EXPERIMENTAL AND THEORETICAL STUDIES OF MULTICOMPONENT VAPOR CONDENSATION

Final Report
for Period 15 May 1992 through 15 May 1994

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August 1994

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EXECUTIVE SUMMARY

This report describes the results of experimental and theoretical studies of nucleation and condensation in multicomponent gas mixtures conducted over the past ten years under funding from the United States Department of Energy, Office of Basic Energy Sciences, Division of Engineering and Geosciences, under Contract No. JDE-AC02-84ER13154 and Grant No. DE-FG02-92ER14257. The program goals were: (1) to improve basic understanding of nucleation and droplet growth, (2) to stringently test theories of nucleation at high nucleation rates and under nonisothermal conditions, (3) to develop improved theories where needed, (4) to enlarge the data base for systems of both fundamental and practical interest, and (5) to provide reliable means for predicting the behavior of mixtures in practical devices and in the atmosphere. Condensible vapors, mixed with a carrier gas, were cooled in a supersonic Laval nozzle to obtain high nucleation rates under steady state conditions. Interferometry and laser light scattering were used to detect the "onset" of condensation and to monitor subsequent droplet growth. Theoretical calculations of the droplet size distribution along the flow axis were performed to assess competing theories of nucleation and droplet growth.

This report summarizes briefly the accomplishments of the first eight years of the program. These include the design, construction, refinement and initial operation of an intermittent, low Mach number supersonic nozzle. The data obtained in this period ultimately led us to an improved understanding of the nature of the condensate particle size distribution at the onset of condensation and how it is affected by experimental operating conditions. Theoretical accomplishments during this period include the development and application of a revised classical theory of binary nucleation. This theory helped to resolve a longstanding disagreement between theory and experiment for binary mixtures exhibiting strong compositional surface enrichment. Extensive modeling calculations were also undertaken in this period to probe the behavior of the condensate particle size distribution at onset.

Following this summary of early work, this report presents a more detailed summary of project accomplishments for the final two years of this program. These consist of joint experimental/modeling studies on the effect of carrier gas pressure on condensation in a supersonic nozzle, and on the influence of nucleation and droplet growth on the onset of condensation in supersonic nozzle expansions; an experimental study of condensation in expansions of binary condensible vapor mixtures in supersonic nozzles; and theoretical studies on the relationship between the Kelvin and self-consistent classical nucleation theories, on the development of a self-consistent binary equilibrium distribution function, and on the formulation and numerical solution of a set of fully self-consistent binary kinetics equations. Each of these studies is described in considerably more detail in a series of appendices to this report.

PAST ACCOMPLISHMENTS

The accomplishments of the first eight years of the program included the design, construction, refinement and initial operation of an intermittent, low Mach number supersonic nozzle. Preliminary results for binary condensation showed good agreement with experimental shock tube data, and nucleation rate theories that explicitly account for surface enrichment. Data obtained in this period from uniary condensation experiments, ultimately led us to an improved understanding of the nature of the condensate particle size distribution at the onset of condensation and how it is affected by experimental operating conditions. Further improvements to the experimental protocol and data analysis let us begin the rather difficult experiments at very low pressures required to explore the effects of the background gas on the nucleation process at these high nucleation rates.

Theoretical accomplishments during this period include the development and application of a revised classical theory of binary nucleation. This theory put classical binary nucleation back on the same conceptual level as that for single condensable vapors. It helped to resolve a longstanding disagreement between theory and experiment for binary mixtures exhibiting strong compositional surface enrichment. Failure of the Reiss-Doyle theory at high water activities had led some researchers to conclude that a purely thermodynamic approach to binary nucleation was untenable. The theory is particularly attractive because it relies only on bulk thermodynamic properties and does not require any intermediate use of a complex cluster or lattice model.

Extensive modeling calculations were also undertaken in this period to probe the behavior of the condensate particle size distribution at onset. This emphasized the use of detailed kinetic models for computing full cluster size distributions formed in the nozzle as a function of position. We developed a discrete-sectional model capable of simulating the nucleation and growth of particles containing up to ten million molecules (40 nm radius). We used this model to elucidate various aspects of the experimental results, and to assess the reliability and self consistency of an older, much simpler computational method for simulating condensation in a nozzle.

Publications associated with this research

1.   Wilemski, G., "Composition of the Critical Nucleus in Multicomponent Vapor Nucleation," J. Chem. Phys., 80, 1370 (1984).

2.   Frish, M.B., Piper, L.G., and Wilemski, G., "Experimental and Theoretical Study of Condensation in Multicomponent Vapors," in Proceedings of the Second Symposium of Energy Sciences, Argonne, IL, April 1984 (NTIS CONF-8404123) p. 71.

