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Let's discuss this!
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SAFETY RELIEF DESIGN
POLYVINYL CHLORIDE PRODUCTION REACTORS

Can we incorporate
it into our manual?
/

BY

HAROLD G. FISHER

PRESENTED TO THE
VINYL CHLORIDE SAFETY ASSOCIATION

TARPON SPRINGS, FLORIDA

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ABSTRACTSAFETY RELIEF DESIGN - POLYVINYL CHLORIDE PRODUCTION REACTORS

TWO-PHASE VAPOR-LIQUID FLOW FROM EMERGENCY RELIEF DEVICES TYPICALLY RESULTS WHEN WORST CREDIBLE INCIDENT RUNAWAY REACTIONS OCCUR IN POLYMER PRODUCTION REACTORS. PROCEDURES FOR SIZING RELIEF DEVICES FOR TWO-PHASE FLOW HAVE RECENTLY BEEN DEVELOPED AND EXPERIMENTALLY CONFIRMED BY THE DESIGN INSTITUTE FOR EMERGENCY RELIEF SYSTEM (DIERS). AN OVERVIEW OF THE DIERS RESEARCH PROGRAM AND THE PROCEDURES APPLICABLE TO THE DESIGN OF SAFETY RELIEF FOR POLYVINYL CHLORIDE PRODUCTION REACTORS WILL BE PRESENTED.

INDEXSAFETY RELIEF DESIGN - POLYVINYL CHLORIDE PRODUCTION REACTORS

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DESIGN BASIS FOR POTENTIAL RUNAWAY REACTIONSSummary

An approach to the safe design of chemical processes, which have the potential to produce runaway reactions, is to identify and analyze worst credible incident scenarios. Reaction, control, process/operations and safety engineering technologies are then used to prevent, moderate (vent) and contain runaway reactions.

Worst Credible Incident Scenario

Many factors must be considered in arriving at the best approach to deal with hazards that may accompany runaway reactions. Thermochemistry, reaction kinetics, thermal stability, process conditions/controls, abnormal operation, contaminants, equipment design, equipment and instrument failures, operating procedures and human error are all examined when evaluating hazard potentials.

Identify the sequence of events that can lead to the greatest potential pressure and flow to the emergency relief system. Make an exhaustive search for conditions which might create a problem, if not prevented, by involving safety specialists, reaction system designers, process engineers and operating personnel. Scrutinize failure modes to arrive at a combination of failures to produce the worst credible incident scenario. Then, utilize reaction, control, process/operations and safety engineering technologies to prevent, moderate (vent) and contain runaway reactions.

Prevention

Design and operating strategies that will prevent catastrophic events from occurring include:

- Acquisition of data to identify potential problems.
- Prevention of contamination by proper design and operating procedures.
- Measurement and control of critical parameters (temperature, pressure, feed rate, coolant, catalyst).
- Redundant instrumentation to increase reliability of measurement and control of critical parameters.
- Operation at conditions (temperature, pressure, concentration) that provide a safe margin from runaway conditions.
- Alarms to warn operators that a critical parameter has changed from its normal condition.
- Operator training and procedures to enable operators to safely react to upset conditions.
- Automatic emergency shutdown when a critical parameter has deviated from normal by a predetermined amount.

These and many other steps ensure that a runaway reaction will not occur as the result of a single failure. However, several failures may occur simultaneously. The analysis of the consequence of multiple failure leads to the identification of the worst credible runaway reaction incident. An emergency relief system is then designed to handle this incident to include safe disposal of vented material.

Runaway Reaction Moderation (Vent with Safe Disposal)

Pressure relief provisions are made for an item of equipment if the associated fluid or energy sources are capable of generating internal pressures in excess of the maximum allowable working pressure (MAWP) of that item. Safety relief device sizing techniques range from scaling of experimental data, through short-cut design methods to rigorous computer simulation of incidents and flow through vent systems. The technique selected depends upon the specific system and/or situation. (Type and number of chemicals involved, complexity of the reactions(s), availability of required data, constraints imposed upon the designer, etc.) A pressure relief system provides full protection if the rise is held within code limits of the equipment for all anticipated scenarios.

Runaway reaction data utilized for direct scaling are obtained in adiabatic equipment and corrected for the thermal inertia of the apparatus. Data requirements for sizing relief devices by computer include kinetics, stoichiometry, vapor-liquid equilibria and thermal and physical properties.

Containment

Containment can be approached in two ways. First, one might design vessels to withstand the maximum pressure that can develop from an upset. Although this approach may be viable for some emergencies such as vapor phase deflagrations, it may not be a feasible alternative for runaway reactions because of the extremely high pressure that can be produced.

The term containment may also be used to describe the decontamination of the discharge from a runaway reaction through a disposal system. Containment/disposal systems may consist of vent stacks, liquid/vapor separators, quench tanks, scrubbers, flares, incinerators or combinations thereof to disperse, quench, scrub, detoxify or burn the fluid.

Runaway Reaction Safety Relief Design Computer Program

The non-linear heat and mass balance differential equations describing a worst credible runaway reaction incident and the fluid dynamic equations describing the flow capacity of an emergency relief system are normally solved by numerical integration in a digital simulation computer program. State-of-the-art computer programs should contain the latest technology developed by AIChE's Design Institute for Emergency Relief Systems (DIERS).

Computer programs may be used to size safety valves, rupture disks or breather vents for process equipment for top or bottom flow of a vapor, liquid or two-phase vapor-liquid mixture as appropriate. These computer programs are valid for runaway reaction with or without a simultaneous fire exposure of the process equipment or heat exchange with the environment.

The kinetics, stoichiometry, heat of reaction, physical properties and vapor-liquid equilibrium constants for the materials present are read into the computer program from a data file. All values should be calculated as a function of temperature in accordance with recognized thermodynamic models.

Program input and output describing the physical situation are checked for consistency and should be printed to provide a written record of the calculations. The mass of each component is continually checked to ensure a balance. A variable step size in temperature and pressure is used to maintain numerical accuracy for stiff (rapid runaway reaction) systems. Warning messages are provided if the emergency relief devices cannot maintain the system pressure to meet ASME pressure vessel code requirements.

TECHNOLOGY .

REACTIVE SAFETY INTEGRATES

REACTION,

CONTROL,

PROCESS/OPERATIONS AND

SAFETY

ENGINEERING TECHNOLOGIES TO

PREVENT,

MODERATE (VENT) AND

CONTAIN

RUNAWAY REACTIONS

DESIGN PHILOSOPHY

IDENTIFY/ANALYZE WORST CREDIBLE INCIDENT SCENARIOS

PROVIDE ADEQUATE PRESSURE RELIEF

CONTAIN/SAFETY DISPOSE OF VENTED MATERIAL

INTRODUCTION TO RISK ANALYSIS

Risk is an expression of probable loss over a specific period of time or over a number of operating cycles. It can be expressed as the probability of an accident times the loss in dollars, personnel injuries, or lives that could occur.

The risk may come from the movement of personnel and be essentially independent of the process or it may be directly associated with the process hazards and specific equipment design. A risk analysis can focus on one specific type of hazard or it can be all inclusive.

Two relatively recent advances in process risk analysis have permitted major improvements in safety. The first is the realization that a relatively minor failure of a part of the process or system can create an unsafe condition in another portion of the system. This examination of the interactions and interfaces is called a system safety analysis. The second advance in safety is centered around improved technical methods to perform the analysis. Examples of some of the improved technical methods are, preliminary hazard analysis, failure modes and effects analysis, cause and consequence analysis, fault tree analysis and network analysis.

Risk is inherent in life and in the things we do to improve the quality of life. Risk can be controlled by the way a process is designed, operated and maintained, but it can not be eliminated. Some of the more rigorous risk analysis technical methods attempt to quantify risk. This quantification of risk is a valuable input to management to permit more objective decisions. The quantification of risk is inexact since it is based on man's imperfect knowledge and on limited statistical data. In addition, fault tree analysis cannot handle a continuum of data and, therefore, attempts to quantify risk in a series of step changes, i.e., changes in pressure, temperature, composition. The resulting risk measurements are, therefore, only relative comparisons between modes of operation or specific hardware configurations.

RISK ACCEPTABILITY

FATAL ACCIDENT FREQUENCY RATE (FAFR)

NUMBER OF DEATHS PER 1,000 PERSONS
 PER 40 HRS/WK
 PER 50 WKS/YR
 PER 50 YRS

(I.E., PER 10^8 HOURS WORKED)

CHEMICAL INDUSTRY - 3.5 FAFR

$$1 \text{ FATALITY/3,300 YRS} = \frac{1E8}{(3.5)(8,760)}$$

ICI RISK ACCEPTABILITY (NEW/EXISTING PLANTS) - 0.35 FAFR

$$1 \text{ FATALITY/33,000 YRS} = \frac{1E8}{(0.35)(8,760)}$$

HAZARD IDENTIFICATION

THERMOCHEMISTRY

REACTION KINETICS

THERMAL STABILITY

PROCESS CONDITIONS/CONTROLS

ABNORMAL OPERATION

CONTAMINANTS

EQUIPMENT DESIGN

EQUIPMENT/INSTRUMENT FAILURES

OPERATING PROCEDURES

HUMAN ERROR

CONTAINMENT/DISPOSAL SYSTEMS

VENT STACKS

VAPOR/LIQUID SEPARATIONS

QUENCH TANKS

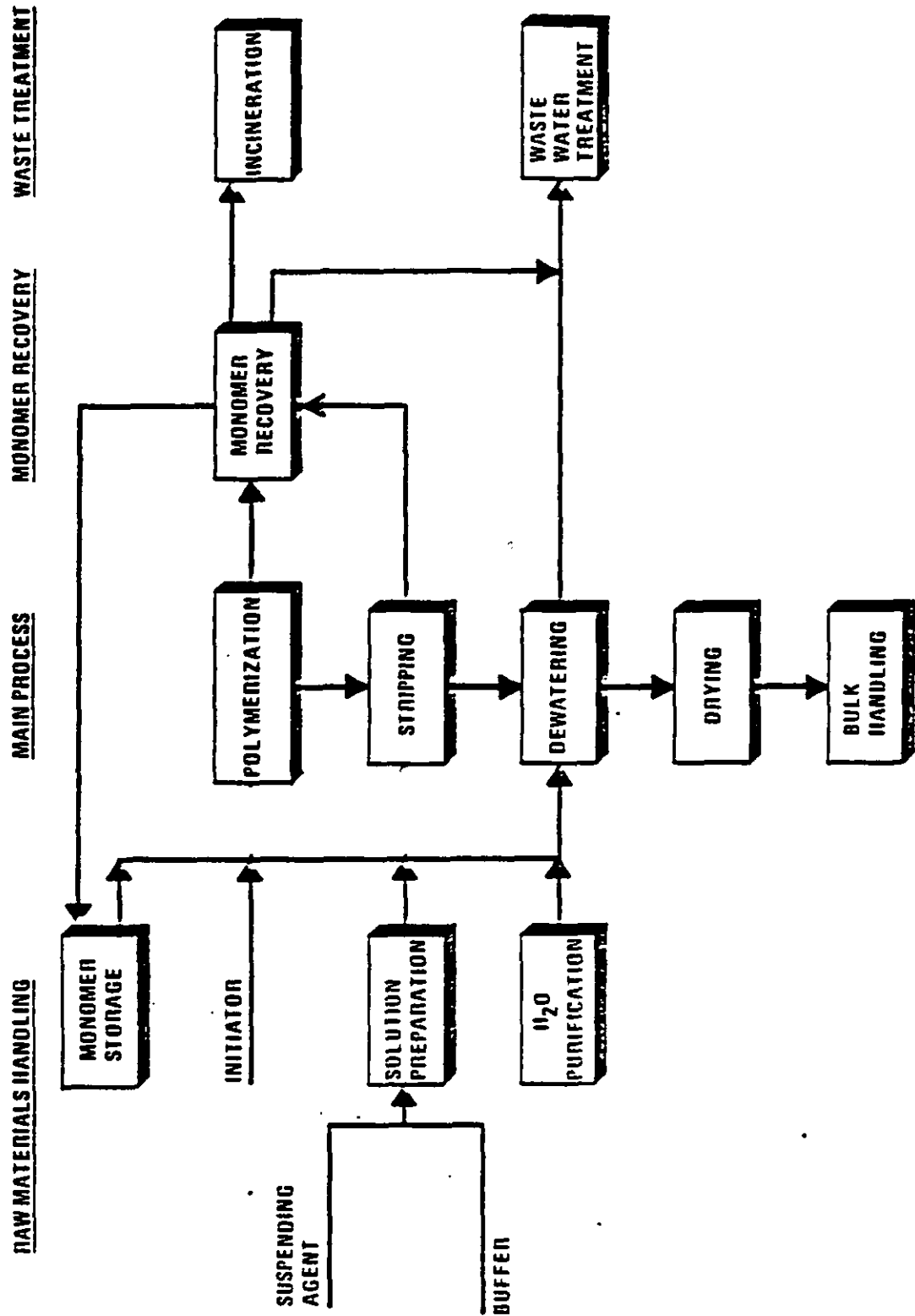
SCRUBBERS

FLARES

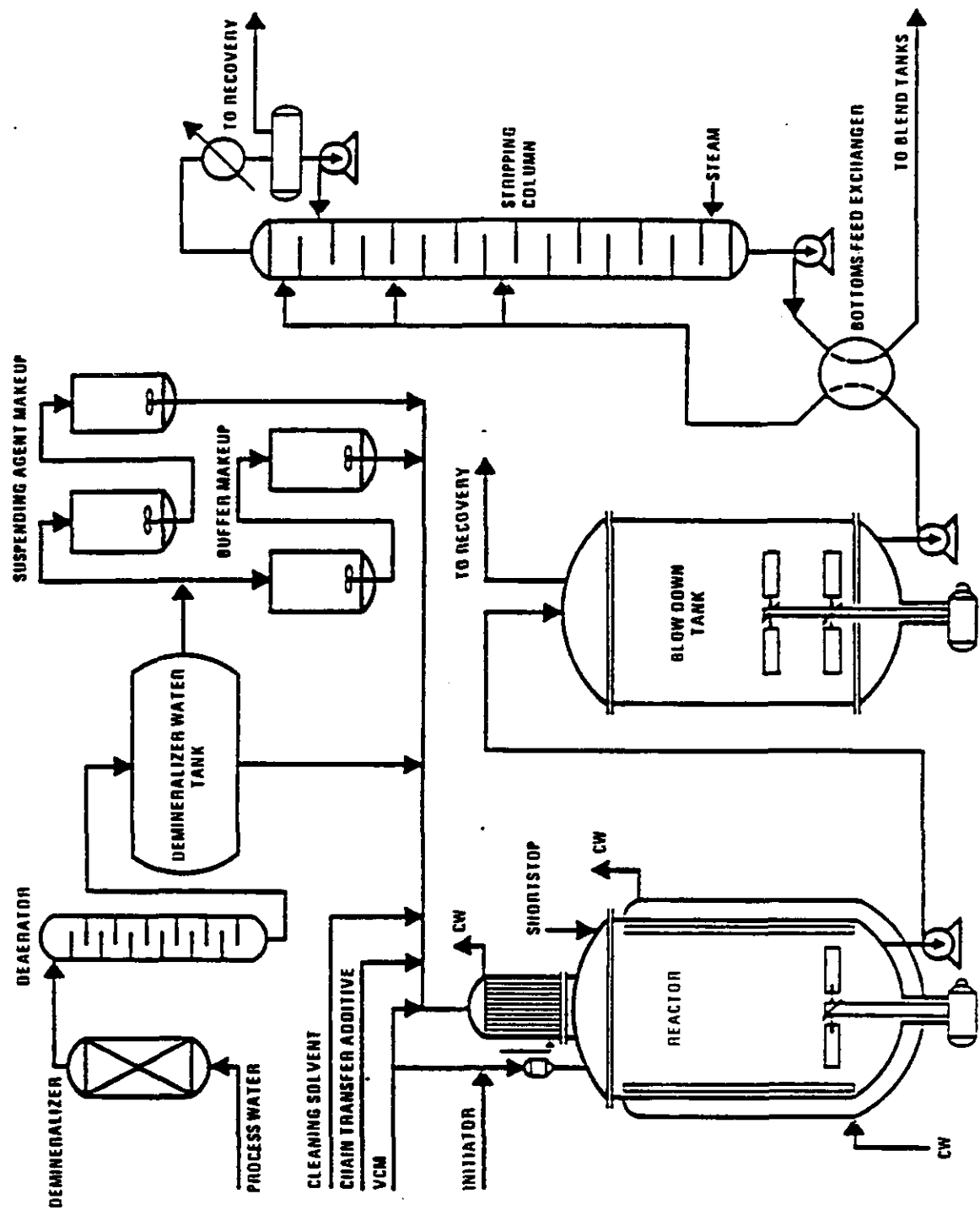
INCINERATORS

INTRODUCTION TO A
SUSPENSION POLYVINYL CHLORIDE
PRODUCTION PROCESS

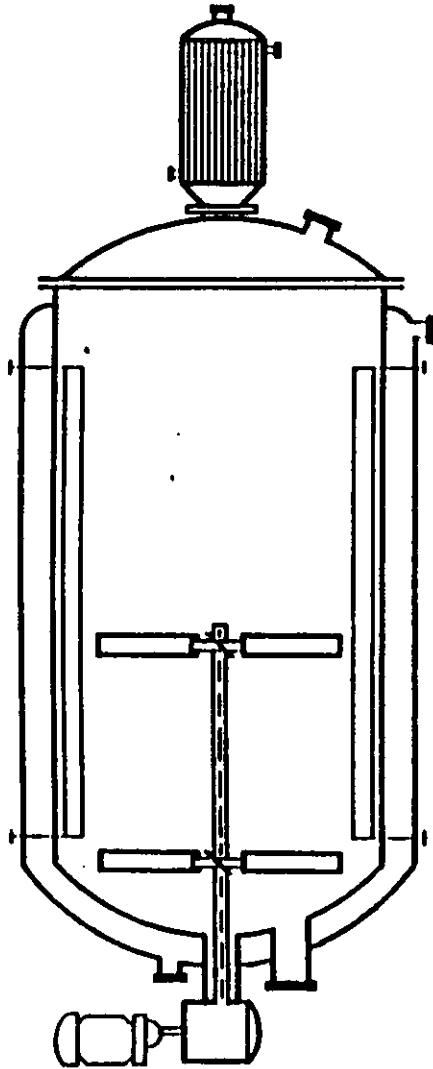
POLYVINYL CHLORIDE BY SUSPENSION PROCESS BLOCK FLOW DIAGRAM



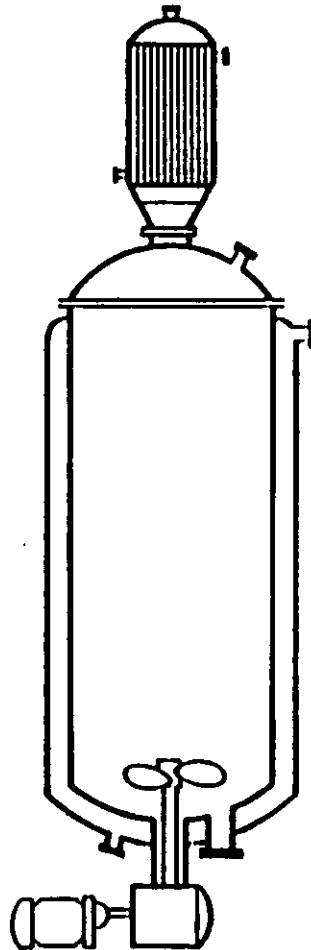
POLYVINYL CHLORIDE BY SUSPENSION PROCESS
POLYMERIZATION AND STRIPPING



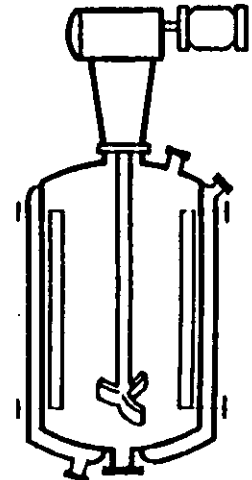
POLYVINYL CHLORIDE BY SUSPENSION PROCESS REACTOR TYPES



10,000 - 50,000 GALS.
STAINLESS STEEL
TURBINE AGITATOR



6,000 - 15,000 GALS.
STAINLESS STEEL
MARINE IMPELLER

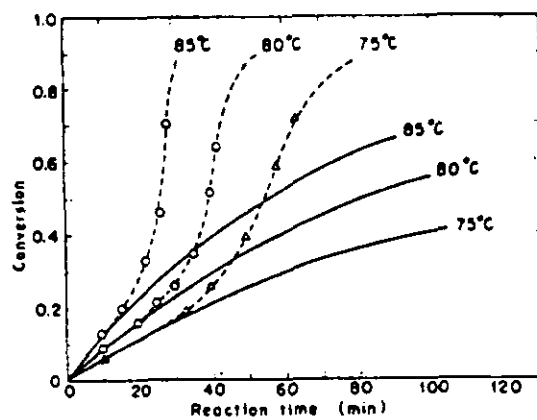


1,200 - 4,000 GALS.
GLASS LINED
3 BLADE RETREAT
AGITATOR

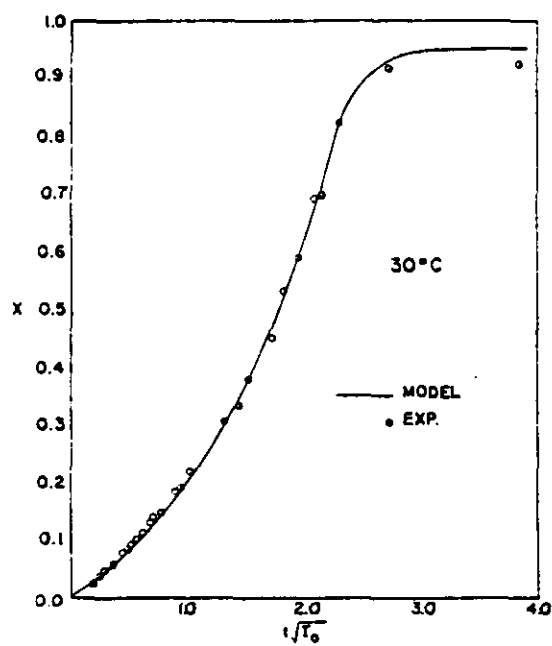
POLYMERIZATION RECIPE (45,000 GAL RX)

<u>COMPONENT</u>	<u>AMOUNT</u>
WATER	25 MGAL
VCL	146 MLB
SUSPENDING AGENTS	30/60 LB
INITIATORS	80 LB
BUFFER SALTS	60 LB
TEMPERATURE	56°C

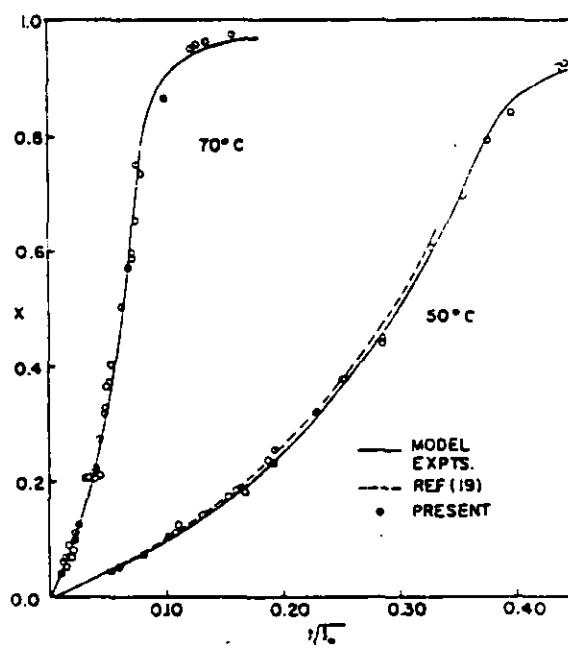
Comparison Between First Order Free Radical and
"Gel" Effect Kinetics for the Suspension Polymerization of MMA



VINYL CHLORIDE POLYMERIZATION

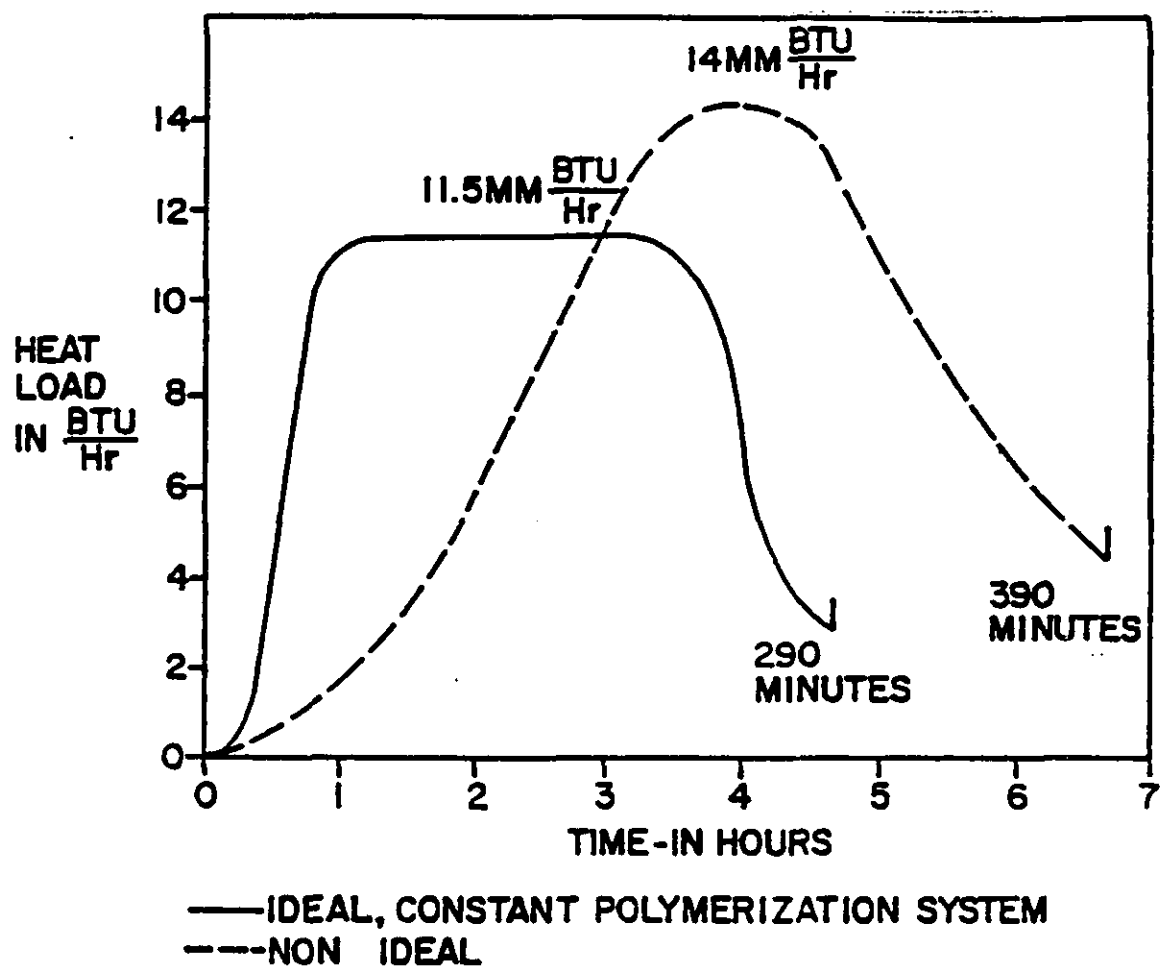


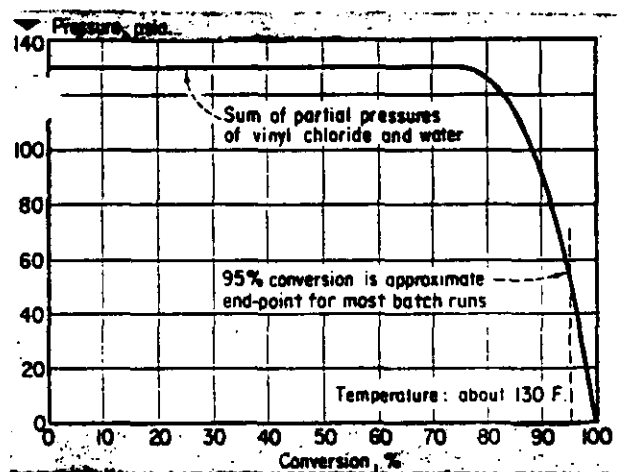
Conversion curve at 30°C; x is conversion, t is reaction time in hr; and t_0 is initial initiator concentration in g/g VC.



