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Of Computers, Chemistry, Chemical Engineering, and Reactivity

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ABSTRACT

With the availability of powerful computers and continued reduction in computing cost, it is routinely possible to calculate the physico-chemical properties of chemicals. This paper is an overview of state-of-the-art calculation models available for data prediction with implications for chemical process safety and especially chemical reactivity.

Hydroxylamine is a highly reactive and poorly characterized compound with important industrial applications. Practical methods for estimation of thermodynamic properties, phase behavior, and solvation energetics are exemplified through calculations on hydroxylamine. Finally, a reaction pathway for hydroxylamine decomposition is proposed, together with a transition state. The techniques discussed in the paper can be extended to other compounds.

Structure based prediction of reactive hazards

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Abstract

There is a considerable interest in the prediction of reactive hazards based on chemical structure. Generally, rules of thumb based on prior experience are used for screening and estimating reactive hazards of compounds. Calorimetric measurements to determine reactivity can be highly resource consuming, so computational methods to predict reactivity hazards are of prime importance.

This paper reviews some of the commonly employed hazard evaluation techniques including the oxygen balance method, ASTM CHETAH, and Calculated Adiabatic Reaction Temperature (CART). It also discusses the development of a study table to correlate and predict reactivity properties of pure compounds. Quantitative structure-property relationships (QSPR) based on semi-empirical quantum calculations are used to correlate the onset temperatures and heats of reaction from calorimetric data with molecular properties.

Introduction:

A question that is frequently encountered during processing, storage, or handling of a chemical is "Does this chemical pose reactive hazards?" An analogous problem is the estimation of chemical incompatibilities. Certain compositions are unstable by nature and susceptible to violent reaction. During the reaction, chemical energy is converted to heat or mechanical energy and poses potential hazards.

Generally, rules of thumb based on prior experience are used for screening and estimating reactive hazards of compounds. For example, the presence of a 'nitro' group is regarded as an indicator of reactivity, as in trinitrotoluene (TNT). Attempts have been made to develop a generalized framework for estimating reactive hazards based on molecular structure, such as the oxygen balance method, CHETAH, and CART. However, these methodologies have limitations, and considerable chemical intuition and experience is required for effective use of these approaches. Also, the reliability of estimations for a variety of compounds and process conditions varies significantly.

A reliable experimental technique for assessing reactivity is calorimetric analysis, which can be highly resource consuming and thus possible only for a limited set of compounds. So, one of the challenges is extending the results of tests on a limited number of compounds to a myriad of compounds and compositions. The methods described in this paper are computational in nature and can be employed quickly. The paper provides a brief review of the available methods and a detailed description of our efforts at estimating reactive hazards.

Review of available methods

This section provides a review of existing methods for reactivity hazard evaluation, including the strengths and limitations of each method. It attempts to provide the reader with enough information to choose a method for a particular situation. A few of these methods are reviewed in reference [1].

Rules of thumb:

The presence of certain functional group, as listed in *Table 1* [2], is considered an indicator of reactivity. This is the simplest possible reactivity screening method and serves as a guideline for further analysis.

$>C=C<$	$-C\equiv C-$	$>C \begin{array}{c} \diagup \\ \diagdown \end{array} C<$
$-O-O-$	$-C \begin{array}{c} O \\ \diagdown \\ Cl \end{array}$	$-O-C \begin{array}{c} O \\ \diagdown \\ Cl \end{array}$
$>S=O$	$-SO_2Cl$	$-O-C \begin{array}{c} S \\ \diagdown \\ SK \end{array}$
$>P(OR)$	$-P(OR)_2$	$P(OR)_3$

Table 1: Functional groups indicative of reactivity

Oxygen balance method:

A quantitative correlation was shown between oxygen balance and various measures of explosive effectiveness for several classes of organic explosives [3]. More than 300 compounds were studied for correlating the explosive properties to oxygen balance. The authors recommend the following formula for calculating oxygen balance for a compound:

$$\text{Oxygen Balance} = \frac{-1600(2X + Y/2 - Z)}{M_w}$$

where,

- X – Number of atoms of carbon
- Y – Number of atoms of hydrogen
- Z – Number of atoms of oxygen
- M_w – Molecular weight