3.   Wilemski, G., "Revised Classical Binary Nucleation Theory for Aqueous Alcohol and Acetone Vapors," J. Phys. Chem. 91, 2492 (1987).

4.   Frish, M.B., Waterhouse,R. and Wilemski, G., "Experimental and Theoretical Studies of Binary Vapor Condensation," in Proceedings of the Fifth Symposium of Energy Sciences, Argonne, IL, June 1987 (NTIS CONF-8706187) p. 115.

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6.   Wilemski, G., "Comparison of Models for the Composition of Binary Nuclei," in Atmospheric Aerosols and Nucleation, Vol. 309 (Lecture Notes in Physics), P.E. Wagner and G. Vali, Eds., (Springer-Verlag, Berlin, 1988) p. 367.

7.   Frish, M.B. and Wilemski, G., "Optical Studies of Condensation Dynamics in a Supersonic Nozzle," in Atmospheric Aerosols and Nucleation, Vol. 309 (Lecture Notes in Physics), P.E. Wagner and G. Vali, Eds., (Springer-Verlag, Berlin, 1988) p.527.

8.   Frish, M.B. and Wilemski, G., "Experimental and Theoretical Studies of Condensation Dynamics in a Supersonic Nozzle," in Proceedings of the Eighth Symposium on Energy Sciences, Argonne, IL, May 1990 (NTIS CONF-9005183) p. 137.

Presentations associated with this research

1.   Frish, M.B., Piper, L.G., and Wilemski, G., "Experimental and Theoretical Study of Condensation in Multicomponent Vapors," Second Symposium on Energy Engineering Sciences, Argonne National Laboratory, Argonne, IL, April 1984.

2.   Wilemski, G., "Revised Classical Theory for Binary Nucleation of Water-Alcohol Vapors," Symposium on Nucleation, 188th National Meeting, American Chemical Society, Philadelphia, PA, August 1984.

3.   Frish, M.B. and Wilemski, G., "Condensation of Binary Systems in a Supersonic Nozzle Flow: A Preliminary Report," 5th Int'l Conf. on Surface and Colloid Science and 59th Colloid and Surface Science Symposium, Clarkson University, Potsdam, NY, June 1985.

4.   Wilemski, G., "Revised Classical Binary Nucleation Theory for Aqueous Alcohol and Acetone Vapors," 5th Int'l Conf. on Surface and Colloid Science and 59th Colloid and Surface Science Symposium, Clarkson University, Potsdam, NY, June 1985.

5.   Wilemksi, G., Waterhouse, R., and Frish, M.B., "Binary Condensation in a Supersonic Nozzle," Seminar on the Thermodynamics of Binary Droplets, Institute for Advanced Study, W. Berlin, 3 July 1986.

6.   Wilemski, G., "Thermodynamics and Models of Binary Cluster Composition," Seminar on the Thermodynamics of Binary Droplets, Institute for Advanced Study, W. Berlin, 3 July 1986.

7.   Wilemski, G., "Homogeneous Nucleation in Binary Vapors: Recent Developments," Physical Chemistry Seminar, Dept. of Chemistry and Biochemistry, UCLA, Los Angeles, CA, 20 October 1986.

8.   Wilemski, G., "Nucleation in Binary Mixtures," Condensed Matter Physics Seminar, Physics Department, Boston University, Boston, MA, 15 December 1986.

9.   Frish, M.B., Waterhouse,R. and Wilemski, G., "Experimental and Theoretical Studies of Binary Vapor Condensation," in Proceedings of the Fifth Symposium of Energy Sciences, Argonne, IL, 18 June 1987.

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12. Wilemski, G., "Binary Homogeneous Nucleation Theory: Current Status," Max Planck Institute for Biophysical Chemistry, Göttingen, Fed. Rep. Germany, 7 November 1989.

13. Frish, M.B. and Wilemski, G., "Experimental and Theoretical Studies of Condensation Dynamics in a Supersonic Nozzle," Eighth Symposium on Energy Sciences, Argonne National Laboratory, Argonne, IL, 10 May 1990.

14. Wilemski, G., "Numerical Simulation of Nucleation and Condensation in Supersonic Jets and Nozzles," 64th Colloid and Surface Science Symposium and Nucleation Symposium, Lehigh University, Bethlehem, PA, 19 June 1990.

