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BINARY CONDENSATION IN A SUPERSONIC NOZZLE

Barbara E. Wyslouzil, Mitzi G. Beals and Gerald Wilemski

I. INTRODUCTION

Binary nucleation measurements were first conducted by Flood[1] using an expansion cloud chamber to study the onset of condensation in the ethanol-water system. Since this pioneering work, binary nucleation has been studied using a variety of techniques, including thermal diffusion cloud chambers,[2,3] shock tubes,[4,5] expansion cloud chambers[6,7] and a fast mixing apparatus.[8,9] Both the onset of condensation and, more recently, isothermal binary nucleation rates have been measured for a large number of ideal and non-ideal systems. However, to date only preliminary experimental results have been reported for binary condensation in supersonic nozzles.[10] Unlike other techniques, supersonic nozzles do not yield nucleation rates directly because the length of time over which nucleation contributes significantly to particle formation is not easy to determine or control. Nonetheless, experiments in nozzles are extremely important because they provide higher rates of cooling, higher supersaturations and higher nucleation rates than any of the other techniques. Their operating conditions are more typical of the important industrial conditions such as aerodynamic and turbomechanical flows where homogeneous nucleation can have serious consequences. Because the fluid mechanics of nozzles are well defined and understood, nucleation experiments in the nozzle are amenable to sophisticated modeling efforts and much useful insight can be gained regarding the nucleation and droplet growth processes under these severe cooling conditions.

This paper summarizes our recent experimental work using a gently diverging supersonic Laval nozzle to investigate 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 should be almost ideal. In §II we briefly describe the experimental apparatus and our method for preparing the binary gas mixtures. We present our experimental results in §III and compare them to relevant experimental data and nucleation rate calculations available in the literature.

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II. EXPERIMENTAL APPARATUS AND DATA ANALYSIS

The experimental apparatus and data analysis were described in detail in a recent publication[11] and are reviewed only briefly here. As illustrated in Figure 1, the apparatus consists of an intermittent, low Mach number, supersonic Laval nozzle equipped with a Mach-Zender interferometer. Gas mixtures of the desired composition are prepared by accurately metering the desired amount of each condensible vapor from its pressurized saturator into the previously evacuated supply tank and plenums. The required amount of N_2 carrier gas is then added to make up the mixture. The nozzle is two dimensional with a 0.5x1.23 cm^2 throat, a 7.9 cm long supersonic portion and an exit-to-throat area ratio of 1.37 that yields a maximum Mach number of 1.72 for a diatomic gas. During a 300 ms run, gas from a heated plenum flows through the nozzle into an evacuated dump tank and steady one dimensional density, temperature and pressure gradients are established. An analysis of the interference fringes measured during the steady flow period, yields the relative density profiles, ρ/ρ_0, as a function of position in the nozzle. The relative density profile for a non-condensing flow follows that described by the one-dimensional adiabatic gas dynamics equations and is used to accurately calibrate the shape of the nozzle. This calibration is critical in a small nozzle because boundary layers significantly alter the effective shape of the nozzle and are a strong function of the pressure. The relative density profiles for the flow of a condensing gas mixture together with the diabatic gas dynamics equations yield the temperature, pressure and condensed mass profiles.

The gas dynamics equations for diabatic flow outlined in our previous paper[11] are readily generalized to binary systems although there is some subtlety involved because we cannot determine the composition of the condensing species from the experiments. Fortunately, the location of onset is not strongly influenced by our assumptions regarding the composition of the condensed species. Even the uncertainties in the derived quantities (temperature, pressure and condensed mass) downstream of onset should not be too sensitive because the molar heats of condensation of these species are not too different.

III. BINARY CONDENSATION

A. Experimental Results

We conducted condensation experiments over a wide range of initial ethanol, propanol and water concentrations. The results from the uniary experiments have been presented elsewhere[12] and will not be repeated here, but we note that our agreement with experimental results from other nozzles and shock tubes was very good. Figure 2 illustrates the variations in the density ratio, temperature, pressure and condensed mass fraction as a function of position in the nozzle for a typical experiment with the water-propanol system. As in our uniary experiments we define the following curves.

(1) Dry Isentrope : The isentropic expansion of the carrier gas that does not contain any condensible vapor. This curve is used to define the effective shape of the nozzle, which differs from the shape of the physical nozzle walls because of the boundary layers.

(2) Wet Isentrope : The isentropic expansion a condensible vapor laden carrier gas would experience if condensation were suppressed. This curve differs from the 'dry isentrope' because

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the addition of the condensible species changes the ratio of the heat capacities of the mixture, γ.

(3) Condensing Flow Curve: The actual expansion followed by the condensing flow. Before condensation becomes significant, the condensing flow curve follows the 'wet' isentrope.

As shown in Fig. 2., the onset of condensation occurs in the region where the condensing flow curve deviates from the wet isentrope. Depending on how rapidly this deviation occurs, there is some uncertainty in precisely pinpointing the onset of condensation. As a working definition, we define the onset of condensation as the point where the temperature on the condensing flow curve first deviates from the temperature of the wet isentrope by 1 K. As discussed more extensively in our previous paper,[11] this definition is not unique but most reasonable definitions of the onset of condensation will be quite close to this one.

