3 Ca	+	WCl ₆	=	W	+	3 CaCl ₂ -2477
5 Ca	+	2 WCl ₅	=	2 W	+	5 CaCl ₂ -2476
4 Pr	+	3 CCl ₄	=	3 C	+	4 PrCl ₃ -2476
Pr	+	MoCl ₃	=	Mo	+	PrCl ₃ -2464
3 Ba	+	C ₂ Cl ₆	=	2 C	+	3 BaCl ₂ -2462
4 Nd	+	3 CCl ₄	=	3 C	+	4 NdCl ₃ -2459
2 Ca	+	C ₂ Cl ₄	=	2 C	+	2 CaCl ₂ -2457
Nd	+	MoCl ₃	=	Mo	+	NdCl ₃ -2444
4 U	+	3 WCl ₄	=	3 W	+	4 UCl ₃ -2436
5 Ca	+	2 MoCl ₅	=	2 Mo	+	5 CaCl ₂ -2432
4 Li	+	CCl ₄	=	C	+	4 LiCl -2408
2 Mg	+	WCl ₄	=	W	+	2 MgCl ₂ -2396
5 Ce	+	3 NbCl ₅	=	3 Nb	+	5 CeCl ₃ -2395
3 Li	+	MoCl ₃	=	Mo	+	3 LiCl -2387
5 La	+	3 NbCl ₅	=	3 Nb	+	5 LaCl ₃ -2386
5 Ce	+	3 TaCl ₅	=	3 Ta	+	5 CeCl ₃ -2374
4 Y	+	3 CCl ₄	=	3 C	+	4 YCl ₃ -2371
2 U	+	WCl ₆	=	W	+	2 UCl ₃ -2369
5 U	+	3 WCl ₅	=	3 W	+	5 UCl ₃ -2368
4 U	+	3 C ₂ Cl ₄	=	6 C	+	4 UCl ₃ -2368
4 Hf	+	3 WCl ₄	=	3 W	+	4 HfCl ₃ -2365
4 Sc	+	3 WCl ₄	=	3 W	+	4 ScCl ₃ -2365
5 La	+	3 TaCl ₅	=	3 Ta	+	5 LaCl ₃ -2365
2 Sr	+	WCl ₄	=	W	+	2 SrCl ₂ -2357
Ce	+	AuCl ₃	=	Au	+	CeCl ₃ -2349

Table 28 (cont.)

Reaction						Enthalpy, cal/cc
Th +	WCl ₄	=	W	+	ThCl ₄	-2347
2 Mg +	C ₂ Cl ₄	=	2 C	+	2 MgCl ₂	-2343
La +	AuCl ₃	=	Au	+	LaCl ₃	-2342
5 Pr +	3 NbCl ₅	=	3 Nb	+	5 PrCl ₃	-2341
5 Mn +	2 ReCl ₅	=	2 Re	+	5 MnCl ₂	-2339
2 Ca +	CCl ₄	=	C	+	2 CaCl ₂	-2339
3 Mg +	WCl ₆	=	W	+	3 MgCl ₂	-2338
Y +	MoCl ₃	=	Mo	+	YCl ₃	-2336
5 Mg +	2 WCl ₅	=	2 W	+	5 MgCl ₂	-2336
2 Sr +	C ₂ Cl ₄	=	2 C	+	2 SrCl ₂	-2324
5 Nd +	3 NbCl ₅	=	3 Nb	+	5 NdCl ₃	-2320
5 Pr +	3 TaCl ₅	=	3 Ta	+	5 PrCl ₃	-2320
4 Sc +	3 C ₂ Cl ₄	=	6 C	+	4 ScCl ₃	-2318
3 Sr +	WCl ₆	=	W	+	3 SrCl ₂	-2316
4 Hf +	3 C ₂ Cl ₄	=	6 C	+	4 HfCl ₃	-2316
5 Sr +	2 WCl ₅	=	2 W	+	5 SrCl ₂	-2315
3 Ca +	2 MoCl ₃	=	2 Mo	+	3 CaCl ₂	-2307
5 U +	3 MoCl ₅	=	3 Mo	+	5 UCl ₃	-2306
4 Zr +	3 WCl ₄	=	3 W	+	4 ZrCl ₃	-2306
2 Sc +	WCl ₆	=	W	+	2 ScCl ₃	-2306
Pr +	AuCl ₃	=	Au	+	PrCl ₃	-2306
5 Sc +	3 WCl ₅	=	3 W	+	5 ScCl ₃	-2305
Th +	C ₂ Cl ₄	=	2 C	+	ThCl ₄	-2304
2 Hf +	WCl ₆	=	W	+	2 HfCl ₃	-2302
5 Hf +	3 WCl ₅	=	3 W	+	5 HfCl ₃	-2301
5 Nd +	3 TaCl ₅	=	3 Ta	+	5 NdCl ₃	-2298
5 Li +	NbCl ₅	=	Nb	+	5 LiCl	-2288
Nd +	AuCl ₃	=	Au	+	NdCl ₃	-2288
3 Th +	2 WCl ₆	=	2 W	+	3 ThCl ₄	-2287
5 Th +	4 WCl ₅	=	4 W	+	5 ThCl ₄	-2285
2 Ba +	WCl ₄	=	W	+	2 BaCl ₂	-2283

Table 28 (cont.)

Reaction						Enthalpy, cal/cc	
5 Mg	+	2 MoCl ₅	=	2 Mo	+	5 MgCl ₂	-2282
5 Al	+	3 ReCl ₅	=	3 Re	+	5 AlCl ₃	-2278
5 Sr	+	2 MoCl ₅	=	2 Mo	+	5 SrCl ₂	-2276
4 Zr	+	3 C ₂ Cl ₄	=	6 C	+	4 ZrCl ₃	-2273
5 Li	+	TaCl ₅	=	Ta	+	5 LiCl	-2270
3 Li	+	AuCl ₃	=	Au	+	3 LiCl	-2266
2 Ba	+	C ₂ Cl ₄	=	2 C	+	2 BaCl ₂	-2265
5 Sc	+	3 MoCl ₅	=	3 Mo	+	5 ScCl ₃	-2248
3 Ba	+	WCl ₆	=	W	+	3 BaCl ₂	-2247
2 Zr	+	WCl ₆	=	W	+	2 ZrCl ₃	-2247
5 Ba	+	2 WCl ₅	=	2 W	+	5 BaCl ₂	-2246
5 Zr	+	3 WCl ₅	=	3 W	+	5 ZrCl ₃	-2245
5 Hf	+	3 MoCl ₅	=	3 Mo	+	5 HfCl ₃	-2240
5 Ti	+	3 ReCl ₅	=	3 Re	+	5 TiCl ₃	-2229
2 Ce	+	3 WCl ₂	=	3 W	+	2 CeCl ₃	-2228
5 Th	+	4 MoCl ₅	=	4 Mo	+	5 ThCl ₄	-2226
2 La	+	3 WCl ₂	=	3 W	+	2 LaCl ₃	-2223
2 Sr	+	CCl ₄	=	C	+	2 SrCl ₂	-2213
5 Ba	+	2 MoCl ₅	=	2 Mo	+	5 BaCl ₂	-2210
4 U	+	3 CCl ₄	=	3 C	+	4 UCl ₃	-2210
5 Ca	+	2 NbCl ₅	=	2 Nb	+	5 CaCl ₂	-2209
5 Y	+	3 NbCl ₅	=	3 Nb	+	5 YCl ₃	-2208
3 Ca	+	2 AuCl ₃	=	2 Au	+	3 CaCl ₂	-2201
2 Ce	+	3 MoCl ₂	=	3 Mo	+	2 CeCl ₃	-2200
2 Mg	+	CCl ₄	=	C	+	2 MgCl ₂	-2198
Y	+	AuCl ₃	=	Au	+	YCl ₃	-2197
2 La	+	3 MoCl ₂	=	3 Mo	+	2 LaCl ₃	-2196
5 Ca	+	2 TaCl ₅	=	2 Ta	+	5 CaCl ₂	-2191
3 Mn	+	C ₂ Cl ₆	=	2 C	+	3 MnCl ₂	-2188
5 Na	+	ReCl ₅	=	Re	+	5 NaCl	-2185
5 Zr	+	3 MoCl ₅	=	3 Mo	+	5 ZrCl ₃	-2185

Table 28 (cont.)

Reaction						Enthalpy, cal/cc
5 Y	+	3 TaCl ₅	=	3 Ta	+	5 YCl ₃ -2184
2 Pr	+	3 WCl ₂	=	3 W	+	2 PrCl ₃ -2182
2 Be	+	C ₂ Cl ₄	=	2 C	+	2 BeCl ₂ -2168
4 Sc	+	3 CCl ₄	=	3 C	+	4 ScCl ₃ -2168
3 Sr	+	2 MoCl ₃	=	2 Mo	+	3 SrCl ₂ -2166
2 Be	+	WCl ₄	=	W	+	2 BeCl ₂ -2164
2 Nd	+	3 WCl ₂	=	3 W	+	2 NdCl ₃ -2162
2 Li	+	WCl ₂	=	W	+	2 LiCl -2159
2 Ba	+	CCl ₄	=	C	+	2 BaCl ₂ -2159
4 Hf	+	3 CCl ₄	=	3 C	+	4 HfCl ₃ -2157
2 Pr	+	3 MoCl ₂	=	3 Mo	+	2 PrCl ₃ -2153
Th	+	CCl ₄	=	C	+	ThCl ₄ -2148
2 Ce	+	3 CuCl ₂	=	3 Cu	+	2 CeCl ₃ -2144
2 La	+	3 CuCl ₂	=	3 Cu	+	2 LaCl ₃ -2141
U	+	MoCl ₃	=	Mo	+	UCl ₃ -2136
2 Al	+	C ₂ Cl ₆	=	2 C	+	2 AlCl ₃ -2135
2 Li	+	MoCl ₂	=	Mo	+	2 LiCl -2134
2 Nd	+	3 MoCl ₂	=	3 Mo	+	2 NdCl ₃ -2132
3 Mg	+	2 MoCl ₃	=	2 Mo	+	3 MgCl ₂ -2130
6 Na	+	C ₂ Cl ₆	=	2 C	+	6 NaCl -2119
4 Zr	+	3 CCl ₄	=	3 C	+	4 ZrCl ₃ -2113
3 Ba	+	2 MoCl ₃	=	2 Mo	+	3 BaCl ₂ -2108
3 Be	+	WCl ₆	=	W	+	3 BeCl ₂ -2106
5 Be	+	2 WCl ₅	=	2 W	+	5 BeCl ₂ -2103
2 Pr	+	3 CuCl ₂	=	3 Cu	+	2 PrCl ₃ -2097
2 Ti	+	C ₂ Cl ₆	=	2 C	+	2 TiCl ₃ -2096
5 V	+	2 ReCl ₅	=	2 Re	+	5 VC ₂ -2092
3 Sr	+	2 AuCl ₃	=	2 Au	+	3 SrCl ₂ -2092
Sc	+	MoCl ₃	=	Mo	+	ScCl ₃ -2090
Ca	+	WCl ₂	=	W	+	CaCl ₂ -2089
2 Li	+	CuCl ₂	=	Cu	+	2 LiCl -2088

Table 28 (cont.)

<u>Reaction</u>						<u>Enthalpy, cal/cc</u>	
5 Sr	+	2 NbCl ₅	=	2 Nb	+	5 SrCl ₂	-2082
2 Nd	+	3 CuCl ₂	=	3 Cu	+	2 NdCl ₃	-2076
Ce	+	FeCl ₃	=	Fe	+	CeCl ₃	-2075
La	+	FeCl ₃	=	Fe	+	LaCl ₃	-2073
Hf	+	MoCl ₃	=	Mo	+	HfCl ₃	-2072
5 Sr	+	2 TaCl ₅	=	2 Ta	+	5 SrCl ₂	-2065
3 Th	+	4 MoCl ₃	=	4 Mo	+	3 ThCl ₄	-2063
Ca	+	MoCl ₂	=	Mo	+	CaCl ₂	-2062
2 Y	+	3 WCl ₂	=	3 W	+	2 YCl ₃	-2056
3 Ba	+	2 AuCl ₃	=	2 Au	+	3 BaCl ₂	-2048
3 Mg	+	2 AuCl ₃	=	2 Au	+	3 MgCl ₂	-2042
Ce	+	3 AuCl	=	3 Au	+	CeCl ₃	-2040
La	+	3 AuCl	=	3 Au	+	LaCl ₃	-2039
U	+	AuCl ₃	=	Au	+	UCl ₃	-2039
5 Be	+	2 MoCl ₅	=	2 Mo	+	5 BeCl ₂	-2037
5 Ba	+	2 NbCl ₅	=	2 Nb	+	5 BaCl ₂	-2031

Table 29

MOST ENERGETIC CHLORIDE REACTIONS WITH METALS,
IN TERMS OF GRAVIMETRIC ENTHALPY

Reaction					Enthalpy, cal/g
Li +	BCl	=	B +	LiCl	-2316
4 Li +	C ₂ Cl ₄	=	2 C +	4 LiCl	-2002
4 Li +	CCl ₄	=	C +	4 LiCl	-1968
6 Li +	C ₂ Cl ₆	=	2 C +	6 LiCl	-1933
Ca +	2 BCl	=	2 B +	CaCl ₂	-1818
Na +	BCl	=	B +	NaCl	-1787
Mg +	2 BCl	=	2 B +	MgCl ₂	-1750
Be +	2 BCl	=	2 B +	BeCl ₂	-1708
Sc +	3 BCl	=	3 B +	ScCl ₃	-1619
2 Ca +	C ₂ Cl ₄	=	2 C +	2 CaCl ₂	-1532
K +	BCl	=	B +	KCl	-1519
4 Na +	C ₂ Cl ₄	=	2 C +	4 NaCl	-1512
2 Ca +	CCl ₄	=	C +	2 CaCl ₂	-1481
Al +	3 BCl	=	3 B +	AlCl ₃	-1465
4 Na +	CCl ₄	=	C +	4 NaCl	-1463
3 Ca +	C ₂ Cl ₆	=	2 C +	3 CaCl ₂	-1462
6 Na +	C ₂ Cl ₆	=	2 C +	6 NaCl	-1444
6 Li +	MoCl ₆	=	Mo +	6 LiCl	-1416
2 Mg +	C ₂ Cl ₄	=	2 C +	2 MgCl ₂	-1416
3 Li +	BCl ₃	=	B +	3 LiCl	-1399
Sr +	2 BCl	=	2 B +	SrCl ₂	-1382
Y +	3 BCl	=	3 B +	YCl ₃	-1368
2 Mg +	CCl ₄	=	C +	2 MgCl ₂	-1350
Li +	AlCl	=	Al +	LiCl	-1337
3 Mg +	C ₂ Cl ₆	=	2 C +	3 MgCl ₂	-1330
2 Be +	C ₂ Cl ₄	=	2 C +	2 BeCl ₂	-1313
4 Li +	CrCl ₄	=	Cr +	4 LiCl	-1294
Ti +	3 BCl	=	3 B +	TiCl ₃	-1294
5 Li +	MoCl ₅	=	Mo +	5 LiCl	-1291

Table 29 (cont.)

Reaction							Enthalpy, cal/g
4 Sc	+	3 C ₂ Cl ₄	=	6 C	+	4 ScCl ₃	-1290
4 K	+	C ₂ Cl ₄	=	2 C	+	4 KCl	-1283
4 Li	+	MnCl ₄	=	Mn	+	4 LiCl	-1250
Zr	+	3 BC ₁	=	3 B	+	ZrCl ₃	-1237
4 K	+	CCl ₄	=	C	+	4 KCl	-1235
2 Be	+	CCl ₄	=	C	+	2 BeCl ₂	-1229
La	+	3 BC ₁	=	3 B	+	LaCl ₃	-1225
5 Li	+	NbCl ₅	=	Nb	+	5 LiCl	-1224
6 K	+	C ₂ Cl ₆	=	2 C	+	6 KCl	-1224
4 Sc	+	3 CCl ₄	=	3 C	+	4 ScCl ₃	-1221
3 Be	+	C ₂ Cl ₆	=	2 C	+	3 BeCl ₂	-1208
Ce	+	3 BC ₁	=	3 B	+	CeCl ₃	-1208
2 Sc	+	C ₂ Cl ₆	=	2 C	+	2 ScCl ₃	-1204
4 Li	+	SiCl ₄	=	Si	+	4 LiCl	-1203
Si	+	4 BC ₁	=	4 B	+	SiCl ₄	-1197
Pr	+	3 BC ₁	=	3 B	+	PrCl ₃	-1196
4 Li	+	MoCl ₄	=	Mo	+	4 LiCl	-1174
Nd	+	3 BC ₁	=	3 B	+	NdCl ₃	-1169
2 Sr	+	C ₂ Cl ₄	=	2 C	+	2 SrCl ₂	-1152
5 Li	+	Sb Cl ₅	=	Sb	+	5 LiCl	-1149
4 Li	+	VCl ₄	=	V	+	4 LiCl	-1146
Li	+	GeCl	=	Ge	+	LiCl	-1131
Mn	+	2 BC ₁	=	2 B	+	MnCl ₂	-1128
V	+	3 BC ₁	=	3 B	+	VCl ₃	-1126
3 Ca	+	MoCl ₆	=	Mo	+	3 CaCl ₂	-1119
6 Na	+	MoCl ₆	=	Mo	+	6 NaCl	-1118
Ba	+	2 BC ₁	=	2 B	+	BaCl ₂	-1116
6 Li	+	WCl ₆	=	W	+	6 LiCl	-1112
Cr	+	3 BC ₁	=	3 B	+	CrCl ₃	-1107
2 Sr	+	CCl ₄	=	C	+	2 SrCl ₂	-1102
3 Sr	+	C ₂ Cl ₆	=	2 C	+	3 SrCl ₂	-1092

Table 29 (cont.)

Reaction						Enthalpy, cal/g
Ca +	2 AlCl	=	2 Al	+	CaCl ₂	-1092
Na +	AlCl	=	Al	+	NaCl	-1092
4 Y +	3 C ₂ Cl ₄	=	6 C	+ 4	YCl ₃	-1090
4 Al +	3 C ₂ Cl ₄	=	6 C	+ 4	AlCl ₃	-1083
4 Li +	GeCl ₄	=	Ge	+ 4	LiCl	-1076
3 Li +	FeCl ₃	=	Fe	+ 3	LiCl	-1072
5 Li +	ReCl ₅	=	Re	+ 5	LiCl	-1050
3 Na +	BCl ₃	=	B	+ 3	NaCl	-1045
3 Ca +	2 BCl ₃	=	2 B	+ 3	CaCl ₂	-1043
5 Na +	MoCl ₅	=	Mo	+ 5	NaCl	-1031
5 Ca +	2 MoCl ₅	=	2 Mo	+ 5	CaCl ₂	-1028
4 Y +	3 CCl ₄	=	3 C	+ 4	YCl ₃	-1027
3 Li +	MoCl ₃	=	Mo	+ 3	LiCl	-1022
5 Li +	WCl ₅	=	W	+ 5	LiCl	-1021
2 Y +	C ₂ Cl ₆	=	2 C	+ 2	YCl ₃	-1016
4 Na +	CrCl ₄	=	Cr	+ 4	NaCl	-1010
2 Ca +	CrCl ₄	=	Cr	+ 2	CaCl ₂	-1007
3 Li +	MnCl ₃	=	Mn	+ 3	LiCl	-1005
Na +	GeCl	=	Ge	+ NaCl		- 997
Ca +	2 GeCl	=	2 Ge	+ CaCl ₂		- 994
4 La +	3 C ₂ Cl ₄	=	6 C	+ 4	LaCl ₃	- 992
4 Al +	3 CCl ₄	=	3 C	+ 4	AlCl ₃	- 992
2 Li +	CuCl ₂	=	Cu	+ 2	LiCl	- 985
6 K +	MoCl ₆	=	Mo	+ 6	KCl	- 984
Hf +	4 BCl	=	4 B	+ HfCl ₄		- 982
4 Na +	MnCl ₄	=	Mn	+ 4	NaCl	- 979
2 Al +	C ₂ Cl ₆	=	2 C	+ 2	AlCl ₃	- 978
K +	AlCl	=	Al	+ KCl		- 977
5 Na +	NbCl ₅	=	Nb	+ 5	NaCl	- 976
4 Ce +	3 C ₂ Cl ₄	=	6 C	+ 4	CeCl ₃	- 975
Rb +	BCl	+ B	+ RbCl			- 975

Table 29 (cont.)

