NBSIR 74-551

An Appraisal of Methods for Estimating Self-Reaction Hazards

W. Tsang and E. S. Domalski

Physical Chemistry Division
Institute for Materials Research
National Bureau of Standards
Washington, D. C. 20234

June 1974

Interim Report for Period January – June 1974

Prepared for
Office of Hazardous Materials
partment of Transportation
shington, D. C. 20024

NBSIR 74-551

AN APPRAISAL OF METHODS FOR ESTIMATING SELF-REACTION HAZARDS

W. Tsang and E. S. Domalski

Physical Chemistry Division
Institute for Materials Research
National Bureau of Standards
Washington, D. C. 20234

June 1974

Interim Report for Period January – June 1974

Prepared for
Office of Hazardous Materials
Department of Transportation
Washington, D. C. 20024

U. S. DEPARTMENT OF COMMERCE, Frederick B. Dent, Secretary

NATIONAL BUREAU OF STANDARDS, Richard W. Roberts, Director

Preface

The production of chemical compounds and their transportation constitutes a vital segment of our nation's technological growth and economic stability. Hazardous materials require appropriate labeling and identification in connection with their handling and transport in commerce and industry. The Hazardous Classification System proposed by the Department of Transportation, Hazardous Materials Regulations Board, describes various classifications for materials, however, thermally unstable or self-reactive materials are indicated only as a secondary descriptor. The possibility of identifying thermal instability of chemical substances without recourse to experimental studies is the basic purpose of this study. Our approach has been to evaluate certain procedures which claim to be capable of estimating hazard potential by a direct comparison with the results of explosive sensitivity tests and the predictions from the hazard evaluation schemes.

In particular, we have examined both the CHETAH program and Stull's modification of the CRUISE programs for estimating the hazard potential of chemical compounds. As presently constituted we believe that these schemes over-emphasize <u>power</u> as opposed to <u>sensitivity</u>. The latter is a vastly more complex property in comparison with the former because it involves a detailed knowledge of the rates and mechanism of the initial decomposition or polymerization reaction. We suspect that no simple computational scheme of the type under discussion here will be adequate for the classification of all materials or serve as a substitute for experimental results. Nevertheless these programs do introduce concepts which when properly utilized are to some degree correlatable with sensitivity test results. They represent important beginnings in the efforts to rationalize a subject which until now must be considered more of an art than science.

We wish to thank Dr. Eli Freedman (U.S. Army, Ballistics Research Laboratories, Aberdeen Proving Ground, Aberdeen, MD), Dr. Daniel R. Stull (Dow Chemical Company, Midland, MI), and Ms. Eleonore G. Kayser (Chemistry Research Department, Naval Ordnance Laboratory, White Oak, MD) for their assistance and for many useful discussions on various aspects of thermal instability appraisal.

Table of Contents page

List of Tables page

List of Figures page

I. Introduction

The Hazardous Materials Regulations Board of the Department of Transportation (DOT) is presently considering the adoption of amendments to its existing regulations which would characterize more definitively thermally unstable materials and would give detailed instructions for their handling and transport. Improved labeling and placarding of hazardous materials are part of DOT's proposed Hazard Information System (HI System) and will furnish appropriate identifiers to persons who might possibly be confronted with an emergency hazard situation. At present, "SELF REACTIVE" or "THERMALLY UNSTABLE" is proposed as a secondary or tertiary descriptor in the HI System after a primary descriptor such as "FLAMMABLE LIQUID" or "OXIDIZER".

Until recently interest in the characterization of materials on the basis of their self-reaction potential has been limited to those with interest in explosives. Numerous investigations have produced ingenious test methods which permit the ranking order of explosives with regard to shock, impact or thermal sensitivity. In the past few years, spurred by the continual introduction of new chemicals by industry (many of which, although unsuitable for use as explosives, may behave as such under appropriate conditions), attempts have been made to rank substances with regard to susceptibility of self-reaction on the basis of various molecular parameters. Two recent thermochemical studies, one by Treweek, Claydon, and Seaton [1]* and the other by Stull [2,3] have attempted to rank substances with respect to self-decomposition. Both studies describe predictive schemes to estimate hazard potential and have been adapted for machine calculation.

The present investigation represents an attempt at evaluating these schemes. Our procedure will be first to outline the two pertinent schemes and then to illustrate their operational procedure by referring to specific compounds. The latter will permit some immediate conclusions to be drawn with regard to the efficacy of these procedures. Following this, we will proceed with an evaluation on a more formal plane. As a result of identifying the important molecular parameters from the earlier discussion that are supposed to be related to sensitivity, we select from the literature sensitivity test results and then demonstrate directly the degree of correlation or non-correlation for the two sets of data. From these results we will select the molecular property or properties of particular pertinence to material sensitivity and attempt to provide a theoretical justification. At the same time this will indicate the situations where the correlations cannot be expected to apply; in particular with polymerization reactions. Ultimately this will lead to our general conclusions and recommendations with regard to the proposed prediction schemes, test methods, and future work.

---

*Numbers in brackets indicate literature references at the end of the paper.

II. Description of Methods

A. CHETAH Computer Program

A computer program called CHETAH (Chemical Thermodynamics And energy Hazard evaluation) has been developed by the American Society for Testing and Materials (ASTM) Committee E-27 to estimate thermodynamic properties of organic compounds between 300 and 1500 K solely from a knowledge of molecular structure. The calculated thermodynamic data are then used by CHETAH to calculate four energy hazard criteria: namely, (1) maximum enthalpy (heat) of decomposition*, (2) the difference between the heat of combustion and maximum heat of decomposition, (3) oxygen balance, and (4) a modification of the maximum heat of decomposition.

The program contains a data bank which consists of Benson's [4,5] second-order group-contribution values for the enthalpy (heat) of formation (ΔHf°) at 298 K, entropy (S°) at 298 K, and heat capacity (Cp°) at 300, 400, 500, 600, 800, 1000, and 1500 K. For certain calculations, the method of group equations described by Janz [6] is used. The data bank also contains thermodynamic information on a large number of individual compounds. At present the sum total of group-contribution values and data on individual compounds amounts to over 850 items. The CHETAH program can accommodate inorganic and organo-

---

* The terms "enthalpy" and "heat" are used interchangeably throughout the text. Endothermic and exothermic reactions correspond to positive and negative enthalpies, respectively.

metallic compounds, however, proper specification of their reaction products will depend upon the contents of the data bank.

The four hazard criteria of the CHETAH program are discussed in more detail below:

(1) Maximum Enthalpy of Decomposition

The first hazard criterion provides a calculation of the maximum enthalpy of decomposition. Input data for a test run consist of identifying the compound or the group-contributions which comprise the compound and the location of the corresponding thermodynamic information within the data bank. Using these data, a linear programming subroutine selects those decomposition products (also specifically identified in the program data bank) which could be formed from the reactant compound and balances the stoichiometry. The decomposition process which gives a maximum (negative) enthalpy is then chosen. The method is also applicable to reactant mixtures and provides the corresponding maximum enthalpy of decomposition.

The basic approach in the CHETAH program for selecting decomposition products in CHNO compounds is for the oxygen in the molecule to use up the maximum number of hydrogens to form water, H_2O. Excess oxygen would form CO_2 while excess hydrogen would combine with the carbon and form CH_4. Nitrogen present in the molecule would usually end up as molecular nitrogen, N_2, in the products, however, an excess of hydrogen, or hydrogen and oxygen could yield ammonia, NH_3, or nitric acid, HNO_3, respectively.

For this criterion, the program lists the energy hazard potential as low if the maximum heat of decomposition is more positive than -0.3 kcal/g, as medium if the maximum heat of decomposition is between -0.3 and -0.7 kcal/g, and as high if it is equal to or more negative than -0.7 kcal/g. These values were established by ASTM Committee E-27 using experimental results for 120 compounds, about half of which were found to be shock sensitive and half of which were believed to be inert to shock.

We have taken twenty-two compounds to illustrate the CHETAH hazard criteria and have arranged them in approximate decreasing order of explosive sensitivity. Given below in Table 1 are: the name of the compound, and the corresponding formula weight, enthalpy of formation at 25°C in kcal mol^{-1}, and reference to the cited value. In addition, we have provided the decomposition reaction which yields the maximum reaction enthalpy (heat) computed by the CHETAH program. Both reactants and products are gaseous unless otherwise identified. Formula weights were calculated from the 1971 table of atomic weights [7] which showed: C = 12.011; H = 1.0079; N = 14.0067; O = 15.9994; Cl = 35.453; Br = 79.904; Pb = 207.2; Ag = 107.868; Hg = 200.59.

Table 2 lists the twenty-two selected compounds, identifies their calculated maximum enthalpy at 298 K, and gives their hazard rating.

Table 1. Decomposition reactions computed by the CHETAH program

1. mercury fulminate; 284.6242; ΔHf° = 64 [9]

   $Hg(ONC)_2(s) \rightarrow CO_2 + Hg(s) + N_2 + C(s)$

2. silver azide; 149.8881; ΔHf° = 73.8 [7]

   $AgN_2(s) \rightarrow Ag(s) + 1.5\ N_2$

3. lead azide; 291.2402; ΔHf° = 114.3 [9]

   $Pb(N_3)_2(s) \rightarrow Pb(s) + 3\ N_2$

4. nitroglycerin; 227.0872; ΔHf° = -64.7 [8]

   $C_3H_5N_3O_9 \rightarrow 3\ CO_2 + 2.4\ H_2O + 1.4\ N_2 + 0.2\ HNO_3$

5. ethylenedinitramine; 150.0938; ΔHf° = 4.8 [10]

   $C_2H_6N_4O_4 \rightarrow 0.5\ CO_2 + 3\ H_2O + 2\ N_2 + 1.5\ C(s)$

6. ethyl nitrate; 91.0664; ΔHf° = -36.80 [9]

   $C_2H_5ONO_2 \rightarrow 0.25\ CO_2 + 2.50\ H_2O + 0.5\ N_2 + 1.75\ C(s)$

7. 2,4,6-trinitrotoluene; 227.133; ΔHf° = 12.3 [8]

   $C_7H_5N_3O_6 \rightarrow 1.75\ CO_2 + 2.5\ H_2O + 1.5\ N_2 + 5.25\ C(s)$

8. azoethane; 86.1364; 32.2 [5,16]

   $C_4H_{10}N_2 \rightarrow 2.5\ CH_4 + 1.5\ C(s) + N_2$

9. nitromethane; 61.0402; ΔHf° = -17.86 [9]

   $CH_3NO_2 \rightarrow 0.25\ CO_2 + 1.5\ H_2O + 0.5\ N_2 + 0.75\ C(s)$

10. diacetyl peroxide; 118.089; ΔHf° = -116.1 [3]

    $C_4H_6O_4 \rightarrow 0.5\ CO_2 + 3\ H_2O + 3.5\ C(s)$

11. peracetic acid; 76.0518; ΔHf° = -97.7 [3]

    $C_2H_4O_3 \rightarrow 0.5\ CO_2 + 2\ H_2O + 1.5\ C(s)$

Table 1 - continued

12. ethylene oxide; 44.053; ΔHf° = -12.58 [9]

$C_2H_4O \rightarrow H_2O + 0.5\ CH_4 + 1.5\ C(s)$

13. propargyl bromide; 118.9607; ΔHf° = 52.5 [10]

$C_3H_3Br \rightarrow 0.5\ CH_4 + HBr + 2.5\ C(s)$

14. vinyl chloride; 62.4987; ΔHf° = 8.4 [9]

$C_2H_3Cl \rightarrow 0.5\ CH_4 + HCl + 1.5\ C(s)$

15. ethylene; 28.0536; ΔHf° = 12.50 [9]

$C_2H_4 \rightarrow CH_4 + C(s)$

16. 1-octene; 112.2144; ΔHf° = -19.82 [11]

$C_8H_{16} \rightarrow 4\ CH_4 + 4\ C(s)$

17. acetic acid; 60.0524; ΔHf° = -103.93 [9]

$C_2H_4O_2 \rightarrow 2\ H_2O + 2\ C(s)$

18. ethyl acetate; 88.1060; ΔHf° = -106.34 [12]

$C_4H_8O_2 \rightarrow 2\ H_2O + 3\ C(s) + CH_4$

19. acetamide; 59.0676; -57.8 [5,16]

$C_2H_5NO \rightarrow H_2O + 0.75\ CH_4 + 1.25\ C(s) + 0.5\ N_2$

20. dimethyl ether; 46.0688; ΔHf° = -43.99 [9]

$C_2H_6O \rightarrow H_2O + CH_4 + C(s)$

21. ethyl chloride; 64.5145; ΔHf° = -26.70 [9]

$C_2H_5Cl \rightarrow CH_4 + HCl + C(s)$

22. n-octane; 114.2302; ΔHf° = -49.82 [11]

$C_8H_{18} \rightarrow 4.5\ CH_4 + 3.5\ C(s)$

Table 2. Maximum Enthalpy of Decomposition

Formula	name	maximum ΔH(decomposition)		hazard rating
		kcal mol^{-1}	kcal g^{-1}	
$Hg(ONC)_2(c)$	mercury fulminate	-158.	-0.56	medium
$AgN_3(c)$	silver azide	-73.8	-0.49	medium
$Pb(N_3)_2(c)$	lead azide	-114.3	-0.39	medium
$C_3H_5N_3O_9$	nitroglycerin	-362.6	-1.60	high
$C_2H_6N_4O_4$	ethylenedinitramine	-225.2	-1.50	high
$C_2H_5ONO_2$	ethyl nitrate	-131.2	-1.44	high
$C_7H_5N_3O_6$	trinitrotoluene	-321.4	-1.41	high
$C_4H_{10}N_2$	azoethane	-76.9	-0.89	high
CH_3NO_2	nitromethane	-92.3	-1.51	high
$C_4H_6O_4$	diacetyl peroxide	-104.3	-0.88	high
$C_2H_4O_3$	peracetic acid	-64.9	-0.85	high
C_2H_4O	ethylene oxide	-54.2	-1.23	high
C_3H_3Br	propargyl bromide	-70.1	-0.59	medium
C_2H_3Cl	vinyl chloride	-39.4	-0.63	medium
C_2H_4	ethylene	-30.4	-1.08	high
C_8H_{16}	1-octene	-51.7	-0.46	medium
$C_2H_4O_2$	acetic acid	-11.66	-0.19	low
$C_4H_8O_2$	ethyl acetate	-27.1	-0.31	medium
C_2H_5NO	acetamide	-13.4	-0.23	low
C_2H_6O	dimethyl ether	-31.7	-0.69	medium
C_2H_5Cl	ethyl chloride	-13.3	-0.21	low
C_8H_{18}	n-octane	-30.7	-0.27	low

Examination of Table 2 shows that (on the basis of intuition) valid predictions of hazard rating are obtained for many compounds; nitroglycerin, trinitrotoluene, ethylenedinitramine, azoethane, nitromethane, and ethyl nitrate are considered explosive and hazardous materials and are rated as high hazards. We acknowledge the large difference in explosive sensitivity between nitroglycerin and TNT, however, such selectivity is beyond the capability of this method. Others, such as n-octane, acetamide, acetic acid, and ethyl chloride are rated as low hazard, as expected. Inconsistencies do occur, however, since detonators like lead azide, silver azide, and mercury fulminate are classed as medium hazard and should really be high hazard because they are the most sensitive explosives in the listing. Similarly, compounds such as dimethyl ether and ethyl acetate are rated as medium hazard and more realistically should be in the low hazard grouping. Ethylene is classed as being of high hazard assuming it decomposes into elemental graphite and methane, however, polymerization is a more likely reaction pathway for this compound. As yet, the CHETAH program has no facility for identifying or classifying compounds which are hazardous on the basis of their tendency to polymerize.

The errors in hazard ratings which have been generated in this hazard criterion are partly related to the maximization of the enthalpy (heat) of decomposition. Although the maximization technique is mathematically convenient, it departs significantly from the decomposition processes of the real world and the decomposition products selected are not what one would always obtain. The decomposition products obtained by CHETAH for the detonators are likely reaction products, however, these errors suggest strongly that this criterion does not clearly correlate with explosive sensitivity.

(2) Enthalpy Difference Criterion

The difference between the enthalpy of combustion and enthalpy of decomposition at 25°C constitutes the second hazard criterion, and is based on the idea that a compound which contains within its own structure sufficient oxygen to convert the compound to its normal oxidation products, presents a greater energy hazard than one which does not. The rating in this criterion is high if [ΔH(combustion) - ΔH(decomposition)] is less negative than -3.0 kcal/g, medium if between -3.0 and -5.0 kcal/g, and low if more negative than -5.0 kcal/g.

Table 3 below gives the results of calculation [ΔH(combustion) - ΔH(decomposition)] at 25°C for the twenty-two compounds and the corresponding hazard rating.

Table 3. ΔH(combustion) - ΔH(decomposition)

		[ΔH(combustion - ΔH(decomposition)		hazard
Formula	name	kcal mol^{-1}	kcal g^{-1}	rating
$Hg(ONC)_2(c)$	mercury fulminate	-115.8	-0.41	high
$AgN_3(c)$	silver azide	-7.4	-0.05	high
$Pb(N_3)_2(c)$	lead azide	-51.9	-0.18	high
$C_3H_5N_3O_9$	nitroglycerin	+1	+0.04	high
$C_2H_6N_4O_4$	ethylenedinitramine	-136.3	-0.91	high
$C_2H_5ONO_2$	ethyl nitrate	-164.8	-1.81	high
$C_7H_5N_3O_6$	trinitrotoluene	-493.8	-2.17	high
$C_4H_{10}N_2$	azoethane	-909.5	-10.56	low
CH_3NO_2	nitromethane	-70.7	-1.16	high
$C_4H_6O_4$	diacetyl peroxide	-329.2	-2.79	high
$C_2H_4O_3$	peracetic acid	-141.1	-1.86	high
C_2H_4O	ethylene oxide	-236.9	-5.38	low
C_3H_3Br	propargyl bromide	-331.0	-2.78	high
C_2H_3Cl	vinyl chloride	-237.0	-3.79	medium
C_2H_4	ethylene	-285.8	-10.19	low
C_8H_{16}	1-octene	-1143.2	-10.19	low
$C_2H_4O_2$	acetic acid	-118.1	-3.13	medium
$C_4H_8O_2$	ethyl acetate	-473.9	-5.38	low
C_2H_5NO	acetamide	-261.4	-4.43	medium
C_2H_6O	dimethyl ether	-285.8	-6.20	low
C_2H_5Cl	ethyl chloride	-285.8	-4.43	medium
C_8H_{18}	n-octane	-1192.1	-10.44	low

Examination of the hazard ratings obtained for the second hazard criterion in Table 3 shows that nitroglycerin holds true to form with essentially a zero value for $[\triangle H(\text{comb})-\triangle H(\text{decomp})]$ indicating this compound contains enough oxygen within its own molecular structure to provide for its own decomposition, and hence merits a high hazard rating. Similarly, the conventional explosive compounds (TNT, ethylenedinitramine, diacetyl peroxide, etc.) are found to have a high hazard rating. The detonators are classed as expected, very close to nitroglycerin in actual value, and henceforth, are high hazards. Both ethylene and ethylene oxide are rated as low hazard here in contrast to the high hazard rating obtained with the first hazard criterion. This low hazard rating for these compounds is not realistic since both are reactive because of their tendency to polymerize. Azoethane is rated low by the second criterion, however, it is known to decompose explosively. Propargyl bromide is rated as being a high hazard in this criterion in contrast to a medium rating with the maximum $\triangle H$(decomposition) criterion. This compound has a very positive enthalpy of formation in addition to being highly unsaturated so that reaction by decomposition and polymerization are both likely.

