FINAL REPORT

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INTERFACIAL CHEMICAL REACTIONS IN FLOW SYSTEMS

Principal Investigator: Daniel E. Rosner

Period Covered: 1 February 1973-30 June 1976

Yale University
Department of Engineering and Applied Science
Chemical Engineering Section, Mason Laboratory
New Haven, Connecticut 06520

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A. D. BLOOM
Technical Information Officer
This report summarizes the results of a 41-month basic research program in the High Temperature Chemical Reaction Engineering (HTC) Laboratory at Yale University. Specific cases which have been studied in detail are energy deposition to solid surfaces which are the site of highly exothermic chemical reactions, methods of extracting heterogeneous kinetic data from flow reactor experiments, the production, dispersion, and coagulation of condensation aerosols, oxidation of refractory solids leading to volatile reaction products, solute loss or gain by refractory metals, the evaporation and combustion of liquid fuel droplet arrays.
("clouds"). nonequilibrium crystallisation kinetics in supercooled liquids and transpiration cooling in chemically reacting environments. These phenomena are, and will continue to be, a central part of advanced engineering systems containing a dispersed condensed phase, or where the condensed phase is used for fluid confinement. Sixteen publications and two Ph.D. theses resulted from this work.
CONTENTS

1. INTRODUCTION 2

2. SYNOPSIS OF MAJOR ACCOMPLISHMENTS 4
   2.1 Gas/Solid Reaction Kinetics
   2.2 Energy Transfer at Surfaces Catalyzing Highly Exothermic Chemical Reactions
   2.3 Understanding of Nucleation, Dispersion and Coagulation Phenomena in Submicron Aerosol Systems
   2.4 Understanding Droplet Energy/Mass Interaction Effects in Fuel Sprays/Clouds
   2.5 Universal Method for Extracting Intrinsic Rate Constants from Duct Flow Reactor Data

3. PUBLISHED RESULTS 9

4. SCIENTIFIC EDUCATION/TRAINING OF RESEARCH PARTICIPANTS 11

5. DDC FORM 1473 13

TABLES 1

1. Subject Matter of Papers Listed in Section 3 3

2. Research Participants in AFOSR Grant 73-2487 11
1. INTRODUCTION

This report summarizes the results of a 41 month basic research program in the High Temperature Chemical Reaction Engineering (HTCRE) Laboratory at Yale University. Specific cases which we have studied in detail (see Section 2) are energy deposition to solid surfaces which are the site of highly exothermic chemical reactions, methods of extracting heterogeneous kinetic data from flow reactor experiments, the production, dispersion and coagulation of condensation aerosols, oxidation of refractory solids leading to volatile reaction products, solute loss or gain by refractory metals, the evaporation and combustion of liquid fuel droplet arrays ("clouds"), nonequilibrium crystallization kinetics in supercooled liquids and transpiration cooling in chemically reacting environments. These phenomena are, and will continue to be, a central part of advanced engineering systems containing a dispersed condensed phase, or where the condensed phase is used for fluid confinement. The design of all advanced propulsion systems, for example, requires fundamental data in these broad categories, and it is hoped that the research results and techniques reviewed here will continue to be widely used in the fields of aeronautical, metallurgical, chemical and mechanical engineering.

Because of the availability of our papers in the archival scientific and/or engineering literature, detailed summaries of their contents here would be redundant. However, the extent and nature of the information resulting from this program is conveyed in Section 3 via comprehensive chronological listing of publications prepared and/or appearing since 1 February 1973. In addition to this material, we have also made progress on the problem of energy deposition to surfaces which are the site of exothermal chemical reactions - these studies are being extended under a new AFOSR contract commencing 1 July 1976, and will be published in due course.

Our papers can be grouped into the categories listed in Table 1, which in effect provides a guide to the references listed in Section 3. Reprints of most of these papers can be obtained, if required, by writing the author. Information on further applications of this work by other
workers (regardless of their specific field) will be especially welcome.

The author would also like to take this opportunity to acknowledge the many valuable contributions to this program made by his colleagues in the Chemical Engineering Section of Yale University, and elsewhere. This includes Prof. P.C. Nordine, my former students: Drs. H. Feng, F. Tolfo, M. Kritz, Mr. R. Cibrian, and post-doctoral research colleagues: Drs. H. Chung, E. Steinheil. The fruits of recent work by Drs. B. Halpern, R. Sau will appear shortly, as an important part of our new AFOSR program.

