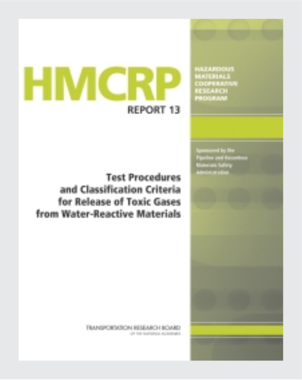

Test Procedures and Classification Criteria for Release of Toxic Gases from Water-Reactive Materials

DETAILS

72 pages | 8.5 x 11 | PAPERBACK
ISBN 978-0-309-30799-4 | DOI 10.17226/22276

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HAZARDOUS MATERIALS COOPERATIVE RESEARCH PROGRAM

HMCRP REPORT 13

Test Procedures and Classification Criteria for Release of Toxic Gases from Water-Reactive Materials

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Research sponsored by the Pipeline and Hazardous Materials Safety Administration

TRANSPORTATION RESEARCH BOARD
WASHINGTON, D.C.
2014
www.TRB.org

HAZARDOUS MATERIALS COOPERATIVE RESEARCH PROGRAM

The safety, security, and environmental concerns associated with transportation of hazardous materials are growing in number and complexity. Hazardous materials are substances that are flammable, explosive, or toxic or that, if released, produce effects that would threaten human safety, health, the environment, or property. Hazardous materials are moved throughout the country by all modes of freight transportation, including ships, trucks, trains, airplanes, and pipelines.

The private sector and a diverse mix of government agencies at all levels are responsible for controlling the transport of hazardous materials and for ensuring that hazardous cargoes move without incident. This shared goal has spurred the creation of several venues for organizations with related interests to work together in preventing and responding to hazardous materials incidents. The freight transportation and chemical industries; government regulatory and enforcement agencies at the federal and state levels; and local emergency planners and responders routinely share information, resources, and expertise. Nevertheless, there has been a long-standing gap in the system for conducting hazardous materials safety and security research. Industry organizations and government agencies have their own research programs to support their mission needs. Collaborative research to address shared problems takes place occasionally, but mostly occurs on an ad hoc basis.

Acknowledging this gap in 2004, the U.S. DOT Office of Hazardous Materials Safety, the Federal Motor Carrier Safety Administration, the Federal Railroad Administration, and the U.S. Coast Guard pooled their resources for a study. Under the auspices of the Transportation Research Board (TRB), the National Research Council of the National Academies appointed a committee to examine the feasibility of creating a cooperative research program for hazardous materials transportation, similar in concept to the National Cooperative Highway Research Program (NCHRP) and the Transit Cooperative Research Program (TCRP). The committee concluded, in *TRB Special Report 283: Cooperative Research for Hazardous Materials Transportation: Defining the Need, Converging on Solutions,* that the need for cooperative research in this field is significant and growing, and the committee recommended establishing an ongoing program of cooperative research. In 2005, based in part on the findings of that report, the Safe, Accountable, Flexible, Efficient Transportation Equity Act: A Legacy for Users (SAFETEA-LU) authorized the Pipeline and Hazardous Materials Safety Administration (PHMSA) to contract with the National Academy of Sciences to conduct the Hazardous Materials Cooperative Research Program (HMCRP). The HMCRP is intended to complement other U.S. DOT research programs as a stakeholder-driven, problem-solving program, researching real-world, day-to-day operational issues with near- to mid-term time frames.

HMCRP REPORT 13

Project HM-14
ISSN 2150-4849
ISBN: 978-0-309-30799-4
Library of Congress Control Number 2014948976

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HAZARDOUS MATERIALS COOPERATIVE RESEARCH PROGRAM

are available from:

Transportation Research Board
Business Office
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Washington, DC 20001

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Printed in the United States of America

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The research reported herein was performed under HMCRP Project HM-14 via a collaboration between ScienceSmith Consulting, Inc., Alliance Technologies, LLC, and Labelmaster Services, Inc.

Gregory M. Smith, PhD, Managing Principal at ScienceSmith Consulting, Inc., served as principal investigator and project lead. The other authors of this report are Jonathan Chun, PhD, Director of Technology, and Anatoly Nemzer, Director of Operations, both of Alliance Technologies, LLC, and Bob Richard, Vice President, Regulatory Affairs, Labelmaster Services, Inc.

Most of the experimental work reported in this research report was carried out by William Poinsett of Alliance Technologies, LLC.

FOREWORD

By Edward T. Harrigan
Staff Officer
Transportation Research Board

This report presents a proposed improved procedure for measuring the rate of gas production when a water-reactive material evolving either a flammable gas or a toxic gas is combined with water.

Water-reactive materials, which are defined in international regulations as substances that, in contact with water, release flammable gases, are assigned to USDOT Hazard Class 4.3. The gases released may also be toxic. For instance, silicon tetrachloride, when in contact with water, releases hydrogen chloride. However, the present test procedures and classification criteria for Hazard Class 4.3 do not take into account (1) water reactions that may lead to the release of toxic gases, (2) the quantity of water-reactive substances being shipped, or (3) the potential effect of water salinity on release of toxic gases.

The objective of HMCRP Project HM-14 was to develop a test procedure and classification criteria for water-reactive materials that take account of the potential release of toxic gases during transport. The research was performed by ScienceSmith Consulting, Inc., Englishtown, New Jersey, with support from Alliance Technologies, LLC, Monmouth Junction, New Jersey, and Labelmaster Services, Inc., Chicago, Illinois.

The initial phase of the research was a critical review of the worldwide literature on water-reactive materials test procedures, test results for various water-reactive materials, and potential flammable and toxic reaction products. Then testing variables that should be specified as part of the testing procedures and shortcomings in present procedures were identified. Based on these results, a laboratory program was carried out to develop and validate a precise, reliable test procedure and classification criteria. The procedure presented in the report is capable of determining the rate at which flammable gas or toxic gas is produced when a substance is combined with water, under laboratory conditions, in a closed vessel, by monitoring the change in pressure as a function of time after the substance and water are mixed.

This report fully documents the research and includes the following Appendixes:

- Appendix A: Full Technical Test Description
- Appendix B: Proposed Classification System
- Appendix C: ASTM Format Test Procedure

CONTENTS

Note: Many of the photographs, figures, and tables in this report have been converted from color to grayscale for printing. The electronic version of the report (posted on the Web at www.trb.org) retains the color versions.

SUMMARY

Test Procedures and Classification Criteria for Release of Toxic Gases from Water-Reactive Materials

This final research report for HMCRP Project HM-14 relates the development of a new test method for measuring the rate of gas production when a water-reactive substance evolving either a flammable gas or a toxic gas is combined with water.

The report includes the following:

- Overview reporting of the background, research approach, and findings for HMCRP Project HM-14 (Chapters 1 through 4).
- Comprehensive technical reporting on an apparatus and experimental validation work demonstrating the test, as well as a documenting example and experimental validation outcomes from testing (within Appendix A).
- A proposed system for classification of water-reactive substances (Appendix B).
- A concise, generalized protocol for the test (in American Society for Testing and Materials [ASTM] format, within Appendix C).

Test N.5 in Section 33.4 of the United Nations' (UNs') *Recommendations on the Transport of Dangerous Goods: Manual of Tests and Criteria*, 5th revised edition (*1*), is applicable to current substances of Division 4.3 within the framework of *Recommendations on the Transport of Dangerous Goods: Model Regulations* (*2*), which in contact with water evolve flammable gas. Test N.5 is used to establish whether a substance should be classified in Division 4.3, and, if so, which of three possible packing groups applies. In its present form, the text provides only very general guidance for conducting the test ("The tap of the dropping funnel is opened to let the water into the conical flask and a stop watch is started. The volume of gas is measured by any suitable means."). The new test, described herein, provides a more comprehensive specification for the test procedure and expands testing to also accommodate materials that in contact with water evolve toxic gas.

The test described herein stipulates (1) an apparatus meeting particular performance criteria and (2) a test procedure that employs that apparatus. The performance criteria require the apparatus to be

- Gas tight
- Safe to operate
- Able to accommodate the combination of test substance/material and water, with either substance/material added to water, or the reverse
- Able to accommodate both solid and liquid test substances/materials
- Capable of accurate monitoring of pressure as gas is produced within the apparatus
- Able to accommodate calibration of a pressure/volume (P/V) response as gas is added to the apparatus
- Capable of operation with an inert atmosphere.

Table S-1. Validation testing results.

Material	Approach	Result (l/kg-min)	Standard Deviation (l/kg-min)	Relative Standard Deviation	UN Number
$(CH_3)_2SiCl_2$	B	36	8	22%	1162
$NaNH_2$	A	9600	2000	20%	1390
$NaBH_4$	A	2 (120 l/kg-h)	0.5 (30 l/kg-h)	25%	1426
CH_3COCl	B	665	60	9%	1717
$AlCl_3$	A	7500	1700	23%	1726
$POCl_3$	A, B	1–3000 (& up)	n/a	n/a	1810
$SiCl_4$	A	1020	210	20%	1818
$SOCl_2$	B	370	110	30%	1836
$TiCl_4$	A	5500	900	16%	1838
Mg_3N_2	A	7900	1800	23%	3132

A = Substance added to water, B = water added to substance

The test procedure using this apparatus then encompasses the following (general) steps:

- Charging the apparatus with water (or test substance, depending on specific test outcomes).
- Checking the P/V calibration and response.
- Charging with the test substance (or water, depending upon specific test outcomes) and combining the test substance and water within the apparatus.
- Accurate and precise measurement of the pressure produced as the reaction proceeds.
- Conversion of the pressure-versus-time results to a specific rate of gas production (liters of gas per kg of substance reacting per hour or per minute).
- Replicating testing to obtain five results that are averaged to find the outcome used for classification.

In addition to defining an improved test, this report includes extensive experimental test validation work. This work includes a comprehensive description of a specific, working apparatus that meets the specific performance criteria stipulated for the test. Although the test does not explicitly dictate an exact configuration for the test apparatus, thereby allowing users to find the best combination of performance and equipment for their particular facilities, the apparatus defined here provides a concrete example of a working apparatus that users may duplicate, should they choose to do so. As noted above, full details of the apparatus and experimental work on test method validation done with it can be found in Appendix A. An ASTM format procedure is also included in Appendix C.

Results from the experimental work on test validation with several model compounds are tabulated in Table S-1.

CHAPTER 1

Background

United Nations (UN) *Model Regulations* (*2*) currently encompasses substances that in contact with water emit flammable gas. As early as 1994, during the course of developing the Globally Harmonized System of Classification and Labeling of Chemicals (GHS), it was noted that there were other regulatory systems that covered substances that in contact with water emit toxic gas (this, and much of the historical information in the next few paragraphs, is drawn from the Organisation for Economic Co-operation and Development's [OECD's] "Detailed Review Document on Classification in OECD Member Countries of Substances and Mixtures which in Contact with Water Release Toxic Gases") (*3*).

During development of the GHS, the OECD played a leadership role in the development of criteria for health hazards and was asked to lead in the development of criteria for substances that on contact with water emit toxic gas. In doing so, the OECD reviewed existing national regulatory frameworks, including the following:

- The Canadian Workplace Hazardous Materials Information System (WHMIS);
- Annex III of European Union Directive 67/548/EEC: Nature of special risks attributed to dangerous substances and preparations; and
- The U.S. DOT Hazardous Materials Regulations (HMR).

The earliest OECD proposal (*4*) regarding classification and labeling of substances that on contact with water emit toxic gas included both gas evolution rate and gas toxicity criteria in the discussion, relying upon Test N.5 from Section 33.4 of the *Manual of Tests and Criteria* (*1*) for gas evolution rate measurements. However, the classification criteria proposed in that document omitted consideration of the rate of gas production.

When these criteria were presented to UN experts, there was concern that the OECD proposals did not address the rate of evolution of toxic gases (*5*). It was also recognized that international model regulations for the transport of dangerous goods did not address materials that emit toxic gases when exposed to water. This led to discussion of the only existing test for the rate of evolution of gases from water-reactive substances, Test N.5 from Section 33.4 of the UN's *Manual of Tests and Criteria*, used to classify substances that are regulated in transport on the basis of their reaction with water and their evolution of flammable gases.

Eventually discussion focused on the test itself, regarding (1) how to adapt it to substances that in contact with water emit nonflammable toxic gas (as opposed to substances that in contact with water emit flammable gas) and (2) how to improve the reproducibility of the test. To help address these issues, HMCRP undertook additional work on this topic.

CHAPTER 2

Research Approach

The research approach for HMCRP Project HM-14 included two phases: Phase I: Test Survey and Planning and Phase II: Method Development. The tasks assigned to each phase are provided below. Phase I included the following:

- Task 1 (Test Survey)
  - A review of the literature on water-reactive materials that give off toxic gases and of procedures used by test laboratories worldwide.
  - Outreach to experts at laboratories engaged in this type of chemical evaluation; chemical manufacturers known to produce water-reactive substances; and to industry associations such as the International Council of Chemical Associations, the American Chemistry Council, and the Dangerous Goods Advisory Council. This outreach specifically included the German Federal Institute for Materials Research and Testing (BAM) as well as the French National Institute for Industrial Environment and Risks (INERIS).
  - Consideration of testing variables such as water introduction rate, particle size, sample size, techniques used to measure gas evolution, and test duration to identify important variables.
  - Development of draft classification criteria for water-reactive materials evolving toxic gases.
  - Preparation of a preliminary list of materials that should be considered for regulation as water-reactive substances evolving toxic gas, identifying the toxic gases that are given off, and providing an estimate of the toxic gas release rate.
  - Briefing of the UN Subcommittee of Experts on the Transport of Dangerous Goods (SCETDG) personnel on status and plans for this project.
- Task 2 (Test Plan Development)
  - Using the recommendations from Task 1, development of plans to explore ways to modify, improve, and standardize existing test methods.
- Task 3 (Interim Reporting)
  - Reporting on (1) the critical review of the worldwide literature on water-reactive material testing; (2) the preliminary list of water-reactive materials and the toxic gases given off when these materials are exposed to water, and (3) a revised work plan incorporating the outcome of Task 2 for review with the HMCRP Project HM-14 Panel.

Phase II included the following:

- Task 4 (Test Development)
  - Execution of the work plan developed in Task 2, including extensive experimentation to develop a workable approach and validate it. The bulk of the work within HMCRP Project HM-14 took place as part of this task.
- Task 5 (Classification System)
  - Creation of a classification system for water-reactive materials based on the test procedures developed in Task 4 and a knowledge of the rate and toxicity of evolved gases. This classification system was used as part of the formal implementation plan in Task 6.
- Task 6 (Implementation Plan)
  - Creation of a plan to potentially implement and standardize new test procedures for water-reactive materials, including a list of substances that should be considered for classification as substances that evolve toxic gases.
- Task 7 (Final Reporting)
  - Final report preparation, documenting results, summarizing findings and conclusions, and including proposed test procedures (in draft ASTM format) and proposed classification criteria.

The single largest task within HMCRP Project HM-14 was Task 4, which encompassed both experimental work to develop the test and then experimental work to validate the test. Outcomes from Tasks 1 through 3 have largely been reported to HMCRP personnel and other stakeholders as interim status and information reports from the project principal investigator. The outcome from the work to develop an approach (as part of Task 4) is embodied in the test procedure and the example experimental apparatus reported on here. The balance of the work under Task 4 includes the experimental validation work, which is reported within Appendix A. This report embodies Task 7.

CHAPTER 3

Findings and Applications

The principal outcome from this research is a complete, detailed, and reproducible test method for measurement of the rate at which gas is produced when a water-reactive substance is combined with water under controlled conditions in the laboratory. This is the "revised test procedure applicable to substances that evolve both toxic and flammable gases" called for in Task 4 of HMCRP Project HM-14. In developing this "improved test methodology," a test has been produced that can encompass substances that produce toxic gas as well as substances that produce flammable gas; furthermore, this test is clearly defined and specified in ways that should enable reproducible, cross-laboratory implementation.

A complete description of the test, test apparatus, and testing results can be found in Appendix A. In brief, the test method developed and described herein determines the rate at which flammable gas or toxic gas is produced when a substance is combined with water, under laboratory conditions, in a closed vessel, by monitoring the change in pressure as a function of time after the substance and water are mixed. Pressure changes are converted to changes in volume by applying a calibration relationship relating change in pressure within the apparatus to amounts of gas (as measured at ambient laboratory conditions) added to the vessel. The test procedure, by default, considers the addition of the test substance to an excess of water. However, when conditions dictate—for instance, if observation of gas production is prevented by absorption of gas by water present in the apparatus—there are provisions for reversing the order of addition.

A specific apparatus is described in Appendix A, but the apparatus may vary from the apparatus described there. Whatever the specifics of the apparatus, however, it must meet the following criteria:

- Be gas tight and capable of safely withstanding internal pressures of at least 50 kPa gauge.
- Allow for the safe combination of water with a water-reactive substance. Provisions for this must include, but are not limited to, pressure relief of the apparatus at a pressure above 50 kPa gauge yet safely below a pressure at which the vessel might rupture; appropriate personal protective equipment for laboratory personnel; and an appropriate laboratory workspace to house the apparatus including fume hoods, proper hazard communication procedures for laboratory personnel, and supervision and operation by qualified personnel.
- Accommodate addition of the substance to water as well as, when required, the reverse order of addition.
- Be capable of use with both solid and liquid substances.
- Include accurate and precise monitoring of pressure as a function of time during testing, preferably using electronic data logging at intervals as short as 2 seconds, with a pressure resolution greater than 0.1 kPa.
- Accommodate calibration of the response of pressure to the volume of gas added to or produced within the apparatus to provide for conversion from observed pressure increases within the apparatus to volume of (as measured at ambient conditions of temperature and pressure) gas added to or produced within the apparatus (this may, for instance, be accomplished via the addition of known aliquots of gas at ambient pressure).
- Allow, when the reactivity of the test substance warrants, for testing to occur under an inert atmosphere.

The procedure (again, in summary) then encompasses the following steps:

- The apparatus is charged with water, or for some substances (determined by test), with the test substance.
- The pressure/volume (P/V) response and calibration of the apparatus is checked.
- The apparatus is then charged with the test substance (or for some substances—water—as determined by test), and test substance and water are combined.
- The pressure produced as any reaction proceeds is measured precisely and accurately as a function of time.

Table 3-1. Validation testing results.

Material	Approach	Result (l/kg-min)	Standard Deviation (l/kg-min)	Relative Standard Deviation	UN Number
$(CH_3)_2SiCl_2$	B	36	8	22%	1162
$NaNH_2$	A	9600	2000	20%	1390
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$POCl_3$	A, B	1–3000 (& up)	n/a	n/a	1810
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$SOCl_2$	B	370	110	30%	1836
$TiCl_4$	A	5500	900	16%	1838
Mg_3N_2	A	7900	1800	23%	3132

A = Substance added to water, B = water added to substance

- The pressure-versus-time results are converted to a specific rate of gas production (liters of gas per kg of substance reacting per hour or per minute) utilizing the pressure/volume response calibration.
- The testing steps listed above, except for the P/V calibration, are repeated to obtain a total of five results, which are then averaged to find final results and sample standard deviation.
- Specifics of the results are then evaluated. The results may be reported as is, unless there is evidence that water present in the flask is masking gas evolution and/or that observed gas evolution merely reflects evaporation of the test substance. If that is the case, then repeat the procedure with the apparatus first charged with test substance, and then aliquots of water added to it, and report those results. Note that, in this latter case, the specific rate of gas evolution will be based upon an estimate of the amount of the substance present that *might* (according to chemical principles) have reacted with the water added. It is not, in that case, based on the total amount of test substance present.

In order to validate the test (i.e., to establish reproducibility and precision of the test within a single laboratory) and to test the method with a range of representative materials, a series of substances were characterized. The results are shown in Table 3-1.

The tasks for HMCRP Project HM-14 called for several other deliverables to be included in this report; these deliverables, along with some other supplementary material, can be found in Appendices A through C. A listing of Appendices A through C and the HMCRP Project HM-14 tasks they fulfill is provided in Table 3-2.

Table 3-2. Appendices A through C.

Deliverable	Task	Appendix
Full Technical Test Description	Task 7	Appendix A
Proposed Classification System	Tasks 5 & 7	Appendix B
ASTM Format Test Procedure	Task 7	Appendix C

CHAPTER 4

Conclusions and Suggested Research

This report records the development and successful validation of a new procedure for measuring the rate of gas production when a water-reactive substance evolving either a flammable gas or a toxic gas is combined with water.

The test is fully defined, is reproducible, and should be suitable for uniform implementation across multiple laboratories. The test relies upon a simple and easily calibrated method for measuring the gas produced (change in pressure within a closed vessel) and takes into account the possibility that some gases may dissolve in water during testing.

Any next steps or further work primarily relates to interlab testing of the method to establish that comparable results can be achieved in independent laboratories. To the extent desired by stakeholders, testing of candidate materials for classification may also be commissioned.

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Abbreviations, Acronyms, and Initialisms

ANL	Argonne National Laboratory
BAM	German Federal Institute for Materials Research and Testing
DI	Deionized (water)
GHS	Globally Harmonized System of Classification and Labeling of Chemicals Program
HMR	Hazardous Materials Regulations
INERIS	French National Institute for Industrial Environment and Risks
OECD	Organisation for Economic Co-operation and Development
PPE	Personal Protective Equipment
P/V	Pressure/Volume
RSD	Relative Standard Deviation
SBH	Sodium Borohydride
SCEGHS	Subcommittee of Experts on the Globally Harmonized System of Classification and Labelling of Chemicals
SCETDG	Subcommittee of Experts on the Transport of Dangerous Goods
UN	United Nations
WHMIS	Canadian Workplace Hazardous Materials Information System

APPENDIX A

Full Technical Test Description

This appendix provides a complete technical description of the test, along with experimental results from validation testing.

Introduction and Generalized Procedure

This section of Appendix A introduces the test and provides a concise, generalized protocol for it. For specifics and details of the test as developed and practiced for the HM-14 project, refer to subsequent sections of this report appendix.

Purpose of the Test

The test procedure given here is intended for use in assessing the *relative* hazards of substances that emit flammable or toxic gases on contact with water by measuring the rate at which the substance produces gas when combined with water.

Apparatus

A block diagram for an apparatus recommended for this test is shown in Figure A-1.

Alternative apparatus may be used. However, regardless of the apparatus used, it should meet the performance criteria outlined here. The apparatus should

1. Be gas tight and capable of safely withstanding internal pressures of at least 50 kPa gauge.
2. Allow for the safe combination of water with a water-reactive substance; provisions for this must include, but are not limited to, pressure relief of the apparatus at a pressure above 50 kPa gauge yet safely below a pressure at which the vessel might rupture. There should also be appropriate personal protective equipment for laboratory personnel and an appropriate laboratory workspace to house the apparatus including fume hoods, proper hazard communication procedures for laboratory personnel, and supervision and operation by qualified personnel.
3. Accommodate addition of the substance to water as well as, when required, the reverse order of addition.
4. Be capable of use with both solid and liquid substances.
5. Include accurate and precise monitoring of pressure as a function of time during testing, preferably using electronic data logging at intervals as short as 2 seconds, with a pressure resolution greater than 0.1 kPa.
6. Accommodate calibration of the response of pressure to the volume of gas added to or produced within the apparatus to provide for conversion from observed pressure increases with the apparatus to volume of (as measured at ambient conditions of temperature and pressure) gas added to or produced within the apparatus (this may, for instance, be accomplished via the addition of known aliquots of gas at ambient pressure).
7. Allow, when the reactivity of the test substance warrants, for testing to occur under an inert atmosphere.

Generalized Procedure

The test method can be applied to solid and liquid substances. In case a pyrophoric or air sensitive substance is tested, the test should be conducted under an inert atmosphere.

When solids are being evaluated, the substance should be inspected for any particles of less than 500 μm diameter. If that powder constitutes more than 1% (mass) of the total, or if the substance is friable, then the whole of the sample should be ground to a powder before testing.

Charge the apparatus with water. Water should be ISO 3696 (1987) grade 2 or better; in cases where it is judged likely that saltwater (3.5% USP grade NaCl in ISO 3696 (1987) grade 2 or better water) will result in a greater rate of gas production, then saltwater should be used. The mass of water should be measured, and the total volume of water should not occupy more than ~ 2.5% of the internal volume of the apparatus.

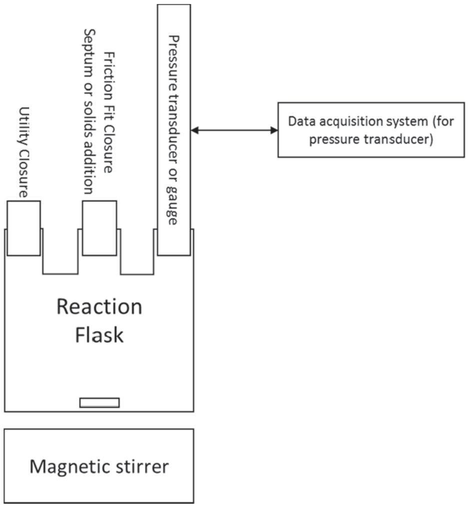

Figure A-1. Block diagram of the recommended apparatus.

For instance, 10.0 g (10.0 ml) could be used in an apparatus with internal volume of 400 ml. Note that if the flammable or toxic gas produced on contact with water is known to have appreciable solubility in water, the amount of water should be reduced to ~0.5% of the internal volume of the apparatus.

If the substance under test is a solid, add it to the apparatus, but in a way that does not yet put it in contact with the liquid water in the apparatus. If the substance under test is a liquid, proceed directly to the next paragraph. Use an amount of test substance chosen so that complete reaction with water, via the reaction expected according to established chemical knowledge or else established in separate testing, would create an amount of gas with a volume of ~ ⅓ of the internal volume of the apparatus.

Close the apparatus and check, or, if not previously measured, measure the apparatus P/V calibration (see item [6] under the apparatus specification).

Equilibrate the apparatus pressure with ambient pressure.

Combine the test substance with the water in the apparatus. In the case of liquid substances, this can be accomplished by adding the test substance directly to the apparatus in a manner that brings it into immediate contact with the water, with good mixing, while maintaining the gas-tight integrity of the apparatus. For a solid substance, operate the apparatus so that the test substance that was inserted as described above is rapidly mixed with the water while maintaining the gas-tight integrity of the apparatus. In the case of liquid substances, use an amount of test substance chosen so that complete reaction with water, according to the reaction expected according to established chemical knowledge, or else established in separate testing, would create an amount of gas with a volume of ~ ⅓ of the internal volume of the apparatus.

Monitor the pressure (and, therefore, volume of gas produced) within the apparatus as a function of time (see item [2] under the apparatus specification). Continue monitoring until a steady state is observed.

If the change in pressure is too low for accurate measurement, repeat the test using a carefully increased amount of substance; exercise care to not exceed the apparatus capacity. If necessary, continue to repeat the test using carefully increased amounts of substance, until a readily and accurately measurable response is observed. An ideal result would be an increase in pressure of from 10 to 25 kPa. Once a satisfactory response is achieved, conduct 4 additional replicate runs to obtain a total of 5 measurements.

For each of the 5 measurements made, find the period of time during the reaction that shows the greatest rate of pressure increase (gas production). This may be as short as the interval between consecutive data points (2 seconds) or a few data points. In this case, convert the observed change in pressure to a net change in volume; this divided by the elapsed time constitutes the raw gas production rate (volume/time; e.g., liters/min or liters/hour). Alternatively, it may be a longer duration over which a nearly linear increase in pressure with time occurs. In this case, convert the rate of pressure increase represented by the slope of a line fitted to the data in that period of time to a rate of gas production, which then constitutes the raw gas production rate (volume/time; e.g., liters/min or liters/hour).

Normalize the raw gas production rate for each measurement to the amount of substance used, to obtain a specific gas evolution rate (volume/(time∗mass); e.g., liters/kg-min or liters/kg-hour). Combine the 5 specific gas evolution rate measurements to obtain an average of the observed specific gas evolution rates, and the sample standard deviation. These form the nominal specific gas evolution rate and precision estimate.

Particularly in the case of liquid test substances, consider whether the observed gas production is due to reaction with water or to evaporation of the material or substance under test. This should be assessed by a qualified chemist, taking into consideration the observed yield of gas vs. the yield expected (low yields of gas may reflect evaporation) and the magnitude of the change in pressure (small changes, comparable to the vapor pressure of the test substance, may reflect evaporation). If the observed gas production may credibly be due simply to evaporation of the test substance, then the measurement should be repeated using a reversed order of addition. For all substances, the possibility that gas evolution has been masked (fully or to some extent) by absorption of gas by excess water in the apparatus should also be considered. If this credibly may be occurring, then the measurement should be repeated using a reversed order of addition. If a low amount of gas is formed relative to the quantity expected, absorption by water may be an issue.

For the reversed order of addition, an amount of water chosen such that complete reaction via the reaction expected according to established chemical knowledge or else established in separate testing, would create an amount of gas with a volume of ~ ⅓ of the internal volume of the apparatus should be added to an excess of the substance under test. The amount of substance under test should not occupy more than 2.5% of the internal volume of the apparatus, and often an amount in the range of 0.5% to 1% of the internal volume of the apparatus will be sufficient. When normalizing the raw gas production rate to a specific production rate, use an amount of test substance in the denominator that corresponds to the amount of test substance predicted by chemical knowledge to be consumed in a complete reaction with the amount of water used. Generally, a comparison of the specific gas evolution rates and overall gas yields from the two orders of addition will make it clear which observation best represents gas production from the reaction between the test substance and water. For instance:

1. If the addition of the substance to water yields an increase in pressure similar to what would be expected solely from the vapor pressure of the substance and the amount of gas produced is low in comparison to what is expected, while the addition of water to the substance produces an amount of gas close to what is expected with a pressure increase greater than the vapor pressure of water, then the latter result should be used.
2. If the addition of the substance to water yields an increase in pressure in excess of what would be expected solely from the vapor pressure of the substance, the amount of gas produced is similar to what is expected, and the specific rate of gas production is greater than for the addition of water to substance, then the former result should form the basis of classification in *Recommendations on the Transport of Dangerous Goods: Manual of Tests and Criteria*, 5th revised edition.
3. For intermediate cases, the judgment of a qualified, independent chemist should be used to determine which result best represents the rate of gas production from reaction with water.

