CRITICAL POINT WETTING DROP TOWER EXPERIMENT

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ABSTRACT

The theory of Critical Point Wetting (CPW) by John Cahn (NBS) was recently proposed (1976) to explain the unusual and unexpected behavior between two immiscible fluids near their critical temperature. Little experimental evidence is available to support the theory. In this series of drop tower experiments, the theory is tested for two-liquid immiscibles. The drop tower provides the low-g environment required to allow surface tension forces to overcome hydrostatic forces generated by the density differences between the two fluid phases in Earth gravity. The theory is proven if the wetting transition temperature can be found. An abrupt change in wetting behavior occurs at this special temperature. It should be possible to find the transition temperature by using several drops over a range of temperatures up to critical temperature.

The second aspect of the experiment utilizes the drop tower as a measurement tool for determining the interfacial free energies (IFE) between two fluids in near-critical systems. Successful drops with different temperatures will give the very important temperature dependence of the IFE. The oscillation frequency depends on the change in acceleration, which for the drop tower can cover five orders of magnitude. By measuring the oscillation of the interface caused by the drop, the IFE may be determined at temperatures close to critical.

The IFE measurements from the tower, together with other IFE data should permit calculation of the wetting transition temperature from the CPW theory.

INTRODUCTION

Wetting phenomena and other fluid behavior can be observed in a microgravity environment by using the MSFC Drop Tower. This facility is being used to test the critical point wetting (CPW) theory of Cahn [1]. Early results of a preliminary feasibility study are the topic of this paper. In this test, transparent binary solutions which form two liquid phases in a monotectic (immiscible) system are used. The shape of the meniscus formed between these two liquid phases contained in an upright cylindrical tube was photographed as the sample experienced the transition from 1 g (at the top of the tower), to approximately 10^{-5} g during the free fall. The meniscus shape changes in response to the acceleration change because of the density difference between the two phases. With the removal of Earth gravity, the forces acting on the interface are solely determined by the balance of interfacial energies (or tensions) between the three phases: liquid 1, liquid 2, and the solid container wall. It is the individual variations of these interfacial energies with temperature that lead to the CPW behavior that is expected to occur. A number of drops, each at a different temperature should reveal the critical wetting transition temperature which should be found somewhat below the critical temperature for the system in question.

The considerable significance of such experiments can be attributed to their fundamental nature. Aspects of studies in crystal growth, nucleation phenomena, solidification of monotectics, superfluidity phenomena, cryogenic liquid storage problems, thin liquid films, and in undercooling of immiscible alloys concern CPW theory [2-7].

EXPERIMENT APPARATUS

The experiment package consists of a circulating water bath, high speed motion picture camera (500 frames per sec. Milliken), lights, batteries, temperature controller and digital timer. Specimen capsules were mounted in the bath cannister in such a way that the camera sees the back-lighted specimen interfaces through the bath window (see Figure 1). Figure 2 shows the optical path in profile view. Figure 3 is the actual set-up shown previously in Figure 2. An idea of the overall dimensions of the experiment can be obtained from Figure 4 which shows M. Tcherneshoff and S. Straits from the University of Alabama in Huntsville working on the package.

The specimens themselves are flame-sealed glass ampoules. The interfaces will be axisymmetric within these cylindrical tubes. The tube axis is oriented parallel with the gravity vector, i.e., up-down. This orientation provides the proper geometry for interface shape analysis.

The two-liquid phase systems which are possible candidates for testing are succinonitrile-H_2O, succinonitrile-ethanol, cyclohexane-methanol, and diethylene glycol-ethyl salycilate. The later two systems already have some interfacial energy data available [8,9]. These systems all have consolute solution temperatures above room temperature but below the boiling point of water. This facilitates temperature control and maintenance of safety.

