



## Thermochemical stability: A comparison between experimental and predicted data



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### ABSTRACT

The first step to be performed during the development of a new industrial process should be the assessment of all hazards associated to the involved compounds. Particularly, the knowledge of all substances thermochemical parameters is a primary feature for such a hazard evaluation. CHETAH (CHEMical Thermodynamic And Hazard evaluation) is a prediction software suitable for calculating potential hazards of chemicals, mixtures or a single reaction that, using only the structure of the involved molecules and Benson's group contribution method, is able to calculate heats of formation, entropies, Gibbs free energies and reaction enthalpies. Because of its ability to predict the potential hazards of a material or mixture, CHETAH is part of the so-called "desktop methods" for early stage chemical safety analysis.

In this work, CHETAH software has been used to compile a complete risk database reporting heats of decomposition and Energy Release Potential (ERP) for 342 common use chemicals. These compounds have been gathered into classes depending on their functional groups and similarities in their thermal behavior. Calculated decomposition enthalpies for each of the compounds have also been compared with experimental data obtained with either thermoanalytic or calorimetric techniques (Differential Scanning Calorimeter – DSC – and Accelerating Rate Calorimeter – ARC).

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### 1. Introduction

Systematic search for hazards, risk assessment and identification of possible remedies are the basic steps of risk analysis (Stoessel, 2008). Chemical industry, more than any others, is perceived as a potential threat for mankind and environment. Nevertheless, all the benefits arising from its activities cannot be disregarded: drugs for human health, crop protection, new materials, colors, textiles and so on. One of the reasons contributing to this negative perception is the occurrence of major accidents, such as those ones which took place in Seveso and Bhopal, that, even if they are rare, unavoidably retain public attention. Therefore, in order to minimize and, if possible, eliminate such catastrophic events, a number of studies about the chemical risk associated to the thermal stability of compounds or reacting mixtures has been carried out throughout the last 35 years (Barontini, Cozzani, & Petarca, 2001; Cardillo, 2001; Cardillo & Cattaneo, 1991; Cardillo, Gigante, Lunghi,

Fraleoni Morgera, & Zanirato, 2008; Cardillo, Gigante, Lunghi, & Zanirato, 2010; Cardillo & Girelli, 1980; Copelli et al., 2011a, 2011b; Di Somma et al., 2010; Dien, Fierz, Stoessel, & Kille, 1994; Fayet, Rotureau, Joubert, & Adamo, 2011; Frurip et al., 1995; Lunghi et al., 2004; Maestri et al., 2009; Roduit et al., 2005; Sato & Sugawara, 1985; Sempere, Nomen, Serra, & Cardillo, 1997).

Chemical risk associated with thermally unstable materials or systems is sometimes predictable from both complete thermodynamic knowledge and correct interpretations of the fundamental laws of physical chemistry. The first step in the identification of thermal dangers consists in evaluating the thermodynamic potential of the system: that is, determining whether the reaction is thermodynamically favored and, subsequently, how much thermal energy releases. The amount of heat evolved can be related to the adiabatic temperature rise and, then, to the instability of reactants, products or reaction mass. Therefore, if it is possible to know or calculate in advance all the thermal effects of an undesired reaction, it is possible, at least as a first approximation, to predict the hazard.

Basing on these features, it is very important to possess suitable tools aimed to determine the thermodynamic potential associated to a chemical compound or a mixture with a quite high level of

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reliability. Particularly, such a fundamental property can be estimated both theoretically, through the use of dedicated evaluation software, and experimentally, performing suitable thermoanalytic and calorimetric tests.

Aim of this work has been the compilation of a complete chemical risk database, capable of constituting an easy tool to be consulted in order to obtain preliminary information about potential hazards associated with a certain compound that needs to be handling for a variety of reasons. Particularly, CHETAH software has been used to compile such a database by reporting heats of decomposition and Energy Release Potential (ERP) for 342 common use chemicals. These compounds have been gathered into classes depending on their functional groups and similarities in their thermal behavior.

In order to validate CHETAH theoretical predictions, calculated decomposition enthalpies for each of the compounds have been compared with experimental data obtained with either thermoanalytic or calorimetric techniques (Differential Scanning Calorimeter – DSC – and Accelerating Rate Calorimeter – ARC).

## 2. Software and laboratory instruments

### 2.1. CHETAH software

An important tool for the theoretical computation of chemical risk is CHETAH (CHEMical Thermodynamic And Hazard evaluation) software, that it was first presented in 1974 (Seaton, Freedman, & Treweek, 1974) and now it is commercialized by ASTM (Harrison, Madas, & Sharma, 2005).

Because of its ability to predict the hazards of a substance or a mixture only by the knowledge of the chemical structure, CHETAH is ideal for a preliminary assessment, performing various calculations such as: (1) estimation of reaction heats; (2) estimation of thermodynamic properties of individual substances; (3) prediction of the tendency of a compound or a mixture to propagate a deflagration or a detonation.

