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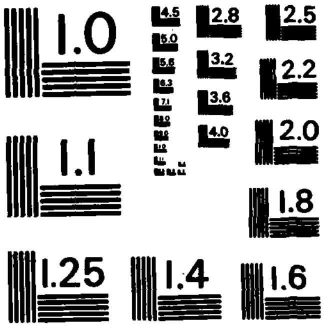

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THERMOCHEMICAL CONSIDERATIONS IN SELF-SUSTAINING SYNTHESIS OF REFRACTORY COMPOUNDS

SPC 814

August 1982

William L. Frankhouser
Stephen T. Sullivan

Advanced Materials Synthesis Program
at Defense Advanced Research Projects Agency (DOD)
Monitored by: Dr. R. P. Gogolewski and
LTC L. A. Jacobson

(Prepared under Contract 6819401 with:
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Thermochemical relationships in synthesis of refractory compounds have been considered. The heat generated from elemental reactants in this synthesis process provides the thermal input for the gasless combustion process. Trends are shown that relate position of the elemental reactants in the periodic table and gram molecular weight of the reacted products to a thermochemical potential factor (TPF). The TPF is obtained by dividing heat of reaction with adiabatic reaction temperature. Suggestions are made to perform laboratory scoping experiments with BeB_2, ScH_2, TiB_2, and W_2C to confirm the thermochemical relationships in self-sustaining synthesis.

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CONTENTS

ABSTRACT

Interest in refractory compounds is intensifying in spite of high costs because of their potentially outstanding performance in structural applications. Self-sustaining synthesis is a relatively new technology that promises low-cost fabrication of these compounds. In the simplest perception, lightly compacted elemental powders can be ignited and made to react to form product compounds and shapes without use of external heating.

Laboratory development is required to select elemental reactants that are most amenable to self-sustaining synthesis and to optimize reaction process technology. The objective in this preliminary study is to provide guidance in selecting reactants for the laboratory development programs by analyzing thermochemical behavior of the reactions. Thermochemical potential factors, measured as the quotient of the thermal effect of the reactions and the adiabatic reaction temperatures, are proposed as criteria for selection of potential reactants.

Specific trends were noted that relate thermochemical potential factors to position of the reactant elements in the periodic table and to stoichiometry of the reacted products. Generally, thermochemical potential factors for compounds diminish as gram molecular weights increase. The relative size and interatomic spacing of the metallic reactant elements may be factors underlying these relationships. Although the highest thermochemical potential factors have been identified for individual borides, carbides, nitrides, and sulfides, the greatest potential for self-sustaining synthesis in overall classes of compounds is attributed to borides. The thermochemical potential factors are especially high for metallic reactants from Groups IIA, IIIA, or IVA in the periodic table. Laboratory screening of self-sustaining reactions that exhibit low, intermediate, and high thermochemical potential factors is suggested. Specific compounds suggested for these screening experiments are BeB_2, TiB_2, ScH_2, and W_2C.

THERMOCHEMICAL CONSIDERATIONS IN SELF-SUSTAINING SYNTHESIS OF REFRACTORY COMPOUNDS

I. BACKGROUND

A. STUDY SUBJECT AND OBJECTIVE

Most useful materials are chemical compounds that were either created through natural occurrences or produced by human-manipulated reactions. In the latter case, heat input-output balances associated with the chemical changes (i.e., the thermochemical aspects) are of considerable technological and economic importance in some commercial industries. Thermal energy supplied from external sources as an input to the reaction is costly, and excess thermal energy generated as a reaction output is often wasted and sometimes causes unwanted disposal expense. A thermally self-sustaining chemical reaction that requires no heat input from external sources and generates no excess heat would be considered as thermochemically ideal. Furthermore, if self-sustaining reactions can produce compounds that are otherwise not available within commercial economic constraints, an additional advantage is accrued. Production of refractory compounds by self-sustaining reactions satisfies both of these conditions.

This report presents an assessment of the thermochemical potential for maintaining self-sustaining reactions that would form specific refractory compounds. The objective is to provide guidance for laboratory development by identifying the most likely candidate reactants for self-sustaining synthesis. Although the thermal balance will not unilaterally determine whether a self-sustaining reaction mode is attainable, it exerts a major influence on that determination. Other influences such as activation energy, geometrical relationships, and additional physical factors will be the subjects of a future broader analysis of combustion technology that concentrates on both thermochemical factors and other aspects of reaction kinetics.

B. REFRACTORY COMPOUNDS

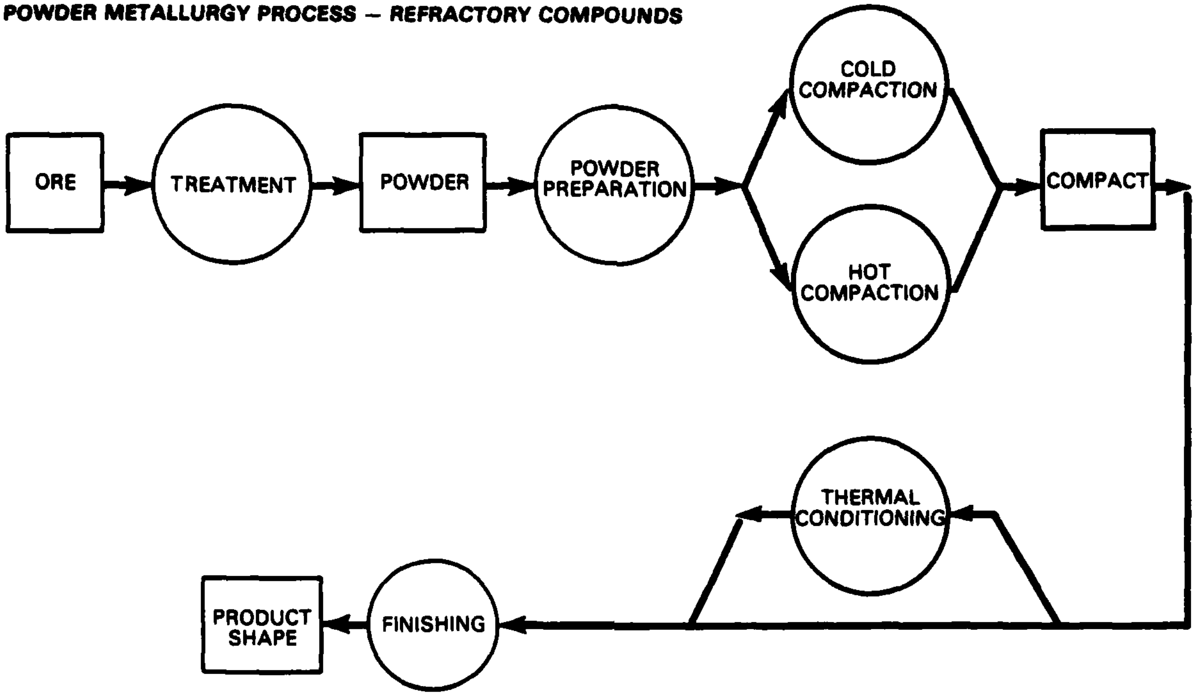
Although a concise definition of refractory compounds has not been universally accepted, the underlying concept implies a group of materials that have unique combinations of high strength and thermal resistance. From a compositional viewpoint, many refractory compounds are ceramics (metal-nonmetal compounds), intermetallics (metal-metal compounds), or cermets (ceramic-metal microscale composites). Often, the metallic components in these refractory compounds are among the transition metals in the periodic table of elements, and the nonmetallic components are among the lighter elements in that table (usually less than atomic number 17). Increased emphasis over the last three decades in industrial, defense, and space programs on materials performance at higher temperature, on greater strength-weight efficiencies, and on specialized electronic and structural properties has intensified interest in refractory compounds.

C. CONVENTIONAL PRODUCTION OF REFRACTORY COMPOUNDS

In comparison to wrought and cast processes that historically have been used to fabricate the most widely known metallic structural materials, fabrication processes for refractory compounds are considered to be less tractable and are generally more costly. Product shapes of refractory compounds have generally been fabricated from the powder form of raw materials by powder metallurgy processes, as shown schematically in Figure 1. These processes are generally characterized with higher costs per unit of product weight than the more conventional approaches such as metal working (also shown in Figure 1) or casting technologies.

Although some of this cost differential can be attributed to the higher cost of materials used in producing refractory materials, the process complexity of powder metallurgy techniques, the smaller production batches, and the need for high-pressure and high-temperature equipment are responsible for more sizable cost increments. High pressures in this case usually require either precision pressing equipment or high-pressure vessels that operate with hot walls or thermally shielded cold walls. High

POWDER METALLURGY PROCESS — REFRACTORY COMPOUNDS



WROUGHT PROCESS — STEELS

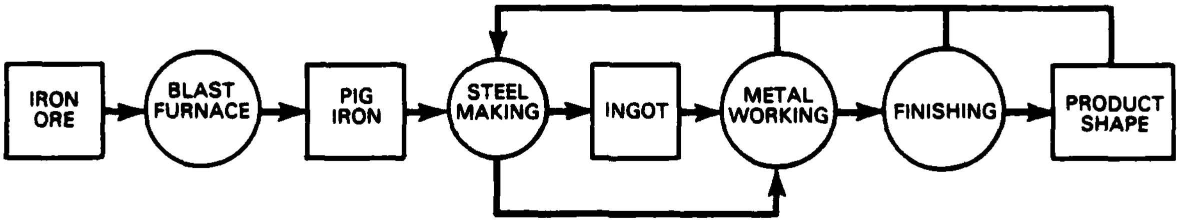


FIGURE 1.
SIMPLIFIED PROCESS FLOW DIAGRAMS

temperatures usually require furnaces with extremely high-temperature capability or integration of high-temperature capability into the pressing equipment. Whereas simple steel shapes may cost typically $1 to $10 per pound, the cost for refractory compounds as product shapes is generally in the range from tens to hundreds of dollars per pound and sometimes may be even more costly.

D. PRODUCTION OF REFRACTORY COMPOUNDS BY SELF-SUSTAINING SYNTHESIS

A self-sustaining reaction requiring no external heat or complex pressure and temperature-producing equipment is considered to be a readily marketable process simplification for production of refractory compounds. In the simplest concept of self-sustaining synthesis, only a relatively thin cold-wall vessel is required for the reaction synthesis of refractory compound products. As shown in Table 1, this concept eliminates much of the sophisticated high-pressure and high-temperature equipment required in conventional powder metallurgy processes and therefore offers significant cost savings.