Precautions

Important Safety Point This test is intended to measure the evolution of gas when *reactive* materials are combined with water. Some of these materials may react violently with water, and many may need to be handled under dry, inert atmosphere prior to their careful reaction with water in order to preserve their integrity and to preclude the possibility of hazardous reactions. Furthermore, some of these materials may (by definition) produce toxic gases when combined with water.

Important Safety Point These materials should be handled by trained, qualified personnel with experience in handling water reactive and/or air-sensitive materials using appropriate laboratory facilities and proper personal protective equipment (PPE). Laboratory facilities should include properly designed and operating fume hoods in addition to other facilities and equipment that may be required. Typical PPE will include flame-retardant laboratory coats (preferably using intrinsically flame-retardant materials, such as Nomex® fabric), safety glasses, face shields, chemically resistant gloves, and other equipment as needed. There are several texts and other resources on the topics of laboratory safety and the handing of air-sensitive materials that should be consulted prior to work.[1]

Important Safety Point This test should be carried out under the supervision of a qualified, experienced chemist who is thoroughly familiar with the materials being handled, their reactivity, and water and air sensitive materials in general. Finally, this report appendix should be read in its entirety prior to attempting any testing.

Example Test Apparatus

A block diagram of an experimental apparatus meeting the requirements set forth in the generalized proposed test procedure above is shown in Figure A-2.

The reaction flask is a heavy walled glass reactor with a total internal volume of ~ 400–450 cc. A typical vendor diagram of such a flask is shown in Figure A-3.

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[1] Information provided here comprises suggestions; personnel on hand, carrying out the experiments, are responsible for taking all needed precautions. Resources on air-free and air-sensitive techniques include:

(a) *CRC Handbook of Laboratory Safety, 5th Ed.* Furr, A. K. (2000).
(b) *Handbook of Chemical Health and Safety*, Alaimo, R. J. Ed. (2001).
(c) *Identifying and Evaluating Hazards in Research Laboratories*, American Chemical Society (2013); available online (as of 2013.09.30) at: http://cen.acs.org/content/dam/cen/static/pdfs/ACSHazardAnalysis20130904.pdf.
(d) University of California online Laboratory Safety Fundamentals training program, available (as of 2013.09.30) at: http://info.ucanr.org/safety/lab/story.html.
(e) *The Manipulation of Air-Sensitive Compounds*, 2nd Edition; Duward F. Shriver; M. A. Drezdzon (1986).
(f) *Synthesis of Organometallic Compounds: A Practical Guide* Komiya, S. (1997).
(g) Sigma-Aldrich Technical Bulletin AL-134 *Handling Air-Sensitive Reagents.* Available online (as of 2013.09.30) at http://www.sigmaaldrich.com/etc/medialib/docs/Aldrich/Bulletin/al_techbull_al134.Par.0001.File.tmp/al_techbull_al134.pdf .
(h) Guidelines for Handling Air-Sensitive Compounds; Gill, GB; Whiting, DA, *Aldrichimica Acta*, 1986, *19(2)*, 31–41. Available online (as of 2013.09.30) at: http://wolfweb.unr.edu/~wchalifoux/PDFs/handlingairsensitivereagents.pdf.
(i) *Safe Laboratory Practices: Working with Air-Sensitive or Highly Reactive Compounds*, Stanford University, 2/13/09, rev 10/15/10—OHS Report#:09-016a, available online (as of 2013.09.30) at: http://www.stanford.edu/dept/EHS/prod/documents/09-016.pdf.
(j) Aluminum Alkyls—Safe Handling, Heck, WB; Johnson, RL *Ind. Eng. Chem.*, 1962, 54 (12), pp. 35–38, DOI: 10.1021/ie50636a007.

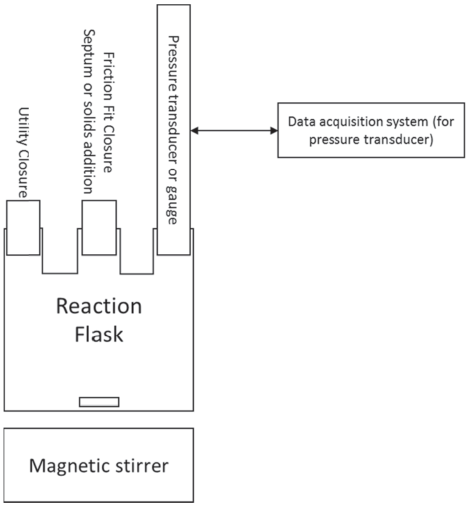

Figure A-2. Block diagram of the recommended apparatus.

Assembled, the apparatus appears as shown in Figures A-4, A-5, and A-6.

The pictured apparatus, along with a selection of gas-tight and disposable syringes, a laboratory balance, a nitrogen purged glove-bag (or, alternatively, a glove-box), a properly installed and functioning fume hood, access to reagents and distilled or deionized water, and an appropriate selection of PPE are all that is required for this test.

Detailed Procedure

Overview

The flow chart shown in Figure A-7 provides an overview of the procedure. Subsequent text and flow charts provide explanation and additional information. "Water" refers to distilled or de-ionized (DI) water, unless otherwise noted (e.g., in tests that intentionally use saltwater containing 3.5% NaCl by weight).

The first issue to consider is whether the identity of gases that might be evolved is known. Generally, this should be the case. Triethylaluminum, for instance (UN 3394; Organometallic substance, liquid, pyrophoric, water-reactive; Division 4.2), is known to produce ethane (or, ethylene, if excess heating occurs) gas on contact with water. Substances like this that produce gases, such as hydrogen or hydrocarbons, with limited solubility in water can usually be tested using Approach (A) (see Figure A-7), with excess water present and without undue concern for absorption of gas into the water influencing the result. Still, care should be taken to either limit the volume of water present to a modest amount (i.e., < 10 g, or < 2.5% of apparatus volume) or to account for its possible impact on the P/V calibration (by conducting the P/V calibration with water present, see below); this limitation is reflected in the proposed next text for Test N.5.

$TiCl_4$ (UN 1838), as another example, is known to produce HCl (g) on contact with water; likewise, anhydrous $AlCl_3$ (UN 1726) can produce HCl (g) in contact with water. HCl (g)

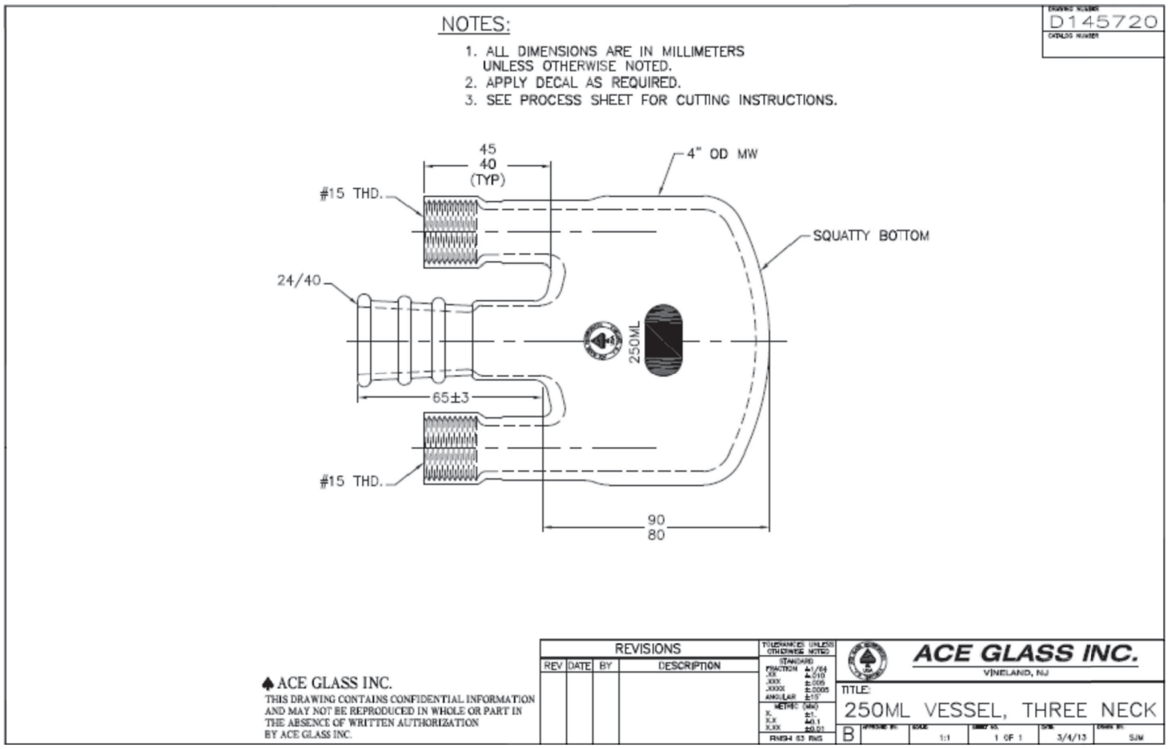

Figure A-3. Vendor drawing of reaction vessel.

Figure A-4. Complete reaction apparatus with analog gauge and timer for manual data acquisition (**far left*****), with pressure transducer (*****center left*****) as configured for use with liquids, with solids addition tube in place (*****center right*****) for use with solids, and with solids addition tube after addition of solids (*****far right*****).***

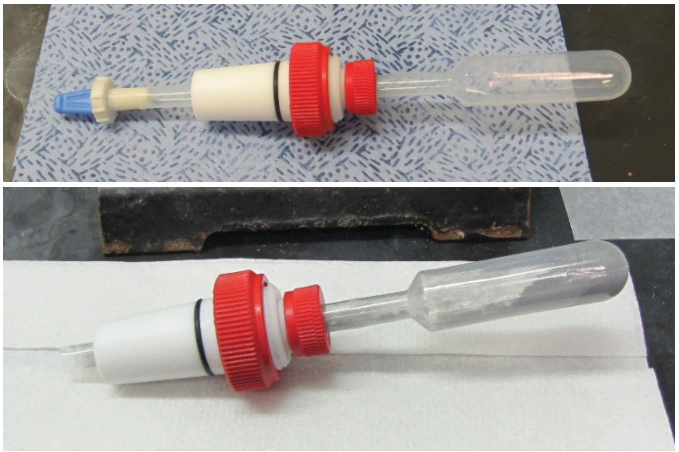

Figure A-5. Detail of solids addition tube assembly empty (**top*****) and after charging (*****bottom*****) with a water reactive (but not air sensitive) solid.***

Figure A-6. Detail of liquid addition/septum closure fitting with septum installed (not visible). Note that this is a friction fit closure of the vessel.

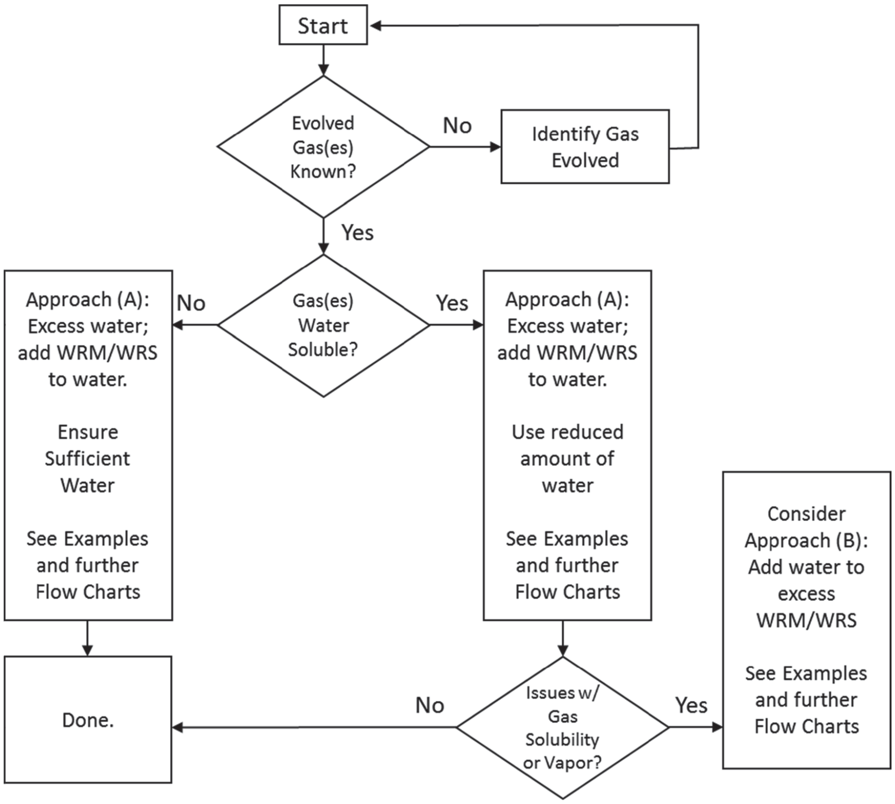

Figure A-7. Flow chart for testing.

is very soluble in water and, as a result, the presence of excess water in the apparatus can mask the formation of gas. For this reason, extra care is needed in work with this type of material. Fortunately, experience shows that in many cases these materials can still be tested using Approach (A), adding the water-reactive materials to water. In this case, however, the amount of water should be kept to a practical minimum.

In some cases, however, work with Approach (A) may make it apparent that it may be desirable to use Approach (B) (see Figure A-7), in which limiting amounts of water are added to the water-reactive materials under test. This approach is discussed further, below.

In all cases, in addition to knowing the identity and properties of gases that may form, it will also be necessary to have at least some idea of the expected *amount* of gas likely to form. If a low amount of gas is formed relative to the quantity expected, absorption by water may be an issue.

With that information in mind, it is possible to turn to the specifics of the testing by either approach, in the sections that follow.

Approach (A)

Approach (A) can be used when absorption of evolved gas by water either will not be an issue or is a manageable issue (as demonstrated by the test). When absorption of evolved gas by the water present becomes a problem, Approach (B) should be used. Note that, particularly when the test material or substance is relatively volatile, Approach (A) may appear to be measuring gas evolution when, in fact, the gas being measured is simply vapor from evaporation of the test material or substance. Personnel conducting the test should be alert to this possibility; if this is the case, Approach (B) should be used.

Specifics of Approach (A) will vary slightly, depending upon whether a solid or a liquid material/substance is being tested (see Figure A-8).

As noted in Figure A-8, assemble the clean and dry apparatus components (as shown in Figures A-2 and A-4) using either a septum closure or a solids addition tube in the center opening of the flask and either a threaded plug or threaded septum adapter in one of the threaded ports (depending upon the type of material under test). When using the solids addition tube, calibration should first be conducted with the empty tube in place, after which the tube should be charged with the required amount of water-reactive material/water-reactive substance. Note that in Figure A-8, within the right-hand branch, where the apparatus is charged with both water and water-reactive material/water-reactive substance, they are kept separate; the water-reactive material/water-reactive substance is kept within the solids addition tube, and the water is charged to

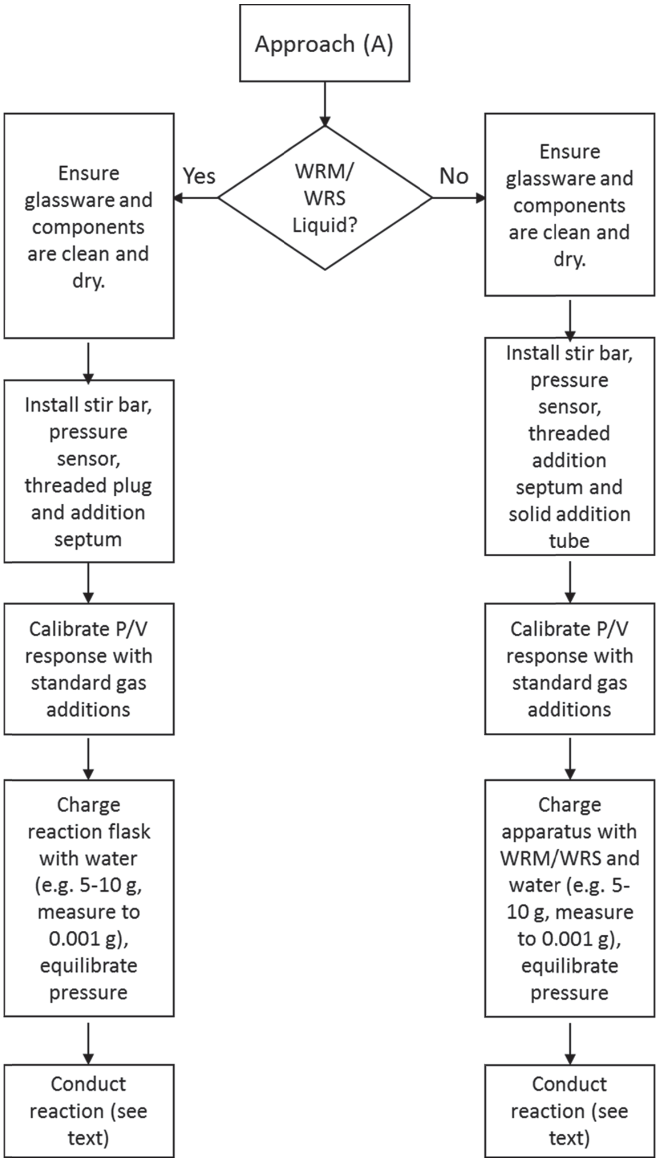

Figure A-8. Flow chart for Approach (A), adding solid or liquid water reactive material/substance to water. Note that, for amounts of water in excess of 10 g, water should be added prior to the P/V calibration check, so that the calibration reflects the free gas-volume in the apparatus, with water present.

the reaction flask. Further, note that in the case of air sensitive and/or highly reactive materials, the solids addition tube may need to be charged under an inert atmosphere. This can be done in a glove box, if available (and necessary), or in a simple nitrogen purged glove bag, with the choice being made by a competent chemist familiar with the materials in question and the safe handling of air-sensitive materials. The weight of the charged solids addition apparatus should be recorded prior to installing it into the apparatus. At the end of the reaction, the empty apparatus will be re-weighed to determine the actual amount combined with water in the test.

The P/V calibration is an important step. This is easily done by using a volume-calibrated syringe[2] to add known volumes of gas under laboratory conditions. The gas should be chosen to match that in use for the experiment (i.e., air or an inert gas such as nitrogen). On commissioning, each flask and associated fittings, assembled as for use, should be characterized by sequential addition of 4 aliquots of 50 cc of gas at ambient conditions. This is readily accomplished with a syringe and via the septum fittings. Figures A-9 and A-10 show a typical calibration exercise.

Note that the result of 4.27 cc/kPa suggests a total internal volume for the apparatus (with that particular flask and configuration) of ~ 430 cc, as an internal pressure of 101 kPa gauge (1 atm gauge) would indicate that a volume of gas equal to the internal volume of the apparatus had been added.

As indicated in Figure A-8, a check of the P/V calibration should be included with each test run. This can be done with the addition of just two aliquots of gas (as illustrated in Figure A-10).

Important Safety Point

At this point, it is worth noting that the apparatus shown in Figures A-2 and A-4 is intended to contain gas as it is produced and therefore will become pressurized (as shown, for instance, in Figure A-9) during testing. *For this reason, estimating the maximum amount of gas that can be produced and scaling of the reaction so that it is within the capacity of the apparatus are part of the protocol* (see below). Figure A-9 illustrates that pressures of at least 40–50 kPa gauge can be tolerated by the apparatus, corresponding to produced volumes of gas of ~ 200 cc. Pressure relief for the apparatus is provided by the friction fit of the septum closure (see Figure A-6) or the friction fit of the solids addition tube (see Figure A-5). If the pressure exceeds ~ 50 kPa, this friction fit closure will yield, venting the apparatus. Experience shows that the closure will vent in the 40–50 kPa gauge pressure range and at somewhat lower pressures if left standing for long periods or not firmly installed. Venting is not violent and occurs with a soft (but definite) "pop" as the closure is expelled. The closure is expelled with enough force to reach the hood ceiling, but the rebound is gentle and is comparable to dropping the closure from a height of a few feet. Users commissioning new apparatus should verify both tolerance of the planned pressures and successful relief performance.

Although the research team's experience has been good, and the few occasions where venting occurred posed no problems, a portable blast shield is employed for initial testing of a new material, until its behavior is well established. During all testing, and particularly during initial screening, all appropriate PPE (such as, but not limited to, lab coats, face shields, and gloves) is employed.

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[2] It is easy to calibrate or verify the volume graduations on a syringe by using DI water, a NIST (or equivalent) traceably calibrated balance, and a NIST (or equivalent) traceably calibrated thermometer, along with standard reference values for the density of water. In our hands, we found that the existing graduations on commercial syringes were accurate to ± 1%.

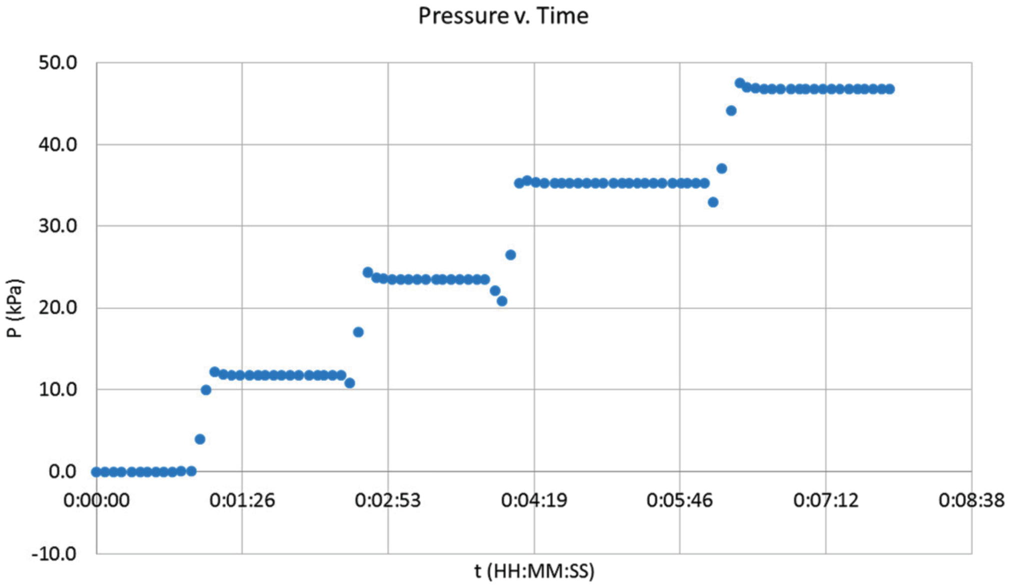

Figure A-9. P/V calibration run. Note that the small drop in pressure on addition of the 2nd and subsequent aliquots is believed to be due to equilibration of the (slightly) pressurized vessel with the ambient pressure volume in the syringe.

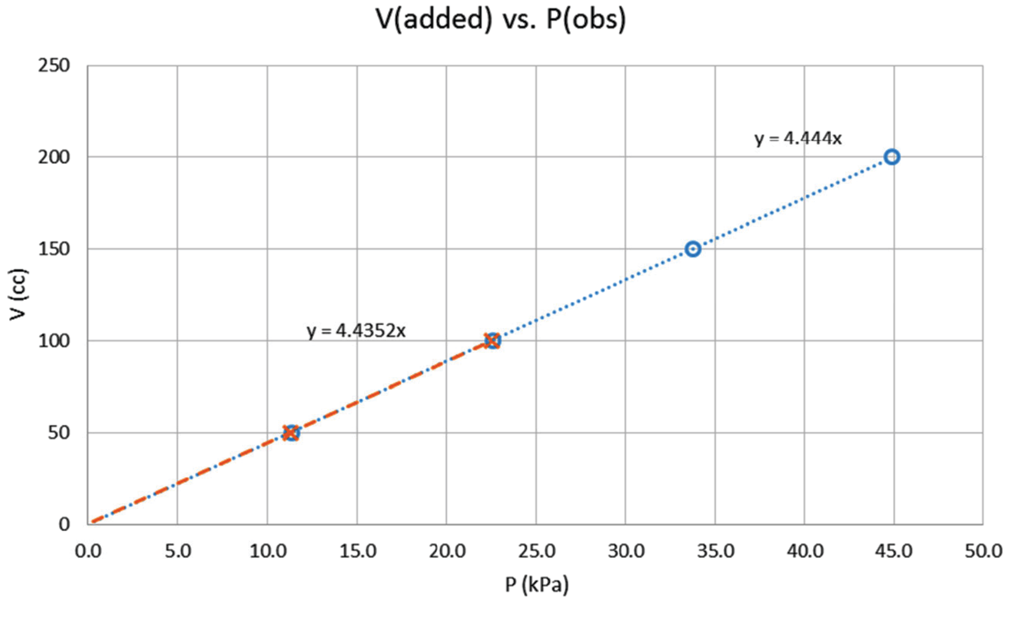

Figure A-10. Example of a P/V calibration curve for an apparatus as shown in Figure A-4 (center left)***. The open circles (4 total, slope of fitted line = 4.444 cc/kPa) represent the series of 4 additions of 50.0 cc of nitrogen gas to an empty apparatus, from the initial commissioning of this apparatus. The crosses (2 total, slope of 4.435 cc/kPa) reflect measurements made immediately prior to a test run, at a later date.***

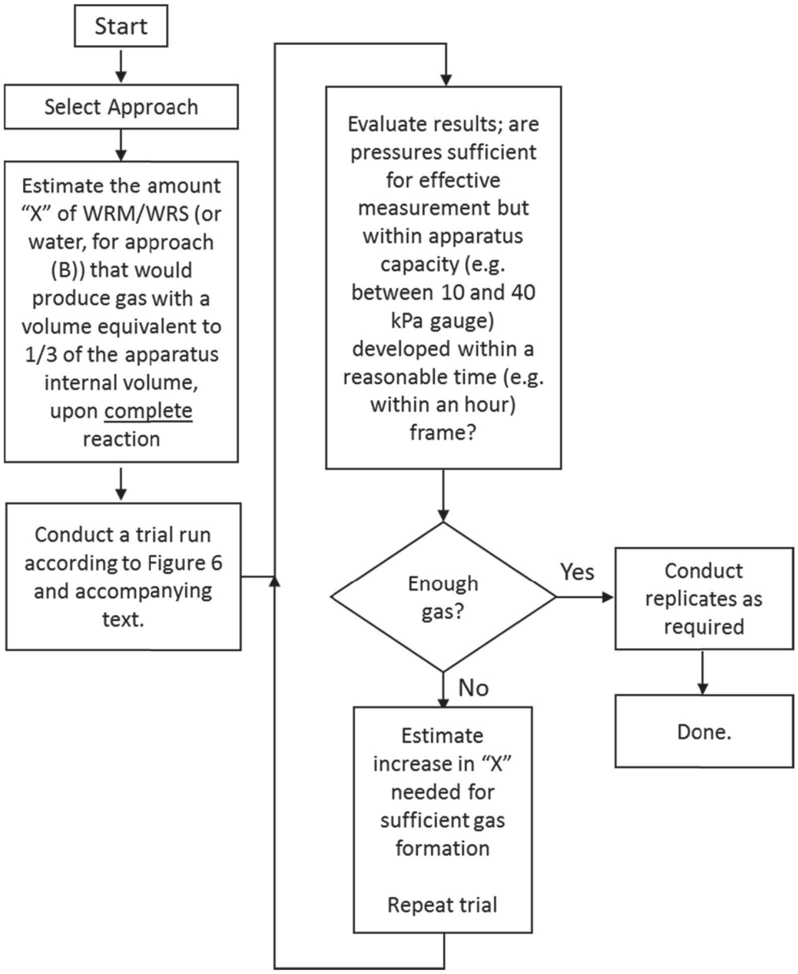

Figure A-11. Flow chart illustrating the process of conducting iterative runs to establish the amounts needed to obtain satisfactory results.

Important Safety Point Particular care to choose and use appropriate equipment and PPE should be taken during handling and dispensing of the water-reactive materials or water-reactive substances. The most reactive materials will require the greatest care and precautions (see Note 1, p.13).

Important Safety Point The amount of water-reactive material/water-reactive substance to use in testing is determined by trial, starting with an amount of water-reactive material/water-reactive substance known (or estimated with confidence by a qualified chemist) to produce *at most* an amount of gas within the capacity of the apparatus (i.e., ≤ ⅓ of the internal volume, ≤ 140 cc in the case of the 430 cc apparatus used in Figures A-8 and A-9). See Figure A-10.[3]

Once the apparatus is calibrated and/or closed, water can be added, either via the septum closure or through the unused threaded opening. After that, the vessel should be vented to equilibrate the internal and external pressure. Water is normally added via syringe, all at once, and the amount delivered is determined by weighing and difference.