Conversion curves at 50°C and 70°C

HEATLOAD VS TIME





CONVERSION is function of pressure in batch reactor

CRITICAL CONTROL PARAMETERS

TEMPERATURE AND TEMPERATURE CONTROL

CATALYST TYPE AND CONCENTRATION

WATER-TO-MONOMER RATIO

WATER QUALITY

SUSPENDING AGENTS AND SURFACTANTS

AGITATOR SPEED AND TYPE

COOLING RATE

SHORTSTOPS

DESIGN

INSTITUTE FOR

EMERGENCY

RELIEF

SYSTEMS



SEVENTY FIVE YEARS OF PROGRESS

345 EAST 47 STREET • NEW YORK, N.Y. 10017

**AMERICAN INSTITUTE
OF CHEMICAL ENGINEERS**

What Is DIERS?

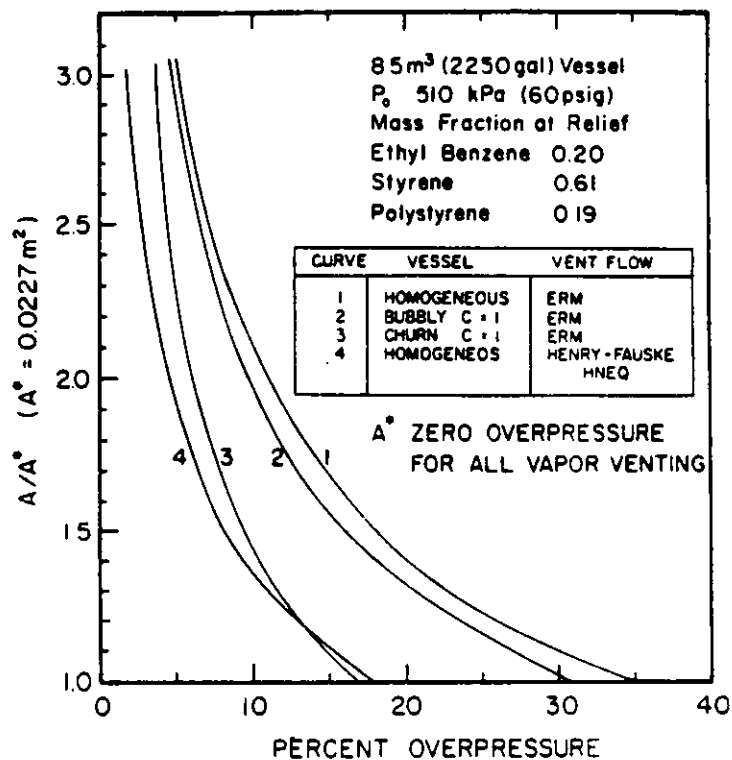
- Founded in 1977 under A.I.Ch.E. auspices to develop technology needed to design safe emergency relief systems in the chemical industry.
- Financed by 28 member companies in USA and abroad. Results presently proprietary to these companies, to be made available to the public after DIERS activity terminates.
- Primary focus on two areas.
 - (1) Hydrodynamics of venting vessels in which runaway reactions occur.
 - (2) Behavior of flashing mixtures flowing through relief devices and vent lines.

What Has DIERS Done?

- Developed mathematical models for venting vessels and flashing flow through relief devices and vent lines.
- Tested models experimentally, first in small scale “separate” effects” tests, later in large scale (500 gal) “integral effects” blowdown tests, followed by runaway reacting system tests on both small (7 gal) and large (500 gal) scales.
- Tested models with a range of fluids: water, ethylene glycol, polyvinyl alcohol, detergents, freons, and the styrene/ethylbenzene/polystyrene reacting system.
- Refined models based on test program results, and recommended appropriate models for relief system design to members.

Major Results of DIERS Work

- Identified the effects of the interrelationship of vessel hydrodynamics, vent flow dynamics and overpressure on vent size, and recommended appropriate models for emergency vent system design to members.



- Identified the need to characterize the “foaminess” of materials under emergency relief conditions.

DIERS Is Currently

- Preparing a technology manual summarizing DIERS work.
- Summarizing design methods for runaway chemical reactions and two phase venting situations.
- Developing a computer model of a runaway chemical reaction in a vessel venting with flashing flow.
- Designing small scale test devices to:
 - (a) Characterize the “foaminess” of systems under emergency venting conditions.
 - (b) Determine heat release rates under emergency venting conditions.
 - (c) Permit venting sizing by direct scale up from small (500 cc) scale tests.
- Investigating stability of relief valves under flashing flow conditions.

DIERS Sponsors

Air Products & Chemicals, Inc.	USA
Allied Chemical Corporation	USA
American Cyanamid Company	USA
Ashland Chemical Company	USA
British Gas Corporation	UK
Ciba-Geigy Corporation	USA
Dow Chemical Company	USA
E. I. Du Pont De Nemours & Company	USA
Dutch State Mines	Netherlands
Eastman Kodak Company	USA
Factory Mutual Research Corporation	USA
FMC Corporation	USA
The Goodyear Tire And Rubber Company	USA
Gulf Research and Development Company	USA
Health And Safety Executive	UK
Hoffman-La Rouche, Inc.	USA
Hooker-Durez Division	USA
Imperial Chemical Industries	UK
Industrial Risk Insurers	USA
The Insurance Technical Bureau	UK
Mobile Research and Development Corporation	USA
Monsanto Company	USA
Olin Corporation	USA
Phillips Petroleum Company	USA
Rohm & Haas Company	USA
Shell Oil Company	USA
Sandoz Ag	Switzerland
Union Carbide Corporation	USA

Principal Contractor For DIERS R&D Work
Fauske & Associates, Inc.

Relief Valve Stability Study By
Obert Associates, Inc.

Chairman, Administrative Committee
Dr. Harold S. Kemp, E. I. Du Pont De Nemours & Co., Inc.
Engg. Dept., Wilm., Delaware 19898 (302) 366-3636

Chairman, Technical Committee
Mr. Harold G. Fisher, Union Carbide Corp., P. O. Box 8361,
Bldg. 2000/4128, S. Charleston, WV 25303 (304) 747-4141

PHASE III TEST SUMMARY

Fluids	Large Scale Depressurization	Large Scale Reacting System	Small Scale Depressurization	Small Scale Reacting System	Test Totals
Water	20		15		35
PVA			2		2
Latex			1		1
Ethylbenzene			4		4
Styrene		5		16	21
Rubber Cement			7		7
	20	5	29	16	70

25 Large Scale Tests

5 Large Scale Reacting

21 Reacting Total

6 Different Fluids

Process Safety

DIERS Research Program on Emergency Relief Systems

The Design Institute for Emergency Relief, a consortium of 29 companies under the auspices of AIChE, has spent 10 years and \$1.6 million to investigate emergency relief systems. This is the first of five articles in this issue on the research findings that can contribute to process safety in the CPI/HPI.

Harold G. Fisher, Union Carbide Corp., South Charleston, W. Va. 25303

The Design Institute for Emergency Relief Systems (DIERS) was formed in 1976 to develop methods for the design of emergency relief systems to handle runaway reactions. Of particular interest were the prediction of when two-phase flow venting would occur and the applicability of various sizing methods for two-phase vapor-liquid flashing flow.

The initial focus of the DIERS program involved an investigation of two-phase vapor-liquid:

1. Onset/disengagement dynamics.
2. Relief system hydrodynamics.
3. Separate effects experimental verification tests. The second phase consisted of:

1. Both small-[85 gal (320 L)] and large-[580 gal (2,200 L)] scale integral blowdown and runaway reaction experimental tests.

2. Computer simulation of the experimental results.
3. Technology revisions as required. The final phase provided:

1. A design computer program.
2. A bench-scale experimental apparatus.
3. An independent review of the basic methodology.

Technology subcommittees were organized to plan and guide the DIERS investigations and to evaluate and validate the results with the help from various contractors. As critical needs were identified, new subcommittees were established.

Technology update

The contributions made by DIERS, therefore, resulted from the joint efforts of various contractors with these subcommittees (see box listing committees and subcommittees).

H. S. Kemp discussed formation of DIERS and functioning of the Administrative and Technical Committees (1), and Swift reviewed information from the open literature and summarized many of the technical findings of the principal contractor (2).

This issue contains five of the 12 papers presented at the Safety and Health Division Symposium on the DIERS Project, AIChE Houston Meeting, March 1985; the others will be published in *Plant/Operations Progress*.

Boyle appears to be the first to publish an article on a

DIERS Committees

Committee	Chairman	Sponsor
Administrative	H. S. Kemp	DuPont
Technical	I. Swift	Union Carbide American Cyanamid Union Carbide Ciba-Geigy
Secretary	H. G. Fisher E. D. Weir	
Advisory Subcommittees		
Onset/ Disengagement Dynamics	H. G. Fisher L. J. Manda	Union Carbide Monsanto
Relief Device Hydrodynamics	J. E. Huff	Dow
Safety Valve Stability/ Capacity	J. E. Huff	Dow
Large Scale Experimental Testing	H. S. Forrest	FMC
High Viscosity Test Program	A. Muller	Goodyear
Bench-scale Experimental Apparatus	J. A. Noronha	Kodak
Design Computer Program	B. J. Tilley	DuPont
Reactor Energy & Material Balance	J. E. Huff	Dow
Containment and Reaction Forces	S. S. Grossel	Hoffmann- LaRoche
Two Immiscible Fluids	H. A. Duxbury	ICI
External Review Project Manual	L. J. Manda D. A. Novak	Monsanto Monsanto

Figure 1. Two-phase flow.

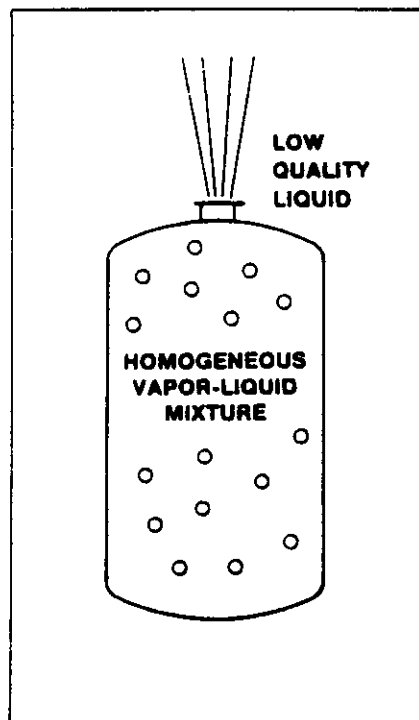


Figure 2. Water blowdown experiment.

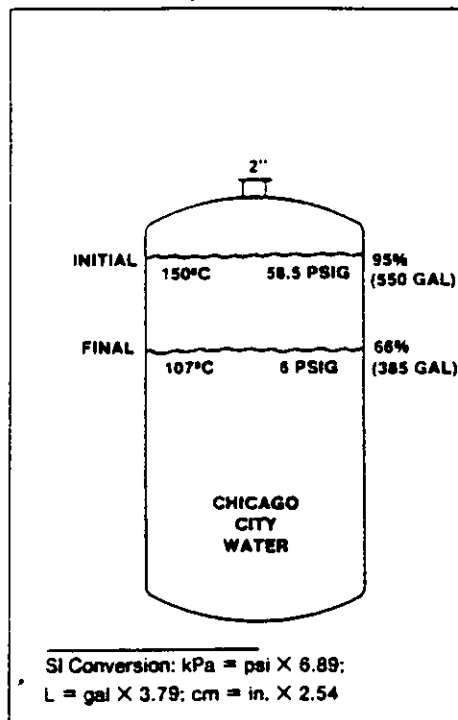
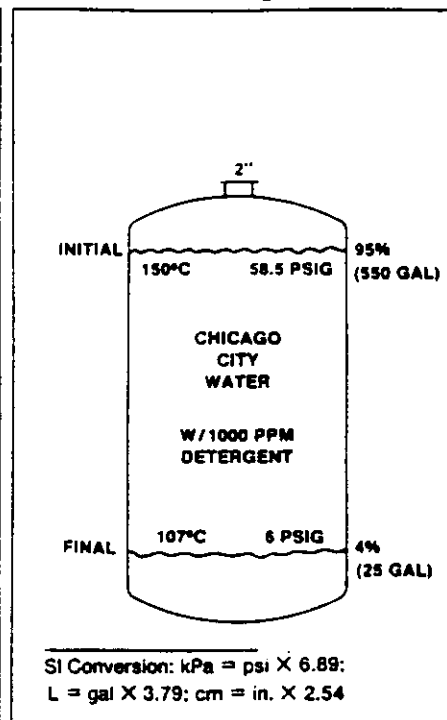


Figure 3. Foamy water blowdown experiment



procedure for sizing relief devices for two-phase venting (3). Duxbury discusses limitations of this method (4). Harmon and Martin subsequently disclosed an experimental area to volume scaling technique for sizing relief devices that is valid only for certain viscous and/or foamy liquids (5). Limitations on experimental area to volume scaling techniques were not clarified until recently (6-8).

Huff (9) was the first to publish details of a comprehensive two-phase flow computational method for sizing emergency relief devices, which with refinements has survived for over a decade (10, 11).

Two-phase vapor-liquid flow

The most significant theoretical and experimental finding of the DIERS program is the ease with which two-phase vapor-liquid flow can occur during an emergency relief situation. The occurrence of two-phase flow during runaway reaction relief almost always requires a larger (two to ten times area) relief system compared to vapor venting (12).

Two-phase vapor-liquid flow of the type that can affect relief system size occurs as a result of vaporization/gas generation during a runaway reaction. Boiling takes place throughout the entire volume of liquid, rather than solely at the surface. Each bubble occupies volume and displaces the liquid surface upward. Individual bubbles are able to rise (slip) through the liquid with a velocity that depends on the buoyancy and surface tension and are retarded by viscosity and the foamy character of the fluid. If a sufficient volume of bubbles become trapped, the liquid surface reaches the height of the relief device and two-phase flow occurs, Figure 1.

A 2-in. (5.1-cm)-diameter relief device (nozzle) was rapidly opened on a tank that was 95% filled with 550 gal (2,080 L) of city water at approximately 150°C and under its own vapor pressure of about 58.5 psig (505 kPa) (13). Approximately 30% of the tank contents vented by two-phase flow, Figure 2. The experiment was repeated, except that 1,000

ppm of a liquid household detergent was added. Approximately 96% of the tank contents vented by two-phase flow, Figure 3. These and the many other DIERS experiments are well predicted by Grolmes and his coworkers of Fauske & Associates (14, 15) and by Klein of JAYCOR, if one can predict *a priori* the foamy character of the fluid during the vent crisis. Failure to do so, however, can result in specification of an undersized relief device (7).

It is most difficult to predict, in an industrial environment, the character of the fluid and thus the quality of the vented material. DIERS has addressed this uncertainty by a two-tracked approach.

1. A conservative relief system can usually be sized for a tempered (cooled via evaporation) reaction by assuming that homogeneous (well-mixed) venting occurs (2). Under this assumption, vapor-liquid disengagement is neglected; i.e., all bubbles formed move at the same velocity as the liquid. Essentially the entire vessel contents are vented during a runaway reaction incident.

2. Experiments can be conducted using the DIERS bench-scale experimental apparatus in an attempt to predict the vapor-liquid disengagement regime. As always, great care must be exercised to ensure that the experiments are an analog of the plant situation and that the vented fluid is truly representative of what would occur during a worst credible incident in the plant.

Experience and future research will allow the designer to take advantage of available technology to reduce relief system size below that required for homogeneous venting. This is particularly important when specifying relief systems for a retrofit, in which nozzle diameters are fixed and great expense is often required to change them.

Relief system sizing

DIERS did not set out to add another two-phase flow computation procedure to the many that already exist, rather to identify a method that could be used to size relief

systems with appropriate conservatism for two-phase vapor-liquid flow for flashing or frozen and viscous or nonviscous fluids (19).

We obtained unique organic and water two-phase vapor-liquid flashing flow data through relief devices and long lines for both blowdowns and runaway reactions. No other organic data bank is as extensive or comprehensive. Hopefully, these data will be the subject of much future analysis and serve as a basis for validation of existing emergency relief system sizing computer programs.

Sallet (20) has obtained steam-water blowdown data that show regions of safety valve instability as predicted by Huff (21). Such data have not been available in the past. These results should guide safety valve manufacturers and others to repeat the tests, confirm or refute the findings and issue appropriate design procedures or cautions.

Design computer program

DIERS sponsored development of a comprehensive computer program that incorporates several one-dimensional, two-phase, vapor-liquid onset/disengagement dynamics and hydrodynamics models. This program has been quite useful in comparing theoretical developments with experimental data. It can also be utilized to size emergency relief systems for runaway reactions in industrial vessels. Appropriate information describing the kinetics, stoichiometry, thermal data, vapor-liquid equilibria and physical properties are input by use of data files. The proper two-phase vapor-liquid onset/disengagement dynamics and relief system hydrodynamics models must also be specified. This program has the potential for widespread use throughout the CPI/HPI.

JAYCOR Corp. modified an existing proprietary computer program to analyze a large number of DIERS large-scale experimental tests. The model determines phase slip from a specified value of a drag coefficient. By this method, the data over a wide range of conditions were reproduced with only two values of the drag coefficient to distinguish between foamy and nonfoamy liquids. This program is also capable of emergency relief system design calculations (16).

Bench-scale experiment

A bench-scale experimental apparatus was developed to measure runaway reaction data under adiabatic conditions in a vessel with a very low thermal inertia. This can predict the vapor-liquid disengagement regime and viscous vs. turbulent pipe flow behavior. It also readily offers data useful for sizing emergency relief devices without a comprehensive computer program.

It is particularly significant, because it combines low thermal inertia (1.05) with high working pressure [2,500 psig (17,340 kPa)] of the test vessel—different from other commercially available calorimeters. The quenching effect due to thermal inertia in a typical calorimeter can reduce the peak rate of temperature rise by one or two orders of magnitude. In contrast, runaway reactions in this apparatus very closely approximate the severity experienced in full-scale vessels.

The ability to characterize the vapor-liquid disengagement regime and viscosity effects is important due to the dramatic effect of these variables on relief system size (13, 18). No other apparatus is known that can predict these variables under runaway reaction conditions.

The ability to size relief systems directly from simple measurements should also be of great value to the safety relief designer. As a minimum, many relief systems can now be readily scoped. Undersizing of a relief system by a factor of two to ten can be eliminated by using this apparatus and current computer programs for safety relief design.

The apparatus was validated by the computer program and kinetics, thermal data, vapor-liquid equilibria, stoichiometry and physical properties from previously well charac-

DIERS Project Manual

The *DIERS Project Manual*, in preparation for early 1986 publication, is a helpful compendium for experienced safety-relief systems engineers. Expected to serve both as a reference and a training tool, it discusses limitations of the methods and the need for further work. To be available as an AIChE publication the manual will contain the following main chapters:

- Studies of vapor-disengagement dynamics, water-blowdown experiments in transparent vessels, and the technology state of the art.
- Relief-system venting dynamics, including relief-valve stability and reactor energy and material balances.
- Large-scale blowdown, reacting-system, and high-viscosity tests in 320-L (85-gal) and 2,200-L (580-gal) vessels.
- Bench-scale experimental relief sizing—computer program and users manual—and calculation of containment and reaction forces on piping and vessels.

After much discussion on the possible user of the manual, DIERS decided that it be directed for use by safety-relief systems specialists. Extensive background and experience are required to properly understand and apply the data. Each user organization is urged to interpret and use the results through the appropriate relief-systems specialists. Help is available from the DIERS contractors and the newly formed DIERS Users' Group.

Darwin A. Novak
Leo J. Manda
Monsanto Co.
St. Louis, Mo.

terized systems. Very favorable measurement vs. calculation comparisons have been obtained for simple as well as kinetically complex systems (23). Additional confidence can be built by comparing computer simulations to test results for many diverse systems (24). Modeling is also quite useful in interpreting and confirming test observations.

DIERS Project Manual

Approximately 50 final experimental and theoretical reports, a comprehensive design computer program, and a prototype bench-scale apparatus resulted from the DIERS research project.

DIERS is also preparing a comprehensive project manual which will be a record of the research. (See box on "DIERS Project Manual") and help organizations acquire and assimilate the vast amount of DIERS information and implement the technology (see box on DIERS Project Manual). The manual is scheduled for completion in late 1985. Publication and sale will be announced by the AIChE DIERS Users Group.

The DIERS research project was effective because of the adequacy of its funding and its unique combination of expertise provided by the sponsoring organizations, and contractor capabilities. To assimilate the DIERS material and implement the recommended technology, many of the previous DIERS sponsors are banding together with other companies interested in adopting the technology by forming an ad hoc organization, the DIERS Users Group. Membership in the DIERS Users Group offers access to refinements of the technology, participation in development of additional technology, and an opportunity to share learning experiences. The purpose of the DIERS Users Group is to:

- Reduce the frequency, severity and consequences of

Sponsors of the DIERS Program

Air Products and Chemicals, Inc.
 Allied Chemical Corp.
 American Cyanamid Co.
 Ashland Chemical Co.
 British Gas Corp., UK
 Ciba-Geigy Corp.
 Dow Chemical Co.
 E. I. Du Pont De Nemours & Co.
 Dutch State Mines, Netherlands
 Eastman Kodak Co.
 Factory Mutual Research Corp.
 FMC Corp.
 General Electric Co.
 The Goodyear Tire & Rubber Co.
 Gulf Research and Development Co.
 Health and Safety Executive, UK
 Hoffmann-LaRoche Inc.
 Occidental Chemical Corp.
 Imperial Chemical Industries, UK
 Industrial Risk Insurers
 The Insurance Technical Bureau, UK
 Mobil Research and Development Corp.
 Monsanto Co.
 Olin Corp.
 Phillips Petroleum Co.
 Rohm & Haas Co.
 Shell Oil Co.
 Sandoz AG, Switzerland
 Union Carbide Corp.

accidental overpressurization of industrial vessels.

- Develop new design techniques that could reduce capital costs of emergency relief systems.

This group will maintain and upgrade the DIERS methodology by providing a forum for discussion, exchange and development of clarifications, modifications, corrections and improvements. The group may solicit and obtain information from industry in the area of emergency relief systems to define research projects, and obtain and evaluate research proposals. It also solicits funds from member companies to support research, award contracts, review the progress of funded projects and make results available to member companies, the CPI/HPI, and the general public on a regular basis.

In summary

DIERS, a consortium of 29 companies under the auspices of AIChE, has spent approximately \$1.6 million to investigate the two-phase vapor-liquid onset/disengagement and

hydrodynamics of emergency relief systems. The theoretical and experimental results are expected to contribute significantly to the safety performance of the CPI/HPI.

Acknowledgments

The author, on behalf of DIERS, would like to acknowledge: financial contributions and support of our sponsors (see box listing their names) and the Engineering Foundation; efforts of AIChE that helped to make the project a success; contributions of technical expertise of the DIERS contractors—Fauske and Assoc. Inc., JAYCOR Inc., and OBERT Assoc.—and Prof. G. B. Wallis; and contributions of members of the DIERS Administrative Committee and its Technical and Advisory Subcommittees. #

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H. G. Fisher, staff engineer, reaction safety in the Engineering and Technology and Services Div. of Union Carbide Corp., has been Chairman of the DIERS Technical Committee since 1982. The holder of a B.S.Ch.E. degree from Syracuse Univ. and M.S.Ch.E., M.S.E. (I.E.) and M.B.A. degrees from West Virginia Univ., he has nearly a dozen years experience in production supervision and more than a decade of experience in reaction safety engineering.

TWO-PHASE FLOW PREDICTION

HYDRODYNAMIC ASPECTS OF THE EMERGENCY

RELIEF SYSTEM DESIGN PROBLEM

General Considerations

Emergency relief system design is a multi-faceted problem and should consider:

- Worst case credible upset.
- Energy release rate for the worst case upset at the relieving condition.
- Vapor or two-phase flow.
- Containment and/or header system for vented fluid.
- Reaction forces.
- System physical properties.
- Economic and process constraints.

The principal hydrodynamic uncertainty is whether the relief system must accomodate single-phase (vapor only) flow or two-phase (vapor and liquid) flow. The rate of pressure increase or decrease is determined by the volumetric discharge rate and the interaction between pressure, temperature, mass loss and reaction rate. If two-phase venting occurs, the volumetric discharge rate and the system mass loss will be affected by the vapor-liquid phase ratio. Generally, two-phase flow design requires a larger relief area than all-vapor. (3-10X)

Problem Definition

The emergency relief system design problem is simply stated. What relief area and set pressure are needed to accomodate specific emergency conditions for:

- A vessel of given size and maximum allowable working pressure,
- A system of known physical and chemical properties and
- Fixed process temperature and pressure requirements?

Two types of behavior are possible when the relief device opens.

-1-

They are:

All-Vapor Flow

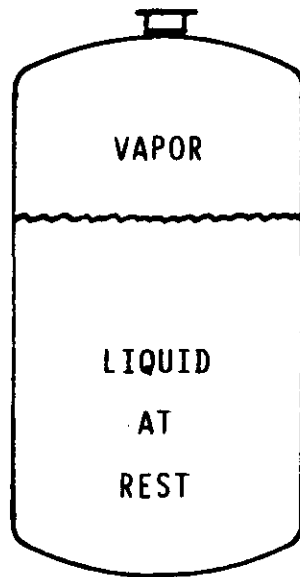
Essentially all-vapor venting occurs when the vapor and liquid phases separate at a plane below the vessel vent location.