Reaction					Enthalpy, cal/g
2 Ca +	MnCl ₄	=	Mn +	2 CaCl ₂	- 974
4 Li +	TiCl ₄	=	Ti +	4 LiCl	- 972
5 Ca +	2 NbCl ₅	=	2 Nb +	5 CaCl ₂	- 971
3 Mg +	MoCl ₆	=	Mo +	3 MgCl ₂	- 969
Ga +	3 BC ₁	=	3 B +	GaCl ₃	- 969
4 Pr +	3 C ₂ Cl ₄	=	6 C +	4 PrCl ₃	- 963
Mg +	2 AlCl	=	2 Al +	MgCl ₂	- 962
4 Zr +	3 C ₂ Cl ₄	=	6 C +	4 ZrCl ₃	- 954
Zn +	2 BC ₁	=	2 B +	ZnCl ₂	- 953
4 Na +	MoCl ₄	=	Mo +	4 NaCl	- 952
Li +	GaCl	=	Ga +	LiCl	- 951
2 Ca +	MoCl ₄	=	Mo +	2 CaCl ₂	- 946
4 Ti +	3 C ₂ Cl ₄	=	6 C +	4 TiCl ₃	- 944
4 La +	3 CCl ₄	=	3 C +	4 LaCl ₃	- 938
4 Nd +	3 C ₂ Cl ₄	=	6 C +	4 NdCl ₃	- 938
5 Li +	TaCl ₅	=	Ta +	5 LiCl	- 937
5 Na +	SbCl ₅	=	Sb +	5 NaCl	- 933
2 La +	C ₂ Cl ₆	=	2 C +	2 LaCl ₃	- 931
4 Li +	ReCl ₄	=	Re +	4 LiCl	- 929
Th +	4 BC ₁	=	4 B +	ThCl ₄	- 928
K +	GeCl	=	Ge +	KCl	- 928
5 Ca +	2 SbCl ₅	=	2 Sb +	5 CaCl ₂	- 927
2 Ba +	C ₂ Cl ₄	=	2 C +	2 BaCl ₂	- 926
4 Ce +	3 CCl ₄	=	3 C +	4 CeCl ₃	- 921
6 Na +	WC ₆	=	W +	6 NaCl	- 917
5 K +	MoCl ₅	=	Mo +	5 KCl	- 917
6 Li +	Al ₂ Cl ₆	=	2 Al +	6 LiCl	- 916
4 Na +	SiCl ₄	=	Si +	4 NaCl	- 916
2 Ce +	C ₂ Cl ₆	=	2 C +	2 CeCl ₃	- 914
3 Ca +	WCl ₆	=	W +	3 CaCl ₂	- 911

Table 29 (cont.)

Reaction						Enthalpy, cal/g
4 Pr	+	3 CCl ₄	=	3 C	+	4 PrCl ₃
4 Li	+	OsCl ₄	=	Os	+	4 LiCl
Mg	+	2 GeCl	=	2 Ge	+	MgCl ₂
2 Ca	+	SiCl ₄	=	Si	+	2 CaCl ₂
3 K	+	BCl ₃	=	B	+	3 KCl
4 Li	+	WCl ₄	=	W	+	4 LiCl
4 Li	+	SnCl ₄	=	Sn	+	4 LiCl
Ge	+	4 BCl	=	4 B	+	GeCl ₄
2 Pr	+	C ₂ Cl ₆	=	2 C	+	2 PrCl ₃
4 Na	+	VCl ₄	=	V	+	4 NaCl
Fe	+	2 BCl	=	2 B	+	FeCl ₂
4 K	+	CrCl ₄	=	Cr	+	4 KCl
Sc	+	3 AlCl	=	3 Al	+	ScCl ₃
2 Ca	+	VCl ₄	=	V	+	2 CaCl ₂
4 Zr	+	3 CCl ₄	=	3 C	+	4 ZrCl ₃
Sr	+	2 AlCl	=	2 Al	+	SrCl ₂
3 Li	+	CrCl ₃	=	Cr	+	3 LiCl
4 Nd	+	3 CCl ₄	=	3 C	+	4 NdCl ₃
2 Sc	+	MoCl ₆	=	Mo	+	2 ScCl ₃
3 Sr	+	MoCl ₆	=	Mo	+	3 SrCl ₂
2 Ba	+	CCl ₄	=	C	+	2 BaCl ₂
5 Na	+	ReCl ₅	=	Re	+	5 NaCl
2 Zr	+	C ₂ Cl ₆	=	2 C	+	2 ZrCl ₃
2 Nd	+	C ₂ Cl ₆	=	2 C	+	2 NdCl ₃
3 Ba	+	C ₂ Cl ₆	=	2 C	+	3 BaCl ₂
5 Mg	+	2 MoCl ₅	=	2 Mo	+	5 MgCl ₂
3 Li	+	VCl ₃	=	V	+	3 LiCl
5 Ca	+	2 ReCl ₅	=	2 Re	+	5 CaCl ₂
5 K	+	NbCl ₅	=	Nb	+	5 KCl
4 K	+	MnCl ₄	=	Mn	+	4 KCl

Table 29 (cont.)

Reaction							Enthalpy, cal/g
Sr	+	2 GeCl	=	2 Ge	+	SrCl ₂	- 865
Sc	+	3 GeCl	=	3 Ge	+	ScCl ₃	- 861
4 Na	+	GeCl ₄	=	Ge	+	4 NaCl	- 853
4 Ti	+	3 CCl ₄	=	3 C	+	4 TiCl ₃	- 857
4 K	+	MoCl ₄	=	Mo	+	4 KCl	- 856
3 Na	+	FeCl ₃	=	Fe	+	3 NaCl	- 855
5 Na	+	WCl ₅	=	W	+	5 NaCl	- 855
3 Li	+	GaCl ₃	=	Ga	+	3 LiCl	- 851
Co	+	2 BCl	=	2 B	+	CoCl ₂	- 851
2 Ca	+	GeCl ₄	=	Ge	+	2 CaCl ₂	- 848
2 Ti	+	C ₂ Cl ₆	=	2 C	+	2 TiCl ₃	- 847
5 Ca	+	2 WCl ₅	=	2 W	+	3 CaCl ₂	- 847
3 Na	+	MoCl ₃	=	Mo	+	3 NaCl	- 846
3 Mg	+	2 BCl ₃	=	2 B	+	3 MgCl ₂	- 846
3 Ca	+	2 FeCl ₃	=	2 Fe	+	3 CaCl ₂	- 846
5 K	+	SbCl ₅	=	Sb	+	5 KCl	- 841
Be	+	2 AlCl	=	2 Al	+	BeCl ₂	- 840
3 Ca	+	2 MoCl ₃	=	2 Mo	+	3 CaCl ₂	- 838
2 Li	+	MoCl ₂	=	Mo	+	2 LiCl	- 837
Ni	+	2 BCl	=	2 B	+	NiCl ₂	- 837
Na	+	GaCl	=	Ga	+	NaCl	- 836
2 Mg	+	CrCl ₄	=	Cr	+	2 MgCl ₂	- 836
2 Li	+	NiCl ₂	=	Ni	+	2 LiCl	- 835
U	+	4 BCl	=	4 B	+	UCl ₄	- 835
6 K	+	WCl ₆	=	W	+	6 KCl	- 833
Be	+	2 GeCl	=	2 Ge	+	BeCl ₂	- 831
Ca	+	2 GaCl	=	2 Ga	+	CaCl ₂	- 830
2 Mn	+	C ₂ Cl ₄	=	2 C	+	2 MnCl ₂	- 825
3 Be	+	MoCl ₆	=	Mo	+	3 BeCl ₂	- 824
3 Li	+	AlCl ₃	=	Al	+	3 LiCl	- 823

Table 29 (cont.)

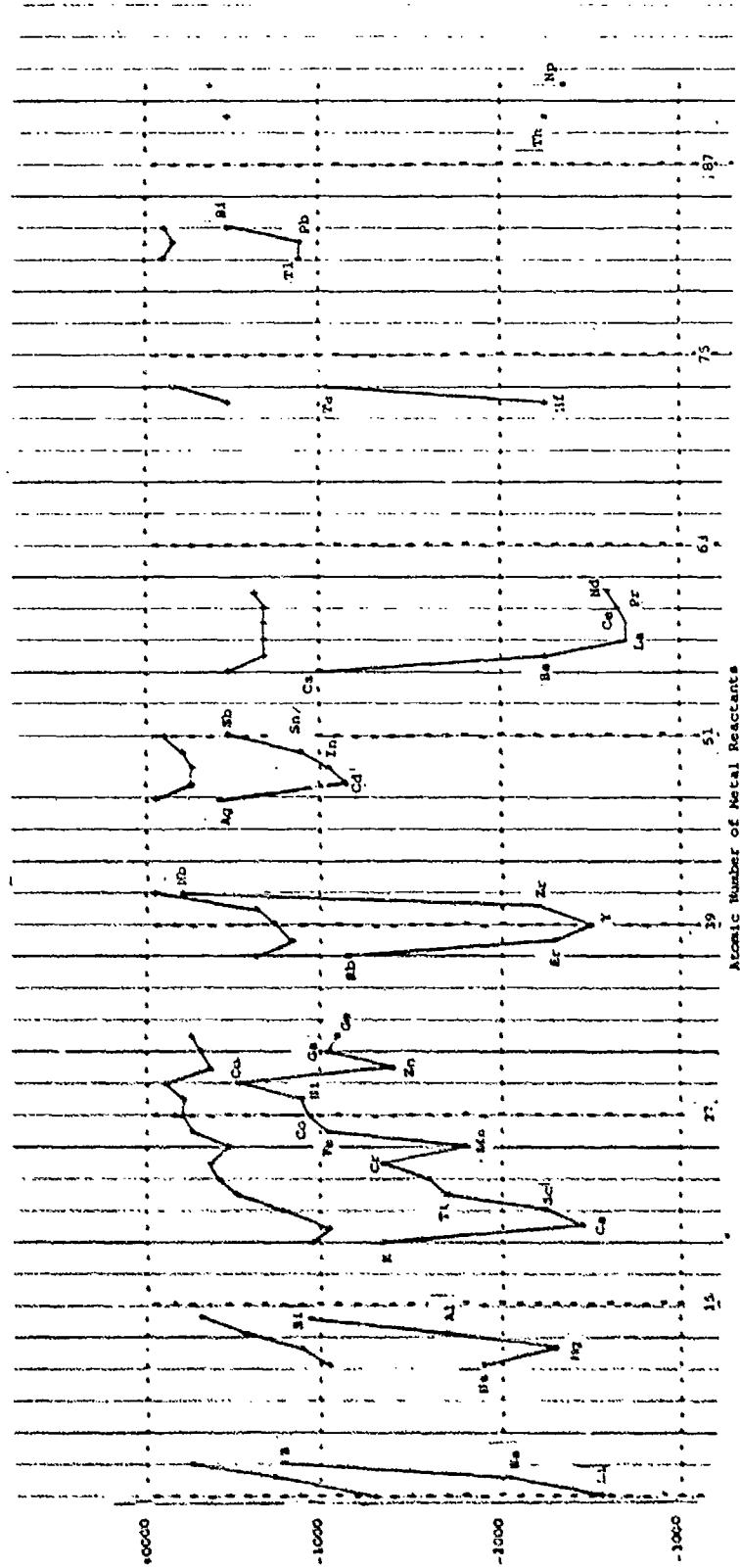
Reaction						Enthalpy, cal/g
5 Sr + 2 MoCl ₅	=	2 Mo	+ 5 SrCl ₂			- 821
2 Li + CoCl ₂	=	Co	+ 2 LiCl			- 818
3 Li + AuCl ₃	=	Au	+ 3 LiCl			- 816
2 Na + CuCl ₂	=	Cu	+ 2 NaCl			- 816
5 Mg + 2 NbCl ₅	=	2 Nb	+ 5 MgCl ₂			- 811
3 Li + SbCl ₃	=	Sb	+ 3 LiCl			- 810
2 Li + FeCl ₂	=	Fe	+ 2 LiCl			- 809
In + 3 BCl	=	3 B	+ InCl ₃			- 808
4 K + SiCl ₄	=	Si	+ 4 KCl			- 808
Ca + CuCl ₂	=	Cu	+ CaCl ₂			- 806
5 K + ReCl ₅	=	Re	+ 5 KCl			- 806
4 Rb + C ₂ Cl ₄	=	2 C	+ 4 RbCl			- 804
Y + 3 GeCl	=	3 Ge	+ YCl ₃			- 804
3 Na + MnCl ₃	=	Mn	+ 3 NaCl			- 802
2 Mg + MnCl ₄	=	Mn	+ 2 MgCl ₂			- 801

(tetrachloroethylene, carbon tetrachloride, and hexachloroethane), chromium tetrachloride, molybdenum hexachloride, and molybdenum pentachloride.

The periodic relationships of the chloride reactions are shown in Figures 21, 22, and 23. It is interesting to compare the general periodic trends, shown by the solid connecting lines, in the chloride, oxide, and fluoride systems. Lithium, which is one of the best reducing agents in the chloride systems, is of moderate efficacy in the oxide and fluoride systems. It occurs at one of the most energetic peaks in the chloride systems. Unlike the oxide systems, magnesium is more energetic than aluminum in the fluoride and chloride systems. Titanium is relatively less energetic in the chloride systems than in the fluoride and oxide systems. The areas including strontium, yttrium, zirconium, the rare earths, hafnium, and tantalum are similar in all three systems.

It is also of interest to compare the trends within the different periodic groups. The trends within each group are similar in all three systems except for the alkaline earths. Thus, most of the groups exhibit less energetic reactions as the atomic number increases. The primary exception to this is the titanium-zirconium-hafnium group, which exhibits an increase in the volumetric energy with increasing atomic number because the lanthanide contraction minimizes the effect of the volume. The behavior of the alkaline earths is therefore striking. Instead of decreasing in energy with increasing atomic number, maximum energy is reached at calcium. This occurs because the heat of formation of the chlorides increases monotonically at a rate which is compensated by the increase in atomic volume and weight when calcium is reached. After calcium, the increase in heat of formation is not enough to overcome the effect of the increase in atomic volume and weight.

The reactions of the chlorides with lithium metal are depicted in Figures 22 and 23. These curves are approximately the inverse of the curves in Figure 21 because the metals that are effective reducing agents form chlorides that are poor oxidizing agents. The chlorides of carbon (hexachloroethane, tetrachloroethylene, and carbon tetrachloride), the transition metal chlorides (vanadium trichloride, chromium trichloride, iron trichloride, cobalt dichloride, nickel dichloride, copper dichloride, molybdenum pentachloride, molybdenum trichloride, tantalum pentachloride, tungsten tetrachloride, tungsten pentachloride and tungsten hexachloride), gold trichloride, mercury dichloride, lead tetrachloride, and bismuth trichloride are effective oxidizers on a volumetric basis. In general, the higher the oxidation state of the metal in the chloride, the more energetic are its reactions. For instance, note the volumetric outputs of molybdenum di-, tri-, and pentachloride. There are many exceptions however, such as vanadium tetra- and trichloride and tungsten tetra- and pentachloride.