(3) Oxygen Balance

The third criterion, or the oxygen balance, is the quantity of oxygen required for the complete conversion of the elements present in a compound to their corresponding normal combustion products. A different mathematical expression is required for compounds with elements comprising their stoichiometries. Examples are given below:

$$C_aH_b + (a + (b/4))O_2 \rightarrow aCO_2 + (b/2)H_2O$$

oxygen balance = $[-1600(2a + b/2)] /(\text{formula wt.})$

$$C_aH_bN_c + (a + (b/4))O_2 \rightarrow aCO_2 + (b/2)H_2O + (c/2)N_2$$

oxygen balance = $[-1600(2a + (b/2))]/(\text{formula wt.})$

$$C_aH_bO_d + (a + (b/4) - (d/2))O_2 \rightarrow aCO_2 + (b/2)H_2O$$

oxygen balance = $[-1600(2a + (b/2)-d)]/(\text{formula wt.})$

$$C_aH_bN_cO_d + (a + (b/4) - (d/2))O_2 \rightarrow aCO_2 + (b/2)H_2O + (c/2)N_2$$

oxygen balance = $[-1600(2a + (b/2)-d)]/(\text{formula wt.})$

$$C_aH_bCl_e + (a + (b/4) - (e/4)O_2 \rightarrow aCO_2 + (b/2) - (e/2)\ H_2O + eHCl$$

oxygen balance = $[-1600(2a + (b/2) - (e/2))]/(\text{formula wt.})$

$$C_aH_bBr_f + (a + (b/4) - (f/4))O_2 \rightarrow aCO_2 + (b/2) - (f/2)\ H_2O + fHBr$$

oxygen balance = $[-1600(2a + (b/2) - (f/2))]/(\text{formula wt.})$

This criterion, like the second criterion, is a measure of the amount of oxygen bonded within the molecular structure which could convert part or all of the molecule to its normal oxidation products. If the oxygen balance is more positive than 240.0 or more negative than -160.0, the energy hazard potential is rated as low. If the oxygen balance is between +240.0 and +120.0 or -160.0 and -80.0, the energy hazard potential is rated as medium. If the oxygen balance is between -80.0 and +120.0, the energy hazard potential is rated as high.

Table 4 provides calculated values of the oxygen balance for the twenty-two compounds and their corresponding hazard rating.

Table 4. Oxygen Balance

Formula	name	oxygen balance	hazard rating
$Hg(ONC)_2(c)$	mercury fulminate	-16.9	high
$AgN_3(c)$	silver azide	-10.7	high
$Pb(N_3)_2(c)$	lead azide	-5.5	high
$C_3H_5N_3O_9$	nitroglycerin	3.5	high
$C_2H_6N_4O_4$	ethylenedinitramine	-32.0	high
$C_2H_5ONO_2$	ethyl nitrate	-61.5	high
$C_7H_5N_3O_6$	trinitrotoluene	-74.0	high
$C_4H_{10}N_2$	azoethane	-241.5	low
CH_3NO_2	nitromethane	-13.1	high
$C_4H_6O_4$	diacetyl peroxide	-94.9	medium
$C_2H_4O_3$	peracetic acid	-63.1	high
C_2H_4O	ethylene oxide	-181.6	low
C_3H_3Br	propargyl bromide	-94.1	medium
C_2H_3Cl	vinyl chloride	-128.0	medium
C_2H_4	ethylene	-342.2	low
C_8H_{16}	1-octene	-342.2	low
$C_2H_4O_2$	acetic acid	-79.9	high
$C_4H_8O_2$	ethyl acetate	-181.6	low
C_2H_5NO	acetamide	-149.0	medium
C_2H_6O	dimethyl ether	-208.4	low
C_2H_5Cl	ethyl chloride	-148.8	medium
C_8H_{18}	n-octane	-350.2	low

The hazard ratings from Table 4 show both the explosives and detonation receiving a rating of high. The oxygen balance criterion failed to identify diacetylperoxide (medium), ethylene oxide (low), or propargyl bromide (medium) as probably worthy of a high hazard rating. On the other hand certain substances were suggested as being hazardous when experience indicates otherwise. For example: acetic acid (high) and ethyl chloride (medium) are more correctly identified as low hazard.

(4) Modified Enthalpy of Decomposition Criterion

The fourth criterion is described by the following equation:

$$y = (10)(\Delta H(\text{decomp}))^2(W)/(n)$$

where $\Delta H(\text{decomp})$ is the maximum enthalpy of decomposition in kcal g^{-1}, W is the formula weight of the compound undergoing decomposition, and n is the number of atoms which make up the latter compound. If y is greater than 110.0, the energy hazard potential is rated as high. If y is between 30.0 and 110.0, the energy hazard potential is rated as medium. If y is below 30.0, the energy hazard potential is rated as low. Table 5 shows the y value and hazard rating for the twenty-two compounds. When a comparison is made between the hazard rating provided in Table 5 and the hazard rating from the enthalpy of decomposition given in Table 2, improvement is found for dimethyl ether, ethyl acetate, and 1-octene in going from medium to low. Similarly, mercury fulminate, a detonator, is rated a high hazard in Table 5 by criterion (4), however, the absolute value of y is nowhere near TNT or nitroglycerin. Lead azide and silver azide are rated incorrectly as being only of medium hazard. Comparison shows diacetyl peroxide, peracetic acid and ethylene oxide as having a medium hazard rating (Table 5) from

Table 5. Modified Enthalpy of Decomposition Criterion

Formula	name	y ($y = 10\ (\Delta H_d)^2 W/n$)	hazard rating
$Hg(ONC)_2(c)$	mercury fulminate	125.2	high
$AgN_3(c)$	silver azide	90.7	medium
$Pb(N_3)_2(c)$	lead azide	63.9	medium
$C_3H_5N_3O_9$	nitroglycerin	291.7	high
$C_2H_6N_4O_4$	ethylenedinitramine	211.1	high
$C_2H_5ONO_2$	ethyl nitrate	171.7	high
$C_7H_5N_3O_6$	trinitrotoluene	215.0	high
$C_4H_{10}N_2$	azoethane	42.6	medium
CH_3NO_2	nitromethane	198.8	high
$C_4H_6O_4$	diacetyl peroxide	65.3	medium
$C_2H_4O_3$	peracetic acid	61.1	medium
C_2H_4O	ethylene oxide	95.2	medium
C_3H_3Br	propargyl bromide	59.1	medium
C_2H_3Cl	vinyl chloride	41.3	medium
C_2H_4	ethylene	54.5	high
C_8H_{16}	1-octene	9.9	low
$C_2H_4O_2$	acetic acid	2.7	low
$C_4H_8O_2$	ethyl acetate	6.0	low
C_2H_5NO	acetamide	3.5	low
C_2H_6O	dimethyl ether	24.4	low
C_2H_5Cl	ethyl chloride	3.6	low
C_8H_{18}	n-octane	3.2	low

criterion (4) whereas they were rated more correctly as high hazard (Table 2) by criterion (1).

Overall, the two fundamental properties of importance in CHETAH are (1) maximum enthalpy of decomposition (criterion 1 and 4) and (2) oxygen balance (criterion 2 and 3). Validation of the program has been provided by the ASTM Committee E-27 and shows that preliminary correlations of the CHETAH hazard criteria with experimental shock-sensitivity data on 218 organic compounds yield correct identification of all of the shock-sensitive compounds (83), but incorrect identification of 16 (or about 12%) of the shock-sensitive compounds. The sensitivity data were obtained from three types of experimental test methods, namely, the impact test (120 kg-cm for liquids and 500 kg-cm for solids), and detonation from the explosion of (#9)-blasting cap and (50 g)-pellet of tetryl.

We have provided a summary of the four hazard criteria for the twenty-two compounds in Table 6. We note that only six (nitroglycerin, ethylenedinitramine, ethyl nitrate, TNT, vinyl chloride, n-octane) out of twenty-two compounds received the same hazard rating for all four criteria while three compounds (azoethane, ethylene oxide, acetic acid) received ratings of low, medium, and high among the four categories.

Table 6. Summary of CHETAH Hazard Criteria

Formula	Name	Hazard Rating*			
		(1)	(2)	(3)	(4)
$Hg(ONC)_2(c)$	mercury fulminate	medium	high	high	high
$AgN_3(c)$	silver azide	medium	high	high	medium
$Pb(N_3)_2(c)$	lead azide	medium	high	high	medium
$C_3H_5N_3O_9$	nitroglycerin	high	high	high	high
$C_2H_6N_4O_4$	ethylenedinitramine	high	high	high	high
$C_2H_5ONO_2$	ethyl nitrate	high	high	high	high
$C_7H_5N_3O_6$	2,4,6-trinitrotoluene	high	high	high	high
$C_4H_{10}N_2$	azoethane	high	low	low	medium
CH_3NO_2	nitromethane	high	high	high	high
$C_2H_4O_3$	peracetic acid	high	high	high	medium
$C_4H_6O_4$	diacetyl peroxide	high	high	medium	medium
C_2H_4O	ethylene oxide	high	low	low	medium
C_3H_3Br	propargyl bromide	medium	high	medium	medium
C_2H_3Cl	vinyl chloride	medium	medium	medium	medium
C_2H_4	ethylene	high	low	low	high
C_8H_{16}	1-octene	medium	low	low	low
$C_2H_4O_2$	acetic acid	low	medium	high	low
$C_4H_8O_2$	ethyl acetate	medium	low	low	low
C_2H_5NO	acetamide	low	medium	medium	medium
C_2H_6O	dimethyl ether	medium	low	low	low
C_2H_5Cl	ethyl chloride	low	medium	medium	low
C_8H_{18}	n-octane	low	low	low	low

---

*(1) Maximum Enthalpy of Decomposition

(2) Enthalpy Difference Criterion

(3) Oxygen Balance

(4) Modified Maximum Enthalpy of Decomposition

The detonators, $Pb(N_3)_2$, AgN_3, and $Hg(ONC)_2$ are more correctly identified by oxygen balance than by the maximum enthalpy of decomposition because their decomposition reactions do not conserve any oxygen and with reasonably high formula weights yield values for criteria 2 and 3 which are small enough to fall into the high hazard range. Compounds with low formula weights and modest oxygen consumption, such as ethyl chloride, and acetic acid, will be classed higher than they actually should be.

Strictly speaking, the maximum enthalpy of decomposition is a measure of explosive power and need not always correspond with explosive sensitivity. This has indeed been borne out by the incorrect rating of criterion 1 (and for the most part with criterion 4) for the detonators. From the standpoint of overall screening of substances, there are dangers in equating detonators with substances such as dimethyl ether, ethyl acetate, and acetamide. For many explosive substances, these criteria can provide an accurate rating, however, for all other compounds large overestimates are made to the extent that the overestimates intrude into the range of values occupied by substances that are truly dangerous.

In an effort to improve the predictive capabilities of the CHETAH program and better establish the separation between shock-sensitive and shock-insensitive compounds a combination of the CHETAH hazard criteria is recommended by ASTM Committee E-27. Hence, an organic compound is identified as shock sensitive if: (1) the heat of decomposition is calculated to be greater than -0.7 kcal g^{-1} or either (2) criterion 2 or 3 (oxygen balance) classes the compound to have medium or high hazard rating. According to this combination only four compounds could be considered as shock insensitive, namely: ethyl acetate, 1-octene, dimethyl ether, and n-octane. Included, in the shock sensitive group, however, would be: acetic acid, acetamide and ethyl chloride.

B. CRUISE Computer Program

The computational method used by D. R. Stull (Dow Chemical Co., Midland, Michigan) is a modification of a computer program reported by D. R. Cruise for the calculation of chemical equilibria [13]. The data base used by Stull consists of the JANAF Thermochemical Tables [8], which contain mostly inorganic compounds, and similar tables compiled for the text by Stull, Westrum, and Sinke [11] on the chemical thermodynamic properties of over 900 organic compounds. The modified Cruise program can accommodate up to eight chemical elements (this includes oxygen) in any stoichiometry required by ten reactive species. Input data to the program consist of specifying the stoichiometries of the reactants and their enthalpies of formation at 298 K. As a result of examining the chemical elements present in the reactant species, the program finds a set of potential decomposition products. The program then calculates the thermodynamically most stable products on the basis of their Gibbs energies, balances the stoichiometry, computes the heat of decomposition at 298 K, total number of moles of products, and the maximum temperature, T_d, and the pressure, P_d, of the products. Both T_d and P_d are based on the assumption that 100 grams of reactant are contained in a gram-molar-volume of 24.5 liters at 298 K and that the process takes place at constant volume.

Dr. Stull has provided us with a copy of the back-up computer calculations on some 80 organic compounds covered in his recent paper, "Linking Thermodynamics and Kinetics to Predict Real Chemical Hazards" [3]. Two computations were made through the CRUISE program for each compound; one for the self-decomposition of the compound, the other for the complete combustion of the compound in oxygen. We have presented some of these data in Table 10 (see page 65).

Stull correlated the T_d calculated for the 80 compounds with literature data on activation energies, E_a, for these compounds. A scale with T_d increasing upward from 0 to 3000 K was plotted on the left side of a square while E_a was plotted on the right side with values from 0 to 100 kcal mol^{-1} increasing in the opposite direction (downward). The Reaction Hazard Index Line (RHI) which connects $T_d = 0$ with $E_a = 0$ is divided into 10 units. Another line is drawn for a given compound from its T_d to its corresponding E_a. A value for RHI is assigned at the interception of the Reaction Hazard Index Line. The relationship is shown below in figure 1.

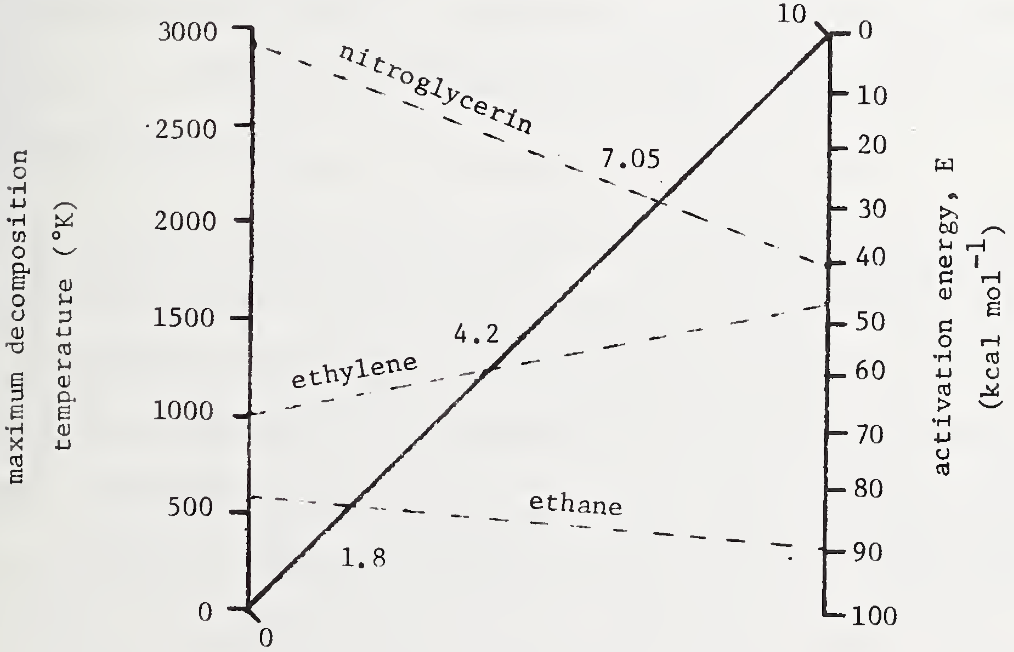


Figure 1. Nomograph of maximum decomposition temperature vs. activation energy. Examples cited are nitroglycerin, ethylene, and ethane.

For validation Stull [2] demonstrates a trend between the RHI values and the reactivity rating values established for these compounds by the National Fire Protection Association (NFPA).

A table of common hazard chemicals has been published by NFPA [15] on almost a yearly basis since 1962. A detailed discussion of the NFPA Hazard Identification System is provided in reference [15] describing ratings for health, flammability, and reactivity. Only the NFPA reactivity ratings are pertinent to our discussion and are given below.

NFPA Reactivity Ratings

(4) Materials which in themselves are readily capable of detonation or of explosive decomposition or explosive reaction at normal temperatures and pressures. Includes materials which are sensitive to mechanical or localized thermal shock. If a chemical with this hazard rating is in an advanced or massive fire, the area should be evacuated.

(3) Materials which in themselves are capable of detonation or of explosive decomposition or of explosive reaction but which require a strong initiating source or which must be heated under confinement before initiation. Includes materials which are sensitive to thermal or mechanical shock at elevated temperatures and pressures or which react explosively with water without requiring heat or confinement. Fire fighting should be done from an explosion-resistant location.

(2) Materials which in themselves are normally unstable and readily undergo violent chemical change but do not detonate. Includes materials which can undergo chemical change with rapid release of energy at normal temperatures and pressures or which can undergo violent chemical change at elevated temperatures and pressures. Also includes those materials which may react violently with water or which may form potentially explosive mixtures with water. In advanced or massive fires, fire fighting should be done from a protected location.

(1) Materials which in themselves are normally stable but which may become unstable at elevated temperatures and pressures or which may react with water with some release of energy but not violently. Caution must be used in approaching the fire and applying water.

(0) Materials which are normally stable even under fire exposure conditions and which are not reactive with water. Normal fire fighting procedures may be used.

A reasonable trend has been shown to exist between the Reaction Hazard Index and the ratings of these compounds by the National Fire Protection Association (NFPA). For illustration we have listed the 80 compounds examined by Stull [2] according to increasing RHI value in Table 7. This arrangement gives a better idea of how the NFPA ratings vary with Stull's scheme. The value of T_d is, of course, calculated by the CRUISE program while the activation energies (not shown in Table 7) were extracted from the literature.