All of our experiments were conducted using a stagnation pressure of 2.5 atmosphere. This is a reasonable compromise between providing clean interferograms while still letting us observe onset even at low condensible vapor conditions. When the stagnation pressure is very high the heat released by the condensing vapor may not be enough to perturb the flow noticeably. When the stagnation pressure is too low, interferometry becomes difficult because the absolute changes in the density are small. Because the most useful test of binary nucleation theory is provided by data at constant temperature, we varied the concentrations of both condensing species to maintain a constant temperature at onset. Experiments in the ethanol-water and ethanol-propanol systems used a stagnation temperature of 316 K while the propanol-water experiments used a stagnation temperature of 310 K.

Tables 1, 2 and 3 summarize the conditions at onset for all of the binary experiments. For the ethanol-water experiments we were able to keep onset between 234 and 239 K, with most of the points between 234.4 and 237 K. For propanol-water, onset was always between 230 and 236 K with most points between 232 and 234 K. Finally for ethanol-propanol, with the exception of the pure ethanol point, onset was observed between 228 and 233.3 K with most points between 231 and 233 K. Figures 4, 5 and 6 summarize the data. Points within the approximately 2 K temperature range are given as open squares, while outliers are indicated as filled squares. We have chosen to plot our data in terms of the pressures at onset rather than the activity because at these low temperatures very slight inaccuracies in the temperature lead to large changes in activity.

We are not able to compare our current experiments to the preliminary results of Frish, Waterhouse and Wilemski.[10] As discussed in our previous paper,[11] this nozzle exhibits some transient behavior that can lead to onset temperatures and pressures that are too high if this transient is not removed during the data analysis. In the absence of other nozzle experiments, shock tube data provide the best comparison because they are the most similar with respect to cooling and nucleation rates. However, at the same onset temperature, supersaturations and nucleation rates are still higher in nozzles than shock tubes. This means that to observe onset at the same temperature as in a shock tube, nozzle experiments must start with higher initial condensible pressure. Thus our data should, on average lie close to but somewhat above the shock tube data on an activity plot, or equivalently on a pressure plot.

Shock tube data are available in the literature for each of these binary pairs. Ethanol-water and ethanol-propanol were studied by Zahoransky and Peters[4] water was investigated by Peters.[5] Their results are shown as filled triangles in Figures 3, 4, and 5. Although a direct comparison is difficult, our data show the same trends for each system and appear to be consistent.

B. Comparison with Nucleation Theory

The curves of onset pressures at constant onset temperature correspond to curves of approximately constant rate. Based on modeling results in uniary condensation experiments,[12] these rates are on the order of 10^{17}. All binary nucleation rate expressions rely on approximations in their development and most are only strictly valid in the limit of a large free energy barrier and a critical cluster size large enough for the continuous approximation to be valid. A key reason, therefore, for conducting experiments in a supersonic nozzle is to test binary nucleation theories in the high rate limit, when free energy barriers and critical clusters become very much smaller than under the conditions typical for diffusion cloud chambers.

There are several versions of nucleation theory available, based on different microphysical models, which are appropriate to compare with our data. In systems that display a high degree of surface enrichment, microphysical models that calculate the free energy of cluster formation based on an average cluster composition fail especially under conditions rich in the higher surface tension species. Thus in the water-alcohol systems, the classical binary nucleation theory of Reiss[13] and Doyle,[14] which finds the saddle point of the free energy surface by solving the generalized Kelvin equations that contain compositional derivatives of the surface tension are not appropriate. The revised classical theory of Wilemski,[15] which gives equivalent results to the theory of Neumann and Döring,[16] implicitely allows for surface enrichment through the use of the Gibbs adsorption isotherm and is a distinct improvement. However at very high nucleation rates and for very non-ideal systems it can predict unphysical behavior.[17] Better results have been obtained by models which try to include surface enrichment explicitly, such as the monolayer-lattice approach of Flageollet-Daniel, Garnier, and Mirabel[18] (FDGM) or more recently the simplified cluster model approach of Laaksonen and Kulmala.[19] Both have been quite successful in reproducing the experimental trends observed in water alcohol systems. Calculations in the literature[4,20] for these systems are shown as solid lines in Figures 3 through 5 and provide qualitative agreement with our experimental results.

IV. SUMMARY AND CONCLUSIONS

We report here the first systematic studies of binary condensation in a supersonic nozzle. Our experiments investigated all three binary pairs in the ethanol-propanol-water ternary system. 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. Further modeling studies, using an integral model which considers both nucleation and growth, will help us understand binary condensation downstream of onset.

V. ACKNOWLEDGMENT

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Table 1. Summary of Experimental Conditions for Ethanol-Water Vapor.