CALORIMETRIC AND VOLUMETRIC ENTHALPIES OF REACTIONS OF METALS WITH HOCl₅

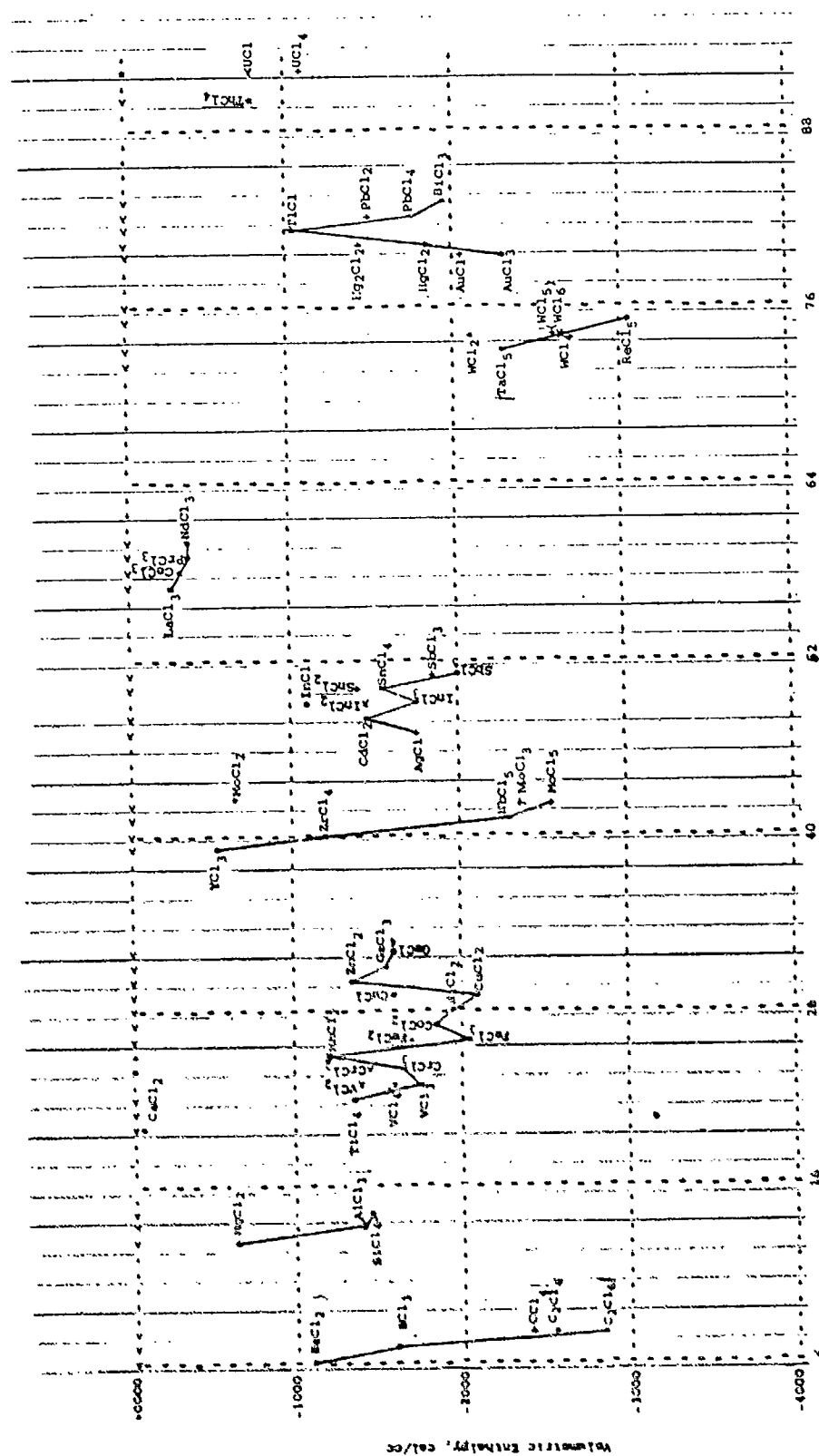
Figure 21

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VOLUMETRIC ENTHALPIES OF REACTIONS OF CHLORIDES WITH Li

Figure 22

Atomic Number of Metal in the Chloride



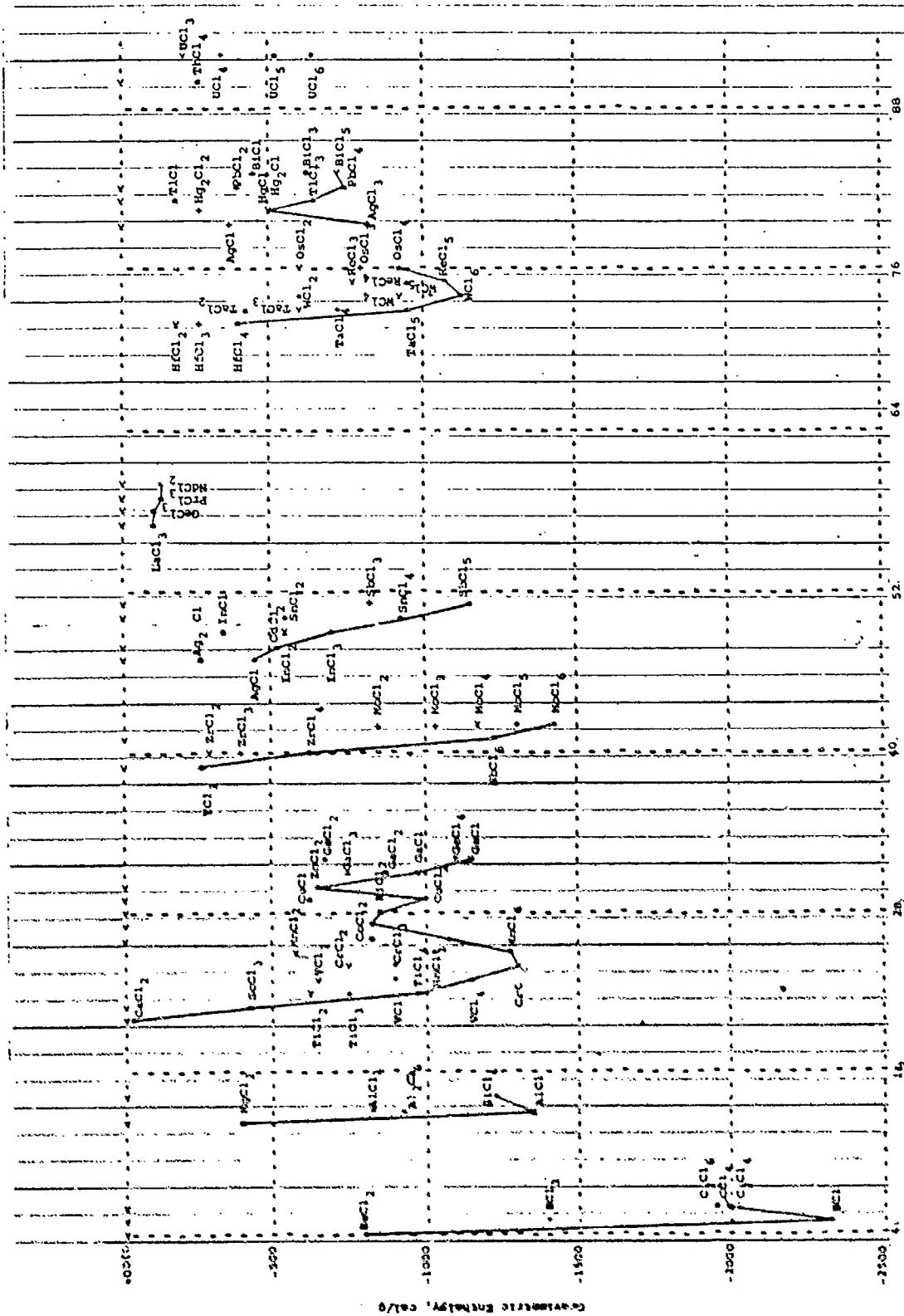


Figure 23
GRAVIMETRIC ENTHALPIES OF REACTIONS OF CHLORIDES WITH Li

The behavior of the chlorides on a gravimetric basis is similar to the volumetric behavior. The chlorides of carbon and the chlorides of many of the transition metals are effective oxidizers. Again, the higher the oxidation state of the metal in the chloride, the more energetic are its reactions. This is illustrated dramatically in Figure 23 by the chlorides of titanium, chromium, manganese, zirconium, molybdenum, indium, tin, antimony, hafnium, tantalum, tungsten, rhenium, osmium, lead, bismuth, and uranium. There are a few exceptions, such as the chlorides of boron, aluminum, gallium, germanium, and mercury. It is interesting that the first three are the first elements in Group IIIA. Evidently, in this group the addition of chloride atoms does not increase the heat of formation of the chloride enough to compensate for the increase in weight of the additional chlorine atoms. Similar charts for the other chlorides and metals indicate similar trends, except for displacement of the vertical scale.

Summaries of the volumetric and gravimetric enthalpies of all the chloride reactions are presented in Tables 30 and 31, respectively. The most energetic reactions are in the upper left-hand corner of the chart. The same trends noted previously are apparent.

Table 30
VOLUMETRIC ENTHALPIES OF REACTIONS OF METALS WITH CHLORIDES
(In descending order from top to bottom and left to right)

Reacts	C-C16	MCl ₄	MCl ₅	MCl ₆	MoCl ₃	CCl ₄	CCl ₃	MoCl ₅	MoCl ₆	TaCl ₅	AuCl ₃	WCl ₂	MoCl ₂	CrCl ₃	NiCl ₂	HgCl ₂	CoCl ₂	
CC	-2736	2047	-2731	-2730	-4670	-2659	-2523	-2395	-2174	-2149	-2223	-2200	-2194	-2075	-2040	-1943	-1843	
Li	-1921	-3025	2784	-2714	-2661	-2643	-2513	-2509	-2196	-2165	-2221	-2142	-2141	-2073	-2019	-1944	-1842	
Fr	-2249	-2946	-3752	-2671	-2659	-2659	-2646	-2644	-2616	-2511	-2406	-2153	-2153	-2075	-1976	-1891	-1749	
Al	-3244	-2970	-2724	-2643	-2652	-2598	-2595	-2444	-2444	-2320	-2298	-2288	-2162	-2132	-2076	-1949	-1848	-1743
Li	-1705	-2814	-2612	-2544	-2555	-2512	-2523	-2508	-2408	-2357	-2270	-2248	-2248	-2159	-2134	-2075	-1918	-1818
T	-3178	-2897	-2632	-2534	-2544	-2363	-2363	-2368	-2368	-2156	-2106	-2194	-2194	-2197	-2055	-1955	-1874	-1742
U	-2906	-2725	-2434	-2434	-2434	-2308	-2308	-2308	-2308	-2150	-2150	-2150	-2150	-2150	-2055	-1955	-1874	-1742
Cd	-2916	-2735	-2529	-2476	-2477	-2474	-2474	-2474	-2474	-2359	-2359	-2359	-2359	-2359	-2201	-2062	-1946	-1846
Nf	-1605	-2655	-2364	-2401	-2302	-2302	-2302	-2302	-2302	-2157	-2054	-1948	-1948	-1948	-1827	-1781	-1656	-1505
Pg	-2672	-2656	-2394	-2394	-2394	-2334	-2284	-2284	-2198	-2130	-2015	-1952	-1952	-1863	-1855	-1781	-1641	-1435
Sf	-2874	-2638	-2364	-2364	-2364	-2347	-2347	-2347	-2347	-2168	-2090	-1948	-1948	-1948	-1808	-1749	-1649	-1540
Iw	-1855	-2629	-2347	-2347	-2347	-2347	-2347	-2347	-2347	-2148	-2063	-1943	-1943	-1943	-1825	-1781	-1673	-1507
Zp	-2628	-2596	-2347	-2347	-2347	-2285	-2285	-2285	-2285	-2113	-2113	-2014	-2014	-2014	-1898	-1871	-1754	-1655
Ge	-2729	-2694	-2347	-2163	-2163	-2057	-2057	-2057	-2057	-1689	-1689	-1689	-1689	-1689	-1522	-1422	-1329	-1021
Sq	-1852	-2517	-2357	-2357	-2357	-2315	-2315	-2315	-2315	-2155	-2155	-2155	-2155	-2155	-2092	-1945	-1858	-1750
Oa	-2576	-2442	-2284	-2284	-2284	-2210	-2210	-2210	-2210	-2159	-2159	-2159	-2159	-2159	-2054	-1945	-1846	-1660
Pn	-2279	-2198	-1847	-1847	-1847	-1750	-1750	-1750	-1750	-1687	-1687	-1687	-1687	-1687	-1475	-1377	-1270	-1139
Al	-2272	-2135	-1791	-1791	-1791	-1693	-1693	-1693	-1693	-1524	-1524	-1524	-1524	-1524	-1470	-1357	-1294	-1142
Tt	-3224	-2096	-1760	-1760	-1760	-1658	-1658	-1658	-1658	-1520	-1520	-1520	-1520	-1520	-1467	-1354	-1295	-1139
Ha	-2163	-2119	-1945	-1945	-1945	-1890	-1890	-1890	-1890	-1748	-1748	-1748	-1748	-1748	-1690	-1593	-1532	-1378
V	-2162	-1997	-1654	-1654	-1654	-1623	-1623	-1623	-1623	-1562	-1562	-1562	-1562	-1562	-1476	-1362	-1296	-1136
Zn	-1836	-1776	-1450	-1450	-1450	-1416	-1416	-1416	-1416	-1357	-1357	-1357	-1357	-1357	-1204	-1119	-1024	-893
Ca	-1803	-1747	-1291	-1291	-1291	-1176	-1176	-1176	-1176	-1045	-1045	-1045	-1045	-1045	-1008	-1020	-963	-817
Co	-1552	-1517	-1162	-1162	-1162	-1115	-1115	-1115	-1115	-1070	-1070	-1070	-1070	-1070	-965	-951	-853	-727
Ga	-1480	-1481	-1114	-1114	-1114	-1046	-1046	-1046	-1046	-983	-983	-983	-983	-983	-872	-852	-744	-624
K	-1445	-1457	-1154	-1154	-1154	-1109	-1109	-1109	-1109	-1050	-1050	-1050	-1050	-1050	-915	-893	-793	-692
Fe	-1654	-1660	-1064	-1064	-1064	-1016	-1016	-1016	-1016	-952	-952	-952	-952	-952	-872	-811	-716	-604
Ja	-1654	-1616	-1073	-1073	-1073	-1009	-1009	-1009	-1009	-932	-932	-932	-932	-932	-876	-824	-743	-646
Co	-1271	-1392	-1016	-1016	-1016	-943	-943	-943	-943	-871	-871	-871	-871	-871	-774	-731	-643	-543
Sl	-1264	-1297	-908	-908	-908	-810	-810	-810	-810	-761	-761	-761	-761	-761	-686	-645	-586	-485
Ge	-1453	-1462	-1114	-1114	-1114	-1054	-1054	-1054	-1054	-910	-910	-910	-910	-910	-812	-760	-685	-591
It	-1453	-1463	-1064	-1064	-1064	-1006	-1006	-1006	-1006	-877	-877	-877	-877	-877	-760	-687	-616	-516
Nt	-1205	-1241	-954	-954	-954	-891	-891	-891	-891	-726	-726	-726	-726	-726	-668	-611	-519	-414
Kp	-1256	-1271	-1160	-1160	-1160	-1159	-1159	-1159	-1159	-1125	-1125	-1125	-1125	-1125	-1088	-1048	-940	-879
B	-1161	-1161	-814	-814	-814	-751	-751	-751	-751	-672	-672	-672	-672	-672	-574	-517	-420	-320
Am	-1209	-1250	-932	-932	-932	-891	-891	-891	-891	-812	-812	-812	-812	-812	-748	-664	-577	-472
Fb	-1206	-1247	-901	-901	-901	-858	-858	-858	-858	-740	-740	-740	-740	-740	-662	-584	-490	-392
Tl	-1090	-1134	-896	-896	-896	-850	-850	-850	-850	-704	-704	-704	-704	-704	-680	-595	-491	-391
Us	-1043	-1063	-964	-964	-964	-919	-919	-919	-919	-841	-841	-841	-841	-841	-769	-679	-583	-483
Se	-786	-899	-534	-534	-534	-492	-492	-492	-492	-732	-732	-732	-732	-732	-686	-597	-497	-397
Cu	-828	-930	-524	-524	-524	-493	-493	-493	-493	-402	-402	-402	-402	-402	-344	-244	-147	-343
Dl	-793	-946	-521	-521	-521	-491	-491	-491	-491	-396	-396	-396	-396	-396	-312	-221	-121	-21
Ag	-651	-767	-452	-452	-452	-476	-476	-476	-476	-341	-341	-341	-341	-341	-246	-146	-784	-784
Po	-429	-421	-.....	-.....	-.....	-.....	-.....	-.....	-.....	-400	-400	-400	-400	-400	-420	-311	-211	-111
G	-235	-465	-.....	-.....	-.....	-.....	-.....	-.....	-.....	-611	-611	-611	-611	-611	-511	-292	-192	-92
Gs	-117	-381	-.....	-.....	-.....	-.....	-.....	-.....	-.....	-553	-553	-553	-553	-553	-454	-226	-126	-226
U	-64	-.....	-.....	-.....	-.....	-.....	-.....	-.....	-.....	-540	-540	-540	-540	-540	-454	-226	-126	-226
Pc	-928	-7112	-465	-297	-232	-232	-232	-232	-232	-662	-662	-662	-662	-662	-462	-362	-262	-162
Ac	-928	-641	-297	-232	-232	-232	-232	-232	-232	-641	-641	-641	-641	-641	-441	-341	-241	-141

Table 30 (cont.)

SnCl ₃	AgCl	PbCl ₃	VCl ₃	FeCl ₃	CrCl ₃	BCl ₃	VCl ₄	CuCl	GeCl ₄	SnCl ₄	GaCl ₃	PbCl ₂	CaCl ₂	Hg ₂ Cl ₂	SiCl ₄	CrCl ₂	InCl ₃	VCl ₂	SnCl ₂	AlCl ₃
Li ₁₆₀₅	-1751	-1722	-1693	-1662	-1561	-1559	-1558	-1558	-1494	-1463	-1463	-1463	-1463	-1463	-1463	-1359	-1359	-1287	-1245	
Li ₁₆₀₄	-1746	-1723	-1692	-1661	-1560	-1558	-1558	-1558	-1494	-1463	-1463	-1463	-1463	-1463	-1463	-1359	-1359	-1287	-1245	
Li ₁₇₄₀	-1441	-1631	-1631	-1630	-1558	-1523	-1523	-1523	-1494	-1463	-1463	-1463	-1463	-1463	-1463	-1359	-1359	-1287	-1245	
Li ₁₇₅₁	-1642	-1642	-1661	-1635	-1593	-1558	-1558	-1558	-1494	-1463	-1463	-1463	-1463	-1463	-1463	-1359	-1359	-1287	-1245	
Li ₁₈₀₇	-1732	-1730	-1711	-1707	-1664	-1598	-1598	-1598	-1494	-1463	-1463	-1463	-1463	-1463	-1463	-1359	-1359	-1287	-1245	
Li ₁₆₁₅	-1449	-1537	-1510	-1426	-1407	-1304	-1327	-1327	-1327	-1327	-1327	-1327	-1327	-1327	-1327	-1327	-1327	-1327	-1327	
Li ₁₄₂₉	-1263	-1253	-1361	-1165	-1110	-1166	-1185	-1185	-1185	-1185	-1185	-1185	-1185	-1185	-1185	-1185	-1185	-1185	-1185	
Ca ₁₇₅₇	-1444	-1664	-1664	-1664	-1664	-1664	-1664	-1664	-1664	-1664	-1664	-1664	-1664	-1664	-1664	-1664	-1664	-1664	-1664	
Ca ₁₃₇₄	-1147	-1510	-1504	-1109	-1136	-1136	-1136	-1136	-1136	-1136	-1136	-1136	-1136	-1136	-1136	-1136	-1136	-1136	-1136	
Ca ₁₄₆₂	-1273	-1419	-1394	-1264	-1272	-1248	-1266	-1266	-1266	-1266	-1266	-1266	-1266	-1266	-1266	-1266	-1266	-1266	-1266	
Ca ₁₆₇₈	-1241	-1263	-1136	-1129	-1145	-1201	-1211	-1211	-1211	-1211	-1211	-1211	-1211	-1211	-1211	-1211	-1211	-1211	-1211	
Ca ₁₃₅₆	-1275	-1320	-1272	-1050	-1118	-1052	-1104	-1104	-1104	-1104	-1104	-1104	-1104	-1104	-1104	-1104	-1104	-1104	-1104	
Ca ₁₂₄₂	-1142	-1280	-1272	-1050	-1118	-1052	-1104	-1104	-1104	-1104	-1104	-1104	-1104	-1104	-1104	-1104	-1104	-1104	-1104	
Ca ₁₁₅₁	-1075	-1061	-1092	-1077	-1060	-1060	-1060	-1060	-1060	-1060	-1060	-1060	-1060	-1060	-1060	-1060	-1060	-1060	-1060	
Ca ₁₆₄₆	-1432	-1609	-1591	-1523	-1526	-1504	-1499	-1499	-1499	-1499	-1499	-1499	-1499	-1499	-1499	-1499	-1499	-1499	-1499	
Ca ₁₆₄₃	-1476	-1564	-1576	-1530	-1616	-1494	-1494	-1494	-1494	-1494	-1494	-1494	-1494	-1494	-1494	-1494	-1494	-1494	-1494	
Fe ₄₀₄	-1579	-1850	-1874	-1467	-1595	-1609	-1721	-1721	-1721	-1721	-1721	-1721	-1721	-1721	-1721	-1721	-1721	-1721	-1721	
Fe ₆₀₄	-1497	-1856	-1864	-1664	-1664	-1664	-1720	-1720	-1720	-1720	-1720	-1720	-1720	-1720	-1720	-1720	-1720	-1720	-1720	
Fe ₁₆₁₀	-1315	-1371	-1363	-1276	-1276	-1243	-1273	-1273	-1273	-1273	-1273	-1273	-1273	-1273	-1273	-1273	-1273	-1273	-1273	
Fe ₆₂₄	-1762	-1762	-1664	-1664	-1664	-1664	-1664	-1664	-1664	-1664	-1664	-1664	-1664	-1664	-1664	-1664	-1664	-1664	-1664	
Fe ₆₀₄	-1769	-1636	-1636	-1636	-1636	-1636	-1636	-1636	-1636	-1636	-1636	-1636	-1636	-1636	-1636	-1636	-1636	-1636	-1636	
Cr ₂₂₂	-1148	-1664	-1730	-1738	-1707	-1633	-1790	-1790	-1790	-1790	-1790	-1790	-1790	-1790	-1790	-1790	-1790	-1790	-1790	
Cr ₆₄₃	-1034	-1384	-1423	-1013	-1013	-1013	-1013	-1013	-1013	-1013	-1013	-1013	-1013	-1013	-1013	-1013	-1013	-1013	-1013	
Cr ₅₇₁	-1354	-1354	-1395	-1395	-1395	-1395	-1395	-1395	-1395	-1395	-1395	-1395	-1395	-1395	-1395	-1395	-1395	-1395	-1395	
Cr ₁₃₀₇	...	-203	-1938	-1938	-1938	-1938	-1938	-1938	-1938	-1938	-1938	-1938	-1938	-1938	-1938	-1938	-1938	-1938	-1938	
Cr ₅₁	-227	-321	-321	-321	-321	-321	-321	-321	-321	-321	-321	-321	-321	-321	-321	-321	-321	-321	-321	
Cr ₆₇	-64	-64	-64	-64	-64	-64	-64	-64	-64	-64	-64	-64	-64	-64	-64	-64	-64	-64	-64	
Cr ₄₁₉	-451	-451	-451	-451	-451	-451	-451	-451	-451	-451	-451	-451	-451	-451	-451	-451	-451	-451	-451	
Cr ₂₆₄	-254	-254	-254	-254	-254	-254	-254	-254	-254	-254	-254	-254	-254	-254	-254	-254	-254	-254	-254	
Cr ₉₀₄	-869	-869	-869	-869	-869	-869	-869	-869	-869	-869	-869	-869	-869	-869	-869	-869	-869	-869	-869	
Cr ₁₁₃	-104	-104	-104	-104	-104	-104	-104	-104	-104	-104	-104	-104	-104	-104	-104	-104	-104	-104	-104	
Cr ₂₅₇	-232	-232	-232	-232	-232	-232	-232	-232	-232	-232	-232	-232	-232	-232	-232	-232	-232	-232	-232	
IF	-2679	-2750	-1764	-653	8880	8880	-714	-707	-720	-713	-708	-651	-659	-658	-658	-658	-658	-658	-658	
CS	
SE	
CU	
DL	-10	-50	-50	-50	-50	-50	-50	-50	-50	-50	-50	-50	-50	-50	-50	-50	-50	-50	-50	
PG	
A	
ME	
US	
All	
KC	

Table 30 (cont.)