Table 1
Subject Matter of Papers Listed in Section 3

<table>
<thead>
<tr>
<th>Subject</th>
<th>Reference(s)</th>
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<tr>
<td>energy transfer to catalyst surfaces</td>
<td>8,11</td>
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<td>experimental techniques: gas/solid reaction kinetics</td>
<td>3,4,5,6,10,15,16</td>
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<tr>
<td>kinetics of gas/solid gasification reactions: results</td>
<td>3,4,5,10</td>
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<tr>
<td>kinetics of atom dissolution/exsolution in metals</td>
<td>4,5,6,15</td>
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<td>diffusion limitations on gas/solid reactions</td>
<td>5,18</td>
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<td>regimes of metal oxidation</td>
<td>5,18</td>
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<td>droplet array combustion</td>
<td>1</td>
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<td>aerosol nucleation, dispersion, coagulation</td>
<td>2,7,19</td>
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<td>droplet/particle evaporation/sublimation</td>
<td>13,14,17</td>
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<td>kinetic/transport limitations in crystallization</td>
<td>9</td>
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<tr>
<td>transpiration cooling in reacting systems</td>
<td>12</td>
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a. Further details on content are given in Section 2
b. Complete bibliography included as Section 3
2. SYNOPIS OF MAJOR ACCOMPLISHMENTS

2.1 Gas/Solid Reaction Kinetics

Our AFOSR-sponsored basic research on (i) energy transfer to catalytic solids in highly dissociated gas mixtures, and (ii) the chemical attack of $\beta$-SiC(s) and graphite by O-atoms and/or N-atoms has strongly influenced the materials selection and design of the leading edge coating system developed by Ling-Temco Vought Aerospace Company* for the NASA re-usable Space "Shuttle" Orbiter Vehicle. Based largely on our AFOSR-supported experience with atom/solid reaction kinetics, we examined the high temperature catalytic activities of specific Space Shuttle thermal protection system materials for O-atom and N-atom recombination. Our final report to NASA-JSC† should have a significant impact on future materials development for hypersonic glide vehicles and arc-jet materials test (flight simulation) procedures. We are currently pursuing the energy transfer aspects of this research (see Section 2.2 below), since this strongly influences surface temperatures and hence ablation rates and materials lifetime in practical systems.

By extending our previous atom/filament flow reactor experimental techniques we demonstrated that by measuring the electrical resistance of a metal filament (i) during isothermal reaction with dissociated oxygen (ii) after isothermal degassing and (iii) after a rapid temperature quench it is possible to infer both the instantaneous dissolved oxygen concentration and the metal "gasification" rate for the important oxygen/tantalum reaction. In this way we have proven that the observed dissolution kinetics for tantalum in both dissociated and undissociated oxygen are well-described as two limiting cases of a simple mechanism involving oxygen adatom intermediates. At high temperature and oxygen pressure

*Vought Missiles and Space Company, Ling-Temco Vought Aerospace Corporation, Dallas, Texas 75222.
adatom penetration into the bulk metal is rate controlling, while at "low"
temperature and oxygen pressure the oxygen adsorption-oxide desorption
process becomes rate-controlling. We have also derived a useful
dimensionless "transition parameter" delineating these two extremes on the
oxygen pressure - surface temperature domain, as well as extracted
elementary rate constants and energy barrier heights for adsorption,
interface crossing, and oxide desorption in the oxygen/tantalum system above
2000K.

An extensive publication on kinetics and transport phenomena in nitrogen/
refractory metal (Ta, Nb, V) systems, based on the dissertation research
of Dr. H. Peng, will be issued under the follow-on AFOSR research program
at Yale HTCRE Laboratory.

2.2 Energy Transfer At Surfaces Catalyzing Highly Exothermic Chemical
Reactions

The fate of the energy release in highly exothermic surface-catalyzed
reactions is not only of considerable fundamental interest, but also
influences catalyst volatilization/sintering, and the aerodynamic heating
and ablation of hypersonic vehicles subject to bombardment by atomic
nitrogen and atomic oxygen. We have quantitatively studied the consequences
of (i) a portion of the energy of reaction appearing in desorbed product
molecules, and (ii) secondary catalyst energy deposition via localized
product molecule quenching. Using the highly exothermic surface-catalyzed
association of nitrogen atoms as the prototype reaction, results are now
available on: 1) vacuum flow reactor experiments indicating incomplete
chemical energy accommodation for metals, 2) the role of homogeneous and

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For this work Dr. Feng was awarded the 1975-1976 Yale University/EAS
Department Harding Bliss Award for outstanding research accomplishment
and academic achievement.