For liquid water reactive materials/substances, the substance is added from a pre-weighed syringe all at once via the septum closure, and the amount added is determined by weighing and difference. For solids, the solids addition tube is simply tipped up and the material added all at once. Again, the actual amount of water-reactive material/water-reactive substance delivered is determined by weighing before and after addition and using the difference as the mass. For both solids and liquids, trials are conducted iteratively (see Figure A-11), starting with amounts known to be within the capacity of the apparatus and increasing until convenient, measurable, and reproducible results are obtained. Pressure and temperature are monitored and recorded as the reaction occurs.

The course of trials and replicate runs should proceed as shown in Figure A-11.

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[3] Calculate expected volumes at 21.1 °C and 101.56 kPa.

Approach (B)

Approach (B) (see Figure A-7) is generally only used with liquid water reactive materials/substances, though solids can be tested if necessary. It should be used when experience with Approach (A) shows that the amount of water present must be severely limited to avoid absorption of the gas produced in a reaction with water by excess water that remains in the reaction vessel. Approach (B) should also be employed when there is evidence that the gas observed in Approach (A) has more to do with evaporation of the test material or substance than its reaction with water.

The overall approach is similar to that in Approach (A), but the order of addition is reversed. Also, the water-reactive material/water-reactive substance is present in excess, and water is the limiting reagent. A suitable amount of water-reactive material/water-reactive substance is charged to the apparatus for testing (2–10 g is typical); for liquids, enough must be used to permit evaporation to saturate the headspace while leaving some liquid within the reaction vessel. Also note that for substances with a significant vapor pressure, it may be necessary to (carefully and momentarily) vent the pressure to allow some of the initially present atmosphere to escape so that the equilibrium pressure is not too far above ambient.

The amount of water is chosen to be such that results are within the capacity of the apparatus. Except for considerations of whether the reaction stoichiometry will be 1, 2, or (occasionally) 3 moles of gas per mole of water, the amounts here can be determined independently of the water-reactive material/water-reactive substance under test. In a 1:1 reaction, 100 mg of water yields 133 cc gas, and in a 1:2 reaction, 50 mg yields the same amount.[4]

Validation Test Results

The examples included in this section illustrate the application of Approaches (A) and (B) within the scope of the new proposed test for N.5 and provide guidance (by way of example) on implementation of the new proposed test N.5.

Example 1—Dimethyldichlorosilane (UN 1162)

Dimethyldichlorosilane ($[CH_3]_2SiCl_2$, Aldrich, > 98.5%, UN 1162) was subjected to testing. This is an example of a liquid material likely to be a water-reactive material.

$$(CH_3)_2\,SiCl_2\,(l) + H_2O\ (l) \rightarrow (-Si(CH_3)_2\,O-)_n + 2\ HCl(g) \tag{1}$$

Equation (1) indicates that the potential for gas evolution from $(CH_3)_2SiCl_2$ is ~ 378 l/kg$_{(CH3)2SiCl2}$ after complete reaction at normal ambient conditions. This suggests that $(CH_3)_2SiCl_2$ is a liquid water reactive material that produces a water soluble gas. The process shown in Figure A-7 suggests that this material should be tested according to Approach (A), using the minimum required water. Given the gas evolution potential for $(CH_3)_2SiCl_2$ and considering the process shown in Figure A-11, preliminary experiments should be limited to ~ 0.3 g ($[CH_3]_2SiCl_2$ maximum expected gas production, ~ 112 cc).

A reaction apparatus as shown in Figure A-4, center left, configured for liquid addition was assembled, the P/V calibration checked (as shown in Figure A-10, data indicated with dash-dot pattern), and a trial run with 0.3230 g $(CH_3)_2SiCl_2$ and 2.0585 g water. The results are shown in Figure A-12.

Experience (see other validation testing results) shows that the results of Figure A-12 may be due to evaporation of the $(CH_3)_2SiCl_2$ rather than gas production and/or that any gas being produced is being absorbed by the water. Indicators of this include the following: (a) the observed pressure increase when the $(CH_3)_2SiCl_2$ was added (~ 1.3 kPa) corresponds to only a small amount of gas evolution (~ 6 cc), and (b) it is a much smaller increase in pressure than would be expected even from just the vapor pressure of $(CH_3)_2SiCl_2$ (b.p. 70 °C). The behavior shown in Figure A-12 was observed in additional experiments, with 0.3–0.5 g $(CH_3)_2SiCl_2$ and 1–2 g water. While a rate could be calculated from the small increase in pressure (e.g., 300–700 l/kg-min observed over 4 tests), it seemed clear that absorption of gas by the water present in the reaction was occurring on a timescale similar to, or faster than, gas evolution (if it was occurring). Because this indicated that there were issues related to the solubility of the evolved gas (HCl) in water (see Figure A-7), tests with Approach (B), adding water to $(CH_3)_2SiCl_2$, were conducted. Figure A-13 shows the results.

Figure A-13 confirmed that the expected increase in pressure from evaporation of $(CH_3)_2SiCl_2$ into the headspace would be larger than that observed on addition of $(CH_3)_2SiCl_2$ in Figure A-12; further, very nearly the theoretical amount of gas evolution (i.e., 90% of theory) was observed when water was added. This supports the contention that gas evolution in Figure A-12 was occurring, but was masked by the absorption of the gas by the water present. Fitting a line to the early, steepest part of the gas evolution curve in Figure A-13 (after correction for the small observed changes in temperature), yielded an initial raw gas evolution rate of 9472 kPa/day. Of the 2.15 g $(CH_3)_2SiCl_2$ present, complete reaction would consume ~ 0.72 g, according to Eq. (1).

Normalizing the raw gas evolution rate to that amount yields a specific gas evolution rate of 42 l/kg-min.

Additional experiments were conducted, adding water to $(CH_3)_2SiCl_2$, producing the results shown in Table A-1.

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[4] Calculated for 21.1 °C and 101.56 kPa.

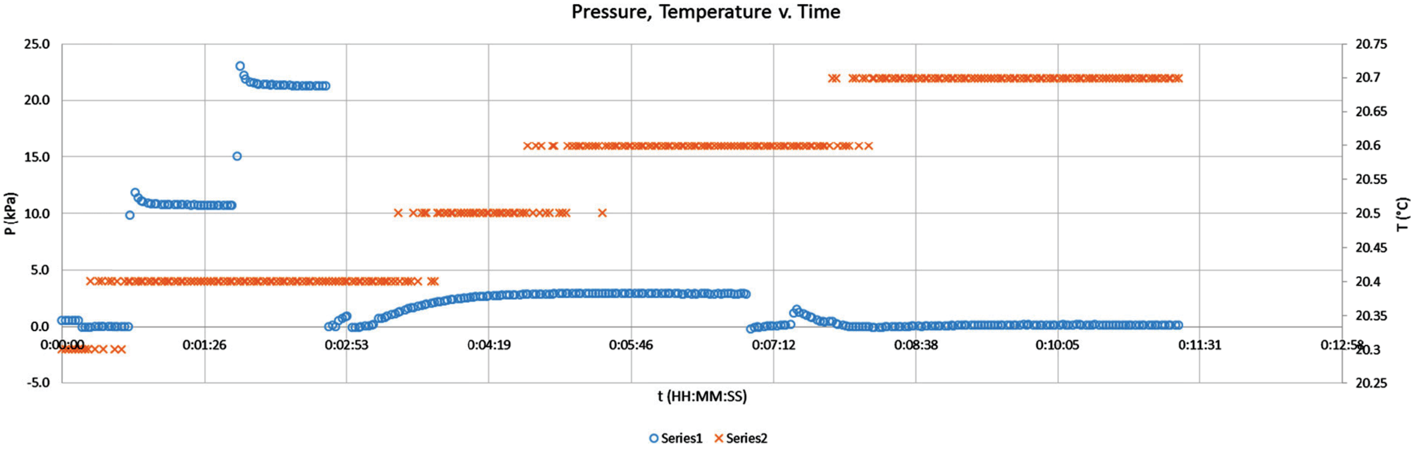

Figure A-12. Pressure vs. time for the pre-run apparatus calibration, water addition, and reaction of 0.3230 g $(CH_3)_2SiCl_2$ with 2.0585 g water. The open circles show the observed pressure, and crosses show the observed temperature, vs. time as the reaction proceeds. Calibration occurred during the 1st 3 minutes of the experiment, with water addition shortly after that. The reaction was vented after water vapor pressure equilibration and the $(CH_3)_2SiCl_2$ added after ~ 7 minutes. The "bump" at ~ 7:30 corresponds to the addition of $(CH_3)_2SiCl_2$.

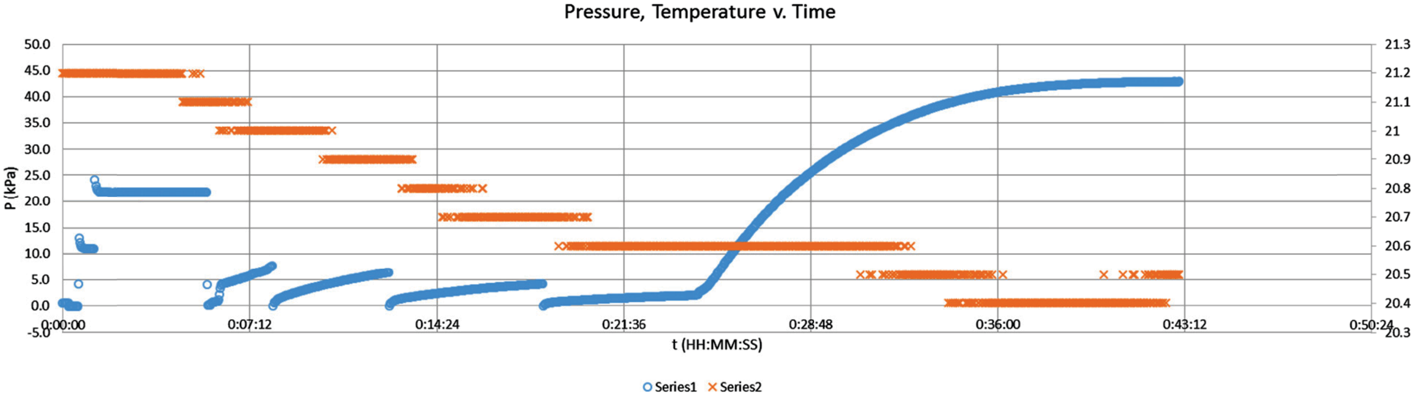

Figure A-13. Pressure vs. time for the apparatus calibration, $(CH_3)_2SiCl_2$ addition, and reaction of 2.1492 g $(CH_3)_2SiCl_2$ with 0.0762 g water. $(CH_3)_2SiCl_2$ addition occurred prior to 7:00, and the reactor was vented several times as the vapor pressure of $(CH_3)_2SiCl_2$ equilibrated in the reactor headspace. Water addition was at ~ 25:00. The net increase in pressure (total) after water addition was ~ 40 kPa, corresponding to ~ 184 cc (~ 90% of theory).

Table A-1. Summary of $(CH_3)_2SiCl_2$ results.

Mass DMDCS	Mass Water	Calibration	Rate	Rate	Net gas observed	Water/ DMDCS
g	g	cc/kPa	kPa/Day	l/kg-min	(% theory)	mole/mole
2.1492	0.0762	4.61	9472	42	97	0.3
2.1710	0.0866	4.47	10203	39	89	0.4
2.1776	0.1357	4.31	11370	27	67*	0.6
1.3428	0.0728	4.72	9672	46	92	0.5
1.3282	0.1013	4.59	9612	32	77*	0.7
1.3933	0.1357	4.42	10208	25	34*	0.9
0.7291	0.0563	4.75	6295	39	73	0.7

*Reaction stopped early, as the pressure increase approached the relief pressure of the apparatus (or, in one case, vented).

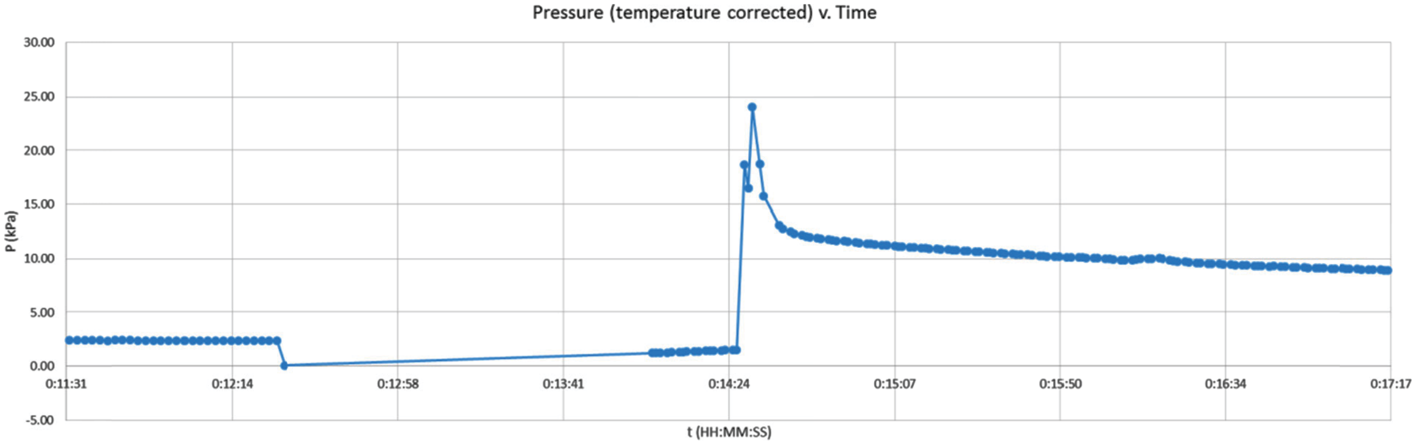

Figure A-14. Pressure vs. time for the reaction of 0.1996 g $NaNH_2$ with 2.0747 g water. Reaction is complete within 6 seconds, after which some absorption of the ammonia by the water present in the reaction occurs. The rate, based on gas formed after 2 seconds, is 12,000 l/kg_{NaNH2}-min. As sometimes happens with reactions of (reactive) solids with water, the reaction is somewhat irregular. In this case, unlike reactions where HCl (g) forms, gas is reabsorbed, but not all of it, as the solubility of NH_3 (g) in basic solution is lower than that of HCl (g) in neutral or basic solutions.

The average of these results is 36 l/kg-min, with a relative standard deviation of 22% for the sample.

Normally it would not be necessary to explore the impact of changes in the ratio of water to test material or substance (though it may often be useful to do this), but in this case that was also explored. In this case, it appears that the specific gas production rate does depend on the water/$(CH_3)_2SiCl_2$, falling as that ratio increases (though, the raw rate increases). These effects are easily rationalized; as the water increases, the raw rate increases from the greater available water, but the specific rate falls because the amount of $(CH_3)_2SiCl_2$ required for reaction (i.e., the denominator in the specific rate calculation) also increases. If the raw rate increases, proportionally, less than the increase in the amount of water used, then the specific rate will fall.

Example 2—Sodium Amide (UN 1390)

Sodium amide ($NaNH_2$, Aldrich, 95%, UN 1390) was subjected to testing. $NaNH_2$ is known[5] to react violently with water to release ammonia.

$$NaNH_2(s) + H_2O(l) \rightarrow NaOH(aq) + NH_3(g) \qquad (2)$$

Equation (2) indicates that the potential for gas evolution from $NaNH_2$ is ~ 620 l/kg_{NaNH2} after complete reaction at normal ambient conditions. This suggests that $NaNH_2$ is a solid water reactive material that produces a water soluble gas. As the process shown in Figure A-7 suggests, this material should be tested according to Approach (A), using the minimum required water. Preliminary experiments should be limited to ~ 0.2 g $NaNH_2$ (maximum expected gas production, ~ 125 cc).

A reaction apparatus as shown in Figure A-4, center-right and far right, configured for solid addition was assembled, the P/V calibration checked (as in Figure A-13, data indicated with circles), and a trial run conducted with 0.1996 g $NaNH_2$ (final weight determined by difference, after completion of the reaction) and 2.0747 g water.

In this case (in contrast to Example 1), rapid initial evolution of a substantial amount of gas (obviously in excess of any vapor pressure from $NaNH_2$ solid) was observed (Figure A-14). While some gas was subsequently absorbed, the initial evolution of gas appears to be substantially faster than the rate at which the gas is absorbed.

As shown in Table A-2 and Figure A-15, similar rates and behavior were observed for a series of experiments with this material, so Approach (A) was judged to be suitable.

Water was always present in excess (Approach [A]), and, while the water/$NaNH_2$ ratio varied somewhat in testing (because of modest changes in the masses used from run to run), there is no obvious correlation of observed rate with the water/$NaNH_2$ ratio. Consequently, all 5 results can be pooled, yielding a result of 9600 l/kg-min with a sample relative standard deviation of 20%.

Example 3—Sodium Borohydride (UN 1426)

Sodium borohydride (SBH, Sigma-Aldrich, ≥98%, UN 1426) was subjected to testing. In principle, Sodium borohydride can

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[5] Cheremisinoff, N. P. *Handbook of Industrial Toxicology and Hazardous Materials*, CRC Press, 1999, p. 366.

Table A-2. Summary of $NaNH_2$ results.

Mass $NaNH_2$	Mass Water	ΔP (Fastest)	ΔV	Rate	Water/$NaNH_2$
G	g	kPa	cc	l/kg-min	mole/mole
0.2929	2.129	16.97	82.3	8430	15.7
0.1996	2.0747	17.13	79.8	11998	22.5
0.223	2.1240	14.70	65.7	8840	20.6
0.2141	2.0513	16.78	80.2	11239	20.7
0.1954	2.1305	10.42	48.0	7375	23.6

Average rate = 9600(2000), 20% relative standard deviation (RSD).

react with water to form 4 moles of hydrogen, and it is already classified as a Division 4.3 WRS, with PG 1 assigned:

$$NaBH_4(s) + 4H_2O(l) \rightarrow NaB(OH)_4 + 4H_2(g) \tag{3}$$

Since the hydrogen produced has low solubility in water, the left side of Figure A-7 applies, and Approach (A) was used.

Equation (3) indicates that Sodium borohydride would release ~2550 l/kg_{SBH} of hydrogen gas after complete reaction at normal ambient conditions. This suggests that initial experiments should use ~ 0.050 g of Sodium borohydride (expected yield, ~125 cc).

An initial reaction with 0.0302 g Sodium borohydride and 2.0448 g water showed a very mild reaction, with ~ 20–25 cc of gas formed over 90 minutes (~ 33% yield of hydrogen), so the reaction was scaled up. Reaction between 0.4541 g Sodium borohydride and 3.9748 g water is shown in Figure A-16.

Subsequently, the reaction was further scaled up to ~ 1 g Sodium borohydride / 8 g water and ~ 2 g Sodium borohydride / 16 g water. These results are summarized in Table A-3 and Figure A-17.

Here, as in Example 2 and despite careful work, significant standard deviations remain in the experimental results. The origin of this is unclear, but presumably it is due to an underlying variability in the reaction—possibly because of a strong dependence on subtle aspects of the experiment (e.g., details of mixing of solid and water). The results were obtained by the same worker, using the same set of apparatus, in the same laboratory, with multiple tests run in a single day. Also, the P/V response of the apparatus was calibrated prior to each run by the addition

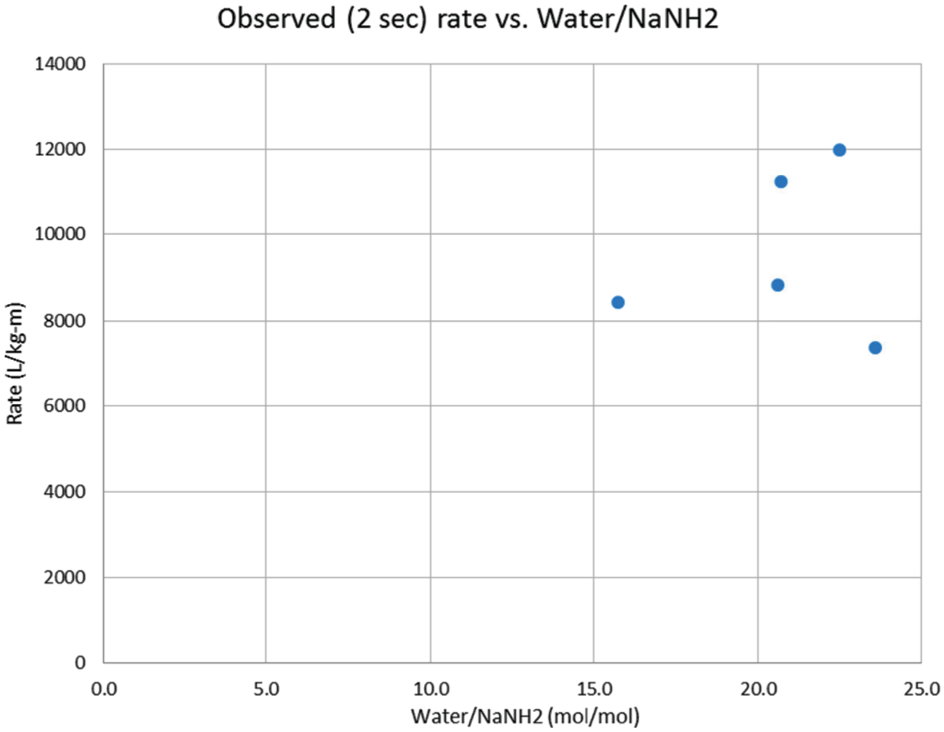

Figure A-15. Results from runs of the reaction of $NaNH_2$ with water at room temperature.

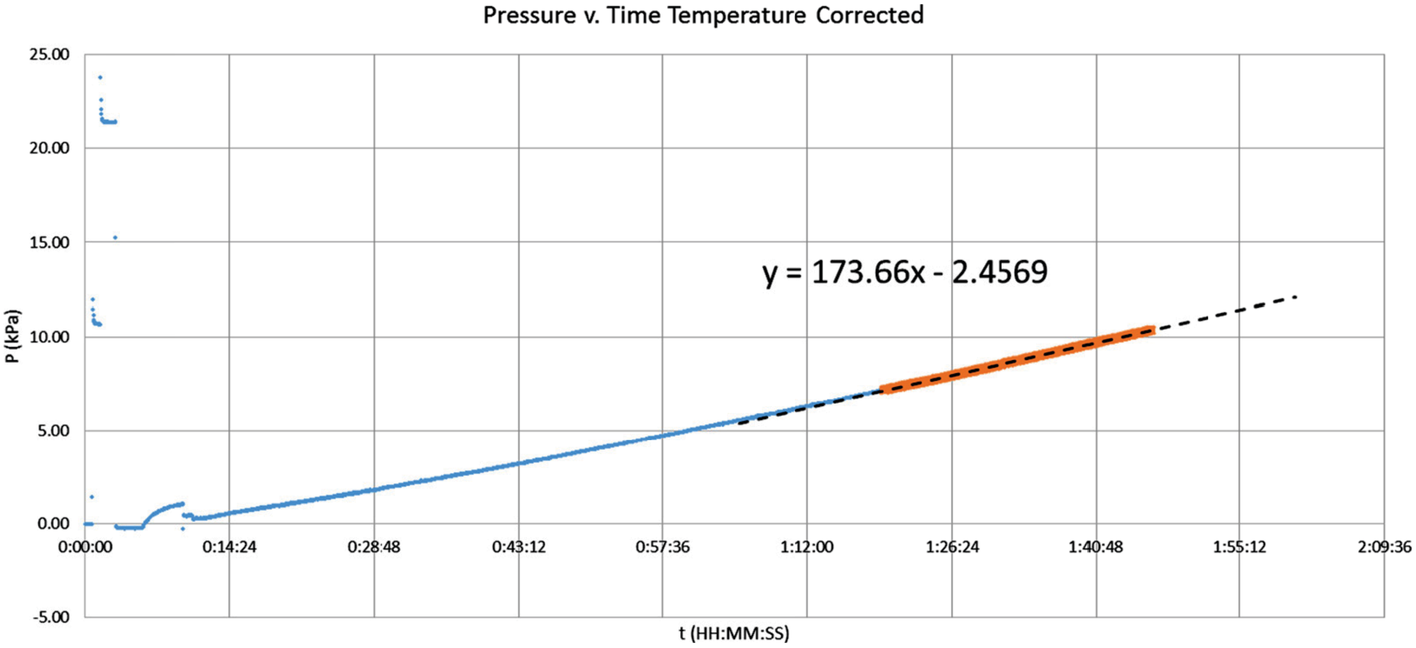

Figure A-16. Results from a reaction between 0.4541 g Sodium borohydride and 3.9748 g water showing the smooth reaction, which achieved a near steady state reaction rate, producing a pressure increase of ~ 173.7 kPa/day in the reaction vessel. Conversion to volume of gas and normalization to the amount of Sodium borohydride used, yielded a specific gas production rate of 74 l/kg$_{SBH}$-h.

of known volumes of gas, as called for in the protocol. It may be that the nature of these reactions intrinsically limits precision.

It is tempting to divide the results shown in Figure A-17 and Table A-3 into the two groups apparent in Figure A-17 and segregate them accordingly. However, a close look at the results shows that while most of the higher results came from the tests with ~2 g sodium borohydride, one of those experiments also yielded the lowest observed rate. Consequently, the case for segregation cannot be made, and all the results were pooled to yield a result of 120 l/kg-hr with a sample relative standard deviation of 25%.

Example 4—Acetyl Chloride (UN 1717)

Acetyl chloride (CH_3COCl, Fluka, ≥99%, UN 1717) was subjected to testing. Acetyl chloride is well known to react vigorously with water; complete hydrolysis proceeds according to Equation (4).

$$CH_3COCl(l)+H_2O(l)\rightarrow CH_3CO_2H(s)+HCl(g) \tag{4}$$

This stoichiometry indicates that the potential for gas evolution from acetyl chloride is ~ 310 l/kg$_{AcCl}$, and that it is a water reactive material that produces a water soluble gas.

Table A-3. Results from tests with Sodium borohydride. Rates were based on the steepest slope portion of the observed curves; reactions were typically monitored for 1.5 hours or more.

Mass SBH	Mass Water	Calibration	Rate	Rate	Water/ SBH
g	g	cc/kPa	kPa/Day	l/kg-hr	mole/mole
0.4541	3.9748	4.65	173.7	74.1	18.4
0.9145	8.0338	4.70	498.7	106.8	18.4
0.9873	7.9741	4.70	601.4	119.3	17.0
1.8549	15.9241	4.73	673.4	71.5	18.0
2.0567	16.4623	4.85	1387	136.3	16.8
1.8373	16.6066	4.73	1234	132.4	19.0
2.0461	16.3986	4.53	1587	146.4	16.8
2.1084	16.3060	4.84	1524	145.8	16.2
1.9692	16.2761	4.70	1556	154.7	17.4

Average rate = 120(30), 25% RSD.

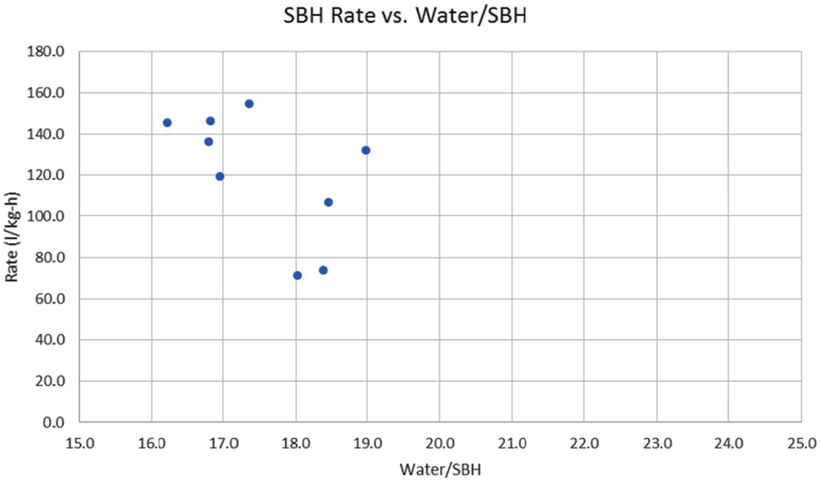

Figure A-17. Results for the 9 replicate runs for the reaction of sodium borohydride with water at room temperature, showing the observed specific rate of gas evolution as a function of water/ sodium borohydride ratio. The scatter in the x-direction (water/ sodium borohydride ratio) reflects the fact that targeted weights are not precisely achieved. This shows that the observed rate is not strongly dependent on water/ sodium borohydride ratio in this range, so all results can be pooled.

This would suggest that ~ 0.4 g of acetyl chloride would yield ~ 125 cc of gas. Because this is a water-reactive material likely to produce a gas soluble in water, the right-hand portion of Figure A-7 applies, and a limited amount of water (e.g., 2.0 g) should be used. Note that with 0.4 g acetyl chloride, 2.0 g water provides ~ 20 moles of water for each mole of acetyl chloride.

A reaction apparatus as shown in Figure A-4, center-left, configured for liquid addition was assembled, the P/V calibration checked (as in Figure A-10, data indicated with dash-dot pattern), and a trial run conducted with 0.4384 g acetyl chloride and 2.0104 g water. As shown in Figure A-18, the rate observed for the first 6 seconds—the fastest period of reaction—was ~ 470 l/kg-min. However, the maximum transient yield of gas was only ~ 25 cc, corresponding to ~ 20% of theory.

Replicate runs gave the results shown in Table A-4 and Figure A-19.