	ZnCl ₂	TiCl ₄	ZrCl ₄	MgCl ₂	KCl ₂	LiCl ₂	BeCl ₂	UCl ₄	TiCl ₄	MgCl ₂	KCl ₂	LiCl ₂	BeCl ₂	NaCl	SiCl ₂	RbCl	CsCl
Ge	-1219	-1217	-1033	-1033	-986	-916	-865	-816	-787	-751	-731	-73	-66	-66	-36	-36	-36
La	-1213	-1213	-1071	-1054	-934	-907	-850	-803	-789	-797	-711	-78	-78	-78	-30	-30	-30
V	-1182	-1182	-1014	-1014	-901	-876	-840	-790	-752	-752	-752	-752	-752	-752	-42	-42	-42
HD	-1153	-1153	-981	-984	-940	-843	-811	-767	-746	-746	-746	-746	-746	-746	-25	-25	-25
I	-1218	-1206	-1189	-1173	-1049	-1034	-1020	-1020	-782	-782	-625	-625	-625	-625	-76	-76	-76
X	-792	-74017	-7493	-7777	-616	-647	-7607	-738	-272	-272	-540	-540	-540	-540	-540	-540	-540
U	-82	-82	-1060	-1060	-1035	-1035	-978	-974	-713	-705	-546	-402	-308	-242	-208	-271	-271
CA	-1266	-1261	-1111	-1090	-1035	-996	-957	-908	-753	-753	-561	-473	-473	-473	-30	-30	-30
Hf	-756	-669	-545	-535	-457	-408	-361	-313	-213	-213	-171	-169	-169	-169	-202	-202	-202
Fe	-857	-824	-690	-677	-571	-534	-513	-471	-411	-411	-392	-392	-392	-392	-92	-92	-92
Sc	-812	-854	-600	-587	-512	-490	-487	-450	-381	-381	-341	-341	-341	-341	-9	-9	-9
Tl	-753	-604	-524	-516	-461	-431	-345	-345	-345	-345	-345	-345	-345	-345	-345	-345	-345
28	-766	-739	-631	-631	-526	-526	-526	-526	-526	-526	-526	-526	-526	-526	-526	-526	-526
82	-962	-932	-7157	-7148	-6426	-531	-531	-531	-531	-531	-531	-531	-531	-531	-323	-323	-323
30	-1224	-1221	-1151	-1158	-948	-979	-979	-979	-782	-782	-596	-517	-517	-517	-17	-17	-17
AA	-1233	-1230	-1119	-1107	-1030	-1023	-1006	-1006	-749	-749	-649	-571	-571	-571	-222	-222	-222
HF	-221	-243	-378	-378	-303	-303	-303	-303	-179	-179	-179	-179	-179	-179	-179	-179	-179
Tl	-1029	-1033	-919	-909	-692	-828	-828	-828	-612	-612	-607	-486	-486	-486	-256	-256	-256
V	-152	-152	-128	-128	-128	-128	-128	-128	-116	-116	-116	-116	-116	-116	-70	-70	-70
Cs	-749	-749	-749	-749	-749	-749	-749	-749	-749	-749	-749	-749	-749	-749	-749	-749	-749
CD	-772	-772	-687	-687	-714	-691	-691	-691	-697	-697	-680	-680	-680	-680	-238	-238	-238
X	-792	-792	-687	-687	-687	-687	-687	-687	-687	-687	-687	-687	-687	-687	-195	-195	-195
TA	-1218	-1218	-1218	-1218	-1218	-1218	-1218	-1218	-1218	-1218	-1218	-1218	-1218	-1218	-192	-192	-192
Al	-221	-221	-221	-221	-221	-221	-221	-221	-221	-221	-221	-221	-221	-221	-192	-192	-192
TL	-298	-298	-298	-298	-298	-298	-298	-298	-298	-298	-298	-298	-298	-298	-5	-5	-5
Sb	-61	-61	-597	-597	-597	-597	-597	-597	-597	-597	-597	-597	-597	-597	-547	-547	-547
As	-61	-61	-61	-61	-61	-61	-61	-61	-61	-61	-61	-61	-61	-61	-546	-546	-546
Se	-61	-61	-61	-61	-61	-61	-61	-61	-61	-61	-61	-61	-61	-61	-53	-53	-53
Pb	-61	-61	-61	-61	-61	-61	-61	-61	-61	-61	-61	-61	-61	-61	-53	-53	-53
CS	-61	-61	-61	-61	-61	-61	-61	-61	-61	-61	-61	-61	-61	-61	-53	-53	-53
Cl	-61	-61	-61	-61	-61	-61	-61	-61	-61	-61	-61	-61	-61	-61	-53	-53	-53
Br	-61	-61	-61	-61	-61	-61	-61	-61	-61	-61	-61	-61	-61	-61	-53	-53	-53
I	-61	-61	-61	-61	-61	-61	-61	-61	-61	-61	-61	-61	-61	-61	-53	-53	-53

Table 31

BRANIMETRIC ENTHALPIES OF REACTIONS OF METALS WITH CHLORIDES (in descending order from top to bottom and left to right)

Table 31 (cont.)

	MgCl ₃	MgCl ₂	CuCl ₂	GeCl ₄	ReCl ₄	TiCl ₄	OsCl ₅	TcCl ₄	HgCl ₄	SeCl ₄	AlCl ₃	NiCl ₃	GaCl ₃	VCl ₃	CrCl ₃	Al ₂ Cl ₆ OCl ₂	AlCl ₃ /SbCl ₃	OsCl ₃	
L1	+1022	+1005	-943	-937	+908	-914	-904	-903	-916	-837	-832	-884	-881	-816	-916	-918	-812	-610	-781
HA	-836	-782	-416	-630	-795	-788	-775	-759	-745	-715	-716	-704	-696	-766	-674	-635	-684	-683	
CA	-518	-501	-646	-763	-774	-766	-752	-731	-712	-695	-705	-674	-650	-696	-640	-616	-616	-671	
K	-778	-724	-744	-730	-724	-722	-682	-716	-696	-675	-670	-639	-645	-637	-618	-627	-584	-672	-644
SX	-695	-670	-674	-661	-669	-654	-652	-648	-609	-607	-605	-563	-560	-557	-554	-552	-574	-574	-558
HO	-69	-607	-616	-750	-652	-625	-637	-529	-520	-570	-519	-572	-500	-490	-492	-460	-490	-524	-524
SC	-620	-537	-666	-667	-603	-572	-587	-434	-579	-512	-512	-524	-449	-423	-411	-414	-434	-514	-514
Y	-582	-499	-554	-637	-566	-532	-532	-532	-492	-492	-492	-492	-497	-429	-405	-412	-371	-474	-474
SE	-543	-420	-546	-630	-553	-467	-515	-216	-506	-510	-469	-405	-357	-284	-216	-215	-316	-452	-446
DA	-594	-473	-682	-562	-501	-572	-457	-457	-560	-524	-524	-519	-531	-487	-476	-478	-416	-416	-523
LA	-581	-511	-627	-630	-567	-561	-561	-432	-534	-496	-496	-511	-507	-453	-438	-427	-410	-469	-501
CF	-570	-497	-633	-633	-562	-547	-547	-545	-514	-514	-514	-514	-514	-421	-421	-426	-410	-446	-446
PF	-561	-489	-617	-617	-562	-534	-534	-530	-482	-482	-482	-482	-482	-473	-473	-473	-460	-486	-486
HD	-546	-477	-621	-621	-530	-530	-530	-530	-477	-477	-477	-477	-477	-468	-468	-468	-451	-474	-474
ZR	-497	-384	-577	-569	-486	-486	-486	-486	-486	-486	-486	-486	-486	-479	-479	-479	-405	-485	-485
TY	-370	-262	-735	-528	-460	-353	-298	-298	-298	-298	-298	-298	-298	-279	-279	-279	-201	-346	-346
RB	-531	-477	-613	-626	-526	-526	-526	-515	-515	-515	-515	-515	-515	-493	-493	-493	-460	-476	-476
AL	-841	-269	-564	-564	-482	-482	-482	-482	-482	-482	-482	-482	-482	-460	-460	-460	-425	-474	-474
IH	-379	-319	-369	-362	-329	-329	-329	-329	-329	-329	-329	-329	-329	-317	-317	-317	-293	-337	-337
TH	-393	-369	-372	-491	-401	-364	-364	-364	-364	-364	-364	-364	-364	-354	-354	-354	-263	-356	-356
V	-367	-214	-317	-382	-262	-262	-262	-262	-262	-262	-262	-262	-262	-250	-250	-250	-232	-313	-313
CS	-408	-355	-348	-422	-411	-386	-386	-386	-386	-386	-386	-386	-386	-358	-358	-358	-326	-391	-391
CD	-274	-137	-743	-429	-320	-238	-238	-238	-238	-238	-238	-238	-238	-216	-216	-216	-188	-249	-249
Hf	-260	-294	-726	-726	-538	-538	-538	-538	-538	-538	-538	-538	-538	-474	-474	-474	-425	-538	-538
ZN	-275	-150	-744	-625	-504	-504	-504	-504	-504	-504	-504	-504	-504	-420	-420	-420	-374	-523	-523
SI	-232	-224	-513	-421	-324	-324	-324	-324	-324	-324	-324	-324	-324	-270	-270	-270	-231	-317	-317
U	-336	-316	-425	-326	-326	-326	-326	-326	-326	-326	-326	-326	-326	-272	-272	-272	-231	-317	-317
Gd	-222	-160	-160	-160	-160	-160	-160	-160	-160	-160	-160	-160	-160	-121	-121	-121	-122	-222	-222
OT	-224	-177	-177	-177	-177	-177	-177	-177	-177	-177	-177	-177	-177	-121	-121	-121	-114	-216	-216
FT	-260	-189	-149	-273	-234	-168	-270	-284	-275	-275	-275	-275	-275	-194	-194	-194	-127	-291	-291
IN	-199	-64	-112	-261	-231	-171	-220	-209	-196	-196	-196	-196	-196	-146	-146	-146	-15	-36	-36
CO	-177	-22	-162	-252	-214	-147	-203	-205	-175	-175	-175	-175	-175	-122	-122	-122	-102	-108	-108
HI	-166	-11	-114	-267	-204	-136	-193	-193	-160	-160	-160	-160	-160	-103	-103	-103	-80	-117	-117
SH	-154	-64	-115	-265	-219	-135	-181	-181	-170	-170	-170	-170	-170	-139	-139	-139	-69	-117	-117
B	-164	-123	-123	-214	-126	-126	-126	-126	-126	-126	-126	-126	-126	-113	-113	-113	-76	-119	-119
CD	-200	-189	-2172	-243	-221	-176	-219	-210	-210	-210	-210	-210	-210	-114	-114	-114	-72	-124	-124
Hg	-15	-251	-171	-122	-122	-122	-122	-122	-122	-122	-122	-122	-122	-113	-113	-113	-68	-116	-116
SB	-121	-60	-202	-163	-111	-88	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-112	-112	-112
TA	-69	-65	-247	-111	-111	-88	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-112	-112	-112
BI	-124	-239	-117	-264	-111	-111	-111	-111	-111	-111	-111	-111	-111	-111	-111	-111	-112	-112	-112
FB	-124	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103
CU	-250	-243	-243	-243	-243	-243	-243	-243	-243	-243	-243	-243	-243	-243	-243	-243	-243	-243	-243
ID	-100	-67	-69	-100	-213	-118	-90	-90	-90	-90	-90	-90	-90	-90	-90	-90	-90	-90	-90
AP	-69	-52	-164	-80	-75	-66	-66	-66	-66	-66	-66	-66	-66	-66	-66	-66	-66	-66	-66
OS	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103
AS	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103
HS	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103
All	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103	-103

Table 31 (cont.)

	FeCl ₃	FeCl ₂	FeCl ₄	CaCl ₂	CaCl ₄	CrCl ₃	TiCl ₄	BeCl ₂	TiCl ₃	HgCl ₂	TiCl ₂	WCl ₂	VCl ₂	ZnCl ₂	TiCl ₄	ZrCl ₂
L1	-169	-734	-740	-740	-715	-715	-715	-715	-715	-618	-618	-618	-618	-618	-618	-618
HA	-671	-646	-632	-624	-616	-603	-599	-595	-595	-594	-594	-594	-594	-594	-594	-594
CA	-640	-640	-640	-640	-640	-640	-640	-640	-640	-530	-530	-530	-530	-530	-530	-530
K	-677	-596	-596	-596	-595	-595	-595	-595	-595	-521	-521	-521	-521	-521	-521	-521
SR	-577	-516	-516	-516	-516	-516	-516	-516	-516	-478	-478	-478	-478	-478	-478	-478
F12	-581	-479	-479	-479	-479	-479	-479	-479	-479	-406	-406	-406	-406	-406	-406	-406
SC	-497	-392	-392	-392	-392	-392	-392	-392	-392	-298	-298	-298	-298	-298	-298	-298
Y	-479	-393	-393	-393	-393	-393	-393	-393	-393	-277	-277	-277	-277	-277	-277	-277
SE	-429	-320	-320	-320	-320	-320	-320	-320	-320	-219	-219	-219	-219	-219	-219	-219
RA	-575	-461	-461	-461	-461	-461	-461	-461	-461	-411	-411	-411	-411	-411	-411	-411
LA	-461	-376	-376	-376	-376	-376	-376	-376	-376	-356	-356	-356	-356	-356	-356	-356
CE	-617	-474	-474	-474	-474	-474	-474	-474	-474	-390	-390	-390	-390	-390	-390	-390
P14	-673	-427	-427	-427	-427	-427	-427	-427	-427	-323	-323	-323	-323	-323	-323	-323
UD	-464	-376	-376	-376	-376	-376	-376	-376	-376	-265	-265	-265	-265	-265	-265	-265
22	-504	-395	-395	-395	-395	-395	-395	-395	-395	-254	-254	-254	-254	-254	-254	-254
F11	-521	-419	-419	-419	-419	-419	-419	-419	-419	-196	-196	-196	-196	-196	-196	-196
R3	-647	-460	-460	-460	-460	-460	-460	-460	-460	-205	-205	-205	-205	-205	-205	-205
AL	-537	-429	-429	-429	-429	-429	-429	-429	-429	-165	-165	-165	-165	-165	-165	-165
IG1	-573	-427	-427	-427	-427	-427	-427	-427	-427	-152	-152	-152	-152	-152	-152	-152
TP1	-265	-265	-265	-265	-265	-265	-265	-265	-265	-152	-152	-152	-152	-152	-152	-152
Y	-264	-264	-264	-264	-264	-264	-264	-264	-264	-148	-148	-148	-148	-148	-148	-148
CF	-571	-419	-419	-419	-419	-419	-419	-419	-419	-130	-130	-130	-130	-130	-130	-130
CK	-263	-263	-263	-263	-263	-263	-263	-263	-263	-120	-120	-120	-120	-120	-120	-120
HP	-518	-376	-376	-376	-376	-376	-376	-376	-376	-115	-115	-115	-115	-115	-115	-115
ZH	-264	-176	-176	-176	-176	-176	-176	-176	-176	-109	-109	-109	-109	-109	-109	-109
S1	-252	-103	-103	-103	-103	-103	-103	-103	-103	-97	-97	-97	-97	-97	-97	-97
U	-307	-255	-255	-255	-255	-255	-255	-255	-255	-87	-87	-87	-87	-87	-87	-87
CA	-207	-112	-112	-112	-112	-112	-112	-112	-112	-76	-76	-76	-76	-76	-76	-76
GZ	-404	-133	-133	-133	-133	-133	-133	-133	-133	-65	-65	-65	-65	-65	-65	-65
PG	-184	-106	-106	-106	-106	-106	-106	-106	-106	-52	-52	-52	-52	-52	-52	-52
CG	-211	-113	-113	-113	-113	-113	-113	-113	-113	-42	-42	-42	-42	-42	-42	-42
SD	-187	-74	-74	-74	-74	-74	-74	-74	-74	-32	-32	-32	-32	-32	-32	-32
TA	-183	-10	-10	-10	-10	-10	-10	-10	-10	-10	-10	-10	-10	-10	-10	-10
SG	-189	-113	-113	-113	-113	-113	-113	-113	-113	-60	-60	-60	-60	-60	-60	-60
CU	-102	-53	-53	-53	-53	-53	-53	-53	-53	-50	-50	-50	-50	-50	-50	-50
PL	-37	-32	-32	-32	-32	-32	-32	-32	-32	-11	-11	-11	-11	-11	-11	-11
TL	-108	-108	-108	-108	-108	-108	-108	-108	-108	-10	-10	-10	-10	-10	-10	-10
RE	-104	-104	-104	-104	-104	-104	-104	-104	-104	-10	-10	-10	-10	-10	-10	-10
OS	-65	-7	-7	-7	-7	-7	-7	-7	-7	-17	-17	-17	-17	-17	-17	-17
AS	-65	-49	-49	-49	-49	-49	-49	-49	-49	-11	-11	-11	-11	-11	-11	-11
EG	-51	-49	-49	-49	-49	-49	-49	-49	-49	-10	-10	-10	-10	-10	-10	-10
AU	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Table 31 (cont.)