Table 7. Ranking of RHI Values

No.	Formula	Name	T_d(K)	RHI	NFPA rating
1.	CH_4	methane	298	0.88	0
2.	C_2H_6	ethane	597	1.82	0
3.	C_4H_{10}	n-butane	633	1.96	0
4.	C_5H_{12}	2,2-dimethylpropane	597	1.98	0
5.	C_2H_{40}	acetic acid	634	2.38	1
6.	$C_4H_{10}O$	diethyl ether	761	2.46	0
7.	C_3H_8	propane	626	2.48	0
8.	C_7H_8	toluene	859	2.52	0
9.	$C_4H_{10}O$	tert.-butyl alcohol	628	2.54	0
10.	CH_3Cl	methyl chloride	744	2.55	0
11.	C_8H_{10}	4-xylene	817	2.55	0
12.	C_6H_{12}	cyclohexane	677	2.60	0
13.	C_5H_{12}	n-pentane	645	2.60	0
14.	C_5H_{12}	2-methylbutane	626	2.62	0
15.	C_3H_6	propylene	866	2.70	1
16.	$C_6H_{14}O$	diisopropyl ether	712	2.72	1
17.	C_4H_8O	2-butanone	755	2.72	0
18.	C_3H_6O	acetone	744	2.75	0
19.	C_7H_{14}	methylcyclohexane	660	2.75	0
20.	C_8H_{10}	ethylbenzene	830	2.75	0
21.	C_4H_{10}	2-methylpropane	611	2.76	0
22.	$C_5H_{12}O$	2,2-dimethylpropanol	725	2.87	0
23.	C_7H_7Cl	benzyl chloride	831	2.89	1
24.	C_4HgCl	n-butyl chloride	701	2.91	0
25.	C_3H_5N	propionitrile	903	2.93	1
26.	C_2H_5Cl	ethyl chloride	701	2.93	0
27.	C_4H_6	1,3-butadiene	991	2.94	2
28.	C_2H_5Br	ethyl bromide	670	2.96	0
29.	C_3H_7Cl	n-propyl chloride	699	2.98	0
30.	C_4HgBr	n-butyl bromide	668	3.04	0

Table 7. Ranking of RHI Values (continued)

No.	Formula	Name	T_d(K)	RHI	NFPA rating
31.	CH_3NH_2	methylamine	767	3.06	0
32.	C_4H_8	cyclobutane	865	3.16	0
33.	C_8H_{12}	vinyl cyclohexene	876	3.18	2
34.	C_4H_8	1-butene	825	3.18	0
35.	C_3H_6	cyclopropane	936	3.22	0
36.	$CHCl_3$	chloroform	683	3.26	0
37.	$C_4H_8O_2$	ethylacetate	735	3.38	0
38.	$C_5H_{10}O_2$	isopropyl acetate	715	3.40	0
39.	$C_6H_{12}O_2$	butyl acetate	715	3.41	0
40.	$C_2H_4Cl_2$	1,1-dichloroethane	847	3.45	0
41.	C_3H_6O	propionaldehyde	819	3.52	1
42.	C_3H_6O	propylene oxide	948	3.53	2
43.	$C_5H_{10}O_3$	diethyl carbonate	753	3.53	1
44.	$C_2H_5NH_2$	ethylamine	740	3.62	0
45.	$C_3H_6O_2$	dioxolane	911	3.64	2
46.	$C_7H_{14}O_2$	tert.-amyl acetate	705	3.68	0
47.	$C_2H_4Cl_2$	1,2-dichloroethane	849	3.76	0
48.	C_2H_4O	acetaldehyde	866	3.76	0
49.	$(CH_3)_2NH$	dimethylamine	792	3.78	0
50.	$C_2H_4O_0$	ethylene oxide	1062	3.81	3
51.	$C_2H_8N_2$	1,1-dimethylhydrazine	953	3.90	1
52.	CH_6N_2	methylhydrazine	1022	3.96	1
53.	C_4H_8O	vinylethyl ether	880	3.98	2
54.	C_4H_8O	crotonyl alcohol	863	4.12	2
55.	C_2H_4	ethylene	1005	4.19	2
56.	C_3H_5Br	allyl bromide	988	4.20	1
57.	$C_3H_7NO_2$	1-nitropropane	1046	4.22	3
58.	N_2H_4	hydrazine	1338	4.24	2
59.	$C_8H_{18}O_2$	di-tert.-butyl peroxide	850	4.30	4
60.	$C_4H_6O_2$	acetic anhydride	793	4.34	1

Table 7. Ranking of RHI Values (continued)

No.	Formula	Name	T_d(K)	RHI	NFPA rating
61.	$C_4H_{10}O_2$	tert.-butylhydroperoxide	919	4.48	4
62.	$C_{10}H_{12}$	dicyclopentadiene-exo	990	4.61	1
63.	$C_2H_5NO_2$	nitroethane	1161	4.62	3
64.	$C_4H_{10}O_2$	diethyl peroxide	968	4.64	4
65.	CH_2O_2	formic acid	800	4.66	0
66.	C_2H_4	ethylene*	1005	4.71	2
67.	$C_{10}H_{12}$	dicylopentadiene-endo	990	4.93	1
68.	$C_2H_4O_3$	peracetic acid	976	5.04	4
69.	$C_5H_{10}O$	vinyl allyl ether	959	5.11	2
70.	$C_4H_6O_4$	acetyl peroxide	983	5.26	4
71.	$C_9H_{12}O_2$	cumene hydroperoxide	989	5.32	4
72.	C_4H_6	1,3-butadiene*	991	5.72	2
73.	CH_3NO_2	nitromethane	2621	5.97	4
74.	$C_{12}H_{16}N_4O_{18}$	cellulose nitrate	2213	6.12	3
75.	C_8H_8	styrene*	993	6.33	2
76.	$C_2H_5NO_3$	ethyl nitrate	2094	6.36	4
77.	$C_3H_5N_3O_9$	nitroglycerin	2895	7.05	4
78.	C_2H_2	acetylene	2898	7.05	4
79.	C_4H_4	vinyl acetylene	2317	7.33	3

(Only 79 compounds are present in this list due to a duplicate listing for di-tert.-butyl peroxide in [2].)

---

* For the polymerization process.

In table 8 we list a series of explosives from reference [2,3] in the order of decreasing adiabatic decomposition temperatures to see if there is a corresponding trend with the reactivity of the compound. Contrary to what is indicated RDX or HMX is not more sensitive than nitroglycerin; nitromethane is not of the same sensitivity as ethylene-dinitramine. For non-explosives [2,3] a similar listing appears in in table 8 and covers the temperature range 850-950°K. Tert-butyl hydroperoxide is not more stable than propylene oxide; di-tert-butyl peroxide is not as stable as toluene. It appears that the use of a maximum decomposition temperature is not a significant improvement over the heat of decomposition criteria. Furthermore in the section on Decomposition Reactions, it will be shown that for non-explosives the products predicted by Stull do not correspond to the observations from experiments, and the use of the Cruise program to calculate T_d provides a parameter of correlating capacity no better than the heat of decomposition.

The introduction by Stull of the activation energy for decomposition is of key importance: for example, the hydroperoxides and peroxides are unstable because of the weak O-O bond and thus have a low bond dissociation energy for decomposition. In order to identify hazard with bond dissociation energies, such values must ultimately refer to a process that generates heat and Stull provides this linkage by correlating the activation energy with the maximum decomposition temperature, T_d. Conflicts arise, however, with respect to the process identified with the activation energy. To be more specific, consider the case of

Table 8. Maximum Decomposition Temperatures Calculated using the CRUISE Program

Decomposition Temperature, °K	Compound
a) Explosives	
2932	cyclonite - RDX
2921	beta - HMX
2880	glycol dinitrate
2865	mannitol hexanitrate
2859	nitroglycerine
2806	dipentaerythritol hexanitrate
2718	glycerol monolactate trinitrate
2698	metriol trinitrate
2673	tetryl
2621	nitromethane
2564	polyvinyl nitrate
2542	ethylenedinitramine
b) Non-explosives	
948	propylene oxide
936	cyclopropane
919	tert-butyl hydroperoxide
911	dioxalane
880	vinyl ethyl ether
876	vinyl cyclohexene
866	propylene
865	cyclobutane
859	toluene
850	di-tert-butyl peroxide

tert-amyl acetate: the reaction hazard index (RHI) according to Stull is 3.68 which will place it in the vicinity of compounds such as ethylene oxide (RHI = 3.81), dioxolane (RHI = 3.64), and propylene oxide (RHI = 3.53). Comparing tert-amyl acetate to these latter compounds is contrary to everyday experience in terms of their expected self-reactivity. The RHI value for tert-amyl acetate was calculated by Stull using an activation energy which corresponds with the formation of acetic acid and the methyl butenes. This latter reaction is endothermic and bears little resemblance to the decomposition process calculated by the CRUISE program.

Both the CHETAH and CRUISE programs have been examined by Davis and Ake [14] in addition to the NASA Lewis equilibrium program and the program TIGER developed by the Army Materiel Command Explosive Research Program. In this study a group of 31 compounds was chosen which included some common stable compounds in addition to some well known explosive materials. Three sensitivity test methods were applied to these compounds, namely, the standard drop-weight shock test, the shock of a #9 blasting cap, and the shock of a 50 gram pellet of tetryl. Each compound was classified as insensitive, borderline, or sensitive. A ranking coefficient equation was devised in which $R = P + aT + 6Q$, where R is the ranking coefficient, P and T are the reaction pressure and temperature and Q is the energy of reaction as computed by TIGER. Rankings were evaluated by correlating the calculated ranking position of each compound with a master ranking based on the test data.

The program TIGER provided the best ranking with the CRUISE program next, followed by NASA-Lewis and CHETAH. No significance should be attributed to the superior performance of the TIGER program according to Davis and Ake [14] because of possible bias in the chosen set of compounds. The basic powers of prediction of all the programs studied appeared to be about the same.

III. Comparison of Certain Parameters with Sensitivity Test Results

A. Test Procedures

In this section several of the test methods which have been used in the assessment of material sensitivity will be described. The experimental results for a wide variety of compounds will be summarized. We will then demonstrate the degree of correlation or non-correlation between the molecular parameters that are considered to be of importance by the predictive schemes, namely: heat of reaction (decomposition), oxygen balance and bond dissociation energy (or lowest bond energy in a molecule) and the test data. It should be noted that in Stull's scheme a key parameter is the activation energy for decomposition. For reactions which proceed by cleavage (into two radicals) the bond dissociation energy is an important if not the most important component of the activation energy for decomposition. For the present we ignore the possibility of decomposition proceeding without free radical intermediates (purely molecular reaction). This is probably satisfactory for the compounds that will now be considered. Discussion on systems for which such an assumption is invalid can be found in a subsequent section.

Until very recently practically all work on the sensitivity of materials with respect to self-reaction has been carried out by investigators with interest in explosives. The importance of this problem in such a context is obvious and has led to the development of a wide variety of test methods and the collection of a large quantity of data. In the absence of any other information it will be necessary to assume that such tests and results, although limited to compounds of a specific type, have general applicability. This may not cause serious problems for organic compounds since the only common factor is an exothermic heat of decomposition and from a cursory examination of the properties of explosives this heat range extends the full gamut from a few tenths of a kcal/gram to 1.6 kcal/gram for nitroglycerine [25]. In any case it is not unreasonable to ask any predictive scheme to give the correct rankings with respect to explosive sensitivity.

For the present purposes, the test methods which appear to be the most appropriate are the following:

a) Explosion Temperature Test [25,26]. This is basically the method developed originally by Henkin and McGill [27]. It involves loosely loading No. 8 blasting caps with a 10 to 20 mg sample of the explosive and determining the temperature at which the sample explodes, ignites or decomposes after a 5 second period of immersion in a Wood's metal bath. The principal uncertainty in this test is whether temperature equilibration is truly obtained. This will be dependent on the thermal conductivity of the sample. Minor problems are in some cases the need to exclude air and to avoid volatilization.

b. Impact Test [25,26]. This is the simplest and most widely used method for assessing material sensitivity. The basic operation is the dropping of a weight from a given height upon a small sample (tens of milligrams). The impact test value is the minimum height (on a statistical basis) which will result in explosion. The interpretation of such data is, however, more difficult. Of particular importance is the physical state of the substance (liquid or solid). In the case of a solid the mesh size of the material must be considered. Also of importance is the receptacle holding the test sample. The absolute values of weight and height are probably less meaningful than the relative ranking of various substances. The actual physical process involves the delivery of a pressure pulse of several hundred to thousands of atmospheres, the generation of small hot spots and ultimately explosion. The overall process takes place in the order of 100 μsec. Note that the explosion appears to be thermal in original. The main difference between this and the explosion temperature test could be that the energy per unit time delivered to the material and the ignition temperature are much higher in these experiments. Bowden and Yoffe [28] have carried out extensive and elegant studies on initiation by impact.

c. Thermal Surge Test [29]. This test method has been developed at the Naval Ordnance Laboratory by Wenograd [29] in 1961. It is not widely used but due to recent work sponsored by the Department of Transportation at the Naval Ordnance Laboratory (NOL) [30] quantitative results are available on materials generally considered non-explosive (but which may nevertheless be dangerous) using this technique. The operation of this test involves the loading of a test sample into hypodermic needle tubing, the discharge of a capacitor across the tubing, the determination of the reaction temperature from measurements on the electrical resistivities of the tubing and, finally, the determination of the delay time preceding the rupturing of the tubing. For purposes of ranking the temperature which yields a delay time of 250 μsec is used. In many ways this test may be considered the high temperature analog of the explosion temperature test. The temperatures and time scales are, however, much more akin to what is found in the impact tests. Wenograd [29] has demonstrated a very satisfactory correspondence between the results of impact and thermal surge tests. Note that this test can only be carried out with liquids that do not interact with the stainless-steel tubing. It is of course necessary to melt any solids previous to insertion into the hypodermic tubing, since the bursting pressure of the hypodermic tubing must be quite. It may be that the test results are truly representative of explosive sensitivity (as opposed to explosive power) only for strong explosives.

In making the selection of test methods we have emphasized sensitivity in contrast to explosive power. The former is intimately connected with the initiation process while the latter is concerned with the initial and final states (more related to thermodynamics). Obviously a true hazard index for self-reaction should take both factors into account. However, in the context of fire and transportation situations even a minor explosion may lead to catastrophic consequences.

One is thus erring on the side of safety when the contribution from sensitivity is considered to be paramount. This appears to be in line with present day regulatory practice. Earlier, it has been noted that the heats of decomposition of high explosives (a measure of explosive power) cover a wide range. Nevertheless, the regulations lump all high explosives into one group and do not take the extent of this range into consideration enough. Finally, it should be noted that although all test methods mentioned here are supposed to measure sensitivity, a perfect one to one correspondence of the results of the different tests should not be expected. The basic difference is the rate at which energy is being fed into the system. Physically this means that the initial temperature is highest in the impact and thermal surge tests, and lowest for the explosion temperature test. This drastic difference in initial temperature may well have serious effects with regard to the mechanism of decomposition and be reflected in sensitivity determinations. From a practical point of view the results of the explosion temperature test are probably most appropriate under fire conditions while the impact test will be applicable in highway and rail collision accidents.

Overall, it is clear that there is no unique test which will permit the categorization of a material with regard to its hazard potential from self-reaction. As suggested earlier there is a need for exact definitions. Furthermore the tests themselves are susceptible to variations in physical state, trace impurities, material handling and the apparatus itself. Thus at best the results can only be interpreted as a probability that under conditions fairly close to those generated in the test apparatus a given substance will be more or less sensitive than another substance. This will become more clear in the subsequent discussion.

B. Test Results

The results of tests on a wide variety of substances are summarize in table 9. Also included are values for the heats of reaction, the oxygen balance and the dissociation energy for the weakest bond in the compound of interest. In the subsequent discussion we will first comment on the test data and then discuss the three molecular parameters which are presumed by the estimation schemes to be of importance with respect to material sensitivity.

There are two entries for the impact tests. One set is derived from the Bureau of Mines apparatus [26] and the other from the Picatinny Arsenal apparatus [26]. They have been included because they are readily available and demonstrate very well the dependence of the results on the nature of the instrument and the handling of the material. The chief difference between the two tests are that in the latter apparatus the sample is held in a small steel die cup and the impulse is transmitted by a vented steel plug. In the Bureau of Mines apparatus the sample is held between two flat steel plates. This also means that for liquid samples the test is carried out with the material dissolved in filter paper. This is considerably different than tests on the pure sample. There are also two sets of results for the thermal surge test. One is from Wenograd's original paper and appear to yield results considerably higher than the subsequent work. The reason for this is unclear. With regard to the explosion temperature test, the tabulated data are in substantial agreement with the original work of Henkin and McGill [27]. This is not really surprising, since the basic experiment may be regarded as a primitive form of differential thermal analysis. One cannot but suspect that in view of the remarkable advances in instrumentation in this field in recent years, the explosion temperature test can be upgraded considerably.

With respect to the parameters used in the estimation schemes, the oxygen balance is a defined quantity (see above) depending only on the elementary composition of the compound in question. The heat of decomposition in these schemes is estimated. For known explosives the estimates of product distribution and enthalpies of reactions are not seriously in error. This can be seen in table 10. The situation for non-explosives is much less favorable. Further comparisons will be reserved for a subsequent section. For the present purposes the experimental numbers will be used. The bond dissociation energies are traceable for the most part from careful kinetic experiments on related molecules and from the use of the fact that within the present context they may be considered a local property. In other words, similar type bonds will have the same energy regardless of the molecular environments. Thus for the aromatic nitro compounds the bond energy is taken to be $\Delta H_f(C_6H_5) + \Delta H_f(NO_2) - \Delta H_f(C_6H_5NO_2) = 71$ kcal/mol. On this basis each of the groups A, organic nitrates; B, aromatic nitro compounds, etc. in table 9 have a characteristic bond energy. This is the reason for the ordering of compounds in table 9. It is suspected that the present approach will bring about an uncertainty of 3-4 kcals/mol.

C. Correlations

Before proceeding with quantitative comparisons some general observations are worthwhile. First of all, the experimental test methods show that detonators are among the most sensitive of explosives. Furthermore the least sensitive explosives are the aromatic nitro compounds while the nitroamines appear to be slightly less sensitive than the organic nitrates. All of this is in accord with general experience and is indicative of the appropriateness of the test methods.