The above formula yields a value of 0 for oxygen-balanced compounds, negative for oxygen-poor and positive for oxygen-rich compositions. This method is one of the criteria used in the CHETAH [5] program. The following classification is recommended for estimating hazard potential based on oxygen balance:

Oxygen Balance	Hazard Rank
More positive than +160	Low
+160 to +180	Medium
+80 to -120	High
-120 to -240	Medium
More negative than -240	Low

Table 2: Oxygen balance and hazard rank [3]

Strengths:

The oxygen balance method is useful for estimating hazards of organic nitro compounds and is universally employed in the explosive industry. In general, it works well for compounds containing C, H, N and O elements.

Weaknesses:

However, it has been shown that there is no necessary connection between oxygen balance and self-reactivity [4]. For example, water (H₂O) has an oxygen-balance value of 0, and it is given a 'high' hazard ranking by this criterion. Also, the method cannot be applied to oxygen free but hazardous compounds such as acetylene. Application of the above oxygen balance equation to low-oxygen content or oxygen-free compounds produces a highly negative, non-hazardous ranking regardless of the actual hazard potential.

CHETAH [5]:

ASTM's Computer Program for Chemical Thermodynamic and Energy Release Evaluation, CHETAH, is popular software for prediction of reactivity hazards. It uses the 'Benson group contribution method' to estimate heat capacity, heat of formation, and heat of combustion for a multitude of compounds. Also, the program includes a database of thermo-chemical properties for selected organic and inorganic compounds. CHETAH classifies chemicals based on their potential for violent explosion, and includes the following hazard evaluation criteria:

1. Maximum heat of decomposition
2. Fuel value minus heat of decomposition
3. Oxygen balance

According to the first criterion, compositions with heats of reaction more negative than -2.929 kJ/g are placed in 'high' hazard category. Detailed explanation of the above evaluation criteria can be found in the CHETAH reference manual [5]. A critical review of CHETAH for predicting reactivity hazards can be found in reference [6]. The first criterion has proved to be a reliable indicator of potential reactive hazard. However, the other criteria may not be effective for all the chemicals and compositions.

Input to the program:

The molecular formula of the compound is the only input to the program. From the included database the thermodynamic properties are estimated and the hazard criteria are determined from these values.

Strengths:

The software is user friendly and offers the flexibility to include user-defined group values. It is computationally inexpensive and can be installed on a PC.

Weaknesses:

The calculations can fail for Benson group values that are not available in the database or if the group values are incorrect. In the evaluation criteria, the program classifies compounds or compositions into hazard categories. Thus the program tries to place a boundary based on a threshold value blurring the distinction between hazardous and non-hazardous chemicals. Also, the program gives no insight into process conditions to be avoided or about the sensitivity of compounds to initiation of a reaction.

CART [1]:

Adiabatic temperature rise due to a reaction is defined as:

$$\Delta T_{\text{Adiabatic}} = \frac{\Delta H_R}{C_p}$$

where,

ΔH_R – heat of reaction

C_p – heat capacity of the reacting mixture

$\Delta T_{\text{adiabatic}}$ – Adiabatic temperature rise

The code developed for CART performs multiphase Gibbs free energy minimization and adiabatic reaction temperature calculations. Based on the calculated $\Delta T_{\text{adiabatic}}$ the substance is classified as [1]:

E - Can explode when unconfined

N- No known explosion hazard when unconfined

An adiabatic temperature rise of 1400 K is considered a cut-off value for the above classification. Thus, substances with adiabatic temperature rise of more than 1400 K are classified as E and lower than 1400 K as N. This value is based on the fact that most combustion reactions leading to formation of CO₂ and H₂O have a threshold temperature value of 1400 K. This value is the

minimum temperature required for carbon monoxide to propagate a self-sustaining flame. The authors recommend a cut-off value of 1200 K for conservative estimations.