Two-Phase Vapor/Liquid Flow

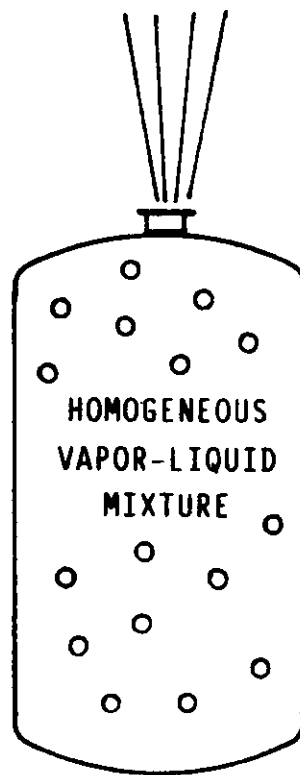
As the pad gas escapes and the pressure falls, bubbles of vapor appear in the body of the liquid to maintain vapor-liquid equilibrium. "Batch swell" or system "boilup" occurs and can fill the vessel with a vapor-liquid mixture. While the boiled-up state is maintained two-phase venting occurs. All vapor venting ensues when vapor separates or disengages from the liquid and forms a vapor space at the top of the vessel. The extreme of two-phase flow is the homogeneous or uniform froth case with no disengagement until the vessel is essentially empty.

TWO-PHASE ONSET/DISENGAGEMENT DYNAMICS

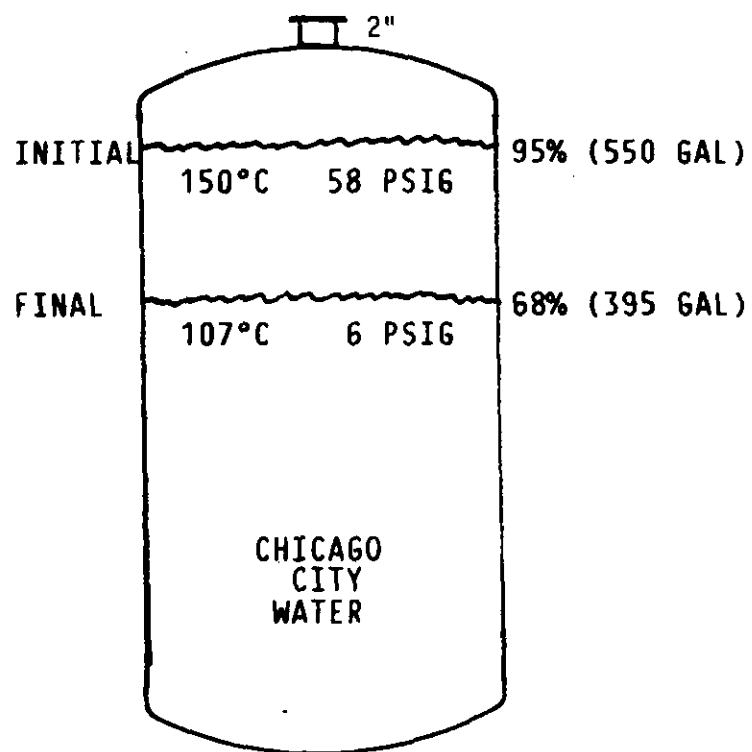
TWO-PHASE FLOW (VENT CLOSED)

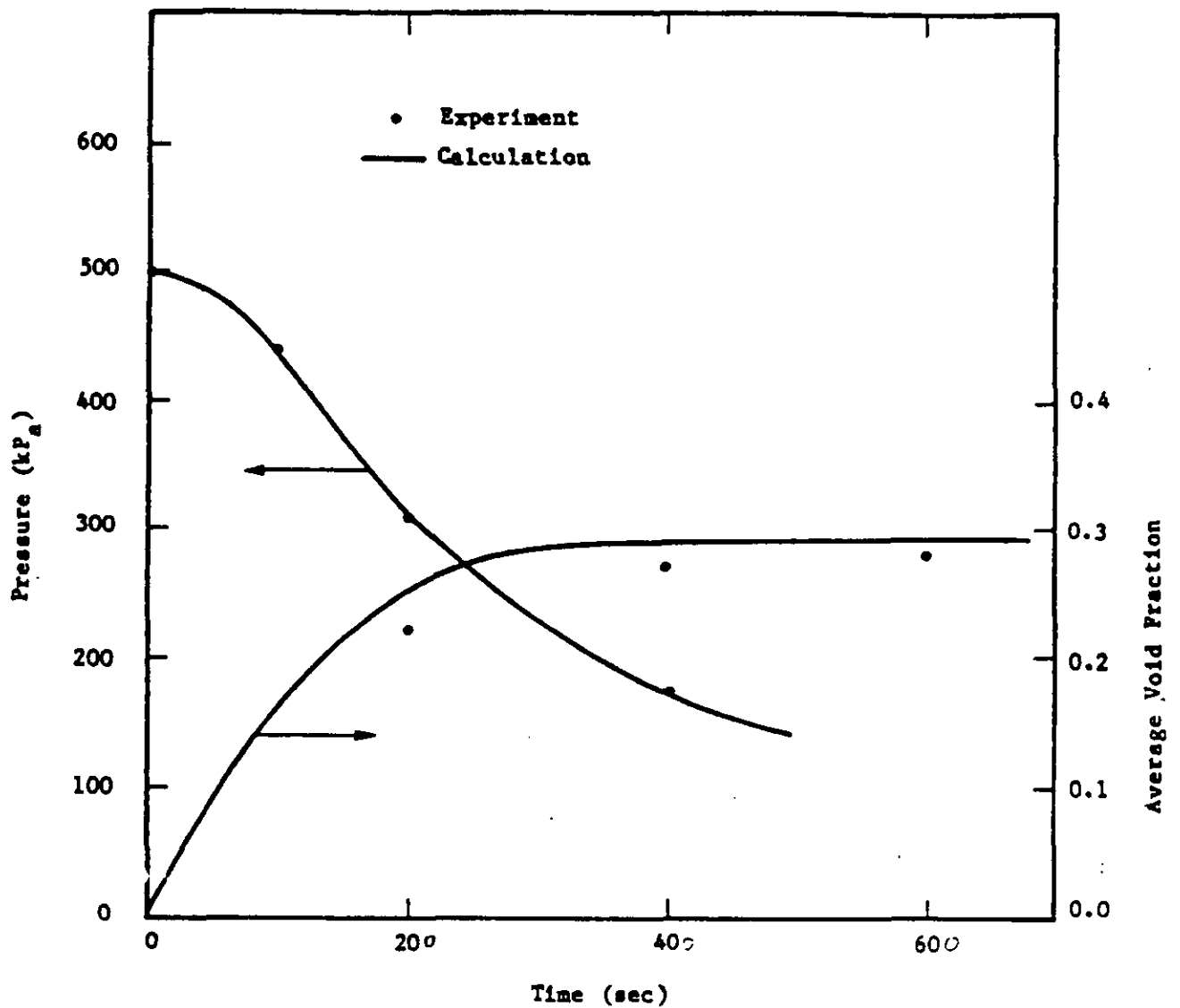


TWO-PHASE FLOW (VENT OPEN)



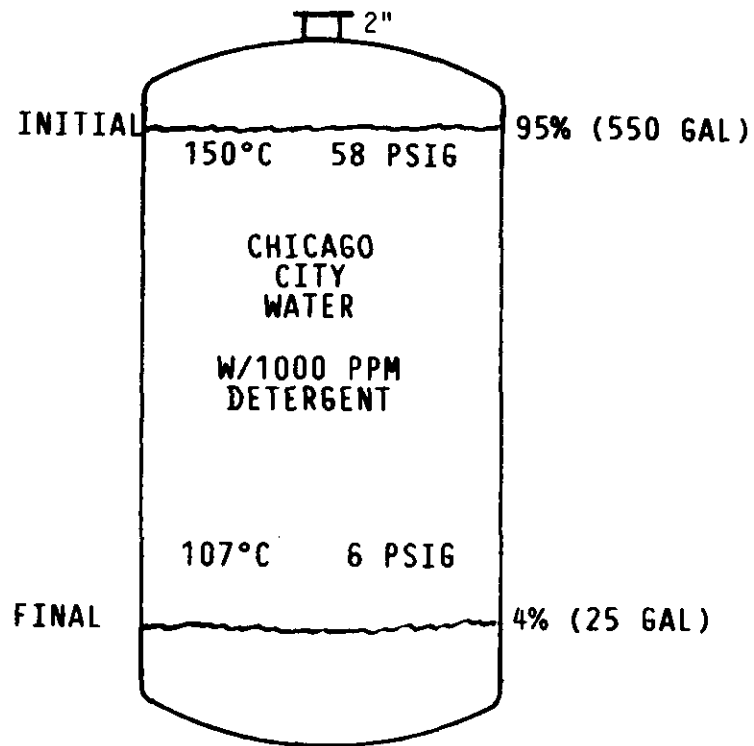
LOW QUALITY LIQUID

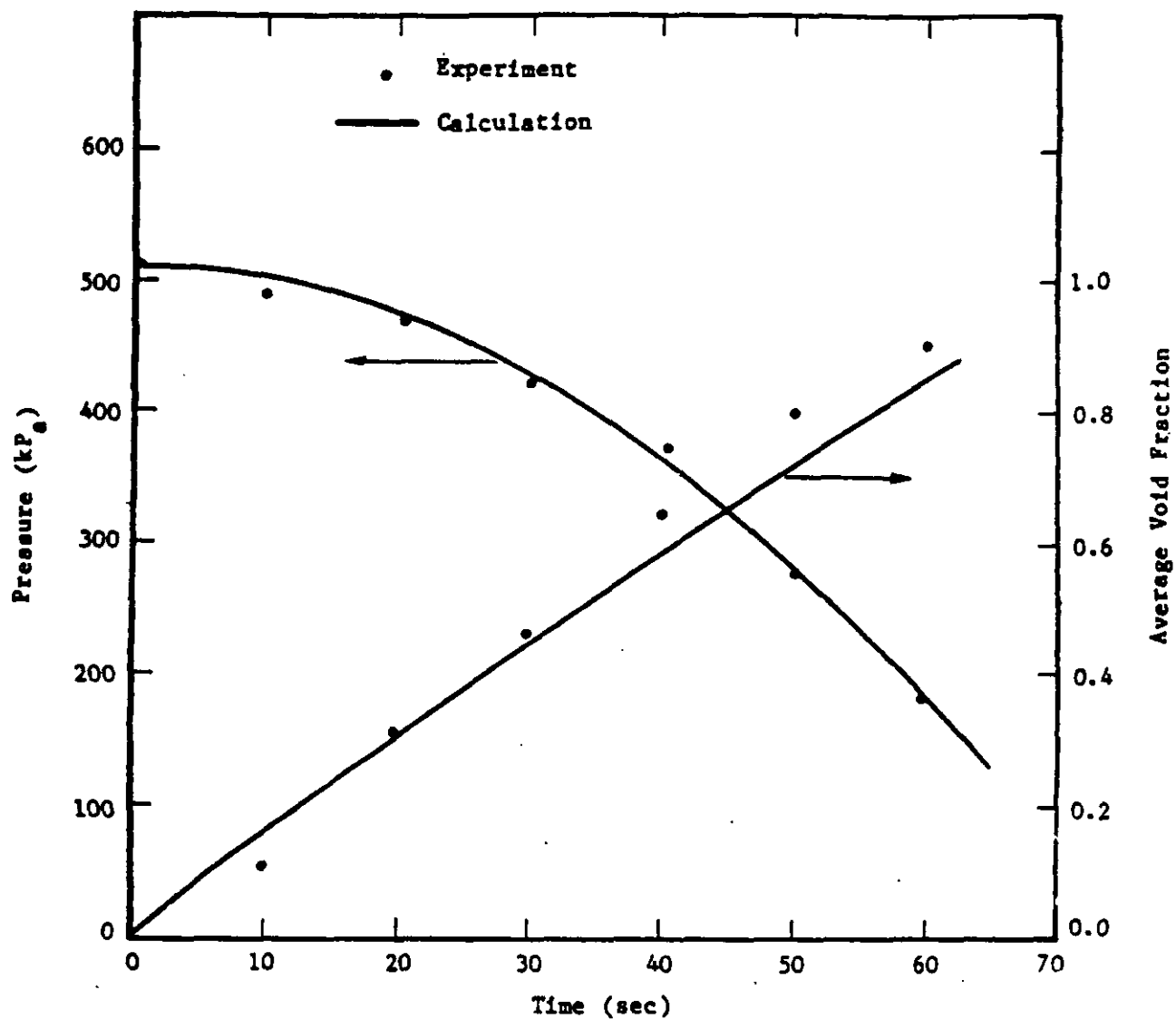
WATER BLOWDOWN EXPERIMENT



PRESSURE AND VOID FRACTION VS TIME

TEST T1C (2 m³, H₂O, 2.03 × 10⁻³ m² VENT)

FOAMY WATER BLOWDOWN EXPERIMENT



PRESSURE AND VOID FRACTION VS TIME

TEST Y20A ($.032 \text{ m}^3$, DETERGENT, $1.27 \times 10^{-4} \text{ m}^2$ VENT)

Best Estimate Procedure to Predict Two-Phase
Vapor-Liquid Vent Flow Onset/Disengagement

The level of a boiling or gas sparged liquid can rise out of a vent if enough bubbles accumulate in a vessel. Gas holdup will be high at low vent rates if the liquid is viscous or foamy. Non-viscous, non-foamy liquids will also swell at high vent rates, which are directly proportional to vent diameter, vessel height or relief pressure.

Two-phase vapor-liquid flow can have a dramatic effect on safety relief sizing for runaway reactions. In general, devices which vent a two-phase mixture must be larger to provide adequate protection than those which vent only a vapor or liquid.

Heat of vaporization cooling due to vapor venting moderates the temperature rise of a volatile liquid. The amount of vaporization during two-phase flow venting is greatly reduced, however, since as much as 99.5 weight percent of the vented material can be liquid. The temperature rise of a vented runaway reaction is therefore more rapid. The rate of reaction increase due to temperature rise is not entirely compensated by mass loss from the vessel. Vent sizes will therefore be larger compared to all vapor venting.

Vessel two-phase vapor-liquid flow onset (start) and disengagement (stop) behavior has been divided into three regimes which are determined by the viscosity and foamy nature of the fluid.

<u>Regime</u>	<u>Viscosity</u>	<u>Stable Foam</u>	<u>C_o</u>	<u>U_{∞}</u>	<u>Expected Disengagement</u>
Churn-turbulent	< 100 cp	no	1.5	$K=1.53$	$\bar{\alpha} \leq 0.63$
Bubbly	≥ 100 cp	no	1.2	$K=1.18$	$\bar{\alpha} \leq 0.83$
Homogeneous	--	yes	--	--	$\bar{\alpha} \leq 1.0$

Constants for equations describing the regimes are also included in the table.

Since two-phase flow can require vent sizes larger in area by a factor of two to ten compared to all vapor venting, the DIERS contractor has recommended use of the homogeneous vapor-liquid regime for runaway reaction vent designs in which the foamy nature of the fluid is not well characterized under venting conditions.

Calculation Procedure (Two-Phase Vapor-Liquid Churn-Turbulent/Bubbly Flow Onset/Disengagement)

1. Determine the vapor capacity (pph) of the relief device(s) at the relief (safety valve)/burst (rupture disk) pressure.
2. Calculate the superficial vapor velocity.

$$j_{g_{\infty}} = \frac{F}{\rho_g A_x}$$

where $j_{g_{\infty}}$ - Superficial vapor velocity (ft/hr)

F - Vapor flow rate (pph)

ρ_g - Vapor density (lb/ft³)

A_x - Vessel cross sectional area (ft²)

3. Calculate the liquid bubble rise velocity.

$$U_{\infty} = \frac{K [980 \sigma (\rho_f - \rho_g)]^{1/4}}{\rho_f^{1/2}}$$

where U_{∞} - Bubble rise velocity (cm/sec)

K - 1.53 (Churn-turbulent)

1.18 (Bubbly)

σ - Surface tension (dynes/cm)

ρ_f - Liquid density (gm/cc)

ρ_g - Vapor density (gm/cc)

4. Calculate the dimensionless superficial vapor velocity due to flow.

$$\psi_F = \frac{j_{g_{\infty}}}{U_{\infty}}$$

where ψ_F - Dimensionless superficial vapor velocity due to flow

$j_{g_{\infty}}$ - Superficial vapor velocity (cm/sec)

U_{∞} - Bubble rise velocity (cm/sec)

$$\text{NOTE: } j_{g_{\infty}} = \frac{j_{g_{\infty}} (2.54)(12)}{3600} = \text{cm/sec}$$

5. Calculate the dimensionless superficial vapor velocity at which two-phase vapor-liquid flow commences.

Churn-turbulent

$$\psi = \frac{2\bar{\alpha}}{1 - C_0 \bar{\alpha}}$$

Bubbly

$$\psi = \frac{\bar{\alpha}(1 - \bar{\alpha})^2}{(1 - \bar{\alpha}^3)(1 - C_0 \bar{\alpha})}$$

where C_0 - Correlating parameter

Best Estimate

Conservative

Best Estimate

Conservative

1.5

1.0

1.2

1.0

ψ - Dimensionless superficial vapor velocity at which two-phase flow commences

$\bar{\alpha}$ - Vessel average void fraction

NOTE: $\bar{\alpha} = \frac{V_T - V_L}{V_T}$

where V_T - Vessel volume (ft³)

V_L - Volume of liquid vessel (ft³)

6. Decision criterion (Two-Phase Vapor-Liquid Flow Onset or Disengagement)

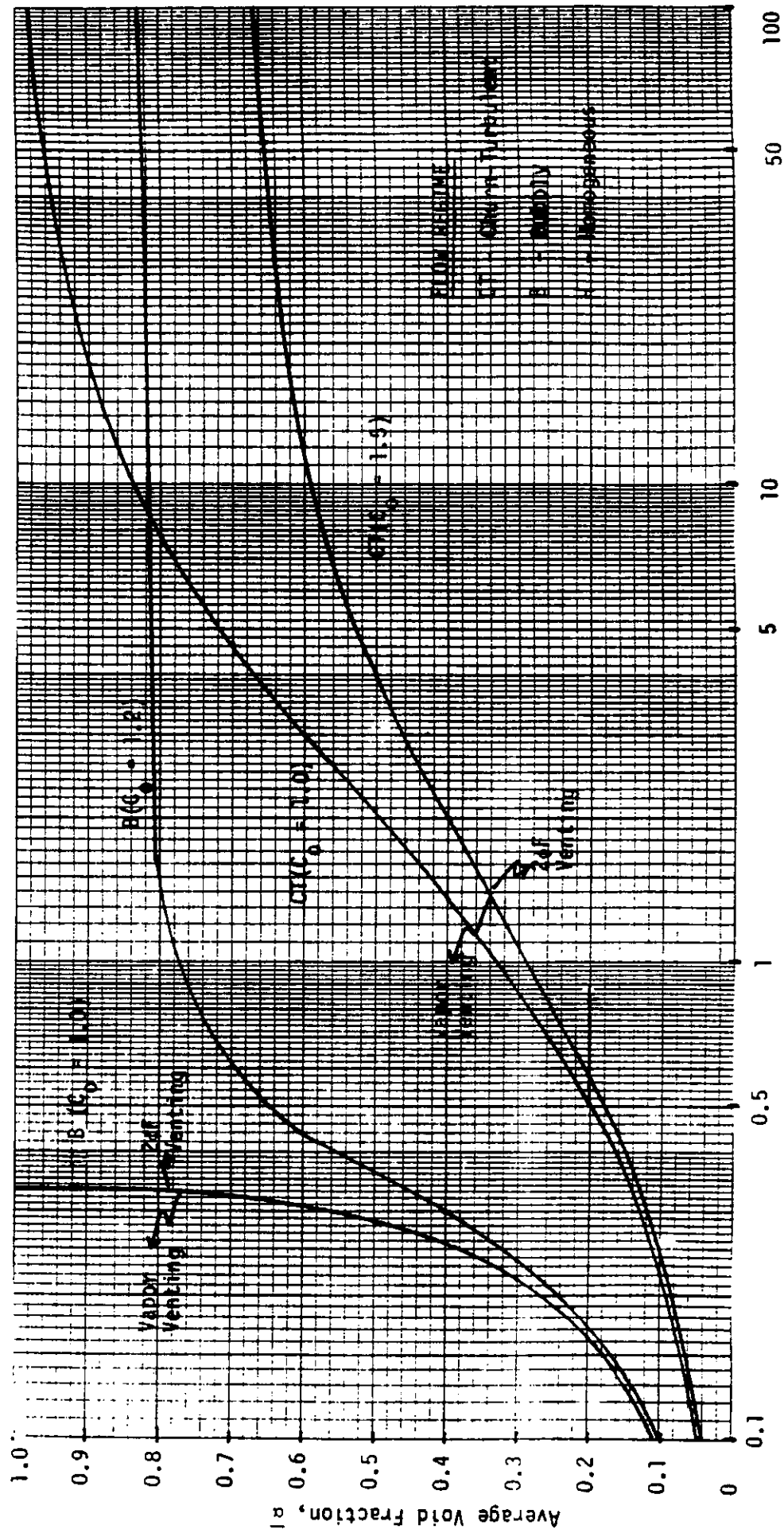
If $\psi_F \geq \psi$, Two-phase vapor-liquid flow onset is predicted.

If $\psi_F < \psi$, All vapor venting is predicted.

If $\psi_F \leq \psi$ and two-phase vapor-liquid flow is in progress, disengagement is predicted.

NOTE: Figure 1 illustrates the functionality of the disengagement relationships.

Two-Phase Vapor-Liquid Churn-Turbulent/Bubbly Flow Onset/Disengagement



Dimensionless Superficial Vapor Velocity, ψ

Figure 1

Sample Calculation

Vessel: Vertical
 Diameter: 10.0 feet
 Fill Ratio: 0.8 (0.2 - void fraction)
 Rupture Disk Diameter: 4 inches
 Burst Pressure: 100 psig
 Equivalent Vent Line Length: 59 feet

1. Relief Device Vapor Capacity

Assume: Vapor venting using water properties, except for surface tension

2. Superficial Vapor Velocity

$$j_{g_{\infty}} = \frac{F}{\rho_g A_x} = \frac{43234 (2.54) (12)}{(0.24) 78.54 (3600)} = 19.4 \text{ cm/sec}$$

3. Bubble Rise Velocity (Churn-turbulent)

$$\begin{aligned}
 U_{\infty} &= \frac{1.53 (980 \sigma (\rho_f - \rho_g))^{1/4}}{\rho_f^{1/2}} \\
 &= \frac{1.53 (980 (20) (0.9 - 0.00386))^{1/4}}{(0.9)^{1/2}} = 18.6 \text{ cm/sec}
 \end{aligned}$$

4. Dimensionless Superficial Vapor Velocity Due to Flow

$$\psi_F = \frac{j_{g_{\infty}}}{U_{\infty}} = \frac{19.4}{18.6} = 1.04$$

5. Dimensionless Superficial Vapor Velocity at Which Two-Phase Flow Commences (Churn-turbulent)

$$\psi = \frac{2\bar{\alpha}}{1 - C_o \bar{\alpha}} = \frac{2(0.2)}{1 - 1.5(0.2)} = 0.57$$

6. Decision Criterion (Two-Phase Flow Onset)

Since $\psi_F (1.04) > \psi (0.57)$, two-phase flow is predicted.

NOTE: Figure 1 may also be used as follows:

@ $\bar{\alpha} = 0.2$, $\psi = 0.57$ from the CT ($C_o = 1.5$) curve.

Since $\psi_F = 1.04$ (the dimensionless superficial vapor velocity due to flow) is greater than $\psi = 0.57$ (the dimensionless superficial vapor velocity at which two-phase flow occurs), two-phase flow is predicted.