Direct comparisons between the results of the three test methods and the three parameters used in the predictive schemes can be seen in figures 2 thru 10. For purposes of identification the points in the figures are given the letters and numbers assigned to the particular compound in table 9. It is clear that there is no quantitative one-to-one correlation between the three molecular parameters in question and the test data. Qualitatively there does appear to be some correlations between bond energy and the sensitivity tests. To a much lesser degree this may also be true for oxygen balance. On the other hand, it is not possible to consider the heat of reaction (decomposition) as an important sensitivity parameter. Indeed, a closer examination of the data shows that the use of the heat of reaction as a sensitivity criterion leads to rather striking conclusions. For example, the heats of decomposition of detonators such as lead azide M1, lead 2,4-dinitroresorcinate (LDNR) L1, lead styphnate K1, mercury-fulminate J1, silver azide I1, tetracene H1, and diazodinitrophenol F1, are: .37 kcal/g, .27 kcal/g, .46 kcal/g, .43 kcal/g, .45 kcal/g, .66 kcal/g, and .82 kcal/g, respectively. An ordinary high explosive such as TNT B6 has a heat of decomposition of 1.08 kcal/g. Similarly the heat of decomposition of tetryl C5 (a nitramine) is less than that for nitromethane D1 but the former is vastly more sensitive both from test data and everyday experience. The lack of relationship between sensitivity and heat of reaction is well known to those with interest in explosives. For example, according to Price [38], "Ease of initiation is associated with the thermodynamic functions of activation and hence the chemical kinetics of decomposition. The kinetics are unrelated to the energy released by the decomposition..." If one apply the same sort of individual comparisons to the oxygen balance criteria similar discrepancies occur, although to a somewhat lesser extent. For example, one still has nitromethane D1 being more sensitive than tetryl C5, tetracene H1, and diazo dinitrophenol F1. In comparison the bond energy criterion does not appear to violate any of the generally held ideas about sensitivity of explosives. This may partly be due to the fact that the inorganic detonators have been excluded from the plots since the bond energies are not well established. But is should be noted that the organic detonators do fall into line.

The above consideration suggests that the bond dissociation energy is the only parameter studied which appears to have a definitive relationship with material sensitivity. Estimation schemes which use as important parameters heats of reaction or oxygen balance or activation energy for decomposition in a manner which includes reactions other than those which involve bond-cleavage may thus lead to serious errors with regard to the identification of reaction hazard.

Table 9. Test Data and Possible Sensitivity Parameters for Various Materials

<table>
<tr><th rowspan="2"></th><th rowspan="2">COMPOUNDS</th><th colspan="2">IMPACT SENSITIVITY</th></tr>
<tr><th>BOM cm/kg/mg[a]</th><th>PA cm/kg/mg[b]</th></tr>
<tr><td>A.</td><td>$RO\text{-}NO_2$ (f) (39 kcal/mol)</td><td></td><td></td></tr>
<tr><td>1)</td><td>1,2,4,-Butanetriol Trinitrate (BTTN) (liq)</td><td>58|2|20 (ℓ)</td><td>2.5|2|liq</td></tr>
<tr><td>2)</td><td>Diethylene Glycol Dinitrate (DEGN) (liq)</td><td>100+|2|20 (ℓ)</td><td>23|2|liq</td></tr>
<tr><td>3)</td><td>Dipentaerythritol Hexanitrate (DPEHN)</td><td>14|2|20</td><td>10|2|10</td></tr>
<tr><td>4)</td><td>Glycerol Monolactate Trinitrate (GLTN) (liq)</td><td>42|2|20 (ℓ)</td><td></td></tr>
<tr><td>5)</td><td>Glycol Dinitrate (GDN) (liq)</td><td>56|2|20 (ℓ)</td><td></td></tr>
<tr><td>6)</td><td>Mannitol Hexanitrate (nitromannite)</td><td>11|2|20</td><td>10|2|11</td></tr>
<tr><td>7)</td><td>Metriol Trinitrate (MTN) (liq)</td><td>4|2|20 (ℓ)</td><td></td></tr>
<tr><td>8)</td><td>Nitrocellulose 12.6% N</td><td>8|2|20</td><td>7.5|2|5</td></tr>
<tr><td>9)</td><td>Nitrocellulose 13.5% N</td><td>9|2|20</td><td>7.5|2|5</td></tr>
<tr><td>10)</td><td>Nitrocellulose 14.14% N</td><td>8|2|20</td><td>7.5|2|5</td></tr>
<tr><td>11)</td><td>Nitroglycerine (liq)</td><td>15|2|20 (ℓ)</td><td>2.5|2|liq</td></tr>
<tr><td>12)</td><td>Nitroisobutylglycerol (NIBTN) (liq)</td><td>25|2|20 (ℓ)</td><td></td></tr>
<tr><td>13)</td><td>Pentaerythritol Tetranitrate (PETN)</td><td>17|2|20</td><td>15|2|16</td></tr>
<tr><td>14)</td><td>Polyvinylnitrate (PVN)</td><td></td><td>10|2|20</td></tr>
<tr><td>15)</td><td>Triethylene Glycol Dinitrate (TEGN) (liq)</td><td>100+|2|20 (ℓ)</td><td>108|2|liq</td></tr>
<tr><td>16)</td><td>Tripentaerythritol Octanitrate (TPEON)</td><td></td><td>23|2|24</td></tr>
<tr><td>17)</td><td>1-Monoglycerine</td><td></td><td></td></tr>
<tr><td>18)</td><td>2-Monoglycerine</td><td></td><td></td></tr>
<tr><td>19)</td><td>1,3-Dinitroglycerine</td><td></td><td></td></tr>
</table>

Explosion Temp. °C	Thermal Surge Test °C	Oxygen Balance	Heat of Reaction -kcal/g
230	374	-17.0	1.46
237	374(c)	-41	.84
255		-26	
223		-30	
257	319(c)	0	1.76
175		7.1	1.34-1.52
235	375(c)	-35	
170		-35	.85
230		-29	.97
		-24	1.06
222	277(c),430(d)	35	1.6
185		0	
225	430(d)	-10	1.39
265			.9
223	432	-89	.36
225		-35	
	541(c)	-53	
	544(c)	-53	
	370(c)	-18	

Table 9. (continued)

	COMPOUNDS	IMPACT SENSITIVITY	
		BOM cm/kg/mg(a)	PA in /kg/mg(b)
20)	1,2-Dinitroglycerine		
21)	Ethylnitrate		
22)	n-Propylnitrate		
B.	$R\phi-NO_2$ (g) (71 kcal/mol)		
1)	2,4-Dinitrotoluene (DNT)		
2)	2,4,6-2',4',6'-Hexanitro-oxanilide (HNO)		
3)	Picric Acid	85 | 2 | 20	
4)	Tetranitrocarbazole	100+ | 2 | 20	
5)	2,4,2',4'-Tetranitro-oxanilide (TNO)		
6)	Trinitrotoluene (TNT)	95-100+ | 2 | 20	
7)	Picramide (TNA)		
8)	Trinitrobenzene		
9)	Trinitroanisole		
10)	Nitrobenzene		
11)	2,4-Dinitrophenol		
12)	m-Dinitrobenzene		

Explosion Temp. °C	Thermal Surge Test °C	Oxygen Balance	Heat of Reaction -kcal/g
	355(c)	-18	
	415(c)	-62	
	550(c)	-99	
310		-114	
384		-53	
320	717(c)	-46	1.0
470		-85	
392		-84	
475	745(c),1040(d)	-74	1.1
		-56	.56
	848(c),1060(d)	-32	
	681(c)	-60	
	1000(c)	-161	
	791(c)	-78	
	790(c)	-95	

Table 9. (continued)

	COMPOUNDS	IMPACT SENSITIVITY BOM cm/kg/mg(a)	 PA cm/kg/mg(b)
C.	$R_1R_2N\text{-}NO_2$ (h) (45 kcal/mol)		
1)	Cyclonite (RDX)	82|2|20	20|2|18
2)	Ethylene Dinitramine (EDNA)	48|2|20	35|2|17
3)	beta HMX	32|2|20	23|2|23
4)	Nitroguanidine	47|2|20	66|2|7
5)	Tetryl	26|2|20	20|2|18
D.	$R\text{-}NO_2$ (i) (59 kcal/mol)		
1)	Nitromethane (liq)	100+|2|20	50|2|liq
E.	$RC(NO_2)_3$ (j) (45 kcal/mol)		
1)	2,2,2-Trinitroethyl-4,4,4-Trinitrobutyrate		
2)	2,2-Dinitropropyl-4,4,4-Trinitrobutyrate		
F.	$R_1R_2C{=}N_2$ (k) (36 kcal/mol)		
1)	Diazodinitrophenol	25|2|20	10 |2| , 18| 1 lb|15
G.	$R_1R_2C\text{-}N_2$ (l) (39 kcal/mol)		
1)	Trinitrotriazidobenzene		
H.	$R_1R_2C\text{-}N\text{-}N{=}N\text{-}$ (m) (35 kcal/mol)		
1)	Tetracene (liq)	7|2|20	5|2|liq, 20|8 oz|liq

Explosion Temp. °C	Thermal Surge Test °C	Oxygen Balance	Heat of Reaction -kcal/g
260		-22	1.28
189		-32	1.28
327		-22	1.36
275		-31	.72
257	880(d)	-47	1.10
430	682(c)	-39	1.22(e)
225	500(d)	-42	
300	830(d)	-29	
195		-61	.82
150		-29	

Table 9. (continued)

	COMPOUNDS	IMPACT SENSITIVITY BOM cm/kg/mg(a)	PA cm/kg/mg(b)
I.	1) Silver Azide (n) (30-40 kcal/mol)	6 | 2 | 20	7.5 | 2 | 8
J.	$Hg(CNO)_2$		
1)	Mercury Fulminate	5 | 2 | 20, 35 | 1 kg | 20	5 | 2 | ?, 10 | 1 lb | 30
K.	1) Lead Styphnate	17 | 2 | 20	7.5 | 2 | ?, 7.5 | 8 oz | 22
L.	1) Lead 2,4-Dinitroresorcinate (LDNR)	30 | 1 kg | 20	7.5 | 2 | 30
M.	1) Lead Azide	10 | 2 | 20	45 | 2 | 18
N.	$R_1R_2C(NO_2)_2$ (o) (49 kcal/mol)		
1)	Bis(2,2-dinitropropyl)Fumarate (DNPF)	100+ | 2 | 20	45 | 2 | 18
2)	Bis(2,2-dinitropropyl)Succinate (DNPS)		
3)	Bis(2,2-dinitropropyl)Formal		
4)	Bis(2,2-dinitropropyl)Acetal		
O.	1) hydrazine (p) (65 kcal/mol)		
P.	1) 1,1 dimethylhydrazine (q) (~60 kcal/mol)		
Q.	1) Tetranitromethane (r) (41 kcal/mol)		

Explosion Temp. °C	Thermal Surge Test °C	Oxygen Balance	Heat of Reaction -kcal/g
290		-5	.45
210		-17	.43
276		-19	.46
265		-32	.27
340		-5.5	.77
250		-59	.77
		-63	
	541(c)	-52	
	545(c)	-59	
	942(c)	-100	
	832(c)	-169	
	709(c)		

a) Bureau of Mines Test, in height (cm), wt (kg), sample size (mg). Liquid samples are in filter paper. Ref. [26].

b) Picatinny Arsenal Test, in height (in), wt (kg), sample size (mg). Liquid samples are in die cup. Ref. [26].

c) Ref. [30].

d) Ref. [29].

e) Ref. [24].

f) From data on ethyl nitrate decomp., Ref. [16], pg. 471.

g) From $Hf(C_6H_5) + Hf(NO_2) - Hf(C_6H_5NO_2) = 80$ [31] + 8 [14] - 17 [32] = 71 kcal/mol.

h) Estimated also see Ref. [33] and Ref. [34], pg. 178.

i) Ref. [16], pg. 473.

j) Estimated from $R_1R_2C(NO_3)_2$ (49 kcal/mol) and $C(NO_2)_4$ (41 kcal/mol).

k) From data on deazomethane and considering possible resonance effects. Ref. [16], pg. 483.

l) From data on ethyl azide and considering possible resonance effects. Ref. [16], pg. 483.

m) From data on tetraethyltetrazine. Ref. [16], pg. 460.

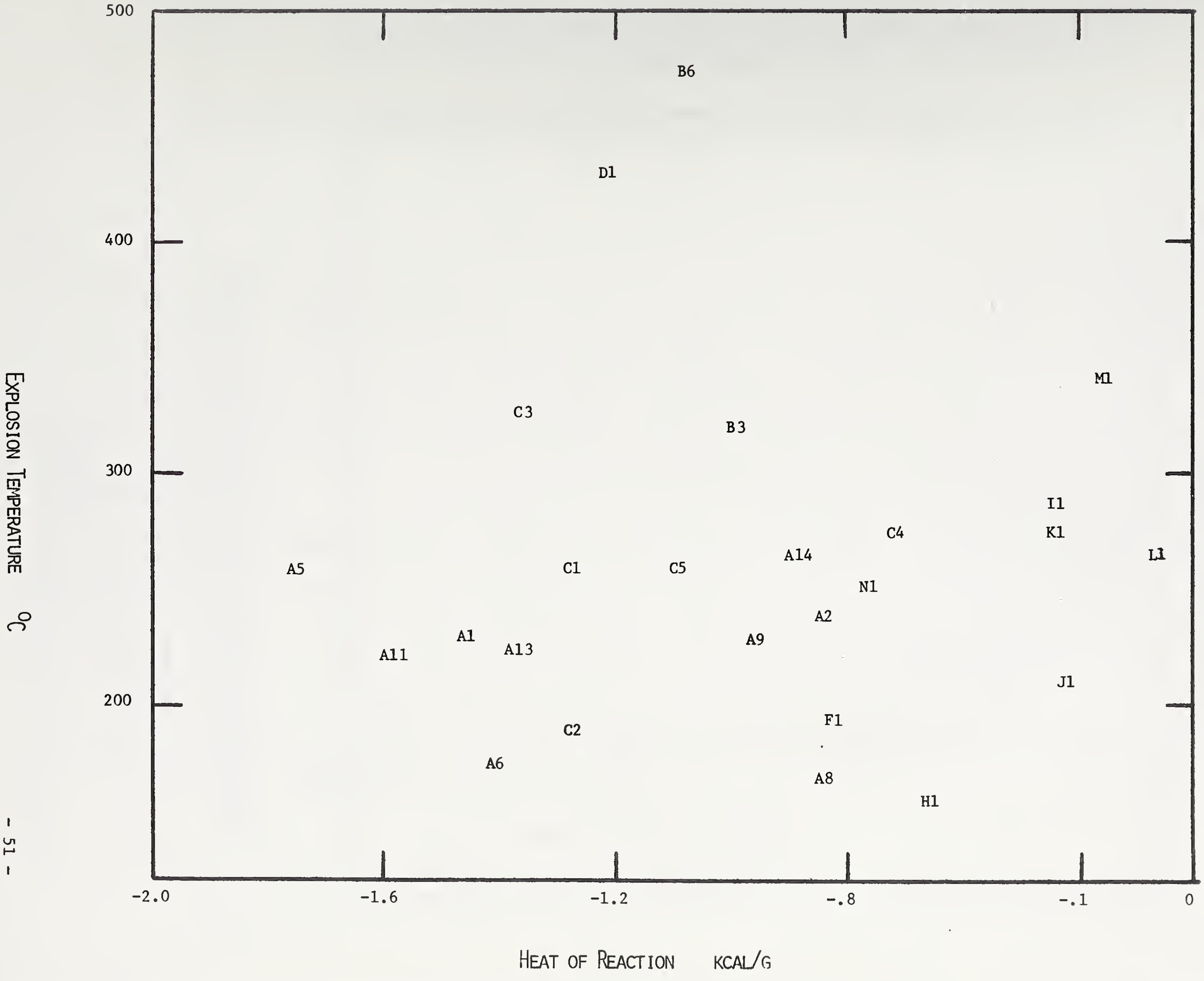
n) Ref. [35].

o) Ref. [36].

p. Ref. [37].

q) Estimated, see Ref. [16, 35].

r) Ref. [16], pg. 477.



Data points from Table 9.

Figure 2. Explosion Temperature results as a function of the Heat of Reaction.

Data points from Table 9.

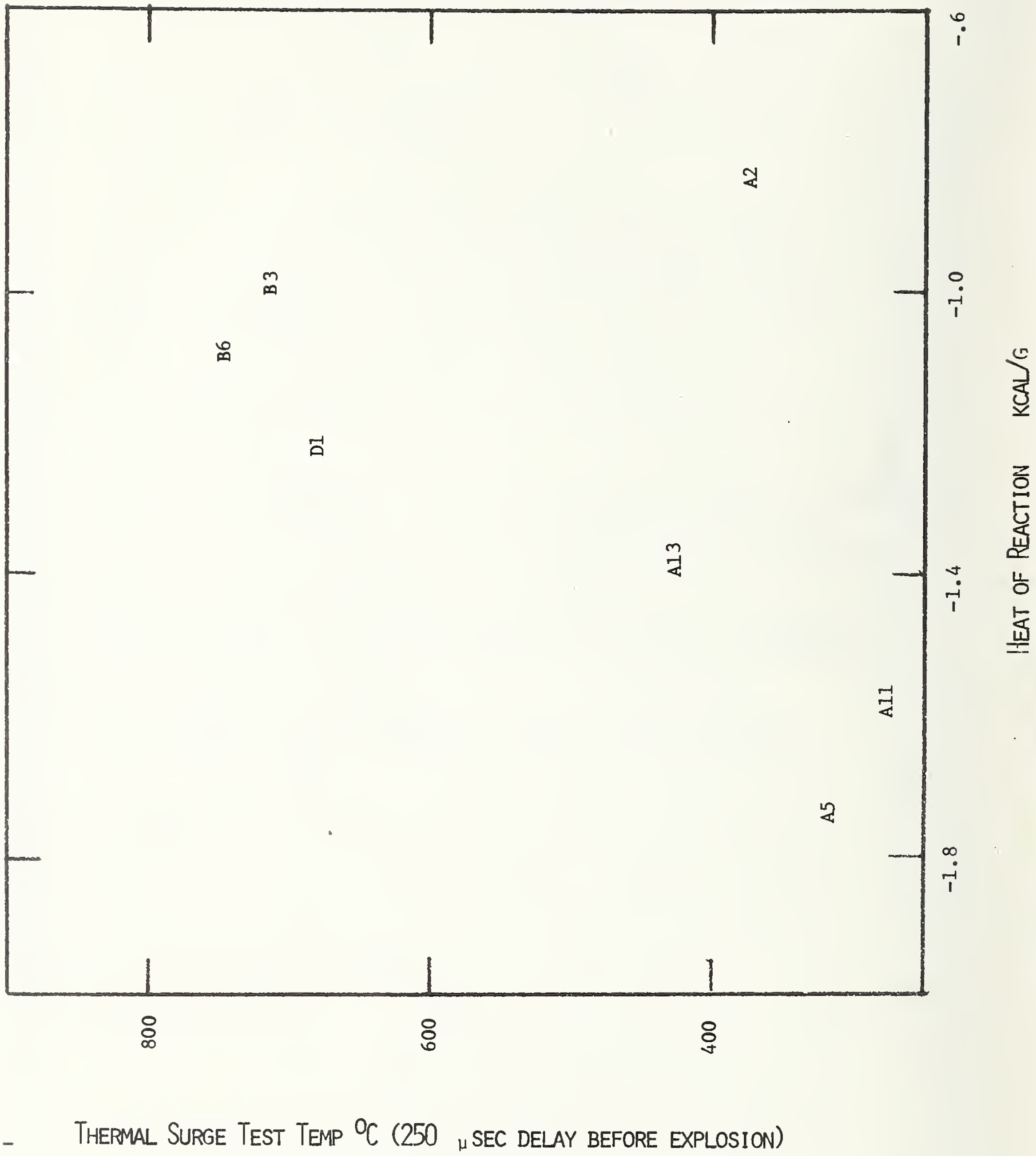


Figure 3. Thermal Surge Test results as a function of Heat of Reaction.