For acetyl chloride, a rapid initial production of gas was observed even though it was ultimately absorbed by the

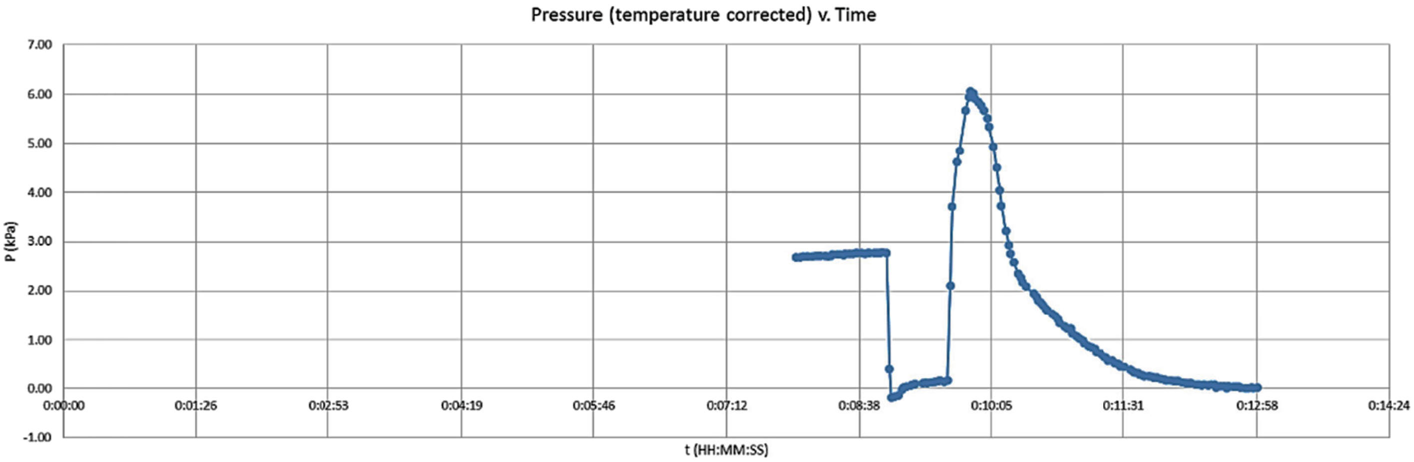

Figure A-18. Pressure vs. time for reaction of 0.4384 g acetyl chloride is combined with 2.0104 g water. The fastest reaction is observed over the first 6 seconds after the materials are combined and corresponds to a rate of 468 l/kg-min. The maximum pressure observed corresponds to 25 cc of gas evolution or ~ 19% of the theoretical yield.

Table A-4. Results from tests with acetyl chloride rates are based on the fastest period of gas evolution (e.g., the first several seconds, the actual duration of the fastest gas evolution varied from run to run).

Mass AcCl	Mass Water	ΔP (Fastest)	ΔV	Duration	Rate	Water/AcCl
g	g	kPa	cc	m	l/kg-min	mole/mole
0.4384	2.0104	4.45	20.5	0.10	468	20.0
0.8765	2.0406	10.53	49.3	0.07	843	10.1
0.8595	2.0420	14.20	63.6	0.13	555	10.4
0.8621	2.0604	5.22	22.6	0.03	787	10.4
0.8649	2.1218	5.67	26.0	0.07	451	10.7

Average rate = 620(180), 30% RSD.

water. In the case of $AlCl_3$, and $TiCl_4$ (see Examples 5 and 9), the initial gas evolution was very rapid, reaction was obvious, the amount of gas transiently observed was a substantial fraction of the expected amount, and the pressure observed was obviously in excess of that likely to be due simply to the vapor pressure of the material under test.

In this case, it is less clear whether the observed initial surge of pressure was due to gas production or vapor pressure of the acetyl chloride. Consequently, a series of experiments were conducted using Approach (B) with ~ 0.050 g of water (chosen because of the theoretical possibility of forming two moles of HCl per mole of water, see prior discussion of Approach [B]). This yielded the behavior shown in Figure A-20, which is much more like the behavior expected for this reaction according to chemical principles, and it yields an amount of gas in line with expectations (See Table A-5). Replicates of the test yielded the results shown in Table A-5, with rates measured in the steepest part of the "S" curve and (as in Example 1) normalized to the amount of acetyl chloride required to react with the water added.

The pooled result here appears to be 665 l/kg-min with a relative standard deviation of 9%.

Example 4 (Repeat with Saltwater)—Acetyl Chloride (UN 1717)

Acetyl chloride was selected for testing with saltwater (3.5% w/w NaCl in DI water) as well as DI water (preceding section). This work used Approach (B) and yielded the behavior shown in Figure A-21.

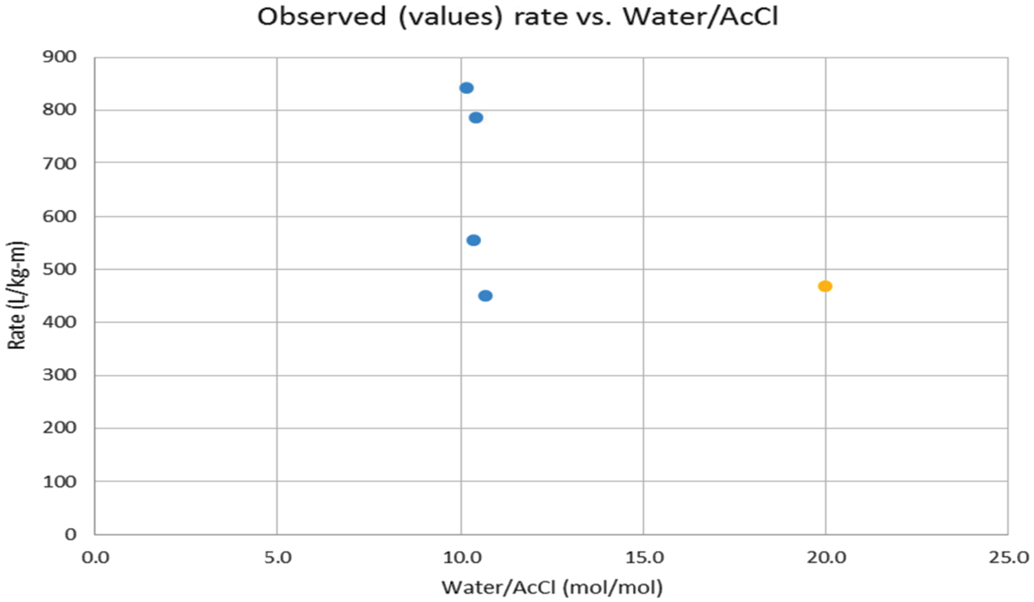

Figure A-19. Results from trial and replicate runs for the reaction of acetyl chloride with water at room temperature. This shows that the observed rate is not strongly dependent on water/acetyl chloride ratio in this range, so all results can be pooled.

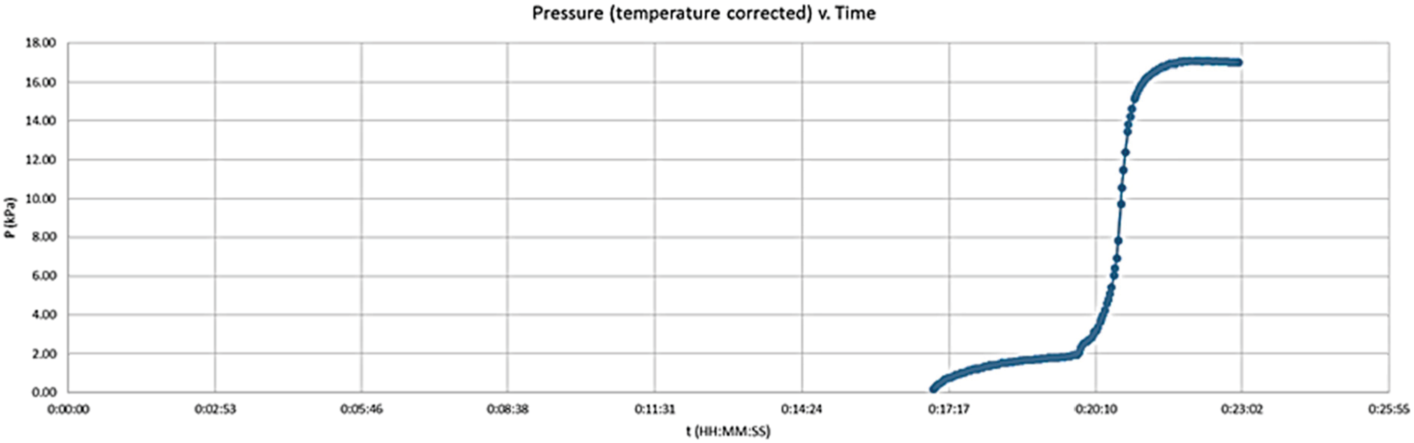

Figure A-20. Pressure observed as a function of time when 0.0535 g water is added to 2.2596 g acetyl chloride.

Table A-5. Results from tests with acetyl chloride rates are based on the fastest period of gas evolution (e.g., the first several seconds, the actual duration of the fastest gas evolution varied from run to run).

Mass AcCl	Mass Water	ΔV (Fastest)	V (total)	V (% of theory)	Duration	Rate	Water/AcCl
g	g	cc	cc		m	l/kg-min	mole/mole
2.2172	0.0561	29.5	76.9	103%	0.17	724	0.110
2.2596	0.0535	25.1	67.3	94%	0.17	646	0.103
2.2133	0.0544	19.7	71.3	98%	0.13	624	0.107
2.2532	0.0585	31.3	79.3	101%	0.17	736	0.113
2.2578	0.0578	15.0	77.3	100%	0.10	596	0.112

Average rate = 665(60), 9% RSD.

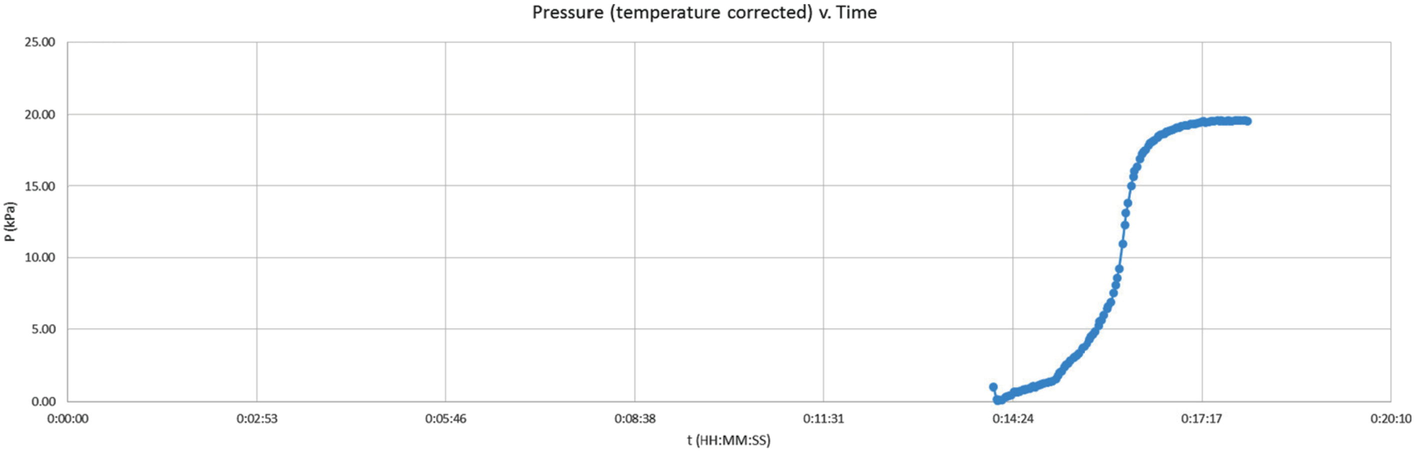

Figure A-21. Pressure vs. time for reaction of 0.0572 g saltwater with 2.2272 g acetyl chloride.

Qualitatively, it is clear that Figure A-21 shows the same behavior apparent in Figure A-20.

Quantitatively, results from 5 replicate runs with saltwater showed an average specific rate of gas production of 790 l/kg-min with a relative standard deviation of 12%. This is slightly higher than the results with DI water (average of 665 l/kg-min with a relative standard deviation of 9%), but given the sample standard deviations, this difference cannot be considered statistically significant.

Example 5—Anhydrous Aluminum Chloride (UN 1726)

Aluminum chloride ($AlCl_3$, Sigma-Aldrich, 98%, UN 1726) was tested. This is an example of a solid material that potentially could be a water-reactive material (if gas is evolved on contact with water). An interesting nuance for $AlCl_3$ is that it is not obvious in advance whether it will produce gas, and if so, whether that could be measured in the presence of water.

$AlCl_3$ is known to react vigorously with water, ultimately forming a hydrated salt:[6]

$$AlCl_3(s) + \text{excess } H_2O(l) \rightarrow [Al(H_2O)_6]^{3+} + 3Cl^-(aq) \qquad (5)$$

However, it is also reported to fume on contact with water and release at least some HCl (g).[7] In principle (and by analogy to materials like $SiCl_4$), this could be due to a reaction such as Equation (6):

$$AlCl_3(s) + 6H_2O(l) \rightarrow Al(OH)_3(H_2O)_3 + 3HCl(g) \qquad (6)$$

If a transient reaction as in Equation (6) occurs, then $AlCl_3$ might need to be classified as a water-reactive material in that it might emit a toxic gas, HCl (g), on contact with water.

Should this (potentially transient) formation of 3 moles of HCl (g) per mole of $AlCl_3$ occur, the potential gas production from $AlCl_3$ is ~ 540 l/kg_{AlCl3}. This would suggest that ~ 0.20 g $AlCl_3$ might yield as much as 110 cc HCl (g). As that amount is within the capacity of the reaction apparatus (see Figure A-11), that was chosen as the starting amount. Because $AlCl_3$ may produce a gas soluble in water, the right-hand portion of Figure A-7 applies, and a limited amount of water (e.g., 2.0 g) used. Note that with 0.20 g $AlCl_3$, 2.0 g water still provides ~75 moles of water for each mole of $AlCl_3$, or > 12 times the amount required for Equation (6) above.

A reaction apparatus (as shown in Figure A-4, center-right and far-right) configured for solids addition was assembled, the P/V calibration checked (as in Figure A-10, data indicated with dash-dot pattern), and charged with 0.2143 g $AlCl_3$ and 2.1085 g water. The $AlCl_3$ was added to the water all at once, and the data shown in Figure A-22 obtained.

As was the case for Example 2, $AlCl_3$ has a negligible vapor pressure at room temperature, so the observed increase in pressure must be due to gas evolution. Since this was well within the apparatus capacity, testing was scaled up to ~ 0.4 g $AlCl_3$ with 2.0 g water and replicates run. A typical result is shown in Figure A-23, all results are tabulated in Table A-6, and the specific rate results are graphed in Figure A-24.

The preceding results suggest that Equation (5) is indeed occurring, but that it occurs by the rapid, stepwise reactions of equations (7)[8] and (8).

$$AlCl_3(s) + 6H_2O(l) \rightarrow Al(OH)_3(H_2O)_3 + 3HCl(g) \qquad (7)$$

$$Al(OH)_3(H_2O)_3 + 3HCl(g) \rightarrow [Al(H_2O)_6]^{3+} + 3Cl^-(aq) \qquad (8)$$

This testing suggests that $AlCl_3$ reacts very rapidly with water to produce HCl (g) with an average observed rate of ~ 7500 l/kg_{ALCl3}-min and an observed relative standard deviation of ~ 20%. While some of this HCl (g) might escape in an open environment, the gas is quickly absorbed by the water present in this closed apparatus, recombining with the intermediate aluminum product.

Example 6—Phosphoryl Chloride (UN 1810)

Phosphoryl chloride ($POCl_3$, Fluka, ≥99%, UN 1810) was subjected to testing. Phosphoryl chloride is well known[9] to react vigorously with water; complete hydrolysis proceeds (in principle) according to Equation (9).

$$POCl_3(l) + 3H_2O(l) \rightarrow H_3PO_4(l) + 3HCl(g) \qquad (9)$$

Equation (9) indicates that the potential for gas evolution from $POCl_3$ is ~ 470 l/kg_{POCL3}. This suggests that $POCl_3$ is a water reactive material that produces a water soluble gas. This would suggest that ~ 0.3 g of $POCl_3$ would yield ~ 140 cc of gas. Because this is a water-reactive material likely to produce a gas soluble in water, the right-hand portion of Figure A-7 applies, and a limited amount of water (e.g., 2.0 g) should be used. Note that with 0.3 g phosphoryl chloride, 2.0 g water provides > 50 moles of water for each mole of phosphoryl chloride.

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[6] Vincoli, J. W., *Risk Management for Hazardous Chemicals*, CRC Press, 1996, p. 75.

[7] Many $AlCl_3$ MSDS note the potential for $AlCl_3$ to fume, producing HCl (g) in contact with water or humid air.

[8] Equation (7) is identical to Equation (6), and reproduced here simply for convenience.

[9] See, for instance, *Inorganic Chemistry*, Cotton, FA; Wilkinson, G; Murillo, CA; Bochmann, M, 1999, John Wiley & Sons, Inc., p. 404.

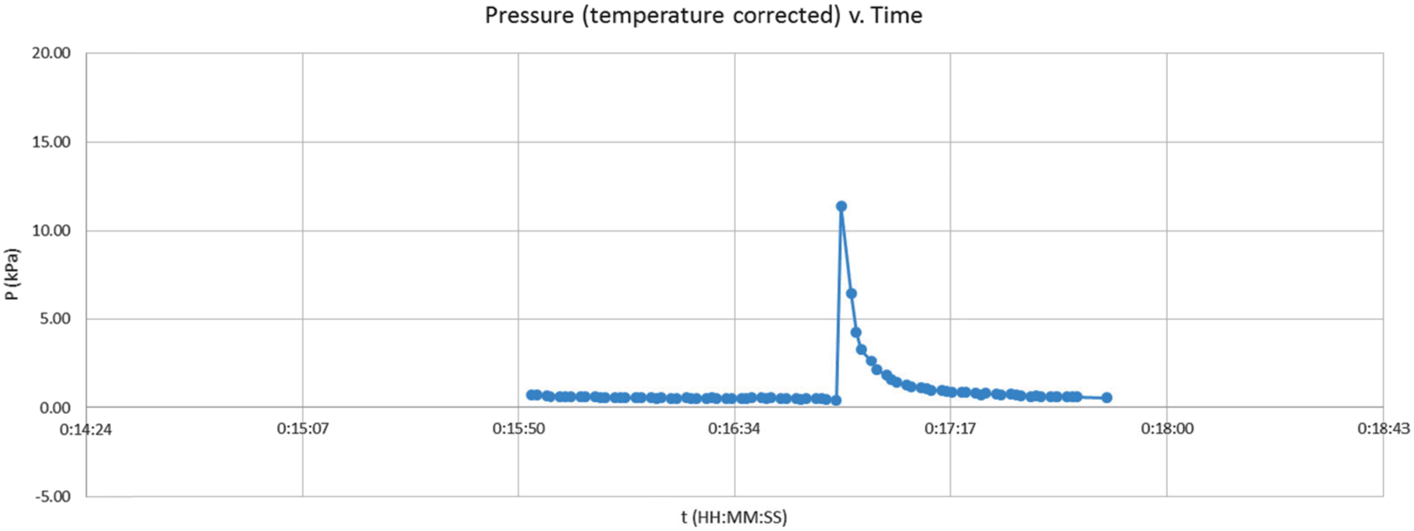

Figure A-22. Pressure vs. time for reaction of 0.2143 g $AlCl_3$ is with 2.1085 g water. Pressures reported are corrected via the ideal gas law for small temperature changes during the course of the reaction to yield an isothermal-equivalent result. Transient gas formation is observed (within the first 2 second interval, data points are separated by 2 seconds), but the gas formed is reabsorbed within 20–30 seconds. Applying the P/V calibration for this apparatus, the transient gas formation amounted to ~ 55 cc of gas (~47% of theory). This corresponds to a (transient) gas evolution rate of ~7700 l/kg$_{AlCl3}$-min.

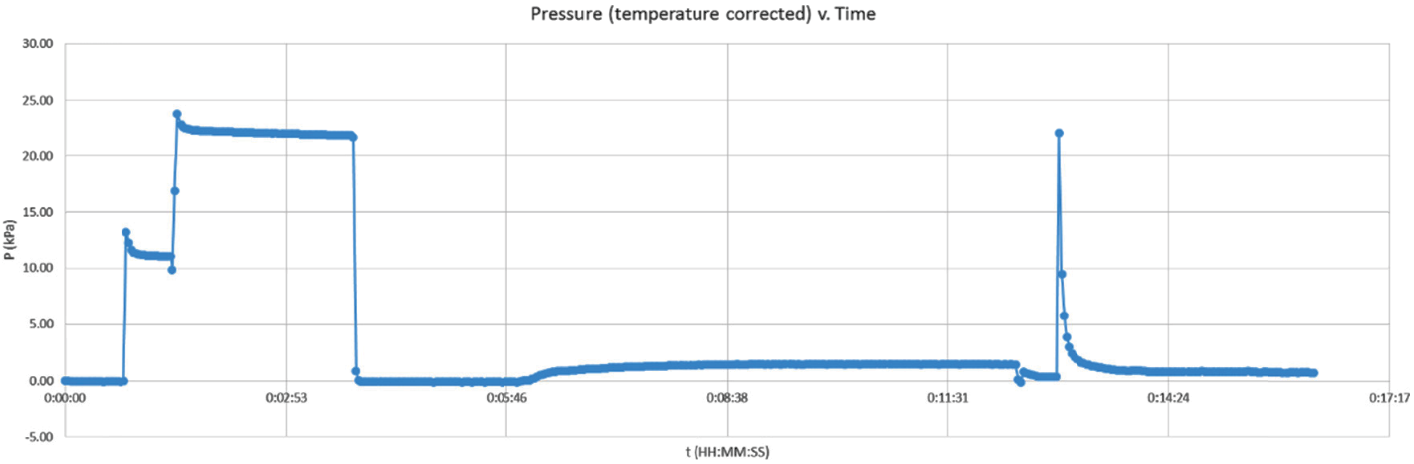

Figure A-23. Pressure vs. time for the reaction of 0.3298 g $AlCl_3$ with 2.1961 g water. The water was added at around 6 minutes, equilibration of reactor pressure with ambient pressure allowed at around 13 minutes. When $AlCl_3$ is combined with the water, transient gas formation is observed, though in this case the gas formed is essentially completely reabsorbed within 20–30 seconds. Applying the P/V calibration for this apparatus, 99 cc of (~ 55% of theory) transient gas formation is observed. Given the short duration of the evolution, this corresponds to a gas evolution rate of ~ 7600 l/kg-min.

Table A-6. Results from 7 runs of $AlCl_3$ reaction with water ($AlCl_3$ added to water).

Mass $AlCl_3$	Mass Water	ΔP (Fastest)	ΔV	Rate	Water/$AlCl_3$
g	g	kPa	cc	l/kg-min	mole/mole
0.2143	2.1085	11.38	55.0	7695	72.8
0.5001	2.0452	31.93	157.4	9443	30.3
0.3184	2.1221	12.97	60.6	5707	49.3
0.3250	2.0760	24.05	107.7	9946	47.3
0.3928	2.1961	22.06	99.5	7599	41.4
0.3582	2.1036	14.66	71.0	5943	43.5
0.3442	2.1060	15.79	73.6	6413	45.3

Average rate = 7500(1700), 23% RSD.

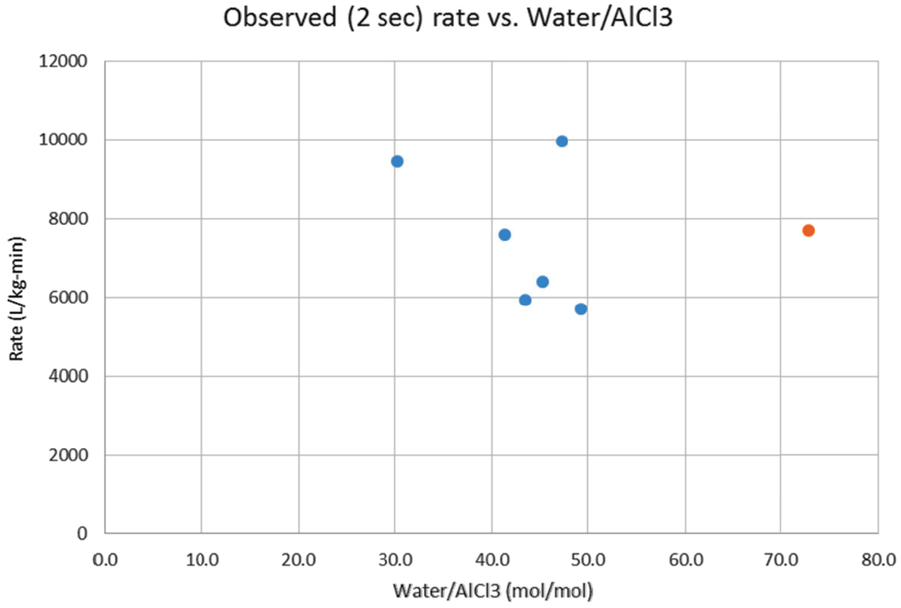

Figure A-24. Results from one trial run (point at > 70 water/$AlCl_3$) and 6 replicate runs for the reaction of $AlCl_3$ with water at room temperature, showing the observed rate of gas evolution, normalized to the amount of $AlCl_3$ used, as a function of the water/$AlCl_3$ ratio. The scatter in the x-direction (water/$AlCl_3$ ratio) reflects the fact that targeted weights are not precisely achieved. This shows that the observed rate is not strongly dependent on the water/$AlCl_3$ ratio in this range, so all results can be pooled.

A reaction apparatus as shown in Figure A-4, center-left, configured for liquid addition was assembled, the P/V calibration checked (as in Figure A-10, data indicated with dash-dot pattern), and a trial run with 0.3485 g phosphoryl chloride and 2.077 g water. For this trial run, fairly slow and modest reaction was observed. In this case, a steady rate was observed, and the slope of the pressure vs. time curve was used to extract a reaction rate. (See Figure A-25.)

Because this reaction rate and yield was modest, increasing amounts of $POCl_3$ were used (see Table A-7). Interestingly, as the water/$POCl_3$ ratio fell (i.e., the amount of $POCl_3$ used increased, while keeping the water constant), the character of the reaction changed. In all cases, there was an induction period, after which a more rapid reaction was observed (see Figure A-26). This more rapid reaction proceeded over a sufficiently short period of time that a simple slope based on the change in pressure and elapsed time could be used to find the maximum raw and specific gas production rate. However, the observed rate was a strong function of the water/$POCl_3$ ratio (see Table A-7 and Figure A-27). Also, at the higher $POCl_3$ charges (lower water/$POCl_3$ ratios), not all the gas was reabsorbed.

These results clearly make it difficult to assign a definite rate to this reaction.

Because of these results, a series of experiments using Approach (B) were also conducted. Interestingly, (see Figures A-28 and A-29) these also showed a strong dependence on water/$POCl_3$ ratio.

In this case, it would appear that the most that can be said is the following:

- $POCl_3$ reacts, when added to water, with a definite induction period. While the materials can be mixed without immediate reaction, a rapid reaction may occur just a few moments after mixing.
- When the reaction occurs, the rate is highly dependent on the amounts of water and $POCl_3$ involved. At water/$POCl_3$ mole ratios below ~15 and above ~ 5, reaction can be rapid and produce gas at rates at least as high as 3000 l/kg-min.

Example 7—Silicon Tetrachloride (UN 1818)

Silicon tetrachloride ($SiCl_4$, Aldrich, ≥99%, UN 1818) was subjected to testing. $SiCl_4$ is well known[10] to react vigorously

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[10] See, for instance, *Inorganic Chemistry*, Cotton, FA; Wilkinson, G; Murillo, CA; Bochmann, M, 1999, John Wiley & Sons, Inc., p. 271.

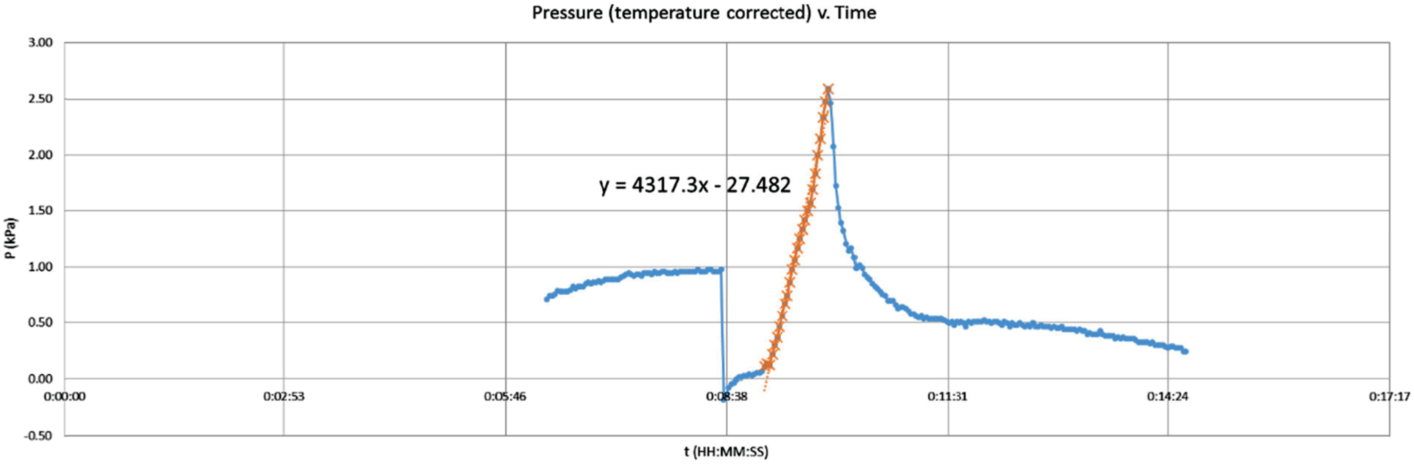

Figure A-25. Pressure vs. time for the reaction of 0.3485 g phosphoryl chloride with 2.077 g water. In this reaction, a modest, sustained raw gas production rate was observed, of ~ 4300 kPa/day. This corresponds to a specific gas evolution rate of ~ 38 l/kg-min. The maximum pressure observed corresponds to ~ 11 cc of gas evolution or ~ 7% of the theoretical yield.