7. Void Fraction at Disengagement

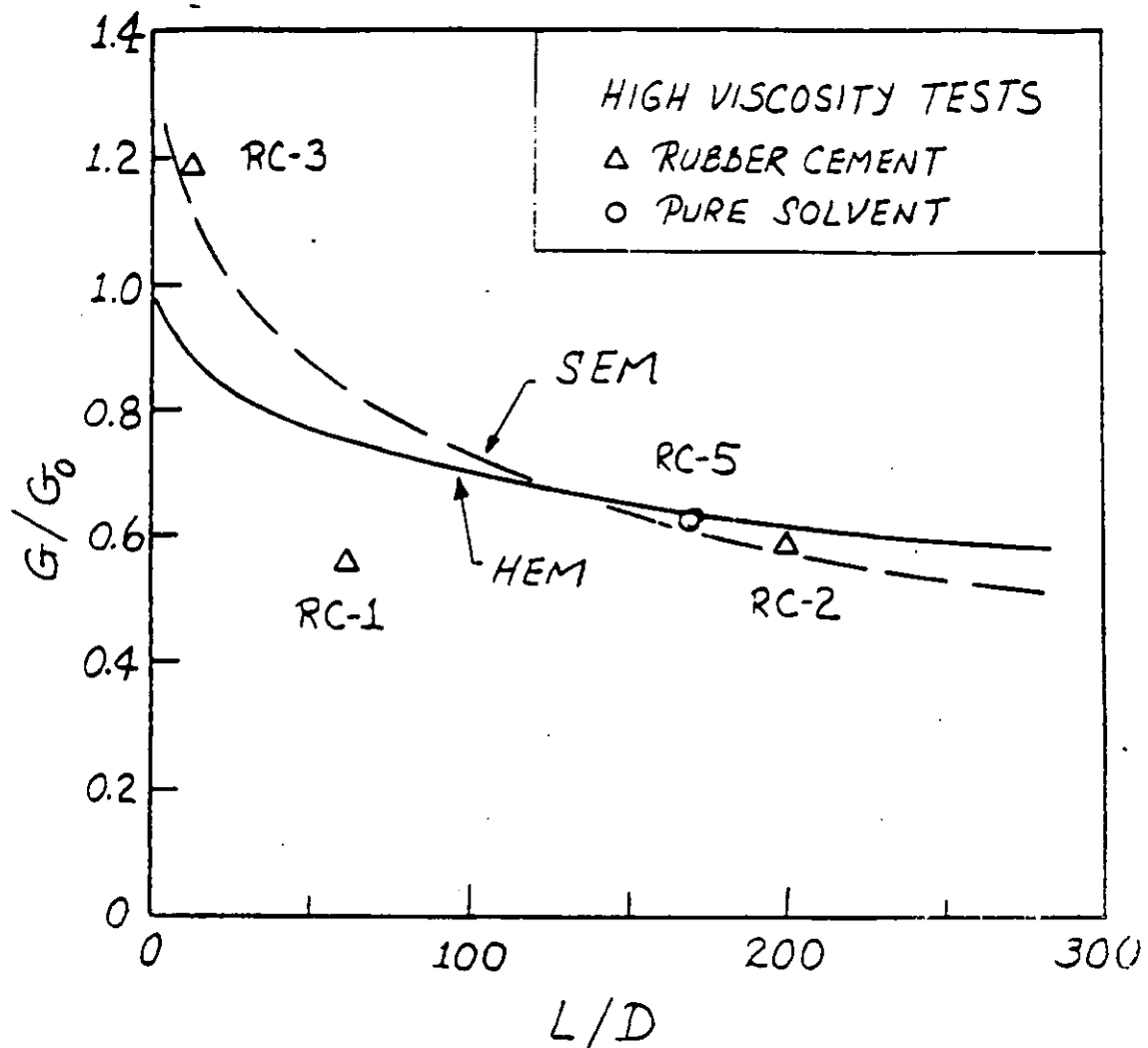
At disengagement $\psi_F = \psi$. Rearrange the churn-turbulent equation and calculate the void fraction.

$$\bar{\alpha} = \frac{\psi}{2 + C_o \psi} = \frac{1.04}{2 + 1.5(1.04)} = 0.29$$

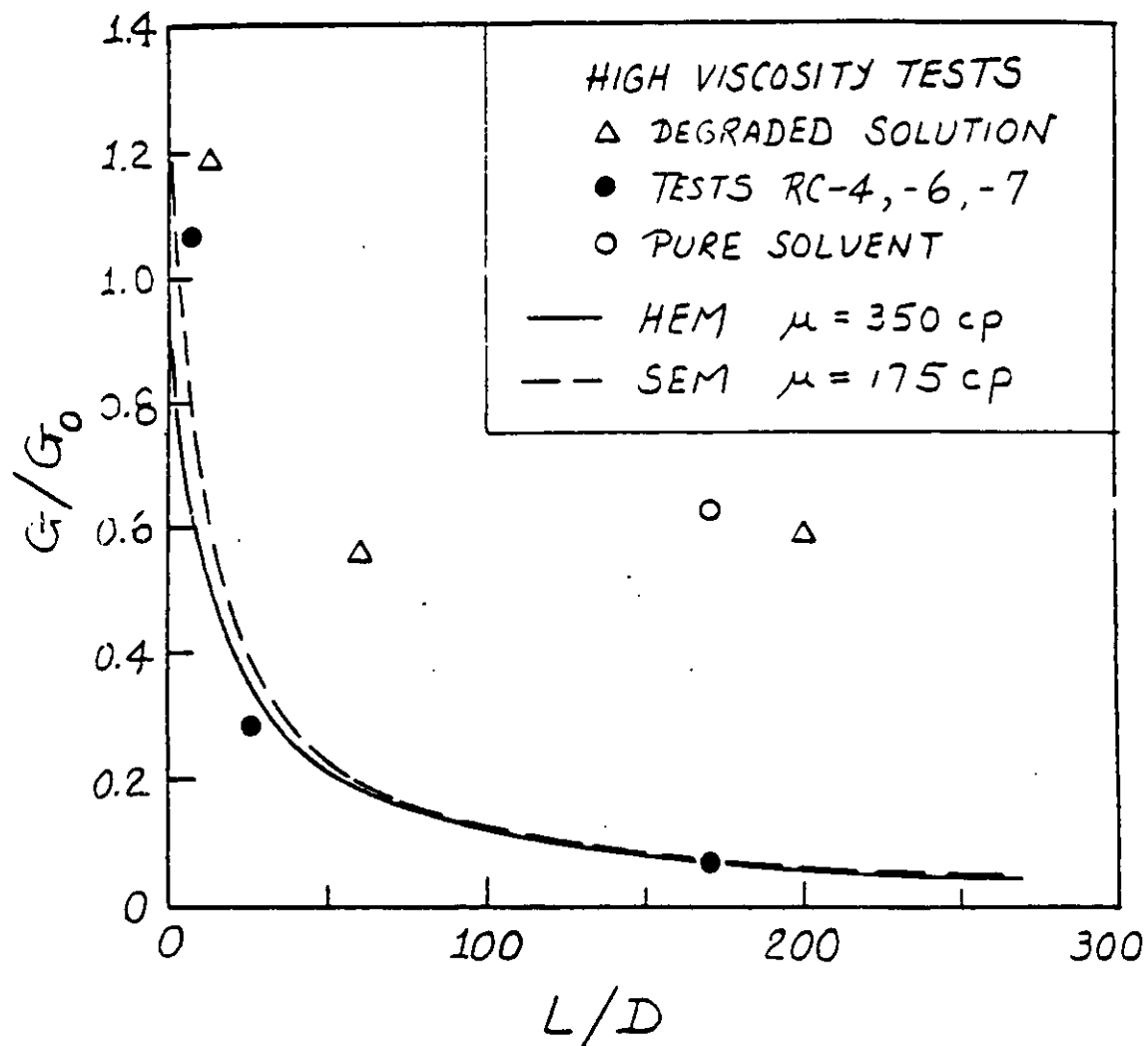
NOTE: Figure 1 may also be used as follows:

@ $\psi_F = \psi = 1.04$, $\bar{\alpha} = 0.29$ from the CT ($C_o = 1.5$) curve.

RELIEF SYSTEM TWO-PHASE HYDRODYNAMICS



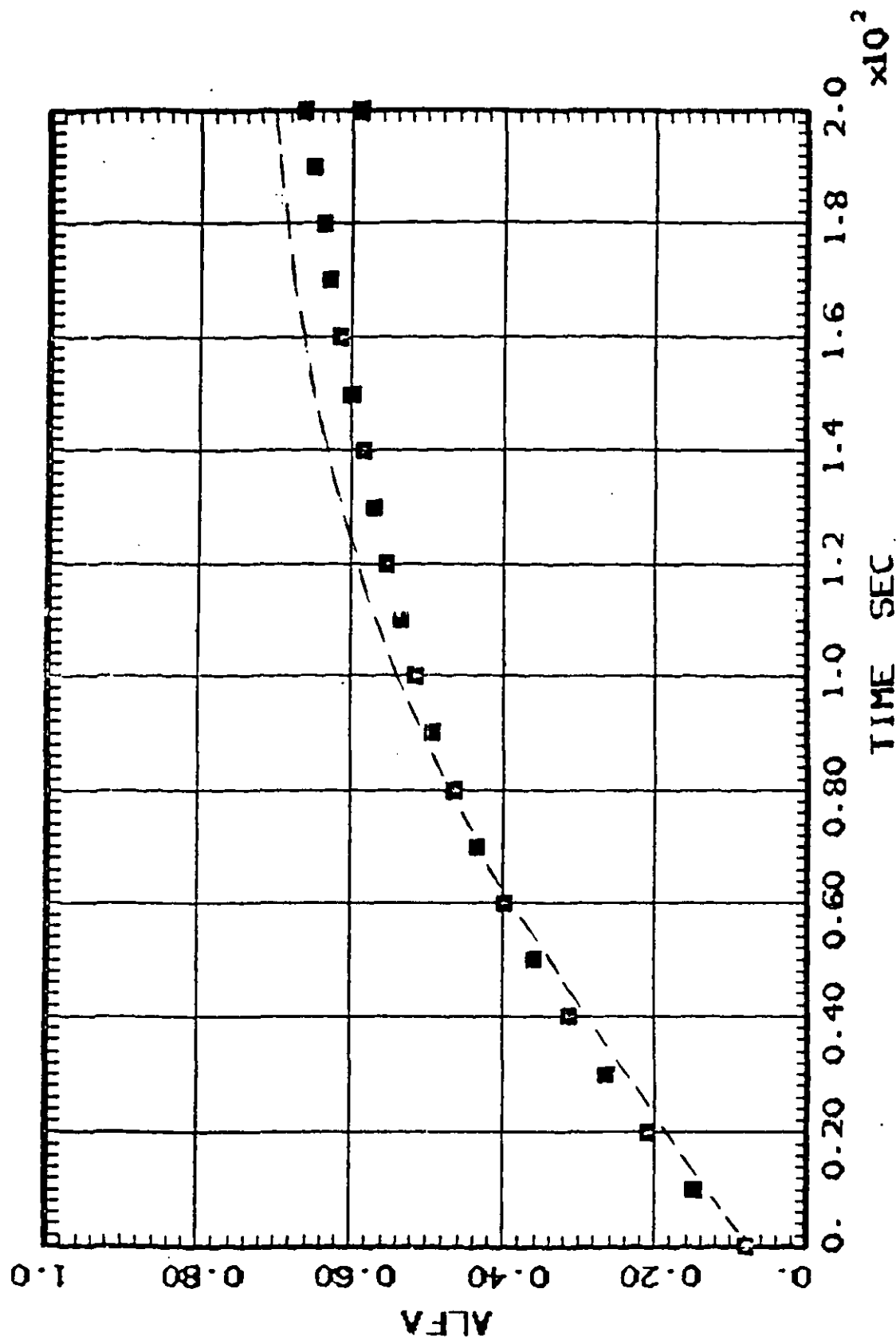
Results of degraded cement solution tests and a pure solvent test and comparison with predictions for nonviscous fluid ($f = 0.005$). (G_0 is based on HEM for a frictionless duct). (SEM uses Lockhart-Martinelli slip correlation).



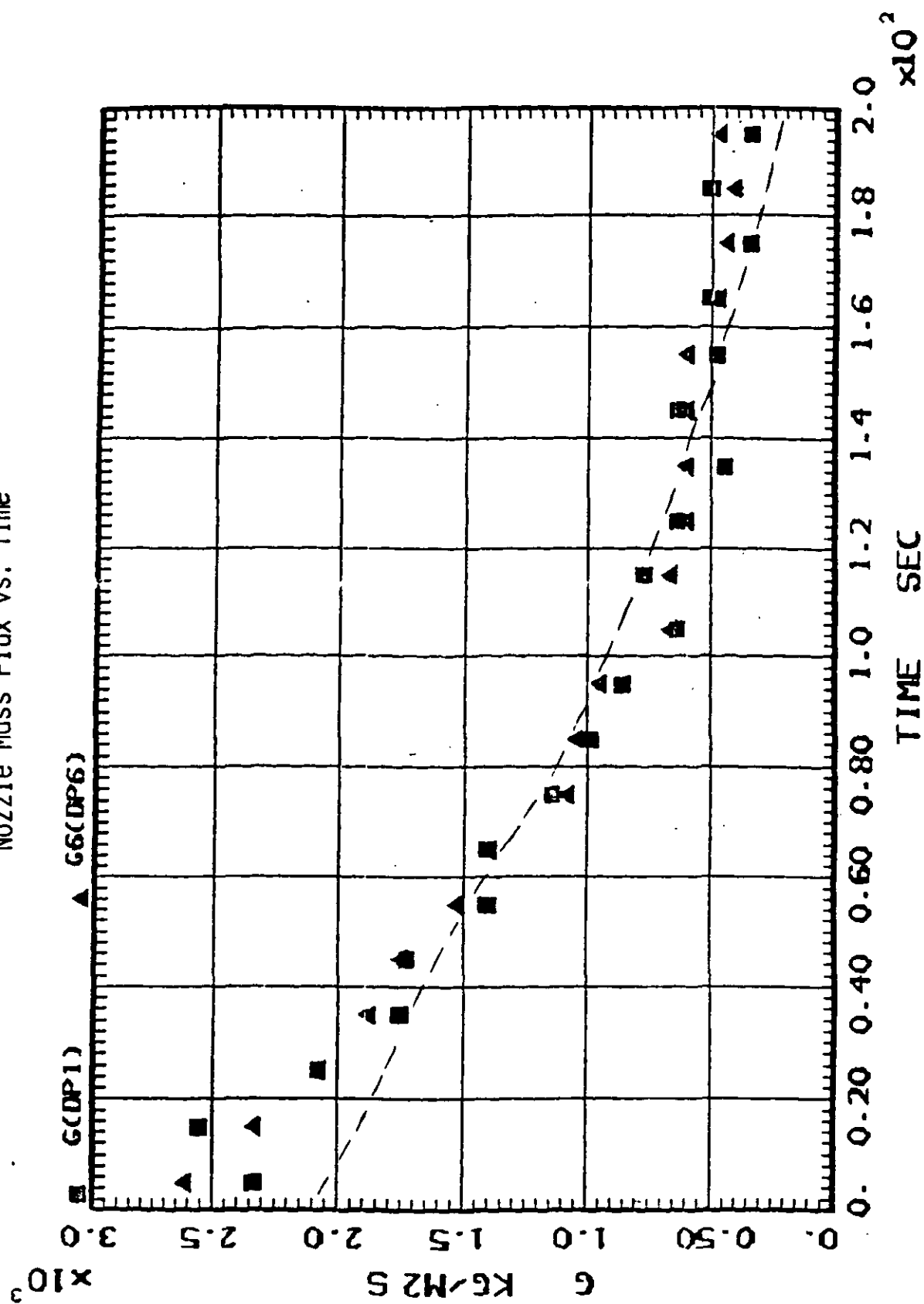
Results of non-degraded cement solution tests (solid circles) and comparison with predictions. (G_0 is based on HEM for a frictionless duct. SEM uses Lockhart-Martinelli slip correlation).

DIERS INTEGRAL EXPERIMENTAL DATA

Vessel Average Void Fraction vs. Time



Nozzle Mass Flux vs. Time



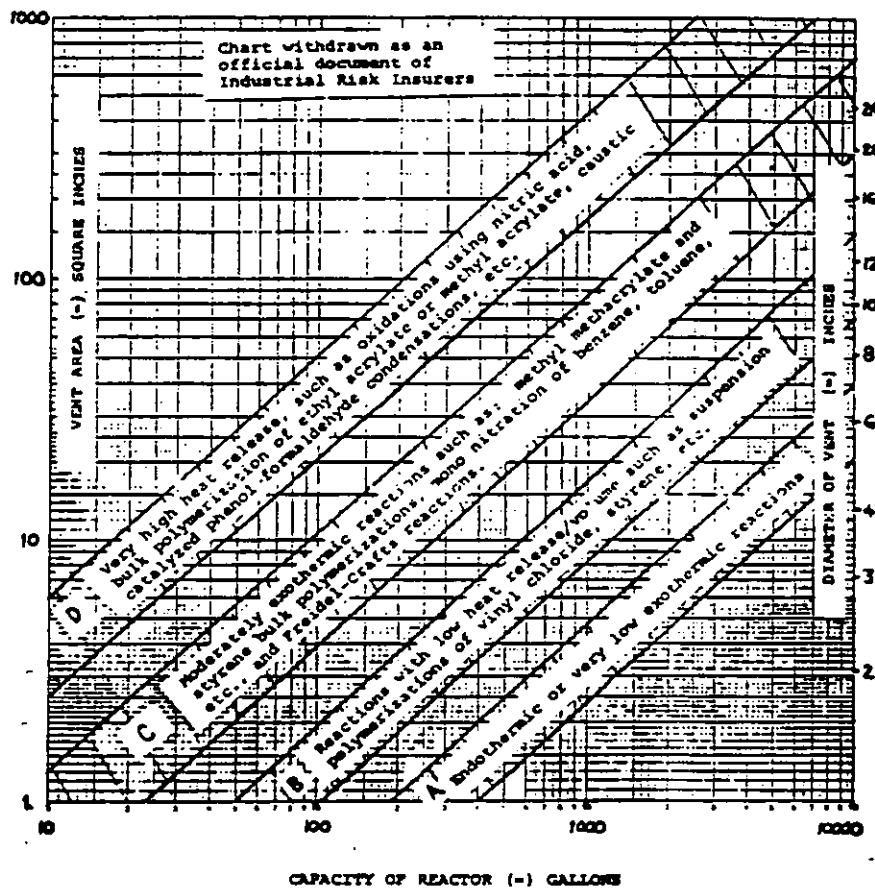
EMERGENCY RELIEF SYSTEM SIZING TECHNIQUES

SHORT-CUT DESIGN METHODS

SCALING OF EXPERIMENTAL DATA

RIGOROUS COMPUTER SIMULATION

FIA chart



RUNAWAY REACTION TESTING IN THE LABORATORY

ADIABATICITY

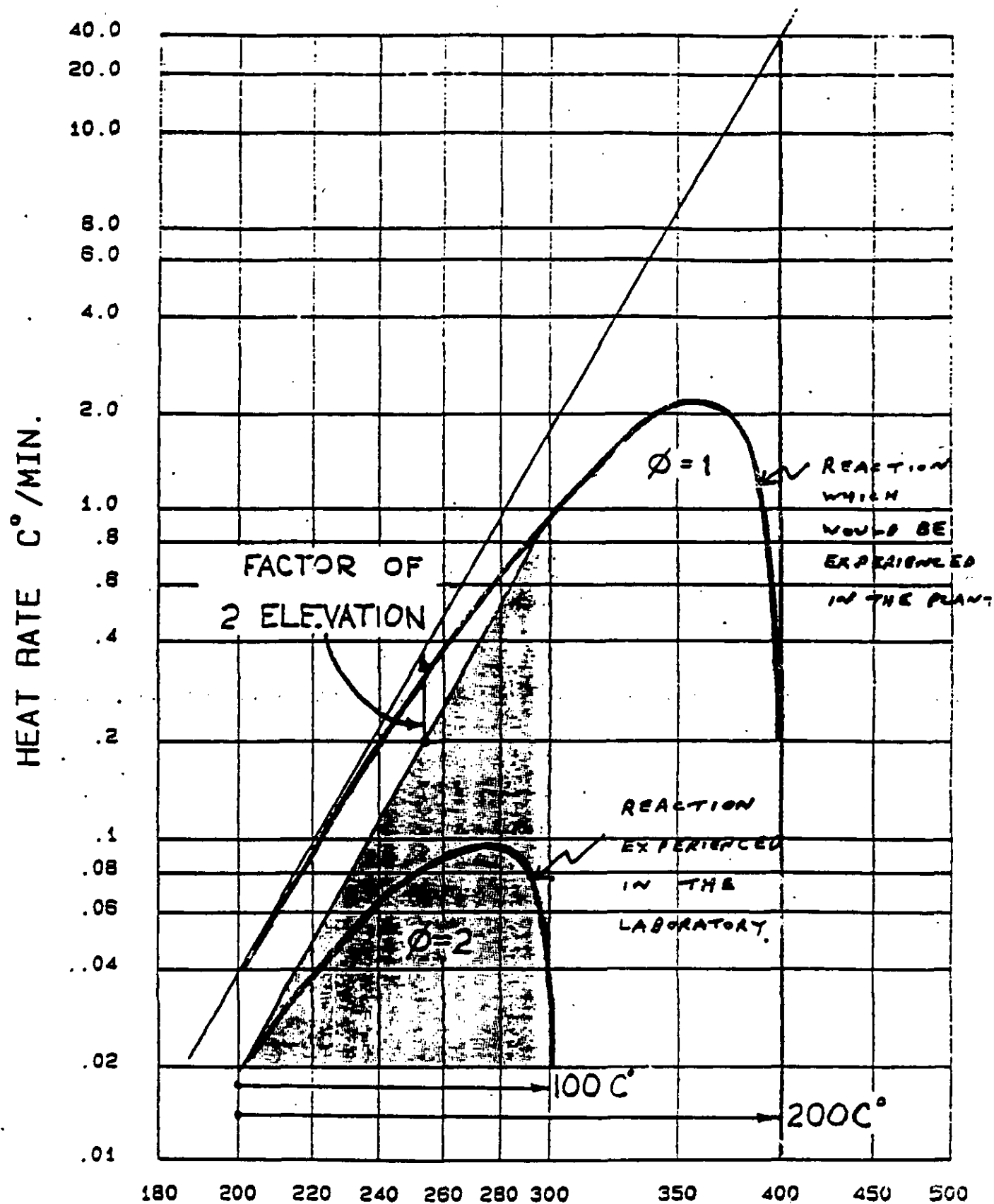
SENSITIVITY

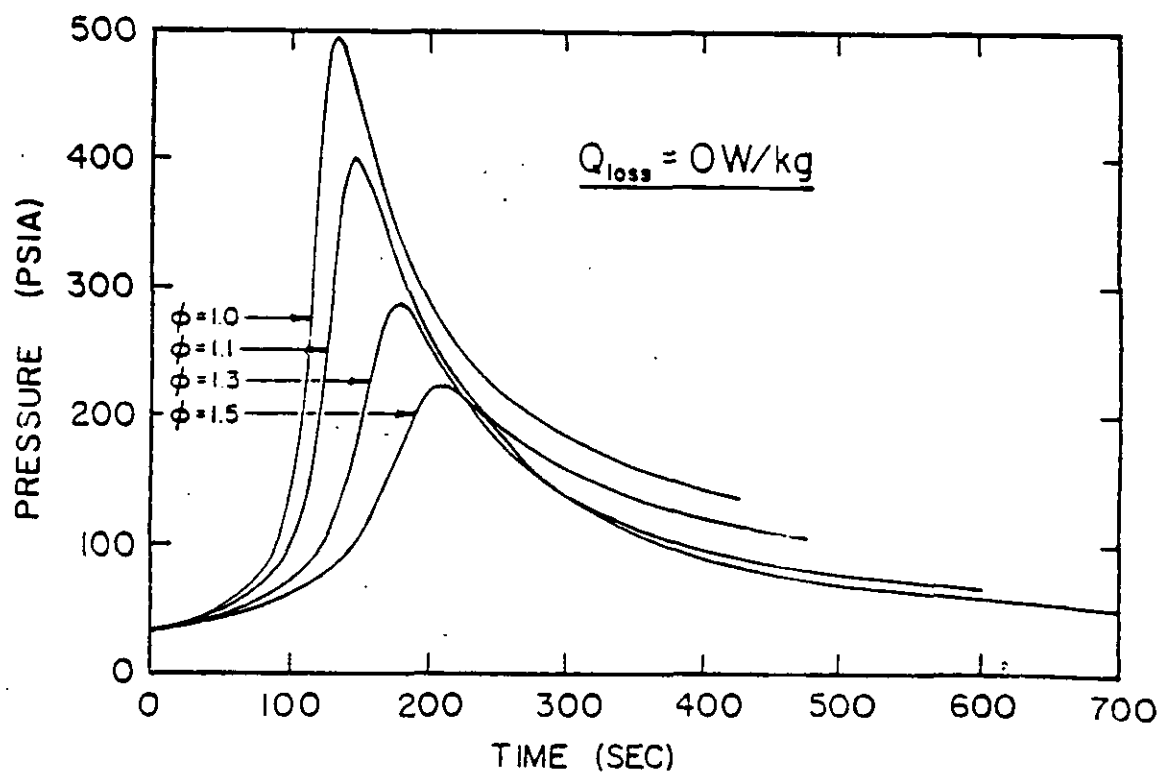
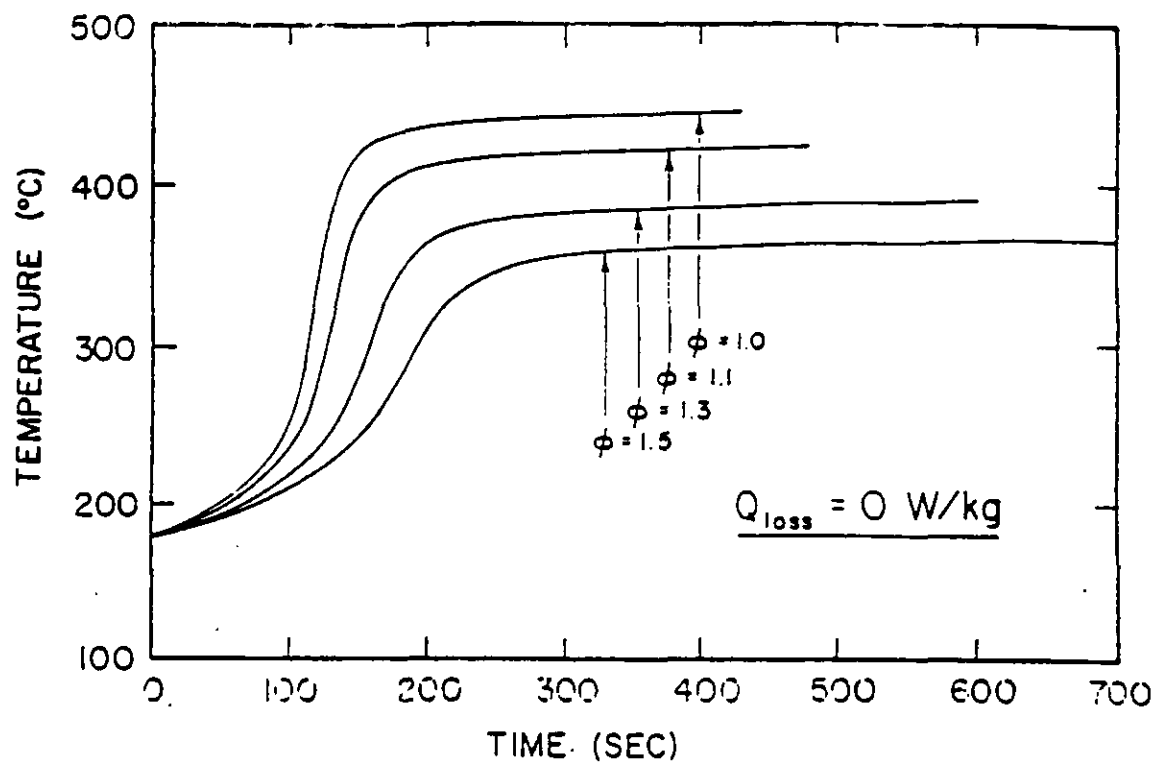
THERMAL INERTIA

