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ESTIMATION OF CHEMICAL INCOMPATIBILITY (*OTHER-CHEMICAL REACTIVITY*) BY COMPUTER[1]

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Abstract. Two simple parameters—the National Academy of Science-National Research Council "Other Chemical" rating and a Lewis acid-base rating were combined in a linear discriminate model to predict the degree of hazard from binary mixtures as measured by Dow Chemical experimental tests. The observed error of 10% compares favorably with 40% error obtained using the NAS–NRC rating system. These results will be incorporated in the American Society for Testing and Materials computer program CHETAH (Chemical Thermodynamics and Energy Hazard Potential).

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The accidental mixing of industrial chemicals during transportation, storage or processing poses a potential energy hazard, defined in terms of both the relatively immediate release of heat and/or gas as a result of chemical incompatibility or "other chemical" reactivity and the potential formation of an explosive mixture that can subsequently be initiated by an appropriate stimulus (mechanical impact, thermal or physical shock). In some cases, the circumstances of an accident (collision, fire, etc.) causing the inadvertent mixing of some unusual combination of chemicals can also serve as the initiation stimulus for a violent deflagration or detonation of such a mixture.

Presently, there are about 1000 chemicals transported in bulk in the U.S. Many thousands more are transported in smaller quantities. Statistically, the number of combinations by which just 2 of the bulk-shipped chemicals might be accidentally mixed is beyond experimental evaluation. Chemical tankers, for instance, may contain thousands of kilograms of a half dozen or more different chemicals in relatively close proximity. Therefore, the astronomical number of unusual combinations that might accidently arise during a transportation mishap make some type of model or simplification highly desirable. Such a model might serve to reduce the potential hazard by identifying hazardous combinations, which can then be precluded by physical separation with relatively inert chemicals.

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Background

A review of the more common hazard rating systems (over 30 have been counted) resulted in the summary of reactivity definitions shown below.

REACTIVITY DEFINITIONS

USCG—(NAS–NRC)—**Other Chemical-Reactivity**
Based on possible reactivity with members of other grades

Water
Based on mixing with equal weight of water at ambient temperature

Self
Usually based on polymerization

Fire Hazard
Based mostly on flash points but noxious gas production or air/water spontaneous ignition considered

DOW—**Binary Mixture**
Based on temperature rise and gas evolution

NFPA—**Reactivity**
Based on shock sensitivity, reactivity with water

Flammability
Based on ignition temperature and tendency to form explosive dusts or mists

ASTM—**Hazard Potential**
Susceptibility to ignition or release of energy under varying environmental conditions

Detailed study of these systems reveals a marked difference in the definition of terms like "reactivity," a vast difference in the degree of subjectivity required to assign a given chemical to a particular hazard class, and in some cases, a lumping of more than one type of hazard into the same rating system to facilitate use by a particular group.

The diversity of these hazard rating systems relating to chemical compatibility is exemplified by the U. S. Coast Guard (National Academy of Science 1973, Department of Transportation 1975), which considers reactivity in 3 distinct rating systems:

Other chemical (see table 1)
Water and Compatibility of Chemicals (see table 2)

whereas NFPA (National Fire Protection Assoc. 1973) lumps many of the same considerations into its reactivity system:

Reactivity shock sensitivity, decomposition or polymerization, reaction with water (see table 3)

TABLE 2
Water (mixing with equal weight of water at ambient temperature).

GRADE	
0	No reaction.
1	Mild reaction.
2	Moderate reaction.
3	May be hazardous.
4	Vigorous—hazardous.

TABLE 3
NFPA Reactivity (shock sensitivity and water reactivity).

GRADE	
0	Stable and unreactive with water.
1	Unstable at high T and P or react slightly with water.
2	Unstable, capable of violent chemical change but not detonation or react violently with water.
3	Shock sensitive but require strong initiating source or high T and P, or react explosively with water.
4	Shock sensitive at normal T and P.

Addressing the chemical incompatibility or "other chemical" hazard exclusively, the Dow Chemical binary mixture rating system (Flynn 1970) developed under contract to the National Academy of Sciences Advisory Committee for the Coast Guard is very explicit about the criteria used to assign a chemical to a particular class (see table 4), whereas the NFPA and NAS–NRC systems use unquantified descriptors like very, normal, moderate, mild, and vigorous. To quantify the NAS–NRC "Other Chemical" system, a flow chart to assist in classifying an unknown was developed (figure 1). A computerized technique based on this flow chart would require a test for

TABLE 1
Other Chemical *Reactivity Hazard Rating System* (mixing results in overflow or rupture of tanks, ignition or evolution of noxious gases).*

GRADE		
0	UNREACTIVE EXCEPT WITH GRADE 4	Saturated hydrocarbons
1	MILDLY REACTIVE WITH GRADE 4	Aromatic and olefinic hydrocarbons
2	MAY REACT WITH GRADES 3 OR 4 ONLY	Alcohols, aldehydes, etc.
3	MAY REACT WITH GRADES 2, 3, OR 4	Organic acids, amines, etc.
4	MAY REACT WITH ALL OTHER GRADES	Conc. mineral acids and bases

*National Academy of Science-National Research Council (NAS 1973).