Input to the program:

The heat of reaction, heat capacity of reaction mixture, and other relevant thermochemical values for a system are required program inputs. These values can be obtained from the literature or estimated using the CHETAH program.

Strengths:

The CART criterion works better than considering just the ΔH_R value (as in first CHETAH criterion) since it takes into account the heat capacity of the reaction mixture. The authors also argue that higher CART values are associated with high sensitivity to initiation and high propagation rates. CHETAH programmers should probably include ‘adiabatic temperature rise’ as one of the hazard evaluation criteria.

Weaknesses:

Thermo-physical values must be estimated, sometimes using CHETAH resulting in limitations similar to CHETAH. The classification works well for estimating hazards of compounds undergoing combustion reactions. For compounds that do not undergo combustion type reactions, deciding a threshold value of $\Delta T_{\text{adiabatic}}$ is difficult. As pointed out by authors in the same reference [1], the CART classification and heats of reaction values fail for correct hazard ranking of organic peroxides. Also, just like CHETAH, this classification places a boundary based on a threshold value.

Modeling Reactivity:

All of the above methods have conceptual deficiencies since they model a part of the actual process with simplified assumptions and then base their classification on certain model outputs. This section discusses the details of a runaway scenario and modeling challenges. The following discussion is from a modeling perspective where our goal is to determine reactive hazards from molecular structure alone.

A reactive accident or incident is the result of conversion of stored chemical energy of the components and can thus be symbolically represented as:



It is the uncontrolled release of this stored energy that causes the damage. A typical fault tree of a reactive accident/incident is represented in *Figure 1*. For a reaction to pose a reactive hazard (generally) it must be exothermic and it must occur at a sufficiently rapid rate.

$\Delta H_R \times r_A$, where r_A refers to the reaction rate, is a coupling term for the mass and the energy balance equations and takes into account both the thermodynamics and kinetics of the process.

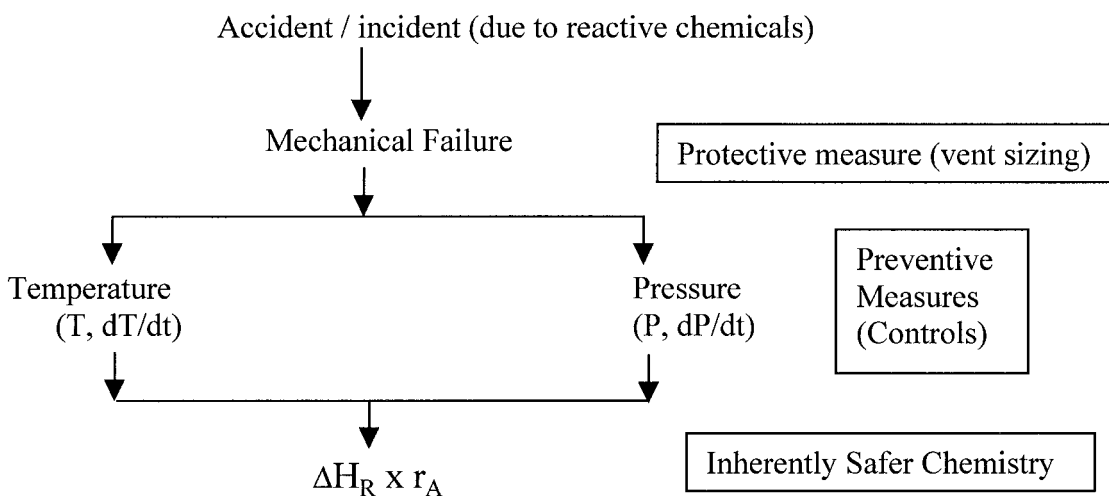


Figure 1: Fault tree for a reactive incident illustrating safety features

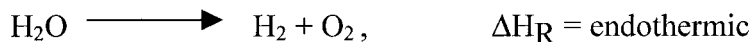
Figure 1 can also be used to illustrate safety principles. The blocks in the figure show the ‘level’ of safety involved in the handling/processing of reactive chemicals. Ideally, one would like to choose an inherently safe reaction pathway with no possible runaways or modify the process conditions to achieve inherent safety. But having accepted a process and the conditions, one accepts the risk of potential reactivity hazards and then uses preventive measures (better control system) and protective measures (vent sizing) to minimize the losses.