Table A-7. Results from tests with phosphoryl chloride. Rates are based on either a sustained reaction or the fastest period of gas evolution.

Mass $POCl_3$	Mass Water	ΔP (Fastest)	ΔV	Duration	Rate	Rate	Water/ $POCl_3$
g	g	cc	cc	m	kPa/day)	l/kg-min	mole/mole
0.3485	2.0767				4317.00	38	51.4
0.6945	2.0399	3.59	15.2	0.07		328	25.3
1.3100	2.0171	56.53	260.6	0.07		2984	13.3
1.0300	2.1082	32.22	142.3	0.07		2072	17.6
0.8449	2.038	10.57	44.7	0.07		794	20.8

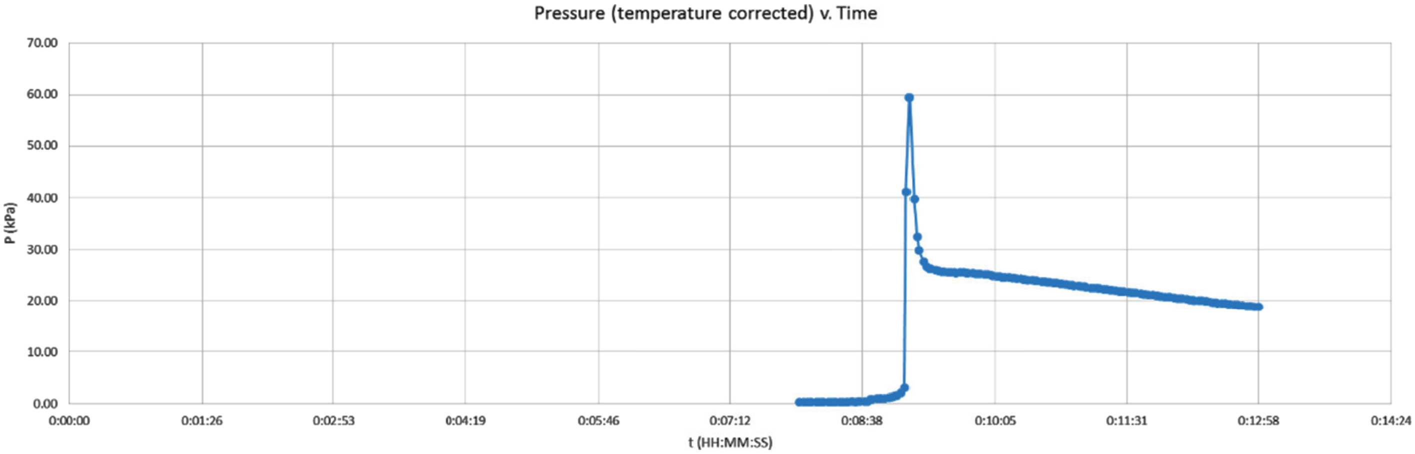

Figure A-26. Pressure vs. time when 1.31 g $POCl_3$ is combined with 2.0171 g water. In this reaction, though not obvious in this trace, a definite induction period was observed, after which a very rapid reaction was observed. For the 4 fastest seconds, the rate was ~ 2900 l/kg-min. The maximum pressure observed corresponds to ~ 261 cc of gas evolution, or ~ 42% of the theoretical yield. Note that, in this case, not all of the gas was reabsorbed by the reaction media; the starting water/$POCl_3$ ratio was ~13.

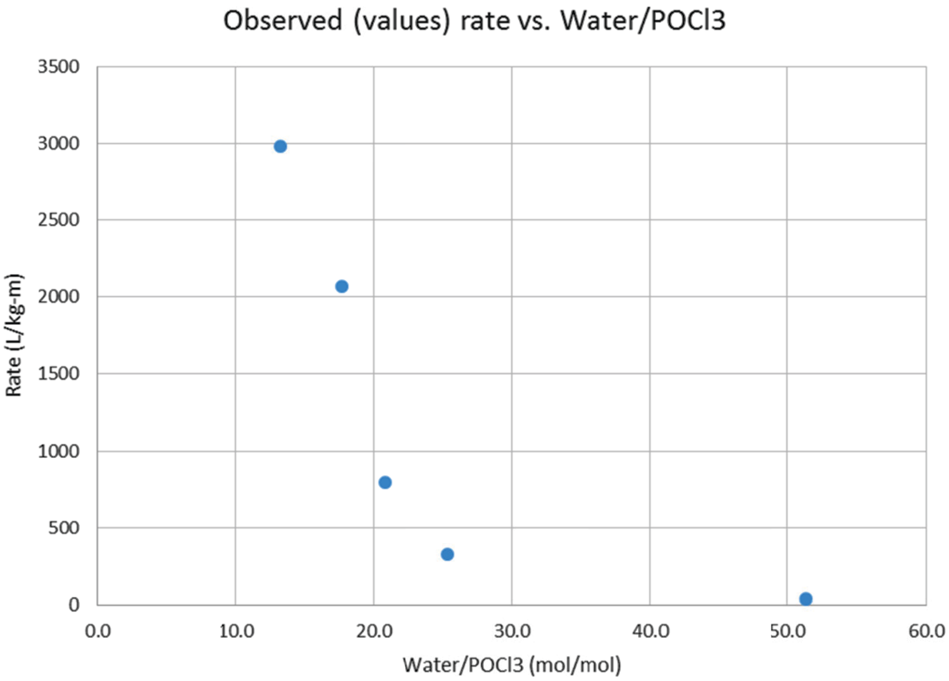

Figure A-27. Results from runs of the reaction of $POCl_3$ with water at room temperature as the water/$POCl_3$ ratio varies. This shows that the observed rate is strongly dependent on the water/$POCl_3$ ratio in this range.

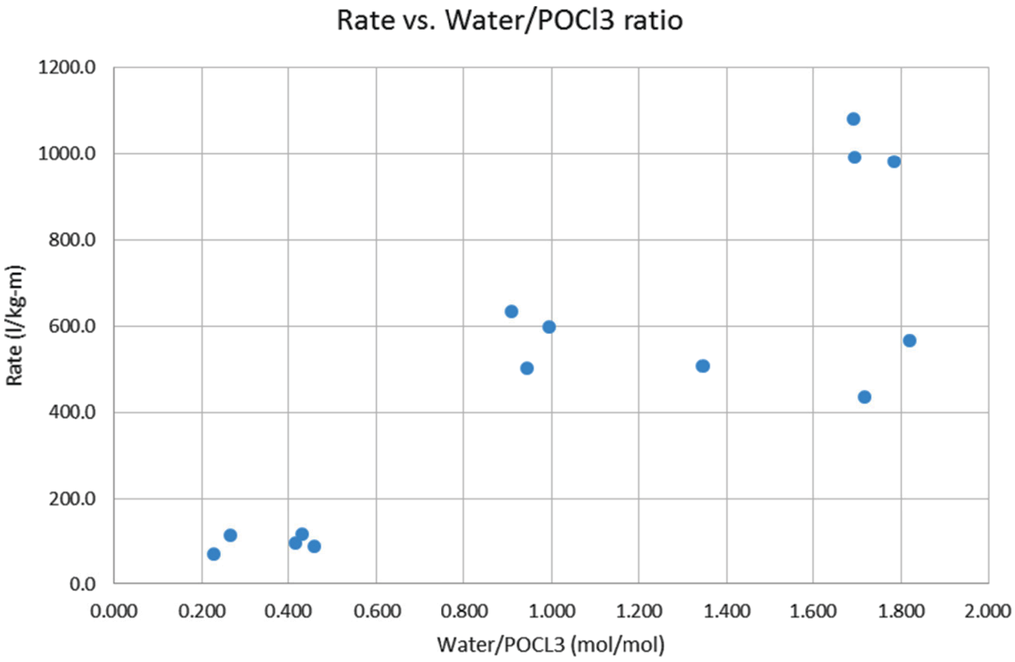

Figure A-28. Specific gas production rates, normalized to $POCl_3$ required for reaction, from the reaction of $POCl_3$ with water via Approach (B). As in Figure A-24, there is a strong dependence on water/$POCl_3$ ratio.

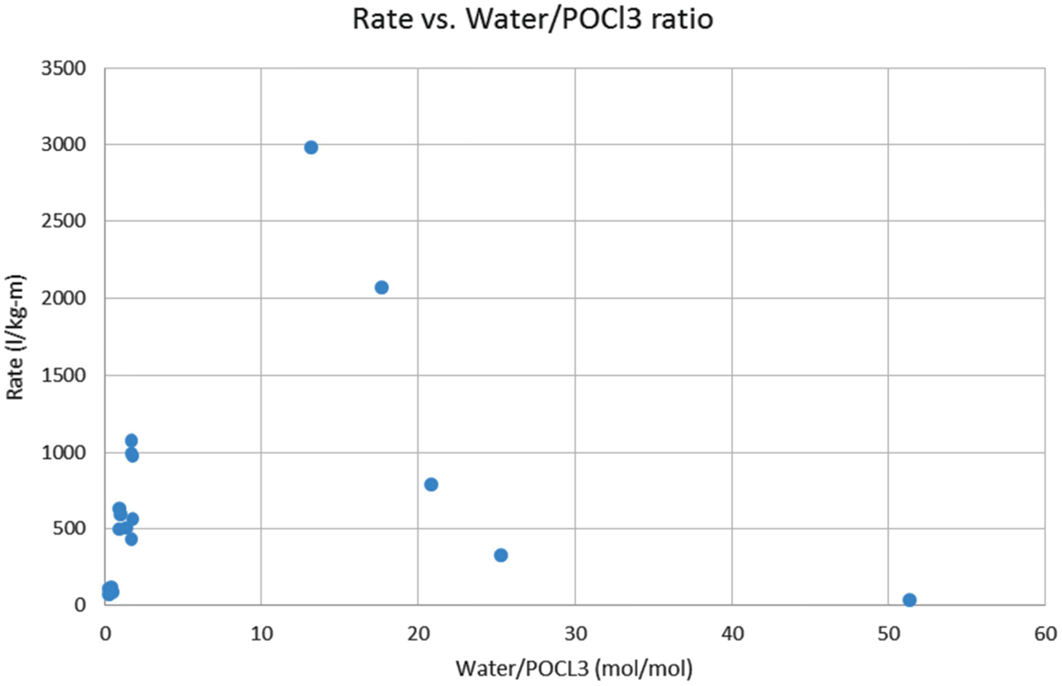

Figure A-29. This figure combines the results shown in Figures A-27 and A-28 for the reaction of $POCl_3$ with water at room temperature, comparing Approach (A) **(right portion)** ***with Approach (B)*** **(left portion)*****. This suggests that the rate of reaction between $POCl_3$ and water depends strongly on the water/$POCl_3$ ratio and peaks at or above 3000 l/kg-min.***

with water; complete hydrolysis proceeds (in principle) according to Equation (10).

$$SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl(g) \qquad (10)$$

This stoichiometry indicates that the potential for gas evolution from $SiCl_4$ is 570 l/kg_{SiCl4}, and that $SiCl_4$ is a water reactive material that produces a water soluble gas. This would suggest that ~ 0.25 g of $SiCl_4$ would yield ~ 140 cc of gas. Because this is a water-reactive material likely to produce a gas soluble in water, the right-hand portion of Figure A-7 applies, and a limited amount of water (e.g., 2.0 g) should be used for Approach (A). Note that with 0.25 g $SiCl_4$, 2.0 g water provides ~ 75 moles of water for each mole of $SiCl_4$, or nearly 20 times the amount required for Equation (10).

A reaction apparatus configured for liquid addition was assembled as shown in Figure A-4, center-left, the P/V calibration checked (as in Figure A-10, data indicated with dash-dot pattern), and a trial run with 0.2462 g $SiCl_4$ and 1.9868 g water. This showed very rapid immediate reaction, but a fairly modest yield of gas, so the amount of $SiCl_4$ was increased to ~ 0.6 g and replicate runs conducted.

Note that the behavior of $SiCl_4$ (i.e., in Figure A-30) is intermediate between that of $(CH_3)_2SiCl_2$ (Figure A-12) and $TiCl_4$ (Figure A-37). It shows a greater pressure increase than $(CH_3)_2SiCl_2$, though it is still only a low fraction of the expected amount (e.g., ~ 12% of theory at max gas production in Figure A-30). In part, the increase relative to $(CH_3)_2SiCl_2$ could be due to its lower boiling point (57.6 vs. 70 °C). It shows substantially slower reaction than $TiCl_4$ (Figure A-38), which also shows a larger fraction of theoretical gas evolution (~ 40%).

The observations noted above make it difficult to be certain that the gas evolution observed in Figure A-30, resulting in the measurements of Table A-8 and Figure A-31 are due to gas evolution from, or evaporation of, $SiCl_4$.

This makes $SiCl_4$ a candidate for testing via Approach (B). However, in this case, attempts to add water to $SiCl_4$ in a controlled fashion (i.e., ~ 0.50 g water to ~ 2.0 g $SiCl_4$) failed because the water was immediately encased by reaction products. Further, though reaction had obviously occurred, there was no strong evidence of a measurable amount of gas evolution.

This leaves no choice but to use the Approach (A) result of a specific rate of gas evolution of 1020 l/kg-hr with a relative sample standard deviation of 20%.

Example 7 (Repeat with Saltwater)—Silicon Tetrachloride (UN 1818)

Silicon tetrachloride was also selected for testing with saltwater (3.5% w/w NaCl in DI water) as well as DI water (preceding section). For the reasons noted in the final paragraph of the preceding section, this work used Approach (A).

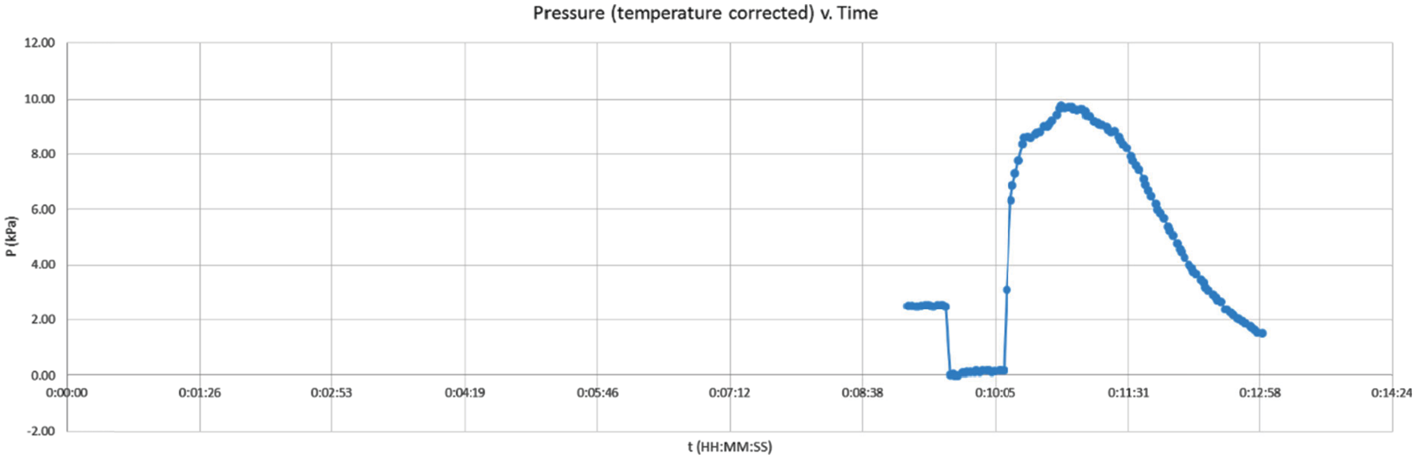

Figure A-30. Pressure vs. time for the reaction of 0.6126 g $SiCl_4$ with 2.0757 g water. The fastest reaction is observed over the first 4 seconds after the materials are combined and corresponds to a rate of 650 l/kg$_{SiCl4}$-min. The maximum pressure observed corresponds to 41 cc of gas evolution, or ~ 11% of the theoretical yield.

Table A-8. Results from tests with $SiCl_4$. Rates are based on the fastest period of gas evolution, (i.e., the first 4 seconds).

Mass $SiCl_4$	Mass Water	ΔP (Fastest)	ΔV	Rate	Water/ $SiCl_4$
g	g	kPa	cc	l/kg-min	mole/mole
0.2462	1.9868	3.82	17.8	1085	76.1
0.603	2.106	8.99	41.2	1025	32.9
0.6000	2.0598	9.81	46.2	1154	32.4
0.6110	2.0694	10.56	48.1	1181	31.9
0.6126	2.0757	6.15	26.6	651*	32.0

Average rate = 1020(210), 20% RSD.

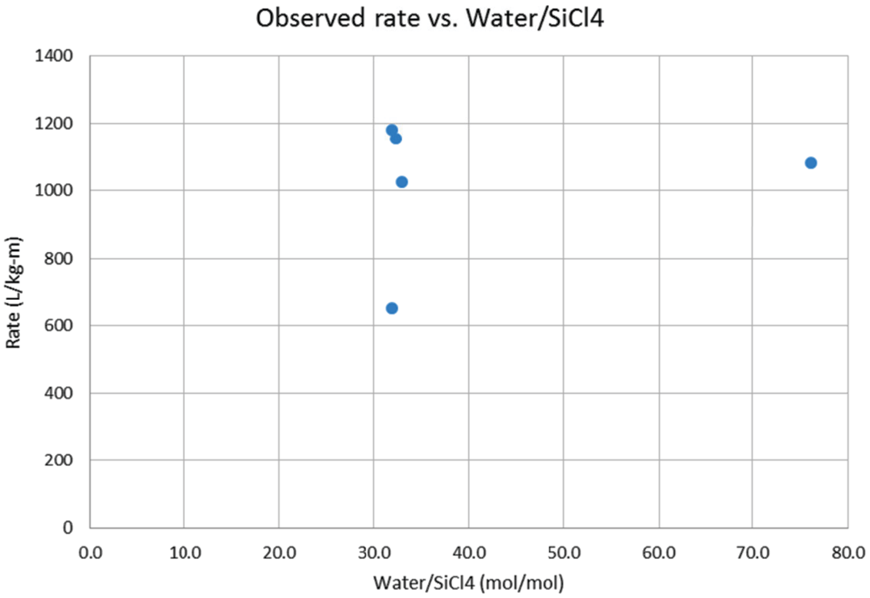

Figure A-31. Results from trial and replicate runs for the reaction of $SiCl_4$ with water at room temperature. This shows that the observed rate is not strongly dependent on the water/$SiCl_4$ ratio in this range, so all results can be pooled.

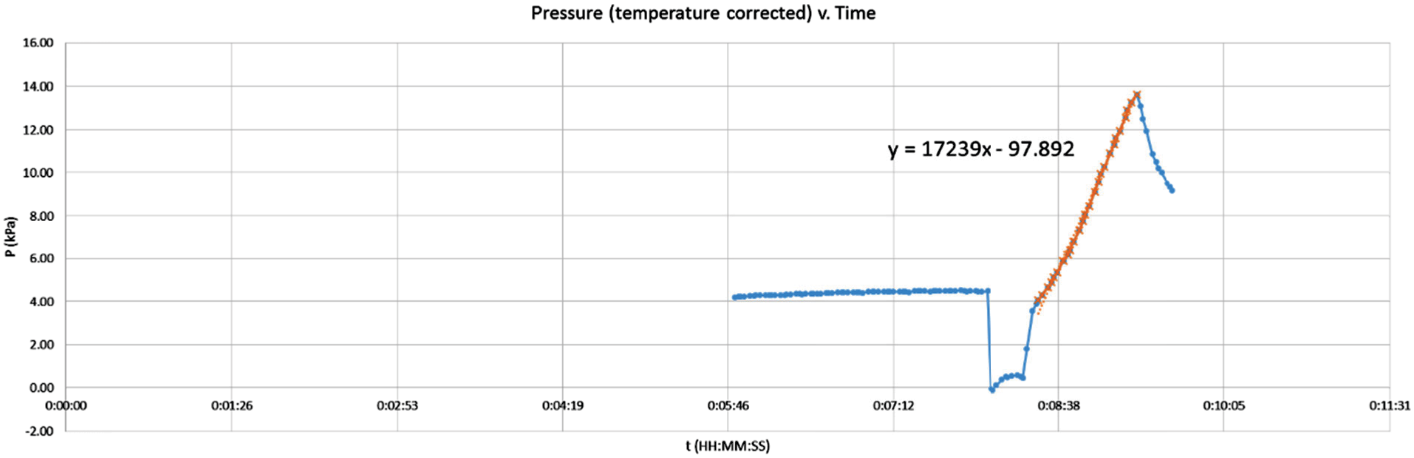

Figure A-32. Pressure vs. time for the reaction of 0.7036 g $SiCl_4$ with 2.1236 g saltwater. As with DI water, the fastest increase in pressure is observed over the first 4 seconds after the materials are combined and corresponds to a rate of 280 l/kg_{SiCl4}-min. However, that pressure increase is very modest (~ 3 kPa, corresponding to only ~ 13 cc of gas), and it is followed by a sustained period of pressure increase (gas production). That pressure increase (~ 10 kPa) production corresponds to ~ 43 cc of gas production at a rate of 17 l/kg-min.

Interestingly, the behavior of $SiCl_4$ with saltwater was (unlike acetyl chloride) qualitatively different than its behavior with DI water, as Figure A-32 illustrates.

It may be that, in this case, it is possible to differentiate between the initial rapid increase in pressure due to evaporation of $SiCl_4$ and a slower, sustained increase in pressure due to HCl (g) release, which either is produced more rapidly, or dissolves less rapidly, with saltwater.

Replicate runs showed the slower, sustained gas evolution to be occurring at an average specific gas production rate of 14 l/kg-min with a relative standard deviation of 40%, while the initial pressure surge corresponded to 300 l/kg-min with a relative standard deviation of 40%. The latter is substantially slower than the 1020 l/kg-min observed with DI water.

Example 8—Thionyl Chloride (UN 1836)

Thionyl chloride ($SOCl_2$, Sigma-Aldrich, >99%, UN 1836) was subjected to testing. It is known to react with water to yield HCl (g) and SO_2(g):

$$SOCl_2(l) + 2H_2O(l) \rightarrow SO_2(g) + 2HCl(g) \qquad (11)$$

This stoichiometry indicates that the potential for gas evolution from $SOCl_2$ is (3 moles/mole) ~ 607 l/kg_{SOCl2}, and that it is a water reactive material that produces water soluble gases. This would suggest that ~ 0.25 g of $SOCl_2$ would yield ~ 150 cc of gas. Because this is a water-reactive material likely to produce gases soluble in water, the right-hand portion of Figure A-7 applies, and a limited amount of water (e.g., 2.0 g) should be used. Note that with 0.25 g $SOCl_2$, 2.0 g water provides ~ 50 moles of water for each mole of $SOCl_2$, or > 25 times the amount required for Equation (11).

A reaction apparatus configured for liquid addition was assembled as shown in Figure A-4, center-left, the P/V calibration checked (as in Figure A-10, data indicated with dash-dot pattern), and the apparatus charged with 2.0263 g water. For the screening test, 0.2495 g $SOCl_2$ was added to the water all at once, with results shown in Figure A-33.

Replicate testing with Approach (A) yielded the results in Table A-9 and Figure A-34.

In this experiment, it is difficult to be certain that the pressure increase is due to gas evolution or simply evaporation of some of the $SOCl_2$ (b.p. 74.6 °C). Because of the uncertainty, Approach (B) was checked.

Figure A-35 shows the behavior observed with Approach (B). The results shown in Table A-10 strongly suggest that the actual rate should be measured with Approach (B).

From these results using Approach (B), it seems clear that the specific rate of gas production for $SOCl_2$ in contact with water is 370 l/kg-min, with a relative standard deviation of 30%.

Example 8 (Repeat with Saltwater)

Thionyl chloride was also selected for testing with saltwater (3.5% w/w NaCl in DI water) as well as DI water (preceding section). For the reasons noted in the preceding section, this work used Approach (B).

From these results (Figure A-36 and Table A-11) using Approach (B) with brine, the specific rate of gas production for $SOCl_2$ in contact with water is 210 l/kg-min with a relative standard deviation of 33%. This is a barely statistically significant difference ($p = 0.02$ in in Student's t-test) from the result with water (370(110) l/kg-min, 30% RSD).

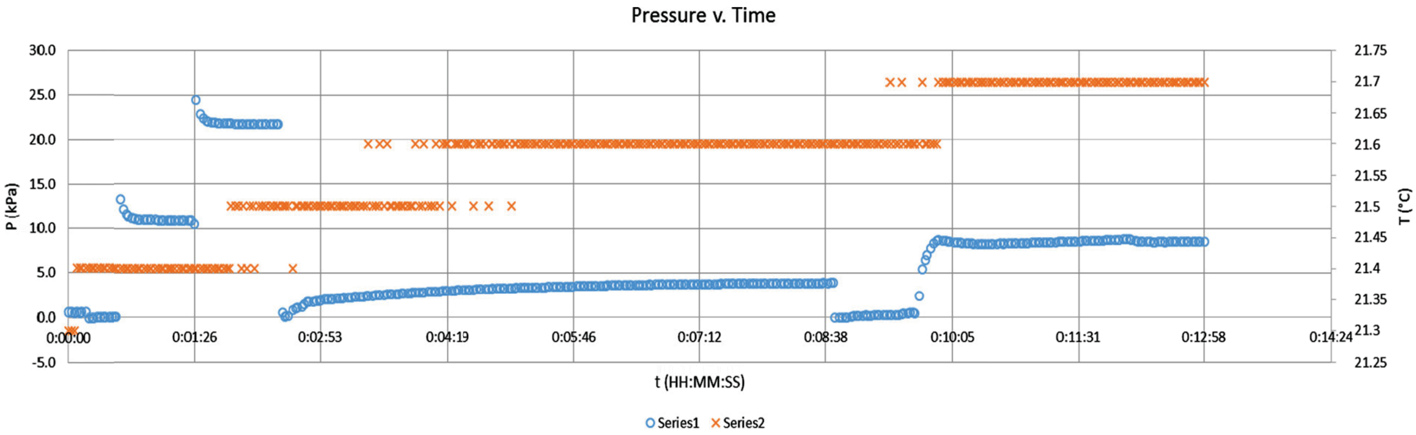

Figure A-33. Pressure vs. time for the reaction of 0.2495 g $SOCl_2$ with 2.0263 g water (observed pressure and temperature shown). Fairly rapid (within ~15 seconds) gas formation is observed. Observed gas formation amounted to ~ 37 cc of gas (~25% of theory). This corresponds to a (transient) gas evolution rate of ~1400 l/kg_{SOCl2}-min.

Table A-9. Results from tests with $SOCl_2$. Rates are based on the initial (4 seconds, maximum rate) gas evolution rate.

Mass $SOCl_2$	Mass Water	ΔP (Fastest)	ΔV	Rate	Water/$SOCl_2$
g	g	kPa	cc	l/kg-min	mole/mole
0.2495	2.0263	4.95	22.7	1366	53.6
0.5022	2.0491	13.09	57.6	1720	26.9
0.5142	2.0619	11.64	49.3	1438	26.5
0.5337	2.0582	8.91	41.1	1154	25.5
0.4849	2.063	7.98	35.3	1091	28.1

Average rate = 1350(250), 20% RSD.

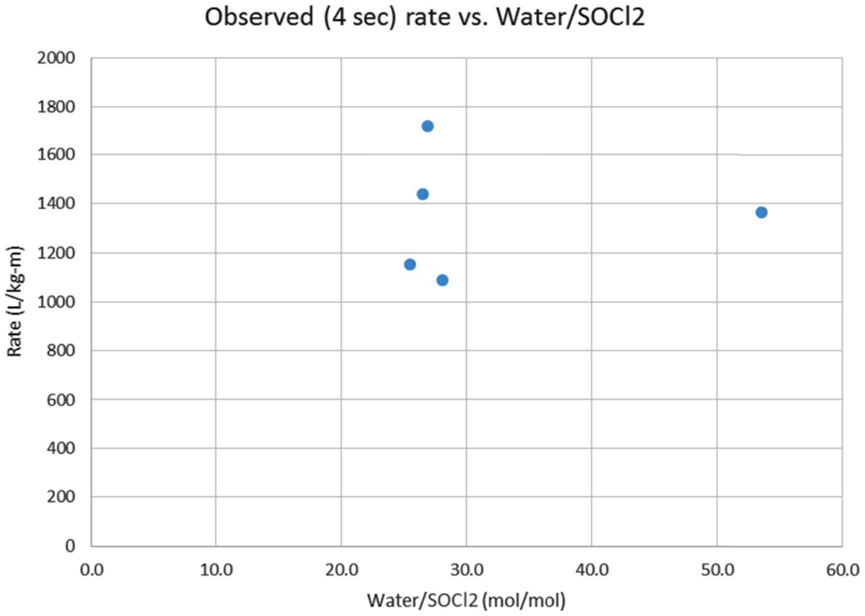

Figure A-34. Results from trial and replicate runs for the reaction of $SOCl_2$ with water at room temperature. This shows that the observed rate is not strongly dependent on the water/$SOCl_2$ ratio in this range, so all results can be pooled.