TABLE 4
Dow binary mixture (temperature rise and gas evolution).

HAZARD DEGREE	
1 NONE	ΔT max. <25 °C, no gas
2 LOW	ΔT max. 25–50 °C, no gas
3 MEDIUM	ΔT max 50–75 °C, no gas
4 HIGH	ΔT max >75 °C *or* gas evolution

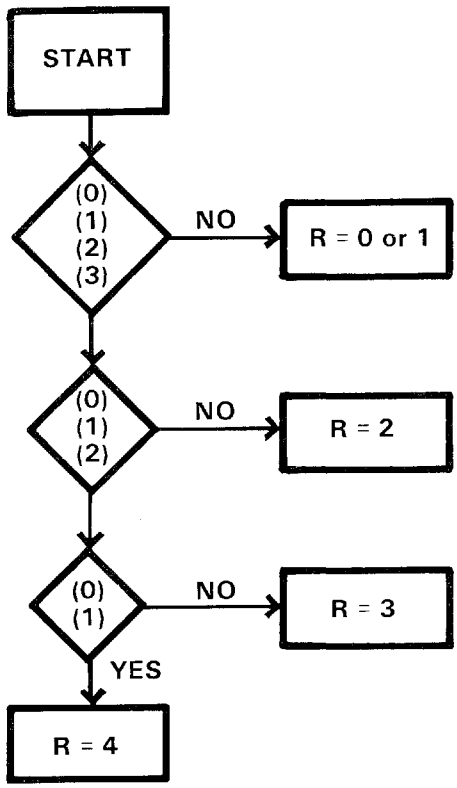


FIGURE 1. Flow chart to classify an unknown into the NAS–NRC **Other Chemical System.** (0), (1), means test for reaction with most reactive member of group 0, 1, etc. R—NAS other chemical hazard rating (NAS 1973).

reactivity with the most reactive member of each grade (0 through 4). Some of the grades contain a variety of types of chemicals; therefore, to account for the possible wide spectrum of reactivity the unknown might exhibit because of its own characteristics and because of those of the other reactant, the test with the most reactive member of each grade might conceivably also require testing with the most reactive member of each type of compound within each grade. Otherwise, the unknown might "fall through" the flow chart with no estimated reaction potential (*i.e.*, 0 grade) when in fact, one type of compound not tested might react quite vigorously with the unknown. For example, if ethylene chlorohydrin was the unknown (actual NAS–NRC "other chemical" grade of 2) and was tested with a representative Grade 3 chemical (*i.e.*, ammonia), no reaction potential would be observed (Flynn 1970) and the unknown would pass the Grade 3 test. This same unknown, however, has been observed experimentally by Dow to be highly reactive with another Grade 3 chemical, ethylene diamine (Δ T–194C, Δ P–13.5 psi, High Hazard) (Flynn 1970). Herein lies the problem in simplifying binary or other chemical reactivity using the NAS–NRC rating system.

The CG Guide to Compatibility of Chemicals (Circular No. NVIC 4–75) provides an ideal working document for field use, but the "GO/NO–GO" simplification that makes this guide so attractive for field use also makes it less suited for quantitative evaluation of a new model.

Thermodynamic parameters were found to have little or no power in predicting binary reaction tendency (Alexander *et al* 1975). Considering the low temperatures generally encountered, this finding is consistent with historical observations on the power of such calculations.

Although the Dow rating system appears to offer many advantages in terms of reference utility to a research study (Flynn 1970), several irreconcilable differences have been encountered as a result of Dow's noble efforts to reduce the amount of experimental data required. Specifically, Dow assigned 209 bulk-shipped chemicals to 59 groups, each with a designated representative working chemical. This reduced the amount of binary experimental data required from 21,736 to 1711.

Ethylene glycol was selected by Dow as the representative working chemical for the alcohols as shown in table 5. In Dow's experimental evaluation of this chemical with 73% nitric acid (another working chemical), no reactivity was observed, and thus no reactivity is predicted for any of the other alcohols of this group with nitric acid. Unpublished experimental data on similar 10 ml quantities of several other alcohols of the same Dow group as ethylene glycol, however, resulted in no reactivity in 3 cases (glycerin, tertiary butyl alcohol and iso-butyl alcohol) and very high, al-

TABLE 5

Comparison of binary mixture data with current ratings.