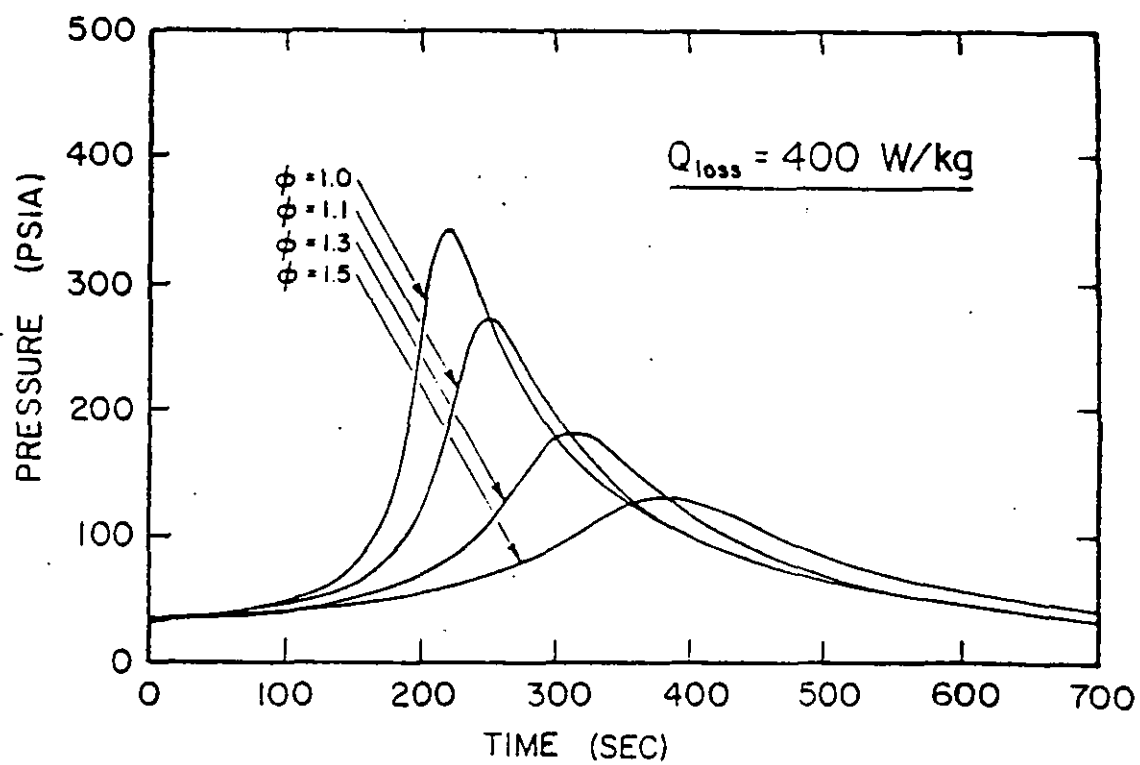
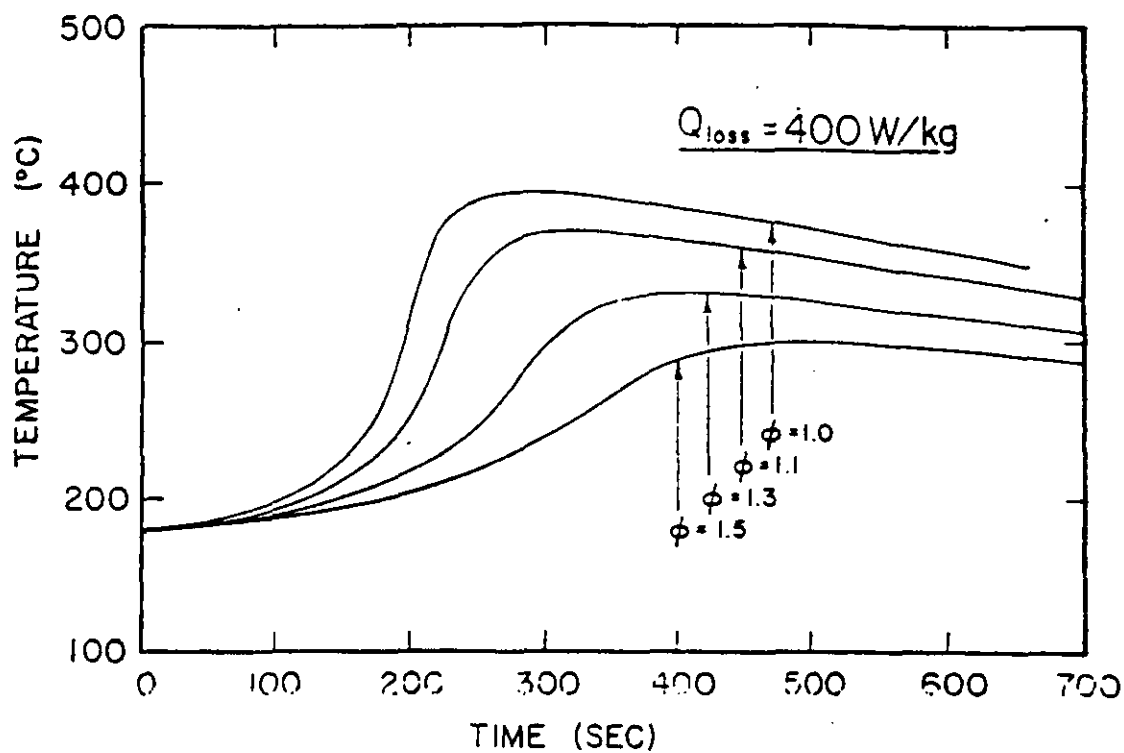
DEFINITION OF PHI

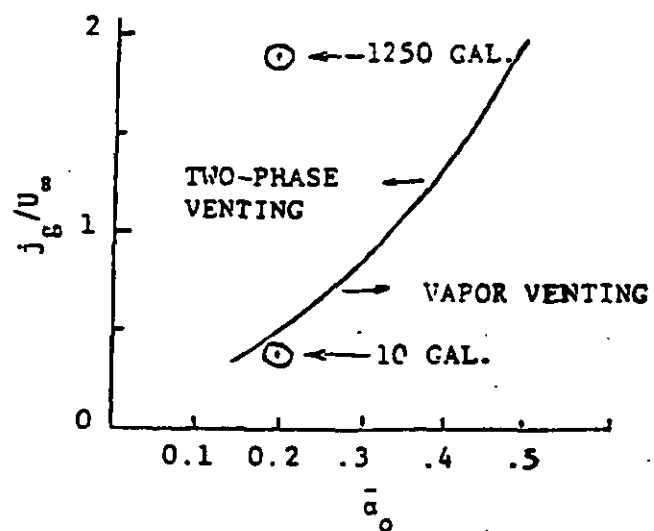
$$\phi = 1 + \frac{M_B C_B}{M_S C_S}$$

$$\frac{1}{\phi} = \text{RATIO OF ACTUAL TEMPERATURE RISE, TO THE TEMPERATURE RISE THAT WOULD OCCUR IF ALL HEAT WENT INTO THE SAMPLE}$$

SCALE-UP USING ϕ







*Illustration of Boundary Between
All-Vapor and Two-Phase Venting
for a Non-Viscous, Non-Foaming
System in a Straight Vessel.*

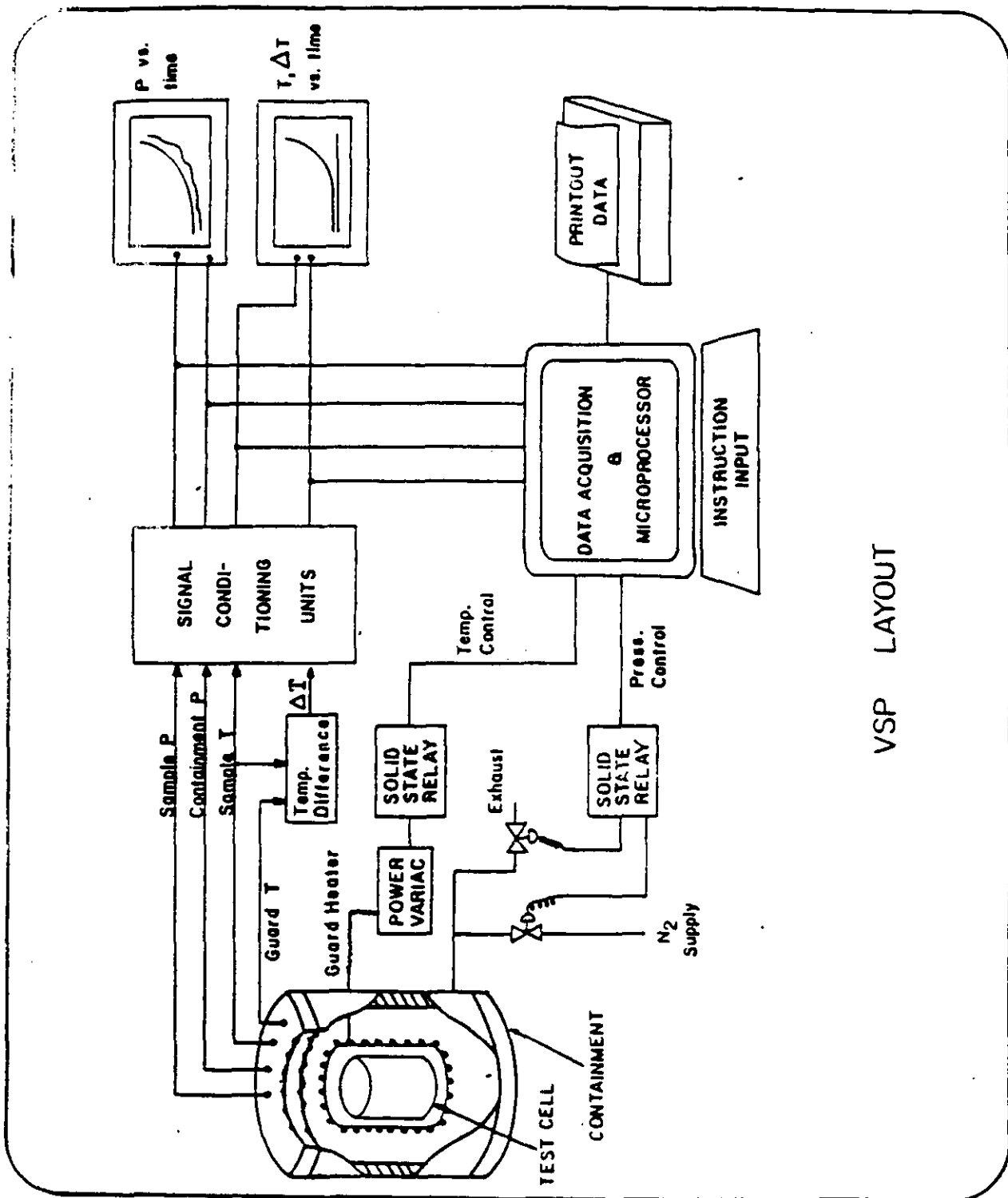
DIERS REACTOR CAPABILITIES

OBTAIN THERMAL STABILITY DATA/KINETICS

CHARACTERIZE TWO-PHASE FLOW REGIME

CHARACTERIZE FLOWING VISCOSITY

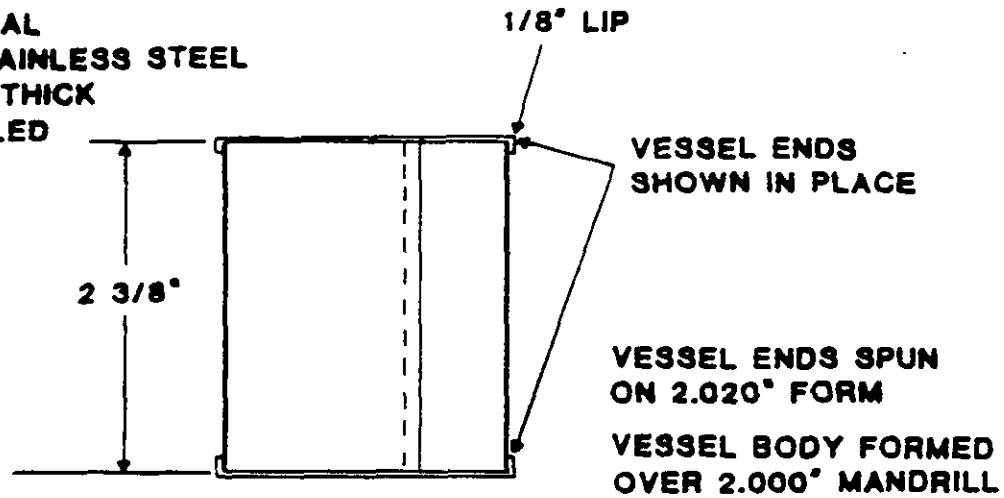
OBTAIN DIRECT ERS SIZING INFO



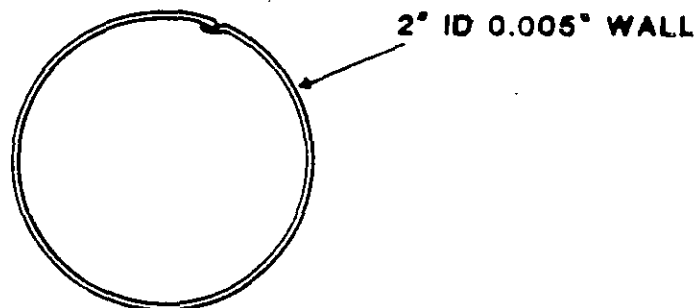
VSP LAYOUT

TEST CELL

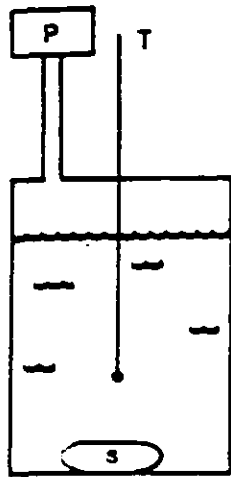
MATERIAL
304 STAINLESS STEEL
0.005" THICK
ANNEALED



ALL SEAMS
SILVER SOLDERED

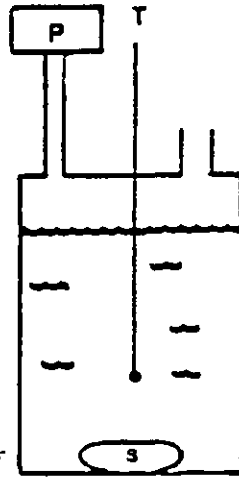


TEST CELL CONCEPTS

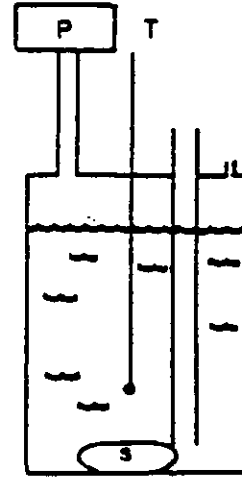


CLOSED SYSTEM

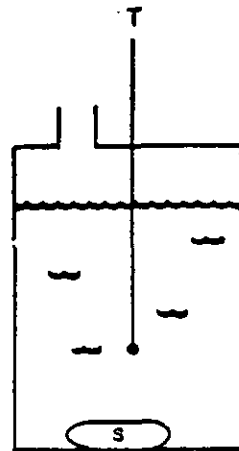
THERMAL DATA



OPEN SYSTEM
'FOAMY'



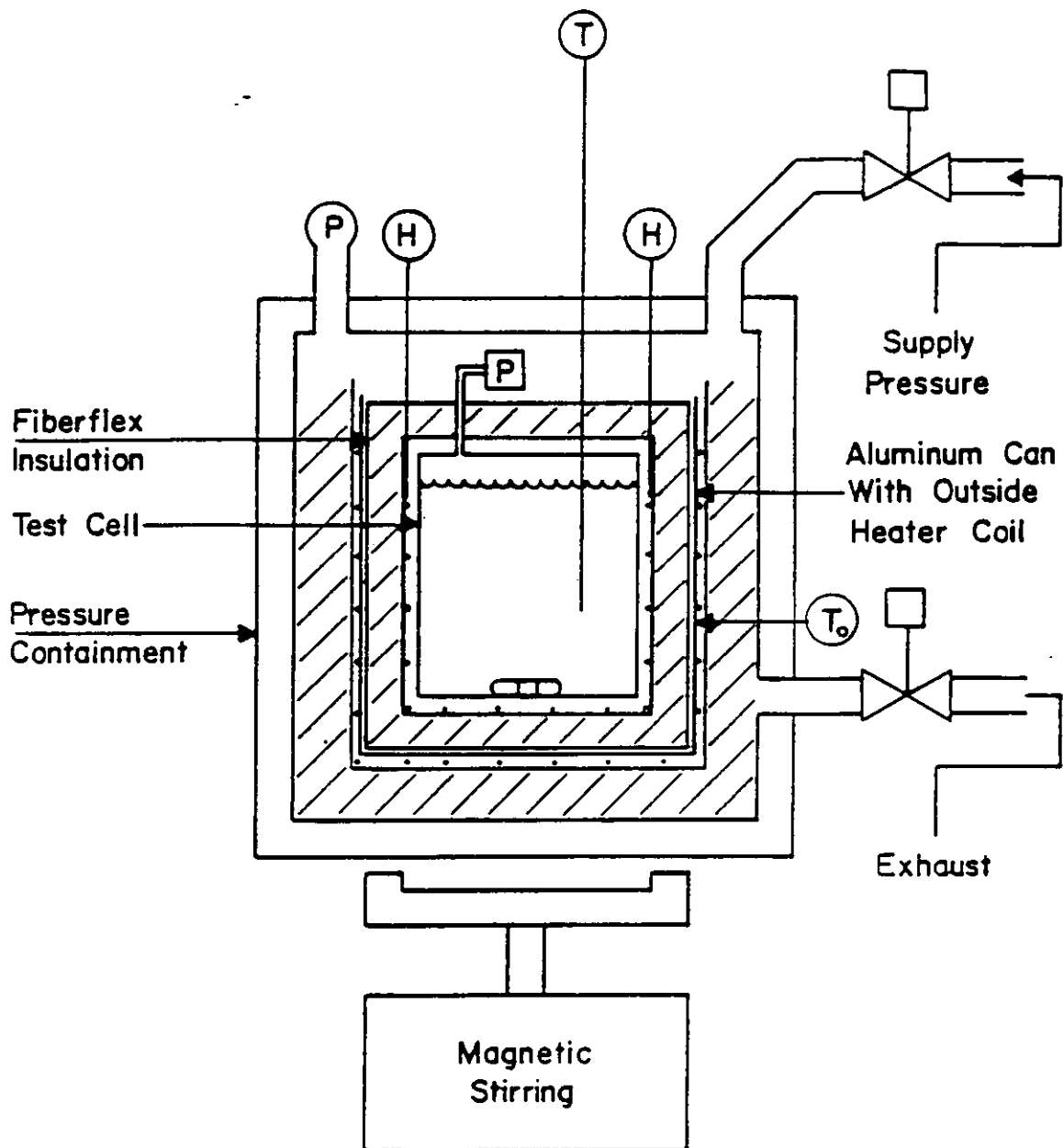
OPEN SYSTEM
'VISCOSITY'



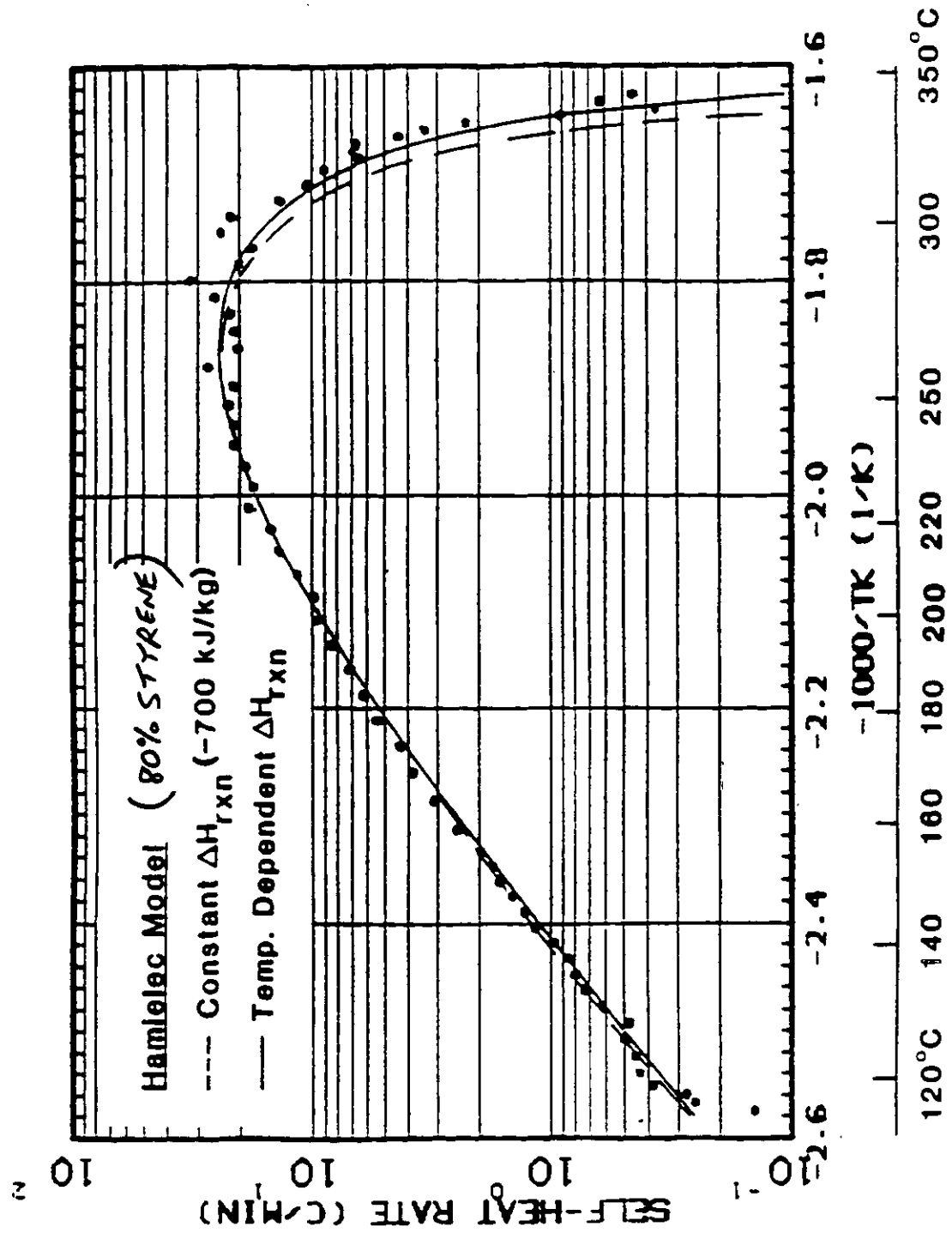
OPEN SYSTEM

DIRECT VENT SIZING
'BLACK BOX'

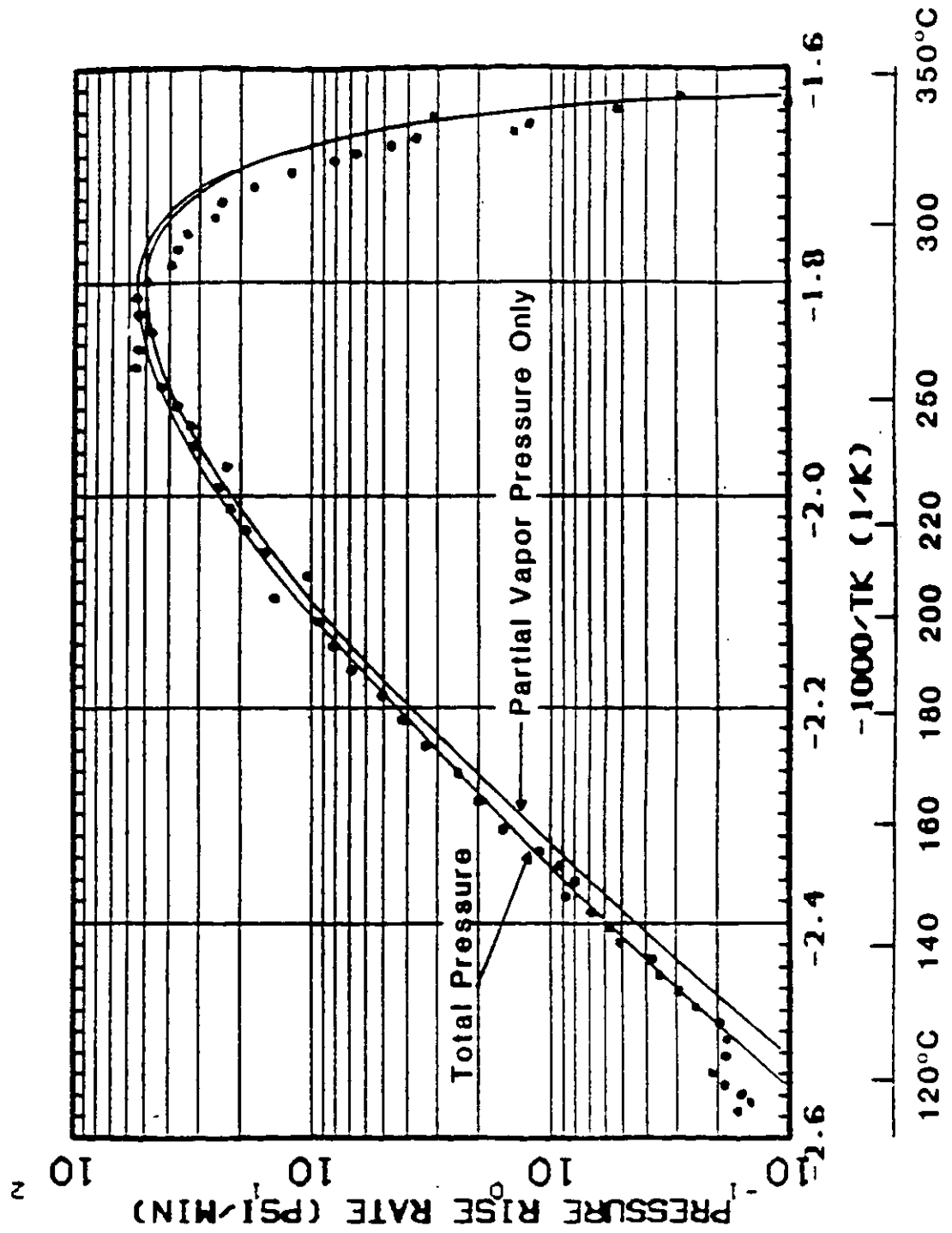
Illustration of the ERS sizing apparatus



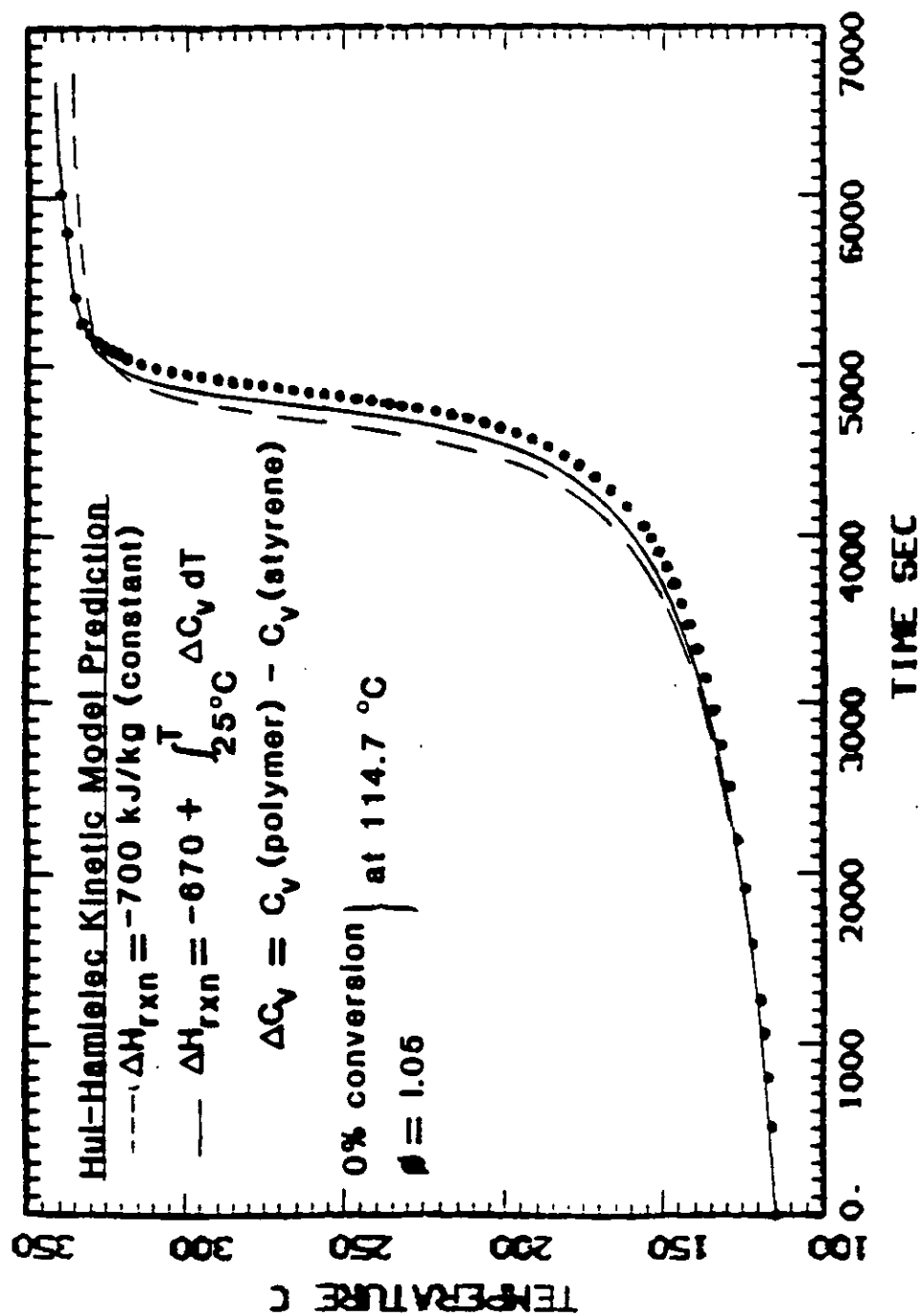
Comparison of self-heat rate data with Hamielec's model

