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**ON THE ESTIMATION OF HAZARD POTENTIAL
FOR CHEMICAL SUBSTANCES**

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On the Estimation of Hazard Potential for Chemical Substances

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There is considerable interest in means for predicting reactivity hazard potential from chemical structure. Such means are intended to provide measures of the likelihood that a given chemical composition can undergo rapid self-reaction, i.e., that it can detonate or deflagrate. The means to be discussed are most useful in predicting behavior under unconfined conditions. As they are computational in nature, they can be deployed quickly and easily to wide ranges of compositions, whether or not these have ever been made. Comparison with better-known compositions is facilitated and can provide additional guidance.

In this paper we provide critical reviews of some commonly used hazard evaluation systems, including the oxygen balance system, and ASTM CHETAH. We also provide a review of our recent studies aimed at the development of more powerful screening systems.

BACKGROUND

Of the myriad chemical compositions existing or capable of existence on earth, many are unstable in the sense that they are thermochemically susceptible to self-reaction with formation of more stable products. Compositions of this description which can persist, if undisturbed, for an appreciable time are termed "metastable". Examples of metastable compositions include hydrogen-oxygen mixtures at room temperature, TNT and other high explosives, black powder, most peroxides and hypochlorites, ammonium salts of oxidizing acids, and other common chemicals. Most aromatic and cyclic organic compounds are metastable, as are ethylene, DMSO, and others.

Some metastable compositions are capable of vigorous or violent reaction when disturbed. As a consequence they can create shock effects, perform mechanical work, and cause damage or injury. These hazardous properties have their roots in stored chemical energy, and in the possibility of very rapid conversion of this energy to heat or mechanical energy. Such compositions may contain mutually-reactive groups in very close proximity, for example in the same molecule. Since reaction can occur without mass transfer, rates can be very high. In the limit, reaction rates may be controlled by hydrodynamic considerations. Such reactions are termed detonations; they represent the fastest possible chemically-driven reactions and the most severe chemical reactivity hazards. Rates of propagation may reach 7000 m/s or higher.

Many metastable compositions can self-react more or less rapidly without converting to detonation. Such reactions, which propagate by thermal diffusion, are termed "deflagrations". Although the fastest deflagrations are an order of magnitude slower than detonations, they can, nonetheless, produce uncontrollable and devastating pressure pulses. The term "deflagration" is frequently used to suggest rapid propagation, on the order of hundreds of m/s. There is, however, no distinction in principle between, say, the reactions in slow burning fuses, warning flares, black powder, and rocket propellants. Table 1 contains examples of energy conversion rates.

For comparison, a typical aircraft jet engine consumes fuel equivalent to about 40,000 kilowatts.

Prodigious energy conversion rates are the basis for all the characteristic effects of explosions. It has been noted, for example, that a few minutes of ordinary sunlight deposits as much energy on a city block as would a WW II blockbuster bomb. In chemical reactivity hazards, the rate's the thing!

It is of considerable practical importance to distinguish metastable compositions capable of detonation or violent deflagration in the *open* from nonhazardous metastable and stable compositions. Presently-used methods have been summarized, for example in reference [1]. Comments on these methods follow:

OXYGEN BALANCE METHOD

In a 1949 Chemical Reviews article, W. C. Lothrop and G. R. Handrick documented a strong correlation between "oxygen balance" and the explosive performance of organic nitrates and nitro compounds. In this context, an

TABLE 1. Some Energy Conversion Rates

Source of Energy	Specific Enthalpy Change (kJ/g)	Propagation Rate (m/s)	Specific Power (kW)
TNT detonation	5.0	6000	4.5×10^6
Lead azide detonation	1.4	4000	2.8×10^6
Black powder deflagration	1.4	400	0.7×10^6
Safety flare	0.1	0.001	< 1

oxygen balance of zero implies an oxygen content just sufficient to convert all carbon to CO₂ and all hydrogen to H₂O. Although valuable and universally used in explosives practice, it has been shown that there is no necessary connection between oxygen balance and self-reactivity in general [2].

Indiscriminate use of the oxygen balance criterion can produce misleading hazard assignments.

ENTHALPY OF FORMATION

Enthalpy of formation data provide information on thermochemical stability with respect to the elements which make up the composition in question. In fact, most explosives are stable with respect to their elements, but are highly unstable with respect to some set of (usually) simpler reaction product. A positive value of the enthalpy of formation provides an early warning of hazard potential. A negative heat of formation provides no hazard potential guidance.

