ASSESSMENT OF REACTIVE CHEMICAL HAZARDS:
SOURCES OF INFORMATION

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Available literature sources of data and methods related to assessment of reactive chemical hazards are presented and discussed, with some speculation on possible future developments in this area.

INTRODUCTION

Many people responsible for the promotion of safety in industrial chemical operations have been concerned for a long time with the difficulty in locating information relevant to the hazards associated with using chemicals in industry. This concern has been expressed by the preparation and publication by many individuals and organisations of various guides to chemical safety. The many and varied forms of these guides will be detailed later, but it will now suffice to note that most of them have related to the reactive chemicals, perhaps a couple of hundred or so, which are of commercial significance, and which have found relatively widespread use, in the process industries.

As an organic chemist working in industrial research and development laboratories, I became concerned some years ago with the extreme difficulty of finding information on the possible reaction hazards associated with the use of various research chemicals not yet in widespread use and not therefore covered in the organised safety literature. The latter includes reference books, review articles and the like where original published material has been subjected to information processing and is presented collectively in a form which stresses safety aspects and is readily usable by the practising technologist.

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During work to compile a comprehensive collection of information on reactive chemical hazards, many references related to the assessment of such hazards were uncovered. It occurred to me that a suitable presentation of some of the more significant of the references might form a useful survey of, and introduction to, some aspects of assessment of reactive chemical process hazards, particularly for the benefit of the newcomer to the chemical process safety field.

The first part of the presentation describes sources of basic information on properties of materials and the use of these in a laboratory context. The second and main part covers ways in which this laboratory information has been applied to the assessment and finally the prediction of chemical hazards associated with pilot-plant and larger scale processing operations.

Information sources have been grouped on the basis of the type of information presented therein, with what are considered to be the most generally useful placed first under each heading. Those marked with an asterisk would together provide a general 'chemical hazards' nucleus for a technical chemical library.

SOURCES OF BASIC AND LABORATORY DATA

Basic Materials Data

Review of thermochemical/ thermodynamic data sources:	Dannhauser (1973)
Tabulated physical data:	*Perry (1973) *Material Factors (1966-7) (1000 materials) Sax (1968)
Chemical data sheets:	M.C.A. series S.D. 1-99 (1947 to date) (99 materials) N.S.C. series 1-604 (1952 to date) (101 materials)
Gas data:	*Braker and Mossmann (1971) (130) B.D.H. Chart (1973) (116)

Data Sources Related to Flammability

Flammability limits:	Zabetakis (1965 a, b)
Flash Points:	B.D.H. (1962) (1500)
(by trade name)	N.F.P.A. 325A (1972) (8,800)

Autoignition temperatures:	Hilado and Clark (1972) (300 organics)
Tabulated data on above 3 aspects:	*N.F.P.A. 325M (1969) (1300) Stephenson (1972) (1121) Material Factors (1966-7) (1000) F.P.A. 24 (1972) (350)
Dusts:	*Palmer (1973) Dorsett and Nagy (1968) Hartmann (1948)
Review of ignition by impact:	Powell (1969)

Data Sources Related to R and D Laboratory Operations

Comprehensive works:	M.C.A. Guide (1972) Steere (1971) Fawcett and Wood (1965)
Safety manuals:	*Quam (1963) *Muir (1971) (poisoning treatment) *Imperial College (1971) (reactive hazards) Everett (1969) (illustrations) Steere et al (1969-70) Schuerch (1972)
Reactive hazards:	*Bretherick (in press, 1974) (5000 single materials and combinations) N.F.P.A. 491M (1971) (2350 single materials and combinations) Steele and Duggan (1959) (structures of single unstable compounds)
Waste disposal:	*Stephenson (1972) (1100 materials tabulated) B.D.H. Chart (1970) (wall chart, 370 materials) Voegelein (1966) (corroded cylinders)
Chemicals in Fires:	*N.F.P.A. 49 (1973) (388 materials) Bahme (1972) Meidl (1972)

The publications listed above, and particularly those grouped under 'Reactive hazards' will provide information upon chemical materials which have been described as hazardous, either because of their instability, or of their violent interactions when brought into contact either deliberately or accidentally with other materials.

However, it is probably more important to be able to predict future reactive hazards than to recognize existing ones, and it is to this aspect that attention is now turned.