Binary Mixture	Battelle Experimental Data	NAS-NRC* Guide	DOW** Rating System	USCG*** NVIC 4-75
Nitric acid (70%)/ethylene glycol	N†	H	N	X
Nitric acid (70%)/glycerin	N	H	N	X
Nitric acid (70%)/butyl alcohol, tert-	N	H	N	X
Nitric acid (70%)/butyl alcohol, iso-	N	H	N	X
Nitric acid (70%)/butyl alcohol, sec-	H	H	N	X
Nitric acid (70%)/isopropyl alcohol	H	H	N	X
Nitric acid (70%)/cyclohexanol	H	H	N	X

*NAS 1973
**Flynn 1970.
***DOT 1975.
†N=no reaction, H=hazardous, and X=unsafe combination.

most hypergolic, reactivity for 3 others (secondary butyl alcohol, isopropyl alcohol and cyclohexanol). On this basis, transportation cost penalties may be imposed on safe combinations and, at the same time, potentially catastrophic combinations may be permitted. In fact, the current Coast Guard chemical compatibility guide (DOT 1975) has been observed to permit mixtures with detonation potential such as nitrobenzene/nitric acid (during WW I, nitrobenzene/nitrogen oxide mixtures were used in aircraft bombs) (Federoff 1962, Van Dolah 1969).

Procedure

Review of the National Academy of Science other chemical rating system (NAS 1973) and its limitations resulted in the generalization that additional information about the reaction tendency between the two particular chemicals might lead to greater accuracy. Specifically, the relative strength of the acidic (proton donating or electron pair accepting) plus basic (proton accepting or electron pair donating)—or Lewis characteristic of the reacting pair was established using a simple ranking similar to the National Academy of Science other chemical system. This ranking was based on known acid-base strengths, bond dissociation energies required to

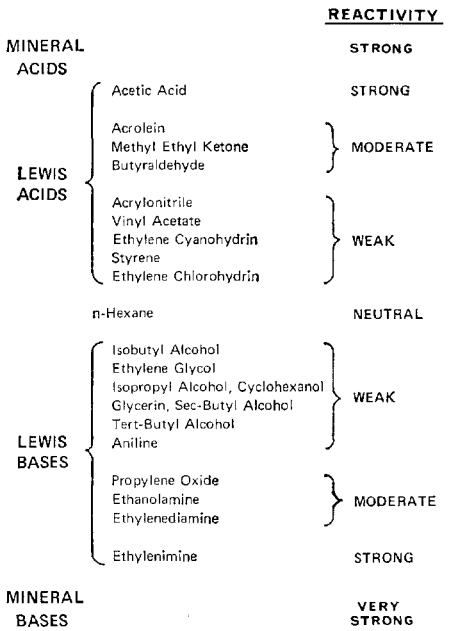
TABLE 6

Relative strength of Acid-Base Reaction Tendency.

GRADE	
0	Weak Lewis acid/weak Lewis base
1	Moderate Lewis acid/weak Lewis base Weak Lewis acid/moderate Lewis base
2	Moderate Lewis acid/moderate Lewis base
3	Strong Lewis acid/strong Lewis base Strong Lewis acid/mineral base Mineral acid/strong Lewis base
4	Mineral acid/mineral base

TABLE 7

Lewis Acid-Base Ratings for chemicals.



produce a proton or proton accepting species, etc.

To develop the acid-base reaction ranking, mineral acids reacting with mineral bases were placed at one end of the spectrum and weak Lewis acids or bases in the middle, as shown in table 6. Specific Lewis acid-base ratings for some of the chemicals considered are shown in table 7. It was noted that some of the chemicals in the center (with weak Lewis characteristics) were amphoteric; other known factors such as free radical parameters, non-polar solvent effects and ionic reaction parameters such as heats of solution, dynamic and static induction, resonance stabilization, hyperconjugation, double bond polarizability and ease of formation of carbonium ions should be considered in future research. Refinement of the Lewis acid-base ranking should also be considered (Drago 1973). We combined the Lewis reaction ranking mathematically with other published

TABLE 8

Vector Classification of Chemical Incompatibility (Flynn 1970) using National Academy of Science "Other Chemical" Hazard Ratings (NAS 1973) and Lewis Acid-Base Reaction Tendency (table 6).