ENTHALPY OF REACTION

The difference between enthalpy of formation of the composition in question and its reaction products represents the enthalpy of reaction. This parameter provides at least a rough guide to the amount of stored chemical energy and, to this extent, to the hazard potential.

ASTM "CHETAH" HAZARD CRITERIA

The well-known CHETAH program provides convenient, computerized means for estimating enthalpy of formation for any composition that can be represented in the Benson group additivity system. CHETAH then uses a linear programming technique to select, from its own data bank, the set of room-temperature reaction products yielding the greatest enthalpy change. The resulting value of $\Delta H(r)$ is reported as CHETAH hazard evaluation Criterion 1. Values of -2.9 kJ/gram or more negative are taken as indicating "high" hazard potential. Note that the specific enthalpy change, as in kJ/gram, is the relevant parameter.

The five additional hazard criteria provided by CHETAH appear to have limited value. A critical review has been published in reference [3].

ADIABATIC REACTION TEMPERATURE, CONDENSED PHASE MATERIALS

As noted above, chemical reactivity hazards originate with stored chemical potential energy. Without stored energy in the form of metastable compositions there would be no self-reactivity hazards. However, it is the rate of energy conversion that distinguishes detonations and fast deflagrations from ordinary chemical reactions. Reaction rates are dominated by temperature, as temperature occurs in the exponent of the rate equation. This effect is well represented by Figure 1. Figure 1 illustrates the impact of temperature on time required for ammonium nitrate to self-heat itself to explosion under adiabatic conditions. Following the above line of reasoning it is to be expected that adiabatic reaction temperature might be useful in hazard prediction. Study of this possibility has been facilitated by the development of computer codes designed to carry out multi-

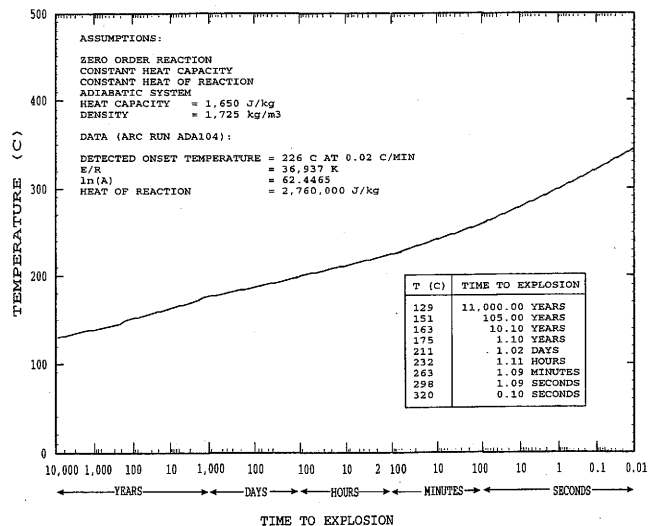


FIGURE 1 Impact of temperature on time to explosion for ammonium nitrate.

phase Gibbs free energy minimization and adiabatic reaction temperature calculations, and by the proliferation of PC's capable of using these codes.

We have explored the relationship between calculated adiabatic reaction temperature (CART) values as calculated by use of the NASA-Lewis CET89 code and the known reactivity hazards of many chemical compositions, including

TABLE 2. CART Values and Hazard Rankings of Selected Carbon-Hydrogen and Carbon-Hydrogen-Oxygen Compounds