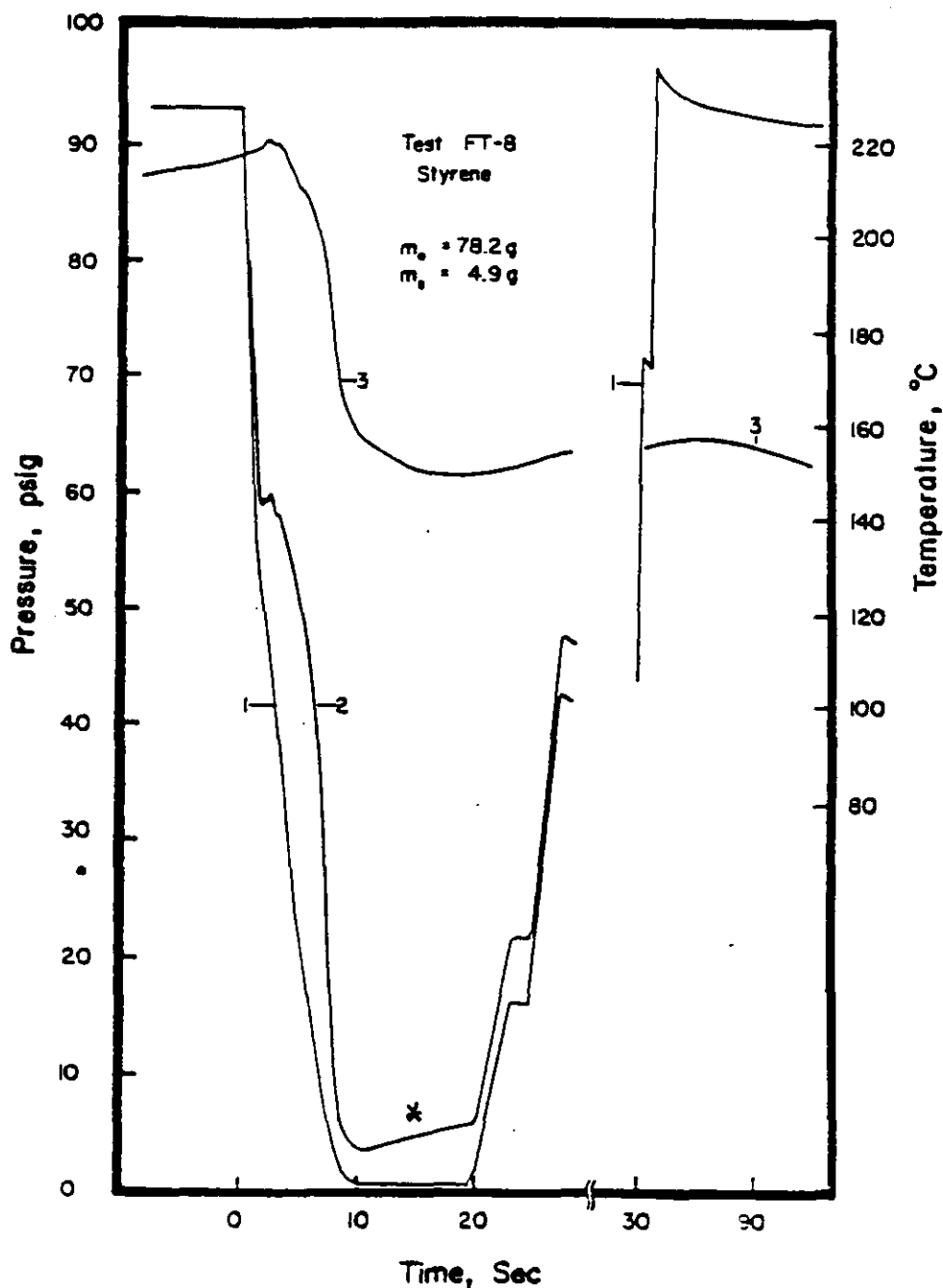


Comparison of total pressure rise rate data with prediction which accounts for pad air effect. (The rise rate due to partial vapor pressure is shown for comparison also.) (80% STYRENE)



Temperature data (80% styrene) and its comparison
with Hamielec's kinetic model predictions.





Depressurization characteristics of styrene (runaway), using a 2.5 mm diameter top vent line. (1) back pressure, (2) test cell pressure, and (3) fluid temperature. m_0 is the initial mass in the test cell and m_s is the mass left behind following completion of the blowdown transient. Note that test cell pressure (2) does not fall to ambient pressure upon completion of the vent transient because the pressure transducer (located inside the containment) is affected by the temperature.

SUMMARY OF FLOW REGIME TEST SERIES

120 cc can (5 mil thick wall), 50.8 mm dia., 60.3 mm ht.

Vent tube dia. 2.5 mm, 19 mm long, top venting

Test No.	Test Fluid	Relief Temperature	P_{sat}	Experimental		Predicted $\alpha_s^{(1)}$		Flow Regime Characterization
				α_0	α_s	Bubbly	Churn	
1	Water	155°C	540 kPa	0.33	0.64	0.98	0.51	Churn *
2	Water	152°C	500 kPa	0.13	0.53	0.98	0.51	Churn *
4	Soapy Water (1000 ppm Joy)	152°C	500 kPa	0.11	0.98	0.98	0.51	Foamy
5	10% Wt. (2) PVA	153°C	515 kPa	0.04	0.89	0.98	0.51	Foamy
6	10% Wt. (3) Polymer in EB	208°C	500 kPa	0.09	0.99	0.99	0.64	Foamy
7	EB	209°C	507 kPa	0.09	0.65	0.99	0.64	Churn
8	Styrene (Runaway)	219°C	510 kPa	0.08	0.95	0.99	0.64	Foamy
10	MMA (4) (Runaway)	160°C	410 kPa	0.1	0.96	0.98	0.60	Foamy
11	PHENOL-HCHO-NaOH (Runaway)	132°C	280 kPa	0.1	0.80	0.99	0.50	Foamy
12	Rubber Cement	128°C	580 kPa	0.14	0.73	0.98	0.62	Churn (5)

(1) $C_0 = 1.0$ in both bubbly and churn regime. Final void fraction α_s is insensitive to flow rate chosen (i.e., HEQ vs. HNEQ flow). These predictions are obtained with the DIERS computer program.

(2) Estimated PVA solution viscosity at relief of 100 cp.

(3) Estimated polymer solution viscosity at relief of 5 cp.

EB = Ethylbenzene

Polymer = Polystyrene (commercial pellet form)

α_0 = Free-board volume fraction at relief

α_s = Free-board volume fraction at the end of blowdown

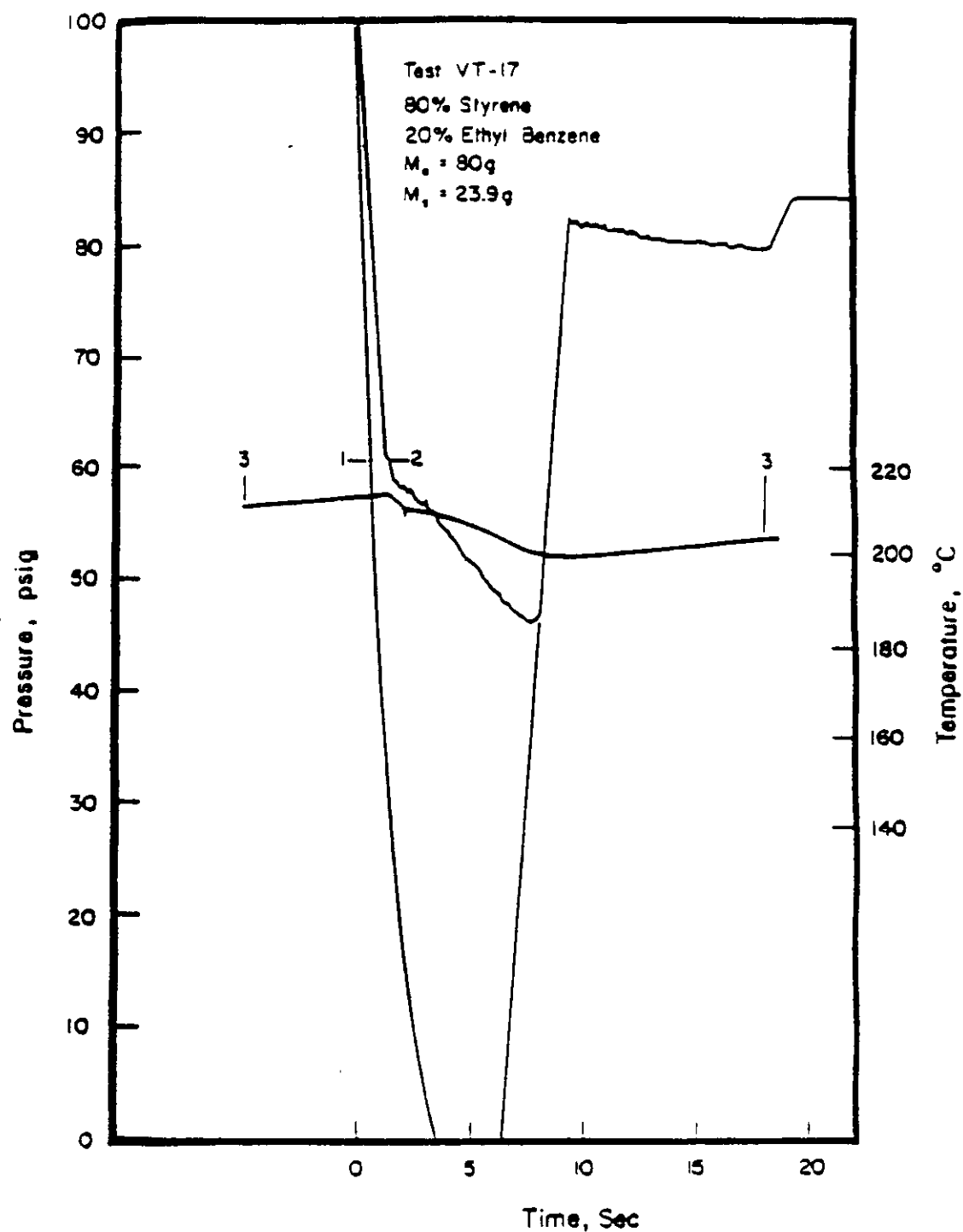
PVA = Polyvinyl alcohol (Elvanol DuPont)

(4) MMA = Methyl Methacrylate

(5) This designation may be misleading since the technique is not capable of discriminating between bubbly and churn-turbulent flow regimes and their transitions at lower void fractions.

* very sensitive to impurities

Illustration of transient blowdown data for 80% styrene - 20% ethylbenzene system using bottom venting. 1) back pressure, 2) test cell pressure, and 3) fluid temperature. M_0 is the initial mass in the test cell and M_s is the mass left behind following the blowdown transient.



*Chester, England
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COMPUTER PROGRAMMING FOR RUNAWAY REACTION VENTING

J.E.Huff*

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The programming details for a generalized simulation of runaway reaction venting are presented. Emphasis is on the determination of vent rate requirements; the approach to relief size selection for the required flows is outlined but not treated in depth. The program versatility is illustrated by application to three example systems of differing degrees of kinetic and pressure-producing complexity. The predictions are in agreement with special-case computer simulation results of others.

INTRODUCTION

A mechanism for the multiphase venting of runaway chemical reactions is proposed in Reference [1], along with an approach to mathematical treatment by the techniques of computer simulation. Though the underlying principles of that paper are quite general, the simulation itself was developed with specific polymerization systems in mind. The treatment is further limited to the proposed well-mixed "uniform froth" concept, which is put forth in that paper to enable the venting to be simulated as a two-phase process. Existing design models at that time were based on all-vapor venting[2], or on an all-liquid venting approximation[3] to the observed multiphase venting phenomena[4].

A refined and generalized version of the computer approach of Reference [1] is described in Reference [5]. The principal equations, programming approach, and example simulation results are presented. This approach yields results in line with the Factory Insurance Association recommendations[6]. An excellent review of published methods is presented in Reference [7].

The purpose of this present paper is to summarize the basic theory and equations of the program of Reference [5] and to describe the program structure in some detail. The versatility of the resulting program is illustrated for three example reaction systems of varying degrees of

* Michigan Division, Dow Chemical USA, Midland, Michigan 48640

complexity. One example serves to compare the present general-purpose simulation with the published results of a program developed independently for that particular system[8]. The agreement is excellent. Other published work employs variations of these same computational models[9,10], and provides valuable additional insight into the nature of the complex venting process.

A further purpose of the present paper is to present an extension of the work of Reference [5] to include the non-uniform vapor distribution model of References [11] and [12]. This extended program was used to generate the simulation results reported in References [13] and [14] for comparison with special-case analytical solutions of the basic equations. Two-phase methods for other classes of fluid systems will be incorporated as they appear. The program of the Design Institute for Emergency Relief Systems ("DIERS", organized under the American Institute of Chemical Engineers) will yield insight and computational methods for the complex and broad subject of vapor-liquid fluid dynamics in venting vessels.

THEORY AND EQUATIONS

General

The physical system of interest in this work is depicted in Figure 1. Vessel geometry is such that the temperature and pressure will be reasonably uniform throughout the contents, with negligible composition gradients within the phases. Also, the time scale of the emergency event is small enough that the event can be formulated as a batch problem. The subscripts on problem parameters refer to the designated locations on Figure 1. Principal parameters also are shown on the figure.

Pressure is computed as the vapor-liquid equilibrium value at the existing condition of temperature and liquid-phase composition. The time for recovery to equilibrium conditions following relief device actuation is assumed to be small with respect to the time scale of the event. This assumption is supported by observation[15].

The above conditions preclude the treatment of non-uniform, propagating events such as vapor or dust deflagrations.

Relief Rate Requirement

The required relief rate at any instant during an event is developed on the basis that the total volume of vapor plus liquid is just equal to the vessel volume. In differential form, this condition is equivalent to setting the volumetric vent rate equal to the rate of volume increase in the vessel at any instant.

The development of the relief rate criterion is presented in Reference [5b]. The resulting Equation 2 of Reference [5a] can be rearranged to relate the rate of vapor generation to the venting rate as follows:

$$(dx_p/d\theta) = [Wv_p/M - (1-x_p)(dv_f/d\theta) - x_p(dv_g/d\theta)]/[v_g - v_f] \quad (1)$$

Vessel Energy Balance

The energy balance on the vessel is developed in Reference [5b] for conditions under which thermal mixing within the vessel is sufficient to allow the properties of all portions of the liquid and vapor phases to be characterized adequately by a single value of temperature. It is assumed also that pressure gradients within the vessel are small with respect to the pressure level so that a single value of pressure may be assigned to the contents. Normal feed and outflow rates are taken as negligibly small with respect to the emergency venting rate, though such terms can be included if desired. The resulting expression in terms of the most commonly available physical property parameters is given as Equation 1 of Reference [5a] for the incompressible liquid-ideal gas case:

$$\begin{aligned} & \{X_r[C_{pg}-R'] + [1-X_r][C_{pf}-T_r(dv_f/dT_r)(dP_r/dT_r)]\}(dT_r/d\theta) \\ & = Q - \{\lambda - P_r(v_g - v_f)\}(dX_r/d\theta) \\ & - \{W/M\}\{[X_0 - X_r][\lambda - P_r(v_g - v_f)] + P_r[X_0 v_g + (1-X_0)v_f]\} \end{aligned} \quad (2)$$

For a given value of the rate of vaporization from Equation 1, a value of the rate of temperature rise, $(dT_r/d\theta)$, can be obtained from Equation 2 using current values of the other parameters. The derivatives of specific volumes and pressure with temperature are approximately equal to the change in the values over a small temperature interval at current phase compositions.

Systems exhibiting a strong effect of composition on pressure require a very small increment size to avoid finite difference errors from equating (dP_r/dT_r) to $(\Delta P_r/\Delta T_r)$ at the current composition. A better result at reasonable increment sizes is obtained by expressing the left side of Equation 2 as follows:

left member of (2)

$$\begin{aligned} & = \{X_r[C_{pg}-R'] + [1-X_r]C_{pf}\}(dT_r/d\theta) \\ & - \{1-X_r\}\{T_r(dv_f/dT_r)(dP_r/d\theta)\} \end{aligned} \quad (2a)$$

Finite-difference values of $(\Delta P_r/\Delta \theta)$ are available after the first time increment for use as an approximation of $(dP_r/d\theta)$ in Equation 2a. Equation 2 must be used for the first increment.

Vapor Content of Two-Phase Streams

The solution of Equation 2 requires a value of the quality (vapor weight flow rate as a fraction of total weight flow) of the vent stream as it leaves the vessel at point "O" of Figure 1. Limiting cases are $X_0 = 1$ (all-vapor venting) and $X_0 = 0$ (all-liquid venting). A more realistic lower limit for venting from the top of the vessel is $X_0 = X_r$, where X_r is the overall weight fraction vapor in the vessel. This criterion is the "well-mixed" or "homogeneous froth" specification as proposed and implemented in Reference [1].

The specification of $X_0 = X_F$ has come into rather wide use as a conservative but realistic basis for taking account of the two-phase venting phenomena[5,7,8,9,10,11,12,13,14,16,17]. However, this criterion can be under-conservative in the cases of multiple and gas-producing reactions if invoked from the first instant of venting[13,14]. Thus, a proper study of a given problem must include an exploration of the sensitivity to assigned values of X_0 . The most conservative results must be accepted in the absence of knowledge of actual values of X_0 .

Ideally, values of the quality at the vent entrance should be obtained from appropriate correlations at given system conditions. The required predictive methods are expected to be one product of the program of the AIChE Design Institute for Emergency Relief Systems. An example of one approach has appeared in recent literature for a specific flow regime and vessel geometry [11,12,18]. This method is based on the use of the "drift flux" concept[19] to relate vapor holdup within a liquid to vapor traffic through the liquid. Vapor flow may result from a bottom feed of gas or from bulk vaporization of a portion of the liquid. The latter source is of interest in the present case of thermal or chemical energy input with subsequent venting and depressurization.

Consider the case of vapor formation within a non-viscous, non-foaming liquid contained in a vertical vessel of constant cross-section. Vapor flow is presumed to be high enough in cases of present interest so that the flow will be in the churn-turbulent flow regime[19]. If the interface is below the top of the vessel, a relationship between vapor holdup below the interface and the vapor flow from the interface is given by Equation 3 of Reference [18]:

$$j_{g\infty} = 2\bar{\alpha}U_{\infty}/(1-C_0\bar{\alpha}) \quad (3)$$

A value of C_0 of 1.5 is suggested[18]. Lower values of C_0 in general will be somewhat conservative in that lower flow rates will be predicted for a given interface level. A value of C_0 of unity is used here, since this value is implicit in the balance of the published model equations.

The parameter U_{∞} of Equation 3 is given by Equation 4 of Reference [18]:

$$U_{\infty} = 1.53[\sigma g v_f(1-v_f/v_g)]^{1/4} \quad (4)$$

Equation 3 is used to test for boil-over conditions. If one assumes that the interface is at the top of the vessel, the value of vapor holdup within the liquid is the same as the total fraction vapor in the vessel (one minus the liquid fill fraction). The corresponding superficial velocity of the vapor is then obtained from Equation 3. If this vapor load exceeds the vapor-handling capacity of the relief system, then the holdup must be less than the overall vapor fraction in the vessel. That is, some of the vapor must be contained in a freeboard space above the interface; only vapor will flow from a top vent. Conversely, a vapor-handling capacity in excess of the flow from equation 3 denotes a boil-over condition; the interface has risen out of the vessel. In this boil-over case, the vapor superficial velocity at the top of the vessel for the churn-turbulent regime with $C_0 = 1$ is given by Equation 12 of References [11] and [12] (note error in [12]; minus sign is missing on density ratio term). Using Equations 9 and 15 in Equation 12 (all of Reference [11] or [12]) and solving for X_0 , one obtains:

$$X_0 = [(U_{\infty}A_r)/(GA_v v_g) + (v_f/v_g)]/[(1-\bar{\alpha})/(2\bar{\alpha}) + (v_f/v_g)] \quad (5)$$

Equation 5 relates X_0 to G for given vessel conditions. The relief system flow models of the following section provide a second relationship between X_0 and G to be solved simultaneously with Equation 5.

According to Equation 5, the vapor content of the vent stream will increase as the vent area is decreased. This trend is consistent with a recommendation to maximize the vapor content by staging large and small relief devices so that the available relief area will change to match the changing requirement during the event[15]. This strategy would minimize the extent of liquid boil-over, provided that reclosing devices are used. However, reducing the liquid content by reducing the vent size can only reduce the degree of protection; two-phase venting must be accepted if boilover occurs at minimum required vapor rates.

Vent System Flow Capacity

The vent system flow capacity most often will be limited by a single piping section or restriction. Thus, only the flow capacity of the limiting section need be formulated in the relief simulation. For orifices and short nozzles*, it is assumed that the residence time is too short for appreciable vaporization of any liquid portion to occur. The resulting flow equation is:

$$G^2/C_d^2 = \{2P_0\} \{ [1-X_0][(v_f)_0][1-n] + [X_0][(v_g)_0][k/(k-1)][1-n^{(k-1)/k}] \} + \{ [1-X_0][(v_f)_0] + [X_0][(v_g)_0][n^{-1/k}] \}^2 \quad (6)$$

Equation 6 is a form of Equation 32 of Reference [20]. The flow rate will reach a maximum ("choked", "critical") value as the outlet-to-inlet pressure ratio is decreased. The value of this ratio at the maximum flow condition is obtained by the method of Reference [20]. This "critical pressure ratio" typically is fairly constant at a value in the range of 0.85 to 0.95 for quality values below 10 weight % vapor. The ratio decreases more or less linearly from the value at 10% vapor to the established values for gas flow at $X_0=1$.

The calculation for pipe flow is complicated by the need to account for frictional losses, significant extent of flashing, and perhaps significant elevation changes. In addition, the possibility that liquid and vapor may flow at different velocities ("slip" flow) must be considered.

One computational approach to the complex pipe problem is to follow the pressure gradient at a given flow rate and upstream condition by stepping down the pipe in small pressure drop increments, keeping track of changing conditions due to equilibrium flashing and changing vapor-liquid ratio. The critical flow condition is attained if the acceleration term becomes equal to the incremental pressure drop, thus leaving nothing for additional frictional length. The known pressure at the pipe outlet location may be attained before this critical flow condition is attained. Either way, the length of pipe for the given problem conditions has been determined. Such an approach based on the mechanical energy balance formulation is presented in Reference [1] and refined in Reference [5]. The working equation is:

*See first paragraph on page 7 for short vs. long nozzle criterion.

$$L = \Sigma(\Delta L) = \Sigma[\Delta P - \Delta K_e / \bar{v}_{av}] / [(\Delta P / \Delta L)_{tf} + g(\Delta Z / \Delta L) / \bar{v}_{av}] \quad (7)$$

$$\text{where } \bar{v} = X v_g + (1-X) v_f$$

$$\text{and } \Delta K_e = 0.5 \Delta \{ G^2 [X^3 v_g^2 / \alpha^2 + (1-X)^3 v_f^2 / (1-\alpha)^2] \}$$

The subscript "av" denotes the arithmetic average value over ΔL .

The momentum balance formulation is also in general use:

$$L = \Sigma(\Delta L) = \Sigma[\Delta P - \Delta K_m] / [(\Delta P / \Delta L)_{tf} + g(\Delta Z / \Delta L) / v_{av}] \quad (8)$$

$$\text{where } 1/v = \alpha / v_g + (1-\alpha) / v_f$$

$$\text{and } \Delta K_m = \Delta \{ G^2 [v_g X^2 / \alpha + v_f (1-X)^2 / (1-\alpha)] \}$$

The potential energy formulation is not strictly correct in Equation 8. The small error in this small term is accepted for mathematical convenience.

Equations 7 and 8 are algebraically identical for the no-slip condition, for which:

$$1/\alpha = 1 + [v_f(1-X)/(v_g X)] \quad (9)$$

The numerical results obtained from Equations 7 and 8 show no important differences for slip flow, at least for the conditions of this present paper. The choice between slip or homogeneous flow must be made based on the best fit to data for similar conditions. Observations of the flow patterns during pressure relief tests have been reported[15].

An auxiliary correlation is required to relate α to X for the slip-flow condition. The Lockhart-Martinelli[21] correlation is used in this present paper, both for the volume fraction holdup and for the two-phase frictional pressure drop computations.

The energy balance for adiabatic two-phase flashing flow is the conventional equation for conservation of enthalpy plus kinetic and potential energy. The energy formulations are those given under Equation 7. The residence time in the relief system is assumed to be too short for appreciable chemical reaction to occur.

Appreciable savings in computer time are realized by generalizing the results of detailed pipe flow computations for use in the venting simulations. Such results are represented well over a sufficiently broad range by an equation of the form:

$$G/P_0^n = a + bX_0 + cX_0^2 \quad (10)$$

It is important to note that valid relief rate requirements can be determined from the venting simulation even if the value of the coefficient C_d in Equation 6 or a similar proportionality on G in Equation 10 is not known. The simulation is run using an "effective" vent flow area. The actual area is determined from auxiliary vent system flow computations, using the vent rates and conditions as computed in the venting simulation. However, the same flow model (short nozzle or long pipe) must be used in both venting and auxiliary sizing computations to avoid ambiguity in the sizing results at different times in the event.