Halpern, B. and Rosner, D.E., "Flow Reactor Studies of Chemical Energy
Deposition at Catalytic Surfaces. I. The Recombination of N-Atoms on
Metals", Faraday Transactions I. Physical Chemistry (in preparation,
October 1976).
heterogeneous quenching in determining energy transfer to smooth, nonporous surfaces, 3) the role of heterogeneous quenching in determining energy transfer to rough, porous surfaces. Fundamental and practical implications of indirect energy transfer in catalytic systems will be documented in publications issued under the follow-on AFOSR program at the Yale HTCRE Laboratory.

2.3 Understanding of Nucleation, Dispersion and Coagulation Phenomena in Submicron Aerosol Systems

Using an oxidizing tungsten filament in a steady gas stream as a continuous "line" source of submicron particulate matter, we have established the dependence of observed aerosol character (size distribution, number density, shape and chemical composition) in the filament wake on controllable system variables (filament surface temperature, oxygen partial pressure, total pressure, gas flow velocity and downstream sampling distance). Experimentally observed trends were quantified by a fit of the log normal function to the observed particle size distribution (PSD) data, from which the various characteristic parameters (count mean diameter, and geometric standard deviation) were derived. These results led to an understanding of the mechanism for aerosol formation/evolution which accounts for the role of the abovementioned system variables on the observed PSD. In a follow-on publication (in preparation) the convection, dispersion and Brownian coagulation of this aerosol is considered in quantitative detail, taking full advantage of the geometrical and fluid dynamic simplicity of our aerosol generator configuration.

In a related aerosol investigation, the important topic of submicron aerosols present in the Earth's stratosphere has been quantitatively studied. In this work quantitative limits are set on the range of these possibilities, particularly the aerosol formation mechanism, by comparing the observed particle size distribution of the stratospheric aerosol with predicted aerosol particle size distributions generated using a numerical model. The model considers the effects of turbulent diffusion, gravitational sedimentation, formation of new particles, particle "growth",
and coagulation on the evolution of the size distribution of aerosol in a region of space, relating these processes to the principal model inputs, which are the nature and initial concentration of aerosol and reactants in air entering the stratosphere, and the rate and mechanism of the aerosol formation process. We have demonstrated that for initial site densities in the range $10^{-1}$ to $10^0$ cm$^{-3}$ either heterogeneous nucleation or heterogeneous oxidation/growth processes can lead to computed aerosol populations dominated (as observed) by large ($r > 10^{-1}$ μm) particles. In contrast, the gas phase oxidation of sulfur compounds followed by homogeneous nucleation would only produce large numbers of Aitken particles ($r < 10^{-2}$ μm) on the geochemical time scales involved. A by-product of this investigation is the development of a computationally efficient particle coagulation algorithm which should facilitate future investigations of aerosol particle size spectrum dynamics under the simultaneous influences of convection, dispersion and chemical reaction. A paper describing this work will be issued under the follow-on AFOSR research program at Yale University/ChE Section.

2.4 Understanding Droplet Energy/Mass Interaction Effects in Fuel Sprays/Clouds

There has been considerable debate and confusion as to when particles in a dispersed fuel droplet cloud can burn with individual envelope flames and when they will "pool" their vapor and burn as a group. We have now determined quantitative conditions for the onset of such "group" behavior. Two conditions are established, viz. i) incipient group combustion, i.e. when the particles at the cloud center pool their vapor and share a single envelope flame, and ii) total group combustion, i.e. when all cloud particles burn with a common envelope flame.

Two different approaches have been used. In the first, a "continuum" view is taken in which the fuel droplets are considered to act as distributed sinks for oxygen (point sources of fuel). By drawing on an analogy to the problem of reactant diffusion through a porous catalyst pellet, group combustion criteria are then proposed based on the
"effectiveness" of gaseous oxidizer penetration into the fuel cloud. In the second approach, actual flame locations for cubical arrays of fuel droplets are calculated using a superposition method. Our results indicate that evaporating fuel particles are so efficient in preventing oxidizer penetration that if a fuel cloud of practical interest were to approach a quasi-steady-state, it would necessarily burn as a group.

Further details on the collective behavior of droplet clouds computed using a more comprehensive transient continuum model will be issued during the follow-on AFOSR program at Yale, based on research by Dr. R. Srivastava under the direction of Professor Rosner.