	TiCl ₃	SnCl ₂	InCl ₂	MnCl ₂	FeCl ₂	CrCl ₂	NiCl ₂	CoCl ₂	W ₂ O ₃	MoO ₃	W ₂ Cl ₂	CrCl ₃	AlCl ₃	AgCl	BiCl ₃	HgCl ₂	PbCl ₂	SrCl ₃	MgCl ₂	InCl	UCl ₄	Hg ₂ Cl ₂	
L1	-577	-249	-244	-273	100	149	149	149	-431	-431	-431	-431	-431	-431	-431	-375	-419	-390	-385	-384	-336	-342	-271
NA	-598	-479	-473	-472	442	442	442	442	-431	-431	-431	-431	-431	-431	-431	-322	-322	-304	-304	-310	-310	-301	-256
CA	-460	-463	-465	-465	445	445	445	445	-431	-431	-431	-431	-431	-431	-431	-312	-312	-298	-298	-270	-270	-267	-267
K	-268	-465	-460	-460	447	447	447	447	-431	-431	-431	-431	-431	-431	-431	-312	-312	-304	-304	-304	-304	-304	-243
SR	-314	-412	-400	-387	321	321	321	321	-431	-431	-431	-431	-431	-431	-431	-267	-269	-269	-269	-269	-269	-260	-260
PD	-345	-325	-317	-253	324	324	324	324	-431	-431	-431	-431	-431	-431	-431	-247	-247	-247	-247	-247	-247	-198	-198
SC	-209	-260	-268	-268	303	303	303	303	-215	-215	-215	-215	-215	-215	-215	-199	-199	-199	-199	-199	-199	-198	-198
Y	-316	-293	-284	-268	266	266	266	266	-361	-361	-361	-361	-361	-361	-361	-229	-229	-229	-229	-229	-229	-124	-124
DE	-397	-194	-184	-51	233	233	233	233	-152	-152	-152	-152	-152	-152	-152	-162	-162	-162	-162	-162	-162	-122	-122
DA	-391	-373	-367	-342	239	239	239	239	-306	-306	-306	-306	-306	-306	-306	-307	-307	-307	-307	-307	-307	-244	-244
LA	-376	-326	-314	-274	238	238	238	238	-291	-291	-291	-291	-291	-291	-291	-263	-263	-263	-263	-263	-263	-177	-177
CE	-319	-217	-210	-204	224	224	224	224	-274	-274	-274	-274	-274	-274	-274	-256	-256	-256	-256	-256	-256	-169	-169
PR	-473	-211	-204	-257	270	270	270	270	-219	-219	-219	-219	-219	-219	-219	-251	-251	-251	-251	-251	-251	-162	-162
HD	-172	-210	-293	-264	405	405	405	405	-211	-211	-211	-211	-211	-211	-211	-174	-174	-174	-174	-174	-174	-191	-191
ZB	-245	-210	-210	-210	221	221	221	221	-159	-159	-159	-159	-159	-159	-159	-174	-174	-174	-174	-174	-174	-144	-144
TI	-195	-127	-110	-110	293	293	293	293	-160	-160	-160	-160	-160	-160	-160	-158	-158	-158	-158	-158	-158	-97	-97
AB	-350	-350	-350	-350	344	344	344	344	-279	-279	-279	-279	-279	-279	-279	-218	-218	-218	-218	-218	-218	-222	-222
AL	-162	-151	-117	-117	303	303	303	303	-142	-142	-142	-142	-142	-142	-142	-98	-98	-98	-98	-98	-98	-68	-68
W1	-156	-192	-184	-112	266	266	266	266	-136	-136	-136	-136	-136	-136	-136	-126	-126	-126	-126	-126	-126	-154	-154
TS	-214	-194	-194	-112	270	270	270	270	-164	-164	-164	-164	-164	-164	-164	-122	-122	-122	-122	-122	-122	-145	-145
V	-190	-279	-260	-234	331	331	331	331	-242	-242	-242	-242	-242	-242	-242	-221	-221	-221	-221	-221	-221	-178	-178
CS	-244	-279	-279	-279	316	316	316	316	-252	-252	-252	-252	-252	-252	-252	-232	-232	-232	-232	-232	-232	-194	-194
CR	-73	-73	-73	-73	292	292	292	292	-163	-163	-163	-163	-163	-163	-163	-214	-214	-214	-214	-214	-214	-97	-97
HP	-263	-166	-134	-97	301	301	301	301	-143	-143	-143	-143	-143	-143	-143	-265	-265	-265	-265	-265	-265	-221	-221
SI	-64	-61	-50	-50	225	225	225	225	-131	-131	-131	-131	-131	-131	-131	-123	-123	-123	-123	-123	-123	-67	-67
U	-146	-167	-166	-166	235	235	235	235	-202	-202	-202	-202	-202	-202	-202	-194	-194	-194	-194	-194	-194	-124	-124
GA	-729	-729	-729	-729	194	194	194	194	-164	-164	-164	-164	-164	-164	-164	-164	-164	-164	-164	-164	-164	-48	-48
GE	-64	-64	-64	-64	226	226	226	226	-161	-161	-161	-161	-161	-161	-161	-156	-156	-156	-156	-156	-156	-54	-54
FZ	-119	-113	-112	-112	229	229	229	229	-87	-87	-87	-87	-87	-87	-87	-189	-189	-189	-189	-189	-189	-67	-67
CD	-64	-64	-64	-64	218	218	218	218	-66	-66	-66	-66	-66	-66	-66	-161	-161	-161	-161	-161	-161	-57	-57
II	-112	-112	-112	-112	213	213	213	213	-64	-64	-64	-64	-64	-64	-64	-176	-176	-176	-176	-176	-176	-52	-52
SH	-22	-22	-22	-22	205	205	205	205	-173	-173	-173	-173	-173	-173	-173	-172	-172	-172	-172	-172	-172	-54	-54
B	-23	-23	-23	-23	218	218	218	218	-161	-161	-161	-161	-161	-161	-161	-175	-175	-175	-175	-175	-175	-6	-6
CO	-253	-234	-234	-234	226	226	226	226	-166	-166	-166	-166	-166	-166	-166	-126	-126	-126	-126	-126	-126	-58	-58
NS	-113	-113	-113	-113	178	178	178	178	-104	-104	-104	-104	-104	-104	-104	-117	-117	-117	-117	-117	-117	-50	-50
SB	-112	-112	-112	-112	193	193	193	193	-104	-104	-104	-104	-104	-104	-104	-160	-160	-160	-160	-160	-160	-44	-44
TA	-111	-111	-111	-111	121	121	121	121	-104	-104	-104	-104	-104	-104	-104	-116	-116	-116	-116	-116	-116	-44	-44
SI	-110	-110	-110	-110	182	182	182	182	-96	-96	-96	-96	-96	-96	-96	-124	-124	-124	-124	-124	-124	-44	-44
PB	-110	-110	-110	-110	121	121	121	121	-96	-96	-96	-96	-96	-96	-96	-117	-117	-117	-117	-117	-117	-44	-44
CU	-110	-110	-110	-110	121	121	121	121	-96	-96	-96	-96	-96	-96	-96	-117	-117	-117	-117	-117	-117	-44	-44
HO	-110	-110	-110	-110	121	121	121	121	-96	-96	-96	-96	-96	-96	-96	-116	-116	-116	-116	-116	-116	-44	-44
C	-110	-110	-110	-110	114	114	114	114	-96	-96	-96	-96	-96	-96	-96	-122	-122	-122	-122	-122	-122	-44	-44
Tl	-110	-110	-110	-110	154	154	154	154	-96	-96	-96	-96	-96	-96	-96	-116	-116	-116	-116	-116	-116	-44	-44
W	-110	-110	-110	-110	121	121	121	121	-96	-96	-96	-96	-96	-96	-96	-115	-115	-115	-115	-115	-115	-44	-44
SE	-110	-110	-110	-110	123	123	123	123	-96	-96	-96	-96	-96	-96	-96	-116	-116	-116	-116	-116	-116	-44	-44
OS	-110	-110	-110	-110	143	143	143	143	-96	-96	-96	-96	-96	-96	-96	-127	-127	-127	-127	-127	-127	-44	-44
AS	-110	-110	-110	-110	116	116	116	116	-96	-96	-96	-96	-96	-96	-96	-116	-116	-116	-116	-116	-116	-44	-44
RS	-110	-110	-110	-110	116	116	116	116	-96	-96	-96	-96	-96	-96	-96	-116	-116	-116	-116	-116	-116	-44	-44
AU	-110	-110	-110	-110	116	116	116	116	-96	-96	-96	-96	-96	-96	-96	-116	-116	-116	-116	-116	-116	-44	-44

Table 31 (cont.)

Ag_2Cl	ZrCl_2	HfCl_3	YCl_3	TaCl_4	UCl_3	TlCl	HfCl_2	NdCl_3	PrCl_3	CeCl_3	LaCl_3	CaCl_2	NaCl	SrCl_2	BaCl_2	RbCl	CsCl
LI	-258	-286	-271	-263	-197	-194	-194	-131	-122	-110	-43	-8					
NA	-245	-247	-239	-226	-231	-197	-187	-171	-16	-159	-78	-41					
PA	-236	-222	-217	-196	-209	-177	-177	-155	-98	-50	-70						
K	-252	-263	-264	-248	-238	-215	-197	-193	-158	-150	-145	-60	-9	-7	-3		
SR	-230	-212	-208	-190	-202	-176	-176	-157	-111	-103	-97	-40	-15	-7			
HG	-173	-45	-62	-51	-44	-109	-130										
SC	-163	-11	-32	-21	-20	-96	-7										
Y	-168	-52	-66	-56	-50	-108	-37										
BE	-118	-202	-200	-183	-194	-173	-174	-156	-118	-111	-110	-82	-73	-65	-55		
BA	-224	-120	-120	-88	-108	-104	-104	-83	-23	-15	-8						
LA	-191	-111	-118	-76	-76	-97	-10	-97	-131	-93	-15						
CE	-187	-111	-112	-68	-70	-92	-92	-83	-128	-79	-8						
PR	-164	-104	-112	-68	-70	-84	-84	-75	-123	-77							
ND	-179	-94	-103	-57	-95	-82	-82	-77	-123	-77							
ZR	-140	-94	-102	-57	-95	-82	-82	-77	-123	-77							
TI	-213	-182	-163	-176	-159	-165	-144	-107	-101	-96	-96	-56	-40	-32	-23	+	
RB	-215	-94	-102	-57	-95	-82	-82	-77	-123	-77							
AL	-94	-95	-88	-57	-91	-81	-81	-76	-123	-77							
AN	-130	-63	-71	-57	-68	-51	-51	-49	-123	-77							
TH	-169	-142	-147	-142	-131	-146	-120	-80	-81	-77	-72	-45	-33	-27	-21	-13	-2
V	-142	-142	-147	-142	-131	-146	-120	-80	-81	-77	-72	-45	-33	-27	-21	-13	-2
CS	-59	-125	-125	-72	-72	-71	-71	-72	-72	-72	-72						
CR	-66	-28	-28	-5	-5	-2	-2										
HP	-66	-121	-121	-72	-72	-71	-71	-72	-72	-72	-72						
ZN	-121	-72	-72	-5	-5	-2	-2										
SI	-121	-72	-72	-5	-5	-2	-2										
U	-121	-72	-72	-5	-5	-2	-2										
GA	-49	-49	-49	-49	-49	-49	-49	-49	-49	-49	-49						
GE	-49	-49	-49	-49	-49	-49	-49	-49	-49	-49	-49						
PB	-41	-41	-41	-41	-41	-41	-41	-41	-41	-41	-41						
IN	-28	-28	-28	-28	-28	-28	-28	-28	-28	-28	-28						
CO	-20	-20	-20	-20	-20	-20	-20	-20	-20	-20	-20						
NI	-25	-25	-25	-25	-25	-25	-25	-25	-25	-25	-25						
SN	-29	-29	-29	-29	-29	-29	-29	-29	-29	-29	-29						
B	-29	-29	-29	-29	-29	-29	-29	-29	-29	-29	-29						
CD	-59	-59	-59	-59	-59	-59	-59	-59	-59	-59	-59						
NB	-33	-33	-33	-33	-33	-33	-33	-33	-33	-33	-33						
SB	-33	-33	-33	-33	-33	-33	-33	-33	-33	-33	-33						
TA	-33	-33	-33	-33	-33	-33	-33	-33	-33	-33	-33						
BI	-33	-33	-33	-33	-33	-33	-33	-33	-33	-33	-33						
PB	-33	-33	-33	-33	-33	-33	-33	-33	-33	-33	-33						
CU	-AO	-AO	-AO	-AO	-AO	-AO	-AO	-AO	-AO	-AO	-AO						
C	-39	-39	-39	-39	-39	-39	-39	-39	-39	-39	-39						
TL	-W	-W	-W	-W	-W	-W	-W	-W	-W	-W	-W						
RE	-OS	-OS	-OS	-OS	-OS	-OS	-OS	-OS	-OS	-OS	-OS						
AG	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1						
HG	-AU	-AU	-AU	-AU	-AU	-AU	-AU	-AU	-AU	-AU	-AU						

J. Chromate Reactions

The reactions between 49 metals and 5 chromates were programmed on the computer. A total of 2920 possible reactions was examined, and 114 of these were printed. As mentioned previously, when two reactants undergo more than one reaction, only the most energetic one is printed. The reactions with positive enthalpies are also discarded. The chromates are the least energetic of the oxide systems examined. The most energetic reaction exhibits an enthalpy of only -3845 cal/cc.

Representative computer data for a few of the chromate reactions are illustrated in Table 32. The relatively low energies of these reactions are due primarily to the high heat of formation of the chromates. The high heats of formation of the product oxides partially compensate for this.

The periodic variation of the enthalpies of the reactions of the metals with lead chromate is shown in Figure 24. The trends are the same as those observed in the other oxide systems. The Group II metals (beryllium, magnesium, and calcium), the Group IVB metals (titanium, zirconium, and hafnium) and the rare earths (lanthanum, cerium, praseodymium, neodymium, samarium, gadolinium, terbium, holmium, erbium, thorium, uranium, and neptunium) are effective reducing agents. With the exception of Group IVB, which is anomalous because of the lanthanide contraction, the energies within a group tend to decrease with increasing atomic number. This is apparent in Group IA (lithium, rubidium, and cesium), Group IIA (beryllium, magnesium, strontium, and barium), Group VB (vanadium, niobium, and tantalum), and Group VIB (chromium, molybdenum, and tungsten). Except for displacement of the vertical scale, the other chromates exhibit similar trends.

The most energetic chromate reactions are listed in Tables 33 and 34. A summary of the enthalpies of all the chromate reactions is presented in Tables 35 and 36. The trends described previously are evident in Tables 35 and 36. Lead and silver chromate are the most effective oxidizers on a volumetric basis, and sodium and lead chromate are the most effective on a gravimetric basis.

Table 32
DATA ON REACTIONS OF VARIOUS METALS WITH CHROMATES

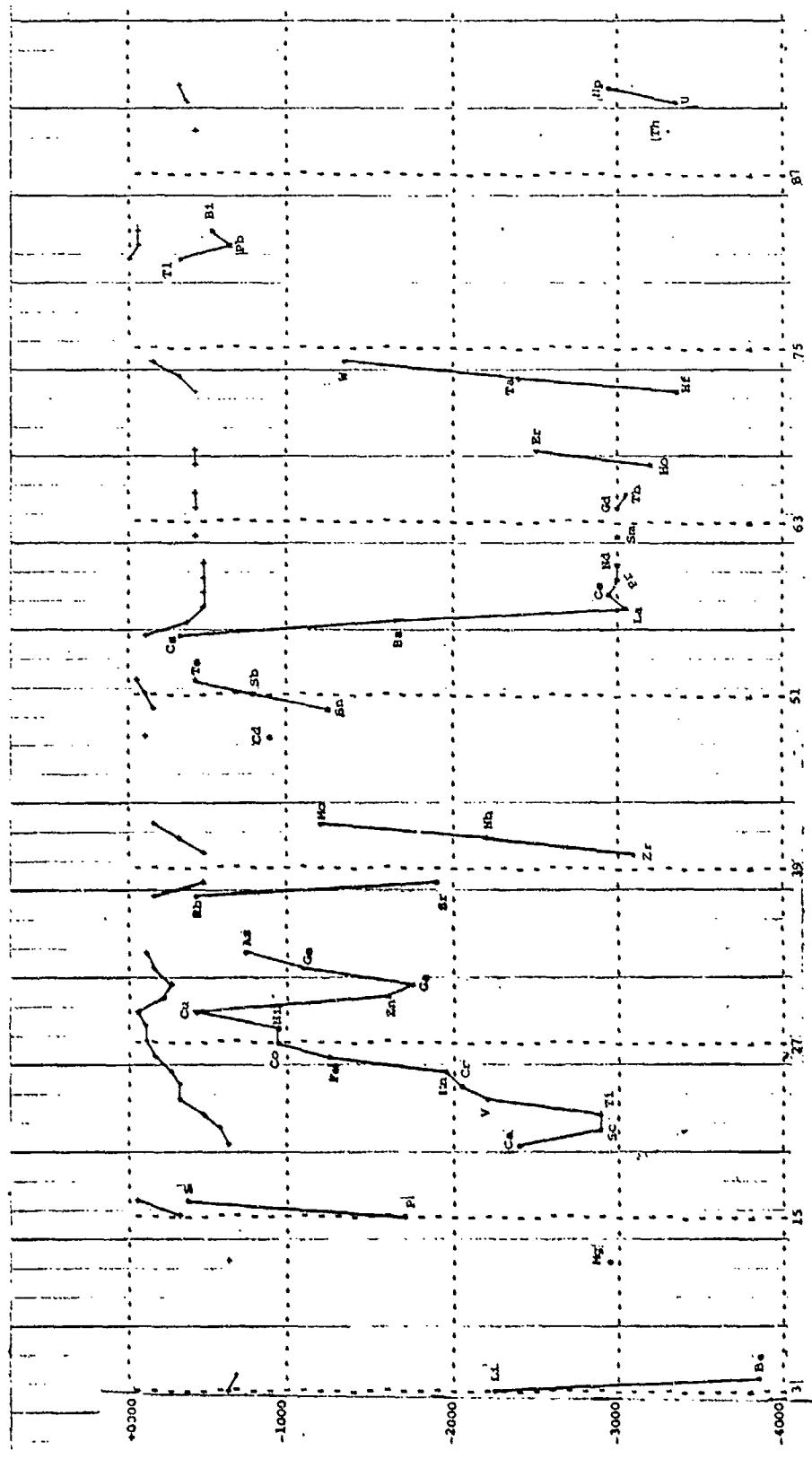
	$3 \text{ Ge} + 4 \text{ Ag}_2\text{CrO}_4 = 4 \text{ Ag}_2\text{O} + 3 \text{ GeO}_2 + 2 \text{ Cr}_2\text{O}_3$			
Heat of formation	-170.15	-7.31	-128.30	-269.70
Molecular weight	331.70	231.76	104.60	152.02
Density	5.63	7.14	4.70	5.21
Melting point, °C				
Boiling point, °C	960.00	300.00	1000.00	2265.00
Heat of reaction, kcal	2700.00			
Reactants' density	-272.92			
Gravimetric enthalpy, cal/g	5.58			
Volumetric enthalpy, cal/cc	-176.66			
	-986.58			
	$3 \text{ Hf} + 4 \text{ Ag}_2\text{CrO}_4 = 4 \text{ Ag}_2\text{O} + 3 \text{ HfO}_2 + 2 \text{ Cr}_2\text{O}_3$			
Heat of formation	-170.15	-7.31	-271.50	-269.70
Molecular weight	331.77	231.76	210.60	152.02
Density	5.63	7.14	9.68	5.21
Melting point, °C				
Boiling point, °C	113.30	3200.00	2810.00	2265.00
Heat of reaction, kcal	2227.00			
Reactants' density	-702.52			
Gravimetric enthalpy, cal/g	6.74			
Volumetric enthalpy, cal/cc	-377.18			
	-2543.64			
	$2 \text{ Ho} + 2 \text{ Ag}_2\text{CrO}_4 = 2 \text{ Ag}_2\text{O} + \text{ Ho}_2\text{O}_3 + \text{ Cr}_2\text{O}_3$			
Heat of formation	-170.15	-7.31	-449.60	-269.70
Molecular weight	331.77	231.76	377.88	152.02
Density	5.63	7.14	5.21	
Melting point, °C				
Boiling point, °C	164.94	300.00	2265.00	
Heat of reaction, kcal	6.38			
Reactants' density	8.76			
Gravimetric enthalpy, cal/g	-396.22			
Volumetric enthalpy, cal/cc	-2529.31			

Table 32 (cont.)

	2 La	+ 2 Ag ₂ CrO ₄	= 2 Ag ₂ O + La ₂ O ₃ + Cr ₂ O ₃
Heat of formation		-170.15	-7.31
Molecular weight	138.92	331.77	231.76
Density	6.15	5.63	7.14
Melting point, °C	880.00		300.00
Boiling point, °C	1800.00		2315.00
Heat of reaction, kcal	-402.01		4200.00
Reactants' density	5.77		
Gravimetric enthalpy, cal/g	-427.95		
Volumetric enthalpy, cal/cc	-2464.22		
	6 Li	+ 2 Ag ₂ CrO ₄	= 2 Ag ₂ O + 3 Li ₂ O + Cr ₂ O ₃
Heat of formation		-170.15	-142.40
Molecular weight	6.94	331.77	231.76
Density	.53	5.63	7.14
Melting point, °C	180.00		300.00
Boiling point, °C	1326.00		1700.00
Heat of reaction, kcal	-371.21		
Reactants' density	3.60		
Gravimetric enthalpy, cal/g	-526.41		
Volumetric enthalpy, cal/cc	-1894.52		
	3 Mg	+ 2 Ag ₂ CrO ₄	= 2 Ag ₂ O + 3 MgO + Cr ₂ O ₃
Heat of formation		-170.15	-143.84
Molecular weight	24.32	331.77	231.76
Density	1.74	5.63	7.14
Melting point, °C	650.00		300.00
Boiling point, °C	1120.00		2800.00
Heat of reaction, kcal	-375.53		
Reactants' density	4.61		
Gravimetric enthalpy, cal/g	-509.89		
Volumetric enthalpy, cal/cc	-2348.64		

Table 32 (cont.)