TABLE 1

COMPARISON OF PROCESS ALTERNATIVES

	Equipment	
Process Step	Conventional Powder Metallurgy	Self-Sustaining Synthesis
1. Powder Preparation	Powder attrition, sizing blending, etc.	Same
2. Cold Compaction	Low-pressure press or cold-wall vessel	Same
3. Product Reaction, Conditioning, Shaping, etc.		
• Pressure Equipment	High-pressure press or hot-wall, high-pressure vessel	Reaction vessel with vacuum or modest pressure capability
• Thermal Equipment	Thermal adaption to high-pressure press, high-temperature furnace, or both	High-temperature furnace only if post-reaction thermal conditioning required

E. DEVELOPMENT HISTORY OF SELF-SUSTAINING SYNTHESIS PROCESSES

The principle of chemically reacting elements and compounds to form useful materials or thermal effects has been mastered for many centuries. Applications have ranged from relatively quiescent metallurgical processes, such as production of pig iron or cast iron, to vigorous reactions, as exemplified by thermite and pyrotechnic processes. Self-sustaining synthesis is a recently conceived concept that is illustrated schematically in Figure 2. In this case, the reactions are used for materials production rather than for generation of heat or explosions, propulsion, etc. The reaction is gasless and proceeds as a combustion wave and not as a volumetric process. Temperatures of more than 4000°C are achievable with reactants in the elemental form and without heating from external sources.

The commercial potential of the self-sustaining synthesis concept has been recognized in at least three countries, and it has already been extensively promoted as an industrial process in the U.S.S.R. Soviet articles on the concept first appeared in the early 1960s [Refs. 1, 2, and 3], and commercial patents have been obtained by Soviet researchers periodically since the late 1960s [Refs. 4, 5, 6, 7, and 8]. An Australian research article and a patent appeared in the late 1960s [Refs. 9 and 10]. Some related U.S. research was published in the early 1970s [Refs. 11, 12, 13, and 14], and at least one U.S. process has been patented for a number of years [Ref. 15].

Related domestic laboratory research is currently under way in at least three locations--at the Army Materials and Mechanics Research Center, at General Electric's RSD facility, and at Lawrence Livermore National Laboratory [Ref. 16]. The laboratory program in Australia was terminated because of a shift in emphasis on project priorities. In the U.S.S.R., self-sustaining synthesis has become a nationally sponsored research and development program in which at least 12 laboratories and 200 researchers participated during the 1970s. As indicated in Table 2, Soviet researchers envision the number of compounds that potentially can be synthesized to have many potential uses. When all possible intercombinations of these compounds and potential composite materials are considered, the total

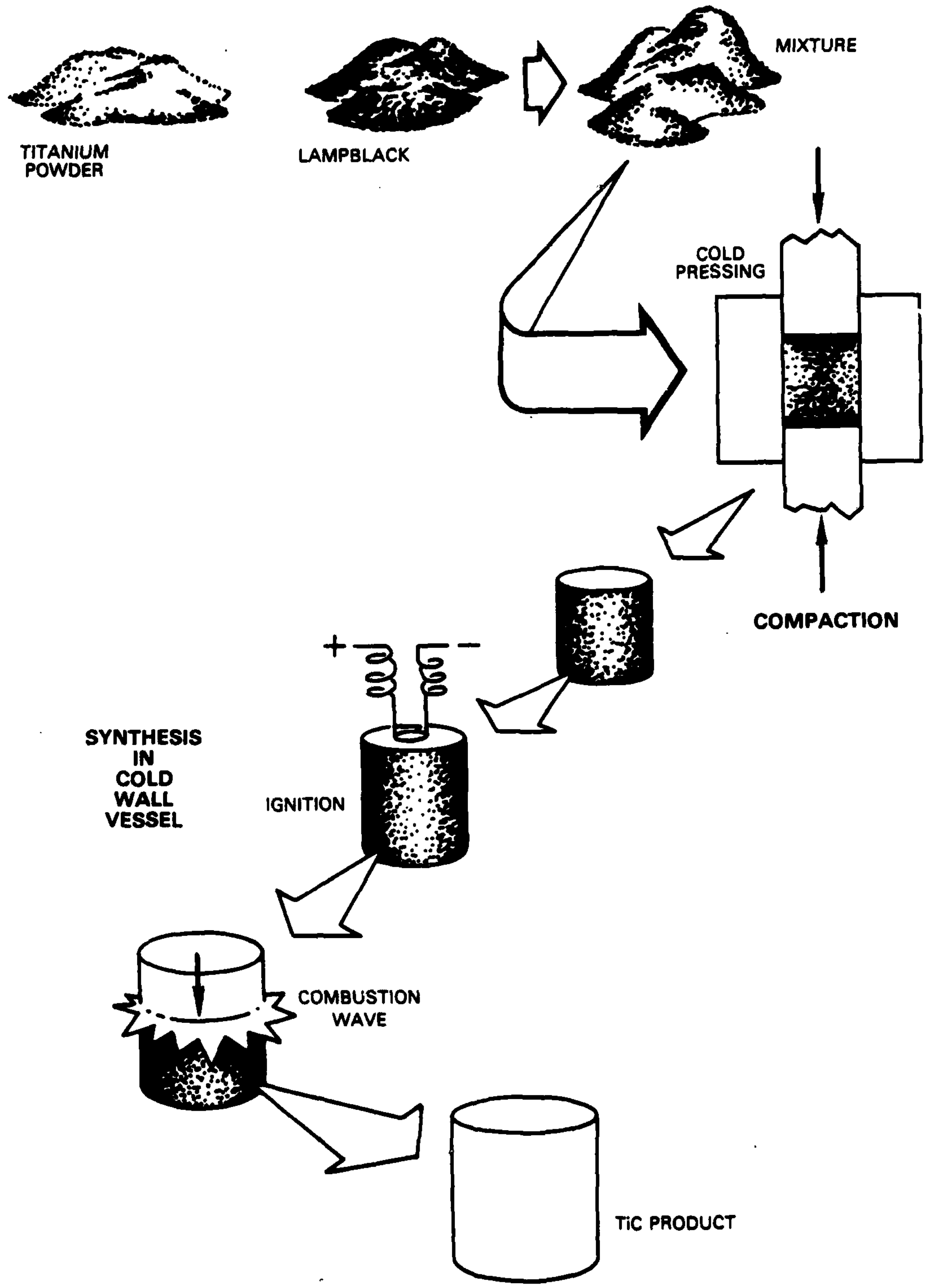


FIGURE 2.
SELF-SUSTAINING SYNTHESIS IN PRODUCTION OF TITANIUM CARBIDE

TABLE 2

POTENTIAL SOVIET APPLICATIONS FOR SYNTHESIS OF REFRACTORY COMPOUNDS

	Applications						
Compounds	Hard Alloys[a]	High-Temperature Structural	Superhard Abrasives	Protective Coatings	Electrical and Electronic	Lubricants	Nuclear Energy
Borides[b]	X	X	X	X	X		X
Carbides[b]	X	X	X	X	X		X
Chalcogenides		X			X	X	
Hydrides							X
Intermetallic Compounds		X		X			
Nitrides[b]	X	X	X	X	X	X	
Oxides		X	X	X	X		
Silicides		X		X	X		

[a] Cemented carbide and related tool industry products.

[b] Researchers also report synthesis of carborides and carbonitrides.

number becomes almost uncountable. Several recent Soviet publications have referred to production or pilot-production applications of the technology, and those operations are listed in Table 3.

TABLE 3

SOVIET PILOT OR FULL-SCALE PRODUCTION OPERATIONS

Compounds	Forms and Uses	Other Remarks
➤ Current Production		
• Chalcogenides	Lubricants	MoS_2, WS_2, WSe_2
• Ferrochromium (nitrided)	Alloying steels	Charged as a master alloy
• $MoSi_2$	Furnace heating elements	Similar to Superkanthal
• TiC	Surface conditioning, turbine blade coatings, grinding pastes, cutting tools, press tooling	Plasma spray claddings, nickel and ferrous-based cermets
• TiNi	Plate and wire forms, aircraft tubular fittings, engine components	Temperature-dependent "shape memory"
➤ Future Production	--	By 1986
• B_4C		
• TiCN		
• B_4C - cermet		

II. CHEMICAL THERMODYNAMIC RELATIONSHIPS IN SELF-SUSTAINING SYNTHESIS

A. CHEMICAL REACTIONS

The chemical reaction used as the basis for this analysis is stated below in the generic form used by Soviet researchers [Ref. 17]. This reaction is the classic form of self-sustaining synthesis in which an elemental metallic "fuel" (M) and nonmetallic "oxidizer" (N) combine to form a refractory product (P):

$$\underbrace{\sum_{i=1}^{m} a_i M_i}_{\text{metal powders}} + \underbrace{\sum_{j=1}^{n} b_j N_j}_{\text{powder, liquid, or gas}} \Longrightarrow \underbrace{P}_{\text{solid compound}}$$

Typically, the M elements are transition metals from the A Groups in the periodic table, and the N elements have low atomic numbers (e.g., B, C, N, S, Si, etc.). Another significant factor in this reaction is that unwanted by-products are not formed.

In the initial Soviet synthesis experiments, values of m and n were 1 (e.g., where titanium and carbon react to form titanium carbide). Later, reactions with m = 1 and n = 2 were examined (e.g., where titanium reacts with carbon and nitrogen to form a carbonitride), and other mixtures with m = 2 and n = 1 have been reacted (e.g., where titanium and chromium react with boron to form a diboride). More recently, Soviet researchers have also examined more complex compounds (e.g., where m = 2 and n = 2, as exemplified by a reaction in which niobium and zirconium form a carbonitride).

Other types of reactions have also been reported in which self-sustaining synthesis is combined with metallothermic (oxidation-reduction) reactions, e.g.:

$$MN_m + X \longrightarrow MX_n + XN_k .$$

In this case, a compound (MN_m) is reacted with an elemental oxidizer-reducer (X) to form a desired refractory product (MX_n) and a by-product (XN_k). A specific example would be the reaction of titanium oxide with boron to form titanium diboride (the product) and a slag that contains boron in the oxide form.

In other combined processes, the oxidizer (O) and reducer (R) have been introduced as separate elements, e.g.:

$$MN_m + O + R \longrightarrow MO_n + RN_k .$$

Obviously, as the chemical reactions become more complex, the thermochemical relationships would be more difficult to comprehend. Also, chemical thermodynamic data are not as readily available for more complex reactions. For those reasons, this initial analysis has been limited to simpler types of chemical reactions.