Table 1: Summary of Experimental Conditions for Ethanol - Water Vapor						
Stagnation Conditions				Onset Condistions		
		Ethanol	Water		Ethanol	Water
T_0, K	P_0, atm	P_0, Torr	P_0, Torr	T, K	P, Torr	P, Torr
316	2.50	0.00	18.00	239.1	0.00	6.66
316	2.50	0.00	15.00	235.6	0.00	5.32
316	2.50	0.71	14.29	234.9	0.25	5.03
316	2.50	1.39	11.81	234.9	0.49	4.15
316	2.50	1.98	9.92	234.4	0.69	3.45
316	2.50	2.78	8.33	235.4	0.99	2.95
316	2.50	3.67	6.20	235.9	1.31	2.21
316	2.50	4.80	4.80	237.0	1.74	1.74
316	2.50	5.92	3.66	236.2	2.11	1.31
316	2.50	6.94	2.78	238.4	2.56	1.03
316	2.50	7.78	1.67	234.4	2.70	0.58
316	2.50	9.04	0.74	235.1	3.18	0.26
316	2.50	12.40	0.00	238.0	4.47	0.00

Table 2. Summary of Experimental Conditions for Propanol-Water Vapor.

Table 2: Summary of Experimental Conditions for Propanol - Water Vapor						
Stagnation Conditions				Onset Condistions		
		Propanol	Water		Propanol	Water
T_0, K	P_0, atm	P_0, Torr	P_0, Torr	T, K	P, Torr	P, Torr
316	2.50	0.00	15.00	235.6	0.00	5.32
310	2.50	0.53	13.60	232.4	0.19	4.93
310	2.50	1.07	10.67	233.3	0.39	3.89
310	2.50	1.60	8.67	231.8	0.57	3.11
310	2.50	1.97	6.58	232.5	0.71	2.39
310	2.50	2.67	3.63	230.9	0.94	1.28
310	2.50	3.38	2.70	230.0	1.17	0.94
310	2.50	3.73	1.33	233.5	1.36	0.49
310	2.50	4.50	0.00	232.1	1.62	0.00

Table 3. Summary of Experimental Conditions for Propanol-Ethanol.

Table 3: Summary of Experimental Conditions for Propanol - Ethanol Vapor						
Stagnation Conditions				Onset Condistions		
		Propanol	Ethanol		Propanol	Ethanol
T_0, K	P_0, atm	P_0, Torr	P_0, Torr	T, K	P, Torr	P, Torr
316	2.50	0.00	7.00	225.2	0.00	2.82
316	2.50	1.47	6.62	233.3	0.50	2.26
316	2.50	2.50	5.00	232.7	0.85	1.69
316	2.50	2.94	3.53	231.8	0.98	1.18
316	2.50	3.47	2.08	228.0	1.09	0.66
316	2.50	4.12	0.74	230.8	1.36	0.24
310	2.50	4.50	0.00	232.1	1.62	0.00