Data points from Table 9.

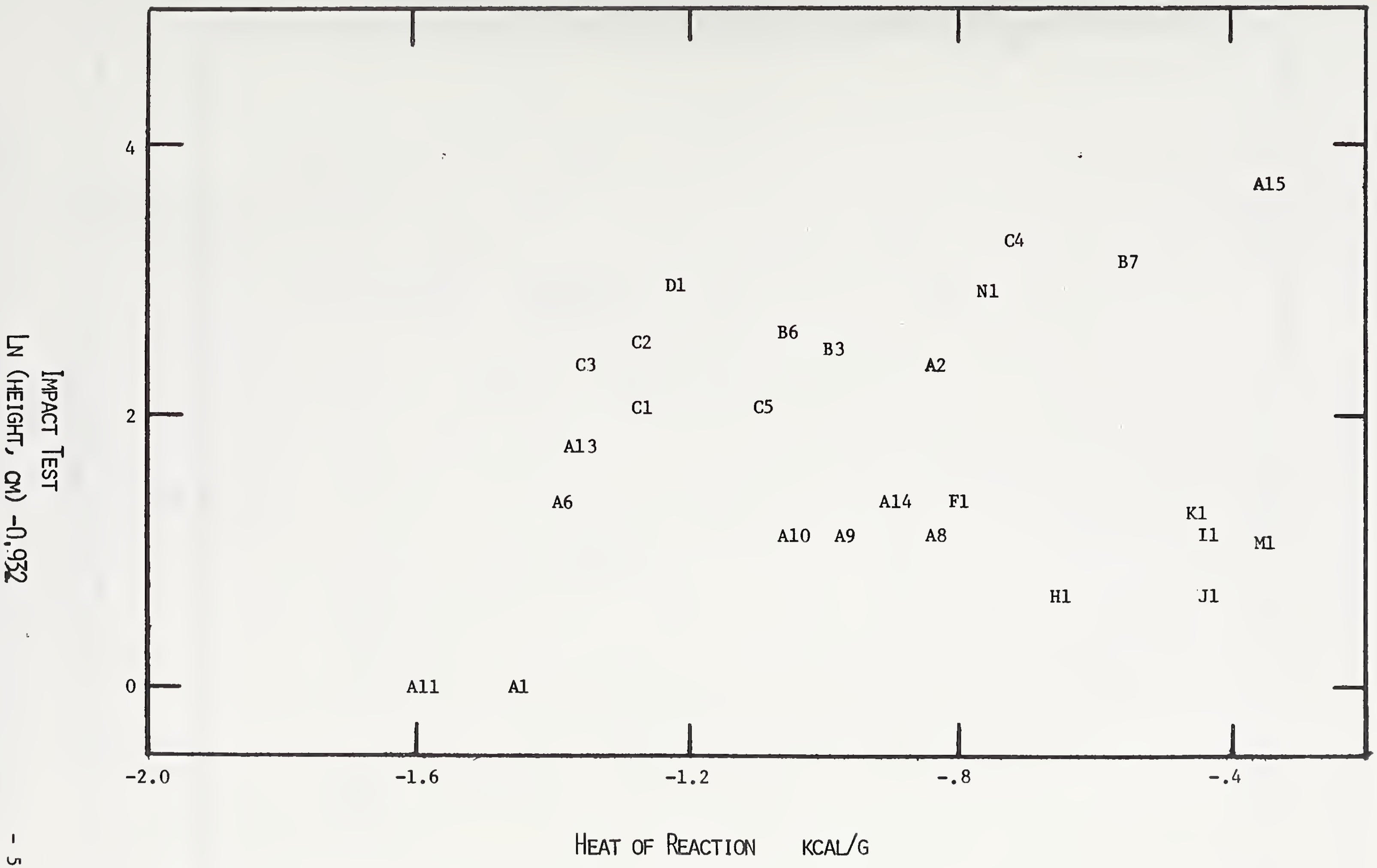
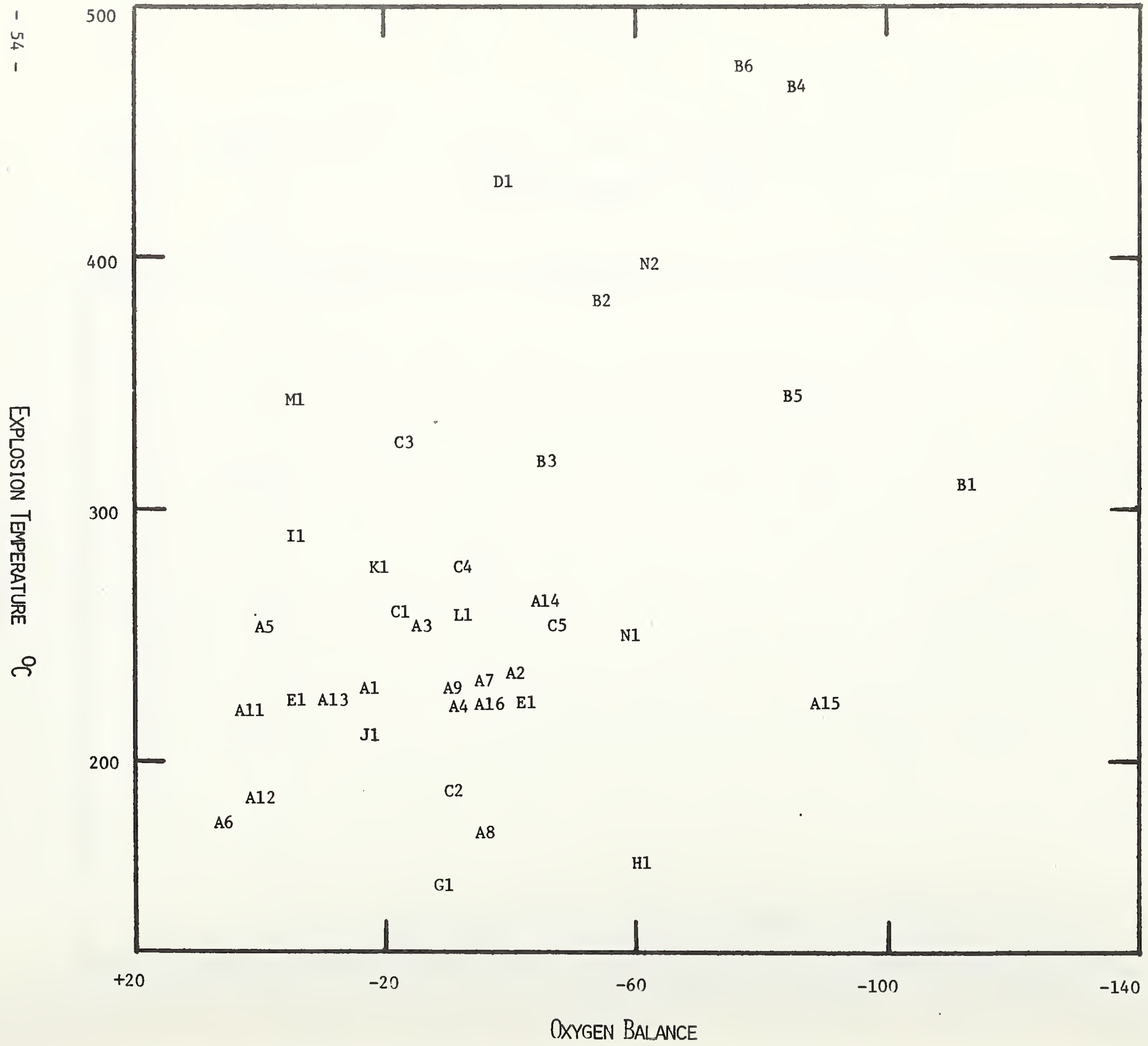
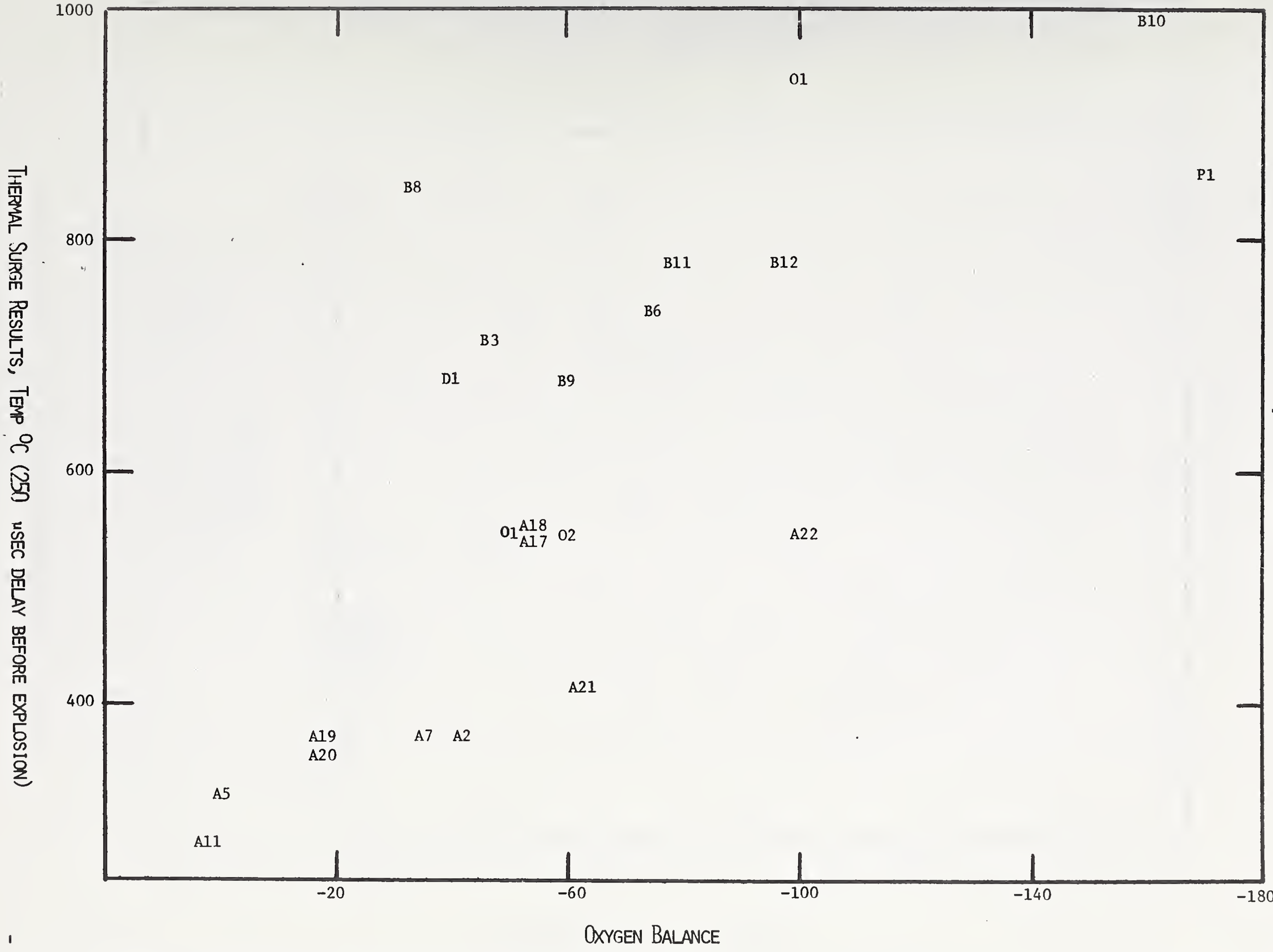


Figure 4. Impact Test results as a function of Heat of Reaction.



Data points from Table 9.

Figure 5. Explosion temperature results as a function of Oxygen Balance.



Data points from Table 9.

Figure 6. Thermal Surge results as a function of Oxygen Balance.

Data points from Table 9.

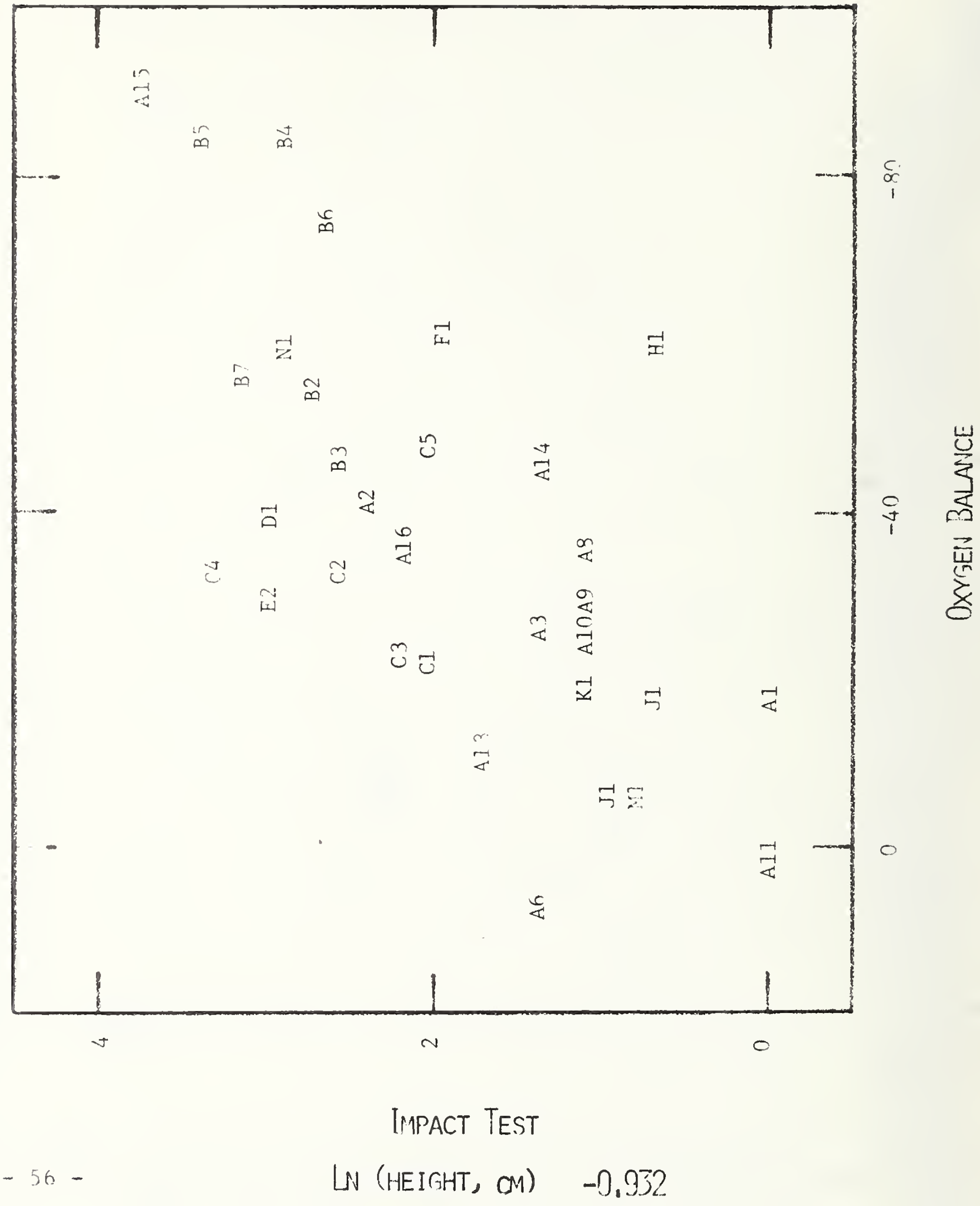


Figure 7. Impact Test results as a function of Oxygen Balance.

Data points from Table 9.