PROGRAM ACCOMPLISHMENTS IN THE CURRENT FUNDING PERIOD

The final two years of this project were extremely productive from both the experimental and theoretical standpoint. Experimental measurements were made on both uniary and binary vapors in nitrogen carrier gas. The uniary experiments were performed to satisfy two goals. First, the effect of carrier gas pressure on the onset of condensation for a fixed amount of condensible vapor was ascertained. Second, condensation measurements were made with varying amounts of several condensible vapors at a constant stagnation pressure to amass a data base spanning the widest range of conditions attainable in our nozzle apparatus. In conjunction with these experimental efforts, modeling of condensation was undertaken to help understand the effect of carrier gas pressure on condensation and to elucidate the nature of the condensate size distribution at onset over a wide range of experimental conditions. The results of these experimental and modeling activities are summarized in Sections A and B below. Building on the uniary condensation measurements, the experimental program was concluded by performing the first systematic measurements in a supersonic nozzle of binary condensation for three binary systems. These data will enable theories of binary nucleation and condensation to be stringently tested under the conditions of extremely high cooling rates that are unattainable with other types of experimental devices. This work is further summarized in Section C below.

Besides the modeling of condensation that was just mentioned and is described further in Sections A and B, theoretical work was performed on both uniary and binary homogeneous nucleation kinetics. Emphasis was placed on a thorough examination of the fundamental consistency of the kinetic and thermodynamic approaches to nucleation using both analytical and numerical techniques. The goal of this work was not merely an abstract reconciliation of apparently disparate results, but the establishment of a rigorously consistent kinetic framework for performing exact numerical solutions of the birth-death equations for binary systems. These solutions provide the first, and to date, only reliable means for evaluating the accuracy of simpler rate expressions based on approximate analytical solutions of the binary kinetics equations. It is important to assess these useful formulas on their own merits before their adequacy is judged by comparisons with high quality binary rate measurements just beginning to become available. This theoretical work is summarized in Sections D, E, and F.

A. Effect of Carrier Gas Pressure on Condensation in a Supersonic Nozzle

In this work, we performed supersonic nozzle experiments with a fixed water or ethanol vapor pressure and varying amounts of nitrogen to test the hypothesis that carrier gas pressure affects the onset of condensation. Such an effect might occur if non-isothermal nucleation were important under conditions of excess carrier gas in the atmospheric pressure range, as has been suggested in the recent literature. Although we observed a small increase in the condensation onset temperature as the stagnation pressure was reduced from 3 to 0.5 atm, we cannot attribute these changes to any non-isothermal effects. To theoretically simulate the observed behavior, we performed calculations of nucleation and droplet growth in the nozzle that took into account the change in nozzle shape with carrier gas pressure due to boundary layer effects and the heat capacity of the flowing gas. We neglected energy transfer limitations in calculating the nucleation rates. The trend of the calculated results matched that of the experimental results very well. Thus, heat capacity and boundary layer effects are sufficient to explain the experimental onset behavior without invoking energy transfer limited nucleation. Our conclusions about the rate of nucleation are consistent with those obtained recently using an expansion cloud chamber, but are at odds with results from thermal diffusion cloud

chamber measurements. This work was recently published in the Physics of Fluids, and a reprint of it is contained in Appendix A.

B.   The Influence of Nucleation and Droplet Growth on the Onset of Condensation in Supersonic Nozzle Expansions

In this experimental work we used our gently diverging supersonic Laval nozzle to investigate the variation of onset temperature and pressure for varying amounts of condensible vapor in an excess of carrier gas. Experiments were performed using water, ethanol, and n-propanol as the condensible species with nitrogen as the carrier gas. Many similar studies have been carried out previously, but the results of these studies are usually not sufficiently well documented to enable us to do modeling studies that permit assessment of the condensate characteristics at onset. By carrying out modeling of the particle size distributions for our own experiments, we can avoid this difficulty. At the onset of condensation in a supersonic nozzle expansion, gas flowproperties begin to deviate from their isentropic values. The latent heat released by condensation heats the flow and causes the pressure and density to increase. While nucleation always initiates condensation, the onset of condensation is not necessarily due to nucleation alone. Our modeling results, indicate that the mechanism for producing observable condensate varies considerably with conditions. The particle size distribution at onset appears to undergo a continuous transition from narrow to broad as the onset temperature and pressure increase. When condensible vapor at a low partial pressure expands to a low temperature, nucleation rates are very high at onset, and the mass of condensate occurs mainly as droplets of near critical size. Droplet growth contributes substantially to the accumulation of condensate only after nucleation subsides. At high pressures of condensible vapor, onset occurs at higher temperatures and lower supersaturations. The condensate mass at onset then occurs overwhelmingly as very large supercritical droplets. While nucleation continues at an appreciable rate in the onset region, freshly nucleated droplets contribute negligibly to the total condensed mass. A more extensive description of the experimental and modeling results produced in this study is contained in Appendix B.