One way to consider the problem of a reactive hazard occurrence is:

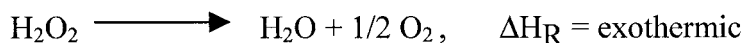
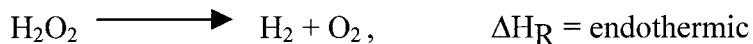


The substance X undergoes a rearrangement following conservation of atoms. Thus hazardous stoichiometries can exist, but except for the simplest system, it is difficult to determine these stoichiometries. Let us assume that the stoichiometries are known as in the following example.

H₂O:



H₂O₂:



It is easy to conclude that water (H₂O) does not pose a self-reactive hazard. However, in the case of hydrogen peroxide (H₂O₂) it is difficult to determine the dominant reaction. We can assume a worst-case scenario that results in maximum heat of reaction, and CHETAH employs the criterion of ‘maximum enthalpy of decomposition’ based on a similar logic. It assumes X goes to

products that maximize the enthalpy of decomposition. An energy release evaluation sheet from CHETAH 7.2 is shown at the end of this paper.

Based on the maximum heat of decomposition, H_2O_2 is given a “high” hazard classification. However, it should be noted that the product spectrum might be hypothetical. Thus, one problem is the thermodynamic feasibility of a proposed stoichiometry under process conditions. This is complicated by the fact the process we are trying to model is an unsteady state process and a multicomponent process, both of which may affect feasibility. The heat of reaction value gives no indication about the sensitivity to initiation of reaction or the process conditions to be avoided. It is difficult to conclude definitively whether H_2O_2 poses a reactive hazard based on such an analysis. Thus, the problem of reactivity is not just a combinatorial problem (stoichiometric analysis).

Knowing the heat capacity of the reacting mixture, we can estimate the adiabatic temperature rise (similar to CART methodology). For H_2O_2 , CHETAH estimates a maximum heat of reaction of -25.27 kcal/mol and C_p as 10.309 cal/mol K, yielding an adiabatic temperature rise of 2450 K. Again, this value gives no indication about the process conditions to be avoided. It is worth noting that in the case of H_2O_2 , the CHETAH criteria and the adiabatic temperature value indicate a potential reactive hazard.

To represent the dynamics of the process we need an unsteady state model for the reaction. For example, let us assume that we know the reaction stoichiometry of H_2O_2 and the necessary kinetics of the reaction. Knowing the kinetics and heat of reaction, one can solve the unsteady state mass and energy balance equations, which would better represent the concentration, temperature, and time profile and better estimate the adiabatic temperature rise. Ideally, we also need an additional equation that estimates pressure with changing temperature and composition for better estimation of hazards. Thus, knowing the kinetic model is not sufficient for reactive hazard estimation. To obtain a realistic model we need to couple kinetic and thermo-physical properties of a system of components with a flow model (similar to “Computational Reacting Fluid Dynamics”). This would include detailed chemical kinetic mechanisms and also account for the hydraulics.

From the above discussion, it is clear that we need an explicit mapping of the reaction into temperature, pressure, and time domain to provide a realistic scenario for identifying reactive hazards. Such an approach is too detailed to be implemented, limited by current computational power, lack of reliable data, and also partly by our lack of understanding of the actual process to be modeled.