B. ELEMENTARY THERMODYNAMIC RELATIONSHIPS

The principles of thermodynamics can be used to illustrate a number of basic properties of reacting systems. The relationships of interest in analyzing self-sustaining reactions include reaction spontaneity, heat capacity of the reactants, the adiabatic reaction temperature, and the equilibrium compositions of the products.

Spontaneity

The spontaneity of a chemical reaction is determined by the extensive thermodynamic quantity of Gibbs free energy (G) or its intensive analogue, the chemical potential (μ).[1] To be spontaneous, a reaction system must have a net decrease in G at constant temperature and pressure.

The Gibbs free energy is defined by the relationship:

$$G = H - TS$$

where H is the enthalpy, S is the entropy, and T is the absolute temperature. Changes in G at constant temperature and pressure may be expressed as:

$$\Delta G = \Delta H - T\Delta S.$$

The characteristics of constant temperature and pressure for self-sustaining reactions require assumptions in order to use the simple expression above. The temperature of the reactants must be raised to a temperature at which the reaction becomes thermodynamically favorable. Since G, H, and S are thermodynamic state functions, the reaction occurs along a path in which it is initiated at some minimum reaction temperature and some of the products are subsequently heated to a higher temperature. The restriction of constant pressure causes no difficulty if the reaction is open to the atmosphere or if a closed reaction vessel is large compared to the reaction zone. Since self-sustaining reactions are essentially gasless, the assumption of constant pressure, therefore, generally holds. Thus, information on enthalpy and entropy of the reactants and products over the temperature range of interest is the basic need in characterizing spontaneity of a reaction.

Adiabatic Temperature

The adiabatic temperature of a reaction system can be approximated by equating the enthalpy (i.e., heat content) of the initial charge with that

---

[1] The chemical potential (μ) is the partial molar Gibbs free energy (G); i.e., the total change in Gibbs free energy of a solution when a mole of solute is added to an infinite amount of solution.

of the final product and assuming that no heat escapes the system during the reaction. Since enthalpy is a function only of the thermodynamic state, the mechanism of the reaction need not be known; only knowledge of the initial and final states (temperature, pressure, volume, and composition) is required.

The initial temperature and composition of the system are usually known quantities in studying the enthalpy of specific systems. The final composition of the system can be determined and used to calculate the adiabatic temperature at which enthalpy is in equilibrium for the system. Therefore, enthalpy data are required for the initial reactants up to the initial temperature and for the products up to the adiabatic reaction temperature.

The available literature generally shows that the enthalpies of the original substances at the initial temperature T_0 and of the final products at the adiabatic temperature T_{ad} must be equal, but does not specify the assumptions concerning the initial temperature. The two obvious candidates for T_0 are the standard ambient temperature (298°K) and the temperature at which the reaction begins to occur. If 298°K is used, account must be made of the heat absorbed by the system from the ignitor that initiates the reaction, which can vary markedly for different reaction systems. Failure to include this heat input will result in a calculated adiabatic temperature that is smaller than the experimental result. Although the initial temperature would ideally be the reaction temperature, this quantity is difficult to measure empirically. It can be calculated when thermodynamic data are available for both reactants and products from standard state to the reaction temperature.

Equilibrium Composition

The equilibrium composition for the reaction is determined by the same argument used to determine spontaneity. If the change in free energy (ΔG) is less than zero, the reaction will occur as written; if ΔG is greater than zero, the reverse reaction is spontaneous. When ΔG is equal to zero, no tendency for further reaction exists. For self-sustaining reactions of concern in this study, the equilibrium composition will depend on the reactants and products and on the initial temperature and pressure.

Heat Capacity Data

The basic thermodynamic quantities of interest are heat capacities and enthalpies of phase transformations. From these, other necessary thermodynamic quantities (i.e., ΔH, ΔS, ΔG) can be calculated. The principal difficulty in performing the calculations is the lack of enthalpy and entropy data for substances in condensed states at elevated temperatures. This problem arises because of the lack of experimentally determined heat capacity data for substances over broad temperature ranges. These thermodynamic functions of substances in condensed states cannot be determined strictly from theoretical principles and must be obtained empirically or calculated from empirical or semi-empirical correlations.

The enthalpy of one mole of pure substance at constant pressure is related to the molar heat capacity by the function

$$\Delta H = \int_{T_o}^{T_f} C(T)_p dT + \sum_i \nu_i \Delta H_i$$

where $C(T)_p$ is the constant-pressure heat capacity, T_0 and T_f are the initial and final temperatures, ν_i is the fraction of the mole that experiences phase change i, and ΔH_i is the molar enthalpy of phase transformation i occurring at temperature T_i. The entropy of one mole of pure substance at constant pressure is related to the molar heat capacity by the function

$$\Delta S = \int_{T_i}^{T_f} \frac{C(T)_p}{T} dT + \sum_i \nu_i \frac{\Delta H_i}{T_i}$$

where T_i is the transition temperature for phase change i.

Some thermodynamic data on materials that are potential candidates for self-sustaining reactions are available in the literature; these are reviewed in the following section. A considerable amount of the Soviet data is keyed to self-sustaining reactions that form refractory compounds.

C. AVAILABLE THERMODYNAMIC DATA

Data are available in the literature in tabular compilations for some reaction systems of potential interest. These values have been derived both from empirical correlations and from semi-empirical correlations based on theoretical postulations. Though no concerted effort has been made here to assess the level of agreement among data from different sources, some inconsistencies have been noted; also, standard reference states are sometimes insufficiently specified in the data. For these reasons, caution is advisable in using the available values.

Heat capacities for solids and liquids cannot presently be precisely determined using theoretical approaches. Although a number of theories have been proposed to account for their behavior, and some have proven to be accurate and reliable for many substances over specific ranges of temperatures, none have been completely successful over all temperature ranges. According to Zefirov [Ref. 18]:

> At the present, practical methods have still not been worked out for calculating heat capacity and other thermodynamic functions of crystalline substances in which the results of experimental measurements of heat capacity are not used....Theoretical calculations of thermodynamic functions of substances in solid and liquid states at high temperatures are also practically impossible, because available methods for calculating the heat and temperature of phase transfer motions and heat capacity in a liquid state are not acceptable.

Theories of the heat capacity of condensed phases range from zero-order correlations such as those based strictly on molecular weights to sophisticated models. For example, Novikov [Ref. 19] uses a simple correlation based on the number of atoms in a product molecule to estimate the heat capacity of the solid product at the melting point and of the liquid product. In contrast, Krikorian [Ref. 20] uses a model for estimating the heat capacities of borides that includes the contributions of electrons and lattice defects.

A number of tabular compilations of thermodynamic data for heat capacities, enthalpies, entropies, and free energies are available. A 1965

Soviet publication [Ref. 18] provides an extensive listing of such data for many inorganic materials and includes other parameters of crystalline structure and equilibrium vapor pressures. The introductory chapter presents a brief review of the basic thermodynamic relationships between thermodynamic variables and summarizes the theoretical approaches and empirical and semi-empirical correlations used by various researchers in deriving the tabulated data. This treatise provides an excellent synopsis of the basic thermodynamic relationships and practical approaches to relevant calculations.

The JANAF Thermochemical Tables [Ref. 21] provide data and annotated information on the availability of data for a large number of substances over broad ranges of temperature. A 1966 Soviet-edited handbook [Ref. 22] presents a tabular compilation of data on approximately 4,000 organic and inorganic compounds and provides references to data sources.

Data on the adiabatic reaction temperature for compounds of the type M_iN_i (where N = B, Si, C, N, or S) are presented in the 1975 paper by Novikov [Ref. 19]. Values are calculated for reactions of formation from elements and from reduction of oxides. The calculations are based on the assumptions that (1) the temperature dependence of heat capacity is linear for all substances between the temperature at which the highest empirically determined heat capacity data are available and the melting temperature, and (2) the heat capacities of the product solid and liquid are given by:

$$C_{sol}\ (T_{melt}) = 7n \left(\frac{\text{cal}}{\text{mol. degree}}\right)$$

$$C_{liq} = 8n \left(\frac{\text{cal}}{\text{mol. degree}}\right)$$

where C_{sol} (T_{melt}) is the heat capacity of the solid at the melting temperature, C_{liq} is the heat capacity of the liquid product (which is essentially independent of temperature), and n is the number of atoms in a molecule of the product. General trends in the level of adiabatic temperatures are related to groups and periods in the periodic table for various M reactants.

A review of the thermochemistry of exothermic intermetallic reactions presented in a 1971 study for the U.S. Air Force [Ref. 23] indicated that thermodynamic data are plentiful, but agreement among reported values is seldom close and reference conditions are often insufficiently specified. After critical review of the data reported in the literature, the study team presented eight tables of data on heats of reaction and adiabatic reaction temperature for the synthesis of selected compounds from elemental powders. Included are data for compounds of the alkali metals, the alkaline earths, borides, aluminides, carbides, silicides, rare earths, and actinides.

The study for the USAF also included a series of laboratory experiments to obtain reaction data on many of the systems that had been reported in the literature. Disagreement between laboratory findings and tabulated values was found in many cases and was attributed in part to:

- Unreliable published data, particularly where these are derived from solution calorimetric or electrochemical data
- Incomplete reaction because of surface cooling or due to the presence of local inhomogeneities
- Incomplete reaction because of poor sintering
- Low total enthalpy changes leading to low precision in calorimetry
- Deviations from greybody behavior
- Ignition technique.

The background review strongly suggests that little agreement exists in either the thermodynamic data base or the theoretical approach to forecasting the potential for the self-sustaining mode of reactions. One researcher proposes, however, that the most reasonable approach to understanding thermochemical relationships is through a preliminary analysis of adiabatic reaction temperatures [Ref. 17]. This approach has been used in the analysis presented in Chapter IV.

III. ANALYSIS OF THE THERMOCHEMICAL POTENTIAL FOR SELF-SUSTAINING SYNTHESIS

A. DATA ANALYSIS

The initial step in the analysis of thermochemical potential for self-sustaining synthesis was to identify a body of thermodynamic data that both encompassed a considerable number of potential reactants and was internally consistent. In spite of the controversy about relative reliability of various data tabulations, the rationale was that significant thermochemical trends would be identifiable within a single well-organized body of data. After completing the literature review described previously, a decision was made to use the data base compiled by Novikov in Reference 19.