A criterion for choosing between short nozzle or long pipe models is presented in Reference [16]. According to this source, equilibrium-flash models should be used for flow passages over about 0.1 m in length. The nozzle length in standard pressure relief valve "orifices" is usually slightly longer than this limit. However, there is no assurance that the orifice is the flow-controlling section in all valves. More work is required to define safety valve behavior in two-phase flashing flow [22]. A project within the DIERS program will add to present knowledge on this question.

Vapor-Liquid Equilibrium

The vapor-liquid equilibrium is formulated for ideal vapor mixtures as:

$$P_r = \sum p_i = \sum (\gamma_i x_i P_i^0) \quad (11)$$

The vapor mole fractions equal the partial pressure fractions. Vapor pressure data are introduced in the form of constants in the Antoine equation:

$$\log P_i^0 = A_i - B_i / (T + C_i - 273.2) \quad (12)$$

Activity coefficients for non-ideal liquid mixtures are computed from equations relating the activity in the mixture to coefficients as determined for the binary pairs. Equation 7.37 of Reference [23] is useful for this purpose in that it is general for both monomeric and polymeric components:

$$\ln \gamma_k = [(v_k'/RT) \sum_{ij} (A_{ik} - A_{ij}/2) \phi_i \phi_j] + [\ln(\phi_k/x_k) + 1 - \phi_k/x_k] \quad (13)$$

$$\text{where } A_{ij} = A_{ji} \text{ and } A_{ii} = A_{jj} = 0$$

Better predictions for monomeric components are obtained in most cases if the Wilson local volume fractions are used in the derivation of the second bracketed term on the right side of Equation 13. The result is Equation 15 of Reference [24] with the addition of the first bracketed term on the right side of Equation 13:

$$\begin{aligned} \ln \gamma_k &= (v_k'/RT) \sum_{ij} [(A_{ik} - A_{ij}/2) \phi_i \phi_j] - \ln(\sum_i x_i \Lambda_{ki}) \\ &+ 1 - \sum_i [x_i \Lambda_{ik} / (\sum_j x_j \Lambda_{ij})] \end{aligned} \quad (14)$$

$$\text{where } \Lambda_{ij} \neq \Lambda_{ji} \text{ and } \Lambda_{ii} = \Lambda_{jj} = 1$$

The first term on the right of Equation 14 is retained only for systems containing polymer; $A_{ij}=0$ if component k is polymeric and neither component i or j is polymeric.

Equation 14 reduces to 13 for the case of $\Lambda_{ij} = v_j'/v_i'$. Equation 13 in turn reduces to the polymer-solvent binary relationship of Reference [25], which can be expressed as:

$$\ln \gamma_1 = \ln(\phi_1/x_1) + [\phi_2(1 - v_1'/v_2') + \mu \phi_2^2] \quad (15)$$

where component 2 is polymeric. The interaction coefficient is:

$$\mu = v_1' A_{12} / RT$$

Equation 14 is quite general, but may not be good enough for two-liquid-phase systems. A totally-immiscible model is readily programmed and is usually good enough for vent size selection purposes.

Systems are often charged in a noncondensable gas atmosphere. The computer program allows the choice of treating this initial pad gas as one of the equilibrium components, or as a non-equilibrated insoluble component. In the latter case, the partial pressure of the pad gas is proportional to the moles of gas and the absolute temperature.

Thermokinetic Model

The reaction rates are determined from the expression:

$$df_i/d\theta = f_i^a m_j^b \exp(K' - E/T) \quad (16)$$

The model is defined for each reaction by specifying the exponents a and b and the component numbers i and j. Forward and reverse reactions for reversible reactions are specified separately. Values of K' and E are required for each reaction. The enthalpy change of each reaction in the liquid state is specified, along with the temperature to which the value applies. The model of Equation 16 will accomodate most systems. Kinetic expressions for special cases can be patched into the subroutine quite easily, as is done for the styrene polymerization example of a later section of this paper.

Heat Transfer Model

Heat transfer to wetted surfaces is formulated as follows:

$$q_w = (UA)(T_r - T_w) = (WC)_w(\Delta T_w/\Delta\theta) \quad (17)$$

A constant "wall" temperature can be specified to simulate heat removal by an external fluid. Otherwise, the heat sink effect of the vessel itself is simulated.

Thermophysical Properties

Thermophysical properties used in the simulation are specific heats of liquid and vapor at constant pressure, molecular weights, liquid density, enthalpy of phase change (vaporization or degassing), vapor pressure, and surface tension. Vapor and liquid viscosities are required for auxiliary flow computations.

Property values are generated in subroutines from specified values of the coefficients in appropriate regression equations. The usual power series in temperature proves to be a good choice. Any pressure dependency is accommodated by using property values at saturation conditions. Such representations do not give a good fit to certain pure-component properties in the critical region. However, properties in mixtures are of more interest than pure-component properties in the runaway reaction case. This is particularly true for noncondensable components, which can have appreciable solubility in the liquid phase even though the pure component exists only as a gas. The power series fits are extrapolated from the sub-critical region, through known or estimated values of the corresponding property values for dissolved gas (latent heats of vaporization extrapolate to heat of solution values, etc.). The standard state for noncondensable components is taken as the hypothetical liquid state ("symmetric convention"[26]).

Non-volatile components are treated by assigning a negligible vapor pressure via the coefficients of Equation 12. The concentration of such components in the vapor phase is thus negligible; dummy vapor property coefficients can be supplied for such components.

The property subroutines use the simple additive volume and weighted sum rules for mixture properties. More complex mixing rules and energetics can be patched into the subroutines as required.

COMPUTER PROGRAM

General

The computer programming strategy presented below is geared more toward unsophisticated coding and speed of execution than toward high precision of the finite-difference integration. Since the primary goal is to choose between standard sizes of relief system components, high precision is not needed. The precision of the suggested programming is more than adequate for sizing purposes, but standard integration routines can be invoked if desired. Suitable error criteria for such routines are identified in the following sections.

A key point in the present strategy is the decision to include only an approximate representation of the vent system flow capacity in the simulation, leaving the details of the vent system component sizing and layout to a separate program. This strategy greatly reduces the size of the program and speeds up execution by roughly an order of magnitude. Some judgement is required to assign coefficients to the flow capacity approximations of Equations 6 or 10 so that the percentage difference between these results and detailed flow simulations will be acceptably constant over the range of a given runaway simulation. In general, little judgement is required to obtain a good representation of the flow up to the peak venting pressure. Obtaining a good flow representation from the peak pressure to the end of the event is more difficult, but is of little importance in determining vent system size requirements. If program size and running time are of little concern, the detailed capacity computations can be carried out at each increment of time by methods outlined in a previous section of this paper.

Overall Program Structure

The diagram of the overall programming is presented in Figure 2. Numbers in parentheses on Figure 2 refer to the following notes.

1. Give problem title, and specify system characteristics: Number of components, number of reactions, choice of reactant to use when determining the maximum depletion per time step ("key" reactant), choice of liquid-phase activity coefficient model, choice of output device and reporting options.

Specify thermokinetics and reaction stoichiometry: Give component numbers of i and j and values of exponents " a " and " b " in Equation 16 for each reaction, give enthalpy change of each reaction (liquid-phase standard states) and temperature at which reported, give number of moles of each component taking part in each reaction (flag products with minus sign on number).

Specify pure-component property equation parameters: Refer to earlier section of this paper for description of thermo-physical property representation; includes specific heats of liquid and vapor, molecular weights, liquid density, enthalpy of phase change (vaporization or degassing), Antoine constants in Equation 12, surface tension, liquid activity coefficient parameters.

Specify problem parameters (see example output of Table 1): Give total weight of liquid charged and relative weight of each component, initial pressure (no gas pad present if value is less than initial Equation 11 pressure), initial temperature in vessel, effective opening pressure of relief device (mean of start-to-open and full-open pressures), effective reclosing pressure, total internal volume of protected system, thermal energy input from temperature-insensitive sources (fire, etc.), cross-sectional flow area at gas-liquid interface, effective diameter of relief system, backpressure on relief system. Also, specify step control parameters: maximum temperature rise per step before vent actuation, number of increments for depletion of key reactant while venting, print frequency before venting, minimum pressure change between prints while venting. Specify values of K' and E in Equation 16 for each reaction, (UA) and (WC) in Equation 17 along with initial wall temperature specification, values of pressure ratio and " k " in Equation 6 (discharge coefficient is included in effective flow area value) or flow coefficients in Equation 10. Specify choice of method for vent stream quality computation.

Compute equilibrium phase inventory and compositions; report initial conditions.

2. The limiting reactant of the current major reaction becomes the key until depleted; increment size is based on the degree of depletion of the key per step.
3. See Figure 3 and notes of the following section.
4. From Equation 1 using latest values of specific volume derivatives (can neglect terms with derivatives for first increment).
5. Heat input from reactions is product of internal energy change of reaction at current temperature times reaction rate (positive heat release for negative energy change). Reduce heat input from fire as wetted area changes with decreasing inventory (effective wetted area taken as proportional to inventory for present purposes; questions as to best model for relating heat transfer coefficient and area to vapor content and interface level remain to be answered). Compute heat flow to walls per Equation 17.
6. Use Equation 2 for first increment with dP_r/dT_r and dv_f/dT_r evaluated over a small temperature range at initial composition. Thereafter use Equation 2a for the left member of Equation 2 and use the current values of $\Delta v_f/\Delta T_r$ and $\Delta P_r/\Delta \theta$ for the differentials. All other values in Equations 2 and 2a are obtained from property subroutines at the current temperature and composition. Maximum $\Delta \theta$ before vent actuation is determined from the specified maximum temperature rise per step and current value of $dT_r/d\theta$. Maximum $\Delta \theta$ after vent actuation is set such that the key component would be depleted in the remaining number of specified increments if reaction and venting should continue at the current rate. If necessary, $\Delta \theta$ is reduced so that not over 90% of the vapor inventory will be vented during the current increment.

7. Obtain change in component inventory from current reaction rates, stoichiometric numbers for components in each reaction, and value of $\Delta\theta$. If a component concentration falls below zero due to finite-difference overshoot, reduce $\Delta\theta$ to obtain zero concentration. Alternatively, $\Delta\theta$ can be left unchanged with an adjustment in the rate of the appropriate reaction (and in $dT_r/d\theta$) such that the component concentration just goes to zero. Add time increment to current value of time; add $[(dT_r/d\theta)\Delta\theta]$ to T_r . New value of X_r is determined from overall material balance rather than from gradient to avoid accumulation of finite-difference error. Integrating routines such as the Runge-Kutta or predictor-corrector codes can use the integrated vs. material balance quality values as an error criterion.
8. Run is terminated if liquid charge expands to fill system before vapor-space pressure reaches relief device set point. Such a premature activation of relief device due to hydrostatic pressure is an under-conservative case.
9. Using current values of vent flow rate and phase compositions.
10. At current temperature and total component inventory; see Figure 4 and associated notes.
11. This trial-and-error routine can be invoked at each re-closing and re-opening of valve-type devices. If the relief system is oversized for current loads, appreciable computer time is required to track the valve cycling. In general, computation time is saved with little loss of realism by specifying smaller increment size to limit the overshoot to acceptable levels without using the trial-and-error approach. Integrating routines may adjust increment size to attain a specified precision on pressure.
12. Crisis is past if all reaction rates have peaked and pressure is falling from peak value.
13. Obtain current finite difference gradients for use as approximations of values of derivatives as required in next increment for Equations 1 and 2a.

Vent Stream Quality and Flow

The routine for the vent stream quality and flow computations, step 3 of Figure 2, is given as Figure 3. The numbers in parentheses on Figure 3 refer to the following notes.

1. The pre-set criterion is the weight fraction liquid in the stream leaving the vessel (weight flow fraction liquid), expressed as a fraction of the weight fraction liquid in the vessel itself. A value of unity specifies the homogeneous-froth model, while a value of zero specifies all-vapor venting. Variations include an option to switch from a value of unity to zero at a specified value of vessel void fraction.
2. The vapor flow rate required to just reach the incipient boil-over condition (interface at the top of the vessel) is obtained from vapor rate vs. holdup correlations such that expressed by Equation 3. The assumption of all-vapor venting for the first trial provides a logical basis to test for boilover conditions. If the vent capacity for all-vapor flow is less than the value corresponding to incipient boilover, then some freeboard volume must be present. A top vent will thus see only vapor flow.

3. As discussed in the text, detailed vent flow computations are left to a separate program. The computations here are based on Equation 6 if the last two flow parameters are given as zero, or on Equation 10 if non-zero values are given.
4. The material balance across the vent entrance plane is given by Equation 5 for the ideal churn-turbulent case. Other cases and models can be added as they become available.
5. The value from the previous time increment provides a good starting point. Linear interpolation or half-interval methods converge rapidly.
6. This result follows from the logic of note 2 above.

Phase Equilibration Routine

The diagram of the phase equilibration routine, step 10 of Figure 2, is given as Figure 4. The numbers in parentheses on Figure 4 refer to the following notes.

1. The quality parameter X_v is the moles vapor phase per mole total liquid plus vapor in the vessel. Conversion to the weight fraction parameter X_r must await knowledge of the equilibrium pressure and phase compositions, which are determined in this routine. Vapor pressures at the current value of vessel temperature are computed from Equation 12.
2. Liquid-phase mole fractions are obtained by combining the phase material balance and the equilibrium criterion of Equation 11 to obtain:

$$x_i = [(\text{moles } i \text{ in vessel})/(\text{total moles in system})]/[1 - X_v(1 - \gamma_i P_i^0)/P_r]$$

Vapor-phase compositions are obtained from equation 11.

3. Newton's method will converge the trials very rapidly for ideal solutions (activity coefficients equal to unity). A bounded linear interpolation routine suffices even with moderate non-idealities; the trailing values of activity coefficients fall into place as convergence is approached. Severe non-idealities may require that the activity coefficient/composition loop be repeated two or three times before changing the trial value of pressure. Convergence can be assured in the worst cases by introducing another level of trial-and-error to establish the precise values of the activity coefficients for each trial pressure value. Activity coefficients are computed from Equation 14.
4. Phase densities are computed at current compositions and conditions. The overall density is known (total inventory divided by vessel volume). Knowledge of phase compositions permits conversion between the weight and mole vapor fractions.

EXAMPLE APPLICATIONS

Styrene Polymerization

The present example is taken from Reference [13]. A vertical tank of styrene is undergoing adiabatic polymerization after being heated inadvertently to 243 K. The following parameters apply:

Vessel outside diameter = 2.44 m
 Vessel inside sectional area = 4.57 m²
 Height of straight side = 2.44 m
 Total internal volume = 13.16 m³
 Maximum allowable working pressure = 5 bar (abs.)
 Relief opening pressure = 4.5 bar (abs.)
 Pressure at allowed 10% accumulation (Section VIII of Reference [27]) = 5.4 bar (abs.)
 Initial styrene charge = 9500 kg
 Normal gas pad = atmospheric air via a small conservation vent (assume air displaced from vessel by styrene vapor after atmospheric boiling point is attained)

The computer simulation is set up for this case by patching the kinetic model for styrene polymerization into the reaction rate subroutine. Both the kinetic model and the thermophysical property parameters are summarized in the appendix of Reference [13].

The pressure, inventory, and temperature histories for this example are presented in Figure 5, for both the homogeneous-froth and the ideal churn-turbulent cases. The homogeneous-froth model gives the more conservative result. The churn-turbulent behavior of Equation 5 is perhaps the least conservative two-phase venting model, giving somewhat smaller vent sizes as the value of the coefficient C_0 is increased. For the present example at $C_0 = 1$, a vent diameter equivalent to an 18.5-cm perfect nozzle is required for the same peak pressure as attained with a 20-cm ideal nozzle for the homogeneous-froth case. The size difference is not large for this "hot" reaction (28 K/min temperature rise rate at relief opening pressure). The difference would be greater for lower initial fill levels.

The main difference between the churn and homogeneous cases is in the rate and amount of material discharged. This difference results from the greater efficiency of energy removal in the churn-turbulent case due to the higher vapor fraction in the vent stream. The conclusion to be reached for this example is that the homogeneous-froth model is a good basis for vent sizing for fast reactions or frothy liquids, but will over-predict the amount and rate of material loss if churn-turbulent behavior in fact prevails. Frothy behavior would be expected in this styrene polymerization system[1].

Phenol-Formaldehyde Condensation

A computer simulation with supporting thermokinetic studies is presented in Reference [17] and summarized in Reference [8]. The example case as presented in Reference [17] is as follows:

Vessel: Vertical, hemispherical heads, 2-m diameter
 Total internal volume = 4.54 m³
 Maximum allowed venting pressure = 2.3 bar (absolute)
 Relief opening pressure = 2.07 bar (absolute)
 Vent pipe configuration: 2-m vertical run, plus 6-m run at 10-degree inclination to an atmospheric header (equivalent length = 6 m + 60 diameters for bend; any flow resistance of the blown rupture disc and holder is neglected)
 Initial charge: 3628 kg; 0.0052 kmol formaldehyde per kg total (566 kg added as 38.3% aqueous solution), 2150 kg phenol
 Initial temperature: 353 K Inert gas pad: none present after charge temperature reaches the atmospheric boiling point
 Fluid dynamics in vessel: homogeneous-froth behavior assumed

The thermophysical and thermokinetic parameters for the example case are given in Reference [17]. The thermophysical values are taken as constant (independent of composition and temperature). System pressure is computed as that of saturated water. The capability of the present program to accept a more sophisticated thermophysical property base is not required for the example data[17]. No program patches are required for this simulation; all system characteristics are coded into the input data.

Results obtained from the computer program of the present paper are shown by the solid and dash lines of Figure 6. The circles on Figure 6 are example results from the tabular computer output of Appendix V of Reference [17] for the 0.3-m vent diameter case. Vent sizes for the present work were chosen to give the same maximum venting pressure as reported in Reference [17]. The plots for the homogeneous-froth case are in excellent agreement. The slight difference during pressure decay is due most likely to differences in precision (increment size). These differences do not affect the vent size specification. The difference in vent diameter for the same vent rate history (same inventory history) results from the different choice of flow model. For the present work, Reference [28] was used as a guide in model selection, since the data are in the range of the present example. Slip flow predictions according to the holdup correlation of Reference [21] give a better fit to the data than obtained by the no-slip assumption[28]. The flow regime criterion used in Reference [17] indicates bubbly flow, so the flow computations in that work are based on a limiting velocity for no-slip flow. Observed flow patterns are complex for the actual unsteady-state case[15]. The no-slip flow model is conservative, so the difference in vent size between present results vs. Reference [17] is consistent with theory. These two models represent a significant advance over an earlier effort[29].

The assumption of ideal churn-turbulent behavior in the vessel yields the results shown by the dash lines on Figure 6. Portions of the computer output for this case are given in Table 1. The difference in vent size between homogeneous-froth and churn-turbulent behavior (24.1 vs. 15.3 cm)* is more pronounced in this case than in the styrene polymerization example. The less severe runaway (15.4 K/min at start of venting, vs. 28 K/min for the styrene case) would be expected to favor higher vapor content of the vent stream. Of course, the initial fill level also influences the difference between churn and homogeneous model results.

The ideal churn-turbulent model provides a near-minimum estimate of vent sizes for two-phase relief flow. However, such behavior cannot be presumed without direct supporting observations under runaway conditions. The conservative homogeneous-froth result must be accepted in the absence of such observations.

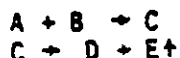
Example of Gassy Secondary Reaction

The previous examples involve a singular reaction yielding lower-boiling products (systems of decreasing volatility). A quite different response to venting is observed if the products are more volatile than the reactants, particularly if non-condensable gases are formed. Such products exhibit limited solubility in the liquid phase, as well as small heats of phase change (heats of solution).

The venting crisis in "gassy" systems usually occurs well past the point of initial venting. The absence of large heats of vaporization results in a continuing temperature rise. The venting crisis can occur at a peak rate condition just before the reactants become exhausted. The presumption of homogeneous-froth venting behavior is under-conservative in such cases, since the vessel would be predicted to empty before the all-vapor venting crisis could occur. Thus, all-vapor venting can require a larger vent size than the homogeneous-froth case[13,14].

A further complication arises if the gas-producing reactant is a product of a prior reaction. A common example is polymerization to form a polymer, which becomes unstable at the temperatures attained in the runaway polymerization. The venting crisis can occur either during the polymerization or during the gassy decomposition period.

The capabilities of the present simulation program in treating such complex systems is illustrated in earlier papers[13,14] for the following hypothetical system of reactions:



The exothermic reactions are carried out in component F as a solvent. Component E is non-condensable at reaction temperature. The assigned thermophysical and thermokinetic properties are given in Reference [14]. No program patches are required for this simulation; all system characteristics are coded into the input data.

*Diameters of 22.6 cm for the homogeneous case and 13.4 cm for the churn case appear in the published version of this paper. The refined values 24.1 and 15.3 are more faithful to the piping equivalent length and simplified thermophysical property base of Reference[17].

The example design case is as follows:

Vessel: Vertical, 1.12-m outside diameter
 Inside Sectional Area = 0.96 m^2 *
 Total internal volume = 1.36 m^3
 Surface area below top tangent line = 5.34 m^2
 Relief opening pressure = 3.04 bar (absolute)
 Pressure at allowed accumulation = 3.47 bar (absolute)
 Initial charge = 410 kg; 20% A, 45% B, 5% C, 30% F (by weight)
 Inert gas pad: none present after atmospheric bubble point is attained

Ignition of a flammable liquid spill occurs at time zero. Neglect any other sources of heat transfer. The initial value of the heat input from the fire is taken as $20,000 \text{ BTU/hr/ft}^2$ on the exposed area[30], or 337 kw. This heat input is reduced as venting proceeds; see the notes on program step 5 for the example approach.

With no fire heat input, the largest vent size results if all-vapor venting behavior prevails[13,14]. Homogeneous-froth behavior results in emptying of the vessel before the more-severe decomposition reaction can occur. The ideal churn-turbulent model predicts all-vapor venting throughout the event in the absence of heat input from fire.

The results obtained with the addition of fire exposure are presented in Figure 7 for all-vapor, ideal churn-turbulent, and homogeneous-froth cases**. A somewhat higher maximum venting pressure is used with fire exposure than without fire. The homogeneous-froth model is now the most conservative. The temperature rises out of control during the second reaction, since the heat required to drive the noncondensables out of solution is less than the heat produced in the reaction. However, the size for the froth case is more than sufficient to vent the product gasses at low pressure levels. The range of vent areas for the three cases of Figure 7 is roughly a factor of two.

This example illustrates one important advantage of the computer simulation approach over the use of simplified formulas in complex cases. One must identify the crisis condition before knowing which simplified formula to use. In the present example, a different worst-case model applies if fire exposure is considered (homogeneous froth) than if there is no fire (all-vapor model applied to the second reaction). Lacking the insight from a simulation, one must use the worst-case condition of homogeneous-froth venting at the gas-free atmospheric bubble point during the second reaction. The peak rate condition must be used if attained before the atmospheric bubble point is reached[14].

*Computations were performed with this value of 0.96, rather than the value of 0.985 given in the published version of this paper.

**Figure 7 of the published version of this paper was prepared from an earlier version of the property data set of Reference [14]; component C is treated as dimeric with a less-vigorous decomposition. That figure appears here as Figure 7'.

CONCLUSIONS

The general approach to computer simulation of runaway reaction venting as presented in Reference [5] is a valid and versatile tool for the determination of emergency pressure relief requirements, both for runaway chemical reactions and for uncontrolled heating with or without chemical reaction. The more-recent published work of others supports the original computational model and computer programming approach based on the proposed well-mixed "homogeneous-froth" concept of two-phase venting.

Recent published work on computational models for non-uniform vapor distribution has been incorporated into the original program. The results show that somewhat smaller vent sizes will result if the use of such models can be supported by direct knowledge of the frothing character of the given system. The AIChE DIERS program will be of great value in this respect. Further refinement of the present theory and computer model must await the results of such programs.