HAZARD ASSESSMENT AND PREDICTION

Publications Related to Process Scale-Up

Process safety analysis:	M.C.A. SG-14 (1962) Smith (1965)
Information transfer:	Perciful and Edwards (1967)
Hazardous materials:	Graf (1967)
Plant design considerations:	Pratt (1965) Hudson (1967) Manchester Symposia (1960-71)
Pre-startup checklists:	Marinak (1967)
Pilot Plant Manual:	*P.P.M. (1972) updates and consolidates above U.S. material.
Disposal:	Deviny (1967) Novak (1972) A.P.I. Manual (1969)

Process Hazard Evaluation and Prediction

Qualitative estimation from unit process or material used:	Shabica (1963)
from chemical structure:	Tomlinson and Audrieth (1950) Bretherick (in press, 1974)
from whole-process view:	Spiegelman (1969)
Preliminary hazard screening:	Albisser and Silver (1960) (simple thermal tests) Prugh (1967) (DTA tests) Silver (1967) (DTA and other tests) Wankel (1967) (10 tests)

Evaluation of explosive materials:	Van Dolah (1961) (energy estimates plus sensitivity tests) Clancey (1971a and b) (available tests discussed)
Whole process evaluation:	* Dow Manual (1966). Now republished in amended form as a CEP Technical Manual, 'Safety and Loss Prevention Guide; Hazard Classification and Protection', AIChE, (1973) * Material Factors (1966-7)
Prediction of energy hazard potential:	Davis and Ake (1973) (computation) only) Treweek et al (1973)
Prediction of real chemical hazards:	Stull (1971, 1973) (computation)
Prediction and assessment of chemical instability:	Coffee (1969, 1971, 1973) (computation, thermal and impact stability tests)
Prediction of flash points:	Prugh (1973)
Prediction of flammability characteristics:	Shimy (1970) Hilado (1970)

This section of the review is very wide in character, covering several published techniques. These range from simple assessment of published data or laboratory test results, with or without the addition of computation techniques to these assessments, through fully quantitative arithmetical assessment of reactivity and equipment hazards existing in a particular plant (or design for a plant), finally extending to computer prediction of potential or real hazards in a particular reaction system. Just how far along this progression of techniques one should go in any particular case will be dictated largely by economic considerations tempered by commonsense and overall safety considerations. It would be, currently, just as unthinkable for a chemist planning a one-off laboratory preparation to apply the full quantitative treatment as it would be for a chemical engineering team planning a pilot or full-scale production plant not to do so.

The whole-process evaluation method introduced in the Dow Process Safety Manual (1966) is particularly valuable in that it separately quantifies all aspects of reactivity hazards and physical plant features, finally producing a numerically significant Plant Hazard Rating. This separate quantification allows potentially hazardous points in existing or projected installations to be recognised and either modified or catered for in physical protective measures and operating procedures.

It has however, been known that plant modifications introduced for the sake of operational convenience during and subsequent to commissioning have sometimes not taken into account the full safety implications of the change. For this reason, any modifications should have management approval.

The purely computational technique of Davis and Ake (1973) and Treweek et al (1973) successfully differentiated between shock-sensitive and shock-insensitive compounds, in fairly good agreement with experimental observations for ranges of 30 to 218 compounds. Since their techniques would also be applicable to criteria other than shock-sensitivity, it should also be of use as a routine method of evaluating compounds for other aspects of their chemical energy hazard potential.

The methods developed by Stull (1971-3) combine computerised assessment of hazard potential from thermodynamic and thermochemical data, with calculation of kinetic behaviour to predict the likely (or "real") chemical hazard, expressible as a Reaction Hazard Index for a particular compound or mixture. In practice, good correlation was found between the RHI and the (subjective) NFPA numerical reactivity ratings established for 80 materials in common industrial use.

The assessment procedure developed by Coffee (1969-73) involves initial computation of maximum possible energy release for a compound or reaction mixture. Materials showing a potential energy release exceeding 2.9 MJ/Kg (0.7 kcal/g) are subsequently subjected to impact sensitivity testing and thermal analysis procedures. Combination of the results from these 3 separate procedures enables a compound or mixture to be rated on a scale (of increasing hazard) of 1-8. Further specific tests and detailed examination will then be required for highly rated materials to permit detailed assessment of processing and plant limitations and requirements.

Methods of predicting flash points and flammability characteristics are somewhat limited in precision and types of compound covered.