	8 La	+ 6 PbCrO ₄	= 3 Pb ₂ O + 4 La ₂ O ₃ + 3 Cr ₂ O ₃
Heat of formation		-217.70	-51.20
Molecular weight	138.92	323.22	430.42
Density	6.15	6.30	8.34
Melting point, °C	880.00	844.00	2315.00
Boiling point, °C	1800.00		4200.00
Heat of reaction, kcal	-1488.50		
Reactants' density	6.24		
Gravimetric enthalpy, cal/g	-487.92		
Volumetric enthalpy, cal/cc	-3046.85		
	8 Li	+ 2 PbCrO ₄	= Pb ₂ O + 4 Li ₂ O + Cr ₂ O ₃
Heat of formation		-217.70	-51.20
Molecular weight	6.94	323.22	430.42
Density	.53	6.30	8.34
Melting point, °C	180.00	844.00	1700.00
Boiling point, °C	1326.00		
Heat of reaction, kcal	-455.10		
Reactants' density	3.40		
Gravimetric enthalpy, cal/g	-648.33		
Volumetric enthalpy, cal/cc	-2203.03		
	4 Mg	+ 2 PbCrO ₄	= Pb ₂ O + 4 MgO + Cr ₂ O ₃
Heat of formation		-217.70	-51.20
Molecular weight	24.32	323.22	430.42
Density	1.74	6.30	8.34
Melting point, °C	650.00	844.00	2800.00
Boiling point, °C	1120.00		
Heat of reaction, kcal	-460.86		
Reactants' density	4.69		
Gravimetric enthalpy, cal/g	-619.67		
Volumetric enthalpy, cal/cc	-2907.31		



GRAVIMETRIC AND VOLUMETRIC ENTHALPIES OF REACTIONS OF METALS WITH $PbCrO_3$

Figure 24

Table 33

MOST ENERGETIC CHROMATE AND DICHROMATE REACTIONS WITH METALS,
IN TERMS OF VOLUMETRIC ENTHALPY

Reaction					Enthalpy, cal/cc
4 Be + 2 Pb(CrO ₄)	=	Pb ₂ O + 4 BeO	+ Cr ₂ O ₃		-3845
2 U + 2 Pb(CrO ₄)	=	Pb ₂ O + 2 UO ₂	+ Cr ₂ O ₃		-3322
2 Hf + 2 Pb(CrO ₄)	=	Pb ₂ O + 2 HfO ₂	+ Cr ₂ O ₃		-3310
2 Th + 2 Pb(CrO ₄)	=	Pb ₂ O + 2 ThO ₂	+ Cr ₂ O ₃		-3259
8 Ho + 6 Pb(CrO ₄)	=	3 Pb ₂ O + 4 Ho ₂ O ₃	+ 4 Ho ₂ O ₃		-3173
2 Zr + 2 Pb(CrO ₄)	=	Pb ₂ O + 2 ZrO ₂	+ Cr ₂ O ₃		-3065
8 Tb + 6 Pb(CrO ₄)	=	3 Pb ₂ O + 4 Tb ₂ O ₃	+ 3 Cr ₂ O ₃		-3048
8 La + 6 Pb(CrO ₄)	=	3 Pb ₂ O + 4 La ₂ O ₃	+ 3 Cr ₂ O ₃		-3046
8 Sm + 6 Pb(CrO ₄)	=	3 Pb ₂ O + 4 Sm ₂ O ₃	+ 3 Cr ₂ O ₃		-2999
8 Nd + 6 Pb(CrO ₄)	=	3 Pb ₂ O + 4 Nd ₂ O ₃	+ 3 Cr ₂ O ₃		-2998
8 Gd + 6 Pb(CrO ₄)	=	3 Pb ₂ O + 4 Gd ₂ O ₃	+ 3 Cr ₂ O ₃		-2986
8 Pr + 6 Pb(CrO ₄)	=	3 Pb ₂ O + 4 Pr ₂ O ₃	+ 3 Cr ₂ O ₃		-2980
8 Ce + 6 Pb(CrO ₄)	=	3 Pb ₂ O + 4 Ce ₂ O ₃	+ 3 Cr ₂ O ₃		-2939
2 Np + 2 Pb(CrO ₄)	=	Pb ₂ O + 2 NpO ₂	+ Cr ₂ O ₃		-2914
4 Mg + 2 Pb(CrO ₄)	=	Pb ₂ O + 4 MgO	+ Cr ₂ O ₃		-2907
3 Be + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + 3 BeO	+ Cr ₂ O ₃		-2881
8 Sc + 6 Pb(CrO ₄)	=	3 Pb ₂ O + 4 Sc ₂ O ₃	+ 3 Cr ₂ O ₃		-2879
8 Ti + 6 Pb(CrO ₄)	=	3 Pb ₂ O + 4 Ti ₂ O ₃	+ 3 Cr ₂ O ₃		-2861
3 Th + 4 Ag ₂ (CrO ₄)	=	4 Ag ₂ O + 3 ThO ₂	+ 2 Cr ₂ O ₃		-2563
3 U + 4 Ag ₂ (CrO ₄)	=	4 Ag ₂ O + 3 UO ₂	+ 2 Cr ₂ O ₃		-2546
3 Hf + 4 Ag ₂ (CrO ₄)	=	4 Ag ₂ O + 3 HfO ₂	+ 2 Cr ₂ O ₃		-2543
2 Ho + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + Ho ₂ O ₃	+ Cr ₂ O ₃		-2529
8 Er + 6 Pb(CrO ₄)	=	3 Pb ₂ O + 4 Er ₂ O ₃	+ 3 Cr ₂ O ₃		-2499
2 La + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + La ₂ O ₃	+ Cr ₂ O ₃		-2464
2 Tb + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + Tb ₂ O ₃	+ Cr ₂ O ₃		-2439
2 Nd + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + Nd ₂ O ₃	+ Cr ₂ O ₃		-2415
2 Pr + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + Pr ₂ O ₃	+ Cr ₂ O ₃		-2408
2 Sm + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + Sm ₂ O ₃	+ Cr ₂ O ₃		-2406
2 Gd + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + Gd ₂ O ₃	+ Cr ₂ O ₃		-2398

Table 33 (cont.)

Reaction					Enthalpy, cal/cc
4 Ca + 2 Pb(CrO ₄)	=	Pb ₂ O + 4 CaO	+ Cr ₂ O ₃		-2393
3 Zr + 4 Ag ₂ (CrO ₄)	=	4 Ag ₂ O + 3 ZrO ₂	+ 2 Cr ₂ O ₃		-2377
8 Ta + 10 Pb(CrO ₄)	=	5 Pb ₂ O + 4 Ta ₂ O ₅	+ 5 Cr ₂ O ₃		-2377
2 Ce + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + Ce ₂ O ₃	+ Cr ₂ O ₃		-2371
3 Mg + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + 3 MgO	+ Cr ₂ O ₃		-2348
2 Sc + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + Sc ₂ O ₃	+ Cr ₂ O ₃		-2306
3 Be + 2 Ba(CrO ₄)	=	2 BaO + 3 BeO	+ Cr ₂ O ₃		-2293
3 Np + 4 Ag ₂ (CrO ₄)	=	4 Ag ₂ O + 3 NpO ₂	+ 2 Cr ₂ O ₃		-2265
2 Ti + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + Ti ₂ O ₃	+ Cr ₂ O ₃		-2233
8 Li + 2 Pb(CrO ₄)	=	Pb ₂ O + 4 Li ₂ O	+ Cr ₂ O ₃		-2203
2 Nb + 2 Pb(CrO ₄)	=	Pb ₂ O + Nb ₂ O ₄	+ Cr ₂ O ₃		-2197
8 V + 6 Pb(CrO ₄)	=	3 Pb ₂ O + 4 V ₂ O ₃	+ 3 Cr ₂ O ₃		-2170
2 Er + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + Er ₂ O ₃	+ Cr ₂ O ₃		-2113
3 Ca + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + 3 CaO	+ Cr ₂ O ₃		-2044
3 Th + 4 Ba(CrO ₄)	=	4 BaO + 3 ThO ₂	+ 2 Cr ₂ O ₃		-2030
3 Be + 2 Na ₂ (CrO ₄)	=	2 Na ₂ O + 3 BeO	+ Cr ₂ O ₃		-2022
8 Cr + 6 Pb(CrO ₄)	=	3 Pb ₂ O + 4 Cr ₂ O ₃	+ 3 Cr ₂ O ₃		-2011
2 La + 2 Ba(CrO ₄)	=	2 BaO + La ₂ O ₃	+ Cr ₂ O ₃		-1976
3 Hf + 4 Ba(CrO ₄)	=	4 BaO + 3 HfO ₂	+ 2 Cr ₂ O ₃		-1966
2 Tb + 2 Ba(CrO ₄)	=	2 BaO + Tb ₂ O ₃	+ Cr ₂ O ₃		-1927
2 Nd + 2 Ba(CrO ₄)	=	2 BaO + Nd ₂ O ₃	+ Cr ₂ O ₃		-1915
2 Pr + 2 Ba(CrO ₄)	=	2 BaO + Pr ₂ O ₃	+ Cr ₂ O ₃		-1912
4 Mn + 2 Pb(CrO ₄)	=	Pb ₂ O + 4 MnO	+ Cr ₂ O ₃		-1904
2 Sm + 2 Ba(CrO ₄)	=	2 BaO + Sm ₂ O ₃	+ Cr ₂ O ₃		-1897
6 Li + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + 3 Li ₂ O	+ Cr ₂ O ₃		-1894
4 Sr + 2 Pb(CrO ₄)	=	Pb ₂ O + 4 SrO	+ Cr ₂ O ₃		-1894
2 Gd + 2 Ba(CrO ₄)	=	2 BaO + Gd ₂ O ₃	+ Cr ₂ O ₃		-1890
2 Ce + 2 Ba(CrO ₄)	=	2 BaO + Ce ₂ O ₃	+ Cr ₂ O ₃		-1870
6 Ta + 10 Ag ₂ (CrO ₄)	=	10 Ag ₂ O + 3 Ta ₂ O ₅	+ 5 Cr ₂ O ₃		-1861
3 Zr + 4 Ba(CrO ₄)	=	4 BaO + 3 ZrO ₂	+ 2 Cr ₂ O ₃		-1799
2 Sc + 2 Ba(CrO ₄)	=	2 BaO + Sc ₂ O ₃	+ Cr ₂ O ₃		-1782

Table 33 (cont.)

Reaction					Enthalpy, cal/cc
2 La + 2 Na ₂ (CrO ₄)	=	2 Na ₂ O + La ₂ O ₃	+ Cr ₂ O ₃		-1768
6 Nb + 8 Ag ₂ (CrO ₄)	=	8 Ag ₂ O + 3 Nb ₂ O ₄	+ 4 Cr ₂ O ₃		-1749
2 V + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + V ₂ O ₃	+ Cr ₂ O ₃		-1732
3 Hf + 4 Na ₂ (CrO ₄)	=	4 Na ₂ O + 3 HfO ₂	+ 2 Cr ₂ O ₃		-1722
8 Ga + 6 Pb(CrO ₄)	=	3 Pb ₂ O + 4 Ga ₂ O ₃	+ 3 Cr ₂ O ₃		-1711
2 Nd + 2 Na ₂ (CrO ₄)	=	2 Na ₂ O + Nd ₂ O ₃	+ Cr ₂ O ₃		-1705
2 Sm + 2 Na ₂ (CrO ₄)	=	2 Na ₂ O + Sm ₂ O ₃	+ Cr ₂ O ₃		-1684
2 Gd + 2 Na ₂ (CrO ₄)	=	2 Na ₂ O + Gd ₂ O ₃	+ Cr ₂ O ₃		-1679
3 Np + 4 Ba(CrO ₄)	=	4 BaO + 3 NpO ₂	+ 2 Cr ₂ O ₃		-1677
3 Sr + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + 3 SrO	+ Cr ₂ O ₃		-1676
2 Al + 2 Na ₂ (CrO ₄)	=	2 Na ₂ O + Al ₂ O ₃	+ Cr ₂ O ₃		-1665
8 P + 6 Pb(CrO ₄)	=	3 Pb ₂ O + 4 P ₂ O ₃	+ 3 Cr ₂ O ₃		-1658
2 Ti + 2 Ba(CrO ₄)	=	2 BaO + Ti ₂ O ₃	+ Cr ₂ O ₃		-1649
4 Ba + 2 Pb(CrO ₄)	=	Pb ₂ O + 4 BaO	+ Cr ₂ O ₃		-1614
2 Sc + 2 Na ₂ (CrO ₄)	=	2 Na ₂ O + Sc ₂ O ₃	+ Cr ₂ O ₃		-1570
4 Zn + 2 Pb(CrO ₄)	=	Pb ₂ O + 4 ZnO	+ Cr ₂ O ₃		-1566
3 Zr + 4 Na ₂ (CrO ₄)	=	4 Na ₂ O + 3 ZrO ₂	+ 2 Cr ₂ O ₃		-1565
3 Mn + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + 3 MnO	+ Cr ₂ O ₃		-1561
3 Ba + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + 3 BaO	+ Cr ₂ O ₃		-1460
2 Ga + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + Ga ₂ O ₃	+ Cr ₂ O ₃		-1426
2 P + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + P ₂ O ₃	+ Cr ₂ O ₃		-1407
3 Zn + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + 3 ZnO	+ Cr ₂ O ₃		-1330
4 W + 6 Pb(CrO ₄)	=	3 Pb ₂ O + 4 WO ₃	+ 3 Cr ₂ O ₃		-1329
3 Sr + 2 Ba(CrO ₄)	=	2 BaO + 3 SrO	+ Cr ₂ O ₃		-1296
3 Fe + 2 Pb(CrO ₄)	=	Pb ₂ O + Fe ₃ O ₄	+ Cr ₂ O ₃		-1230
2 Sn + 2 Pb(CrO ₄)	=	Pb ₂ O + 2 SnO ₂	+ Cr ₂ O ₃		-1206
2 Mo + 2 Pb(CrO ₄)	=	Pb ₂ O + 2 MoO ₂	+ Cr ₂ O ₃		-1198
3 Sr + 2 Na ₂ (CrO ₄)	=	2 Na ₂ O + 3 SrO	+ Cr ₂ O ₃		-1162
W + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + WO ₃	+ Cr ₂ O ₃		-1136
2 Al + 2 K ₂ (CrO ₄)	=	2 K ₂ O + Al ₂ O ₃	+ Cr ₂ O ₃		-1113

Table 33 (cont.)

Reaction					Enthalpy, cal/cc
2 Ge + 2 Pb(CrO ₄)	=	Pb ₂ O + 2 GeO ₂	+ Cr ₂ O ₃		-1095
9 Fe + 8 Ag ₂ (CrO ₄)	=	8 Ag ₂ O + 3 Fe ₃ O ₄	+ 4 Cr ₂ O ₃		-1076
3 Sn + 4 Ag ₂ (CrO ₄)	=	4 Ag ₂ O + 3 SnO ₂	+ 2 Cr ₂ O ₃		-1068
3 Ge + 4 Ag ₂ (CrO ₄)	=	4 Ag ₂ O + 3 GeO ₂	+ 2 Cr ₂ O ₃		-986
3 Ni + 2 Pb(CrO ₄)	=	2 PbO + 3 NiO	+ Cr ₂ O ₃		-933
3 Co + 2 Pb(CrO ₄)	=	2 PbO + 3 CoO	+ Cr ₂ O ₃		-903
3 Ni + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + 3 NiO	+ Cr ₂ O ₃		-865
3 Cd + 2 Pb(CrO ₄)	=	2 PbO + 3 CdO	+ Cr ₂ O ₃		-859
3 Cd + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + 3 CdO	+ Cr ₂ O ₃		-806
4 Sb + 4 Pb(CrO ₄)	=	4 PbO + Sb ₄ O ₆	+ 2 Cr ₂ O ₃		-773
2 As + 2 Pb(CrO ₄)	=	2 PbO + As ₂ O ₃	+ Cr ₂ O ₃		-739
3 Pb + 2 Pb(CrO ₄)	=	2 PbO + 3 PbO	+ Cr ₂ O ₃		-611
3 Bi + 2 Pb(CrO ₄)	=	2 PbO + 3 BiO	+ Cr ₂ O ₃		-533
3 Te + 4 Pb(CrO ₄)	=	4 PbO + 3 TeO ₂	+ 2 Cr ₂ O ₃		-417
3 Te + 4 Ag ₂ (CrO ₄)	=	4 Ag ₂ O + 3 TeO ₂	+ 2 Cr ₂ O ₃		-407
3 Cu + 2 Pb(CrO ₄)	=	2 PbO + 3 CuO	+ Cr ₂ O ₃		-406
6 Rb + 2 Pb(CrO ₄)	=	2 PbO + 3 Rb ₂ O	+ Cr ₂ O ₃		-401
6 Rb + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + 3 Rb ₂ O	+ Cr ₂ O ₃		-399
S + 2 Pb(CrO ₄)	=	2 PbO + SO ₃	+ Cr ₂ O ₃		-370
6 Cs + 2 Pb(CrO ₄)	=	2 PbO + 3 Cs ₂ O	+ Cr ₂ O ₃		-315
6 Tl + 2 Pb(CrO ₄)	=	2 PbO + 3 Tl ₂ O	+ Cr ₂ O ₃		-314
6 Rb + 2 Ba(CrO ₄)	=	2 BaO + 3 Rb ₂ O	+ Cr ₂ O ₃		-202
6 Rb + 2 Na ₂ (CrO ₄)	=	2 Na ₂ O + 3 Rb ₂ O	+ Cr ₂ O ₃		-154
6 Rb + 2 K ₂ (CrO ₄)	=	2 K ₂ O + 3 Rb ₂ O	+ Cr ₂ O ₃		-38

Table 34

MOST ENERGETIC CHROMATE AND DICHROMATE REACTIONS WITH METALS,
IN TERMS OF GRAVIMETRIC ENTHALPY

Reaction					Enthalpy, cal/g
3 Be + 2 Na ₂ (CrO ₄)	=	2 Na ₂ O + 3 BeO	+ Cr ₂ O ₃		-772
4 Be + 2 Pb(CrO ₄)	=	Pb ₂ O + 4 BeO	+ Cr ₂ O ₃		-687
8 Li + 2 Pb(CrO ₄)	=	Pb ₂ O + 4 Li ₂ O	+ Cr ₂ O ₃		-648
4 Mg + 2 Pb(CrO ₄)	=	Pb ₂ O + 4 MgO	+ Cr ₂ O ₃		-619
2 Al + 2 Na ₂ (CrO ₄)	=	2 Na ₂ O + Al ₂ O ₃	+ Cr ₂ O ₃		-614
4 Ca + 2 Pb(CrO ₄)	=	Pb ₂ O + 4 CaO	+ Cr ₂ O ₃		-611
2 Sc + 2 Na ₂ (CrO ₄)	=	2 Na ₂ O + Sc ₂ O ₃	+ Cr ₂ O ₃		-590
8 Sc + 6 Pb(CrO ₄)	=	3 Pb ₂ O + 4 Sc ₂ O ₃	+ 3 Cr ₂ O ₃		-565
3 Be + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + 3 BeO	+ Cr ₂ O ₃		-553
3 Be + 2 Ba(CrO ₄)	=	2 BaO + 3 BeO	+ Cr ₂ O ₃		-546
6 Li + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + 3 Li ₂ O	+ Cr ₂ O ₃		-526
3 Ca + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + 3 CaO	+ Cr ₂ O ₃		-509
3 Mg + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + 3 MgO	+ Cr ₂ O ₃		-509
8 La + 6 Pb(CrO ₄)	=	3 Pb ₂ O + 4 La ₂ O ₃	+ 3 Cr ₂ O ₃		-487
2 Zr + 2 Pb(CrO ₄)	=	Pb ₂ O + 2 ZrO ₂	+ Cr ₂ O ₃		-484
8 Ti + 6 Pb(CrO ₄)	=	3 Pb ₂ O + 4 Ti ₂ O ₃	+ 3 Cr ₂ O ₃		-484
2 La + 2 Na ₂ (CrO ₄)	=	2 Na ₂ O + La ₂ O ₃	+ Cr ₂ O ₃		-484
3 Zr + 4 Na ₂ (CrO ₄)	=	4 Na ₂ O + 3 ZrO ₂	+ 2 Cr ₂ O ₃		-478
2 Sc + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + Sc ₂ O ₃	+ Cr ₂ O ₃		-471
8 Pr + 6 Pb(CrO ₄)	=	3 Pb ₂ O + 4 Pr ₂ O ₃	+ 3 Cr ₂ O ₃		-467
8 Nd + 6 Pb(CrO ₄)	=	3 Pb ₂ O + 4 Nd ₂ O ₃	+ 3 Cr ₂ O ₃		-460
8 Ce + 6 Pb(CrO ₄)	=	3 Pb ₂ O + 4 Ce ₂ O ₃	+ 3 Cr ₂ O ₃		-456
4 Sr + 2 Pb(CrO ₄)	=	Pb ₂ O + 4 SrO	+ Cr ₂ O ₃		-451
2 Nd + 2 Na ₂ (CrO ₄)	=	2 Na ₂ O + Nd ₂ O ₃	+ Cr ₂ O ₃		-449
8 Er + 6 Pb(CrO ₄)	=	3 Pb ₂ O + 4 Er ₂ O ₃	+ 3 Cr ₂ O ₃		-448
8 Ho + 6 Pb(CrO ₄)	=	3 Pb ₂ O + 4 Ho ₂ O ₃	+ 3 Cr ₂ O ₃		-446
2 Sc + 2 Ba(CrO ₄)	=	2 BaO + Sc ₂ O ₃	+ Cr ₂ O ₃		-443
8 Sm + 6 Pb(CrO ₄)	=	3 Pb ₂ O + 4 Sm ₂ O ₃	+ 3 Cr ₂ O ₃		-443
3 Sr + 2 Na ₂ (CrO ₄)	=	2 Na ₂ O + 3 SrO	+ Cr ₂ O ₃		-437

Table 34 (cont.)