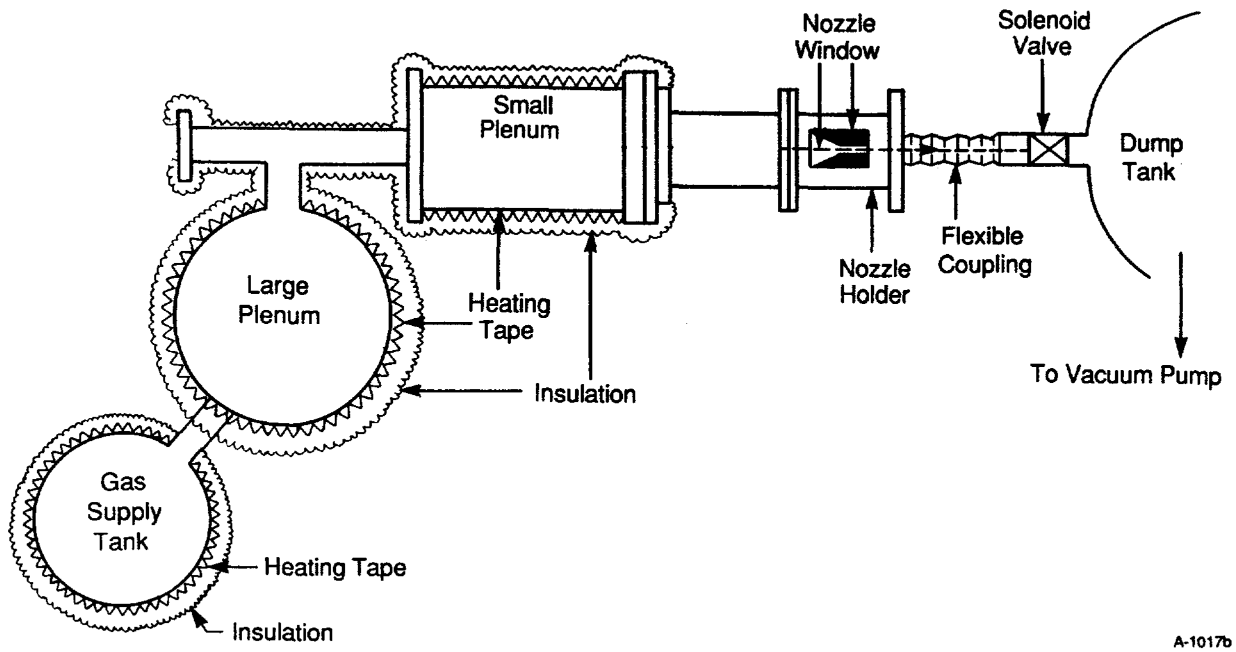
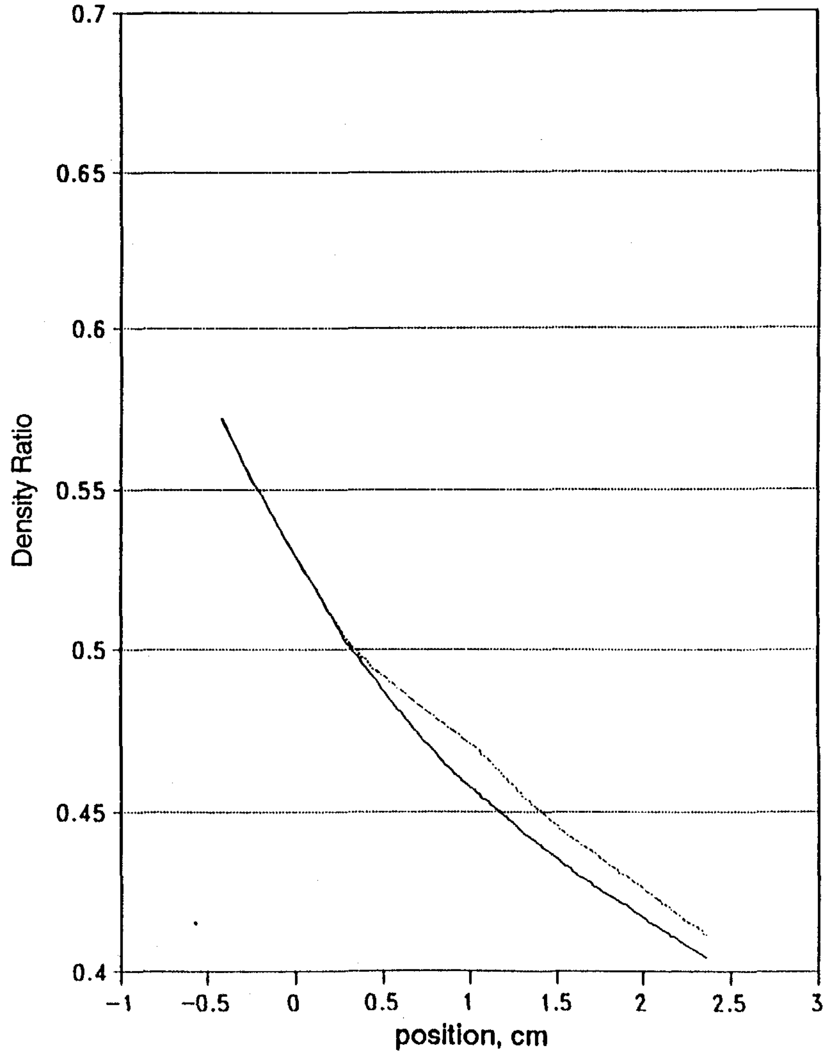
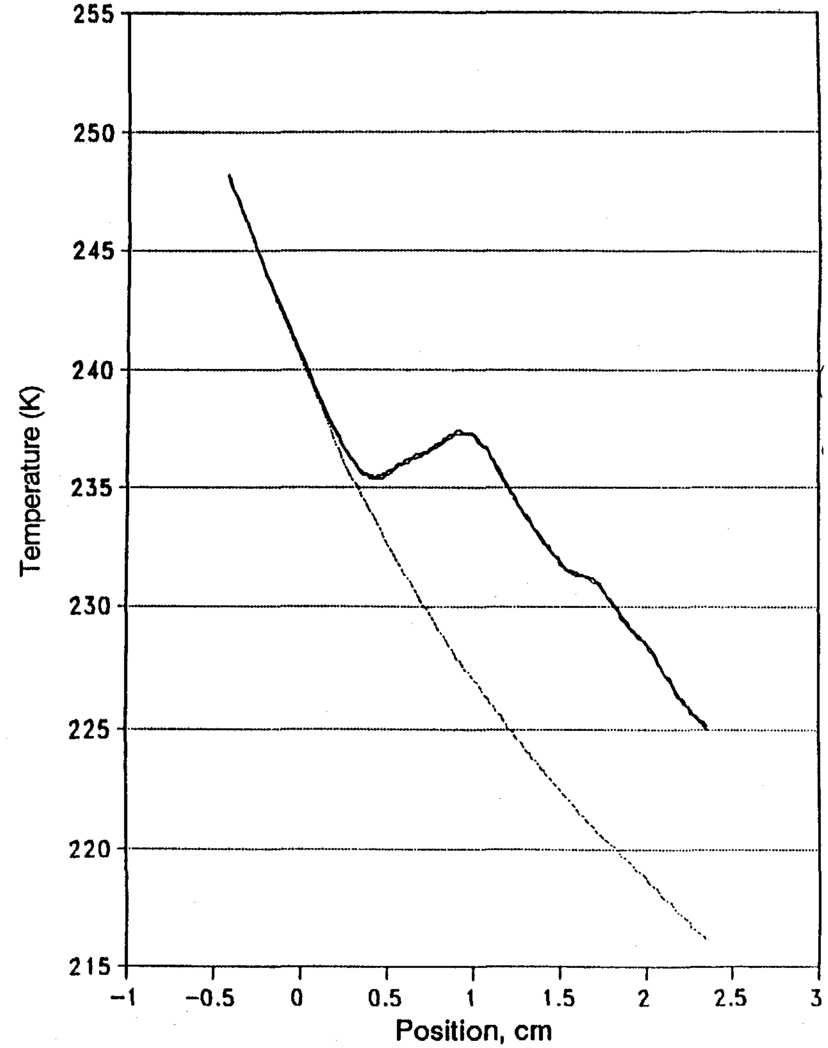