The second step in performing the analysis was to identify one or more parameters that could be used to assess the relative thermochemical potentials for different compounds. The criterion for making this selection was that the parameter(s) should be readily calculable, since the questionable reliability of existing data would not warrant precise or sophisticated calculations. On this basis, a decision was made to concentrate the analysis on adiabatic reaction temperatures (T_{ad}) and the thermal effect (Q) or enthalpy of individual reactions. This decision carries with it an assumption that heat liberated in the reactions equals exactly the heat required to heat the products from the initial temperature (T_0) to the adiabatic reaction temperature (T_{ad}).

Location in Periodic Table

The initial analysis has been concentrated on 55 reactions of Group IV through VIIIA[1] transition metals of the periodic table in forming borides,

---

[1] Also restricted to elements in Periods 4 through 6 in the periodic table.

carbides, nitrides, silicides, and sulfides (as shown in Figure 3). Since Novikov calculated the Q and T_{ad} values for these reactions and reported trends linking levels of reaction heat and temperature to position of the reactants in the periodic table, that aspect was examined first.

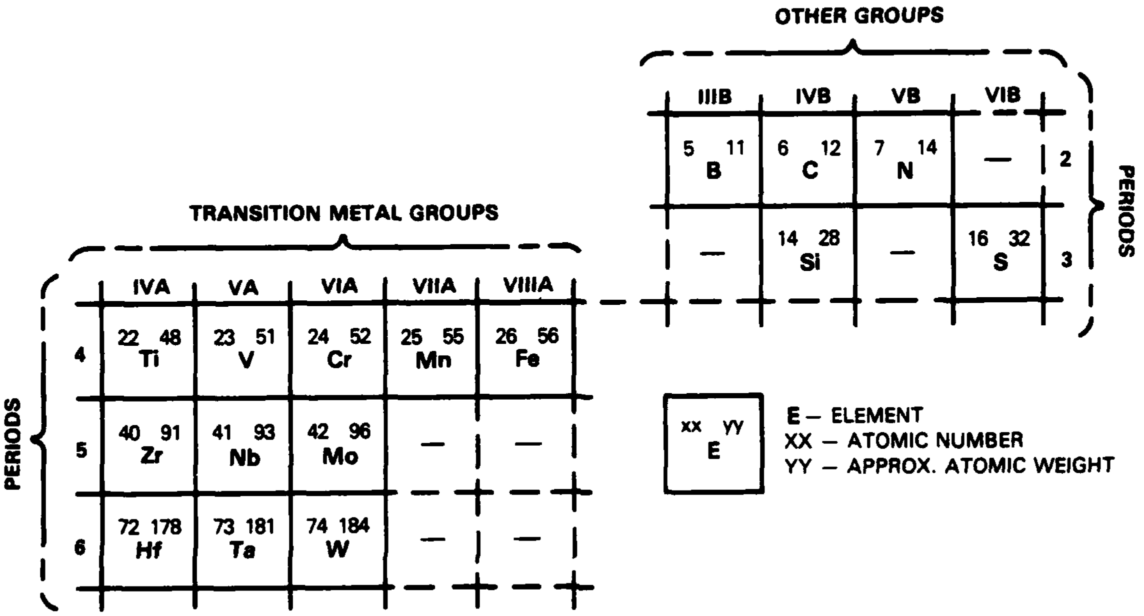


FIGURE 3.
APPLICABLE REGIONS OF PERIODIC TABLE OF ELEMENTS

The Q and T_{ad} data are grouped in Figures 4 and 5 as averages for all compounds studied for each position on the periodic table occupied by the metallic reactant. In general, $\overline{T_{ad}}$ values tend to be higher for Group IV and V elements involved in reactions than for elements from Groups VI through VIII. In the case of $\overline{Q}$ values, the same relationship of higher values for Group IV and V elements holds within each of the periods. Definite overall trends are noticeable in both Figures 4 and 5. Values decrease from left to right (as periodic groups get higher), excepting for the anomaly attributable to Group VII that included only two values. The vertical trends (by period) are reversed in the two cases. $\overline{T_{ad}}$ values diminish as periods get lower, excepting for Group VI, and $\overline{Q}$ values diminish as periods get higher.

$\overline{T_{ad}}$ Values[a]

PERIODS	Transition Metal (A) Groups				
	IV	V	VI	VII	VIII
4	$\boxed{2993}$	2555	1868	2275[b]	1700[c]
5	$\boxed{3116}$	2893	1578	–	–
6	$\boxed{4173}$	2915	1271	–	–

HIGH-LOW TREND ⟶ (EXCLUDING GROUP VII)

HIGH-LOW TREND ↑ (EXCLUDING GROUP VI)

☐ = 3 LARGEST VALUES

[a] T_{ad} VALUES ARE REPORTED AS THE AVERAGE ADIABATIC REACTION TEMPERATURE WITHIN EACH GROUP OF COMPOUNDS (M_iN_j).

[b] TWO VALUES ONLY.

[c] ONE VALUE ONLY.

FIGURE 4.
AVERAGE T_{ad} VALUES FOR 55 COMPOUNDS

$\overline{Q}$ Values[a]

PERIODS	Transition Metal (A) Groups				
	IV	V	VI	VII	VIII
4	$\boxed{687}$	$\boxed{530}$	270	385[b]	255[c]
5	$\boxed{427}$	347	253	–	–
6	382	197	62	–	–

HIGH-LOW TREND ↓

HIGH-LOW TREND ⟶ (EXCLUDING GROUP VII)

☐ = 3 LARGEST VALUES

[a] Q VALUES ARE REPORTED AS AVERAGE CALORIES PER GRAM OF REACTION PRODUCT (M_iN_j) WITHIN EACH GROUP.

[b] TWO VALUES ONLY.

[c] ONE VALUE ONLY.

FIGURE 5.
AVERAGE Q VALUES FOR 55 COMPOUNDS

After examination of these data, a decision was made to select the quotient of $Q \div T_{ad}$ as the parameter best representative of thermodynamic potentials for self-sustaining synthesis. The rationale is that larger quantities of heat released per gram of product should act as a thermal driving force for the reaction. The driving force should also be intensified if the temperature range of heating is more restricted (i.e., for smaller temperature ranges of T_{ad} minus T_0). This rationale is buttressed by the similarity of the quotient $Q \div T_{ad}$ and the entropy of mixing,

$$S_{mix} = \int_{T_i}^{T_{ad}} \frac{Q}{T} \, dT$$

which is the driving force behind the change in chemical potential, or free energy. In fact, once the reaction occurs at the reaction temperature, this increased entropy of mixing makes the absorption of the heat of reaction *spontaneous, and the product temperature is raised to* T_{ad}. The reaction parameter is identified as the thermochemical potential factor (TPF), and numerical values are obtained from the following relationship [$TPF = (Q \div T_{ad}) \times 100$]. When the average Q and T_{ad} values of Figures 4 and 5 are converted to average TPF values in Figure 6, the highest thermochemical potentials are shown for compounds formed with elements from Periodic Groups IV and V of the transition metals that appear in Period 4 of the periodic table (titanium and vanadium). In fact, any of the five elements in Period 4 (Ti, V, Cr, Mn, and Fe) have values of thermochemical potential factors as high or higher than the other six values in Figure 6.

Compound Type (by non-metallic element)

The final data comparisons of average thermochemical potential factors ($\overline{TPF}$) are shown in Figures 7 and 8, where the values are related to types of chemical compounds in regard to position of the metallic reactant in the periodic table. The data in Figure 7 indicate that titanium and vanadium borides (TiB, TiB_2, VB, VB_2, and V_3B_2) have by far the highest TPF values. Similarly, data in Figure 8 indicate that titanium and vanadium nitrides

$\overline{\text{TPF}}$ Values[a]

PERIODS	Transition Metal (A) Groups				
	IV	V	VI	VII	VIII
4	$\boxed{23}$	$\boxed{21}$	14	17[b]	15[c]
5	14	12	10	–	–
6	9	7	5	–	–

HIGH-LOW TREND ↓

HIGH-LOW TREND → (EXCLUDING GROUP VII)

☐ = 2 LARGEST VALUES

[a] TPF VALUES ARE REPORTED AS AVERAGE THERMOCHEMICAL POTENTIAL FACTORS FOR EACH GROUP OF REACTION PRODUCTS (M_iN_j).

[b] TWO VALUES ONLY.

[c] ONE VALUE ONLY.

FIGURE 6.
AVERAGE TPF VALUES FOR 55 COMPOUNDS

(TiN and VN) have the highest ranking as a group of compounds, and other groups that follow closely in the ranking are Period 5 nitrides (NbN, Nb_2N, and ZrN), Period 4 carbides (TiC and VC), and Period 4 borides (CrB_2, TiB, TiB_2, VB, VB_2, and V_3B_2).

Although these data strongly suggest that borides and nitrides have the greatest potential for self-sustaining synthesis, a limited number of values available for sulfides also indicated some possibilities there. The TPF values of 14 for MoS_2 (a Group VI-Period 5 combination) and 19 for MnS (a Group VII-Period 4 combination) appear to exceed the other trends.