But the reactivity problem cannot be solved by experimentation alone. For example, the two hydrogen atoms in hydrogen peroxide can be any of the following 10 groups: H, C1-C6 (aliphatic chains), benzene, toluene, or xylene. Thus, 100 different peroxide compounds must be evaluated to obtain the reactivity data. Assuming two runs per compound (at least) and a day per calorimetric run, the analysis would take at least 200 days. But there are many different possible combinations of functional groups (e.g., alkenes, alkynes, isomers) and compositions (e.g., 10, 20, 80 % H_2O_2). Sometimes experimentation is not feasible because of the toxic nature of chemicals or products.

The computational methods cannot be employed independently to estimate reactive hazards but must be cleverly implemented together with experimental measurements to reduce experimental effort and to expedite reactive hazard evaluation. The following section describes another approach to the reactivity problem, wherein we attempt to bridge the gap between macroscopic (calorimetric data) and microscopic (molecular) properties within the above limitations.

Structure based screening tool:

It is intuitive to assume that a similar change in structure will produce a similar change in reactivity. This is the theoretical basis of Hammett's linear free energy formulation for reactivity [7] and we use it to correlate and predict calorimetric data, namely:

- a. *Onset Temperature (Tonset): Measure of kinetics*
- b. *Energy of decomposition*

We build a Quantitative Property Structure Relationship (QSPR) study table to develop the correlation. The first column of this table is either Tonset or energy of decomposition, obtained from calorimetric experiments and is called the dependent variable. The remaining columns are the independent variables (characteristic of the molecules) called descriptors. A descriptor value can be obtained by experimental measurement or calculated based on molecular structure. We have used calculated descriptors to facilitate prediction of properties for unknown molecules.

Data Set Selection:

The data for Tonset and energy of decomposition are taken from references [2,8] and are presented in *Tables 2* and *3*, respectively. The data are from DSC / DTA measurements. We chose compounds belonging to the organic nitro family since a better correlation of properties is expected within a family of similar compounds. This set of compounds used to develop the correlation is called a 'training set'. Depending on the type of calorimeter, sample size, and scanning rate, the Tonset can vary by 5-50 °C, and the value for heat of decomposition can vary by 5-40 Kcal/kg. Hence, the choice of data is critical for an effective correlation.

Discussion of a few descriptors:

- a. **Highest Occupied Molecular Orbitals (HOMO):**
HOMO is the highest ground state energy level in the molecule that contains electrons. Molecules with high energy HOMOs are more easily able to donate their electrons and are hence relatively reactive compared to molecules with lower HOMO values.
- b. **Lowest Unoccupied Molecular Orbitals (LUMO):**
LUMO is the lowest ground state energy level in the molecule that contains no electrons. Molecules with lower LUMO values are able to accept electrons more easily than those with higher LUMO values.

c. Superdecentralizability (Sr):

Sr an index of reactivity in aromatic hydrocarbons as proposed by Fukui. The index is based on the idea that interaction between orbitals may be regarded as a mutual perturbation so that the relative energies of the two orbitals change together and maintain a similar degree of overlap as the reactants approach each other.

Calculations were performed using the QSPR module in the Cerius² modeling environment, version 4.2, from Accelrys Inc. [9]. Quantum mechanic descriptors are based on the semi-empirical quantum calculation method Austin Model-1 (AM1) as implemented in the MOPAC application in the Cerius² modeling environment [9]. Higher levels of theory were not tested to keep the method computationally inexpensive. The details of the descriptors used are available on request.

Correlation:

The predicted values for compounds in *Tables 3* and *4* were obtained by performing genetic partial least square regression analysis on the training set of molecules. The developed correlation has the form

$$Y = A_1X_1 + A_2X_2 + A_3X_3 + \dots + A_nX_n$$

where,

Y – Dependent variable

X – Independent variable (descriptor)

A – Regression constant

To test the predictability within the training set, the value for the dependent variable for each compound is predicted by leaving out that compound and performing a regression analysis on the remaining 12 compounds. From the predicted decomposition energy value, nitromethane appears to be an outlier.