Figure 1. Schematic diagram of the supersonic nozzle flow system.

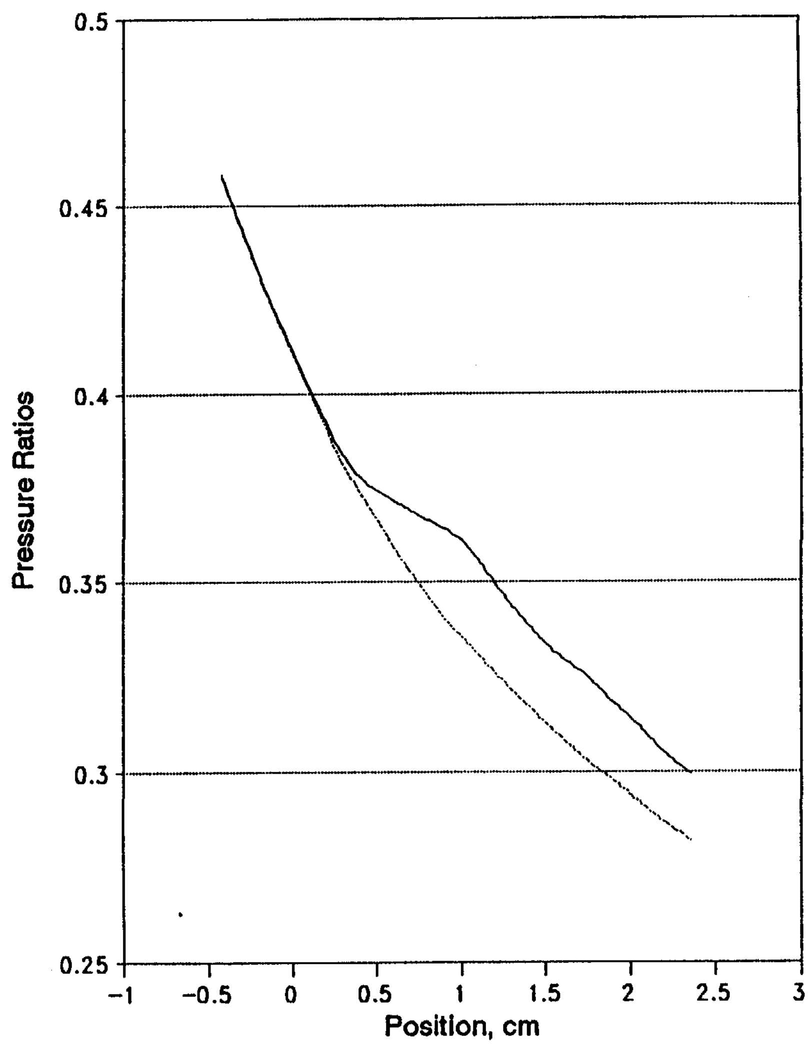


(a)