Reaction					Enthalpy, cal/g
8 Tb + 6 Pb(CrO ₄)	=	3 Pb ₂ O + 4 Tb ₂ O ₃ + 3 Cr ₂ O ₃			-437
8 Gd + 6 Pb(CrO ₄)	=	3 Pb ₂ O + 4 Gd ₂ O ₃ + 3 Cr ₂ O ₃			-435
2 Sm + 2 Na ₂ (CrO ₄)	=	2 Na ₂ O + Sm ₂ O ₃ + Cr ₂ O ₃			-427
2 La + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + La ₂ O ₃ + Cr ₂ O ₃			-427
2 Hf + 2 Pb(CrO ₄)	=	Pb ₂ O + 2 HfO ₂ + Cr ₂ O ₃			-427
2 Th + 2 Pb(CrO ₄)	=	Pb ₂ O + 2 ThO ₂ + Cr ₂ O ₃			-422
2 Gd + 2 Na ₂ (CrO ₄)	=	2 Na ₂ O + Gd ₂ O ₃ + Cr ₂ O ₃			-418
3 Zr + 4 Ag ₂ (CrO ₄)	=	4 Ag ₂ O + 3 ZrO ₂ + 2 Cr ₂ O ₃			-413
2 Pr + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + Pr ₂ O ₃ + Cr ₂ O ₃			-410
2 Ti + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + Ti ₂ O ₃ + Cr ₂ O ₃			-409
2 Al + 2 K ₂ (CrO ₄)	=	2 K ₂ O + Al ₂ O ₃ + Cr ₂ O ₃			-408
3 Hf + 4 Na ₂ (CrO ₄)	=	4 Na ₂ O + 3 HfO ₂ + 2 Cr ₂ O ₃			-406
2 Nd + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + Nd ₂ O ₃ + Cr ₂ O ₃			-405
2 Ce + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + Ce ₂ O ₃ + Cr ₂ O ₃			-401
2 Er + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + Er ₂ O ₃ + Cr ₂ O ₃			-398
2 La + 2 Ba(CrO ₄)	=	2 BaO + La ₂ O ₃ + Cr ₂ O ₃			-397
3 Sr + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + SrO + Cr ₂ O ₃			-396
2 Ho + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + Ho ₂ O ₃ + Cr ₂ O ₃			-396
2 Sm + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + Sm ₂ O ₃ + Cr ₂ O ₃			-391
2 Tb + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + Tb ₂ O ₃ + Cr ₂ O ₃			-388
2 Gd + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + Gd ₂ O ₃ + Cr ₂ O ₃			-386
2 U + 2 Pb(CrO ₄)	=	Pb ₂ O + 2 UO ₂ + Cr ₂ O ₃			-379
2 Pr + 2 Ba(CrO ₄)	=	2 BaO + Pr ₂ O ₃ + Cr ₂ O ₃			-378
3 Th + 4 Ag ₂ (CrO ₄)	=	4 Ag ₂ O + 3 ThO ₂ + 2 Cr ₂ O ₃			-377
3 Hf + 4 Ag ₂ (CrO ₄)	=	4 Ag ₂ O + 3 HfO ₂ + 2 Cr ₂ O ₃			-377
3 Zr + 4 Ba(CrO ₄)	=	4 BaO + 3 ZrO ₂ + 2 Cr ₂ O ₃			-374
2 Nd + 2 Ba(CrO ₄)	=	2 BaO + Nd ₂ O ₃ + Cr ₂ O ₃			-372
2 Ce + 2 Ba(CrO ₄)	=	2 BaO + Ce ₂ O ₃ + Cr ₂ O ₃			-367
2 Ti + 2 Ba(CrO ₄)	=	2 BaO + Ti ₂ O ₃ + Cr ₂ O ₃			-366
3 Sr + 2 Ba(CrO ₄)	=	2 BaO + 3 SrO + Cr ₂ O ₃			-360
2 Sm + 2 Ba(CrO ₄)	=	2 BaO + Sm ₂ O ₃ + Cr ₂ O ₃			-356

Table 34 (cont.)

Reaction					Enthalpy, cal/g
2 Tb + 2 Ba(CrO ₄)	=	2 BaO + Tb ₂ O ₃	+ Cr ₂ O ₃		-352
2 Gd + 2 Ba(CrO ₄)	=	2 BaO + Gd ₂ O ₃	+ Cr ₂ O ₃		-350
4 Ba + 2 Pb(CrO ₄)	=	Pb ₂ O + 4 BaO	+ Cr ₂ O ₃		-350
8 V + 6 Pb(CrO ₄)	=	3 Pb ₂ O + 4 V ₂ O ₃	+ 3 Cr ₂ O ₃		-347
3 U + 4 Ag ₂ (CrO ₄)	=	4 Ag ₂ O + 3 UO ₂	+ 2 Cr ₂ O ₃		-341
3 Th + 4 Ba(CrO ₄)	=	4 BaO + 3 ThO ₂	+ 2 Cr ₂ O ₃		-341
3 Hf + 4 Ba(CrO ₄)	=	4 BaO + 3 HfO ₂	+ 2 Cr ₂ O ₃		-337
2 Np + 2 Pb(CrO ₄)	=	Pb ₂ O + 2 NpO ₂	+ Cr ₂ O ₃		-336
8 P + 6 Pb(CrO ₄)	=	3 Pb ₂ O + 4 P ₂ O ₃	+ 3 Cr ₂ O ₃		-336
2 Nb + 2 Pb(CrO ₄)	=	Pb ₂ O + Nb ₂ O ₄	+ Cr ₂ O ₃		-328
3 Ba + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + 3 BaO	+ Cr ₂ O ₃		-320
8 Cr + 6 Pb(CrO ₄)	=	3 Pb ₂ O + 4 Cr ₂ O ₃	+ 3 Cr ₂ O ₃		-312
3 Np + 4 Ag ₂ (CrO ₄)	=	4 Ag ₂ O + 3 NpO ₂	+ 2 Cr ₂ O ₃		-307
2 V + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + V ₂ O ₃	+ Cr ₂ O ₃		-305
8 Ta + 10 Pb(CrO ₄)	=	5 Pb ₂ O + 4 Ta ₂ O ₅	+ 5 Cr ₂ O ₃		-304
2 P + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + P ₂ O ₃	+ Cr ₂ O ₃		-294
4 Mn + 2 Pb(CrO ₄)	=	Pb ₂ O + 4 MnO	+ Cr ₂ O ₃		-292
6 Nb + 8 Ag ₂ (CrO ₄)	=	8 Ag ₂ O + 3 Nb ₂ O ₄	+ 4 Cr ₂ O ₃		-292
6 Ta + 10 Ag ₂ (CrO ₄)	=	10 Ag ₂ O + 3 Ta ₂ O ₅	+ 5 Cr ₂ O ₃		-277
8 Ga + 6 Pb(CrO ₄)	=	3 Pb ₂ O + 4 Ga ₂ O ₃	+ 3 Cr ₂ O ₃		-275
3 Mn + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + 3 MnO	+ Cr ₂ O ₃		-265
3 Np + 4 Ba(CrO ₄)	=	4 BaO + 3 NpO ₂	+ 2 Cr ₂ O ₃		-258
2 Ga + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + Ga ₂ O ₃	+ Cr ₂ O ₃		-251
4 Zn + 2 Pb(CrO ₄)	=	Pb ₂ O + 4 ZnO	+ Cr ₂ O ₃		-240
3 Zn + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + 3 ZnO	+ Cr ₂ O ₃		-225
3 Fe + 2 Pb(CrO ₄)	=	Pb ₂ O + Fe ₃ O ₄	+ Cr ₂ O ₃		-187
2 Sn + 2 Pb(CrO ₄)	=	Pb ₂ O + 2 SnO ₂	+ Cr ₂ O ₃		-184
9 Fe + 8 Ag ₂ (CrO ₄)	=	8 Ag ₂ O + 3 Fe ₃ O ₄	+ 4 Cr ₂ O ₃		-182
3 Sn + 4 Ag ₂ (CrO ₄)	=	4 Ag ₂ O + 3 SnO ₂	+ 2 Cr ₂ O ₃		-180
2 Ge + 2 Pb(CrO ₄)	=	Pb ₂ O + 2 GeO ₂	+ Cr ₂ O ₃		-179
3 Ge + 4 Ag ₂ (CrO ₄)	=	4 Ag ₂ O + 3 GeO ₂	+ 2 Cr ₂ O ₃		-176
2 Mo + 2 Pb(CrO ₄)	=	Pb ₂ O + 2 MoO ₂	+ Cr ₂ O ₃		-173

Table 34 (cont.)

Reaction						Enthalpy, cal/g
4 W + 6 Pb(CrO ₄)	=	3 Pb ₂ O + 4 WO ₃	+ 3 Cr ₂ O ₃			-171
1 W + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + WO ₃	+ Cr ₂ O ₃			-170
6 Rb + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + 3 Rb ₂ O	+ Cr ₂ O ₃			-153
6 Rb + 2 Pb(CrO ₄)	=	2 PbO + 3 Rb ₂ O	+ Cr ₂ O ₃			-151
3 Ni + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + 3 NiO	+ Cr ₂ O ₃			-141
3 Ni + 2 Pb(CrO ₄)	=	2 PbO + 3 NiO	+ Cr ₂ O ₃			-138
3 Co + 2 Pb(CrO ₄)	=	2 PbO + 3 CoO	+ Cr ₂ O ₃			-134
3 Cd + 2 Ag ₂ (CrO ₄)	=	2 Ag ₂ O + 3 CdO	+ Cr ₂ O ₃			-126
3 Cd + 2 Pb(CrO ₄)	=	2 PbO + 3 CdO	+ Cr ₂ O ₃			-123
4 Sb + 4 Pb(CrO ₄)	=	4 PbO + Sb ₄ O ₆	+ 2 Cr ₂ O ₃			-120
2 As + 2 Pb(CrO ₄)	=	2 PbO + As ₂ O ₃	+ Cr ₂ O ₃			-119
6 Cs + 2 Pb(CrO ₄)	=	2 PbO + 3 Cs ₂ O	+ Cr ₂ O ₃			-115
6 Rb + 2 Ba(CrO ₄)	=	2 BaO + 3 Rb ₂ O	+ Cr ₂ O ₃			-88
6 Rb + 2 Na ₂ (CrO ₄)	=	2 Na ₂ O + 3 Rb ₂ O	+ Cr ₂ O ₃			-83
3 Pb + 2 Pb(CrO ₄)	=	2 PbO + 3 PbO	+ Cr ₂ O ₃			-75
3 Te + 4 Ag ₂ (CrO ₄)	=	4 Ag ₂ O + 3 TeO ₂	+ 2 Cr ₂ O ₃			-70
3 Bi + 2 Pb(CrO ₄)	=	2 PbO + 3 BiO	+ Cr ₂ O ₃			-69
3 Te + 4 Pb(CrO ₄)	=	4 PbO + 3 TeO ₂	+ 2 Cr ₂ O ₃			-66
S + 2 Pb(CrO ₄)	=	2 PbO + SO ₃	+ Cr ₂ O ₃			-64
3 Cu + 2 Pb(CrO ₄)	=	2 PbO + 3 CuO	+ Cr ₂ O ₃			-60
6 Tl + 2 Pb(CrO ₄)	=	2 PbO + 3 Tl ₂ O	+ Cr ₂ O ₃			-34
6 Rb + 2 K ₂ (CrO ₄)	=	2 K ₂ O + 5 Rb ₂ O	+ Cr ₂ O ₃			-20

Table 35

VOLUMETRIC ENTHALPIES (cal/cc) OF REACTIONS OF METALS
 WITH CHROMATES AND DICHROMATES
 (In descending order from top to bottom and left to right)

Metal	PbCrO_4	Ag_2CrO_4	BaCrO_4	Na_2CrO_4	K_2CrO_4
Be	-3845	-2881	-2293	-2022	
U	-3322	-2546			
Hf	-310	-2543	-1966	-1722	
Th	-3259	-2563	-2030		
Ho	-3173	-2529			
Zr	-3065	-2377	-1799	-1565	
Tb	-3048	-2439	-1927		
La	-3046	-2464	-1976	-1768	
Sm	-2999	-2406	-1897	-1684	
Nd	-2998	-2415	-1915	-1705	
Gd	-2986	-2398	-1890	-1679	
Pr	-2980	-2408	-1912		
Ce	-2939	-2371	-1870		
Np	-2914	-2265	-1677		
Mg	-2907	-2348			
Sc	-2879	-2303	-1782	-1570	
Ti	-2861	-2233	-1649		
Er	-2499	-2113			
Ca	-2393	-2044			
Ta	-2377	-1861			
Li	-2203	-1894			
Nb	-2197	-1749			
V	-2170	-1732			
Cr	-2011				
Mn	-1904	-1561			
Sr	-1894	-1676	-1296	-1162	
Al				-1665	-1113
P	-1658	-1407			
Ba	-1614	-1460			
Zn	-1566	-1330			
Ga	-1711	-1426			
W	-1329	-1136			
Fe	-1230	-1076			
Sn	-1206	-1068			
No	-1198				
Ge	-1095	-986			
Ni	-933	-865			
Co	-903				
Cd	-859	-806			
Sb	-773				
As	-739				
Pb	-611				
Bi	-533				
Te	-417	-407			
Cu	-406				
Rb	-401	-399	-202	-154	-38
S	-370				
Cs	-315				
Tl	-314				

Table 36
 GRAVIMETRIC ENTHALPIES (cal/g) OF REACTIONS OF METALS
 WITH CHROMATES AND DICHROMATES
 (In descending order from top to bottom and left to right)

<u>Metal</u>	<u>Na₂CrO₄</u>	<u>PbCrO₄</u>	<u>Ag₂CrO₄</u>	<u>BaCrO₄</u>	<u>K₂CrO₄</u>
Be	-772	-687	-553	-546	
Li		-648	-526		
Mg		-619	-509		
Al	-614				-408
Ca		-611	-509		
Sc	-590	-565	-471	-443	
La	-484	-487	-427	-397	
Zr	-478	-484	-413	-374	
Ti		-484	-409	-366	
Pr		-467	-410	-378	
Nd	-449	-460	-405	-372	
Ce		-456	-401	-367	
Sr	-437	-451	-396	-360	
Er		-448	-398		
Ho		-446	-396		
Sm	-427	-443	-391	-356	
Tb		-437	-388	-352	
Gd	-418	-435	-386	-350	
Hf	-406	-427	-377	-337	
Th		-422	-377	-341	
U		-379	-341		
Ba		-350	-320		
V		-347	-305		
Np		-336	-307	-258	
P		-336	-294		
Nb		-328	-292		
Cr		-312			
Ta		-304	-277		
Mn		-292	-265		
Ga		-275	-251		
Zn		-240	-225		
Fe		-187	-182		
Sn		-184	-180		
Ge		-179	-176		
Mo		-173			
W		-171	-170		
Rb	-83	-151	-153	-88	-20
Ni		-138	-141		
Co		-134			
Cd		-123	-126		
Sb		-120			
As		-119			
Cs		-115			
Pb		-75			
Te		-66	-70		
Bi		-69			
S		-64			
Cu		-60			
Tl		-34			

K. Boride Reactions

The reactions of 3 metals with 8 borides resulted in 14 reactions. Although the properties for only a few reactions were calculated, they are of interest because of the refractory nature of the products and reactants. Some representative reactions are shown in Table 37, and the volumetric and gravimetric enthalpies of all the boride reactions are listed in Tables 38 and 39. Except for boron carbide, the enthalpies are low. However, the reactions of titanium and zirconium with boron carbide are energetic. It would be interesting to examine these reactions experimentally to determine the effect of the refractoriness of the reactants and products on the behavior of the reactions.

Table 37

DATA ON REACTIONS OF VARIOUS METALS WITH BORIDES

	4 N	+	CB ₄	=	C	+	4 NB
Heat of formation			12.20		12.01		60.30
Molecular weight	14.01		55.29		2.25		24.83
Density	.81		2.50				2.20
Melting point, °C			2450.00				3000.00
Boiling point, °C			3500.00				
Heat of reaction, kcal	-229.00						
Reactants' density	1.22						
Gravimetric enthalpy, cal/g	-2057.10						
Volumetric enthalpy, cal/cc	-2503.76						
	2 Ti	+	CB ₄	=	C	+	2 TiB ₂
Heat of formation			12.20		12.01		70.00
Molecular weight	47.90		55.29		2.25		69.54
Density	4.50		2.50				4.5
Melting point, °C	1812.00		2450.00				
Boiling point, °C	3000.00		3500.00				
Heat of reaction, kcal	-127.80						
Reactants' density	3.48						
Gravimetric enthalpy, cal/g	-845.85						
Volumetric enthalpy, cal/cc	-2944.37						
	2 Zr	+	CB ₄	=	C	+	2 ZrB ₂
Heat of formation			12.20		12.01		76.40
Molecular weight	91.22		55.29		2.25		112.86
Density	6.40		2.50				6.08
Melting point, °C	1852.00		2450.00				
Boiling point, °C	2900.00		3500.00				
Heat of reaction, kcal	-140.60						
Reactants' density	4.70						
Gravimetric enthalpy, cal/g	-591.43						
Volumetric enthalpy, cal/cc	-2777.43						

Table 37 (cont.)

	2 N	+	TiB ₂	=	Ti	+	2 NB
Heat of formation			70.00		47.90		-60.30
Molecular weight	14.01		69.54		4.50		24.83
Density	.81		4.5				2.20
Melting point, °C							3000.00
Boiling point, °C							
Heat of reaction, kcal							
Reactants' density							
Gravimetric enthalpy, cal/g							
Volumetric enthalpy, cal/cc							
	5 N	+	Ti ₂ B ₅	=	2 Ti	+	5 NB
Heat of formation			-105.00		47.90		-60.30
Molecular weight	14.01		149.90		4.50		24.83
Density	.81		4.63				2.20
Melting point, °C							3000.00
Boiling point, °C							
Heat of reaction, kcal							
Reactants' density							
Gravimetric enthalpy, cal/g							
Volumetric enthalpy, cal/cc							
	5 Zr	+	2 Ti ₂ B ₅	=	4 Ti	+	5 ZrB ₂
Heat of formation			-105.00		47.90		-76.40
Molecular weight	91.22		149.90		4.50		112.86
Density	6.40		4.63				6.08
Melting point, °C							
Boiling point, °C							
Heat of reaction, kcal							
Reactants' density							
Gravimetric enthalpy, cal/g							
Volumetric enthalpy, cal/cc							

Table 38

VOLUMETRIC ENTHALPIES (cal/cc) OF REACTIONS OF METALS WITH BORIDES
(In descending order from top to bottom and left to right)

Metal	<u>CB₄</u>	<u>Ti₂B₅</u>	<u>TiB₂</u>	<u>ZrB₂</u>	<u>TiB</u>
Ti	-2944				
N	-2503	-1650	-1037	- 830	- 804
Zr	-2777	-1264	- 221		- 110

Table 39

GRAVIMETRIC ENTHALPIES (cal/g) OF REACTIONS OF METALS WITH BORIDES
(In descending order from top to bottom and left to right)

Metal	<u>CB₄</u>	<u>ZrB₂</u>	<u>Ti₂B₅</u>	<u>TiB₂</u>	<u>TiB</u>	<u>ZrB₂</u>	<u>Ti₂B</u>	<u>ZrB</u>
N	-2057	-1551	- 893	- 518	- 334	- 313	- 201	- 183
Ti	- 845	- 277			- 20			
Zr	- 591		- 227	- 39				

L. Phosphide Reactions

A total of 25 phosphides and 500 reactions was surveyed. The phosphides do not form an energetic class of reactions. The most energetic revealed in these studies,



yields only -1439 cal/cc. A few representative reactions are shown in Table 40.