Gram Molecular Weight

Since comparisons of group averages of thermochemical potential factors demonstrated a relationship with position on the periodic table, potential relationships for individual compounds were examined next. Gram molecular weights were used for differentiation between compounds; Figure 9 shows the data for all compounds represented in Figures 7 and 8 that have

$\overline{\text{TPF}}$ Values[a]

Type of Compound	Transition Metal (A) Groups		
	IV	V	VI
BORIDES	$\boxed{20}$	$\boxed{21}$	9
CARBIDES	12	10	5
NITRIDES	17	14	–
SILICIDES	13	9	9

☐ = 2 LARGEST VALUES

[a] TPF VALUES ARE REPORTED AS AVERAGE THERMOCHEMICAL POTENTIAL FACTORS FOR EACH GROUP OF REACTION PRODUCTS

FIGURE 7.
AVERAGE TPF VALUES FOR 52 COMPOUNDS IN THREE PERIODIC GROUPS

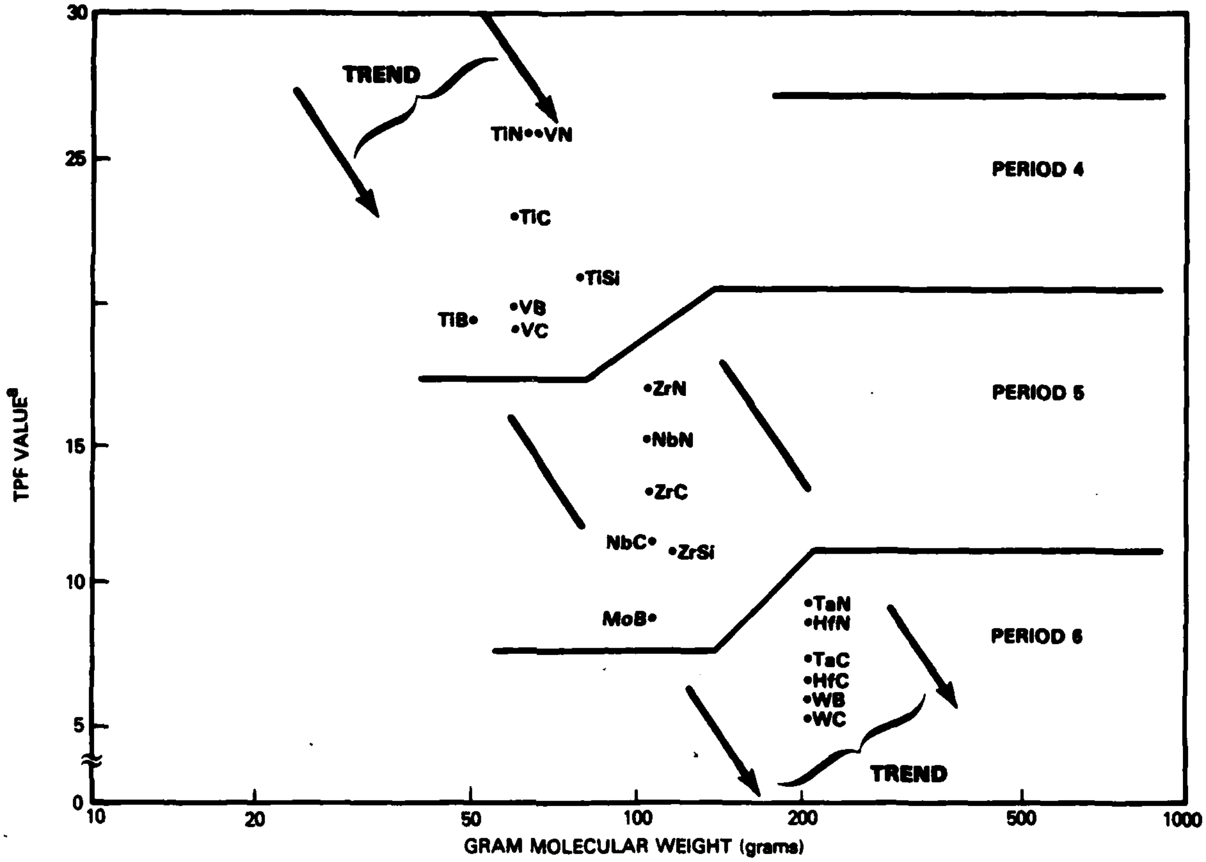
$\overline{\text{TPF}}$ Values[a]

Type of Compound	Periods		
	4	5	6
BORIDES	$\boxed{20}$	12	6
CARBIDES	$\boxed{21}$	9	5
NITRIDES	$\boxed{26}$	$\boxed{22}$	12
SILICIDES	15	10	6

☐ = 4 LARGEST VALUES

[a] TPF VALUES ARE REPORTED AS AVERAGE THERMOCHEMICAL POTENTIAL FACTORS FOR EACH GROUP OF REACTION PRODUCTS

FIGURE 8.
AVERAGE TPF VALUES FOR 52 COMPOUNDS IN THREE PERIODS



^{a}[(Q + T_{ad}) × 100] VALUES FOR COMPOUNDS

FIGURE 9.
TPF VALUES FOR INDIVIDUAL MN COMPOUNDS

an MN stoichiometry. A trend of decreasing TPF values with increasing molecular weights is very definite, as revealed by the slanted lines that enclose the 19 values reported. Although a few values overlap, groupings of metallic elements from Periods 4, 5, and 6 are also apparent. Similar trends are also indicated within these three periods for most relationships among Group IV, V, and VI elements for the same chemical types of compounds but these relationships are not always consistent. Six other stoichiometric combinations (M_2N_5, MN_2, M_3N_2, M_5N_3, M_2N, and M_3N) were also examined, and the same trends shown in Figure 9 were evident in each instance (i.e., thermochemical potentials diminished as gram molecular weights increased).

Compound Stoichiometry

In view of the demonstrated relationship between thermochemical properties and atomic number and mass, thermochemical potentials were checked in several series of compounds (M_iN_j) in which only the stoichiometric ratio ($i \div j$) varied. In this case also, relationships that linked molecular mass and thermochemical potential were confirmed. As shown in Figure 10, values of the thermochemical potential factor diminish as the stoichiometric ratio increases for 14 of the 15 M-N groupings (gram molecular weights necessarily increase with increases in this ratio). In the case of the exception, $TiSi_2$, Reference 19 indicated that the T_{ad} values used in Figure 10 were suspect for that group of compounds.

Other relationships that are apparent in Figure 10 are the trends of decreasing TPF values with increasing elemental periods (for Periods 4 through 6) for the M elements. Within each period as well, a tendency is shown for TPF values to decrease as the elemental "A" group numbers increase from left to right for the M elements within each period.

Additional Data on Thermochemical Potentials

Some Q and T_{ad} data were also available on compound-forming reactions among elements outside the areas on the periodic table that were shown previously in Figure 3. Locations of these elements are shown in Figure 11, and values for thermochemical potential (TPF) for self-sustaining synthesis are plotted vs. gram molecular weights for these compounds in Figure 12. With the exception of the TPF value for Be_3N_2, the same general trends observed previously in Figure 9 apply in Figure 12 (i.e., the TPF values tend to diminish for heavier molecular weights). Compounds formed with metallic elements from Periods 2 and 3 (Be and Mg) on the A-Group side of the periodic table tend to follow the normal trend established previously for elements from Periods 4 through 6. Also, compounds formed between elements in Periods 2 and 3 on the B-Group side follow the trend (see points for AlN, Al_4C_3, B_4C, BN, SiC, and Si_3N_4). Elements from lower periodic groups than Group IVA (Be, Mg, Ca, La, Ce, Th, and U) and from higher periodic groups than Group VIIIA also follow the trend (see values for Ni from Group XA and Cd from IIB), and elements from higher periods than