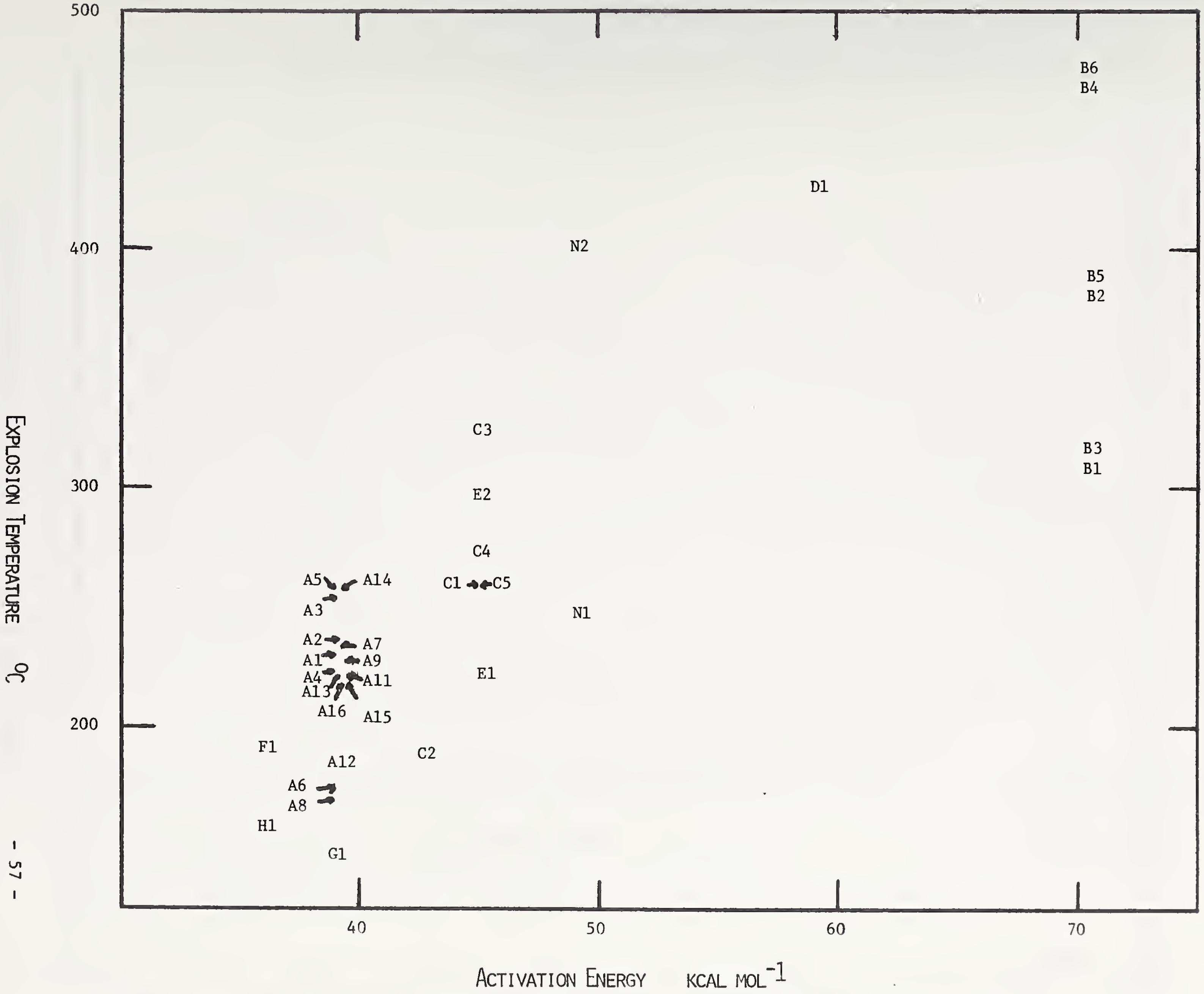


Figure 8. Explosion Temperature results as a function of Activation Energy (bond energy).

Data points from Table 9.

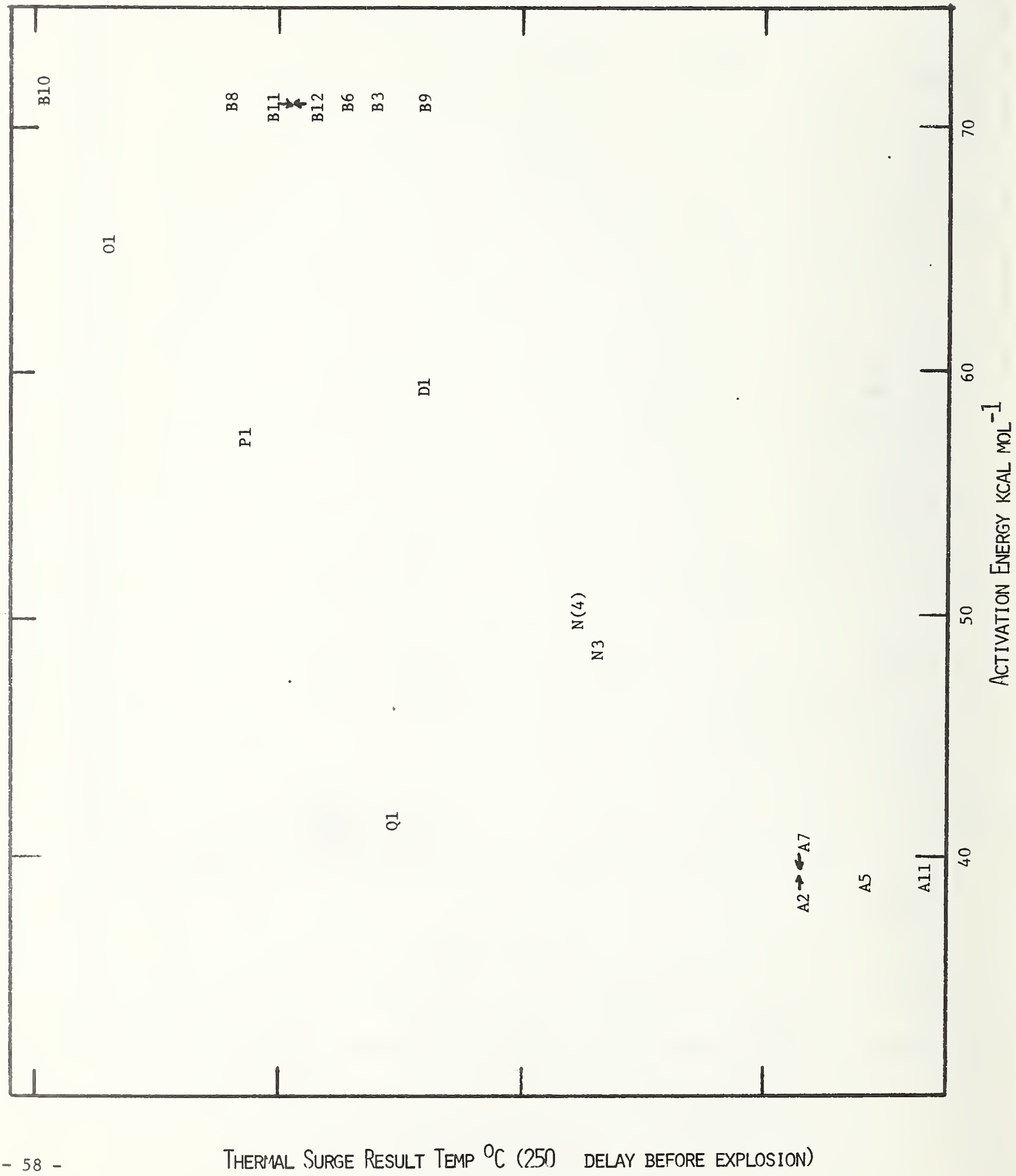


Figure 9. Thermal Surge results as a function of Activation Energy (bond energy).

Data points from Table 9.

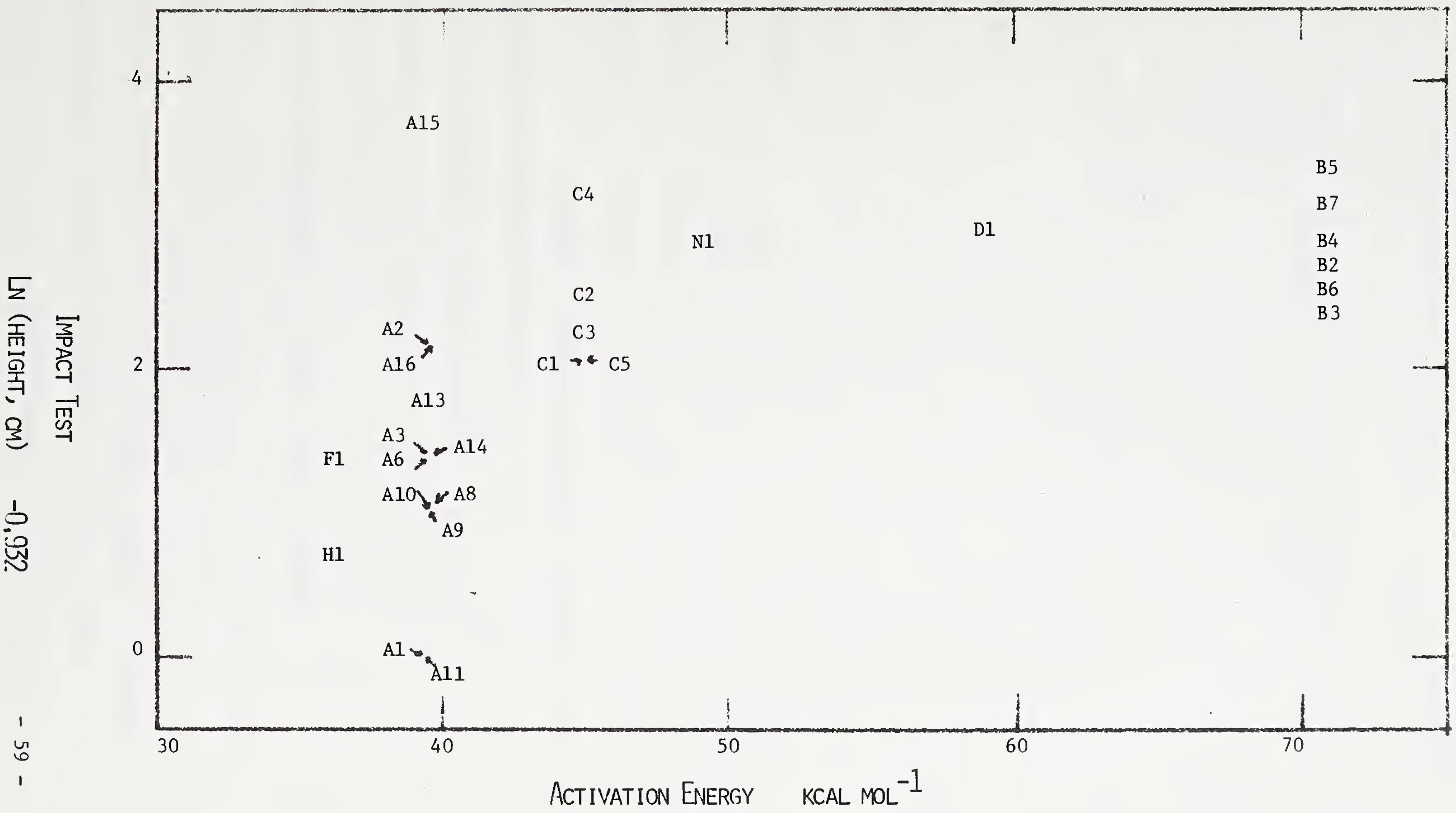


Figure 10. Impact Test results as a function of Activation Energy (bond energy).

IV. Discussion

The data presented in the earlier sections provide the raw material for consideration of the sensitivity problem from a more generalized point of view. Our approach will be to take each of the designated molecular parameters, heat of reaction, activation energy for decomposition, and oxygen balance and consider how they may be related to material sensitivity on a theoretical basis. Finally we will consider the situation with respect to polymerization processes.

A. Heat of Reaction (Decomposition)

In the earlier discussion, we have demonstrated that for explosives the heat of reaction (decomposition) and sensitivity are at best only indirectly related. However, from a general standpoint, it is possible that the heat of decomposition can be a valuable criterion because if self-reaction is endothermic, then in practically all cases, no possible danger from self-decomposition should be expected. The questions remains: can the available estimation schemes provide reasonable heats of decomposition, i.e., heat of decomposition which will approach physical reality?

We have compiled a table (Table 10) of decomposition reactions of substances for the purpose of comparison with decomposition reactions and enthalpies derived from the estimation schemes we had mentioned earlier. The arrangement of reactions in the table begins with the decomposition of stable compounds and then progresses to increasingly more hazardous materials. The decomposition reactions and their enthalpies at 298 K were obtained from observed experimental studies and are numbered throughout table 10. Accompanying the decomposition reactions and enthalpy are: the reference from which the reaction was obtained, the name of the compound, formula weight, and enthalpy of formation of the reactant at 298 K and the reference from which the latter was taken.

The decomposition reactions and enthalpies derived from estimation schemes are listed in table 10 according to assigned letters. We have listed the results of the CHETAH program calculation of the reaction and maximum enthalpy of decomposition under a). We shall briefly repeat the basic rationale of the CHETAH program with respect to decomposition products: the oxygen present is allowed to exhaust the hydrogens forming water with any remaining oxygen to form CO_2. Unreacted carbon atoms and nitrogen atoms yield C (graphite) and gaseous N_2 as decomposition products. In the event of an excess of hydrogen atoms (as with hydrocarbon molecules) CH_4 or NH_3 are formed. We have entered the data obtained from Dr. Stull under b) derived from calculations of the CRUISE program for a given substance. In b), a set of possible products are defined from the stoichiometry and the relative concentrations of the products are determined on the basis of equilibrium considerations.

Examination of table 10 shows that both the CHETAH and CRUISE programs yield heats of decomposition which are exothermic while most experimentally observed results for these processes indicate that they are endothermic. As a general trend the CRUISE program calculates a heat of decomposition which is always less negative than that obtained from the CHETAH program. We do not mean to suggest that this observation is always appropriate.

As would be expected, both the experimental and calculated heats of decomposition of nitromethane and 2,4,6-trinitrotoluene are exothermic (negative). A compound having such a large predicted heat of decomposition should be suspected as being hazardous. The fact that the observed decomposition products and those predicted by the CRUISE and CHETAH program are basically the same, and that although not always in close agreement, both experimental and predicted decomposition heats are very negative, suggests that these programs are more generally accurate when applied to explosives than when predicting heat values for thermally stable materials. The empirical rules have not come into play with nitromethane or TNT because no serious projection of hydrocarbon fragments was required to specify decomposition products.

In other words, the CRUISE and CHETAH programs grossly overestimate the heats of reaction of "safe" compounds. It is seen that the predicted decomposition heats for some of these compounds are well in the range of explosives. The reader will recall that for explosives these programs yield heats of reaction which are fairly close to the experimental numbers. The overall effect is to compress and show the range of possible heats of reaction. There is no chance of using these schemes as a means of ruling a substance "safe" purely on the basis that its heat of decomposition is endothermic or sufficiently less exothermic than explosives. This is due to that fact that neither the maximization of the heat of decomposition (CHETAH) nor minimization of the Gibbs energies of the products (CRUISE), although computationally convenient, provides the appropriate basis for selecting the proper decomposition products and, hence, an accurate ranking of substances from very hazardous to very stable is not deduced. At best, the maximization over-emphasizes explosive power, and this we have found does not always correspond to explosive sensitivity.

There are several approaches toward arriving at more accurate heats of decomposition. First of all one can make use of the large volume of data on decomposition processes. From the product analysis it is easy to deduce whether the reaction is endothermic or exothermic. Furthermore in the case of molecular reactions (as opposed to chain decompositions), the fact that a molecule with a particular grouping decomposes in some fashion implies that analogous molecules will decompose in a similar manner. For example, the fact that ethyl acetate decomposes to ethylene and acetic acid suggests that alkyl esters will decompose to the olefin and acid with similar rates. Then, from standard heats one can determine the enthalpy of reaction. A particularly helpful compendium is the review by Benson and O'Neal [16]; an older text by Hurd [17] is also of use. When no data are available one must rely on chemical intuition.

Alternatively, we have attempted to set up rules which for bond-breaking reactions at least are kinetically more realistic. Referring to Table 10 again these possibilities include: under entry c), if the reactant contains a carbonyl group or an ether linkage, C-O-C, we assumed carbon monoxide, CO, to be a decomposition product. A carboxyl group, -COO-, will give CO_2 for a product. If the reactant contains the groups, -C-O-H, $-NO_2$, $-ONO_2$, the H_2O can be assumed to be a decomposition product. Under entry d) we have limited the formation of CH_4 as a decomposition product to only those situations in which the structure of the reactant contained methyl groups; otherwise the formation of decomposition products is similar to those selected in c). The provisions of entry e) are identical to those of entry d) except that the presence of methyl groups in the reactant structure results in the formation of gaseous ethane, C_2H_6, as a decomposition product. In entry f), the presence of CH_2 or CH fragments in the reactant structure results in the formation of ethylene, C_2H_4, or C_2H_4 and graphite as reaction products, respectively; otherwise product formation is similar to those identified in entry e). The provisions of entry g) are the same as those for entry f) except that methyl groups in the reactant appear as CH_4 in the products instead of C_2H_6. The presence of a halogen atom in a reactant compound yields the corresponding hydrogen halide as a decompositon product.

Table 10. Comparison of Decomposition Reactions and their Enthalpies at 25°C

Table Format

---

(1) Name of compound; formula weight; enthalpy of formation at 25°C [enthalpy reference]. Observed decomposition reaction, [reaction reference], enthalpy in kcal mol^{-1}

(a) Decomposition reaction calculated by CHETAH program; enthalpy.

(b) Decomposition reaction calculated by CRUISE program; enthalpy.

(c) If reactant has a carbonyl group, or a C-O-C bond, assume carbon monoxide, CO, as a decomposition product. If reactant contains C-O-H bond, then H_2O can be assumed as a decomposition product; enthalpy.

(d) Formation of CH_4 as a decomposition product takes place only if CH_3 groups are part of the molecular structure. The remaining carbon and hydrogen form solid graphite and H_2 gas; enthalpy.

(e) Same as (d) except that C_2H_6 instead of CH_4 is formed from CH_3 groups; enthalpy.

(f) Same as (e) except that the remaining CH_2 fragments combine to form C_2H_4 and the CH fragments combine to form C_2H_4 and graphite; enthalpy.