<u>General Safety Data Sources</u>

Sources which may yield data in related areas or on specific topics include the following:

Plant Design Considerations:	Yelland (1966)
Bibliographies etc:	Fawcett (1965) Vervalin (1972) C.I.A. List (1973) M.C.A. List (1973)

Collected Papers:	Loss Prevention (1967-1973) Manchester Symposia (1960-1971) Major Loss Prevention (1971) Combustion Institute Symposia 1 - 14 + European (1928-1973)
Selected Abstracts:	A.B.C.M. Summaries (1930-1964) B.C.I.S.C. Summaries (1965 to date) M.C.A. Case Histories (1950 to date) C.I.S. Cards. Publication as separate cards was discontinued in 1973, but subject matter continues to be available in C.I.S. Abstracts Bulletin. A new computerised index-searching service has become available covering the C.I.S. material

THE PRESENT POSITION AND FUTURE POSSIBILITIES

The 80-odd references which have been assembled in this review on assessment of chemical process hazards collectively contain a great deal of relevant information, but the majority is qualitative data.

The overall future aim in this area of technology will undoubtedly be to provide better and more quantitative evaluation and prediction mechanisms. This will involve application of existing hazard-test procedures more widely and development of improved and new assessment methods, both for preliminary screening and in-plant purposes.

Better ways of classifying and presenting basic data will be essential, and in this context the use of a computer-based system for the analysis and handling of nuclear safety information was described by Buchanan and Hutton (1968). To handle the needs of the chemical process industries adequately, involvement of chemical structure in the classification system seems inevitable. In U.S.A. a computer-based information system (covering toxicity and related data for 60,000 compounds) has recently become generally accessible (Chem. Eng. News, 1974, 52 (4), 22-3). Access to a particular compound may be via alternative nomenclatures, C.A.S. registry number, molecular formula or the structure - related Wisswesser Line Notation.

Better ways of subsequently using the increasingly available data to produce meaningful quantitative assessments and predictions will also undoubtedly involve computer-based procedures. As the more highly developed testing and data-processing procedures become more readily available, they will be applied with greater frequency to hazard-assessment problems, and at a lower economic threshold on the processing size-scale.

Parallel with these technical developments, there will be improved training (and, hopefully, career prospects) in this important specialisation, both in industrial and academic circles. The establishment in 1972 of a Chair of Industrial Safety at Aston under Professor Atherley, and of Professor Burgoyne in 1973 at City University, may be seen as further milestones on the long road upon which we all travel hopefully, towards satisfactory methods of predicting and controlling or eliminating the hazards associated with modern chemical process operations.

The following quotation from a chapter peering into the future of chemical safety by Christian (1960) may be of general interest·

"With knowledge, a safety vaccine could be designed. Given to new employees, and older employees as needed, it could induce a desirable level of safety awareness and performance through increased conscious thought flow and altertness, just as methedrine is used intravenously as a modern psychiatric technique. Environmental tempering, such as addition of gases to air conditioning, might be an effective technique."

Personally, I feel that eternal vigilance is likely to be a more suitable price to pay for chemical process safety than sending our older employees on "air-conditioned trips" as foreseen by Christian.

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European Sources of Information Related to Chemical Hazards

Allgemeine Unfallversicherungsanstalt - Unfallverhutungsdienst
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Outline of forthcoming book

'Handbook of reactive chemical hazards'
L. Bretherick (Butterworths, 1974)

The Handbook is designed to provide chemists and students with a condensed guide to available information on chemical materials which are known to be hazardous because of their instability, or their violent interactions when brought into contact either deliberately or accidentally with other materials.

All information of this type available up to July 1973 has been scanned, evaluated, condensed, and presented in a form which permits the ready retrieval and understanding of information relevant to some 1700 single elements or compounds, 3100 dual combinations, and 220 combinations of three or more materials. Over 3400 references to published data and 120 private communications are included. Information is presented in one of two ways, depending on its type.

Information specific to an individual element or compound is indexed in the main section of the Handbook on the basis of the conventionally expressed empirical molecular formula corresponding to the compound, names in accordance with IUPAC recommendations.

General information upon groups of compounds possessing common features of structure of potentially hazardous reactivity is indexed alphabetically under a suitably descriptive group name, of which there are some 200.

An unusually comprehensive system of cross-references (4000) relates each individual element or compound to its group name and, conversely, each of the latter to all the materials which comprise that group.

Collectively, these features are intended to facilitate decisions on the likely hazards which may be associated with materials or combinations of materials which have not been previously described.

Future Information

Further information on reactive chemical hazards is now being sought for a supplementary volume for publication in 1976-7.

If you or your colleagues have, or become aware of, information relevant to this topic, please send it to:

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Sources of all items included will be acknowledged on publication.