Table 40

DATA ON REACTIONS OF VARIOUS METALS WITH PHOSPHIDES

	9 Mg	+	2 Au ₂ P ₃	=	4 Au	+	3 Mg ₃ P ₂
Heat of formation			-24.10		197.00		-128.00
Molecular weight	24.32		487.34		19.30		134.91
Density	1.74		6.67				
Melting point, °C	650.00				1063.00		
Boiling point, °C	1120.00				2660.00		
Heat of reaction, kcal	-335.80						
Reactants' density	4.39						
Gravimetric enthalpy, cal/g	-281.34						
Volumetric enthalpy, cal/cc	-1254.91						
	3 Mg	+	Ba ₃ P ₂	=	3 Ba	+	Mg ₃ P ₂
Heat of formation			-118.00		137.36		-128.00
Molecular weight	24.32		474.03		3.50		134.91
Density	1.74				704.00		
Melting point, °C	650.00				1638.00		
Boiling point, °C	1120.00						
Heat of reaction, kcal	-10.00						
Reactants' density							
Gravimetric enthalpy, cal/g							
Volumetric enthalpy, cal/cc	-18.28						
	3 Mg	+	Ca ₃ P ₂	=	3 Ca	+	Mg ₃ P ₂
Heat of formation			-120.50		40.08		-128.00
Molecular weight	24.32		182.20		1.55		134.91
Density	1.74		2.24				
Melting point, °C	650.00				850.00		
Boiling point, °C	1120.00				1240.00		
Heat of reaction, kcal	-7.50						
Reactants' density	2.07						
Gravimetric enthalpy, cal/g	-29.39						
Volumetric enthalpy, cal/cc	-60.81						

Table 40 (cont..)

	3 Mg	+	2 Cu ₃ P	=	6 Cu	+	Mg ₃ P ₂
Heat of formation			-36.40				-128.00
Molecular weight	24.32		221.60		63.54		134.91
Density	1.74		6.40		8.92		
Melting point, °C	650.00				1083.00		
Boiling point, °C	1120.00				2582.00		
Heat of reaction, kcal	-55.20						
Reactants' density	4.64						
Gravimetric enthalpy, cal/g	-106.94						
Volumetric enthalpy, cal/cc	-496.49						
	3 Mg	+	CuP ₂	=	Cu	+	Mg ₃ P ₂
Heat of formation			-28.90				-128.00
Molecular weight	24.32		125.49		63.54		134.91
Density	1.74				8.92		
Melting point, °C	650.00				1083.00		
Boiling point, °C	1120.00				2582.00		
Heat of reaction, kcal	-99.10						
Reactants' density	4.64						
Gravimetric enthalpy, cal/g	-499.37						
Volumetric enthalpy, cal/cc							
	3 Mg	+	2 FeP	=	2 Fe	+	Mg ₃ P ₂
Heat of formation			-28.00				-128.00
Molecular weight	24.32		86.83		55.85		134.91
Density	1.74		5.20		7.86		
Melting point, °C	650.00				1535.00		
Boiling point, °C	1120.00				2800.00		
Heat of reaction, kcal	-72.00						
Reactants' density	3.27						
Gravimetric enthalpy, cal/g	-291.95						
Volumetric enthalpy, cal/cc	-955.83						

M. Organic Fluoride Reactions

A limited survey was made of the reactions of organic fluorides with metals. The properties were tabulated for 76 organic fluorides for which data on heat of formation were available. These included perfluorinated compounds, partially fluorinated hydrocarbons, mixed halogenated organics, and organics containing various combinations of hydrogen, oxygen, nitrogen and fluorine. The enthalpies of reactions of 89 metals* with carbon tetrafluoride and hexafluoroethane were calculated. Both of these compounds are effective oxidizers.

The volumetric enthalpies for the 30 most energetic reactions of each fluoride are listed in Tables 41 and 42. Each reaction is represented by the metal reactant and the product fluoride. The Group IIA metals (beryllium, magnesium, calcium, strontium, and barium), the Group IVB metals (titanium, zirconium, and hafnium), and the rare earth metals (yttrium, lanthanum, neodymium, praseodymium, uranium, and thorium) are very energetic with these fluorides.

* In this instance each valence state of a metal is considered as a separate unit.

Table 41

VOLUMETRIC ENTHALPIES OF REACTIONS OF METALS
WITH ORGANIC FLUORIDES C_2F_6

<u>Reaction</u>	<u>Product</u>	<u>Enthalpy, cal/cc</u>
Be	BeF_2	-5.75
Y	YF_3	-5.14
La	LaF_3	-5.02
Nd	NdF_3	-4.98
Pr	PrF_3	-4.97
U	UF_3	-4.74
Mg	MgF_2	-4.73
Hf	HfF_3	-4.54
U	UF_4	-4.53
Th	ThF_4	-4.50
Sc	ScF_3	-4.47
Zr	ZrF_3	-4.46
Zr	ZrF_4	-4.45
Hf	HfF_4	-4.36
Li	LiF	-4.18
Ca	CaF_2	-4.14
Ti	TiF_3	-4.07
Th	ThF_3	-4.05
Ce	CeF_3	-4.05
Al	AlF_3	-4.04
Hf	HfF_2	-3.92
U	UF_5	-3.85
Zr	ZrF_2	-3.84
V	VF_2	-3.59
Ti	TiF_4	-3.48
B	BF_3	-3.47

Table 41 (cont.)

<u>Reaction</u>	<u>Product</u>	<u>Enthalpy, cal/cc</u>
Si	SiF ₄	-3.42
Mn	MnF ₂	-3.36
Ti	TiF ₂	-3.32
Ce	CeF ₄	-3.30
V	VF ₃	-3.29
Cr	CrF ₃	-3.26
Ba	BaF ₂	-3.23
U	UF ₆	-3.16
Cr	CrF ₂	-3.15
Ta	TaF ₃	-2.90
V	VF ₄	-2.83
Zn	ZnF ₂	-2.82
Ta	TaF ₂	-2.80
Ga	GaF ₃	-2.75
Na	NaF	-2.67
Mn	MnF ₃	-2.63
Fe	FeF ₃	-2.59
Ni	NiF ₂	-2.53
Co	CoF ₂	-2.51
In	InF ₃	-2.45
Ge	GeF ₂	-2.34
Cd	CdF ₂	-2.25
Cr	CrF ₄	-2.22
Ta	TaF ₅	-2.19
Ga	GaF ₂	-2.18
Cr	CrF ₅	-2.16

Table 41 (cont.)

<u>Reaction</u>	<u>Product</u>	<u>Enthalpy, cal/cc</u>
W	WF ₆	-2.09
In	InF ₂	-1.97
Mo	MoF ₆	-1.96
Nb	NbF ₅	-1.94
V	VF ₅	-1.91
Ge	GeF ₄	-1.91
Sn	SnF ₂	-1.89
Mo	MoF ₅	-1.89
Pb	PbF ₂	-1.83
Bi	BiF ₄	-1.76
Sb	SbF ₃	-1.75
N	NF ₃	-1.70
Bi	BiF ₃	-1.64
K	KF	-1.63
Mo	MoF ₄	-1.62
Co	CoF ₃	-1.53
W	WF ₄	-1.52
Fe	FeF ₂	-1.50
Sn	SnF ₄	-1.50
Cu	CuF ₂	-1.47
Rb	RbF	-1.34
Sb	SbF ₅	-1.31
Bi	BiF ₂	-1.30
Mn	MnF ₄	-1.22
W	WF ₅	-1.16

Table 42

VOLUMETRIC ENTHALPIES OF REACTIONS OF METALS
WITH ORGANIC FLUORIDES CF_4

<u>Reaction</u>	<u>Product</u>	<u>Enthalpy, cal/cc</u>
Be	BeF_2	-5.14
Y	YF_3	-4.69
La	LaF_3	-4.57
Nd	NdF_3	-4.57
Pr	PrF_3	-4.51
Mg	MgF_2	-4.24
C	UF_3	-4.167
Th	ThF_4	-3.94
Sc	ScF_3	-3.93
U	UF_4	-3.90
Zr	ZrF_4	-3.83
Li	LiF	-3.82
Ca	CaF_2	-3.75
Hf	HfF_4	-3.72
Ce	CeF_3	-3.64
Th	ThF_3	-3.52
Al	AlF_3	-3.37
Sr	SrF_2	-3.23
U	UF_5	-3.14
V	VF_2	-2.93
Ba	BaF_2	-2.88
Ce	CeF_4	-2.76
Ti	TiF_4	-2.73
Si	SiF_4	-2.68
B	BF_3	-2.66
Mn	MnF_2	-2.65
V	VF_3	-2.54

Table 42 (cont.)

<u>Reaction</u>	<u>Product</u>	<u>Enthalpy, cal/cc</u>
Cr	CrF ₃	-2.48
Cr	CrF ₂	-2.42
U	UF ₆	-2.36
Na	NaF	-2.33
Ta	TaF ₃	-2.16
Ta	TaF ₂	-2.12
Zn	ZnF ₂	-2.12
Ga	GaF ₃	-2.00
V	VF ₄	-1.99
Mn	MnF ₃	-1.80
Fe	FeF ₃	-1.75
In	InF ₃	-1.75
Ni	NiF ₂	-1.73
Co	CoF ₂	-1.71
Au	AuF	-1.71
Cd	CdF ₂	-1.58
Au	AuF ₃	-1.45
K	Kf	-1.41
Os	OsF ₈	-1.39
Os	OsF ₆	-1.35
In	InF ₂	-1.33
Cr	CrF ₄	-1.31
Ta	TaF ₅	-1.30
Sn	SnF ₂	-1.26
Pb	PbF ₂	-1.22
Cr	CrF ₅	-1.22
Ge	GeF ₄	-1.56
Rb	RbF	-1.14

Table 42 (cont.)

<u>Reaction</u>	<u>Product</u>	<u>Enthalpy, cal/cc</u>
Nb	NbF_5	-1.03
Sb	SbF_3	-1.03
Mo	MoF_6	-1.01
Bi	BiF_4	-1.01
V	VF_5	-1.01
Bi	BiF_3	- .95
Mo	MoF_5	- .95
Cs	CsF	- .88
Mo	MoF_4	- .69
Sn	SnF_4	- .66
Fe	FeF_2	- .64
Cu	CuF_2	- .60
W	WF_4	- .58
Co	CoF_3	- .58
In	InF	- .57
Sb	SbF_5	- .43
Tl	TlF	- .37
Cu	CuF	- .30
Ag	AgF	- .28

IV. ENTHALPY BEHAVIOR PATTERNS

The groups examined in the present study are compared in Table 43 according to the energy of their reactions. The most meaningful comparison would involve reactions between one metal and the compounds of another metal, e.g., the reactions of magnesium with the carbide, nitride, oxide, fluoride, silicide, phosphide, and sulfide of lithium. Because of the limited data available, however, the values in Table 43 apply to reactions of the metals with different compounds in each system. These compounds are listed at the top of each column.

Table 43

COMPARISON OF THE REACTION ENERGIES OF THE GROUPS STUDIED

Family	Volumetric Enthalpy, kcal/cc				
	Group IV	Group V	Group VI	Group VII	
2	Li_2C_2	Fe_2N	$\text{Ba}(\text{N}_3)_2$	LiNO_3	CoF_3
Be	-	-2.4	-3.3	-7.8	-5.1
Mg	0	-1.3	-1.3	-5.0	-4.1
Al	-0.1	-1.9	-2.5	-6.4	-3.0
Ta	-2.5	-1.8	-2.5	-5.1	-1.8
Ba	-	-0	-	-2.2	-2.8
Th	-0.6	-2.2	-2.6	-5.9	-3.8
3	CoSi_2	N_3P_5	FeS_2	CoCl_2	WCl_4
Be	-	-	-2.1	-1.2	-2.2
Mg	-0.1	-1.4	-2.4	-1.5	-2.4
Al	-	-	-1.2	-1.0	-1.8
Ta	-	-	-	-	-1.1
Ba	-5.1	-	-1.4	-1.7	-2.3
Th	-	-	-3.2	-1.4	-2.4

The oxide and fluoride reactions tend to be the most energetic. The nitrates and nitrites are included in the oxide system since the reaction products are invariably oxides. The nitrides, including the more energetic azides, the chlorides, the sulfides, and the carbides, are the next most energetic, in that order. The phosphides are the least energetic. Among the metals this order is followed by the reactions of beryllium,

magnesium, aluminum, tantalum, and thorium, with minor irregularities associated with each metal. Except for the highly energetic barium silicide system, barium follows a similar order.

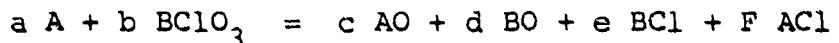
The silicide and chloride systems are unusual in that the heats of formation, in Group II at least, increase greatly with increasing atomic number. In the other systems the heats of formation tend to remain relatively constant or to decrease with increasing atomic number.

Although the data are limited, it appears that compounds of the elements of the second period, i.e., the carbides, nitrides, oxides, and fluorides, are more energetic than those of the third period, i.e., the phosphides and sulfides. Again, the silicides are an exception, being more energetic than the carbides.

V. RELATION OF THE DATA TO REALITY

In using or interpreting the calculated data, the stoichiometry, free energy, and kinetics associated with experimental conditions must be considered.

In almost all cases, the calculated values represent the stoichiometric reaction that has the highest calculated enthalpy. However, many of the reactant combinations can undergo, theoretically at least, several different stoichiometric reactions which produce different combinations of products. The reactions of a metal with a chlorate, for instance, may produce different combinations of oxides and chlorides; i.e., the coefficients c, d, e, and f in the following equation can have values of zero or higher in any combination that will yield a balanced equation.



There is no way of predicting the stoichiometry of a reaction in an experimental situation. Thus, experimentally, a reaction may not yield the maximum energy outputs that were calculated. Also, the reaction mixtures that function most satisfactorily in practical applications usually deviate appreciably from the stoichiometric ratio.

Only enthalpies were considered in the present program. The enthalpy (ΔH) is of most interest for present purposes because it is a measure of the amount of heat energy liberated by a reaction at a particular temperature. Conceptually, a reaction such as



can be considered to occur at an infinitesimal rate at 298°K and to liberate 380.2 kcal of thermal energy. This energy will be dissipated by conduction, convection, and radiation. Since radiative transfer is an inefficient process at such a low temperature, most of the energy will be lost by conduction and convection. Conversely, the reaction may be carried out under adiabatic conditions, in which case the energy liberated will be used to heat the products of the reaction to a temperature determined by the heat content of the products and by the manner in which the enthalpy, entropy, and free energy of the reaction vary with temperature.

In reality, however, these types of reactions proceed rapidly under partially adiabatic conditions after they are initiated, and the products of the reaction are heated to very high temperatures by the energy liberated. As the products cool from a high temperature to 298°K, they effectively convert a sizeable portion of the thermal energy to radiative energy. And since radiation is our primary concern, the

the enthalpy is the most significant thermodynamic quantity. Fortunately, it also is the function which is most frequently available in the literature.

The free energy (ΔF) defines the equilibrium state of a reaction and thus indicates the extent to which a reaction can occur. The free energy can be considered the enthalpy minus a correction term consisting of $T\Delta S$, where T is the temperature and ΔS is the entropy change. In most instances and especially in the present case, where large negative enthalpies are involved, the correction term is small compared with the enthalpy, and $\Delta H_{298} \sim \Delta F_{298}$. The change of the enthalpy with temperature is small because it depends on the change in heat capacity between the products and the reactants, and this change is usually small if no phase changes occur. The amount of energy liberated per mole of reaction will therefore be relatively independent of temperature. On the other hand, the free energy is strongly dependent on temperature. In fact, there is usually a temperature at which the free energy of a reaction passes through zero, indicating that the direction of the reaction has reversed. This means that although the energy output for a mole of reaction may be the same at different temperatures, the reaction will only occur to a small extent when the free energy is near zero.

Thus, although a theoretical reaction may be very energetic, it may, in fact, proceed to such a small extent that the thermal output will be greatly reduced. In a future program it may be interesting to examine the behavior of the free-energy function of some of the more interesting reactions for which free-energy data of the constituents are available.

A factor not considered but very important for practical applications is the kinetics of the reactions. There is no way of predicting the kinetics of these types of reactions. Although a reaction may be highly energetic, its kinetics may be such that the output of thermal energy is too slow to be utilized practically. In addition, these reactions must be heated to a temperature at which they can propagate at a finite rate. This temperature cannot be predicted, but is very important for practical applications and even for theoretical studies.

Because of all these unknown factors in the experimental and practical realizations of these reactions, an extensive experimental program involving several areas of study is necessary. Calorimetric studies can be used to determine the validity of the present calculations. The thermal output can be studied as a function of the stoichiometry of the reaction and the physical variations of the reactants. To further substantiate the calculations, the products of the reactions can be chemically analyzed. For theoretical and practical applications the kinetics and mechanisms of the reactions can

be studied by burning rate, radiation, and spectroscopic studies, and differential thermal analysis and thermogravimetric analysis at different stoichiometries, different ambient conditions, and different variations of the physical properties of the reactants.

In summary, the thermal data presented in this report provide a rational method for choosing reactions to be studied experimentally for theoretical and practical applications. The ancillary data included on the physical properties of the reactants and the products of each reaction aid in the selection, since these properties may be important for the theoretical and practical applications.

VI. SUMMARY

The heats of reactions of metals with oxides, nitrites, chlorates, perchlorates, chromates, chlorides, fluorides, sulfides, nitrides, azides, carbides, phosphides, and silicides were tabulated on a Univac 1105 computer. The reactions involving chlorates, oxides, nitrates, nitrites, and fluorides tend to be the most energetic. The metals associated with the highest energies released are beryllium, magnesium, aluminum, lithium, calcium, titanium, zirconium, hafnium, lanthanum, cesium, neodymium, praseodymium, thorium, and uranium. The highest energy, -9459 cal/cc, is realized by the reaction of beryllium with magnesium perchlorate.

In all, about 20,000 reactions were tabulated. Each reaction was recorded in the primary tabulation in the form of a balanced equation. This was followed by a tabulation of input data, consisting of heats of formation, molecular weight, melting and boiling points, and also output data, consisting of reaction density and heat of reaction on molar, gravimetric, and volumetric bases.

In consequence of this large amount of detail, a page of data consists of only three equations and the data are voluminous. Therefore, only the most significant results are presented in this report and the remainder summarized. The full utility of the compilation is best realized by the establishment of secondary computer programs, designed to present the data in forms to meet specific requirements. Thus, computer programs were prepared to summarize the data in each class of reactions in descending orders of volumetric and gravimetric heats of reaction. Other programs were used to present graphically the heats of the reactions of a metal with all the oxidants of a particular class or an oxidant with all the metals, on molar, volumetric, and gravimetric bases. Still other programmed tabulations show in grid form the data for all metals with oxidizers (oxides, fluorides, chlorates, etc.), arranged in order of the energy of reaction.

The tabulations of the data presented in this report were prepared to meet the requirements of a specific problem. However, the special merit of the system lies in its versatility, since the possible treatments of the data can be varied to cope with innumerable applications involving other uses of these data.

VII. FUTURE WORK

The studies presented here have been essentially completed as far as the enthalpies are concerned. Almost all systems of potential interest for which data are available are included. It would be of interest, however, to calculate the free energy and equilibria of certain reactions as a function of temperature. These calculations would predict the maximum temperature and the extent of the reactions. They would be limited to reactions for which free energy and specific heat data are available.