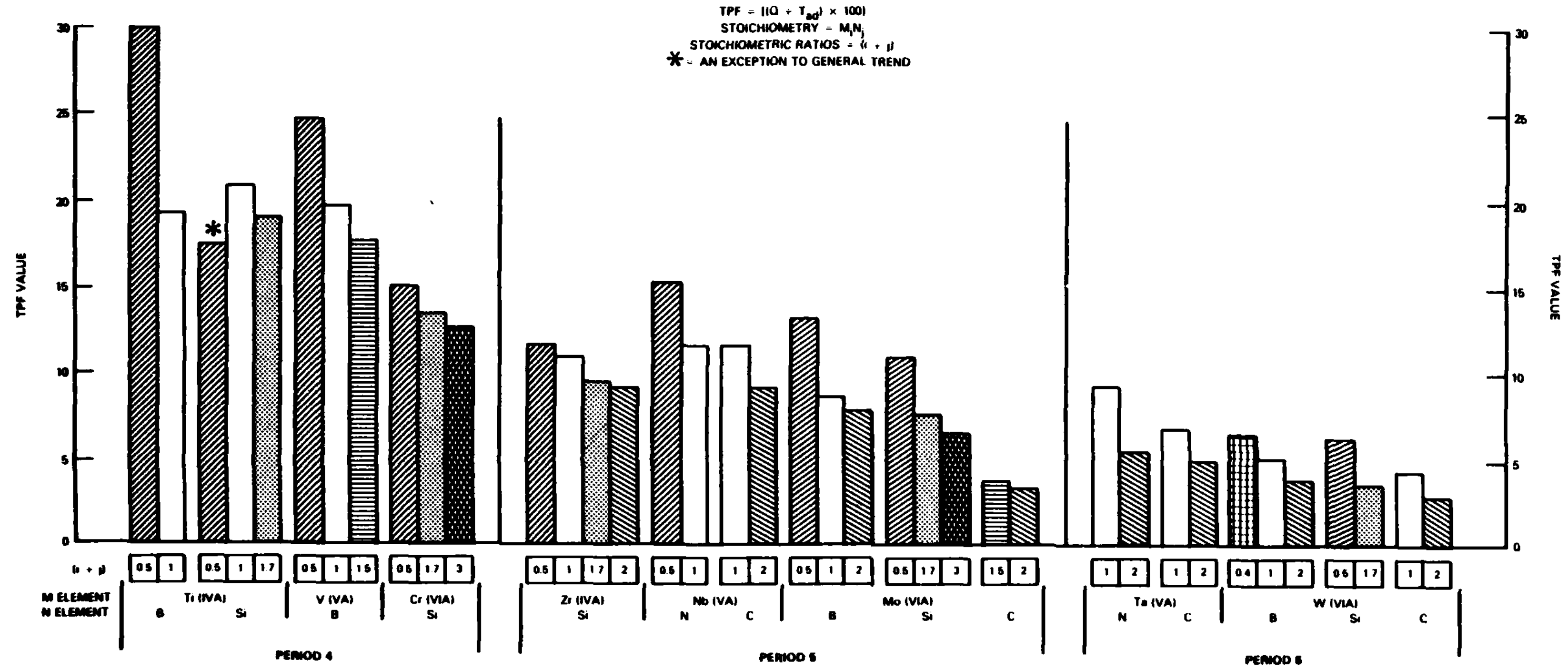


FIGURE 10.
TPF VALUES FOR COMPOUNDS WITH VARYING STOICHIOMETRIC RATIOS FOR SAME REACTANTS

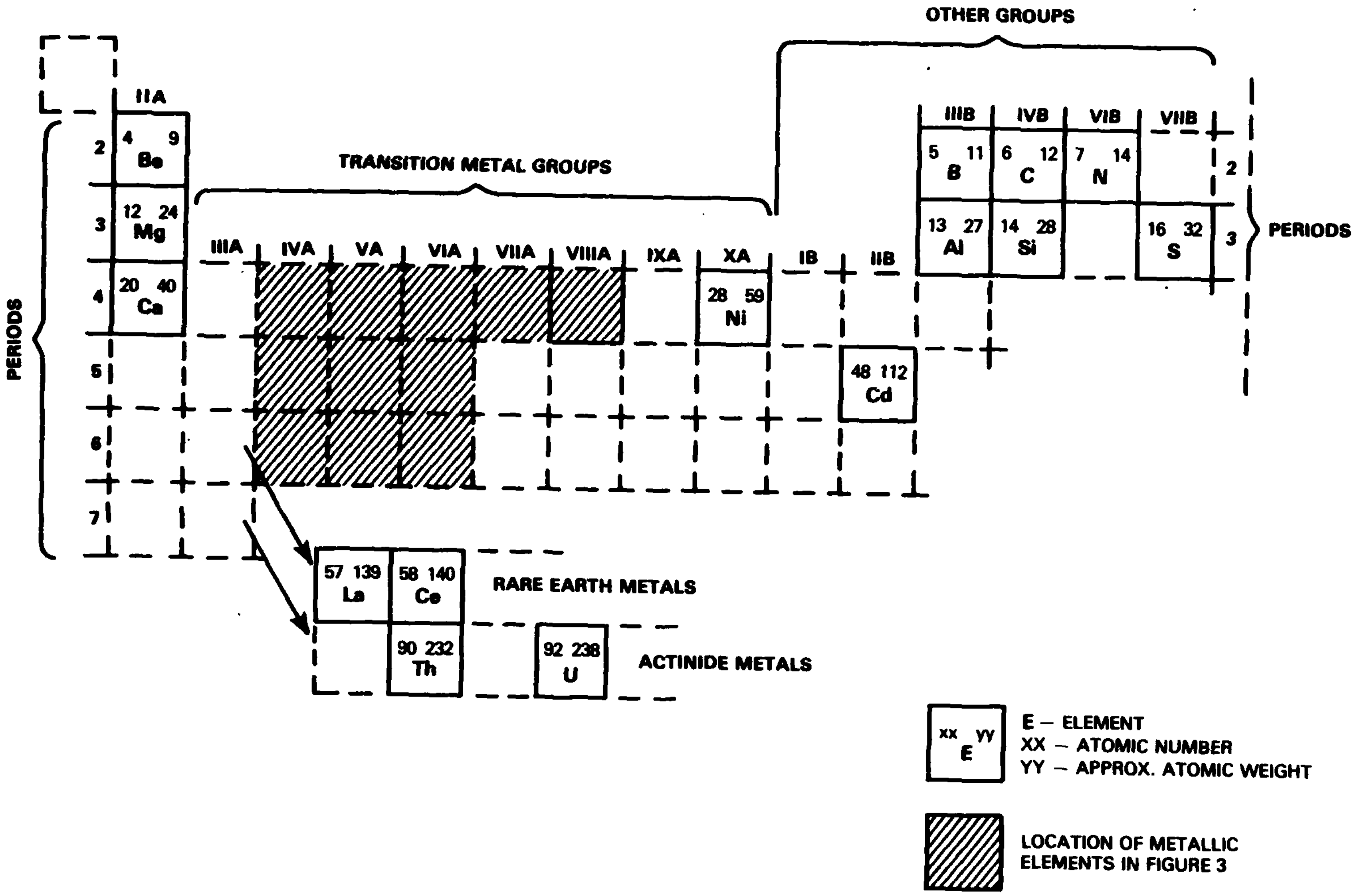
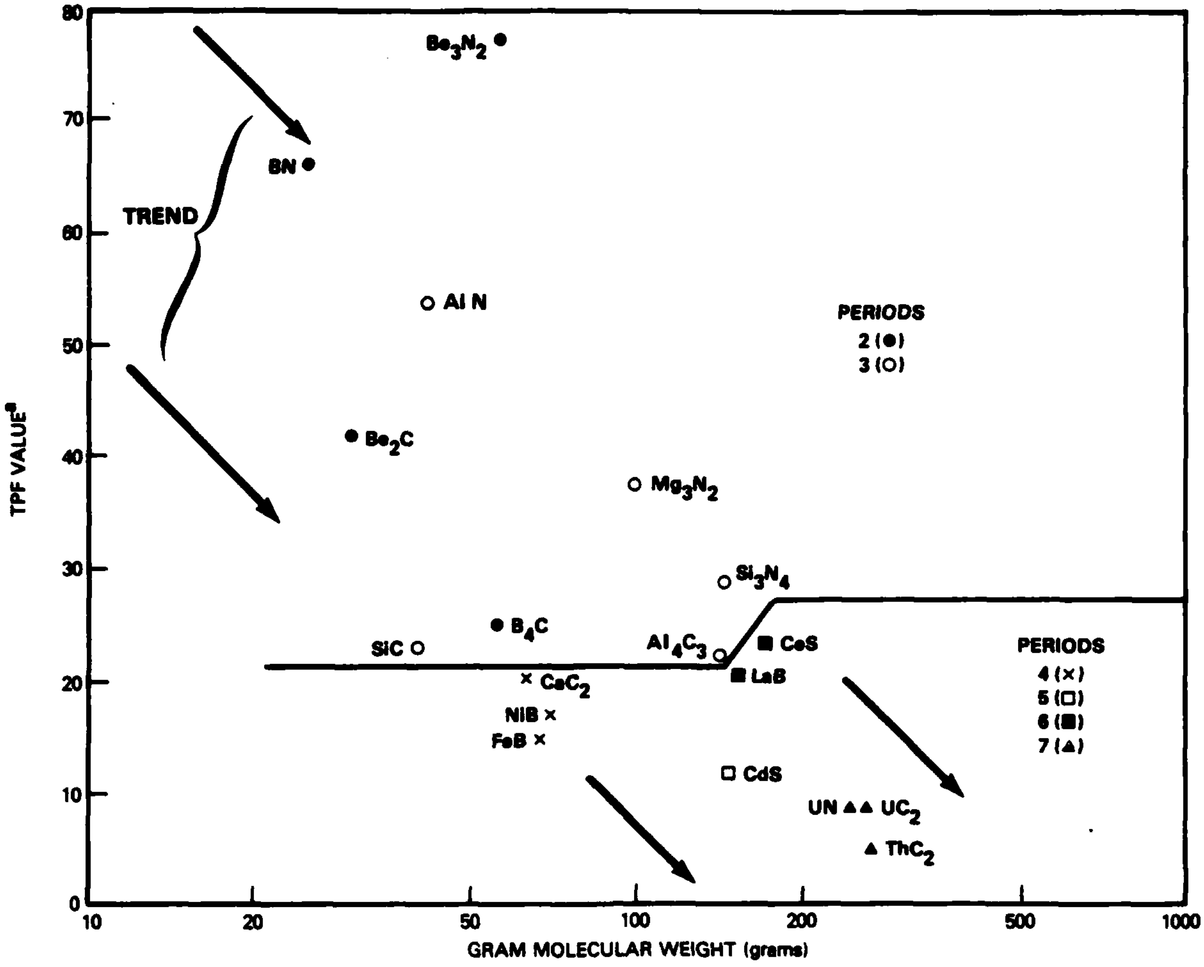


FIGURE 11.
LOCATIONS ON PERIODIC TABLE OF ADDITIONAL REACTANTS



[a][(Q÷T_{ad}) × 100] VALUES FOR COMPOUNDS NOT INCLUDED IN PREVIOUS COMPARISONS.

FIGURE 12.
TPF VALUES FOR MISCELLANEOUS COMPOUNDS

Period 6 likewise tend to follow the trend (see values for actinide metals thorium and uranium from Period 7). In addition, note that the two compounds formed with metals from the rare earth transition series of elements (LaB and CeS) tend to reverse the quantitative levels shown for elements from Periods 4 through 7. TPF values over 20 are extremely high for transition metals from Period 6. Values for Group 7 elements, thorium and uranium, tend to fall more within the established trend than those plotted for Period 6 elements.

Melting Point Data

In exploring the thermochemical potential for self-sustaining synthesis, melting points of the compounds formed are also of interest. The rationale in this regard is that the tendency for forming non-porous products should be greater if a liquid phase is formed during the synthesis process. For that reason, melting potential factors (MPFs) were explored for all compounds for which thermochemical potentials had been examined previously. The MPF values are calculated by dividing the heat of reaction with the melting point of the synthesis product $[(Q \div T_m] \times 100]$. The basic finding in this instance, shown in Table 4, is that MPF values for many nitride compounds are considerably higher than those obtained for the other types.

TABLE 4

MELTING POTENTIAL FACTORS (MPFs) FOR POTENTIALLY SYNTHESIZABLE COMPOUNDS

Highest MPF Values[a]	
Among Nitride Compounds	Among Compounds in Other Chemical Groups
Be_3N_2 - 99	Borides
Mg_3N_2 - 84[b]	TiB_2 - 30
BN - 75[b]	TiB - 26
AlN - 62	VB_2 - 25
Si_3N_4 - 58[b]	NiB - 25[b]
VN - 40	Carbides
TiN - 40	Be_2C - 33
ZrN - 36	TiC - 23
	Sulfides
	MnS - 31
	CeS - 25
	Silicides
	TiSi - 19

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[a] MPF = $[(Q \div T_m) \times 100]$, where Q is the thermal effect of the reaction (cal per gm of product) and T_m is the melting point.

[b] Probably sublimes or decomposes instead of melting.

Although the nitrides do not have the highest melting points among the reaction products examined, the amount of heat released per degree of temperature is greater for them than for other chemical types of compounds.Two other observations possibly relate to this difference between the nitrides and other compound types. First, some of the nitrides with the highest MPF values tend to decompose rather than melt; and second, oxidation resistance of nitrides is generally ranked below other compounds such as borides and carbides. These factors may imply that some nitrides are too thermochemically reactive for self-sustaining synthesis. Both this aspect and the potential role of liquid phases in reaction kinetics will be explored further in the subsequent analysis of combustion technology.

A comparison was also made of the difference between adiabatic reaction temperature (T_{ad}) and melting point (T_m) for potential synthesizable compounds. When these temperature differentials are greater, synthesized products might have a greater tendency to be less porous because of the more extensive superheating. The data reported in Table 5 for the largest temperature differentials among the various types of chemical compounds reveal that some nitride compounds rank well above those in the other groups. Also, carbide and silicide compounds, which have relatively low thermochemical potentials for the transition metal groups (see Figure 7), have the lowest temperature differences in Table 5. On this basis, carbides might not be preferred candidates to form non-porous products in self-sustaining synthesis.