(g) Same as (d) except that the remaining CH_2 fragments combine to form C_2H_4 and the CH fragments combine to form C_2H_4 and graphite; enthalpy.

butane; 58.1230; ΔHf° = -30.15 [11]

$$1)\quad \left.\begin{array}{ll} C_4H_{10} \rightarrow CH_4 + CH\ CH{=}CH_2 & 44\% \\ C_4H_{10} \rightarrow C_2H_6 + C_2H_4 & 40\% \\ C_4H_{10} \rightarrow H_2 + C_4H_8 & 5\% \\ C_4H_{10} \rightarrow 2\ H_2 + C_4H_6 & 4\% \end{array}\right\} \qquad +22.3$$

---

a)	$C_4H_{10} \rightarrow 2.5\ CH_4 + 1.5\ C(s)$	-14.6
b)	$C_4H_{10} \rightarrow 2.3067\ CH_4 + 0.3865\ H_2 + 1.6933\ C(s)$	-11.1
c)	--	
d)	$C_4H_{10} \rightarrow 2\ CH_4 + 2\ C(s) + H_2$	-5.6
e)	$C_4H_{10} \rightarrow C_2H_6 + 2\ C(s) + 2\ H_2$	+9.9
f)	$C_4H_{10} \rightarrow C_2H_6 + C_2H_4$	+22.4
g)	$C_4H_{10} \rightarrow 2\ CH_4 + 0.5\ C_2H_4 + C(s)$	+0.6

---

isobutane; 58.1230; ΔHf° = -32.15 [11]

2) $C_4H_{10} \rightarrow .62iC_4H_8 + .04\ C_3H_8 + .31\ C_3H_6 + .02\ C_2H_6$
$+ .41\ CH_4$ [19] +28.5

---

a)	$C_4H_{10} \rightarrow 2.5\ CH_4 + 1.5\ C(s)$	-12.6
b)	$C_4H_{10} \rightarrow 2.3557\ CH_4 + 0.2885\ H_2 + 1.6443\ C(s)$	-10.0
c)	--	
d)	$C_4H_{10} \rightarrow 2.5\ CH_4 + 1.5\ C(s)$	-12.6
e)	$C_4H_{10} \rightarrow 1.5\ C_2H_6 + C(s) + 0.5\ H_2$	+1.4
f)	$C_4H_{10} \rightarrow C_2H_6 + C_2H_4$	+24.4
g)	$C_4H_{10} \rightarrow 2\ CH_4 + 0.5\ C_2H_4$	+2.6

	neopentane; 72.1498; $\Delta Hf° = -40.27$ [12]	
3)	$C_5H_{12} \rightarrow (CH_3)_2C{=}CH_2 + CH_4$ [20]	+18.3
a)	$C_5H_{12} \rightarrow 3\ CH_4 + 2\ C(s)$	-13.4
b)	$C_5H_{12} \rightarrow 2.8573\ CH_4 + 2.1427\ C(s) + 0.2854\ H_2$	-11.5
c)	--	
d)	$C_5H_{12} \rightarrow 3\ CH_4 + 2\ C(s)$	-13.4
e)	$C_5H_{12} \rightarrow 2\ C_2H_6 + C(s)$	-0.2
f)	$C_5H_{12} \rightarrow 2\ C_2H_6 + C(s)$	-0.2
g)	$C_5H_{12} \rightarrow 2\ CH_4 + C_2H_4$	+17.0
	acetone; 58.0798; $\Delta Hf° = -51.90$ [12]	
4)	$CH_3COCH_3 \rightarrow CH_2{=}C{=}O + CH_4$ [17]	+22.4
a)	$CH_3COCH_3 \rightarrow H_2O + CH_4 + 2\ C(s)$	-23.8
b)	$CH_3COCH_3 \rightarrow 0.9030\ H_2 + 0.7149\ CH_4 + 0.6671\ H_2O + 2.0992\ C(s) + 0.0388\ CO + 0.1470\ CO_2$	-14.2
c)	$CH_3COCH_3 \rightarrow CO + 1.5\ CH_4 + 0.5\ C(s)$	-1.4
d)	$CH_3COCH_3 \rightarrow CO + 1.5\ CH_4 + 0.5\ C(s)$	-1.4
e)	$CH_3COCH_3 \rightarrow CO + C_2H_6$	+5.2
f)	$CH_3COCH_3 \rightarrow CO + C_2H_6$	+5.2
g)	$CH_3COCH_3 \rightarrow CO + CH_4 + 0.5\ C_2H_4$	+13.8

n-butyl acetate; 116.1596; ΔHf° = -116.10 [12]

5) $CH_3COOC_4H_9 \rightarrow CH_3COOH + 1\text{-}C_4H_8$ [16] +12.3

a) $CH_3COOC_4H_9 \rightrightarrows 2\ H_2O + 2\ CH_4 + 4\ C(s)$ -34.7

b) $CH_3COOC_4H_9 \rightarrow 1.4667\ H_2O + 1.7219\ CH_4 + 4\ C(s)$
$+ 1.0896\ H_2 + 0.2552\ CO_2 + 0.0229\ CO$ -23.5

c) $CH_3COOC_4H_9 \rightarrow CO_2 + 3\ CH_4 + 2\ C(s)$ -34.5

d) $CH_3COOC_4H_9 \rightarrow CO_2 + 2\ CH_4 + 3\ C(s) + 2\ H_2$ -16.6

e) $CH_3COOC_4H_9 \rightarrow CO_2 + C_2H_6 + 3\ C(s) + 3\ H_2$ -1.0

f) $CH_3COOC_4H_9 \rightarrow CO_2 + C_2H_6 + 1.5\ C_2H_4$ +20.6

g) $CH_3COOC_4H_9 \rightarrow CO_2 + 2\ CH_4 + C_2H_4 + C(s)$ -1.2

n-butyl chloride; 92.5681; ΔHf° = -35.1 [12]

6) $C_4H_9Cl \rightarrow 1\text{-}C_4H_8 + HCl$ [16] +13.1

a) $C_4H_9Cl \rightarrow HCl + 2\ CH_4 + 2\ C(s)$ -22.6

b) $C_4H_9Cl \rightarrow HCl + 1.6065\ CH_4 + 0.7870\ H_2 +$
$2.3935\ C(s)$ -15.6

c) --

d) $C_4H_9Cl \rightarrow HCl + CH_4 + 3\ C(s) + 2\ H_2$ -4.8

e) $C_4H_9Cl \rightarrow HCl + 0.5\ C_2H_6 + 3\ C(s) + 2.5\ H_2$ +3.0

f) $C_4H_9Cl \rightarrow HCl + 0.5\ C_2H_6 + 1.25\ C_2H_4 + 0.5\ C(s)$ +18.5

g) $C_4H_9Cl \rightarrow HCl + CH_4 + 0.5\ C_2H_4 + C(s)$ +1.4

di-tert.butyl peroxide; 146.229; ΔHf° = -83.4 [12]

7) $C_8H_{18}O_2 \rightarrow 2\ CH_3COCH_3 + C_2H_6$ [16] -43.5

---

a) $C_8H_{18}O_2 \rightarrow 2\ H_2O + 3.5\ CH_4 + 4.5\ C(s)$ -96.7

b) $C_8H_{18}O_2 \rightarrow 1.2127\ H_2O + 1.6525\ CH_4 + 5.8065\ C(s)$
$+ 4.4824\ H_2 + 0.2462\ CO_2 + 0.2948\ CO$ -49.1

c) $C_8H_{18}O_2 \rightarrow 2\ CO + 4.5\ CH_4 + 1.5\ C(s)$ -51.4

d) $C_8H_{18}O_2 \rightarrow 2\ CO + 4.5\ CH_4 + 1.5\ C(s)$ -51.4

e) $C_8H_{18}O_2 \rightarrow 2\ CO + 3\ C_2H_6$ -31.2

f) $C_8H_{18}O_2 \rightarrow 2\ CO + 3\ C_2H_6$ -31.2

g) $C_8H_{18}O_2 \rightarrow 2\ CO + 3\ CH_4 + 1.5\ C_2H_4$ -6.2

---

nitromethane; 61.0402; ΔHf° = -17.86 [9]

8) $CH_3NO_2 \rightarrow 0.882\ H_2O + 0.55\ CO + 0.095\ C(s) + 0.394\ N_2$
$+ 0.261\ CO_2 + 0.294\ H_2 + 0.118\ NH_3 + 0.083\ CH_4 +$
$0.008\ HCN + 0.001\ C_2H_6$ [23] -74.9

---

a) $CH_3NO_2 \rightarrow 1.5\ H_2O + 0.25\ CO_2 + 0.75\ C(s)$ -92.4

b) $CH_3NO_2 \rightarrow 0.8148\ H_2O + 0.8355\ CO + 0.4994\ N_2 +$
$0.6472\ H_2 + 0.1644\ CO_2 + 0.0584\ H + 0.0005\ O_2 +$
$0.0175\ OH + 0.0012\ NO + 0.001\ O$ -63.5

c) $CH_3NO_2 \rightarrow 1.5\ H_2O + 0.5\ CO + 0.5\ N_2$ -82.0

d) --

e) --

f) --

g) --

2,4,6-trinitrotoluene; 227.133; ΔHf° = 12.3 [12]

9) $C_7H_5N_3O_6 \rightarrow 1.25\ CO_2 + 1.98\ CO + 3.65\ C(s) + 1.32\ N_2$
$+ 1.60\ H_2O + 0.46\ H_2 + 0.162\ NH_3 + 0.099\ CH_4 + 0.02\ HCN$
$+ 0.004\ C_2H_6$ [23] -248.3

---

a) $C_7H_5N_3O_6 \rightarrow 1.75\ CO_2 + 2.5\ H_2O + 1.5\ N_2 +$
$5.25\ C(s)$ -321.4

b) $C_7H_5N_3O_6 \rightarrow 0.9613\ C(s) + 1.4806\ N_2 + 0.0002\ H_2O$
$+ 0.0001\ CO_2 + 5.9996\ CO + 2.4760\ H_2$
$+ 0.0078\ H + 0.0387\ HCN + 0.0002\ CH_4$
-374.5

c) $C_7H_5N_3O_6 \rightarrow 2.5\ H_2O + 1.75\ CO + 0.875\ CO_2 +$
$1.5\ N_2 + 4.375\ C(s)$ -285.3

d) --

e) --

f) --

g) --

For the first three compounds in Table 10, butene, isobutane, and neopentane, the experimentally observed heats of decomposition are endothermic, however, both the CRUISE and CHETAH programs calculate exothermic values. Accommodation for the formation of C_2H_6 and C_2H_4 as decomposition products in empirical rules e), f), and g) allows for reasonable prediction of the endothermicity for butane and isobutane by rule f) and for neopentane by rule g) (between 1 and 4 kcal mol^{-1}).

Endothermic heats of decomposition are observed for acetone, n-butyl acetate, and n-butyl chloride. These decompositions, however, are molecular elimination reactions, and without a knowledge of the actual mechanism prediction of the decomposition products is nearly impossible. Hence, the agreement between the heats of decomposition allowed by the empirical rules and the experimental values is not as good (between 5 and 9 kcal mol^{-1}). The calculated decomposition heats for these compounds as obtained by the CRUISE and CHETAH programs still yield exothermic values. Thus although our empirical rules do result in some improvement, the products of decomposition processes are frequently so specific that we do not believe it is possible to set up an algorithm for the computation of realistic heats of decomposition without recourse to a chemical knowledge on the specific mechanism of decomposition.

B. Activation Energy for Decompositon

Of all the molecular properties that have been considered as a sensitivity parameter, the activation energy for decomposition (as defined here) appears to display the most clearcut relationship with the sensitivity test data. This is in apparent accord with what may be derived from thermal ignition theory. The fundamental relationship is [25, 28]:

$$\rho c(\frac{\partial T}{\partial t}) = \lambda \nabla^2 T + \rho Q(\frac{d\varepsilon}{dt})$$

where T = temperature(°K); c = specific heat (cal/g °K); ρ = density (g/cm^3); λ = temperature independent thermal conductivity (cal/cm-°K-sec); Q = heat of reaction (cal/g); and ε = fractional amount of explosive reacted. The physical **picture** is that of a block of matter reacting exothermally (third term of above reaction represents heat generation) and thus subject to self-heating (first term) while at the same time heat is lost through conduction (second term). For the present purposes it is of interest to consider the special case where the rate of heat generation is much greater than that of the heat loss or where one can assume adiabatic self-heating. Then, since

$$\frac{d\varepsilon}{dt} = (1 - \varepsilon)\ Z\ \exp(- E/RT)$$

where Z = a constant pre-exponential factor and E = activation energy for decomposition.

It is possible to define an induction time:

$$t = \frac{cRt_o^2}{QZE} \exp(E/RT_o),$$

that is, starting at a temperature T_o, then is the time necessary prior to a point where the system temperature "taken off". To some degree it can be regarded as a sensitivity parameter. Obviously the longer the induction time, the less sensitive a material since there will be a longer interval for the heat to leak out of the system. Indeed under such an eventuality the above relationship will not be strictly applicable and the resulting induction time will be an underestimate.

For a complete discussion of these relations the reader is referred to standard texts [25, 28].

In the case of bond-breaking reactions, the activation energy E has been identified as equivalent to the bond dissociation energy. This means that the bond dissociation process is the rate determining step and the exothermicity is generated by subsequent fast reactions. Although this involves some approximation, nevertheless the observed correlation suggest that this picture retains some connection with reality. Note that in the formulation given above the key quantity is really the rate constant. The fact that the activation energy is highlighted means that the pre-exponential factor Z does not fluctuate widely for the compounds that have been considered. This is in accord with modern day kinetic results which suggests that these numbers are in the range of $10^{16 \pm 1.5}$ $\sec^{-1}$ [16]. In the temperature range of interest this is equivalent to an uncertainty in the activation energy by 2 to 3 kcal mol^{-1} and is insignificant within the present context. The exponential dependence on the activation energy compared with the linear dependence on heat generation provides a satisfactory explanation for the absence of a clear-cut correlation with the heat of reaction. Nevertheless it must be emphasized that the heat of decomposition is a necessary parameter. In the case where it is endothermic obviously there is no possibility of explosion. This is the reason for the prolonged earlier discussion on methods of estimating decomposition heats. In the cases where it is small the heat conduction effects cannot be neglected.

C. Oxygen Balance

The above discussion suggests that the observed correlation between sensitivity and oxygen balance may be accidental, since in the original paper on the oxygen balance concept Lothrop and Handrick [39] demonstrate a correlation between the heat of reaction and oxygen balance for nitrates, nitramines, aliphatic nitro, aromatic nitro compounds, and their hybrids. Alternatively this suggests that the present comparison between oxygen balance and heat of reaction should be made in the absence of the inorganic detonators. When one does this for the heats of reaction it is possible to discuss the same sort of vague correlation as has been observed for the oxygen balance. This indicates that the data may have to be treated with more respect. The following represents a possible explanation. For the CHNO compounds considered by Lothrop and Handrick [39] the oxygen balance can be considered to be a measure of the excess hydrocarbons present. It is well known that the thermally stable products of hydrocarbon decomposition at the temperature range of interest are the unsaturated compounds. These are generally quite effective as inhibitors in chain decomposition. Obviously as the quantity increases decomposition rates will be slowed leading to a decrease in sensitivity. This is of course superimposed upon the main parameter which is the bond dissociation energy.

D. Polymerization Reaction

The above discussion has to do with decomposition reactions. An alternative source of self-reaction hazard comes from polymerization. Unfortunately both of the schemes that have been considered here ignore this possibility. Furthermore unlike the situation with disintegration where the existing data on explosives furnish a firm tie point, there does not appear any quantitative data on monomer sensitivity. In any case the lack of a general theory of thermal polymerization leaves one without any framework for extrapolation. Note that unlike the situation with explosives, very few polymer chemists are interested in thermal polymerization since catalytic processes are generally more efficient and in any case the products from an uncontrolled polymerization are not usable. At the present time the only method of deriving a hazard rating will be to use the semi-quantitative ideas of polymer chemists as to what special molecular groupings are conductive to polymerization. Work and progress [40,41] along this line due to its obvious importance has been impressive and extensive. The main problem is that of quantitation, that is, while it may be possible to say that one monomer is more polymerizable than another it may be considerably more difficult to assign a numerical value to such conclusions.

It may soon be possible to make ratings on the basis of thermodynamic considerations. The specific variable of interest is the ceiling temperature T, or the enthalpy of polymerization divided by the entropy of polymerization. Above this temperature polymerization will not occur. Obviously, a substance that is shipped above its ceiling temperature represents no hazard at all. Alternatively if a substance is shipped as a liquid and the ceiling temperature is below the boiling point, then it should be a lesser hazard than if the converse is true. All of this presupposes a considerable degree of knowledge of the polymers in question, and this is currently unavailable. Benson's group additivity scheme [16] as embodied in the work of Treweek and coworkers [1] can calculate the required numbers. It is not expected to be accurate since it neglects 1-3, 1-4, etc. interactions, i.e., interactions beyond nearest next-neighbor interactions, and these are precisely the interactions which permit the differentiation of polymerizability among monomers. The scheme of Zwolinski and Somayajula [42] is more promising and has been applied with success to the polymerization of alkanes. If the data are sufficient to permit them to be extended to CHONS systems, this will be of great importance on the present context.

Overall, the need remains for test results. Some thermal surge experiments have been carried out at the Naval Ordnance Laboratory [30] on various monomers, however, this test may not be suitable for polymerization reactions. Explosion temperature as well as DSC and DTA results may be more meaningful. Note that in order to place all materials on the same hazard scale, they must obviously be subject to the same test procedure.

The above comments should not lead one to the conclusion that the predicative schemes are neutral with regard to polymerization. Actually,due to the particular manner of selecting products, the rank ordering that is calculated on the basis of maximum heat of decomposition measures the relative degree of strain in a molecule. Since one way such strain is relieved is by polymerization, monomers may score relatively high as potential hazard. However, many strained molecules do not polymerize and as for disintegration the schemes maximizes hazard to such an extent that all distinctions are lost.

V. Conclusions and Recommendations

Our general conclusions are as follows:

1. CHETAH. Hazard prediction is based on the heat of decomposition and oxygen balance. Both parameters overemphasize explosive power as opposed to explosive sensitivity and, in general, the hazard criteria label many compounds as hazardous when in reality they are not.
2. CHETAH. Maximization of the heat of decomposition is primarily a computational convenience. Although this feature appears in tune with non-explosive materials, significant differences arise between calculation and reality when decomposition products are selected.
3. CRUISE: The activation energy for decomposition, when properly used, is an important parameter for material sensitivity. The maximum decomposition temperature is at best a measure of explosive power and has very little to do with sensitivity. It is a parameter very similar to the maximum heat of decomposition.
4. CRUISE. Decomposition products (as specified by Stull) and the product distributions as calculated by the program are significantly different from those determined experimentally from pyrolysis or thermal decomposition studies for non-explosive compounds. Here also, minimization of the Gibbs energies of the products ignores the mechanism of decomposition (bond scission, molecular elimination, polymerization, etc.).

5. CHETAH and CRUISE. Neither scheme is applicable to self-reaction hazards arising from polymerization.
6. Test Methods. Explosive sensitivity correlates poorly with the heat of decomposition. There may be some correlations with oxygen balance and a somewhat closer relationship to the bond dissociation energy. In the case of bond-breaking processes the bond dissociation energy appears to have a definitive relationship to material sensitivity, and in this context the bond dissociation energy and activation energy are equivalent.
7. Test Methods. Explosion temperature test data are more applicable to fire hazard situations while impact test data relate to hazards in handling and transport.

We recommend that:

1. There is a paramount need for sensitivity test data, particularly on monomers, borderline hazardous compounds, and new substances considered hazardous. Success for future correlations with thermochemical and kinetic parameters will depend on these data.
2. At present, regulations specifying the handling and transport of commodities should follow the concept of self-reactivity based on functional group (nitro, peroxide, azide, nitramine, etc.) [43]. This makes use of the fact that bond dissociation energies are to some degree a localized property. We do not feel the predictive schemes as they now exist justify any high degree of confidence. Certainly experimental test data should be preferred to predictive schemes to evaluate reaction hazard.

3. Accurate predictive schemes must be based on a detailed understanding of the mechanism of self-reaction. Although more complex and more difficult to work with, separate schemes for polymerization, bond cleavage, and molecular elimination reaction could result in a better identification of hazard potential. This area should be explored.

VI. References

[1] Treweek, D. N., Claydon, C. R., and Seaton, W. H., Chem. Eng. Prog., Loss Prevention, 7, 21-27 (1973).

[2] Stull, D. R., Chem. Eng. Prog., Loss Prevention 4, 16-24 (1970).