	Experimental+		Pattern Recognition (estimated)		**Other Chemical** Hazard†	
	Degree	Class	Vector Class++	Error*	Estimated Class**	Error*
Ethylene Chlorohydrin/Ethylene Diamine	H	4	3	U	H	—
Vinyl Acetate/Ammonia, 28%	L	2	1	U	H	O
Aniline/Acrolein	M	3	2	U	H	O
Acetic Acid/Caustic Soda, 50%	H	4	4	—	H	—
Acrylonitrile/Ethanolamine	H	4	4	—	H	—
Styrene/Sulfuric Acid, 96%	H	4	4	—	H	—
Propylene Oxide/HCL, 35%	H	4	4	—	H	—
Ethanolamine/Acetic Acid	H	4	4	—	H	—
Acrylonitrile/Ethylenimine	L	2	2	—	H	O
Ethylene Chlorohydrin/Caustic Soda, 50%	H	4	4	—	H	O
Ethylene Diamine/Acrolein	H	4	4	—	H	—
Butyraldehyde/Ethylenediamine	M	3	3	—	H	O
Butyraldehyde/Ethanolamine	M	3	3	—	H	O
Aniline/Butyraldehyde	L	2	2	—	H	O
Ethylene Diamine/Methyl Ethyl Ketone	L	2	2	—	H	O
Ethylene Diamine/Ethylene Cyanohydrin	L	2	2	—	H	O
Acetic Acid/Aniline	N	1	1	—	H	O
Ethylene Chlorohydrin/Ethanolamine	N	1	1	—	H	O
Aniline/Ethylene Diamine	N	1	1	—	H	O
Ethylene Diamine/Ethanolamine	N	1	1	—	H	O
N-Hexane/Ethylene	N	1	1	—	N	—
N-Hexane/Acrylonitrile	N	1	1	—	N	—
N-Hexane/Styrene	N	1	1	—	N	—
N-Hexane/Acetic Acid	N	1	1	—	N	—
N-Hexane/Aniline	N	1	1	—	N	—
N-Hexane/Butryaldehyde	N	1	1	—	N	—
N-Hexane/Ethylenediamine	N	1	1	—	N	—
N-Hexane/Ethanolamine	N	1	1	—	N	—
N-Hexane/Propylene Oxide	N	1	1	—	N	—
N-Hexane/Ethylene Chlorohydrin	N	1	1	—	N	—
Totals				3(10%)		12(40%)

*U = underestimated, O = overestimated.
**H = hazardous, incompatible; N = non-hazardous, compatible.
+See table 4, Flynn (1970).
++See table 9.
†National Acad. Sci. (NAS, 1973).

chemical hazard ratings of the chemicals (NAS 1973) using a linear discriminant analysis approach of pattern recognition (Kowalski 1972).

FINDINGS

Chemical incompatibility was estimated using only two parameters—the NAS other chemical rating for each component of the mixture plus the Lewis acid-base rating—with about 10% error compared to 40% using the NAS hazard rating system alone (table 8). Since all binary mixtures with a Dow hazard class of 2 or more are considered unacceptable (DOT 1975), the performance of this model is better than 10% in terms of field use.

The linear discrimanant vector coefficients used to assign these binary mixtures with known chemical incompatibility hazards are given in table 9. These vectors take the form:

$$\text{VECTOR} = a_o + \sum_{i=1}^{NVR} a_i \text{VAR}_i$$

where: NVR = number of variables
a = coefficients published
VAR = variables in order listed.

In order to classify additional unknowns, one need only compute the sign of VECTOR; positive values lie on the lower class side of the vector and negative on the higher side of the vector consistent with DOT product conventions employed.

The substantial reduction in error compared with the best rating system available prompts inclusion of this new method into the ASTM computer program CHETAH (Seaton *et al* 1974). Further improvement of the model will be required to be consistent with this program's self-reactivity hazard predictions; however the many relevant reaction parameters not considered should further improve the demonstrated estimation capability for binary mixtures.

Acknowledgment. We would like to thank Ralph Wilson for his assistance with our computer work and Ann Bertagnolli for rearranging the tables.

TABLE 9

Linear discriminant vector coefficients to classify chemicals in table 8.*

	a_0	a_1	a_2	a_3
Vector for:				
Classes 1 and 2	2.6994E	−3.7935E	4.0874E	−5.3298E
Classes 1 and 2	1.0666E	−2.7525E	1.4428E	−7.1032E
Classes 2 and 3	6.0000E	−3.3333E	−1.3333E	−1.0000E
Classes 1 and 4	1.8688E	−1.8702E	−1.7661E	−6.7407E
Classes 2 and 4	3.5823E	−1.5190E	−5.8228E	−8.9114E
Classes 3 and 4	6.1048E	−8.0645E	−8.1452E	−9.1129E

$$\text{*Vector} = a_0 + \sum_{i=1}^{NVR} a_i \text{Var}_i$$

$\text{Var}_{1 \text{ or } 2}$ = National Academy of Science "Other Chemical" Reactivity Hazard Rating (NAS 1973) for each chemical and Var_3 = Relative strength of Acid–Base Reaction Tendency (see table 6).

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