B. POSSIBLE ATOMISTIC RELATIONSHIPS

Although the thermodynamic data used in this analysis are not considered to be of suitable quality for a quantitative statistical investigation of the demonstrated relationships, many of the trends shown are well defined and are considered to warrant a qualitative exploration of underlying causes. Because reaction temperature and thermal effect were related to position of reactants in the periodic table, those properties were selected for an initial exploration of potential atomistic relationships. In this connection, the most obvious fields to explore are atomic and crystal structures.

TABLE 5

GREATEST DIFFERENCES BETWEEN ADIABATIC REACTION TEMPERATURES (T_{ad}) AND MELTING POINTS (T_m)

Largest (T_{ad} - T_m) Differences (^{o}K)	
Among Nitride Compounds	Among Compounds in Other Chemical Groups
Si_3N_4 - 2130[a]	Borides
Mg_3N_2 - 1600[a]	TiB - 850
HfN - 1520	NiB - 600[a]
VN - 1180	Carbides
NbN - 760	No positive values
Be_3N_2 - 730	Sulfides
TiN - 680	MnS - 1200
ZrN - 650	MoS_2 - 520
	Silicides
	ZrSi - 280
	Zr_5Si_3 - 280

---

[a] Probably sublimes or decomposes instead of melting.

In the case of atomic orbitals, the following properties were examined:

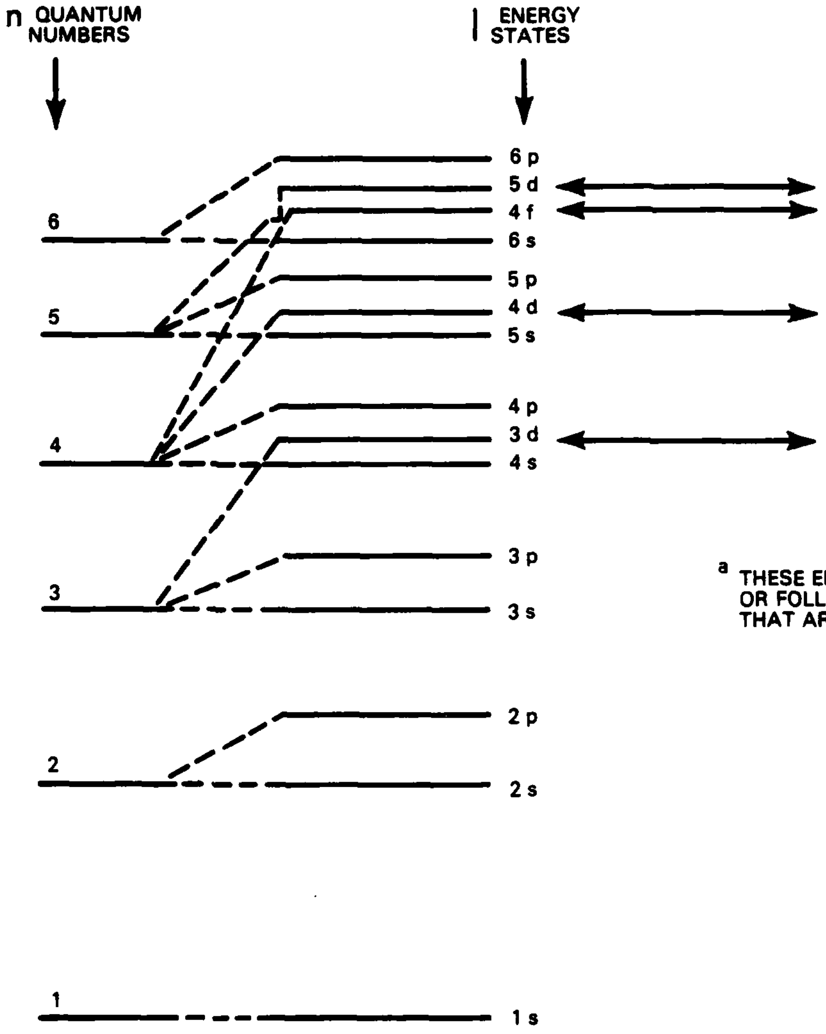
- Electronic structure and energy state in regard to n and l quantum numbers for atoms of metallic reactants and products
- Atomic size of the metallic reactants.

In the case of crystal structures, interatomic spacing was investigated.

The first relationship considered was that the thermal effect (Q) of the reactions in forming compounds appears to vary inversely in magnitude with the electron charge levels of the metallic reactants. Note in Figure 5, Q values tend to decrease within each period as atomic numbers (electron charges in the atoms) increase. With this relationship, the higher charged atoms tend to give up less heat in chemical reactions. Thus, as shown in Figure 11, the highest Q values for the metallic elements shown would be expected for compounds of beryllium, magnesium, and calcium, and even higher values would be expected for the Group IA (alkali metals) elements that are located to the left of those three elements. This relationship appears to hold for beryllium compounds, since Be_2C and Be_3N_2 have by far the largest Q values among the 34 carbide and nitride compounds for which data were available. However, CaC_2 and Mg_3N_2 do not rank second among the carbide and nitride compounds, and no compounds were reported for the Group IA elements. Regardless, in these latter cases, the relatively low melting point of the metallic elements may well account for the lack of stable compounds or for the relatively low thermal releases in forming compounds. For the other compounds, formed with metallic elements listed in Figures 3 and 11, the relationship of lower heat releases with increasing electron charges holds true for each period.

After each electron shell is filled in moving to the right side of the periodic table for Periods 4, 5, and 6, the charge level is increased on the left side of the tables by 18 units between Periods 4 and 5 and between Periods 5 and 6. In the Group IVA column of elements, these differences are 18 and 32 charges, respectively. Thus, the inverse relationship of heat release to charge level is also indicated in Figure 5 by the Q values of 687, 427, and 328 cal per gm for the Group IVA column.

In regard to the second quantum number l (energy states s, p, d, and f), abrupt changes are apparent in energy levels for states 3d, 4d, 4f, and 5d. As shown in Figure 13, the energy level advances in those cases beyond that of one or more energy states in the next n level. Thus, relatively high heat releases might be expected for elements in the periodic table just prior to those abrupt increases or at the beginning of the shell fillings following the abrupt changes. Identities of elements in those positions related to shell fillings are also provided in Figure 13 (on the right hand side). In the case of those elements, only scandium and yttrium are of potential interest to self-sustaining synthesis of refractory compounds; melting points of the other elements are too low to merit consideration. Scandium and yttrium are located in the periodic table to the immediate left of titanium and zirconium, which exhibit two of the largest



POSITIONS OF ELEMENTS[a]

PRECEDING	FOLLOWING
BARIUM	LANTHANUM
LANTHANUM	CERIUM
STRONTIUM	YTTRIUM
CALCIUM	SCANDIUM

[a] THESE ELEMENTS IMMEDIATELY PRECEDE OR FOLLOW ENERGY-STATE OVERLAPS THAT ARE DESIGNATED BY THE ARROWS.

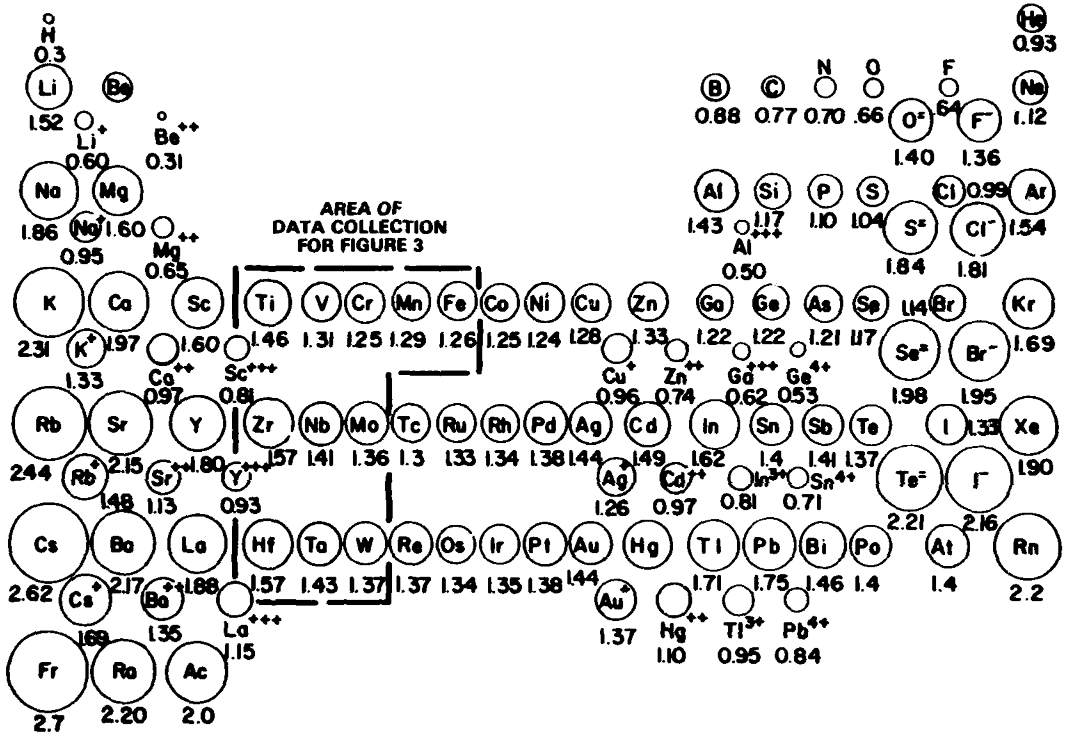
SOURCE: *Figure 3-4 of Reference 24.*

FIGURE 13.
RELATIVE LEVELS OF ENERGY STATES WITHIN PRIMARY QUANTUM NUMBERS

Q values in Figure 5. In addition, the elements lanthanum and cerium, listed in Figure 13, formed compounds (LaB_6, LaN, and CeS) that had higher Q values than any other compounds formed with Period 6 elements.