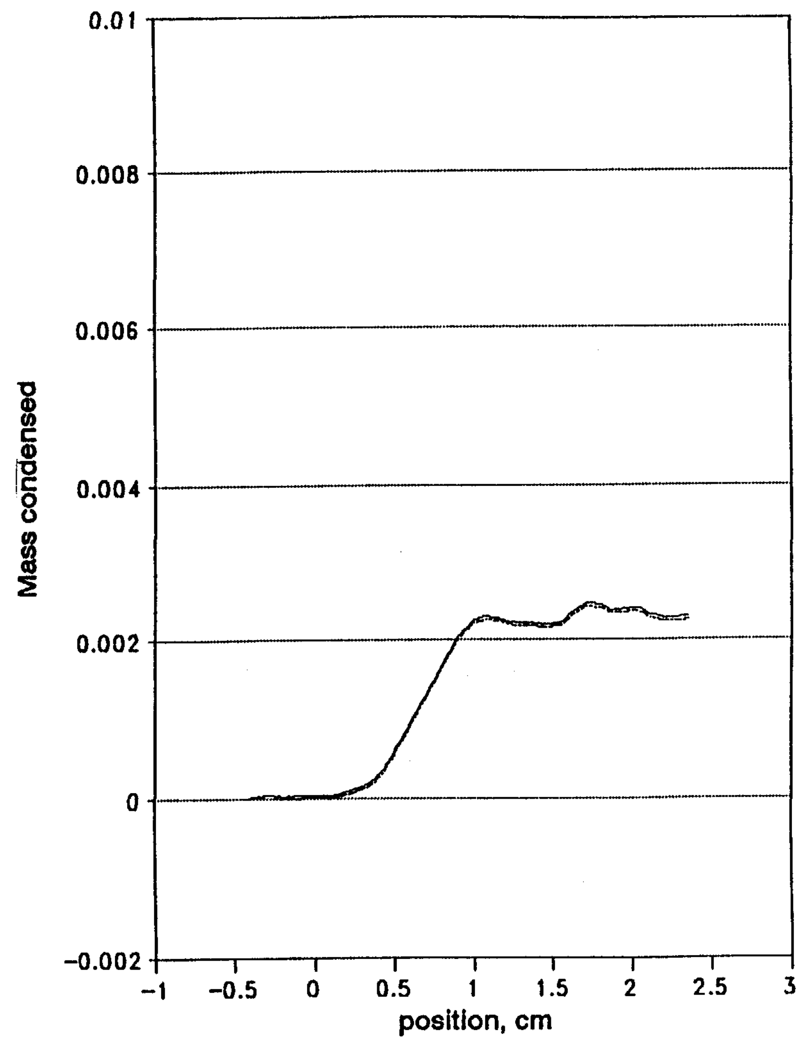


(b)

Figure 2. Typical examples of (a) smoothed experimental density ratios and the derived quantities (b) temperature (c) pressure and (d) condensed mass ratio for a propanol-water condensation experiment. The stagnation conditions were T_0 = 310 K, P_0 = 2.5 atm, $P_{c,water}$ = 7.14 Torr and $P_{c,propanol}$ = 2.14 Torr.



(c)



(d)

Figure 2 (cont). Typical examples of (a) smoothed experimental density ratios and the derived quantities (b) temperature (c) pressure and (d) condensed mass ratio for a propanol-water condensation experiment. The stagnation conditions were T_0 = 310 K, P_0 = 2.5 atm, $P_{c,water}$ = 7.14 Torr and $P_{c,propanol}$ = 2.14 Torr.