2.5 Universal Method for Extracting Intrinsic Rate Constants from Duct Flow Reactor Data

Continuous-flow unpacked-duct chemical reactors are not only widely used in the fuel processing industry, but they are also useful for laboratory studies of the rates of important surface (catalyzed) chemical reactions (e.g. carbon gasification, oxidation of the combustion products SO$_2$(g), CO(g); or NH$_3$, decomposition of NO(g) or H$_2$O$_2$(g); association of atomic oxygen or nitrogen, etc.). As is well known, the interpretation of reaction-rate data for active catalysts is, however, complicated by the need to correct for internal transverse composition gradients which depend on details of the reactor geometry, flow rate, diffusion coefficients, etc. We have developed and tested a correlation which drastically simplifies the interpretation of reaction rate data for reactors of various convenient cross-sectional shapes, in turbulent or laminar flow. A preliminary report on the method was given at the Third International Symposium on Chemical Reaction Engineering (Evanston, Ill., 1974). A complete written account of this work* is currently being prepared, and will be issued in Spring 1977.

*The author is collectively indebted to Summer research students T. Beck, L. Belfiore, L. Skoble (cf. Table 2) for their role in testing this method against available exact solutions to the convective diffusion equation in catalytic ducts of various cross-sections.
3. PUBLISHED RESULTS


*Supported in part by the present Grant (73-2487).

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†Complements documentation of research initiated under previous AFOSR program (Contract F44620-70-C-0026).

4. SCIENTIFIC EDUCATION/TRAINING OF RESEARCH PARTICIPANTS

The education and training of scientists and engineers in the general area of high temperature chemical reaction kinetics/engineering is an important byproduct of this AFOSR grant. Table 2 below lists the graduate students, postdoctoral associates and College undergraduates who have contributed to this research program, together with their completion date and affiliation.

Table 2
Research Participants in AFOSR Grant 73-2487

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<tr>
<td>H. Feng</td>
<td>Ph.D. Student</td>
<td>1975</td>
<td>Stauffer Chemical Company</td>
</tr>
<tr>
<td>P. Tolfo</td>
<td>Ph.D. Student</td>
<td>1975</td>
<td>Universite Catholique du Louvain</td>
</tr>
<tr>
<td>M. Kritz</td>
<td>Ph.D. Student</td>
<td>1975</td>
<td>Centre des Faibles Radioactivites, France</td>
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<tr>
<td>T. Tanaka</td>
<td>GRA\textsuperscript{a}</td>
<td>-</td>
<td>National Space Development Agency of Japan</td>
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<tr>
<td>E. Cibrian</td>
<td>GRA</td>
<td>1974</td>
<td>Empresa Nacional del Uranio, S.A., Spain</td>
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<tr>
<td>H.M. Chung</td>
<td>PDRA\textsuperscript{b}</td>
<td>1973</td>
<td>Argonne National Laboratory</td>
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<tr>
<td>B. Halpern</td>
<td>PDRA</td>
<td>-</td>
<td>Yale University</td>
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<tr>
<td>R. Sau</td>
<td>PDRA</td>
<td>-</td>
<td>Yale University</td>
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\textsuperscript{a} Graduate Research Assistant
\textsuperscript{b} Postdoctoral Research Assistant/Associate
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<td>R. Srivastava</td>
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<td>UGRA$c$</td>
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<td>D. Jaffee</td>
<td>UGRA</td>
<td>-</td>
<td>Yale University</td>
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<tr>
<td>P. Wong</td>
<td>UGRA-$d$</td>
<td>1973</td>
<td>SUNY-Stony Brook</td>
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<tr>
<td>C. DeJong</td>
<td>UGRA-S</td>
<td>1973</td>
<td>University of South Dakota</td>
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<tr>
<td>T. Beck</td>
<td>UGRA-S</td>
<td>1974</td>
<td>North Dakota State University</td>
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<tr>
<td>C.V. Thompson</td>
<td>UGRA-S</td>
<td>1974</td>
<td>New Mexico Institute of Mining &amp; Tech.</td>
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<tr>
<td>L. Belfiore</td>
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<td>1975</td>
<td>Stevens Institute of Technology</td>
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<tr>
<td>L. Skoble</td>
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<td>1976</td>
<td>Smith College</td>
</tr>
<tr>
<td>D. Bernard</td>
<td>UGRA-S</td>
<td>1976</td>
<td>University of Vermont</td>
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</table>

$c$. Undergraduate Research Assistant  
$d$. Undergraduate Research Associate for Summer (affiliation given is student’s College at time indicated)