Compound	Formula	ΔH_r (kJ/g)	CART (K)	Hazard Index
Methane	CH ₄	0.00	298	N
Oxalic acid	C ₂ H ₂ O ₄	-1.21	416	N
n-Butyric acid	C ₄ H ₈ O ₂	-0.96	445	NX
Formic acid	CH ₂ O ₂	-1.30	501	N
Caprylic acid	C ₈ H ₁₆ O ₂	-1.05	546	N
Octane	C ₈ H ₁₈	-1.13	552	N
Ethanol	C ₂ H ₆ O	-1.76	564	NX
Me Isopropyl ketone	C ₅ H ₁₀ O	-0.84	677	NX
Succinic anhydride	C ₄ H ₄ O ₃	-1.26	691	NX
Diisopropyl ether	C ₆ H ₁₄ O	-1.38	701	NX
Acetone	C ₃ H ₆ O	-1.72	706	NX
Ethyl ether	C ₄ H ₁₀ O	-1.92	723	NX
Decene	C ₁₀ H ₂₀	-1.80	747	N
Acetic anhydride	C ₄ H ₆ O ₃	-1.42	754	N
Acrylic acid	C ₃ H ₄ O ₂	-2.18	789	NX
Hydroquinone	C ₆ H ₆ O ₂	-2.34	805	NX
Toluene	C ₇ H ₈	-2.18	810	N
p-Toluic acid	C ₈ H ₈ O ₂	-1.67	840	NX
Acetophenone	C ₈ H ₈ O	-2.22	842	NX
Benzene	C ₆ H ₆	-2.51	864	N
Maleic anhydride	C ₄ H ₂ O ₃	-2.43	901	NX
Phthalic anhydride	C ₈ H ₄ O ₃	-1.80	933	N
Anthracene	C ₁₄ H ₁₀	-2.59	983	N
Furan	C ₄ H ₄ O	-3.60	995	NX
Ethylene oxide	C ₂ H ₄ O	-2.59	1009	N
Ethylene	C ₂ H ₄	-4.18	1253	N
Acetylene	C ₂ H ₂	-10.13	2824	E

TABLE 3. CART Values and Hazard Rankings of Organic Nitro Compounds and Nitrates

Compound	Formula	ΔH_r (kJ/g)	CART (K)	Hazard Index
m-Nitrobenzoic acid	$C_7H_5NO_4$	-3.01	998	NX
Mononitrotoluene	$C_7H_7NO_2$	-4.23	1104	N
p-Nitroaniline	$C_6H_6N_2O_2$	-3.39	1109	NX
Mononitrobenzene	$C_6H_5NO_2$	-4.64	1318	N
Dinitrotoluene	$C_7H_6N_2O_4$	-5.27	1511	E
Nitroguanidine	$CH_4N_4O_2$	-3.77	1840	E
Dinitrobenzene	$C_6H_4N_2O_4$	-5.56	1843	E
TNT	$C_7H_5N_3O_6$	-5.73	2066	E
Trinitrobenzene	$C_6H_3N_3O_6$	-6.07	2344	E
Nitromethane	CH_3NO_2	-6.32	2419	E
Glycerol dinitrate	$C_3H_6N_2O_7$	-6.02	2813	E
Glycerol trinitrate	$C_3H_5N_3O_9$	-6.78	2859	E
HMX	$C_4H_8N_8O_8$		2875	E
RDX	$C_3H_6N_6O_6$	-6.78	2935	E

carbon-hydrogen compounds, organic nitrates and nitro compounds, nitrogen compounds other than nitrates or nitro compounds, redox compositions, and organic peroxides. The data in Tables 2 through 6 illustrate our findings. The hazard index notations, E, N, and X are defined as follows:

- E Can be exploded when unconfined
- N No known explosion hazard when unconfined
- X Tests are described in CHETAH 4.4 Manual on page 177

TABLE 4. CART Values and Hazard Rankings of Nitrogen Compounds other than Organic Nitro Compounds and Nitrates

Compound	Formula	ΔH_r (kJ/g)	CART (K)	Hazard Index
Nitrogen trichloride	NCl_3	-1.92	1930	E
Hydrazoic acid	HN_3	-6.90	3369	E
Lead azide	PbN_6	-1.59	3900	E
Silver azide	AgN_3	-2.05	>4000	E
Silver fulminate	$AgONC$	-1.21	>4000	E
Mercury fulminate	$Hg(ONC)_2$	-2.09	5300	E

ADIABATIC REACTION TEMPERATURE, GASEOUS COMPOSITIONS

The majority of heats of reaction data reported in Tables 2 through 6 were obtained from CHETAH. Heats of reaction data were also obtained from literature sources.

It is known that many of the reactions leading to the formation of CO_2 and H_2O have "freeze-out" temperatures on the order of 1400 K. This "freeze-out" limit is most likely related to the minimum temperature required for carbon monoxide to propagate a self-sustaining flame which is around 1400 K. The concept of a "freeze-out" temperature can be used to estimate flammability limits for multicomponent gas mixtures with diluents and can be used to assess the impact of initial mixture temperature/pressure on flammability limits.¹ Figure 2 illustrates the use of constant

¹This is currently performed using a chemical/physical equilibrium code based on direct minimization of the Gibbs free energy.