C.   Binary Condensation in a Supersonic Nozzle

In this experimental work, we used our supersonic Laval nozzle to investigate the condensation behavior of all three binary pairs in the water-propanol-ethanol ternary system. Of these three binary systems, ethanol-water and propanol-water are both non-ideal and strongly influenced by surface enrichment, while ethanol-propanol is almost ideal. These are the first systematic studies of binary condensation in a supersonic nozzle, and the wide range of mixture properties used will be valuable for assessing the influence of mixture non-ideality on condensation behavior under high cooling rate conditions. By varying the stagnation pressures of the two species independently we were able to observe the onset of nucleation in a narrow range of temperature. Our data are consistent with experiments conducted in shock tubes. When combined with further modeling studies, these data will be invaluable in helping us understand binary nucleation and droplet growth under extreme conditions. More details on the experimental results are presented in Appendix C.

D.   The Kelvin Model and Self-Consistency in Nucleation Theory

In this theoretical work, the self-consistency of several uniary equilibrium cluster distributions based on the traditional capillarity approximationwas reviewed, and some apparent difficulties of interpretation were resolved. The capillarity approximation treats small clusters as liquid drops with volumetric and surface contributions to their reversible work of formation. In the self-consistent

classical (SCC) theory, developed independently by Gershick and Chiu and by Shizgal and Barrett, the equilibrium cluster distribution is modified to both satisfy the law of mass action and satisfy limiting consistency, i.e. equal the monomer concentration when evaluated for a single monomer unit. In this work, the kinetic approach to nucleation theory was used to show that the influence of the self-consistency corrections on the nucleation rate was due to differences in the dimer evaporation rates for various versions of classical theory. This work also considered the relationship between the self-consistent classical theory and the Kelvin model. The Kelvin theory treats homogeneous nucleation using the Kelvin equation as the basis for evaluating droplet evaporation rates. The self-consistent classical theory and the Kelvin theory were shown to give quantitatively similar results. A simple analytical rate expression was also derived for the Kelvin theory making it easy to calculate rates for this model. The similarity of these two approaches was shown to be due to the closeness of the dimer evaporation rates for these different models. However, given the questionable applicability of the Kelvin equation to dimers and other small clusters, it is not clear that the SCC theory should be regarded as fundamentally improved in this respect. Despite this last objection, it is clear that the SCC and Kelvin approaches do provide the best predicted temperature dependence of the nucleation rate for capillarity based nucleation theories. Nevertheless, the predicted temperature dependence is still far from satisfactory, and quantitative improvement in the magnitudes of the predicted rates is not always found. A detailed presentation of the arguments and conclusions of this work has been prepared for publication. It forms Appendix D of this report.

E.   Self-Consistent Size Distribution in Binary Nucleation Kinetics

This work continues the analysis described in Section D and Appendix D and extends it to binary systems, where the considerations become considerably more complex. Using the principle of detailed balance, we derived a new self-consistency requirement, referred to as the kinetic product rule, relating the evaporation coefficients and equilibrium cluster distribution for a binary system. We first used this result to demonstrate and resolve an inconsistency in the results for an idealized Kelvin model of a simple binary mixture. We then examined several forms of the binary equilibrium distribution based on the capillarity approximation. We showed that although each distribution yields sets of evaporation coefficients that are formally consistent with the kinetic product rule, all or some of these coefficients are physically unacceptable because they are functions of the monomer vapor concentrations. We then proposed new forms for the binary distribution function and evaporation coefficients based on the capillarity approximation that satisfy all the degrees of self-consistency investigated here. Finally, we compared experimental binary nucleation rates and vapor activities with theoretical values predicted using our binary SCC distribution in combination with Stauffer's rate formula. While we neither expected nor found perfect agreement, we did note improvement in the predicted slope of the vapor activity dependence at constant rate, and we anticipate that the predicted temperature dependence of the rate will also improve. Appendix E contains a detailed exposition of this work that has been prepared for publication.