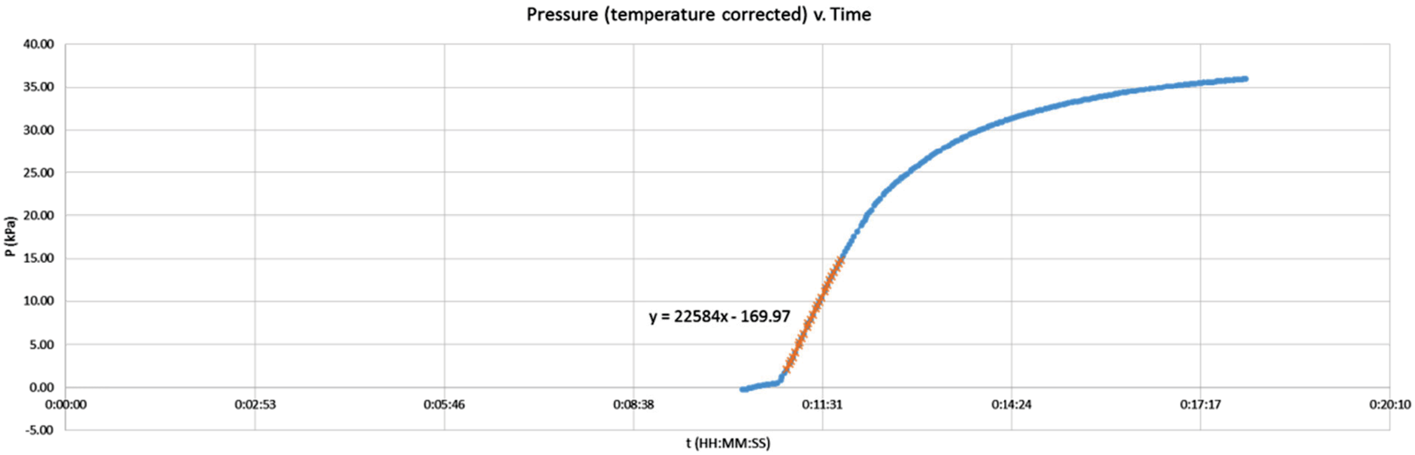

Figure A-35. Pressure vs. time for reaction of 0.0416 g water with 2.2269 g $SOCl_2$. Smooth reaction with gas formation is observed. Observed gas formation here amounted to ~ 160 cc of gas, which was 96% of theory. The line fitted to the steepest part of the curve yielded a specific gas evolution rate, based on $SOCl_2$ required for complete reaction, of 500 l/kg-min.

Table A-10. Results from tests with $SOCl_2$ using Approach (B).

Mass $SOCl_2$	Mass Water	V (total)	V (% of theory)	Rate	Rate	Water/ $SOCl_2$
g	g	cc		kPa/day	l/kg-min	mole/mole
2.0583	0.0307	122.1	99%	9584	306	0.10
2.2269	0.0416	159.7	96%	22584	502	0.12
2.3782	0.0322	125.8	97%	14089	400	0.09
2.3617	0.0319	126.9	99%	16087	493	0.09
1.1189	0.029	128.5	111%	6746	224	0.17
1.1663	0.0271	119.8	110%	9086	301	0.15

Average rate = 370(110), 30% RSD.

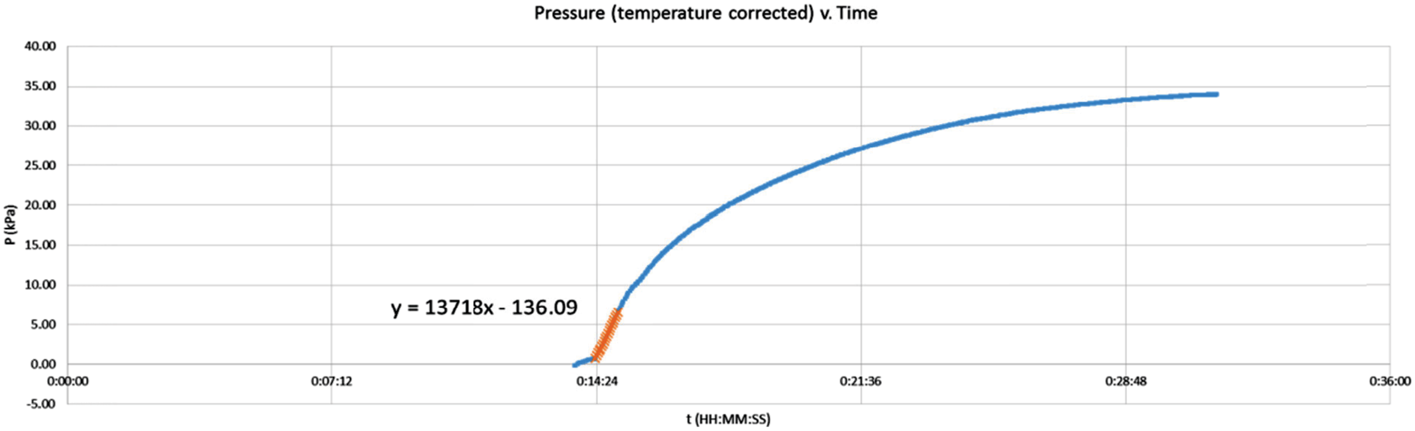

Figure A-36. Pressure vs. time for reaction of 0.0398 g brine (3.5% NaCl) with 2.109 g $SOCl_2$. Smooth reaction with gas formation is observed. Observed gas formation here amounted to ~ 150 cc of gas, which was 95% of theory. The line fitted to the steepest part of the curve yielded a specific gas evolution rate, based on $SOCl_2$ required for complete reaction, of 330 l/kg-min.

Table A-11. Results from tests with $SOCl_2$ using Approach (B) and brine (3.5% NaCl).

Mass $SOCl_2$	Mass Brine	V (total)	V (% of theory)	Rate	Rate	Water/ $SOCl_2$
g	g	cc		kPa/day	l/kg-min	mole/mole
2.109	0.0398	151.4	95%	13718	331	0.12
2.1869	0.038	140.8	92%	9128	221	0.11
2.1801	0.0425	156.7	92%	7344	153	0.13
2.0493	0.0405	148.0	91%	7592	179	0.13
2.0379	0.0309	118.2	95%	5388	167	0.10

Average rate = 210(70), 33% RSD.

Example 9—Titanium Tetrachloride (UN 1838)

Titanium tetrachloride ($TiCl_4$, Fluka, ≥99%, UN 1838) was subjected to testing. $TiCl_4$ is well known[11] to react vigorously with water; complete hydrolysis proceeds (in principle) according to Equation (12), though partial hydrolysis to oxyhalide species is often observed in practice.

$$TiCl_4(l) + 2H_2O(l) \rightarrow TiO_2(s) + 4HCl(g) \qquad (12)$$

This stoichiometry indicates that the potential for gas evolution from $TiCl_4$ is 510 l/kg_{TiCl4} and that $TiCl_4$ is a water reactive material that produces a water soluble gas. This would suggest that ~ 0.15 g of $TiCl_4$ would yield ~ 75 cc of gas. In principle, one could start with as much as 0.30 g $TiCl_4$ (~150 cc of gas formation anticipated), but as an extra precaution, initial runs with $TiCl_4$ used ~ 0.15 g. Because this is a water-reactive material likely to produce a gas soluble in water, the right-hand portion of Figure A-7 applies, and a limited amount of water (e.g., 2.0 g) should be used. Note that with 0.15 g $TiCl_4$, 2.0 g water provides ~ 140 moles of water for each mole of $TiCl_4$, or > 70 times the amount required for Equation (12).

A reaction apparatus configured for liquid addition was assembled as shown in Figure A-4, center-left, the P/V calibration checked (as shown in Figure A-10, data indicated with dash-dot pattern), and the apparatus charged with 2.0218 g water. For the screening test, 0.2638 g $TiCl_4$ was added to the water all at once, with results shown in Figure A-37.

Since this was well within the apparatus capacity, testing was scaled up to target 0.3 g $TiCl_4$ and then 0.5 g $TiCl_4$ with 2.0 g water and replicates run (see Table A-12 and Figure A-38). Because the amount of gas produced scaled up with increasing $TiCl_4$ charge, and the rate remained relatively constant (when normalized to $TiCl_4$ amount), it seems likely that this was due to actual gas production. Evaporation also generally does not proceed quite this quickly (though, see Example 8), nor yield quite this much gas.

Example 10—Magnesium Nitride (UN 3132)

Magnesium nitride (Mg_3N_2, Aldrich, 99.5%, UN 3132) was obtained and subjected to testing. Magnesium nitride is known[12] to react with water to release ammonia.

$$Mg_3N_2(s) + 6H_2O(l) \rightarrow 3Mg(OH)_2 + 2NH_3(g) \qquad (13)$$

Equation (13) indicates that the potential for gas evolution from Mg_3N_2 is ~ 480 l/kg_{Mg3N2}. This suggests that magnesium nitride is a solid water reactive material that produces a water soluble gas. Figure A-7 suggests that this material should be tested according to Approach (A), using the minimum required water. Preliminary experiments should be limited to ~ 0.25 g Mg_3N_2 (~120 cc gas evolution expected).

A reaction apparatus configured for solids addition was assembled as shown in Figure A-4, center-right and far-right, the P/V calibration checked (as in Figure A-10, data indicated with dash-dot pattern), and charged with 0.2281 g Mg_3N_2 and 2.0526 g water. The Mg_3N_2 was added to the water all at once, and the result shown in Figure A-39 observed.

As was the case for Examples 2 and 5, Mg_2N_2 has a negligible vapor pressure at room temperature, so the observed increase in pressure must be due to gas evolution. Since the observed increase was within the apparatus capacity, replicates were run (see Table A-13 and Figure A-40).

Discussion—Comparisons to Prior Results

A complete tabulation of the validation testing results is shown in Table A-14.

A more selective tabulation of the validation testing results, including only the "final" results, is shown in Table A-15.

The primary data available for comparison are the rate measurements made by personnel at Argonne National Labs (ANL) during and prior to 2007 in support of the 2008 and earlier editions of the Emergency Response Guidebook. Their

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[11] See, for instance, *Inorganic Chemistry*, Cotton, FA; Wilkinson, G; Murillo, CA; Bochmann, M, 1999, John Wiley & Sons, Inc., p. 699.

[12] See, for instance, http://en.wikipedia.org/wiki/Sodium_amide#Safety.

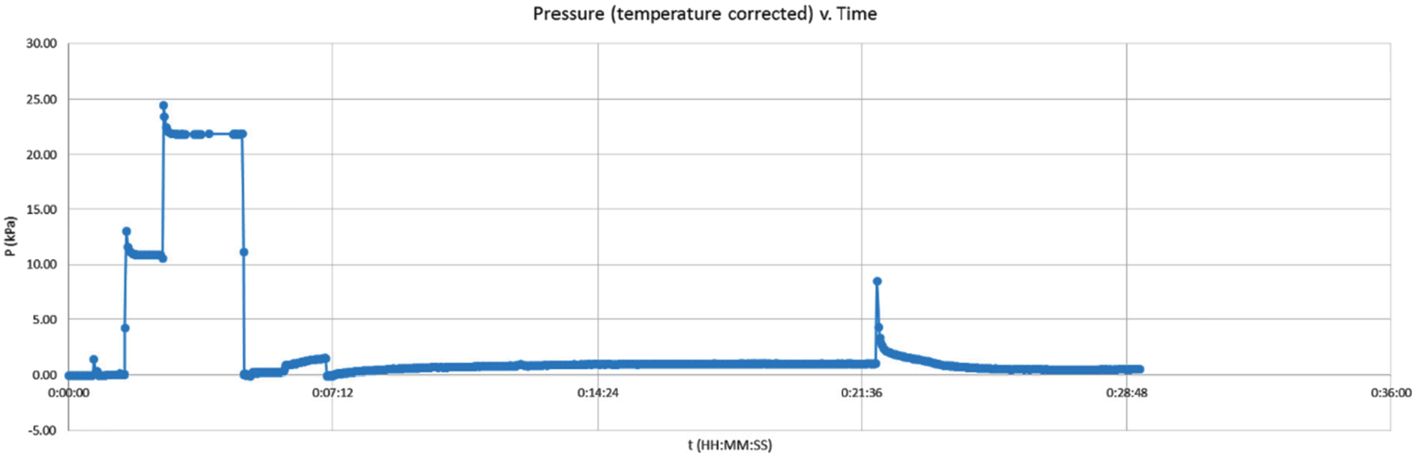

Figure A-37. Pressure vs. time for reaction of 0.1638 g $TiCl_4$ with 2.0218 g water. As in other examples, pressures are corrected for small temperature changes during the course of the reaction. Rapid (within 2 seconds) transient gas formation is observed (at around 21:40), but the gas formed is reabsorbed within ~ 2 minutes. The transient gas formation amounted to ~ 35 cc of gas (~40% of theory). This corresponds to a (transient) gas evolution rate of ~6400 l/kg$_{TiCl4}$-m.

Table A-12. Results from tests with $TiCl_4$. Rates are based on the maximum amount of gas observed (uniformly observed in 2 seconds).

Mass $TiCl_4$	Mass Water	ΔP (Fastest)	ΔV	Rate	Water/ $TiCl_4$
g	g	kPa	cc	l/kg-min	mole/mole
0.1638	2.0218	7.57	34.7	6364	130.0
0.3463	2.1076	10.36	48.4	4191	64.1
0.5420	2.0725	23.34	104.6	5788	40.3
0.5720	2.0725	21.01	94.8	4970	38.1
0.5783	2.1515	24.52	118.7	6157	39.2

Average rate = 5500(900), 16% RSD.

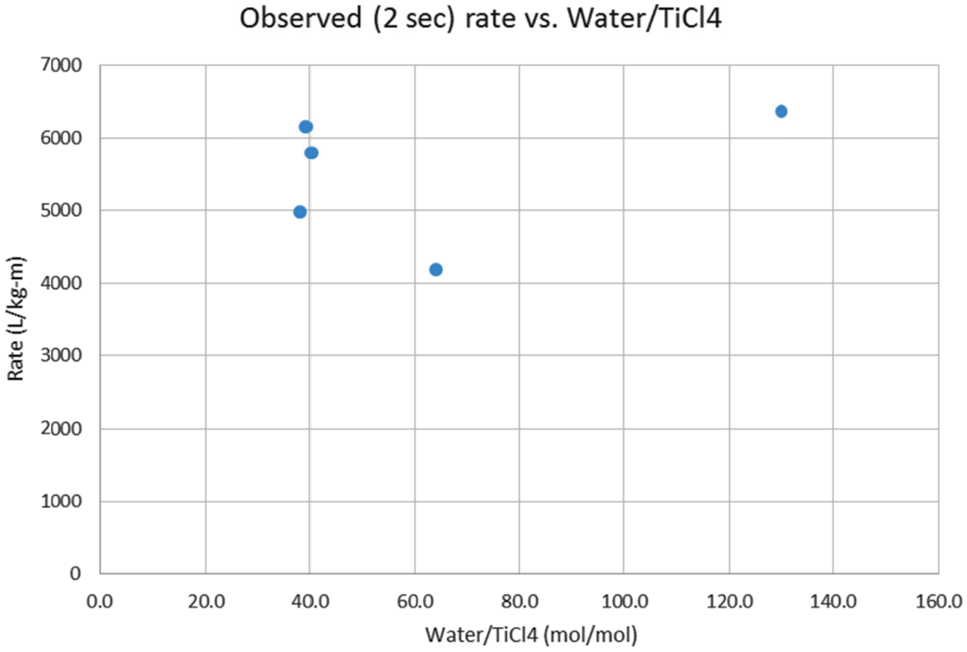

Figure A-38. Results from trial and replicate runs for the reaction of $TiCl_4$ with water at room temperature. This shows that the observed rate is not strongly dependent on the water/$TiCl_4$ ratio in this range, so all results can be pooled.

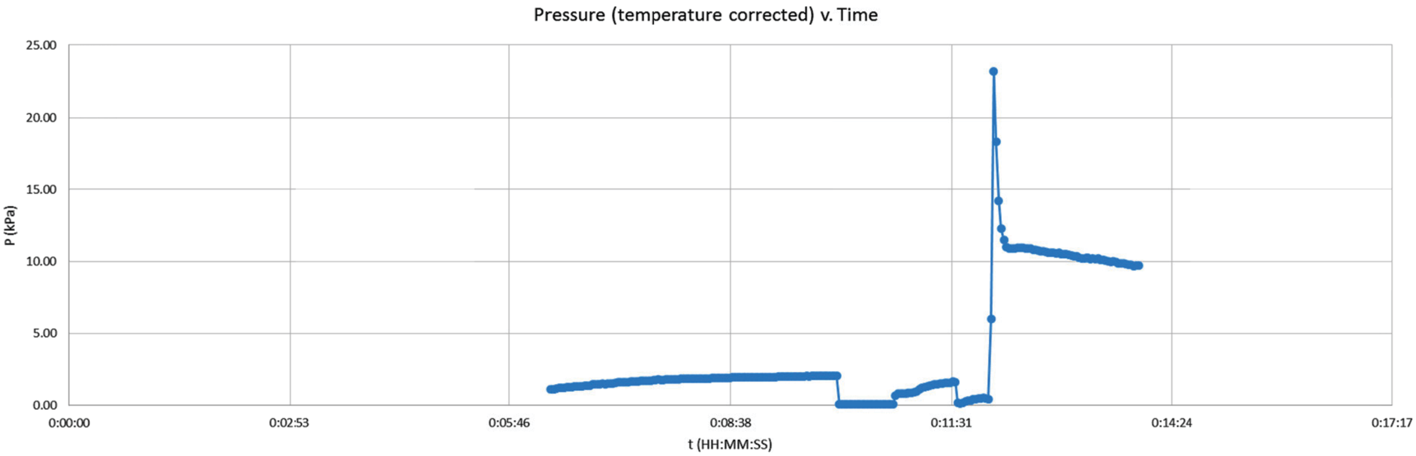

Figure A-39. Pressure vs. time for the reaction of 0.2281 g Mg_3N_2 with 2.0526 g water. Pressures reported are corrected via the ideal gas law for small temperature changes during the course of the reaction, to yield an isothermal-equivalent result. Transient gas formation is observed within the first 4-second interval; data points are separated by 2 seconds. Applying the P/V calibration for this apparatus, the transient gas formation amounted to ~ 104 cc of gas (~96% of theory). This corresponds to a (transient) gas evolution rate of ~6850 l/kg$_{Mg3N2}$-min.

Table A-13. Results from tests with Mg_3N_2. Rates are based on the maximum amount of gas observed (uniformly observed in 4 seconds).

Mass Mg_3N_2	Mass Water	ΔP (Fastest)	ΔV	Rate	Water/ Mg_3N_2
g	g	kPa	cc	l/kg-min	mole/mole
0.2400	2.0043	19.5	86.6	5406	46.8
0.2281	2.0526	22.8	104.0	6848	50.4
0.2114	2.0510	30.5	138.3	9816	54.4
0.2330	2.0689	30.6	139.6	8986	49.8
0.2206	2.1200	28.2	125.9	8579	53.8

Average rate = 7900(1800), 23% RSD.

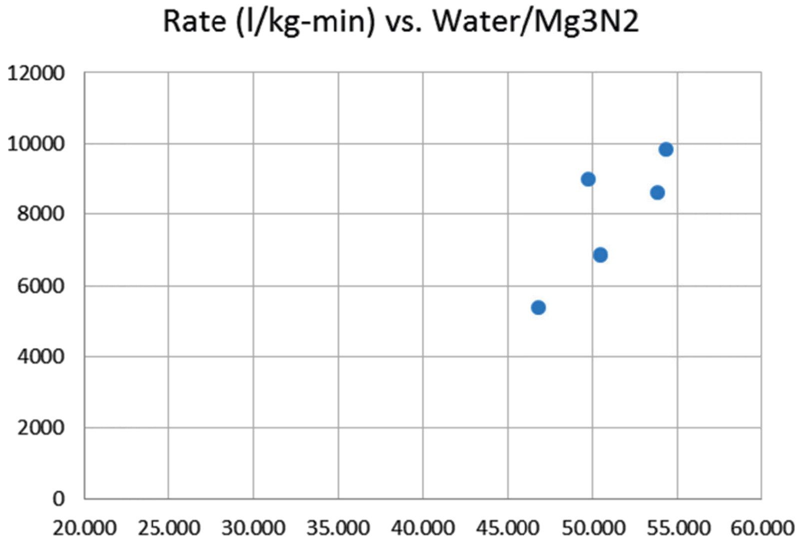

Figure A-40. Results from trial and replicate runs for the reaction of Mg_3N_2 with water at room temperature. This shows that the observed rate is not strongly dependent on the water/Mg_3N_2 ratio in this range, so all results can be pooled.

Table A-14. Complete validation testing results.

Material	Approach	Result (l/kg-min)	Std. Dev. (l/kg-min)	RSD	UN Number
$(CH_3)2SiCl_2$	B	36	8	22%	1162
$NaNH_2$	A	9600	2000	20%	1390
$NaBH_4$	A	2 (120 l/kg-h)	0.5 (30 l/kg-h)	25%	1426
CH_3COCl	A	620	180	30%	1717
CH_3COCl	B	665	60	9%	1717
CH_3COCl	B (saltwater)	790	95	12%	1717
$AlCl_3$	A	7500	1700	23%	1726
$POCl_3$	A, B	1-3000 (& up)	n/a	n/a	1810
$SiCl_4$	A	1020	210	20%	1818
$SiCl_4$	A (saltwater initial)	300	120	40%	1818
$SiCl_4$	A (saltwater steady)	14	6	40%	1818
$SOCl_2$	A (prob. evaporation)	1350	250	20%	1836
$SOCl_2$	B	370	110	30%	1836
$SOCl_2$	B (saltwater)	210	70	34%	1836
$TiCl_4$	A	5500	900	16%	1838
$Mg3N_2$	A	7900	1800	23%	3132

Approach: A = Substance added to water, B = water added to substance
(Salt) indicates a test that used saltwater (3.5% NaCl in DI water)

Table A-15. Selected final validation testing results.

Material	Approach	Result (l/kg-min)	Std. Dev. (l/kg-min)	RSD	UN Number
$(CH_3)2SiCl_2$	B	36	8	22%	1162
$NaNH_2$	A	9600	2000	20%	1390
$NaBH_4$	A	2 (120 l/kg-h)	0.5 (30 l/kg-h)	25%	1426
CH_3COCl	B	665	60	9%	1717
$AlCl_3$	A	7500	1700	23%	1726
$POCl_3$	A, B	1-3000 (& up)	n/a	n/a	1810
$SiCl_4$	A	1020	210	20%	1818
$SOCl_2$	B	370	110	30%	1836
$TiCl_4$	A	5500	900	16%	1838
$Mg3N_2$	A	7900	1800	23%	3132

Approach: A = Substance added to water, B = water added to substance

latest report was made in 2009.[13] Workers at ANL used an apparatus where small quantities of water-reactive materials/water-reactive substances could be combined either with stoichiometric amounts of water (ANL Method A) or 5:1 molar excess over the stoichiometric ratio of water: water-reactive material/water-reactive substance (ANL Method B).

In the 2007 ANL work, gas evolution was measured by the displacement of a lubricated syringe, and the evolution of gas vs. time fitted with a first order rate equation to arrive at parameters that described the reaction. These parameters were λ, a first order rate constant, and β, a ratio of the amount of gas evolution observed (Gas_{obs}) to that expected (Gas_{theory}). These, in principle,[14] can be used to model the progress of reaction ($Gas_{obs}(t)$) via the following equations:

Let $\varphi(t)$ ∫ extent of reaction (i.e., from 0.000 to 1.000, where 0.000 = no reaction and 1.000 = complete reaction), where t ∫ time since the start of reaction.

Then:

$$\varphi(t) = (1 - \exp(-\lambda t)), \text{ and} \tag{14}$$

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[13] See the report *Development of the Table of Initial Isolation and Protective Action Distances for the 2008 Emergency Response Guidebook* prepared by D. F. Brown, H. M. Hartmann, W. A. Freeman, and W. D. Haney. ANL/DIS-09-2. Currently available online at http://phmsa.dot.gov/staticfiles/PHMSA/DownloadableFiles/Files/Argonne_Report.pdf.

[14] i.e., to the extent that the parameters are accurate and that the reaction proceeds in a first order fashion, based on water-reactive materials/water-reactive substances.

$$\text{Gas}_{\text{obs}}(t) = \text{Gas}_{\text{theory}}\beta\varphi(t) = \text{Gas}_{\text{theory}}\beta(1-\exp(-\lambda t)) \qquad (15)$$

In making comparisons, it should be recalled that the rates shown in Tables A-14 and A-15 are observed *initial* rates of *gas production*, while the results from Argonne are parameters for an assumed (possibly, though not necessarily, correct) *rate law*. Equation (15) can be used to calculate the amount of gas expected to be formed at some time (t) and, from that, initial rates estimated for comparison. Because of the varying nature and time frame for the reactions, it is difficult to directly compare the parameters and their predictions to the results here in a general sense. Instead, it is best to consider the comparisons on a case-by-case basis.

Dimethyldichlorsilane ($[CH_3]_2SiCl_2$, UN 1162)

In the present work, Approach (B) (addition of water to water-reactive materials, from the present protocol) was used to test $(CH_3)_2SiCl_2$. Reactions were run with a mole ratio of between 0.3:1 and 1.5:1 (water:$[CH_3]_2SiCl_2$) and yielded an initial rate of 36 (8)[15] l/kg-min. Behavior was as shown in Figure A-13 (see Example 1).

The 2007 ANL work found behavior as shown in Figure A-41.[16]

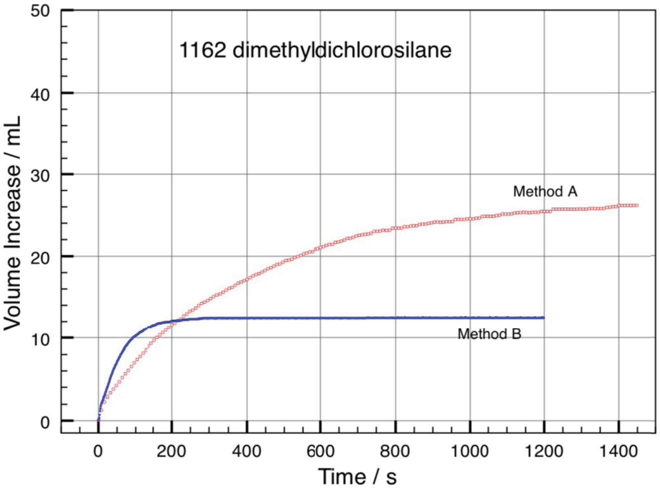

Figure A-41. Results from ANL for $(CH_3)_2SiCl_2$.

Qualitatively, the behavior apparent in Figure A-13 is comparable to that in Figure A-41.

The ANL workers reported values for λ and β of 0.93 min^{-1} and 0.25, respectively, for Method B, which used a 5:1 molar excess over the stoichiometric ratio of water: water-reactive material/water-reactive substance.

When comparing predictions from Equation (15) to results here, gas production needs to be compared for a similar point (i.e., the start) in the reaction and for a similar duration. Many of the tests here showed rapid initial rates and the determination of rates on a time frame of seconds. Given that, it seems reasonable to calculate the overall rate of gas evolution from the start of the 1st order reaction for a duration that matches the observations here.

For dimethyldichlorosilane, given the values for λ and β, Equation (15) predicts a rate of gas generation of 82 l/kg-min over the first 6 seconds. This is actually fairly good (i.e., < one order of magnitude in difference) agreement for kinetic data like these, acquired with different apparatus and conditions.

Acetyl Chloride (UN 1717)

In the present work, Approach (B) was found to be correct for acetyl chloride, and reactions were run with a mole ratio of between ~0.1:1.0 (water: acetyl chloride). These yielded an initial rate of 665 (60) l/kg-min (note that Approach (A) actually yielded very similar results, of ~620 (180) l/kg-min). Behavior with Approach (A) was as shown in Figure A-20 (see Example 4).

The 2007 ANL work found behavior as shown in Figure A-42.[17]

These results have a reasonable amount of similarity to the present results.

The ANL workers reported values for λ and β of 6.38 min^{-1} and 0.70, respectively, for both Method A and B results.[18] Since observed rates in this work were based on observations over the first 4–8 seconds of gas evolution, it seems appropriate to compare these predictions of gas production over the first 6 seconds of a 1st order reaction with these values for λ and β. This has been done, and it yields a predicted net rate of gas evolution for 6 seconds of ~ 1000 l/kg-min with an apparent extent of reaction of 33%. This is actually fairly good agreement with the results reported here, of ~660 (60) l/kg-min. Considering the different apparatus, methods of measuring rates, the intrinsically fast nature of the reaction, the rapid reabsorption of HCl(g), and the differing water: acetyl chloride ratios, this is an acceptable level of agreement.

Aluminum Chloride (UN 1726)

In the present work, reactions were run with mole ratios of ~ 30:1 to ~75:1 (water:$AlCl_3$) and showed results that did not depend strongly upon the water:$AlCl_3$ ratio (see Figure A-24, in

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[15] Parenthetical value is a sample standard deviation.

[16] As a work of the U.S. government, ANL/DIS-09-2 is in the public domain. Figure A-41 is reproduced from p. D-17 of that report.

