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It is a matter of considerable practical importance to recognize metastable, potentially hazardous chemical compositions so that suitable thermal hazard management means can be provided as a part of process safety management. This communication is a report on our evaluation of the oxygen balance criterion as a screening technique for thermal hazard assessment.

THE OXYGEN BALANCE

Numerous chemical compositions are subject to spontaneous self-reaction, i.e. reaction within themselves to yield more stable products. Some substances of this nature are stable in storage though capable of vigorous or explosive reaction if heated or otherwise disturbed. Commercial and military explosives, usually organic nitro compounds, are obvious examples of such compositions. Additional examples include other nitrates, many peroxy and diazo compounds, azides, nitrides, and fulminates, and many metastable compositions made up of oxidizing and reducing components that can be mixed or compounded without reaction.

Hazard assessment may be accomplished by heating, mechanical impact and explosive impact tests, by thermochemical and kinetic studies, and by other means. The oxygen balance test, widely used in explosives technology, is one of the simplest of such means.

Most explosives are metastable redox compositions. If the proportions of oxidant and fuel are such that all of the oxygen in the composition appears in the form of water and/or carbon dioxide in the reaction products, the composition is said to be "oxygen balanced", or simply "balanced". It is reasonable to look for correlations between oxygen balance and other characteristics of potentially hazardous compositions. As noted, most commercial and military explosives are organic nitro compounds or nitrate esters. In general such compounds are not exactly oxygen balanced. Glycerol trinitrate (nitroglycerin), is a (rare) example of an oxygen-rich explosive.

$$C_3H_5O_9N_3 \rightarrow 3CO_2 + \frac{5}{2} H_2O + \frac{3}{2} N_2 + \frac{1}{4} O_2 \qquad (1)$$

Most common explosives such as TNT, RDX, nitrocellulose, and others are oxygen-deficient for complete combustion. They are said to have negative oxygen balances. In contrast to single-compound explosives, most composite explosives such as nitroglycerin dynamites, modern ammonium nitrate explosives, and others can be and usually are blended for oxygen balance. In addition to the obvious efficiency and power advantages, balanced explosives produce benign explosion products "white shots" in contrast to the "black shots" (soot) of oxygen-poor compositions or the "red shots" (nitrogen oxides) of oxygen-rich compositions.

In a 1949 Chemical Reviews article, W. C Lothrop and G. R. Handrick [1] demonstrated quantitative correlations between oxygen balance and various measures of explosive effectiveness for several classes of organic explosives. This study drew upon the large data base accumulated during the years of World War II explosive research. The properties of more than 300 individual explosive compounds were considered and correlated. The authors provided a convenient formula for evaluating the oxygen balance of compositions containing the elements carbon, hydrogen, and oxygen.

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

Table 1 Oxygen Balance vs. Hazard Rank [*2*]

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

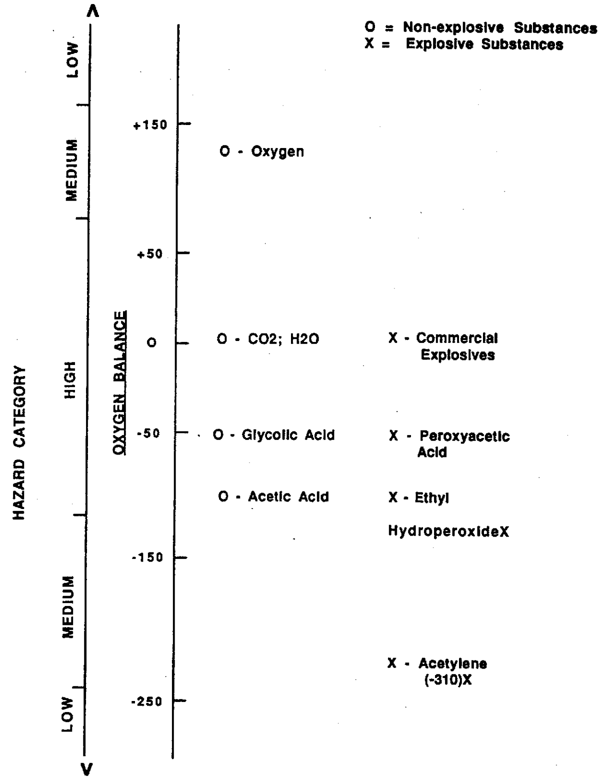

FIGURE 1. Oxygen-balance vs. hazard selected compositions.

Where X is the number of atoms of carbon, Y is the number of atoms of hydrogen, Z is the number of atoms of oxygen and M_w is the molecular weight. This formula produces a value of zero for perfectly oxygen-balanced compositions, negative values for oxygen-poor compositions and positive values for oxygen-rich compositions. For example, negative values produced by the formula represent 100 times the weight fraction of the original composition required in additional oxygen in order to achieve oxygen balance. The authors pointed out the utility of the oxygen balance criterion in evaluating the relative power of new explosive compositions, even in advance of synthesis.