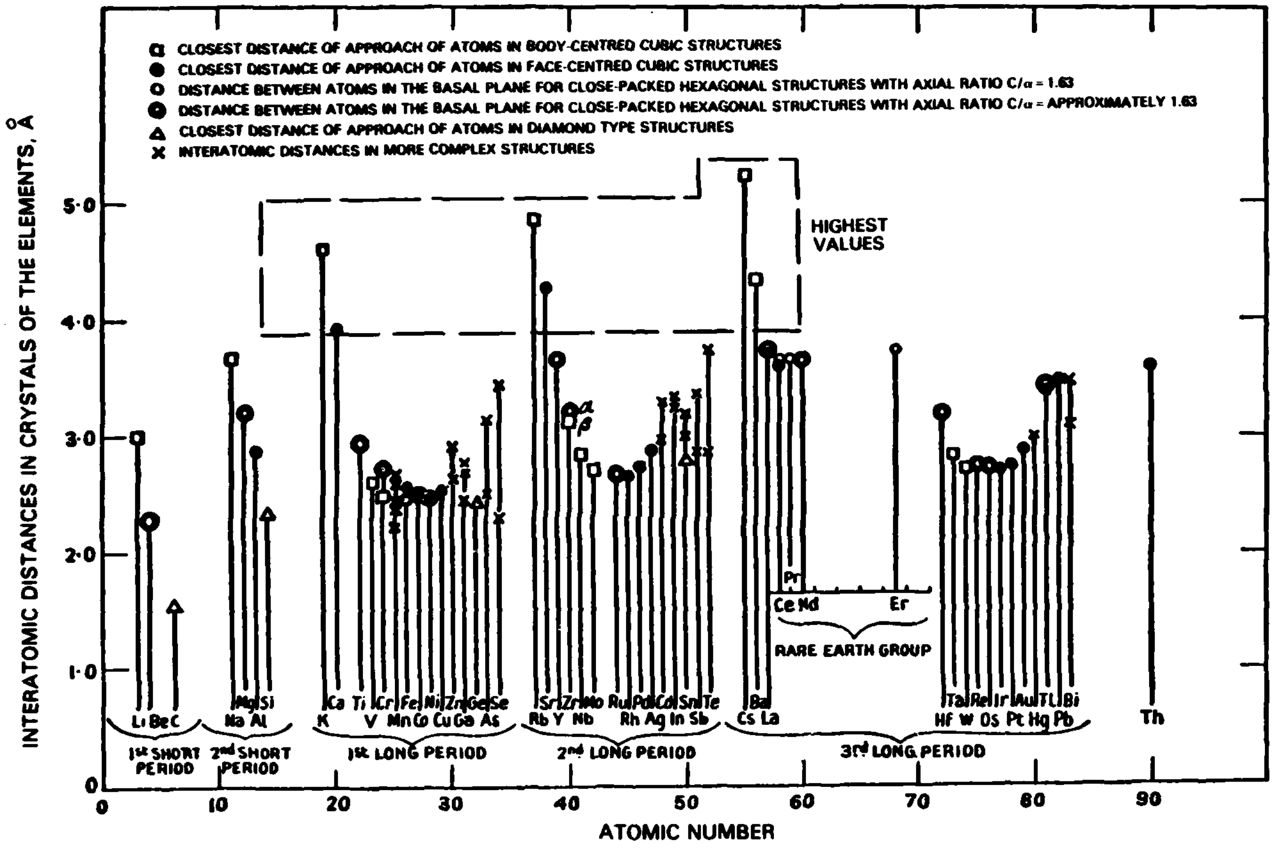
The adiabatic reaction temperature data (T_{ad} values) shown in Figure 4 have a different trend direction (vertical) in the elemental groups than shown for Q values (Figure 5), but both charts exhibit the same trend direction for the elemental periods (horizontal). In Figure 14, trend directions for T_{ad} values can be related somewhat to trends in atomic radii within and between elemental periods. Generally, reaction temperatures tend to be higher for the larger metallic reactant atoms. Perhaps, the larger atomic nuclei tend to act as thermal shields in retaining the heat of reaction.

This statement must be tempered somewhat because interatomic spacing could also have a similar influence on heat release. Figure 15 reveals, for example, that beryllium has a relatively close atomic packing even though its atomic radius is one of the smallest. Thus, it might be expected to have T_{ad} values at intermediate levels compared to the other elements listed in Figure 15, and this is, in fact, true. These data also suggest that some elements in Groups IA and IIA, namely sodium, potassium, calcium, rubidium, strontium, cesium, and barium, have relatively open interatomic structures, and might therefore be expected to exhibit extremely low T_{ad} values. This relationship was true for the single T_{ad} value reported for this group of elements, since CaC_2 had a reaction temperature of only 1100°K.



SOURCE: *Figure 3.6 of Reference 24.*

FIGURE 14.
PERIODIC TABLE OF ATOMIC AND IONIC SIZES



SOURCE: Figure 25 of Reference 25.

FIGURE 15.
INTERATOMIC SPACING VS. ATOMIC NUMBER OF ELEMENTS

IV. GUIDANCE FOR LABORATORY DEVELOPMENT

In spite of the limited scope of this study, trends in thermochemical relationships have been demonstrated that should be useful in planning laboratory research and development. The concept of thermochemical potential for self-sustaining reaction should provide considerable insight for selection of preferred elemental reactants and products.

The thermochemical potential factor is greatest for compounds formed with metallic elements from Groups II, III, IV, and V and from the lower numbered periods in the periodic table. Thermodynamic data support this contention in the case of high-potential compounds formed with beryllium, magnesium, titanium, vanadium, and zirconium. Although no data were available for scandium and yttrium compounds, thermochemical trends suggest that these elements should exhibit high thermochemical potential for forming refractory compounds. Aluminum and boron, from Periods 2 and 3, respectively, have also showed some promise for high thermochemical potential in forming nitrides.

Although some individual nitride compounds exhibit rather high thermochemical potentials for self-sustaining synthesis, the boride compounds are highest when compared as groups including large numbers of compounds. Many nitrides are known to suffer from poor oxidation resistance at elevated temperatures [Ref. 26]. Diborides, on the other hand, have excellent thermal stability [Ref. 27]. Borides are acknowledged to have melting points and hardnesses in ranges comparable to many carbides and nitrides (see bold type in Tables 6 and 7). Borides have also been well researched as chemical compounds and shown to have many potential commercial uses [Ref. 29].

TABLE 6

TYPICAL MELTING TEMPERATURES FOR SOME REFRACTORY AND OTHER MATERIALS

Material	Temperature (°F)
Hafnium carbide	7520
Tantalum carbide	7025
Graphite	6870
Zirconium carbide	6370
Tungsten	6100
Tantalum nitride	6050
Titanium carbide	5660
Thoria	5630
Zirconium boride	**5530**
Titanium boride	**5250**
Magnesia	5072
Silicon carbide	4892
Zirconia	4850
Molybdenum	4748
Beryllia	4660
Zircon	4530
Boron carbide	4430
Silicon carbide (volatilizes)	4160
Spinel	3860
Alumina	3720
Magnesium sulfide	3460
Forsterite	3430
Mullite	3400
Platinum	3220
Silica	3038
Titania	2920
Iron	2995
Clinoenstatite	2835

Source: Table II of Reference 28.

The combination of beryllium and boron is particularly intriguing for self-sustaining synthesis because of the potentially high thermochemical potential for reaction. This combination also results in compounds that have favorable strength-mass ratios for applications where weight constraints are important, and high hardness and melting points (e.g., BeB_2 and BeB_6, per Ref. 30).

TABLE 7

TYPICAL HARDNESSES FOR SOME REFRACTORY AND OTHER MATERIALS

Material	Hardness
Diamond	7000
Boron carbide	2800
Titanium boride, 31%, and boron carbide, 69% (by weight)	**2750**
Titanium boride	**2720**
Silicon carbide	2500
Titanium carbide	2460
Zirconium carbide	2090
Alumina	2000
Tungsten carbide	1880
Cemented carbide	1400 to 1800
Zirconium boride	**1560**
Beryllia	1220
Quartz	800
Hardened steel (60.5 Rockwell C)	740
Glasses	300 to 500
Calcite	130
Gypsum	30

Source: Table IV of Reference 28.

The thermochemical data also demonstrated that the potential for self-sustaining synthesis is generally higher for compounds that have lower gram molecular weights and have stoichiometries that emphasize the nonmetallic element in the M_iN_j relationship. For example, Be_2C, with a gram molecular weight of 30, has a considerably higher reaction potential than W_2C, with a gram molecular weight of 380; likewise, TiB_2, in which the i-to-j stoichiometric ratio is 0.5, has a considerably higher thermochemical reaction potential than TiB, which has an i-to-j ratio of 1.0.

The next logical step would be to perform laboratory screening experiments to determine whether these thermochemical relationships can be exploited in a practical way. Perhaps the simplest approach would be to choose potential reactants and products from opposite ends and the middle of this demonstrated thermochemical spectrum (e.g., BeB_2 vs. ScH_2 vs. TiB_2 vs. W_2C) and to compare their behavior in laboratory synthesis experiments.

The level of porosity in the reacted products would be of considerable interest in determining whether differences in thermochemical potential are manifested in the product and whether a high or low reaction potential is more favorable.

Whereas Soviet researchers have concentrated on transition metals in Periodic Groups IVA through VIIA (in Periods 4 through 6), no thermochemical basis is apparent for limiting research to this restricted portion of the periodic table. In fact, since Soviet patents may constrain commercialization of self-sustaining synthesis processes, selection of elements outside this restricted area could be advantageous.

List of Symbols

C_{liq}	molar heat capacity
$C(T)_p$	molar heat capacity at constant pressure
C_{sol} (T_{melt})	molar heat capacity of solid product at the melting temperature
E	element in periodic table
G	Gibbs free energy
ΔG	molar Gibbs free energy relative to standard and state
H	enthalpy
ΔH	molar enthalpy of pure substance relative to standard state
ΔH_i	molar enthalpy of phase transformation i occurring at transformation temperature T_i
$i \div j$	stoichiometric ratios in M_iN_j compounds
M	elemental metallic reactant
MPF	melting potential factor $[(Q \div T_m) \times 100]$
N	elemental nonmetallic reactant
O	elemental oxidizer reactant
P	reacted product
Q	thermal effect (calories per gram) of individual reactions
$\overline{Q}$	average of thermal effects of a number of reactions
R	elemental reducer reactant
S	entropy
ΔS	molar entropy relative to standard state
ΔS_{mix}	entropy of mixing
T	absolute temperature (°K)
T_{ad}	adiabatic reaction temperature
$\overline{T_{ad}}$	average adiabatic reaction temperature
T_f	final temperature
T_i	temperature of phase transformation

T_m	melting (fusion) temperature
T_o	initial temperature
TPF	thermochemical potential factor $[(Q \div T_{ad}) \times 100]$
$\overline{TPF}$	thermochemical potential factor average
X	elemental oxidizer-reducer reactant

Greek Letters

η	number of atoms in a molecule of product
ν_i	fraction of mole experiencing phase change i

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