[17] As a work of the U.S. government, ANL/DIS-09-2 is in the public domain. Figure A-42 is reproduced from p. D-34 of that report.

[18] See Table C.1 of ANL/DIS-09-2 (footnote 13).

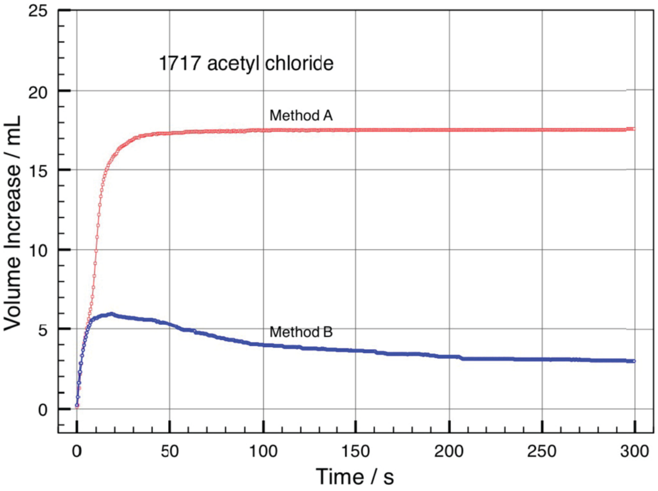

Figure A-42. Results from ANL for acetyl chloride.

Example 5). The rates observed were in the range of ~ 6000 to 10,000 l/kg-min, or 7500 (1700) l/kg-min. Typically, gas formation was transient, with rates based on 2 seconds of gas production, and ~ 55% was a typical maximum yield (see Figure A-23).

In the 2009 report, ANL workers reported values for λ and β of 30 min^{-1} and 0.20, respectively,[19] for both Method A (3 mmol water, 1 mmol $AlCl_3$) and Method B (15 mmol water, 1 mmol $AlCl_3$). Those results were based on experiments conducted during 1999 and reported in 2000.[20] These values are reported, even though the comments on the reaction stated that "Gaseous product did not appear."[21] While the 2009 report (see footnote 13) included graphs of gas production vs. time, the earlier work did not. Given the report of values for λ and β, and the observation of no (net?) gaseous product, it seems likely that the gas formation that led to the parameter values was transient—but this is not certain.

Taking the reported values for λ and β at face value, they predict gas evolution over the 1st 2 seconds (to be comparable to the observations here) at a rate of ~ 2000 l/kg-min (and ~ 15% apparent reaction, 60% actual extent of reaction)—this is again within order of magnitude agreement with the present results. As above, considering the different apparatus and methods and the nature of the reaction, this is an acceptable level of agreement.

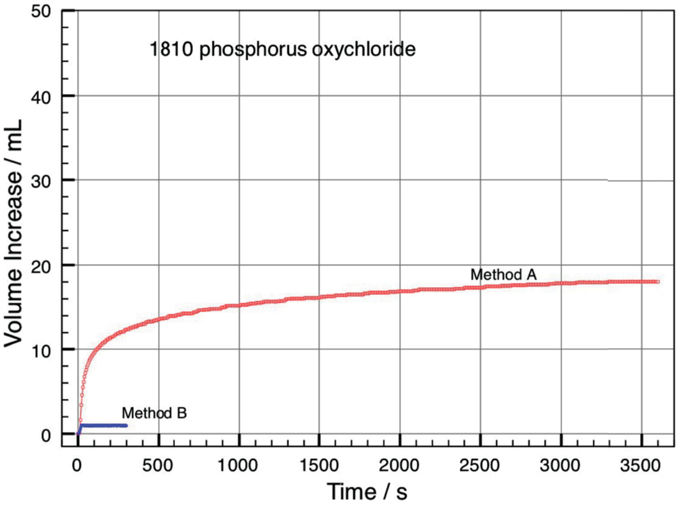

Figure A-43. Results from ANL for phosphoryl chloride.

Phosphoryl Chloride (UN 1810)

In the present work, reactions were run with a mole ratio of between 0.2:1 and 50:1 (water:$POCl_3$) and showed results that depended strongly upon the water/$POCl_3$ ratio (see Figure A-29). For most tests using Approach (A), reported in this work, reactions occurred over 4 seconds.

In the 2007 ANL work, behavior for $POCl_3$ was as shown in Figure A-43.[22]

The ANL workers reported values for λ and β of 6.0 min^{-1} and 0.23, respectively, based on the Method A result (3 mmol water, 1 mmol $POCl_3$). For Method B (15 mmol water, 1 mmol $POCl_3$), parameters could not be fit, and much less gas was observed. ANL workers also note that in their 2003 work the Method B experiment showed a transient spike of gas, followed by absorption of the gas.

Using the ANL values of for λ and β, from their Method A, and finding the gas evolution rate over the first 4 seconds of reaction gives a result of ~ 500 l/kg-min. When compared with the results shown in Figure A-28 (see Example 6) for water:$POCl_3$ mole ratios of ~ 1:1 (not quite the 3:1 of Method A, but close), the present results actually overlap with the prediction of 500 l/kg-min.

However, with higher water/$POCl_3$ ratios (e.g., 14–18 mol water/1 mole $POCl_3$, see Table A-7) that are not too far from the ANL Method B water:$POCl_3$ ratios (i.e., 15:1), the current test shows much faster gas evolution from $POCl_3$ and water (e.g., 2000–3000 l/kg-min).

Thus, on an equal conditions basis, the results from the present work agree with those of the ANL work; however,

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[19] See Table C.1 of ANL/DIS-09-2 (footnote 13).

[20] See the report *Development of the Table of Initial Isolation and Protective Action Distances for the 2000 Emergency Response Guidebook* prepared by D. F. Brown, A. J. Polcastro, W. E. Dunn, R. A. Carhart, M. Lazaro, W. A. Freeman, and M. Krumpolc. ANL/DIS-00-1. Currently available online at http://urbansurvivallibrary.com/uploads/Hazmat_Protective_Action_Distances.pdf.

[21] See p. 143 of ANL/DIS-00-1 (footnote 20).

[22] As a work of the U.S. government, ANL/DIS-09-2 is in the public domain. Figure A-43 is reproduced from p. D-65 of that report.

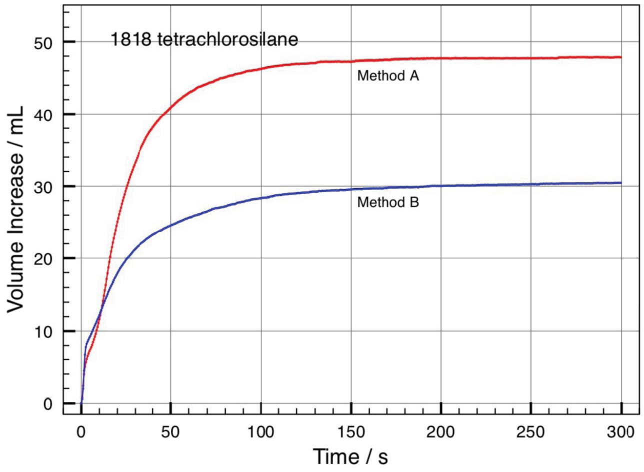

Figure A-44. Results from ANL for silicon tetrachloride.

the wider exploration of conditions here showed that higher rates are possible.

Silicon Tetrachloride (UN 1818)

In the present work, reactions were run with a mole ratio of (mainly) ~ 30:1 (water:$SiCl_4$) and showed results that did not depend strongly upon the water/$SiCl_4$ ratio (see Figure A-31). Most of the rates observed were in the range from 1,000 to 1,200 l/kg-min, though one result was ~ 600 l/kg-min; overall, 1000 (215) l/kg-min. Typically, gas formation was transient, and ~ 10% was the maximum yield (see Figure A-30).

In the 2007 ANL work, behavior for $SiCl_4$ was as shown in Figure A-44.[23]

The ANL workers reported values for λ and β of 1.81 min^{-1} and 0.30, respectively, based on the Method B result (10 mmol water, 1 mmol $SiCl_4$, which is 5 times the stoichiometric ratio), which had the conditions closest to those reported here.

Using the ANL values of for λ and β, from their Method B, and finding the gas evolution rate over the first 4 seconds of reaction gives a result of ~ 290 l/kg-min. When compared with the results in Table A-8 (see Example 7) for water:$SiCl_4$ mole ratios of ~ 30:1 (600–1,200 l/kg-min), there is again rough (order of magnitude) agreement. As for other materials discussed so far, considering the different apparatus and methods and the nature of the reaction, this is an acceptable level of agreement

Thionyl Chloride (UN 1836)

In the present work, under Approach (A) (see Example 8), reactions were run with mole ratios ~ 25:1 to 50:1 (water:$SOCl_2$) and showed results that did not depend strongly upon water/$SOCl_2$ ratio (see Figure A-34). The rates observed were in the range of 1,000 to 1,800 l/kg-min; 1,350 (250) l/kg-min. Typically, gas formation was rapid, occurring over ~20 seconds, and ~ 25% was a typical maximum yield (see Figure A-33). However, work with Approach (B) suggested that in Approach (A) the observed gas production rate was biased by evaporation of thionyl chloride. Approach (B) showed results more clearly due to reaction, in the range of 200–500 l/kg-min, with water limited.

The ANL workers reported values for λ and β of 2.75 min^{-1} and 1.00, respectively, for both Method A (2 mmol water, 1 mmol $SOCl_2$) and Method B (10 mmol water, 1 mmol $SOCl_2$) That result is based on experiments conducted in prior exercises (1999) and reported in 2005.[24] Method A achieved 100% of the theoretical yield of gas after 5 minutes, and Method B after 2 minutes.

Using the reported values of λ and β for Method B, as before, predicts an initial (6 seconds) rate of ~ 1,500 l/kg-min. The present work suggests that this rate may be biased by gas formation from evaporation of thionyl chloride and that the actual rate of gas production from reaction with water is somewhat lower.

Titanium Tetrachloride (UN 1838)

In the present work, reactions were run with mole ratios ~ 40:1 to 140:1 (water:$TiCl_4$) and showed results that did not depend strongly upon water/$TiCl_4$ ratio (see Figure A-38). The rates observed were in the range of 4,000 to 6,500 l/kg-min; 5,500 (900) l/kg-min. Typically, gas formation was transient, occurring over 2 seconds, and ~ 40% was a typical maximum yield (see Figure A-37, in Example 9).

The ANL workers reported values for λ and β of 1.35 min^{-1} and 0.13, respectively, for the Method B result (10 mmol water, 1 mmol $TiCl_4$) and 1.35 min^{-1} and 0.20 for the Method A result (2 mmol water, 1 mmol $TiCl_4$). Those results were based on experiments conducted in prior exercises (1999, 2003), and reported in 2005.[25] In that work, it was reported that for Method A the water was immediately covered with a crust and that for Method B there was a peak of gas production followed by absorption.

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[23] As a work of the US government, ANL/DIS-09-2 is in the public domain. Figure A-44 is reproduced from p. D-69 of that report.

[24] See the report *Development of the Table of Initial Isolation and Protective Action Distances for the 2004 Emergency Response Guidebook* prepared by D. F. Brown, W. A. Freeman, R. A. Carhart, and M. Krumpolc. ANL/DIS-05-2. Currently available online at http://www.ipd.anl.gov/anlpubs/2005/09/53554.pdf.

[25] See the report *Development of the Table of Initial Isolation and Protective Action Distances for the 2004 Emergency Response Guidebook* prepared by D. F. Brown, W. A. Freeman, R. A. Carhart, and M. Krumpolc. ANL/DIS-05-2. Currently available online at http://www.ipd.anl.gov/anlpubs/2005/09/53554.pdf.

Those observations are in qualitative agreement with the present work and, using the reported values of λ and β for Method B as before, predict ~ 90 l/kg-min as the rate of gas formation for the first 2 seconds of reaction. This represents poorer agreement between the ANL work and present work than for most of the other materials for which comparison is possible.

Summary of Comparisons

Overall, the comparison between the present work and the prior ANL work shows generally good agreement:

- For $(CH_3)_2SiCl_2$ the present work suggests a rate of 36 (8) l/kg-min. ANL workers reported qualitatively similar results and suggested that an initial rate of gas generation would be ~ 80 l/kg-min.
- For acetyl chloride, the present work suggests a rate of 665 (60) l/kg-min. ANL workers reported qualitatively similar results and suggested that an initial rate of gas generation would be ~ 1000 l/kg-min.
- For $AlCl_3$, the present work suggests a rate of 7,500 (1,700) l/kg-min. ANL workers appear to report qualitatively similar results, suggesting that an initial rate of gas generation would be ~ 2000 l/kg-min.
- For $POCl_3$, the present work suggests a rate that depends strongly on water/$POCl_3$ ratio and which can be as high as 2,000–3,000 l/kg-min, or possibly more. The ANL work appears to share some of this character, with their Method A and B results differing. The parameters reported there suggest an initial rate of gas generation of ~ 500 l/kg-min, which actually is in agreement with observations under similar conditions in the present work, but which is also somewhat lower than the highest rate observed here.
- For $SiCl_4$, the present work suggests a rate of ~1,000 (200) l/kg-min. ANL workers appear to report qualitatively similar results, suggesting that an initial rate of gas generation would be ~ 300 l/kg-min.
- For $SOCl_2$, the present work suggests a rate of ~ 370 (110) l/kg-min. ANL workers appear to report higher results, which this work suggests were influenced by gas from the evaporation of $SOCl_2$.
- For $TiCl_4$, the present work suggests a rate of 5,500 (900) l/kg-min. ANL workers appear to report qualitatively similar results, but suggest a much lower initial rate of gas generation of ~ 90 l/kg-min. Possibly, this was due to poor mixing in their work, where "crust" formation was reported.

The generally good agreement between the results begs the question: "Should the ANL approach be considered as a test methodology?"

The answer to that question is, in principle, "Yes." However, the HMCRP Project HM-14 team thought that the method outlined in this appendix had several advantages. These include the following:

- Easy acquisition of data with a commercial, off-the-shelf pressure/temperature transducer.
- Easy calibration of the P/V response via additions of known volumes of gas, without concern about the force needed to displace the syringe or "whiplash" in the syringe displacement.
- Ability with Approach (A) to use larger molar excesses of water than the 5:1 ratio used in the ANL work.
- Ability to vary the relative amounts of water and test material used.
- Ease of achieving a leak-tight apparatus by eliminating the presence of tubing.

APPENDIX B

Proposed Classification System

This appendix provides a starting point proposal for discussion of a system that could be used to classify water-reactive substances for transport.

Candidate Classification System

Classification of Substances as Water Reactive

This classification would apply to substances that in contact with water emit flammable or toxic gases during testing, as outlined in Appendix C of this report:

1. Spontaneous ignition of the emitted gas takes place in any step of the test procedure;
2. There is evolution of a flammable gas at a specific rate of gas evolution greater than 1 l/kg-hr; or
3. There is evolution of a toxic gas with an LC_{50} (based on testing with albino rats and 1 hour exposure) less than 5000 ml/m^3 (ppm) at a specific rate of gas evolution greater than 1 l/kg-hr.

Categorization into Subgroups—Substances Evolving Flammable Gases

Substances should be categorized as subgroup I (most hazardous) should they be found to react vigorously with water at ambient temperatures and demonstrate generally a tendency for the gas produced to ignite spontaneously, or should testing measure a specific rate of flammable gas evolution at ambient temperatures equal to or greater than 10 l/kg-min.

Substances should be categorized as subgroup II (moderately hazardous) should testing measure a specific rate of flammable gas evolution at ambient temperatures equal to or greater than 20 l/kg-hr and if the substance does not otherwise qualify for subgroup I.

Substances should be categorized as subgroup III (least hazardous) should testing measure a specific rate of flammable gas evolution at ambient temperatures equal to or greater than 1 l/kg-hr and if the substance does not meet the criteria for subgroups I or II.

Categorization into Subgroups—Substances Evolving Toxic Gases

Substances should be categorized as subgroup I (most hazardous) should testing measure a specific rate of toxic gas evolution at ambient temperatures equal to or greater than 1 l/kg-hr, when the gas produced would be classified as a Division 2.3 toxic gas according to sub-section 2.2.2.1(b) of the *UN Model Regulations* or is already listed as a Division 2.3 substance in the Dangerous Goods List of Chapter 2.3 of the *UN Model Regulations*, and when the ratio of the LC_{50} (based on testing with albino rats and 1-hour exposure) in units of ml/m^3 (ppm) to the specific rate of toxic gas evolution in units of l/kg-hr is less than or equal to 1 (see Figure B-1).

Substances should be categorized as subgroup II (moderately hazardous) should testing measure a specific rate of toxic gas evolution at ambient temperatures equal to or greater than 1 l/kg-hr, when the gas produced would be classified as a Division 2.3 toxic gas according to sub-section 2.2.2.1(b) of the *UN Model Regulations* or is already listed as a Division 2.3 substance in the Dangerous Goods List of Chapter 2.3 of the *UN Model Regulations*, and when the ratio of the LC_{50} (based on testing with albino rats and 1-hour exposure) in units of ml/m^3 (ppm) to the specific rate of toxic gas evolution in units of l/kg-hr is less than or equal to 20, and when the substance does not otherwise meet the criteria for subgroup I (see Figure B-1).

Substances should be categorized as subgroup III (least hazardous) should testing measure a specific rate of toxic gas evolution at ambient temperatures equal to or greater than 1 l/kg-hr, when the gas produced would be classified as a Division 2.3 toxic gas according to sub-section 2.2.2.1(b) of the *UN Model Regulations* or is already listed as a Division 2.3 substance in the Dangerous Goods List of Chapter 2.3 of the *UN Model Regulations*, and when the substance does not otherwise meet the criteria for subgroups I or II (see also Figure B1).

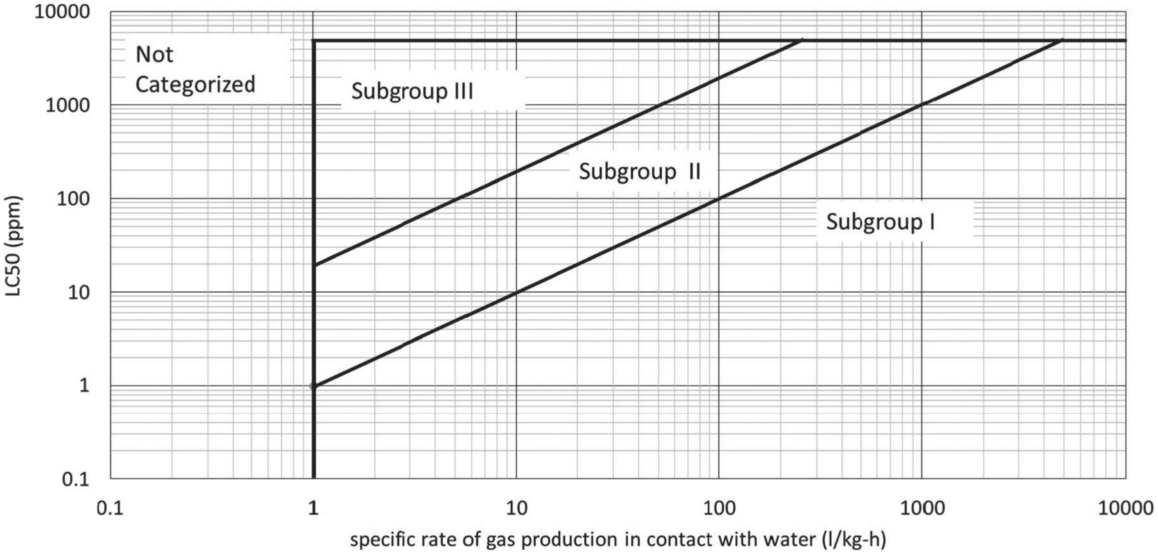


Figure B-1. Chart illustrating the categorization of substances that in contact with water emit toxic gases.

APPENDIX C

ASTM Format Test Procedure

This appendix provides a test procedure for measuring the specific rate of gas production on contact with water for water-reactive substances, cast in a format that corresponds to that expected for draft (still in committee) ASTM procedures.

Standard Test Method for
Characterization and Classification of Water Reactive Substances That Produce Flammable Gas or Toxic Gas on Contact with Water

1. Scope

1.1 This test method describes the determination of the rate at which flammable gas or toxic gas is produced when a substance is combined with water under laboratory conditions in a closed vessel by monitoring the change in pressure as a function of time after the substance and water are mixed. Pressure changes are converted to changes in volume by applying a calibration curve relating change in pressure within the apparatus to amounts of gas (as measured at ambient laboratory conditions) added to the vessel.

1.2 This test method is applicable to solid or liquid substances that react with water to produce gas at specific rates of gas production equal to or greater than 1 (one) liter per kg of substance per hour.

1.3 Units — The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D1193 Specification for Reagent Water

E2586-13 Standard Practice for Calculating and Using Basic Statistics

E681-09 Standard Test Method for Concentration Limits of Flammability of Chemicals (Vapors and Gases) [Note, for international purposes this should be replaced by ISO 10156:2010]

3. Terminology

3.1 *Definitions:*

3.1.1 *competent authority: n*—a person or organization that has the legally delegated or invested authority, capacity, or power to define a property or set a regulation for a political or geographic region.

3.1.2 *flammable gas: n*—a gas which, at 20 °C and a standard pressure of 101.3 kPa is: (a) ignitable when in a mixture of 13% or less by volume with air; or (b) has a flammable range with air of at least 12 percentage points regardless of the lower flammability limit. Flammability shall be determined by tests or by calculation in accordance with methods adopted by ISO (see ISO 10156:2010; corresponding to ASTM E681-09). Where insufficient data are available to use these methods, tests by a comparable method recognized by a competent authority may be used.

3.1.3 *gas: n*—a substance which (a) at 50 °C has a vapor pressure greater than 300 kPa; or (b) is completely gaseous at 20 °C at a standard pressure of 101.3 kPa.

3.1.4 *LC_{50}: n*—the concentration of vapor, mist or dust which, administered by continuous inhalation to both male and female young adult albino rats for one hour, is most likely to cause death within14 days in one half of the animals tested.

3.1.5 *toxic gas: n*—a gas which is (a) known to be so toxic or corrosive to humans as to pose a hazard to health; or (b) presumed to be toxic or corrosive to humans because it has an LC_{50} value equal to or less than 5,000 cm^3/m^3 (ppm).

3.1.6 *water-reactive substance: n*—a substance that reacts with water to product a toxic or a flammable gas at a specific rate of gas production equal to or greater than 1 (one) liter per kg of substance per hour.

4. Summary of Test Method

4.1 The test procedure encompasses the following steps:

4.1.1 The apparatus is charged with water (Method A), or for some substances (determined by test), with the test substance (Method B).

4.1.2 The pressure/volume response and calibration of the apparatus is determined.

4.1.3 The apparatus is then charged with the test substance in Method A, or for some substances water (as determined by test, see 4.1.1) in Method B, and test substance and water within it combined.

4.1.4 The pressure produced as any reaction proceeds is measured as a function of time.

4.1.5 The pressure vs. time results are converted to a specific rate of gas production (liters of gas per kg of substance reacting per hour or per minute), utilizing the pressure/volume response calibration of 4.1.2.

4.1.6 The testing of 4.1.1 through 4.1.5, except for 4.1.2, is repeated to obtain a total of 5 results, which are then averaged to yield a final result, sample standard deviation, and coefficient of variation.

5. Significance and Use

5.1 During commercial transport of reactive chemicals, small but finite chances for leaks and spills exist, and in many cases the spilled chemicals may encounter water. For substances that may react with water to produce flammable gases or toxic gases, it is therefore important to understand the rate at which those gases may be produced, for purposes of understanding and managing the attendant risks during transport.

5.1.1 This test, therefore, is used to make a quantitative measurement of the rate of gas production; this makes it possible to evaluate the relative risks of various substances in transit, and properly plan for emergency response.

5.1.2 The results from this test are generally useful for this application, in that the result is a rate that represents both the highest observed rate and a rate of gas production that is normalized to the amount of substance—it therefore is valuable in understanding outcomes as a function of the size of any possible spill.

5.1.3 Because this test provides a specific rate of gas production, under very specific conditions its utility may be limited. However, this is necessary to ensure that the results allow an equitable comparison of different substances. There are necessarily limitations on the ability to extrapolate from these test results to outcomes in the field.

5.1.4 As a result, the use of these test results should be primarily for identifying the *relative* reactivity of these substances. This assessment of relative reactivity may then be considered within assessments of the potential risk of spills involving these substances, but it should not form the only basis for this assessment; many other factors may also need to be considered. Utilization of these test results for modeling or predicting outcomes within spill scenarios can be considered, but that is a secondary, and less certain, application than the assessment of relative reactivity.

6. Apparatus

6.1 The apparatus used in this test method is illustrated by the schematic diagram of Fig. 1. Materials and configurations other than those stipulated here may be used, so long as they achieve comparable performance and meet the performance stipulations of 6.2. Key elements of the apparatus include:

6.1.1 A reaction vessel. This will typically be a custom fabricated glass vessel, such as that illustrated in Fig. 2, with two standard size threaded fittings which can reliably form hermetic seals, and a third standard taper ground-glass joint. A convenient size is based on a 250 ml "blank," heavy walled glass flask, which yields an apparatus of ~ 400 cm^3 total internal volume.

Note 1: Glass may not be suitable for use in systems where HF or fluoride ions are present.

6.1.2 Closures and adapters to fit the standard size threaded fittings and the standard taper ground-glass joint; solid plug types, as well as types that accept threaded fittings, and "thermometer adapter" types should be available. The thermometer adapter types should further accept rubber septa while maintaining a hermetic seal, even after one or more small punctures of the septum. Examples are shown in Fig. 3. Rubber, elastomer, and plastic components (such as o-rings, septa, and fittings) must be suitable for and compatible with the materials under test and the gases likely to be formed.

6.1.3 An arrangement that allows pre-charged solid substances to be kept separate from water in the main reaction vessel until they are deliberately and suddenly combined, maintaining vessel integrity against gas leaks throughout. An example arrangement is shown in Fig. 4.

6.1.4 A PTFE coated magnetic stirring bar to provide agitation within the reaction vessel.

6.1.5 A magnetic stirring apparatus to spin the magnetic stirring bar during reaction.

6.1.6 A pressure transducer, reporting both pressure and temperature; with a resolution of 0.1 kPa and 0.1 °C, or better.

6.1.7 A data acquisition system for recording the pressure and temperature outputs at intervals of 2 seconds.

6.1.8 Gas-tight syringes of a convenient size for the pressure/volume calibration of 4.1.2, and precision liquid syringes of convenient sizes for adding water and liquid substances to the reaction apparatus.

6.2 Regardless of the specific components used, the apparatus must:

6.2.1 Be gas tight and capable of safely withstanding internal pressures of at least 50 kPa gauge.

6.2.2 Allow for the safe combination of water with a water-reactive substance; provisions for this must include, but are not limited to, pressure relief of the apparatus at a pressure above 50 kPa gauge yet safely below a pressure at which the vessel might rupture. Appropriate personal protective equipment for laboratory personnel and an appropriate laboratory workspace to house the apparatus including fume hoods, proper hazard communication procedures for laboratory personnel, and supervision and operation by qualified personnel.

6.2.3 Accommodate addition of the substance to water as well as, when required, the reverse order of addition.

6.2.4 Be capable of use with both solid and liquid substances.

6.2.5 Include accurate and precise monitoring of pressure as a function of time during testing, preferably using electronic data logging at intervals as short as 2 seconds, with a pressure resolution greater than 0.1 kPa.

6.2.6 Accommodate calibration of the response of pressure to the volume of gas added to or produced within the apparatus to provide for conversion from observed pressure increases with the apparatus to volume of (as measured at ambient conditions of temperature and pressure) gas added to or produced within the apparatus (this may, for instance, be accomplished via the addition of known aliquots of gas at ambient pressure).