It has been proposed more recently that oxygen balance, as calculated above, could serve as a general indicator of energy release hazard. The criteria listed in Table 1 have been suggested in reference [2], although we are aware of no published justification of these limits. We have tested this scheme by calculating oxygen balance values for a number of familiar compounds of known hazard potential. Our findings are summarized in Figure 1 and Table 2. As can be seen in Figure 1, oxygen balance values do not correlate well with the known hazard potential of the compounds included. The cases of carbon dioxide and water are especially instructive. Having oxygen balance values of zero, both are assigned "High" hazard rankings. This highlights the fact that oxygen balance bears no necessary relationship to hazard potential. In fact, most oxygen-balanced or near oxygen-balanced compositions are inert in respect to energy release potential. Relatively unusual compositions bearing a substantial proportion of weakly bonded oxygen (the "effective oxygen" of Lothrop and Handrick), together with an oxidizable moiety can be self-reactive and hazardous. Organic nitrates and nitro compounds represent one class of self-reactive and hazardous substances. This

Table 2 Hazard ranking by oxygen balance for specific compounds

Compound	O Balance	O Balance Hazard Rank	Observed Hazard Rank
Oxygen	100	Medium	None
Ozone	100	Medium	High
Hydrogen Peroxide 100%	47	High	Medium-High
Ammonium Nitrate	20	High	Low
Nitroglycerin	4	High	High
Carbon Dioxide	0	High	None
A.N. + HC Fuel	0	High	Medium
Water	0	High	None
Oxalic Acid	−18	High	None
Hydrazoic Acid	−19	High	High
Tetranitrotoluene	−47	High	High
Fulminic Acid	−56	High	High
Glycolic Acid	−63	High	None
Peroxyacetic Acid	−63	High	High
Trinitrotoluene	−74	High	High
Acetyl Peroxide	−95	High	High
Acetic Acid	−107	High	None
Ethyl Hydroperoxide	−107	High	High
Dinitrotoluene	−114	High	Medium
Diazomethane	−114	High	High
Nitrobenzoic Acid	−120	High-Medium	Low-Medium
Nitroaniline	−151	Medium	Low-Medium
Benzene Diazonium Cl.	−166	Medium	Medium
Mononitrotoluene	−181	Medium	None
Benzoyl Peroxide	−192	Medium	High
t-Butyl Peroxide	−252	Low	High
Ethylene	−286	Low	Medium
Benzene	−308	Low	None
Acetylene	−308	Low	High

class includes most commercial and military explosives and all compositions examined by Lothrop and Handrick. As previously noted, the oxygen balance parameter is a standard and valuable consideration in explosive technology provided that only the "effective" oxygen is included in the calculation.

Table 2 contains examples of additional anomalies. For example, the oxygen balance criterion, based only on empirical formulas, is necessarily blind to isomerism. Cyanates are ranked identically with fulminates. Inert glycolic acid is rated identially with isomeric, explosive peroxyacetic acid. Additional examples abound.

The oxygen balance scheme is not applicable to oxygen-free but hazardous compounds such as, for example, acetylene, acetylides, diazo compounds, explosive nitrides, azides, and other compounds. Although it should not be applied to such compounds, a literal use of the oxygen balance equation produces highly negative, non-hazardous rankings for all low-oxygen-content or oxygen-free compositions, regardless of their actual hazard potential.

As noted above, Lothrop and Handrick demonstrated a correlation between oxygen balance and explosive energy in the case of organic explosives. The practical hazard afforded by energetic compositions is also affected by the sensitivity to initiation. But, oxygen balance correlates very poorly with sensitivity. For example, ammonium nitrate, an extremely insensitive explosive, is more nearly oxygen-balanced than such extremely sensitive explosives as acetyl peroxide, ethyl hydroperoxide, or diazomethane. Nitrobenzoic acid and nitroaniline, though placed in the "medium" oxygen balance hazard category, have been shown to be insensitive to mechanical shock and powerful explosive initiators. In these and many additional cases we have found that oxygen balance provides no useful guidance regarding sensitivity to initiation.

CONCLUSION

In summary, oxygen balance is a standard and valuable concept in explosive and propellant technology. It is conceptually flawed and often dangerously misleading as a guide to energy release hazards in general. Stoichiometric considerations cannot resolve questions of energy release hazard potential. Thermochemical and kinetic considerations are required for such resolution.

LITERATURE CITED

1. **W. C. Lothrop and G. R. Handrick**, "The Relationship between Performance and Constitution of Pure Organic Explosive Compounds, *Chemical Reviews*, **44**, pp. 419–445, (1949).
2. **Davies et al.**, CHETAH 4.4 Reference Manual, The ASTM Chemical Thermodynamic and Energy Release Evaluation Program, 2nd Edition, ASTM DS 51A, ASTM, (1990).