TABLE 5. CART Values and Hazard Rankings of Redox Compositions

Reactant(s)/Reaction	ΔH_r (kJ/g)	CART (K)	Hazard Index
Nitric acid 70% aq. $HNO_3 + 1.5 H_2O = \text{No reaction}$			N
Perchloric acid 70% aq. $HClO_4 + 2.4 H_2O = \text{No reaction}$			N
Hydrogen peroxide, 70% aq. $H_2O_2 + 0.81 H_2O = 1.81 H_2O + 0.5 O_2$	-0.38	494	N
Ammonium nitrate $NH_4NO_3 = 2 H_2O + N_2 + 0.5 O_2$	-2.76	1250	N
Ammonium perchlorate $NH_4ClO_4 = 1.5 H_2O + 0.5 N_2 + 1.25 O_2 + HCl$	-0.84	1381	N
Conc. nitric acid + ethanol, balanced $2.2 HNO_3 + 3.3 H_2O + C_2H_6O = 2 CO_2 + 6.8 H_2O + 1.1 N_2$	-2.59	1775	E
Hydrogen peroxide 70% aq. + ethanol, balanced $6 H_2O_2 + 4.9 H_2O + C_2H_6O = 2 CO_2 + 13.9 H_2O$	-3.97	2109	E
Perchloric acid, 70% aq. + acetic acid, balanced $HClO_4 + 2.4 H_2O + C_2H_4O_2 = 2 CO_2 + 4.4 H_2O + HCl$	-3.47	2125	E
Ammonium nitrate + Urea, balanced $3 NH_4NO_3 + CON_2H_4 = CO_2 + 8 H_2O + 4 N_2$	-4.14	2314	E
Ammonium perchlorate + Carbon, balanced $NH_4ClO_4 + 1.25 C = 1.25 CO_2 + 1.5 H_2O + 0.5 N_2 + HCl$	-4.94	2684	E

NOTE: All reactants in condensed state; all products in gas state.

TABLE 6. CART Values and Hazard Rankings of Selected Organic Peroxides

Compound	Formula	ΔH_r (kJ/g)	CART (K)	Hazard Index
Benzoyl peroxide + 50% H ₂ O	C ₁₄ H ₃₇ O ₁₇	-0.17	336	N
Lauroyl peroxide	C ₂₄ H ₄₆ O ₄	-0.43	779	N
Di-t-butyl peroxide	C ₈ H ₁₈ O ₂	-0.65	847	E
t-butyl perpivalate	C ₉ H ₁₈ O ₃	-0.59	848	E
Dicumyl peroxide	C ₁₈ H ₂₂ O ₂	-0.66	925	N
Acetyl peroxide	C ₄ H ₆ O ₄	0.78	956	E
Benzoyl peroxide	C ₁₄ H ₁₀ O ₄	-0.70	972	E
t-butyl perbenzoate	C ₁₁ H ₁₄ O ₃	-0.51	973	E
Ethyl hydroperoxide	C ₂ H ₅ O ₂	-1.38	1058	E

temperature limit of 1400 K to calculate the flammability envelope for ethane with two different diluents, carbon dioxide and nitrogen. The data compares favorably to values reported by the Bureau of Mines Bulletin 627. Figure 3 illustrates the use of constant temperature to estimate the flammability envelope for a hydrocarbon mixture where water is the diluent. As shown by Figure 3 the selection of a lower temperature limit such as 1200 K results in a wider flammability envelope, a conservative estimate for hazard prediction. With few exceptions, the majority of reported experimental flammability limits correspond to adiabatic flame temperatures in the range of 1200 to 1500 K.

Most compositions yielding adiabatic temperatures lower than these values will not continue to react even if initiated at higher temperatures [4]. The known explosive compositions included in Tables 2-5 all have CART values higher than 1200 K, while the non-sensitive compositions all have CART values lower than 1200 K.