Prediction:

To test the predictability of the correlation, the entire set of 13 molecules in the two tables was used as a training set. Predicted values are based on 78 molecular descriptors. To test the correlation, values were predicted for 2,4 dinitro toluene, which is outside the training set. Based on this training set the onset temperature of 2,4 dinitro toluene is predicted to be 278 °C, whereas the experimental values are 312 °C [2] and 250 °C [8]. Similarly, the decomposition energy for 2,4 dinitro toluene is predicted as 919.7 Kcal/kg as compared to the experimental value of 829.4 Kcal/kg [2] and 854.2 Kcal/kg [8]. It is important to note that the onset temperature is not a fundamental quantity and is sensitive to the measurement technique. However, using such an approach a correlation can be successfully developed to predict values within experimental uncertainty.

		Tonset (°C)	G/PLS *	Residual ⁺	Descriptors		
		Observed	Predicted		HOMO	LUMO	Sr
1	Nitromethane	320	347.9	-27.9	-13.35	0.98	2.90
2	Trinitromethane	128	127.8	+0.2	-14.88	-1.60	0.27
3	Tetranitromethane	137	137.4	-0.4	-15.34	-2.23	3.43
4	Nitrobenzene	360	346.3	+13.7	-12.85	0.50	0.49
5	1,2 dinitrobenzene	280	275.8	+4.2	-13.29	-0.63	0.70
6	1,3 dinitrobenzene	270	295.3	-25.3	-13.41	-0.51	0.70
7	1,4 dinitrobenzene	350	352.5	-2.5	-13.45	-1.16	0.70
8	2 nitrotoluene	290	302.0	-12.0	-12.80	0.59	1.89
9	3 nitrotoluene	310	300.1	+9.9	-12.79	0.54	2.05
10	4 nitrotoluene	320	324.2	-4.2	-12.77	0.50	1.90
11	2,6 dinitrotoluene	290	290.2	-0.2	-13.33	-0.16	1.28
12	3,4 dinitrotoluene	280	267.1	+12.9	-13.20	-0.54	1.03
13	TNT	250	244.5	+5.5	-13.77	-1.03	2.36

Table 3: Onset Temperature (Tonset) - observed and predicted

		Decomposition	G/PLS*	Residual ⁺	G/PLS**	Residual**
		Eney (Kcal/kg)				
		Observed	Predicted		Predicted	
1	nitromethane	1265.5	-391.7	+1657.3	1264.9	+0.7
2	trinitromethane	540.2	534.4	+5.6	549.9	-9.7
3	tetranitromethane	800.7	803.7	-3.0	794.0	+6.7
4	nitrobenzene	418.2	408.4	+9.8	411.4	+6.9
5	1,2 dinitrobenzene	791.1	785.2	+5.9	822.0	-30.9
6	1,3 dinitrobenzene	833.7	845.2	-11.5	833.3	+0.3
7	1,4 dinitrobenzene	884.6	870.1	+14.4	858.9	+25.7
8	2 nitrotoluene	574.6	576.3	-1.7	548.7	+25.8
9	3 nitrotoluene	494.7	534.0	-39.7	507.8	-13.0
10	4 nitrotoluene	554.9	533.5	+21.4	559.2	-4.3
11	2,6 dinitrotoluene	824.8	844.5	-19.7	837.8	-13.0
12	3,4 dinitrotoluene	952.9	939.8	+13.1	953.2	-0.3
13	TNT	1050.4	1049.9	+0.5	1045.1	+5.3

Table 4: Energy of decomposition: observed and predicted

* The values are predicted by leaving out one compound and applying Genetic Partial Least Square (G/PLS) algorithm on the remaining 12 compounds

⁺ Difference between observed and predicted

** Regression performed on all 13 molecules

Conclusion:

Computational screening methods are needed for efficient evaluation of reactive hazards. The earlier methods attempted to classify the substances into 'hazard' categories. We have attempted to correlate DSC/DTA data for the nitro family of compounds with molecular descriptors. The QSPR technique can provide a realistic estimation of hazards and can be further improved by using a larger training set and higher levels of theory.