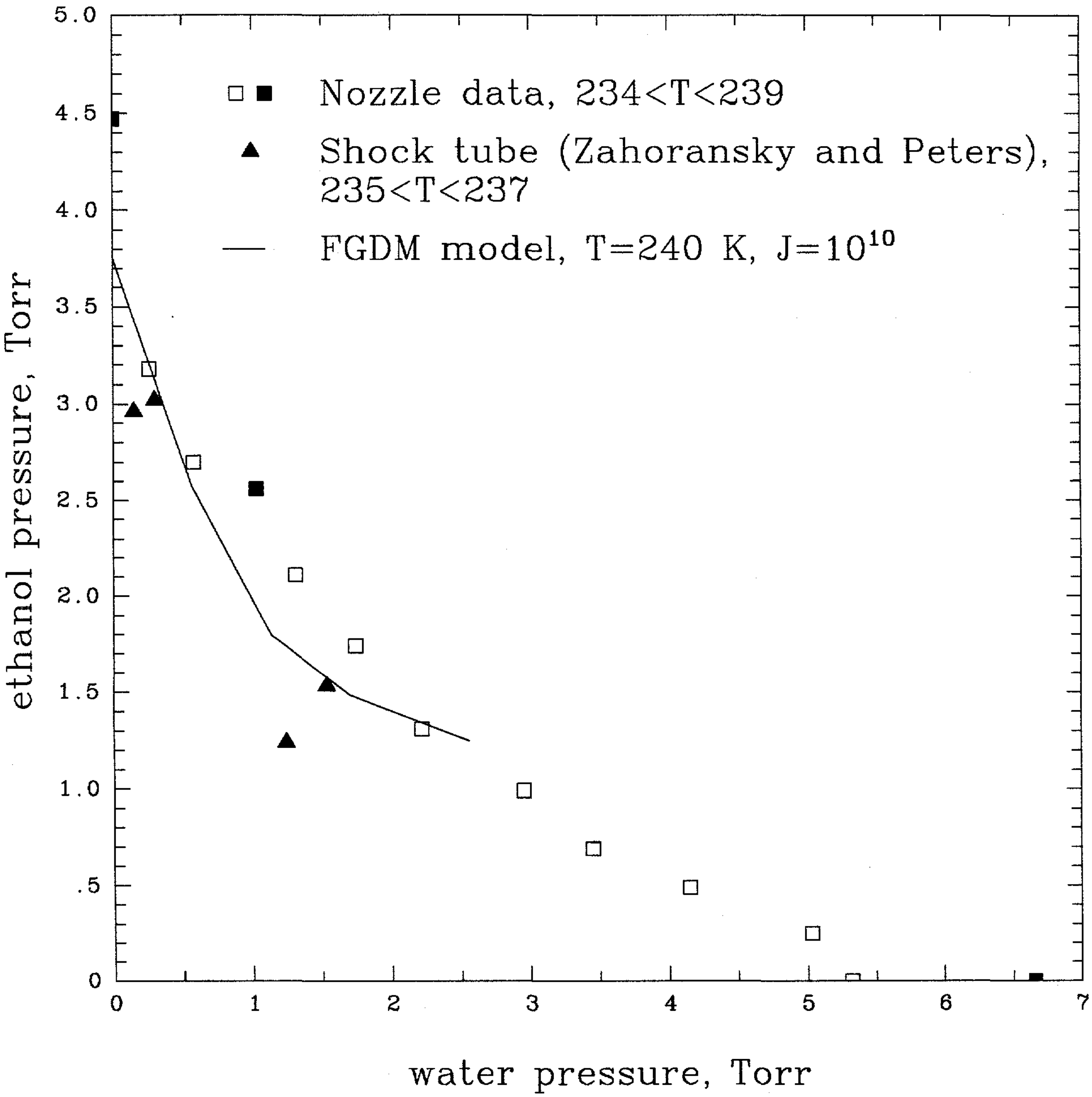


Figure 3. Comparison of the onset pressures for ethanol-water measured in the supersonic nozzle with the shock tube data of Zahoransky and Peters.[4] Their theoretical curve calculated with the FDGM theory is also shown.