SUMMARY

CART rankings are in better agreement with the known properties of the compositions evaluated than are enthalpy of reaction, $\Delta H(r)$, data. For example, by CHETAH 4.4 criteria, ethyl ether and toluene, along with many other com-

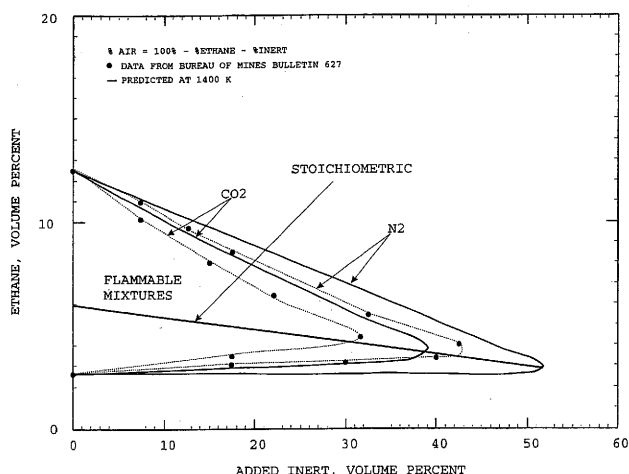


FIGURE 2 Estimation of flammability limits using a constant temperature value of 1400 K.

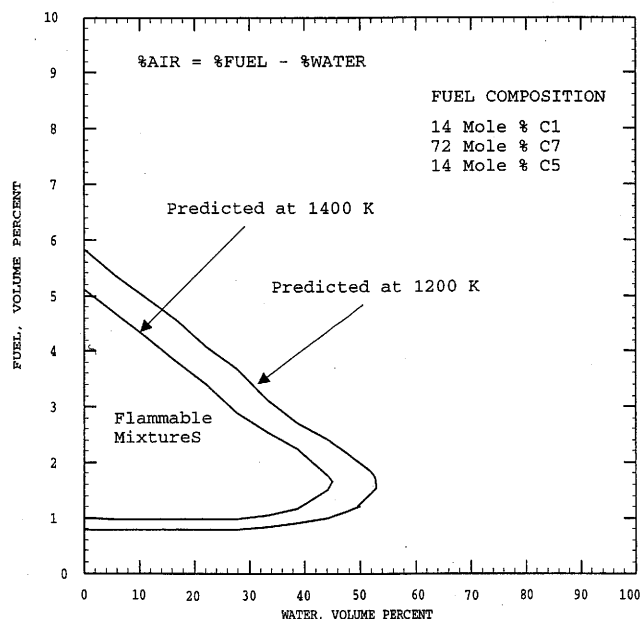


FIGURE 3 Impact of temperature limit on flammability envelope.

pounds of no known self-reactivity hazard are placed in the "medium" hazard category [$\Delta H(r)$ more negative than -1.7 kJ/g]. By the CHETAH 7.0 criterion, *m*-nitrobenzoic acid and mononitrotoluene are placed in the "High" hazard category. [$\Delta H(r)$ more negative than -2.9 kJ/g], although neither appears susceptible to vigorous self-reaction. Also striking is the contrast in classification of nitrogen compounds other than nitro compounds or nitrates. Few such compounds can be evaluated in CHETAH, but manually calculated $\Delta H(r)$ values place some of them in the "medium" or "low" hazard category, in contrast with the high CART values and known high hazard potential.

We suggest that CART values reflect hazardous properties more accurately than $\Delta H(r)$ values because the former take heat capacity into account while the latter do not. For example, the reaction products of the explosive metal-bearing nitrogen compounds have exceptionally low specific heats, hence reach extremely high temperatures even though heats of reaction are modest by CHNO compound standards. The high temperatures are believed to be associated with both high sensitivity to initiation and high propagation rates [5]. In other cases, CHNO compounds in Table 4 for example, relatively high enthalpy of reaction values are counterbalanced by the relatively high specific heat of the product mix. Reaction temperatures are too low to permit formation of the thermochemically favored products at an appreciable rate.

Table 6 contains thermochemical and CART data for selected organic peroxides.

Clearly, neither CART nor enthalpy of reaction values are very effective in predicting the hazard rankings of these compounds, many of which are much more sensitive to initiation than are standard high explosives. The above and additional data indicate that many organic peroxides are able to explode, probably via deflagration [6], even though the calculated adiabatic temperatures are lower than conventional freeze-out temperatures. $\Delta H(r)$ values for the compounds listed in Table 6 are qualitatively consistent with observed properties, but do not suggest the enormous

differences in hazard potential between acetyl and benzoyl peroxides, for example. The evidence suggests that organic peroxides explode by mechanisms different from those of the other classes of compounds considered above

CONCLUSIONS

We have demonstrated that calculated adiabatic reaction temperature (CART) is an effective screening tool in evaluating the reactivity hazard potential of many classes of chemical compositions. As demonstrated by our organic peroxide findings, computational methods should always be viewed as screening tools rather than as substitutes for empirical testing.

ACKNOWLEDGMENTS

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