[3] Stull, D. R., Chem. Eng. Prog., Loss Prevention 7, 67-73 (1973); J. Chem. Ed. 51, A21 - A25 (1974).

[4] Eigenmann, H. K., Golden, D. M., and Benson, S. W., J. Phys. Chem. 77, 1687-1691 (1973).

[5] Benson, S. W., Cruickshank, F. R., Golden, D. M., Haugen, G. R., O'Neal, H. E., Rodgers, A. S., Shaw, R., and Walsh, R., Chem. Rev. 69, 279-324 (1969).

[6] Janz, G. J., "Estimation of Thermodynamic Properties of Organic Compounds", Revised Edition, Academic Press, Inc., New York, NY, 1967.

[7] Commission on Atomic Weights, IUPAC, Pure and Applied Chem. 30, 637-649 (1972); "Atomic Weights of the Elements 1971".

[8] Stull, D. R. and Prophet, H., JANAF Thermochemical Tables Second Edition, NSRDS-NBS-37, June 1971 (U.S. Government Printing Office, Washington, DC 20402).

[9] Wagman, D. D., Evans, W. H., Parker, V. B., Halow, I., Bailey, S. M., and Schumm, R. H., NBS Technical Note 270-3, January 1968.

[10] Estimated using group-contribution values in references [4] and [5] when possible. Take N - (H)(C)(NO_2) = +9.0 kcal mol^{-1}.

[11] Stull, D. R., Westrum, E. F., Jr., and Sinke, G., "Thermodynamics of Organic Compounds" (J. Wiley and Sons, Inc., New York, 1969).

[12] Cox, J. D. and Pilcher, G., "Thermochemistry of Organic and Organometallic Compounds", (Academic Press, Inc., Publishers, New York and London, 1970).

[13] Cruise, D. R., J. Phys. Chem. 68, 3797-3802 (1964).

[14] Davis, E. J. and Ake, J. A., Chem. Eng. Progess Loss Prevention 7, 28-34 (1973).

[15] "Hazardous Chemicals Data" 1973, NFPA No. 49, (National Fire Protection Association, 470 Atlantic Avenue, Boston, MA 02210).

[16] Benson, S. W. and O'Neal, H. E., "Kinetic Data on Gas Phase Unimolecular Reactions", NSRDS-NBS-21, U.S. Government Printing Office, 1970.

[17] Hurd, C. D., The Pyrolysis of Carbon Compounds ACS Monograph Series #50, (1929).

[18] Crynes, B. L. and Albright, L. F., Ind. and Eng. Chem. Process Design and Development 8, 25-31 (1969).

[19] Buehens, A. G. and Froment, G. F., Ind. Eng. Chem. Process and Design Dev. 10, 309-315 (1971).

[20] Baronnet, F., Dzierzynski, M., and Come, G. M., Martin, R., and Niclause, M., Int. J. Chem. Kinetics 3, 197-213 (1971).

[21] Joshi, R. M. and Zwolinski, B., in Vinyl Polymerization, G. Ham, editor, (Marcel Dekker, New York, 1967, pg. 445).

[22] Benson, S. W., "Foundations of Chemical Kinetics" (McGraw Hill, New York, 1960, pg. 379).

[23] Ornellas, D. L., J. Phys. Chem. 72, 2390-2394 (1968).

[24] Ornellas, D. L., Carpenter, J. H., and Gunn, S. R., Rev. Sci. Instruments 37, 907-912 (1966).

[25] Headquarters, U.S. Army Materiel Command, Engineering Design Handbook, Principles of Explosive Behavior AMCP 706-180, April 1972.

[26] Headquarters, U.S. Army Materiel Command, Engineering Design Handbook, Explosives Series Properties of Explosives of Military Interest AMCP 706-171, January 1971.

[27] Henkin, H. and McGill, R., Ind. Eng. Chem. 44, 1391-1395 (1952).

[28] Bowden, P. H. and Yoffe, A., Fast Reactions in Solids (Buttersworth Publishers London, 1958).

[29] Wenograd, J., Trans. Faraday Soc., 57, 1612-1620 (1961).

[30] Kayser, E., Final Report to Dept. of Transportation TES-20-74-1 (NOLTR 74-44) February 1974.

[31] Golden, D. and Benson, S. W., Chem. Rev. 69, 125-134 (1969).

[32] Shaw, R., J. Phys. Chem. 75, 4047-4049 (1971).

[33] Voskoboynikov, I. M., Bogomolov, V. M., and Apin, A. Ya., Fiz. Goreniya Vzryva, 5, 471 (1969); Technical Translations FSTC-HT-23-975-71.

[34] Cook, M. A., The Science of High Explosives (Reinhold Publishing Corp., New York, 1958).

[35] Bartlett, B. E., Tompkins, F. C., and Young, D. A., Proc. Royal Soc., 246, 206-216 (1958).

[36] Shaw, R., Int'l. J. Chem. Kinetics, 5, 261-269 (1973).

[37] Tsang, W., Interim Report on the Thermodynamics of Chemical Species Important in Aerospace Technology, National Bureau of Standards Report 10904.

[38] Price, D., Chem. Rev., 59, 801-825 (1959).

[39] Lothrop, W. C., and Handrick, C. R., Chem. Rev. 44, 419-445 (1949).

[40] Dainton, F. S. and Ivin, K. J., Quarterly Rev. 12, 61-92 (1958).

[41] Ivin, K. J., Angew. Chem. Int'l. Edition 12, 487-494 (1973).

[42] Joshi, R. M., Zwolinski, B. J., and Hayes, C. W., Macromolecules, 1, 30-36 (1968).

[43] Pletz, V., J. Gen. Chem. (USSR) 5, 173 (1935); quoted in [39].

[44] Egger, K. W. and Cocks, A. T., Helv. Chim. Acta 56, 1516-1536 (1973).

VIII. Appendix - Bond Dissociation Energies

In a recent paper, Egger and Cocks [14] have critically evaluated the literature data on heteropolar and homopolar two-center bond dissociation energies in organic compounds in the gas phase and the corresponding heats of formation of radicals and ions. We have extracted the tabular data on homopolar two-center bond dissociation energies and provide these data in Table 11. This information is useful in estimating the weakest bond in a molecule and thus gives some insight toward the mechanism of decomposition and, at times, product formation. The vertical axis (extreme left) provides the formula and/or name of the radical, R, along with its heat of formation at 25°C, while the horizontal axis (top) gives similar data for the other reactant, X. Bond dissociation energies are tabulated for the general dissociation reaction in the gas phase:

$$RX \rightarrow R + X$$

Generally speaking, the lower the value shown in the table, the lower the bond dissociation energy and the greater the tendency toward decomposition.

For details as to the source or magnitude of the values tabulated, the reference by Egger and Cocks [44] should be consulted.

Table 11. Bond Dissociation Energies

	$\Delta H_f^\circ(X)$	H	CH_3	C_2H_5	n-C_3H_7	i-C_3H_7	t-C_4H_9	F
$\Delta H_f^\circ(R)$		52.1	34.0	25.7	20.8	17.8	7.5	18.9
H- hydrogen	52.1	104.2	104	98	98	95	92	135.8
CH_3- methyl	34	104	88.2	84.8	85.2	84.2	81.8	108.8
C_2H_5- ethyl	25.7	98	84.8	81.8	81.6	80.4	77.9	107.1
n-C_3H_7- n-propyl	20.8	98	85.2	81.6	81.5	80.4	77.5	107.3
i-C_3H_7- i-propyl	17.8	95	84.2	80.4	80.4	78.2	74.2	106.1
t-C_4H_9- t-butyl	7.5	92	81.8	77.7	77.5	74.2	68.8	108.4
C_3H_5- cyclopropyl	61.3	100.7	89.6	86.2	86.3	85.4	82.7	110.9
C_4H_7- cyclobutyl	51.2	96.5	85.8	82.5	82.5	81.6	79	107.2
C_5H_9- cyclopentyl	24.3	94.8	83.6	80.3	80.5	79.6	77	105.2
C_6H_{11}- cyclohexyl	13.9	95.5	84.9	80.6	80.9	80.4	77.8	106
C_7H_{13}- cycloheptyl	12.2	92.5	81.5	78.2	78.2	77.3	74.7	102.9
C=C- vinyl	68.4	108	97.5	94.3	94.5	92.8	90.4	118.7
C_6H_5- phenyl	77.7	110	99.7	96.3	96.6	94.5	90.6	123.9
C=C-C- allyl	41.4	88.6	75.6	72.4	72.2	71.5	68.3	97.7
C=C-C- C butenyl	30.4	82.5	71.0	67.9	67.2	65.8	64.4	93.5
C_5H_7- cyclopentenyl	38.4	82.3	71.6	67.8	67.2	65.6	61.6	93.5

Cl	Br	I	OH	OCH_3	HN_2	$NHCH_3$	$N(CH_3)_2$	NO	NO_2
29.0	26.7	25.5	9.0	3.4	47.2	45.2	38.2	21.6	7.9
103.1	87.4	71.3	119	105	110	103	95	49	79
83.6	69.8	56.1	91.1	81.4	86.7	83.6	77.9	40	60
80.8	67.6	53.2	90.9	80.8	84.3	82.3	76.3	38	58
80.1	68.0	53.4	91.0	81.0	84.8	82.3	76.4	38	59
80.4	68	53.1	91.9	81.4	85	83	77.1	37	59
80.2	66.1	50.4	91.2	80.6	83.6	80.8	74.9	36	58
85.4	73.7	58.6	97.5	87.8	91.2	88.7	82.8	42.7	67.3
81.7	69.9	54.9	93.7	84	87.4	84.9	79	38.9	63.6
79.7	67.9	52.9	91.3	82	85.4	82.9	77	36.2	61.5
82	68.7	51.6	91.3	82.8	86.2	83.7	77.8	37	62.4
77.4	65.6	50.6	89.4	79.7	83.1	80.6	74.7	37	59.2
88.8	76.4	63	100.4	88.2					
94.5	79.2	64.4	109.7	98.4	104.1				
71.2	57.2	44.1	80	70.3	75.2	72.7	66.8	28	49.4
67.8	55.4	40.5	79.3	68.8	72.4	70.4	64.5	24	46
67.8	55.4	40.5	79.3	68.8	72.4	70.4	64.5	23.6	48.9

	$\Delta H_f^\circ(X)$	H	CH_3	C_2H_5	n-C_3H_7	i-C_3H_7	t-C_4H_9	F
$\Delta H_f^\circ(R)$		52.1	34	25.7	20.8	17.8	7.5	18.9
C≡C-C- propargyl	86.2	93.9	81.1	77.5	77.4	76.3	73.4	103.2
C=C C=C>C- pentadienyl	48.3	75.2	64.2	60.4	60.4	58.2	54.2	86.1
C=C-C=C-C- trans pentadienyl	48.3	82.3	69.5	65.9	65.8	64.7	61.8	91.6
C_5H_5- cyclo- pentadienyl	55	75.2	64.2	60.4	60.4	58.2	54.2	86.1
C_6H_7- 2,5-cyclo- hexadienyl	44	69.8	59	55.2	55.2	53	49	80.9
C_6H_7- 2,4-cyclo- hexadienyl	44	70.1	59.3	55.5	55.5	53.3	49.3	81.2
C_7H_7- cyclo- heptatrienyl	65	73.2	61.2	57.9	57.9	57	54.4	81.9
$C_6H_5CH_2$- benzyl	44.9	85	71.8	68.7	69	67.8	65	96.3
$CH_3C_6H_4CH_2$- 4-methyl- benzyl	37	84.8	71.8	68.4	68.4	67.6	65	95.1
$CH_3C_6H_4CH_2$- 3-methyl- benzyl	37	85	71.4	68.5	68.4	67.6	65	95.1

Cl	Br	I	OH	OCH_3	NH_2	$NHCH_3$	$N(CH_3)_2$	NO	NO_2
29	26.7	25.5	9.0	3.4	47.2	45.2	38.2	21.6	7.9
76.7	63.9	49.3	86.9	76.9	80.7	78.2	72.3	33.9	54.9
60.4	48	33.1	71.9	61.4	65	63	57.1	17	39
65.1	52.3	37.7	75.3	65.3	69.1	66.6	60.7		
60.4	48.0	33.1	71.9	61.4	65	63	57.1		
55.2	42.8	27.9	66.7	56.2	59.8	57.8	51.9	12.4	37.8
55.5	43.1	28.2	67	56.5	60.1	58.1	52.2		
56.4	44.6	29.6	68.4	58.7	62.1	59.6	53.7	16	38.2
69.4	54.7	40	77.9	66.9	71.9			25	45.9
69	56.5	40	76.3	66.6	71.9			25	45.9
69	56.5	40	76.3	66.6	71.9			25	45.9

	$\Delta H_f^\circ(X)$	H	CH_3	C_2H_5	$n\text{-}C_3H_7$	$i\text{-}C_3H_7$	$t\text{-}C_4H_9$
$\Delta H_f^\circ(R)$		52.1	34	25.7	20.8	17.8	7.5
$O{=}\underset{\substack{\mid\\ H}}{C}{-}$	9.5	87.5	83.2	80.7	79.2	79.6	75.2
$O{=}\underset{\substack{\mid\\ C}}{C}{-}$	-5.8	86	80.1	76.9	76.9	74.8	71
C_6H_5CO- benzoyl	26.1	86.9	80.8	77.8	77.5	77.3	73.6
$O{=}\underset{\substack{\mid\\ C}}{C}{-}C{-}$	-5.5	98.5	85.5	82.1	82.2	80.9	78.3
$HO{-}C{-}$	-4.6	95.6	85.6	82.3	82	81	76.3
$HO{-}\overset{\substack{C\\ \mid}}{\underset{\substack{\mid\\ C}}{C}}{-}$	-27.1	90.1	81.6	77.7			
$O{=}\underset{\substack{\mid\\ OH}}{C}{-}$	-52.7	90	84.6	81.4	80.5	80.8	77.3
$O{=}\underset{\substack{\mid\\ OCH_3}}{C}{-}$	-40.4	95.3	91.5	88.2	88.2	89.6	89.9
$O{=}\underset{\substack{\mid\\ C}}{C}{-}O{-}$	-45	110.4	86.9	87	87	87.9	87.1
C_6H_5O- phenoxy	9.9	85	61.2	61.9	62.1	62.8	62.1
CH_3O- methoxy	3.4	103.6	81.4	80.8	81	81.4	80.6
$C{-}O{-}C{-}$	-2.8	93.3	82.9	79.7	80.3	79.3	76.7

F	Cl	Br	I	OH	OCH_3	NH_2	$NHCH_3$	NO	NO_2
18.9	29	26.7	25.5	9.0	3.4	47.2	45.2	21.6	7.9
122	84	69	52	109.1	96.1	101.2	98.8		
119.5	81.6	66.5	49.8	106.5	95.5	99.2	96.8		
115	80.5	64.4	49.1	105.2	95.1	94.8	92.4		
102	77	64.2	50.2	89.9	80.2				
101	82.2	69.7	55.1	97.9	88.2				
106	80	67	53	94.6	85				
				42.8	38.5				
				25	17.7	38.5	39.1	23.7	21.2
				44	36.9	56.8	57.4	42.9	40.4
106	79.9	67.4	52	95.6	83.9				

	$\Delta H^\circ_f(X)$	H	CH_3	C_2H_5	$n\text{-}C_3H_7$	F	Cl	Br	I	OH	OCH_3
$\Delta H^\circ_f(R)$		52.1	34	25.7	20.8	18.9	29	26.7	25.5	9.0	3.4
CH_2F-	$\gtrsim -5.3$	102.7	91.2	88	87.3	122	89	73		97.6	87.5
CHF_2-	$\gtrsim -57$	103.2	95.8	93	93	128	87.6	70			
CF_3-	-112.5	105.9	99.5	96.6	96.7	129.7	85.5	69.2	53.6		
CH_2Cl-	29	101.7	89.1	85.7	84.9	113	81	65		95.7	85.6
$CHCl_2$-	24.1	99.2	88.8	85	85	109	77.7	60	52		
CCl_3-	18.7	96	87.7	85.3	85.4	104	72.9	54.7			
CH_2Br-	40.5	101.7	89.7	86.7	86.9	111	79	64		97.0	86.9
$CHBr_2$-	54.3	103	93.3			113	78	62			
CBr_3-	72	96	98			115	79	56.2			
CH_2I-	54.0	102.7	90	86.8					51.3	96.4	87
CHI_2-	79.9	102.7							45.7		

U.S. DEPT. OF COMM. **BIBLIOGRAPHIC DATA SHEET**	1. PUBLICATION OR REPORT NO. NBSIR 74-551	2. Gov't Accession No.	3. Recipient's Accession No.

4. TITLE AND SUBTITLE

An Appraisal of Methods for Estimating
Self-Reaction Hazards

5. Publication Date
June 1974

6. Performing Organization Code

7. AUTHOR(S)
W. Tsang and E. S. Domalski

8. Performing Organ. Report No.

9. PERFORMING ORGANIZATION NAME AND ADDRESS

NATIONAL BUREAU OF STANDARDS
DEPARTMENT OF COMMERCE
WASHINGTON, D.C. 20234

10. Project/Task/Work Unit No.
3160415

11. Contract/Grant No.

12. Sponsoring Organization Name and Complete Address *(Street, City, State, ZIP)*

Office of Hazardous Materials
Department of Transportation
2100 Second Street, S.W.
Washington, DC 20024

13. Type of Report & Period Covered
Final
1-1-74 thru 6-30-74

14. Sponsoring Agency Code

15. SUPPLEMENTARY NOTES

16. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)*

The ability to identify and specify the thermal instability of chemical substances has been appraised as a result of examining certain test methods used to measure explosive sensitivity, and certain computer programs designed to estimate reaction hazards from a thermochemical approach. The bond dissociation energy emerges as the parameter giving the best correlation with material sensitivity. The computer programs overemphasize explosive power as opposed to explosive sensitivity and label many compounds hazardous when they are not. At present, regulations specifying the handling and transport of commodities should follow the concept of self-reactivity based upon functional groups.

17. KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)*

Activation energy; bond dissociation energy; computer programs; explosive sensitivity tests; heat of decomposition; oxygen balance.

18. AVAILABILITY ☒ Unlimited

☐ For Official Distribution. Do Not Release to NTIS

☐ Order From Sup. of Doc., U.S. Government Printing Office
Washington, D.C. 20402, SD Cat. No. C13

☐ Order From National Technical Information Service (NTIS)
Springfield, Virginia 22151

19. SECURITY CLASS (THIS REPORT)
UNCLASSIFIED

20. SECURITY CLASS (THIS PAGE)
UNCLASSIFIED

21. NO. OF PAGES
99

22. Price


AMERICAN REVOLUTION BICENTENNIAL
1776-1976