6.2.7 Allow, when the reactivity of the test substance warrants, for testing to occur under an inert atmosphere.

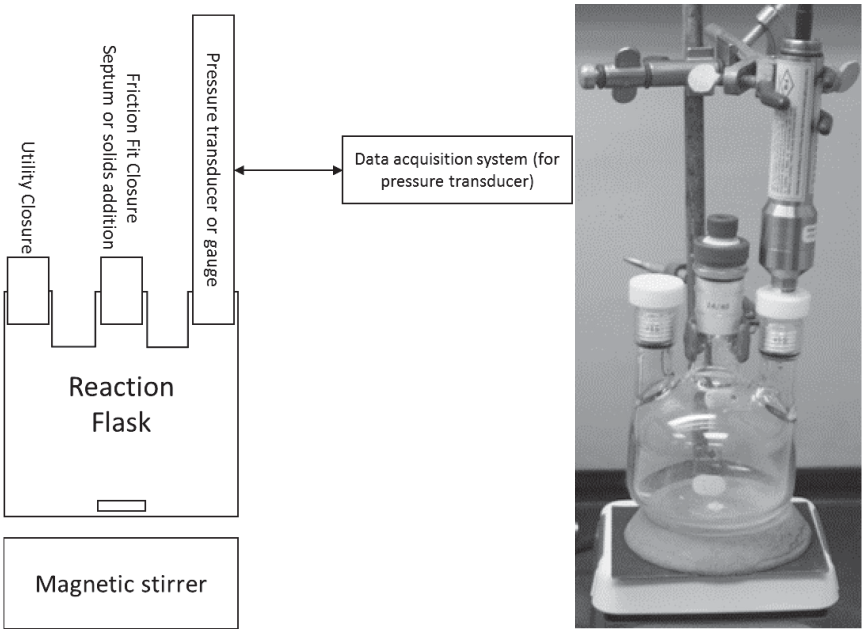
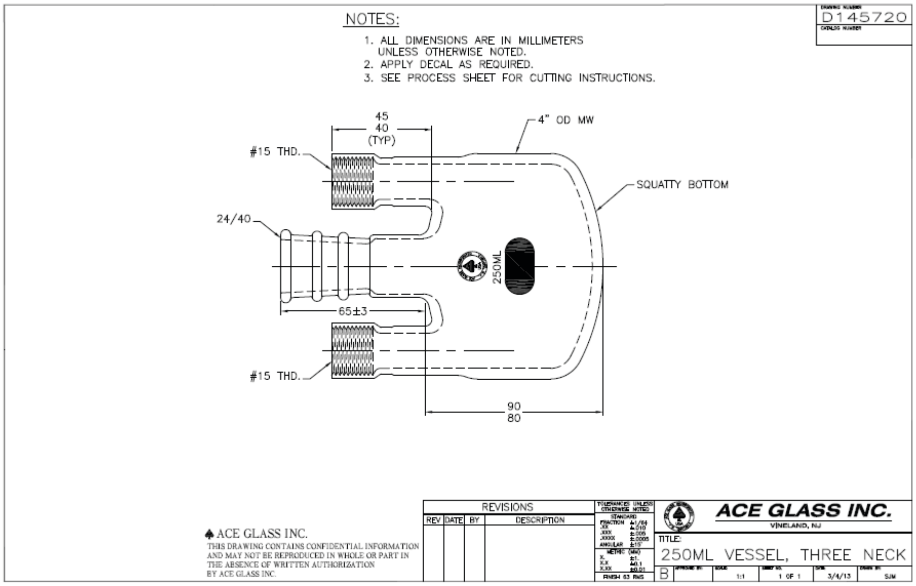


FIG. 1. Schematic diagram (left) and physical example (right) of the test apparatus.



NOTES:

1. ALL DIMENSIONS ARE IN MILLIMETERS UNLESS OTHERWISE NOTED.
2. APPLY DECAL AS REQUIRED.
3. SEE PROCESS SHEET FOR CUTTING INSTRUCTIONS.

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FIG. 2. Vendor drawing of a reaction vessel.

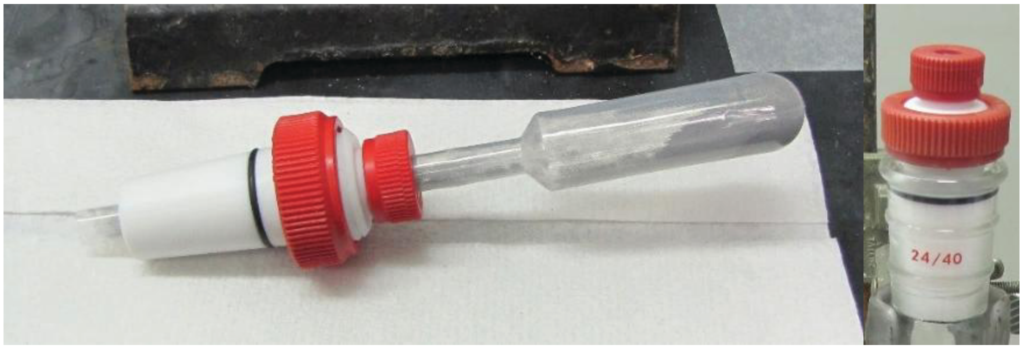

FIG. 3. Detail (left) of a solid addition apparatus and (right) a friction fit closure that accommodates both a septum and provides (via the friction-fit) pressure relief for the test apparatus.

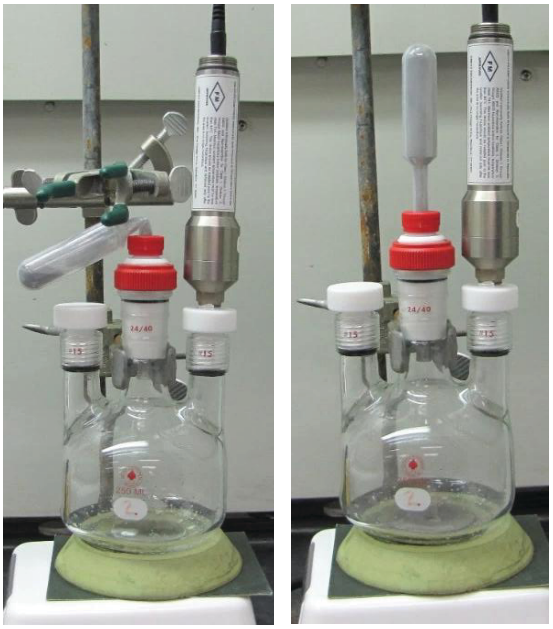

FIG. 4. Test apparatus configured for solid addition, before (left) and after (right) solid test substance is added to water.

6.3 The apparatus should be assembled and used in a modern, properly equipped chemical laboratory and positioned within a properly designed and functioning fume hood when tests are conducted. Ambient conditions in the laboratory must be such that the air temperature in the laboratory is between 18 °C and 24 °C, with a nominal temperature of 21 °C preferred, and that the absolute atmospheric pressure (i.e., not corrected to sea level) is between 96 and 106 kPa, with a nominal pressure of 101.3 kPa preferred.

7. Reagents and Materials

7.1 Other than the test substance, the reagents required are:

D1193 Type IV purified water

ACS Reagent grade sodium chloride, NaCl.

When required, a dry, inert gas supply.

8. Hazards

8.1 *Warning, Reactive Materials*—This test is intended to measure the evolution of gas when reactive materials are combined with water.

8.1.1 Some of these materials may react violently with water, and many may need to be handled under dry, inert atmosphere prior to their careful reaction with water in order to preserve their integrity and to preclude the possibility of hazardous reactions. Furthermore, some of these materials may produce toxic gases when combined with water.

8.1.2 These materials should be handled by trained, qualified personnel with experience in handling water-reactive and/or air-sensitive materials using appropriate laboratory facilities and proper personal protective equipment. Laboratory facilities should include properly designed and operating fume hoods in addition to other facilities and equipment that may be required. Typical personal protective equipment will include flame-retardant laboratory coats (preferably using intrinsically flame-retardant materials, such as Nomex® fabric), safety glasses, face shields, chemically resistant gloves, and other equipment as needed. A transparent shield may be used to deflect debris from the hood when the door is opened. There are several texts and other resources on the topics of laboratory safety and the handing of air-sensitive materials that should be consulted prior to work (see References).

8.1.3 This test should be carried out under the supervision of a qualified, experienced chemist who is thoroughly familiar with the materials being handled, their reactivity, and water- and air-sensitive materials in general.

8.2 *Warning, Elevated Pressures within Closed Apparatus*—The test apparatus shown in Fig. 1 and Fig. 2 is intended to contain gas as it is produced, and therefore will become pressurized during testing.

8.2.1 Pressure relief for the apparatus must be provided. In the apparatus shown in Fig. 1 and Fig. 2, it is provided by the friction fit of the closure in the central, standard taper ground glass joint. Experience with the type of closures shown in Fig. 1, Fig. 2, and Fig. 4 shows that if the pressure exceeds ~ 50 kPa, this friction fit closure will yield, venting the apparatus. Venting is not violent and occurs with a soft (but definite) "pop" as the closure is expelled. The closure is expelled with enough force to reach the hood ceiling, but the rebound is gentle and is comparable to dropping the closure from a height of a few feet. *Users commissioning new apparatus must verify both tolerance of the planned pressures and successful relief performance*.

8.2.2 During the application of this test procedure, prior to charging the apparatus with the substance to be tested and/or water, *estimates of the maximum amount of gas that can be produced must be made, and the amounts charged chosen so that anticipated pressure is within the capacity of the apparatus*. See Annex A-1 for sample calculations.

9. Sampling, Test Specimens, and Test Units

9.1 Samples being evaluated in order to better understand the relative risks of substances in commercial transport should be representative of the larger bulk of the substance as it is to be offered for transport. Samples shall be withdrawn from well mixed containers of the substance, with smaller samples taken from multiple positions within the container, if necessary, and then thoroughly mixed. If, at any time, subsamples—such as small aliquots for each test run—are required, the sample shall be thoroughly mixed in advance to ensure that the subsample is representative of the whole of the sample.

9.2 In the case of solid substances, the substance shall be inspected for any particles of less than 500 μm diameter. If that powder constitutes more than 1% (mass) of the total, or if the substance is friable, then the whole of the sample shall be ground to a powder before testing.

9.3 In the case of substances known to be, or which are discovered to be, pyrophoric or air sensitive, sampling and testing shall be conducted under an inert atmosphere; the atmosphere shall also be dry (dew point -40° C), with the exception of the atmosphere within the apparatus when the substance and water are combined.

10. Calibration and Standardization

10.1 Prior to the first use, and at reasonable intervals afterward, the apparatus must be assembled (without a test substance or water included) and measurements of the pressure/volume response of the apparatus made. While any equivalently effective approach may be used, this can conveniently be accomplished by using calibrated and standardized syringes to add known volumes of gas (at ambient conditions within the laboratory) to the apparatus. For an apparatus with ~ 400–500 cm^3 total internal volume, 4 aliquots of 50 cm^3 each are convenient (See Fig. 5). This procedure can also be used to test the pressure relief provided for the apparatus; the apparatus should safely vent at an internal pressure between 40 and 60 kPa gauge. Note that the pressure volume response of the apparatus also yields the internal volume of the apparatus (see Annex A1 for Sample Calculations).

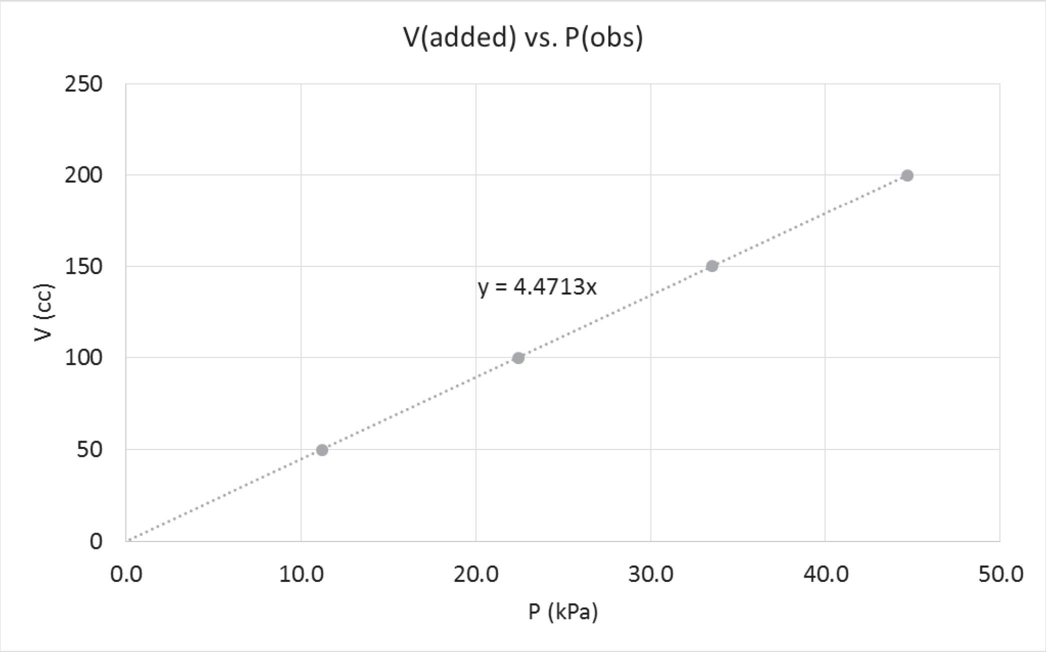

FIG. 5. For a test apparatus with total internal volume of ~ 450 cm^3.

10.2 The gas syringes must be calibrated to deliver known volumes, and this may be either via NIST (or equivalent) traceable calibration or else by conducting a local calibration with reagent grade water and, a NIST traceably calibrated balance and temperature measurement, and standard reference tables for the density of water as a function of temperature.

10.3 Temperature and pressure measurements must be made with NIST traceably calibrated instrumentation.

11. Procedure

11.1 Method A: This is the starting point method (see 12.3 below) and shall be conducted first. It assesses the rate of gas production when a water-reactive substance is added to an excess of water.

11.1.1 Assemble a test apparatus.

11.1.2 Charge the apparatus with purified water; in cases where it is judged likely that saltwater (3.5% w/w ACS Reagent grade NaCl in purified water) will result in a greater rate of gas production, then saltwater shall be used. The mass of water shall be measured, and be such that the total volume of water does not occupy more than ~ 2.5% of the internal volume of the apparatus. For instance, 10.0 g (10.0 ml) could be used in an apparatus with internal volume of 400 ml. Note that if the flammable or toxic gas produced on contact with water is known to have appreciable solubility in water, the amount of water shall be reduced to ~0.5% of the internal volume of the apparatus. The mass of water added shall be determined weighing the syringe before and after the water is charged to the vessel. The mass is determined by difference and is recorded to ±0.0001 g.

11.1.3 If the substance under test is a solid, add it to the apparatus, but in a way that does not yet put it in contact with the liquid water in the apparatus. If the substance under test is a liquid, proceed directly to 11.1.4. Use an amount of test substance chosen so that complete reaction with water, via the reaction expected according to established chemical knowledge, or else established in separate testing, would create an amount of gas with a volume of ~ 1/3 of the internal volume of the apparatus calculated at 20° C and 101.3 kPa. See Annex A.1 for sample calculations.

11.1.4 Close the apparatus and check the apparatus pressure/volume response calibration (see 10.1). The result (the slope of a line fitted to the volume vs. pressure measurements) should be within 5% of the apparatus calibration curve. If it is, proceed, using this check result for test calculations; if not, then the apparatus should be checked and, if necessary, a full pressure/volume response calibration conducted.

11.1.5 Equilibrate the apparatus pressure with ambient pressure.

11.1.6 Combine the test substance with the water in the apparatus. In the case of liquid substances, this can be accomplished by adding the test substance directly to the apparatus in a manner that brings it into immediate contact with the water, with the stirrer operating, while maintaining the gas-tight integrity of the apparatus. When adding liquids via syringe, the syringe needle should be long enough to reach nearly to the liquid (i.e., water) in the reaction vessel, and the syringe operated so that the liquid is added rapidly, and as nearly all at once as possible. For a solid substance, operate the apparatus so that the test substance that was inserted as described above is rapidly mixed with the water while maintaining the gas-tight integrity of the apparatus. In the case of liquid substances, use an amount of test substance chosen so that complete reaction with water, according to the reaction expected according to established chemical knowledge, or else established in separate testing, would create an amount of gas with a volume of ~ 1/3 of the internal volume of the apparatus (see Annex A.1 for sample calculations.). In all cases, the amount of water present in the reaction vessel must be sufficient for complete reaction, according to reactions expected from accepted chemical principles.

11.1.7 Monitor the pressure (and, therefore, volume of gas produced) within the apparatus as a function of time. Continue monitoring until a steady state is observed.

11.1.8 If the change in pressure is too low for accurate measurement, repeat the test (starting at 11.1.1) using an increased amount of substance, but [Important!] do not exceed the apparatus capacity. If necessary, continue to repeat the test using increased amounts of substance, until a readily and accurately measureable response is observed. An ideal result would be an increase in pressure within the apparatus, as reaction proceeds, of from 10 to 25 kPa. Once a satisfactory response is achieved, conduct 4 additional replicate runs, to obtain a total of 5 measurements.

11.2 Method B: This is an alternative method (see 12.3 below) that may be required if Method A proves unsatisfactory because of interference from the vapor pressure of the test substance, or if the gas evolved appears to be absorbed by excess water in the reaction vessel more rapidly than it is produced. It is only necessary to conduct Method B if called for in 12.3. It assesses the rate of gas production when water is added to an excess of water reactive substance. This is a reversal of the conditions in Method A, and is generally most applicable to liquid test substances.

11.2.1 Assemble a test apparatus

11.2.2 Close the apparatus and check the apparatus pressure/volume response calibration (see 10.1). The result (the slope of a line fitted to the volume vs. pressure measurements) should be within 5% of the apparatus calibration curve. If it is, proceed, using this check result for test calculations; if not, then the apparatus should be checked and, if necessary, a full pressure/volume response calibration conducted.

11.2.3 Charge the apparatus with test substance; the mass of test substance shall be measured, and be such that the total volume of substance under test shall not occupy more than 2.5% of the internal volume of the apparatus. Often, an amount in the range of 0.5% to 1% of the internal volume of the apparatus will be sufficient. The mass of substance added shall be determined by weighing the syringe before and after the substance is charged to the vessel. The mass is determined by difference and is recorded to ±0.0001 g.

11.2.4 Equilibrate the apparatus pressure with ambient pressure.

11.2.5 Prepare a syringe with an amount of water chosen such that complete reaction via the reaction expected according to established chemical knowledge, or else established in separate testing, will create an amount of gas with a volume of ~ 1/3 of the internal volume of the apparatus. See Annex A1 for sample calculations.

11.2.6 Add the water to the test substance by adding the water directly to the apparatus in a manner that brings it into immediate contact with the test substance, with the stirrer operating, while maintaining the gas-tight integrity of the apparatus. The syringe needle should be long enough to reach nearly to the liquid (i.e., test substance) in the reaction vessel and the syringe operated so that the water is added rapidly, and as nearly all at once as possible.

11.2.7 Monitor the pressure (and, therefore, volume of gas produced) within the apparatus as a function of time. Continue monitoring until a steady state is observed.

11.2.8 If the change in pressure is too low for accurate measurement, repeat the test (starting at 11.2.1) using an increased amount of water, but [Important!] do not exceed the apparatus capacity. If necessary, continue to repeat the test using increased amounts of water, until a readily and accurately measureable response is observed. An ideal result would be an increase in pressure within the apparatus, as reaction proceeds, from 10 to 25 kPa. Once a satisfactory response is achieved, conduct 4 additional replicate runs, to obtain a total of 5 measurements.

12. Calculation or Interpretation of Results

12.1 For each of the 5 measurements made (starting with Method A; only continue to Method B if required in 12.3), find the period of time during the reaction that shows the greatest rate of pressure increase (gas production). This may be as short as the interval between consecutive data points (2 seconds) or a few data points. In this case, convert the observed change in pressure to a net change in volume; this divided by the elapsed time constitutes the raw gas production rate (volume/time; e.g., liters/min or liters/hour). Alternatively, it may be a longer duration over which a nearly linear increase in pressure with time occurs. In this case, convert the rate of pressure increase represented by the slope of a line fitted to the data in that period of time to a rate of gas production, which then constitutes the raw gas production rate (volume/time; e.g., liters/min or liters/hour). See Annex A1 for sample calculations.

12.2 Divide the raw gas production rate for each measurement by the amount of substance used to obtain a specific gas evolution rate (volume/(time*mass); e.g., liters/kg-min or liters/kg-hour) normalized to the mass of substance used. In the case of Method A, the mass of substance used is simply the amount of substance added to the vessel in 11.1.6. In the case of Method B, use chemical principles to estimate the amount of substance that, in theory, would react with the water used. This estimated amount of the “mass of substance used” then becomes the basis (denominator) for the calculation of the specific rate of gas production. Combine the 5 specific gas evolution rate measurements to obtain an average of the observed specific gas evolution rates, the sample standard deviation, and the coefficient of variation (standard deviation divided by the average expressed in percent). These form the nominal specific gas evolution rate and precision estimate. See Annex A1 for sample calculations.

12.3 For results obtained with Method A, and particularly in the case of liquid test substances, consider whether the observed gas production is due to reaction with water or to evaporation of the material or substance under test. This should be assessed by a qualified chemist, taking into consideration the observed yield of gas vs. that expected (low yields of gas may reflect evaporation) and the magnitude of the change in pressure (small changes, comparable to the vapor pressure of the test substance may reflect evaporation). If the observed gas production may credibly be due simply to evaporation of the test substance, then the measurement (with 5 replicates) shall be repeated *using a reversed order of addition*—charging the apparatus first with test substance, then adding water for the measurement, using Method B. In addition, should it be apparent that production of gas may be masked by absorption of the gas by excess water within the reaction vessel during Method A, then the measurement (with 5 replicates) shall be repeated *using a reversed order of addition*—charging the apparatus first with test substance, then adding water for the measurement, using Method B.

12.4 Generally, a comparison of the specific gas evolution rates and overall gas yields from the two orders of addition (Method A and Method B) will make it clear which observation best represents gas production from the reaction between the test substance and water. Criteria to consider in this determination include the following.

12.4.1 If the addition of substance to water yields an increase in pressure similar to what would be expected solely from the vapor pressure of the substance, and the amount of gas produced is low in comparison to what is expected, while the addition of water to substance produces an amount of gas close to what is expected with a pressure increase greater than the vapor pressure of water, then the latter result shall be used.

12.4.2 If the addition of substance to water yields an increase in pressure in excess of what would be expected solely from the vapor pressure of the substance, the amount of gas produced is similar to what is expected, and the specific rate of gas production is greater than for the addition of water to substance, then the former result shall be used.

12.4.3 For intermediate cases, the judgment of a qualified, independent chemist should be used to determine which result best represents the rate of gas production from reaction with water.

13. Report

13.1 The report shall include:

13.1.1 The full IUPAC chemical name and, if applicable, proper shipping name of the substance tested.

13.1.2 The average result for the specific rate of gas production found in 12.1, as well as the sample standard deviation and coefficient of variation for that result. Any significant increase in temperature during the test shall also be noted.

13.1.3 An indication of whether the test result was based on Method A, adding the substance to water, or Method B, adding water to the substance.

14. Precision and Bias

14.1 Interlaboratory precision testing for this method is pending.

14.1.1 *Precision:* The precision of Test Methods A and B consists of repeatability, which is the agreement that occurs when identical specimens are run sequentially in the same laboratory by the same operator and equipment, and reproducibility, that is, the agreement that occurs when identical specimens are run with the same method at different laboratories. The interlaboratory testing has not yet been completed. However, the repeatability has been measured on 9 substances by a single lab.

Table 1. Validation testing results.

Material	Method	Result (l/kg-min)	Std. Dev. (l/kg-min)	Coeff. Var.	UN Number
$(CH_3)2SiCl_2$	B	36	8	22%	1162
$NaNH_2$	A	9600	2000	20%	1390
$NaBH_4$	A	2 (120 l/kg-h)	0.5 (30 l/kg-h)	25%	1426
CH_3COCl	B	665	60	9%	1717
$AlCl_3$	A	7500	1700	23%	1726
$SiCl_4$	A	1020	210	20%	1818
$SOCl_2$	B	370	110	30%	1836
$TiCl_4$	A	5500	900	16%	1838
$Mg3N_2$	A	7900	1800	23%	3132

Method: A = Substance added to water, B = water added to substance

14.2 In these cases, the standard deviations were found to be proportional to the average gas generation rates so that the coefficient of variation, CV, is the proper measure of precision variability. The value obtained from the combined CVs of the 9 substances tested was:

$CV_r = 21\%$,

Repeatability, r, is defined as 2.8 times CV_r.

$r = 59\%$

14.3 *Bias*—These test methods have no bias because the gas generation rate measured by these test methods is defined only in terms of these methods. Observations in uncontrolled field conditions may vary from those observed with this test.

ANNEX

A1. SAMPLE CALCULATIONS

A1.1 P/V Calibration of test apparatus.

A test apparatus as in Fig. 1 is assembled and calibrated according to Section 10. Using a syringe with an internal volume of 50.0 cc and adding 4 sequential aliquots of gas, the following data results:

Gas Addition	Net Volume Added cc	Pressure Observed kPa
Zero	0	0.0
1st add.	50	11.2
2nd add.	100	22.4
3rd add.	150	33.5
4th add.	200	44.7

This is the data shown in Fig. 5. A line fit to this data by least-squares linear regression yields a slope of 4.4713 cc/kPa. This indicated that the volume of the apparatus is 453 cc, if the ambient pressure was 101.325 kPa.

$$101.325\ kPa \times \frac{4.4713\ cc}{kPa} = 453\ cc$$

A1.2 Estimation of the amount of gas likely to be formed in a test reaction.

Suppose that the test substance is $TiCl_4$. This is expected to react according to Equation (1):

$$TiCl_4\ (l) + 2\ H_2O\ (l) \rightarrow TiO_2\ (s) + 4\ HCl\ (g) \qquad (1)$$

For the case where $TiCl_4$ was to be tested with Method A, and from Equation (1), for ambient pressure of 101.325 kPa and ambient temperature of 21.1 °C, 0.150 g of $TiCl_4$ would be expected to form 76.4 cc of gas.

$$0.150\ g\ TiCl_4 \times \frac{1\ mol\ TiCl_4}{189.679\ g} \times \frac{4\ mol\ HCl}{1\ mol\ TiCl_4} = 0.00316\ mol\ HCl$$

$$0.00316\,mol\,HCl \times \frac{8.314462\,l\cdot kPa}{K\cdot mol} \times \frac{(21.1+273.15)\,K}{101.325\,kPa} = 0.0764\,l\,HCl$$

76.4 cc would be, for instance, less than 1/3 of the volume of a reaction apparatus with total internal volume of 453 cc, so this would be a suitable starting amount for testing, as in 11.1.3.

For the case where $TiCl_4$ was to be tested with Method B, Equation (1) shows production of two moles of gas per mole of water. In that case, 0.050 g of water would be expected to form 134 cc of gas:

$$0.050\,g\,H_2O \times \frac{1\,mol\,H_2O}{18.0153\,g} \times \frac{2\,mol\,HCl}{1\,mol\,H_2O} = 0.00555\,mol\,HCl$$

$$0.00555\,mol\,HCl \times \frac{8.314462\,l\cdot kPa}{K\cdot mol} \times \frac{(21.1+273.15)\,K}{101.325\,kPa} = 0.134\,l\,HCl$$

134 cc would be, for instance, less than 1/3 of the volume of a reaction apparatus with total internal volume of 453 cc, so this would be a suitable starting amount for testing, as in 11.1.3.

A1.3 Estimation of the amount of test substance that would react with water in Method B.

For the case where $TiCl_4$ was to be tested with Method B, Equation (1) shows that every two moles of water would consume 1 mole of $TiCl_4$. For the case where 0.050 g of water was added to excess $TiCl_4$, the amount of $TiCl_4$ consumed would be:

$$0.050\,g\,H_2O \times \frac{1\,mol\,H_2O}{18.0153\,g} \times \frac{1\,mol\,TiCl_4}{2\,mol\,H_2O} \times \frac{189.679\,g\,TiCl_4}{1\,mol\,TiCl_4} = 0.263\,g\,TiCl_4$$

A1.4 Calculation of the raw rate of gas production and specific rate of gas evolution from a test run.

Suppose that 0.1638 g of $TiCl_4$ was added to 2.0218 g water, in an apparatus with a P/V calibration of 4.584 cc/kPa, yielding a change in pressure of 7.57 kPa over 2 seconds. Then:

$$7.57\ kPa\ \times \frac{4.584\ cc}{kPa} \times \frac{1}{2\ sec} \times \frac{60\ sec}{min} = 1041\ cc/min$$

and

$$1041\ cc/min\ \times \frac{1}{0.1638\ g\ TiCl_4} \times \frac{1\ l}{1000\ cc} \times \frac{1000\ g}{kg} = 6355\ l/kg \cdot min$$

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(7) ISO 10156:2010 *Gases and gas mixtures—Determination of fire potential and oxidizing ability for the selection of cylinder valve outlets.*

Abbreviations and acronyms used without definitions in TRB publications:

A4A	Airlines for America
AAAE	American Association of Airport Executives
AASHO	American Association of State Highway Officials
AASHTO	American Association of State Highway and Transportation Officials
ACI–NA	Airports Council International–North America
ACRP	Airport Cooperative Research Program
ADA	Americans with Disabilities Act
APTA	American Public Transportation Association
ASCE	American Society of Civil Engineers
ASME	American Society of Mechanical Engineers
ASTM	American Society for Testing and Materials
ATA	American Trucking Associations
CTAA	Community Transportation Association of America
CTBSSP	Commercial Truck and Bus Safety Synthesis Program
DHS	Department of Homeland Security
DOE	Department of Energy
EPA	Environmental Protection Agency
FAA	Federal Aviation Administration
FHWA	Federal Highway Administration
FMCSA	Federal Motor Carrier Safety Administration
FRA	Federal Railroad Administration
FTA	Federal Transit Administration
HMCRP	Hazardous Materials Cooperative Research Program
IEEE	Institute of Electrical and Electronics Engineers
ISTEA	Intermodal Surface Transportation Efficiency Act of 1991
ITE	Institute of Transportation Engineers
MAP-21	Moving Ahead for Progress in the 21st Century Act (2012)
NASA	National Aeronautics and Space Administration
NASAO	National Association of State Aviation Officials
NCFRP	National Cooperative Freight Research Program
NCHRP	National Cooperative Highway Research Program
NHTSA	National Highway Traffic Safety Administration
NTSB	National Transportation Safety Board
PHMSA	Pipeline and Hazardous Materials Safety Administration
RITA	Research and Innovative Technology Administration
SAE	Society of Automotive Engineers
SAFETEA-LU	Safe, Accountable, Flexible, Efficient Transportation Equity Act: A Legacy for Users (2005)
TCRP	Transit Cooperative Research Program
TEA-21	Transportation Equity Act for the 21st Century (1998)
TRB	Transportation Research Board
TSA	Transportation Security Administration
U.S.DOT	United States Department of Transportation