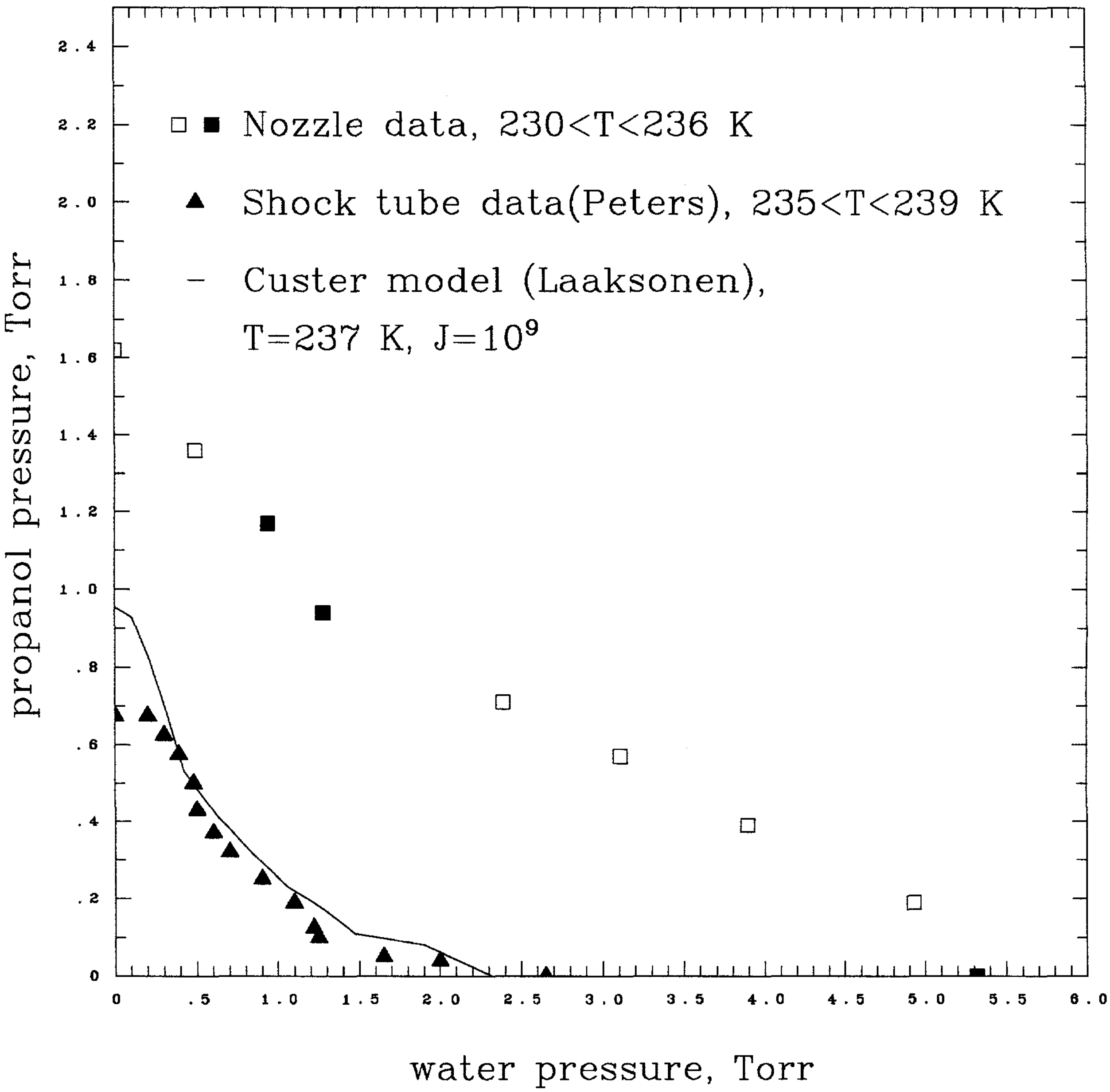


Figure 4. Comparison of the onset pressures for propanol-water measured in the supersonic nozzle with the shock tube data of Peters.[5] The theoretical curve calculated by Laaksonen[20] using a cluster model is also shown.

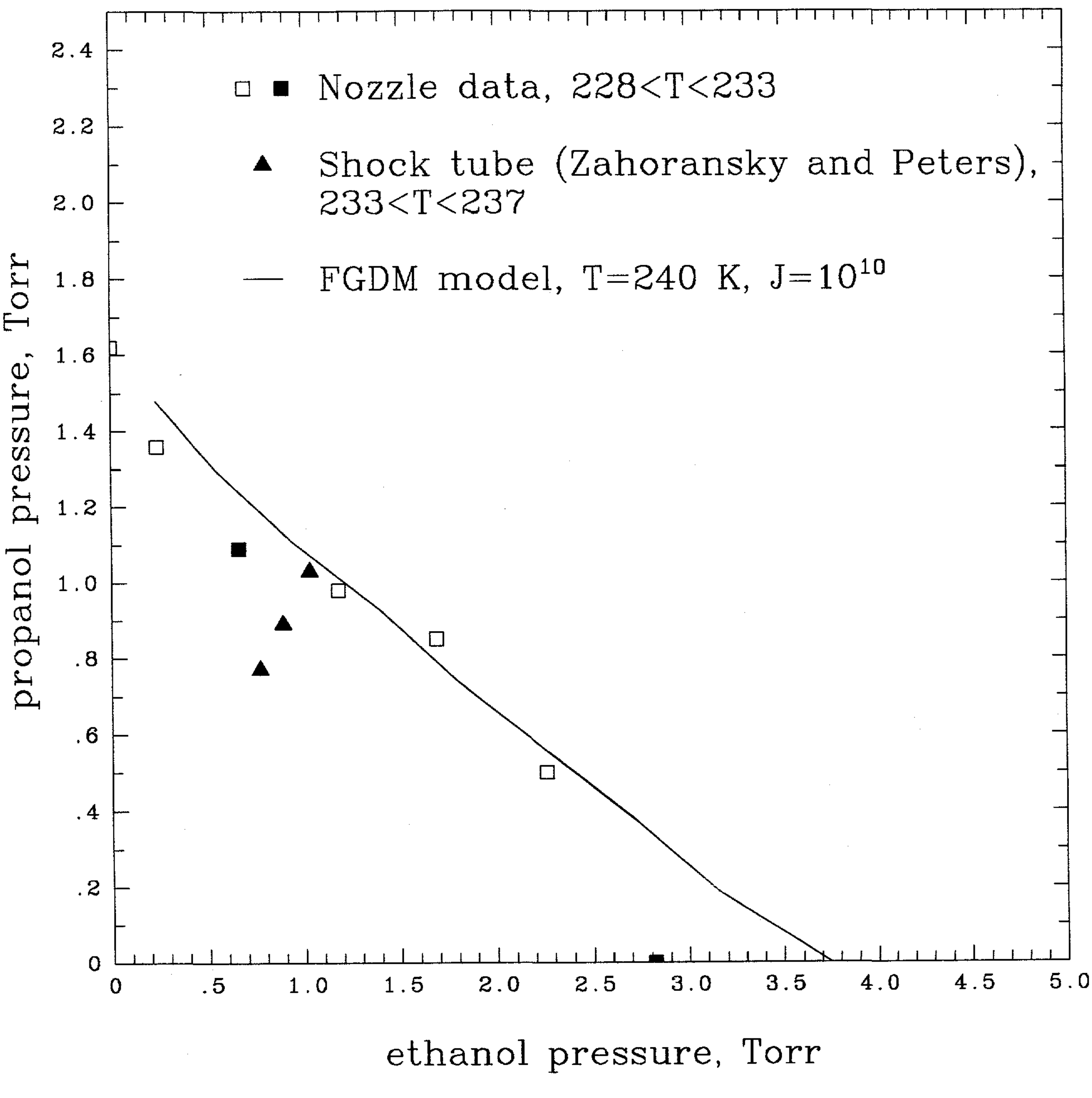


Figure 5. Comparison of the onset pressures for propanol-ethanol measured in the supersonic nozzle with the shock tube data of Zahoransky and Peters.[4] Their theoretical curve calculated using the FDGM theory is also included.