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NOMENCLATURE

The designated units apply for the parameters in equations. Numerical values may be given in related units (temperature in Celsius = $K - 273.2$, absolute pressure in bar = $N/m^2 \times 10^{-5}$, time in minutes).

a	= general constant
A'	= cross-sectional flow area, m^2
A _i	= first Antoine constant of component i (pressure in N/m^2)
A _{ij}	= coefficients in Equations 13 and 14
b	= general constant
B _i	= second Antoine constant of component i (temperature in K)
c	= general constant
C _i	= third Antoine constant of component i, K
C _d	= nozzle flow coefficient
C _o	= distribution parameter in equation 3
C _p	= specific heat at constant pressure, J/kg.K
E	= parameter in Equation 16 (activation energy over R), K
f _i	= weight fraction of component i in mixture
g	= gravitational acceleration m/s^2
G	= total mass flow rate, $kg/m^2.s$
j _g	= superficial vapor velocity at a level below interface, m/s
j _{g∞}	= vapor velocity from interface, m/s
k	= isentropic expansion exponent
K _e	= kinetic energy term in Equation 7, J/kg
K _m	= momentum term in Equation 8, N/m^2
k _i	= parameter in Equation 16
L	= vent pipe length, m
m _i	= concentration of component i in liquid, $kmol/m^3$
M	= mass of liquid plus vapor in vessel, kg
n	= general constant
p _i	= partial pressure of component i in vapor, N/m^2
P	= absolute pressure N/m^2 (ΔP is pressure drop, upstream minus downstream values)
P _i	= pure component vapor pressure, N/m^2
q	= heat flow, W
Q	= net rate of heat input and generation per unit mass, W/kg
R	= gas law constant, J/kmol.K
R'	= gas law constant, J/kg.K
T	= temperature, K
U _∞	= bubble rise rate parameter, m/s
UA	= value of heat transfer coefficient times area, W/K
v	= specific volume, m^3/kg (note $v_r = V/M$)
$\bar{v}$	= effective specific volume in Equation 7
v'	= specific volume, $m^3/kmol$
V	= volume of vessel, m^3
WC	= heat capacity at constant volume, J/K
W	= weight rate of relief flow, kg/s
x _i	= mole fraction component i in liquid phase
X	= weight fraction vapor in mixture (weight flow fraction basis for flowing streams)
X'	= mole fraction vapor phase
y _i	= mole fraction component i in vapor phase
Z	= elevation, m

Greek Letter Symbols:

- α = volume fraction vapor
- $\bar{\alpha}$ = overall volume fraction vapor below interface
- γ_i = activity coefficient of component i
- Δ = finite difference
- η = ratio of nozzle throat and inlet pressures
- θ = time, s
- λ = latent heat of vaporization at constant pressure, J/kg
- Δ_{ij} = Wilson constants
- μ = polymer-solvent interaction parameter
- σ = surface tension, N/m
- Σ = summation
- ϕ_i = volume fraction of component i

Subscripts:

- av = arithmetic average
- f = liquid phase
- g = gas (vapor) phase
- i,j,k = indices
- r = in vessel
- tf = two-phase friction
- v = vent pipe
- w = vessel wall (or other heat sink)
- 0,1,2,3 = locations per Figure 1

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TABLE 1. EXAMPLE COMPUTER OUTPUT

VESSEL RELIEF SIMULATION (VENTRX/JEH):

PHENOL-FORMALDEHYDE EXAMPLE

CHARGE COMPOSITION BY WEIGHT:

15.60% FORMALDEHYDE 59.26% PHENOL
 25.14% WATER 0.00% RESIN(F)
 0.00% RESIN(P)

KG CHARGE = 3627.99 BAR = -1.00 CELSIUS = 80.0
 BAR SET = 2.068 RESEAT BAR = 1.013 RX VOL. M³ = 4.542
 WATT FIRE = .0000E+00 EFF. TANK A, M² = 3.14 VENT SIZE = .134
 RECEIVER BAR = 1.013 MAX T RISE/STEP = 1.0 VENT STEPS = 40
 PRINT INTERVAL BEFORE VENTING = 5
 MINIMUM PRESSURE CHANGE BETWEEN PRINTS WHILE VENTING = 0.00 BAR

RATE PARAMETERS = 0.27401E+02 0.12389E+05

HEAT SINK: UAM = 0.0000E+00 CSVR = 0.0000E+00 TSINKO = 0.0000E+00
 FLOW CONSTANTS = -0.44000E+00 0.31123E+03 -0.29094E+02 0.94011E+00

LIQUID CARRYOVER FOR $C_0 = 1$ IN CHURN-TURBULENT REGIME

TIME, MIN.	V E S S E L							VENT INLET	
	BAR	TEMP	WT% V	KG LIQ	WT% I	C/MIN	Twall	KG/SEC	WT% L
0.00	0.47	80.0	0.01	3628.	15.601		80.0		
5.82	0.58	85.0	0.01	3628.	15.117	1.03	85.0		
9.64	0.70	90.0	0.01	3628.	14.633	1.55	90.0		
- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
16.95	1.98	120.0	0.02	3627.	11.727	13.57	120.0		
17.04	2.07	121.3	0.02	3627.	11.599	15.40	121.3	45.02	99.38
17.07	2.09	121.6	0.02	3549.	11.559	10.34	121.6	44.97	99.28
- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
17.25	2.18	123.1	0.05	3073.	11.303	5.97	123.1	43.44	98.53
17.28	2.19	123.2	0.05	2992.	11.259	4.80	123.2	42.90	98.37
17.31	2.20	123.3	0.06	2911.	11.214	3.46	123.3	42.26	98.18
17.35	2.21	123.4	0.07	2829.	11.168	1.94	123.4	40.58	97.76
17.41	2.20	123.3	0.08	2668.	11.079	-1.74	123.3	39.57	97.52
17.44	2.19	123.2	0.08	2593.	11.038	-3.81	123.2	38.46	97.26
17.47	2.18	123.0	0.09	2523.	11.000	-5.97	123.0	37.27	97.00
- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
17.93	1.54	112.2	0.12	1865.	10.700	-33.50	112.2	9.78	85.02
17.96	1.50	111.5	0.12	1852.	10.698	-33.79	111.5	9.43	84.63
17.98	1.47	110.7	0.12	1839.	10.696	-34.02	110.7	9.11	84.26
18.00	1.43	109.9	0.12	1927.	10.696	-34.19	109.9	8.80	83.90
- -	- -	- -	- -	- -	- -	- -	- -	- -	- -
18.24	1.08	101.8	0.10	1722.	10.722	-33.46	101.8	5.57	78.22
18.26	1.05	101.1	0.10	1715.	10.726	-33.21	101.1	5.13	76.74
18.28	1.03	100.4	0.10	1708.	10.730	-32.93	100.4	4.44	73.59
18.30	1.01	99.7	0.09	1703.	10.735	-32.60	99.7	0.00	73.59

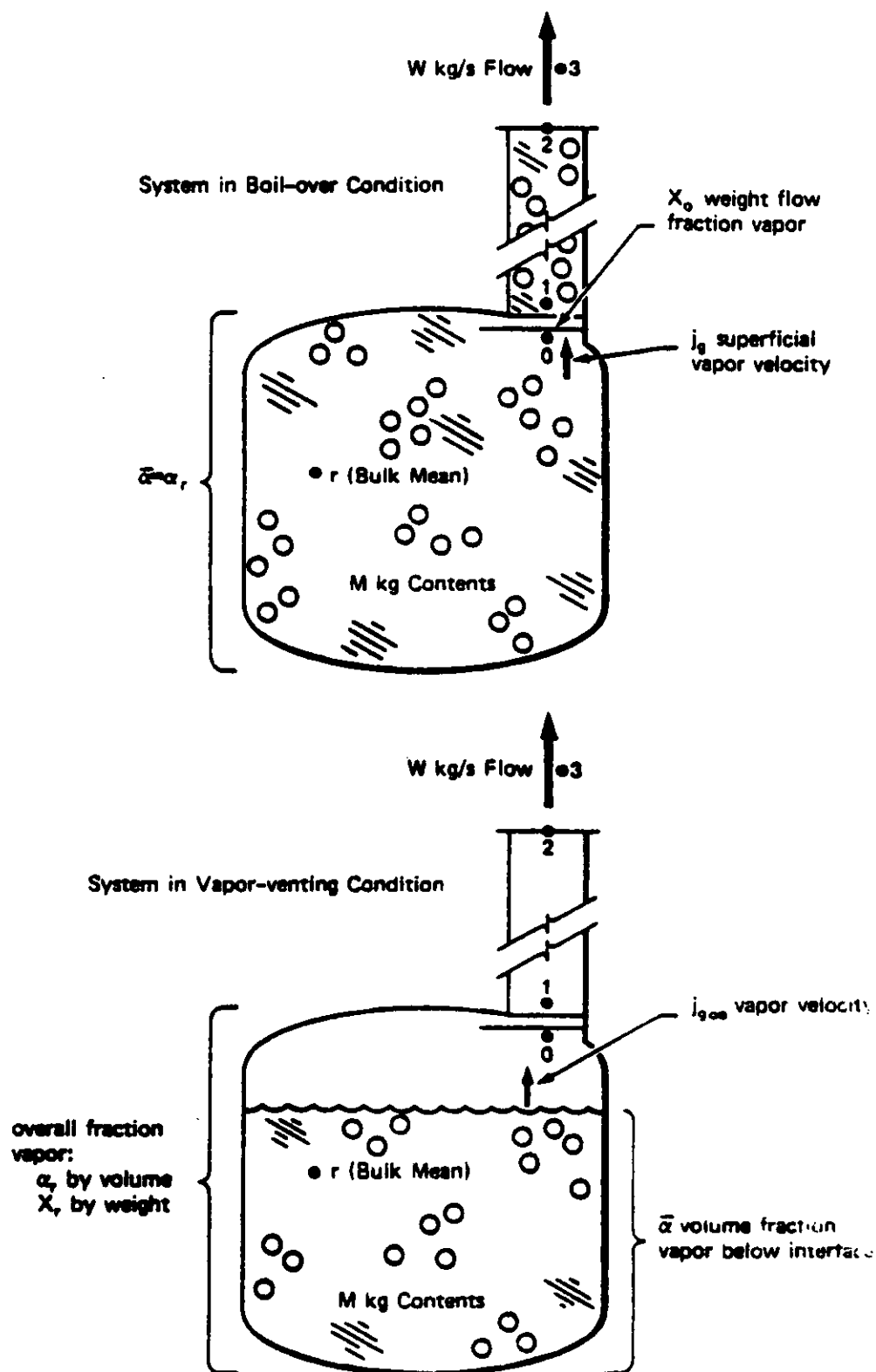


Figure 1. Physical System and Principal Parameters

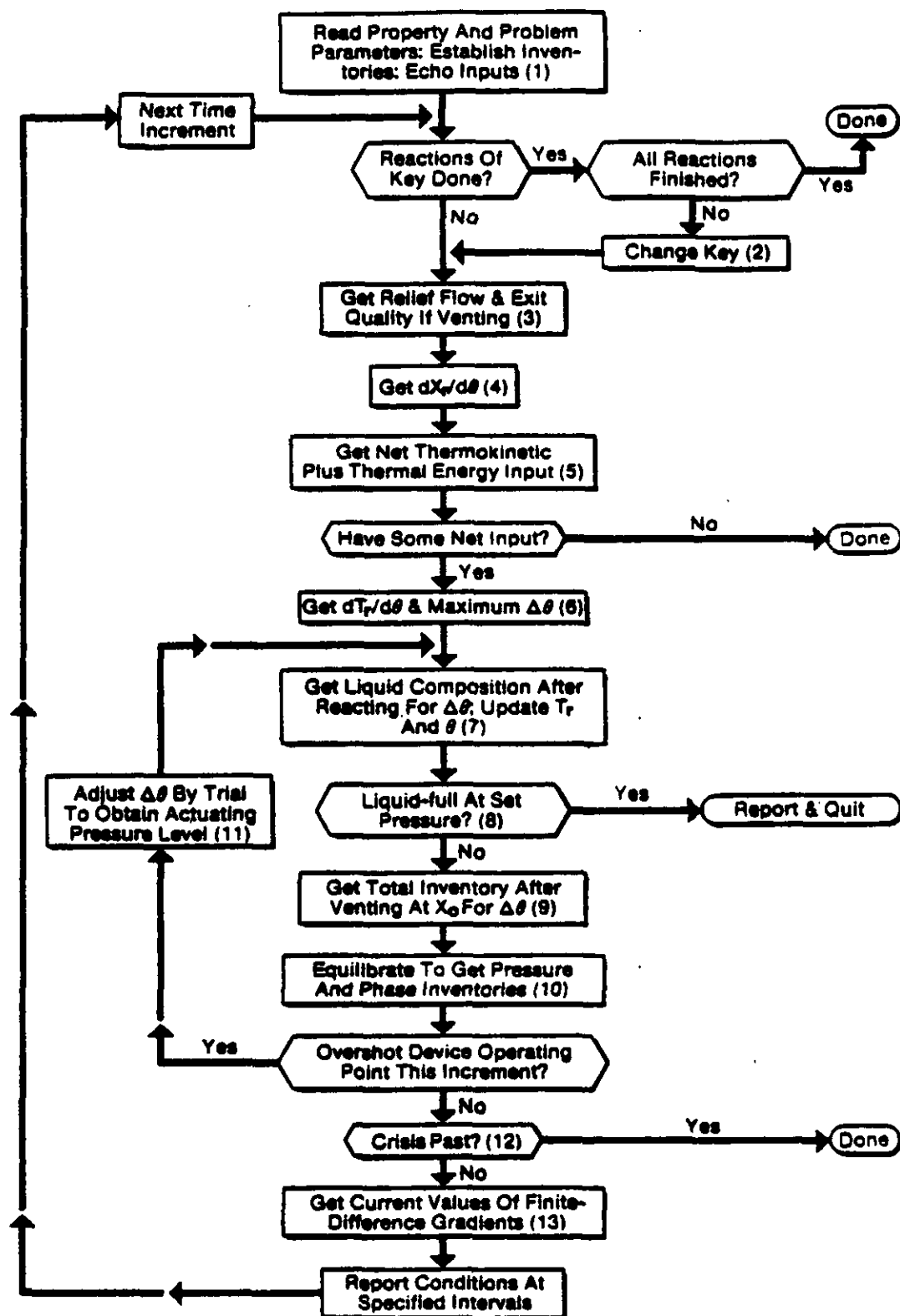


Figure 2. Program Structure

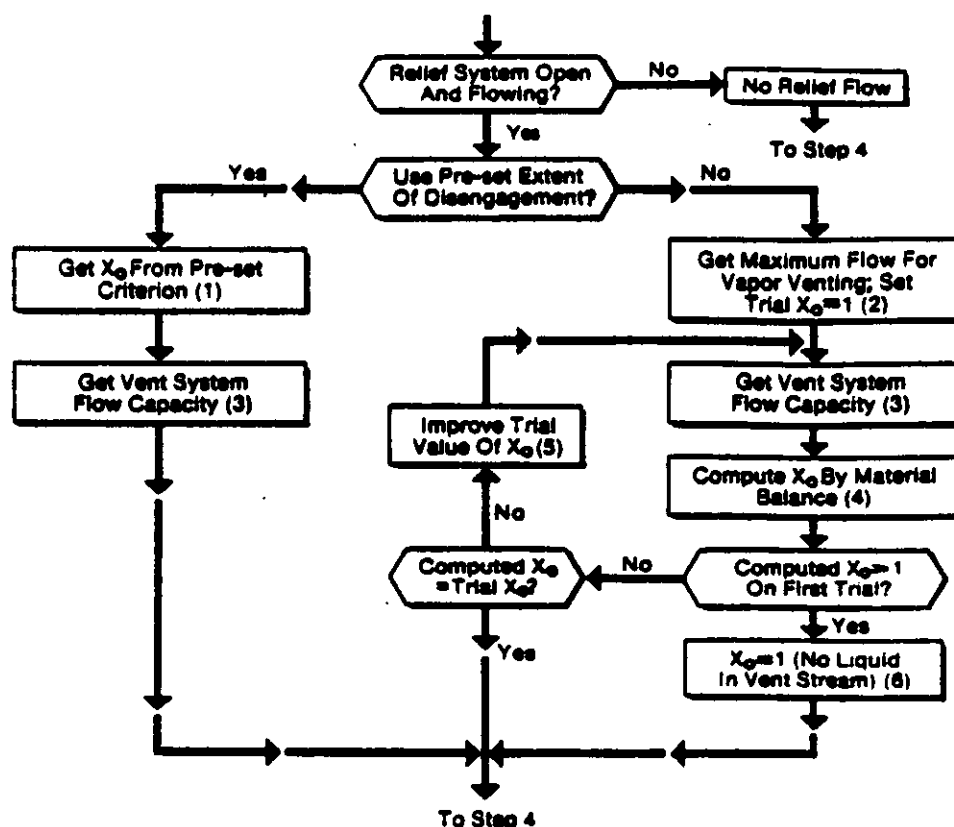


Figure 3. Vent Stream Quality and Flow Routine (Step 3 of Figure 2)

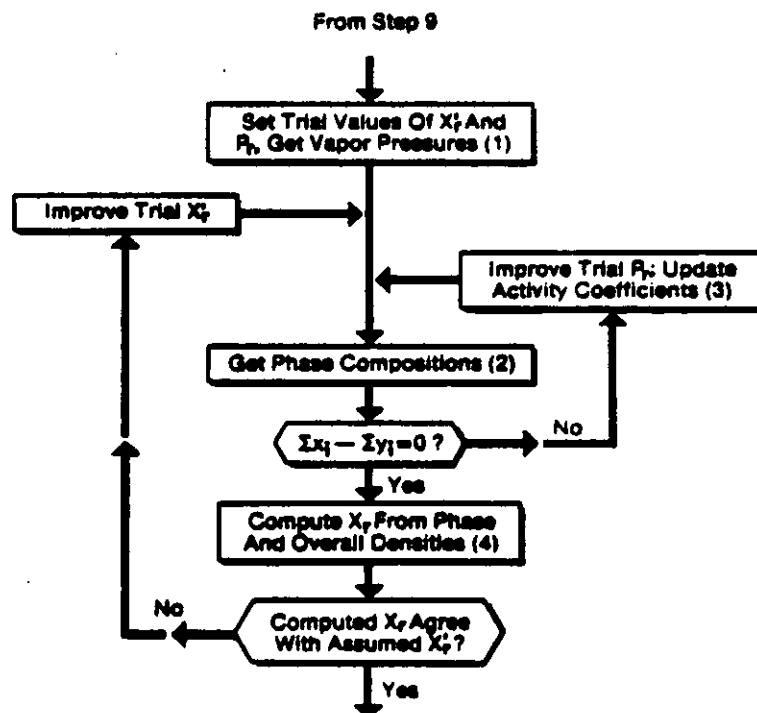


Figure 4. Phase Equilibration Routine (Step 10 of Figure 2)

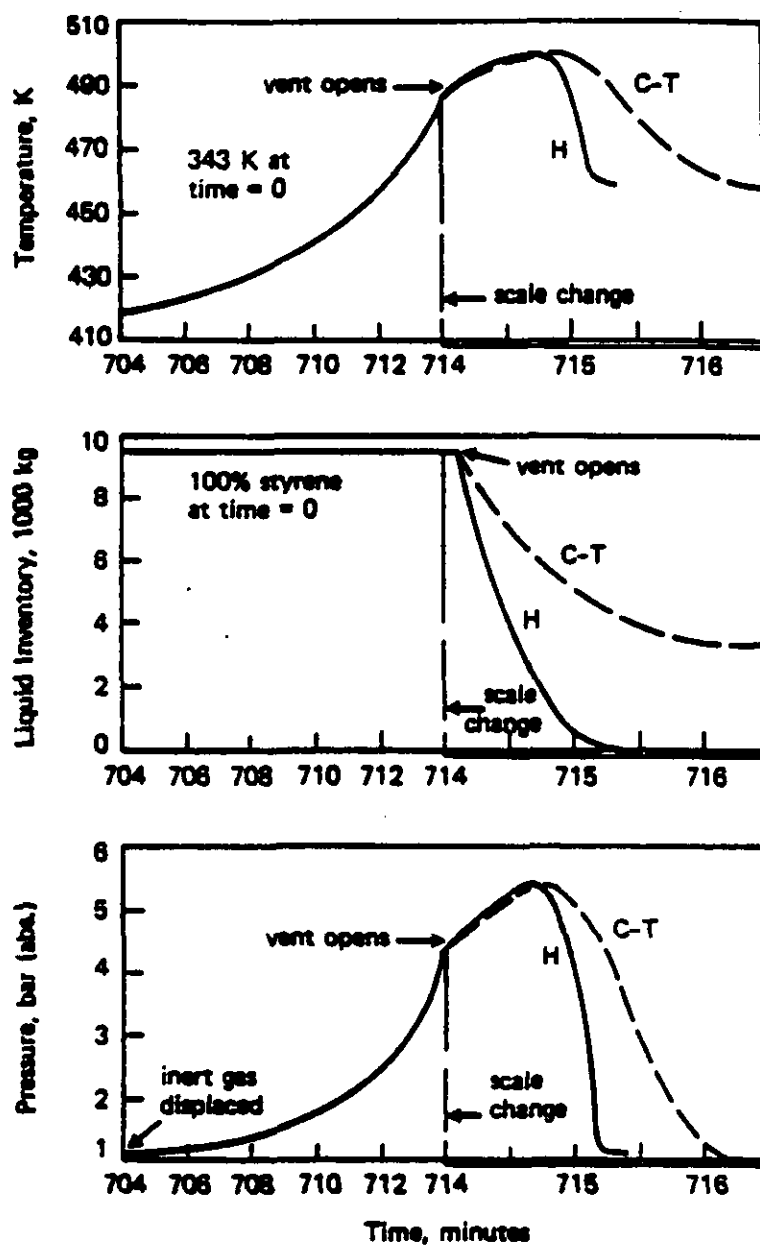


Figure 5. Runaway and Venting History for Styrene Polymerization Example. Solid line: homogeneous-froth behavior ("H", 20.2-cm vent). Dash line: ideal churn-turbulent behavior ("C-T", 18.5-cm vent). Vent size is in terms of diameter of equivalent ideal nozzle.

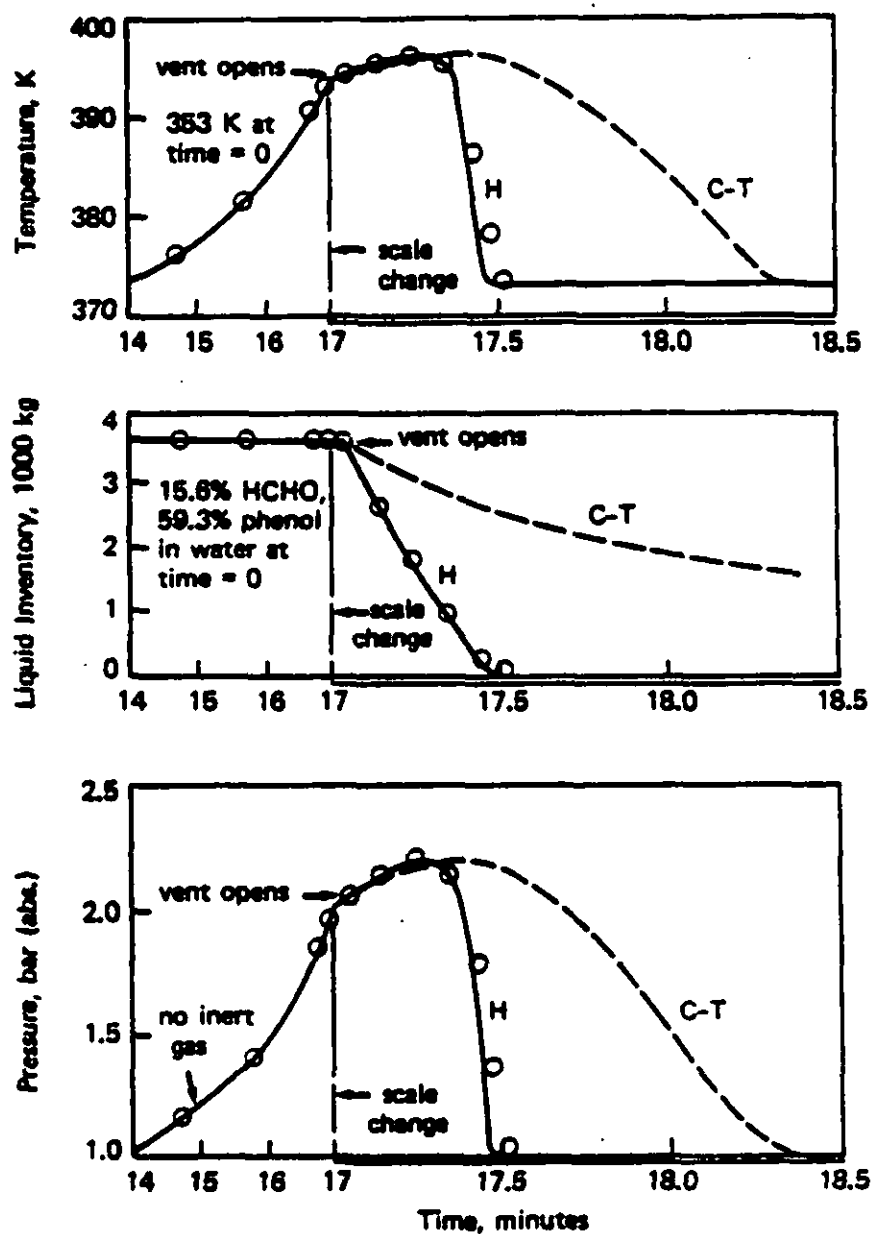


Figure 6. Runaway and Venting History for Phenol-Formaldehyde Example. Solid line: homogeneous-froth behavior ("H", 24.1-cm vent pipe diameter). Dash line: ideal churn-turbulent behavior ("C-T", 15.3-cm vent pipe diameter). Slip flow in vent pipes. Circles are from simulation of Reference [17]. ("H", 30-cm vent pipe diameter, no-slip critical flow model); displaced 14 seconds to the left to match up time at vent opening.

See footnote on p. 15

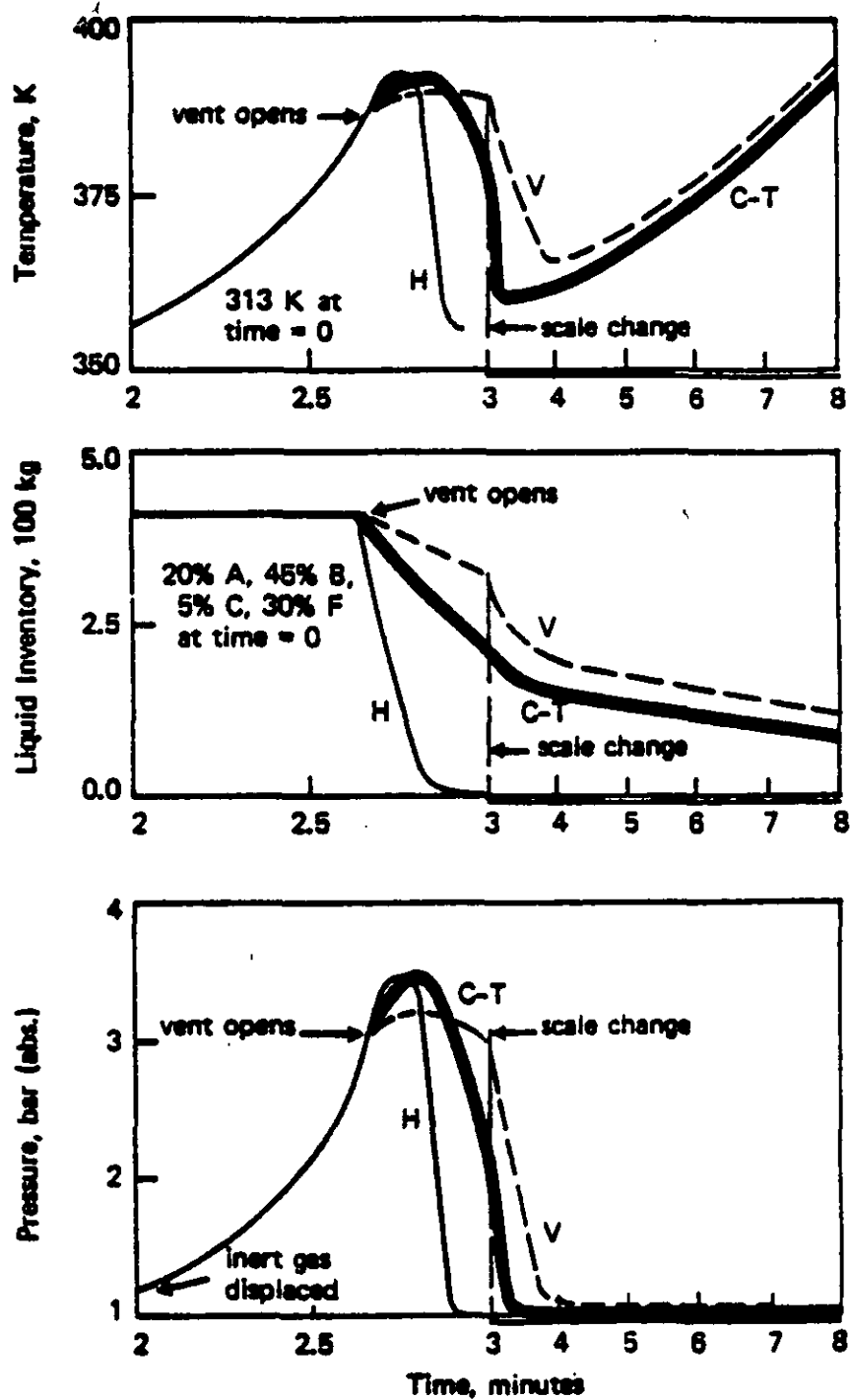


Figure 7: Runaway and Venting History for Gassy Secondary Reaction Example. Dash line: all-vapor venting ("V", 7.4-cm vent). Heavy line: ideal churn-turbulent behavior ("C-T", 9.7-cm vent). Light line: homogeneous-froth behavior ("H", 11.4-cm vent). Vent size is in terms of diameter of equivalent ideal nozzle.

See footnote on p. 16