F.   Exact Numerical Solution of the Birth-Death Equations in Binary Nucleation Kinetics

This work uses the self-consistent binary distribution function described in Appendix E to formulate a fully self-consistent kinetics scheme describing binary nucleation kinetics. The goal of this work was to investigate both the steady state and transient periods in binary nucleation by setting up and numerically solving the coupled differential equations governing the evolution of the cluster population. We have solved these equations for binary systems that display both positive and negative deviations from ideality in the liquid phase and for a wide range of relative rates of monomer impingement. In all cases we assume ideal gas phase behavior. We have investigated the

evolution to the steady state and compared the numerical results to appropriate analytical rate and time lag expressions. We have emphasized systems and conditions that have been investigated experimentally or which are accessible experimentally. For all of the systems we examined, the numerical nucleation rates agree extremely well with the appropriate analytical theory based on the assumption of a saddle crossing. The latter finding is very significant since there have been several suggestions in the recent literature that contrary behavior known as ridge crossing would dominate under some conditions. We have yet to find any evidence for this type of behavior. The transition from binary to uniary nucleation is followed very well by a modified version of the rate prescription first developed by Wilemski in 1975. During the transient period, the total flux through the subcritical clusters overshoots the final steady state nucleation rate in a manner analogous to the uniary case. Numerically derived time lags are usually within about 20-30\% of those predicted using the simple theory of Wilemski. This work is nearly ready for publication, and a detailed summary of it is contained in Appendix F.

Publications associated with this research

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2.   G. Wilemski, B.E. Wyslouzil, M. Gauthier, and M.B. Frish, in Proceedings of the Eleventh Symposium on Energy Engineering Sciences, Argonne IL, May 1993 (NTIS CONF-9305134) (1993) p.J56.

3.   G. Wilemski, B.E. Wyslouzil, M. Gauthier, and M.B. Frish, "Effect of Carrier Gas Pressure on Water Condensation in a Supersonic Nozzle," in Nucleation and Atmospheric Aerosols, Proceedings of The Thirteenth International Conference on Nucleation and Atmospheric Aerosols, N. Fukuta and P.E. Wagner, Eds. (A. Deepak Publishing, Hampton, 1992) p. 23.

4.   G. Wilemski, "Modeling of Water Condensation in a Supersonic Nozzle," in Nucleation and Atmospheric Aerosols, Proceedings of The Thirteenth International Conference on Nucleation and Atmospheric Aerosols, N. Fukuta and P.E. Wagner, Eds. (A. Deepak Publishing, Hampton, 1992) p. 71.

Presentations associated with this research

1.   Wyslouzil, B.E.and Wilemski, G.,"Numerical Solution of the Binary Evolution Equations," 68th Colloid and Surface Science Symposium, Stanford University, Stanford, CA, 22 June 1994.

2.   Wilemski, G., Wyslouzil, B.E., Beals, M.G., and Frish, M.B.,"The Influence of Nucleation and Droplet Growth on the Onset of Condensation in Supersonic Nozzle Expansions," 68th Colloid and Surface Science Symposium, Stanford University, Stanford, CA, 22 June 1994.

3.   Wilemski, G., Wyslouzil, B.E., Gauthier, M., and Frish, M.B., "Effect of Carrier Gas Pressure on Water Condensation in a Supersonic Nozzle," Eleventh Symposium on Energy Sciences, Argonne National Laboratory, Argonne, IL, 3 May 1993.

4. Wilemski, G., Panel Member for "Panel Discussion on Nucleation," at the Nucleation and Crystallization Symposium, Glass and Optical Materials Meeting, The American Ceramic Society, Stone Mountain, GA, 19 August 1992.

5. Wilemski, G., Wyslouzil, B.E., Gauthier, M., and Frish, M.B., "Effect of Carrier Gas Pressure on Water Condensation in a Supersonic Nozzle," Thirteenth International Conference on Nucleation and Atmospheric Aerosols, University of Utah, Salt Lake City, Utah, 24 August 1992.

6. Wilemski, G., "Modeling of Water Condensation in a Supersonic Nozzle," Thirteenth International Conference on Nucleation and Atmospheric Aerosols, University of Utah, Salt Lake City, Utah, 26 August 1992.

7. Wilemski, G., "Vapor Condensation in Supersonic Flow," Staub- und Aerosolkolloquium, Institute for Experimental Physics, University of Vienna, Vienna, Austria, 21 October 1992.

APPENDIX A

Effect of Carrier Gas Pressure on Condensation in a Supersonic Nozzle
(reproduced in its entirety)

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APPENDIX B

The Influence of Nucleation and Droplet Growth on the Onset of
Condensation in Supersonic Nozzle Expansions

APPENDIX C

Binary Condensation in a Supersonic Nozzle

APPENDIX D

The Kelvin Model and Self-Consistency in Nucleation Theory

APPENDIX E

Binary Nucleation Kinetics I
Self-Consistent Size Distribution

APPENDIX F

Binary Nucleation Kinetics II
Exact Numerical Solution of the Birth-Death Equations