Heats of formation, entropies and free energies of the substances in question are calculated using the Benson's criterion (Benson, 1976).

The estimation of the hazard associated to a substance is formulated on the basis of four criteria.

The first criterion consists in the calculation of the maximum amount of energy released during a decomposition event (maximum heat of decomposition,  $\Delta\hat{H}_{\text{dec, max}}$ ). In order to perform such a calculation, the software assumes that, when a generic compound of formula  $C_xH_yO_zN_k$  decomposes, the obtained products are:  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{N}_2$ ,  $\text{CH}_4$ ,  $\text{C}$ ,  $\text{H}_2$  and  $\text{O}_2$ . Then, the software calculates the combination of these products that maximizes the heat of decomposition. As the sake of example, if the decomposition of pure water is considered, the set of products that maximizes the heat of decomposition (calculated basing on Benson's groups additive method) is:  $\text{H}_2$  and  $\text{O}_2$ . CHETAH considers the risk as low, medium or high depending on the value assumed by such a maximum heat of decomposition (see Table 1). In a similar way, that is assuming complete combustion ( $\text{CO}_2$  and  $\text{H}_2\text{O}$  as final products), the maximum heat of combustion,  $\Delta\hat{H}_{\text{comb, max}}$ , is evaluated.

**Table 1**  
First CHETAH criterion for chemical risk evaluation.

High level risk	$\Delta\hat{H}_{\text{dec, max}} < -0.7 \text{ kcal/g}$
Medium level risk	$-0.7 \text{ kcal/g} < \Delta\hat{H}_{\text{dec, max}} < -0.3 \text{ kcal/g}$
Low level risk	$\Delta\hat{H}_{\text{dec, max}} > -0.3 \text{ kcal/g}$

**Table 2**  
Third CHETAH criterion for chemical risk evaluation.

High level risk	$-80 < B_0 < 120$
Medium level risk	$120 < B_0 < 240$ $-160 < B_0 < -80$
Low level risk	$B_0 < 240$ $B_0 < -160$

The second criterion is based on the assumption that the most reactive substances almost always contain many oxygen atoms in their structure; with these materials the difference between the maximum heat of decomposition,  $\Delta\hat{H}_{\text{dec, max}}$ , and the maximum heat of combustion,  $\Delta\hat{H}_{\text{comb, max}}$ , at stoichiometric conditions is small. This means that almost all oxygen required for a complete combustion and/or decomposition is available directly into the analyzed molecule. Therefore, the second criterion is represented by the difference  $\Delta\hat{H}_{\text{comb, max}} - \Delta\hat{H}_{\text{dec, max}}$ . More such a difference tends to zero, the greater the risk is.

The third criterion is based on the concept of "oxygen balance" proposed by Lathrop and Handrix. For a molecule containing  $x$  carbon atoms,  $y$  oxygen atoms and  $z$  hydrogen atoms, the oxygen balance  $B_0$  is obtained by the following formula:

$$B_0 = \frac{1600(2x + y/2 - z)}{\text{PM}} \quad (1)$$

where PM is the molecular weight of the analyzed compound (kg/kmol).

In practice, the oxygen balance defines how much oxygen grams are required to completely oxidize 100 g of compound. More this index is close to zero (that is, all the oxygen required for the full oxidation is already present in the molecule), the more the risk is high (see Table 2). Nevertheless, oxygen balance must be critically assessed; as an example, two isomers with the same value of  $B_0$ , may be, the first, an explosive and, the second, a stable substance: peracetic acid  $\text{CH}_3\text{CO-O-OH}$  is an explosive while glycolic acid  $\text{HO-CH}_2\text{-COOH}$  is not. In fact, in the calculation of  $B_0$  are counted, without distinction, all the oxygen atoms regardless of the type of linkage in which they are involved. But, as it is well known, the explosive character depends largely on the nature of these links.

The fourth criterion is represented by the following equation:

$$Y = \frac{10 \times \Delta\hat{H}_{\text{dec, max}}^2 W}{n} \quad (2)$$

where  $W$  is the compound weight and  $n$  is the number of atoms in the molecule. Such a formula takes into account both the maximum decomposition enthalpy and the average molecular weight of an atom in the molecule. The square associated to  $\Delta\hat{H}_{\text{dec, max}}$  is merely empirical and it is used to magnify the value of the decomposition enthalpy (especially when it is close to (or major of) 1 kcal/g). Moreover, the higher the average molecular weight of a single compound atom is, the higher the decomposition risk of such a compound will be. The associated risk level is reported in Table 3.

Finally, CHETAH provides a risk value for each of the four criteria and a total risk value, the so-called Energy Release Potential (ERP) (Frurip et al., 1995; Treweek et al., 1978).

**Table 3**  
Forth CHETAH criterion for chemical risk evaluation.

High level risk	$Y > 110$
Medium level risk	$30 < Y < 110$
Low level risk	$Y < 30$

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