References:

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ASTM PROGRAM CHETAH 7.2
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ENERGY RELEASE EVALUATION

Compound Name : Molecule 1¹
 Formula : H2O2
 Molecular Weight : 34.015
 Amount : 1 Mole(s)
 Heat of Formation at 25 C : -32.530 kcal/mol

Plusive Hazard Classification Section

Plusive Hazard Classification:

Over-all Energy Release Potential is HIGH Value: -1.375

Contributing Details:

Criterion	Value	Units	Hazard Classification(#1)
Maximum heat of decomposition (#2)	-0.743	kcal/g	HIGH
Fuel Value - Heat of Decomposition	0.000	kcal/g	HIGH
Oxygen Balance(#3)	47.037	percent	HIGH
CHETAH ERE Criterion 4	46.934	kcal ² /mol	MEDIUM
Total Number of Peroxide Bonds	1.000		
Net Plusive Density(#4)	0.435		PLUSIVE

- Warning: These ratings only apply to hazards associated with strong mechanical shock. This does not imply the absence of other hazards.
- Notes: #1 This evaluation was developed to classify a composition as able or not able to decompose with violence, if subjected to the proper conditions. Information on the interpretation of the hazard classification criteria used by CHETAH may be found in the CHETAH documentation (ASTM publication DS-51A) and in J Chem Ed. v66, A137 (1989)
- #2 For decomposition products shown.
- #3 Experience has shown that the oxygen balance criterion is useful only for compounds composed of the elements C, H, N, and O.
- #4 Sum of auxoplosive and plosophoric weights per gram of mixture.

Decomposition Products (chosen to maximize heat of decomposition):

Moles	State	Species
0.500	ref-gas	O2 Oxygen
1.000	gas	H2O water

Heat of Combustion Section

Fuel Value (Net Heat of Combustion):

Mass Basis	Mole Basis
-0.743 kcal/g	-25.270 kcal/mol
-3.108 kJ/g	-105.730 kJ/mol
-1337.246 Btu/lb	

Combustion Products (Chosen for Fuel Value and Net Heat of Combustion):

Moles	State	Species
1.000	gas	H2O water

Groups Present in this Compound:-

Description	Count
H2O2 hydrogen peroxide	1

Figure2: Hazard evaluation and ranking for hydrogen peroxide using CHETAH 7.2

ASTM PROGRAM CHETAH 7.2
COMMITTEE E-27 CHEMICAL THERMODYNAMIC AND ENERGY APPRAISAL PROGRAM

PURE COMPOUND THERMOCHEMISTRY

Compound Name : Molecule 1¹
Formula : H2O2
Molecular Weight : 34.015

Standard State Pressure = 1 atm and Enthalpy Reference Temperature = 298.150K

T	Cp	S	gef	Ht-H298	delHF	delGF	logKf
K	cal/(mol-K)	cal/(mol-K)	cal/(mol-K)	kcal/mol	kcal/mol	kcal/mol	kcal/mol
298.15	10.309	55.660	55.660	0.000	-32.530	-25.225	18.490

Literature References

- 1 Stull, D.R., Westrum, E.F., and Sinke, G.C., "The Chemical Thermodynamics of Organic Compounds," John Wiley, New York, N.Y., 1969.
- 2 (a) Benson, S.W., "Thermochemical Kinetics", 1st ed., pp18-54, pp178-203, John Wiley, New York, N.Y., 1968
 (b) Benson, S.W., "Thermochemical Kinetics", 2nd ed., pp272-298, John Wiley, New York, N.Y.

Total Symmetry Number used in Calculations: 2

Number of Optical Isomers used in Calculations: 0

Warning: Default values for Symmetry Number and/or Optical isomers were used in the calculations. This can cause values for entropy and Gibb's free energy to be in error.

Contributing Details :-

Description	Count	S [cal/mol-K]	delHF [kcal/mol]
H2O2 hydrogen peroxide	1	55.660	-32.530

Notes about Data for this Compound:-

Number of optical isomers not given.. estimated or set = 0

Figure 3: Thermo-chemical data for hydrogen peroxide using CHETAH 7.2