The experiment package, Figure 4, sits inside the drop tower dragshield for the duration of the test drop. The dragshield is shown in Figure 5. The drop height is 100 meters and a high pressure gas rocket nozzle on top of the shield helps keep the package accelerating with the rate:g, despite air resistance. Upon release, the thruster pushes the shield down from under the package inside. From that moment on, the package falls free of outside interference and experiences minimal g-forces in all three axis. Potentially superior low-g levels can be obtained over that experienced in the KC-135 airplane during Keplerian flight. The cost per unit time of low-g is lower as well. Up to 4 seconds of low-g can be obtained with the drop tower. Turn around time on the tower can be as little as one hour per drop.

Drop towers have been used for low-g fluids experiments in the past [10-14]. The facility at MSFC was constructed to study the behavior of rocket propellants within fuel tanks in order to ensure reliable fuel and oxidant flow to the engine. The facility is now dedicated to the performance of materials science experiments in low-g.

Oscillations of the fluid in the tank models mentioned above, were observed and the behavior of the fluid was determined to be dependent on the interfacial energy (surface tension) of the fluid-vapor interface. The period of oscillation for the given geometry and liquid combination varied with surface tension. This very behavior is useful to measure the (unknown) surface energy of a fluid as a function of temperature. This technique almost requires a drop tower type of facility. It is the sudden unloading of the pull of gravity which sets the interface into motion. The restoring force of the surface tension causes the interface to change shape to accommodate the new balance of forces since the hydrostatic forces caused by the density differences of the two fluid phases (in that case, vapor and liquid) were removed [11]. Although damped by fluid viscosity, the interface acts like a taut skin and oscillates like a weight on a spring.

INTERFACE SHAPES

These drop tower experiments involve the study of interphase interfaces from the motion picture film taken during the drop. It should be possible to measure the interfacial free energy and to determine the wetting transition temperature for the CPW theory from the film or a series of films from drops performed at various temperatures. The static interface shape can be calculated using the Bond number, B_o:

$$B_o = \Delta\rho\alpha r^2/\sigma_{lv}$$

where $\Delta\rho$ is the density difference between the liquid phases, α is the acceleration level, r is the tube radius, and σ_{lv} is the surface tension of the interface. Figure 6 shows calculated interface shapes for some systems with the contact angle fixed at 5 degrees, the tube diameter 1 cm and 1 g acceleration. The final interface shape at static equilibrium can be calculated and compared to the interface shape measured in the specimen if the oscillations damp-out. Interfacial energy and/or contact angle measurements are possible from such comparisons.

PRELIMINARY RESULTS

At the present time, only a couple of successful drops were performed. Figures 7 and 8 are a pair of individual frames taken from the 16-mm film of the latest drop. One frame is that of the specimens in 1 g just before the drop, Figure 7. The other is of the specimens after a 1 sec period of low-g (10^{-3} g approximately). In the left ampoule is the immiscible system, succinonitrile-ethanol; in the middle ampoule is cyclohexane-methanol; and in the third ampoule is the third immiscible, succinonitrile-water. The center ampoule is 1 cm in diameter. Two interfaces are seen in each ampoule. The uppermost interface is that of the top liquid phase and the vapor, the lower of the two is the interface between the upper and lower liquid phases. The higher surface tension of the liquid-vapor interface causes it to form a near spherical ullage. The low interfacial energy of the left sample is clearly seen by looking at the relative flatness of this interface in 1 g. As expected, this interface curvature increases after the acceleration of gravity is removed. The other interfaces also respond as expected, for example, the right hand sample increases its interfacial curvature dramatically in low-g. Note how the different refractive indeces of the liquid phases change the spacing of the reference grid lines on either side of the interfaces. The response to the unloading of gravity was different at another temperature.

At this time, no test of the CPW theory has been made. However, some experimental evidence for this theory can be found in the literature [15-18]. This experiment will be the first to use the drop tower to test the CPW theory. A brief explanation of the theory is given in the Appendix.

CONCLUSIONS

Preliminary results for the CPW Drop Tower Experiment have been produced with immiscible systems. Much of the observed phenomena conformed to the anticipated behavior. More drops will be needed to test the CPW theory with these immiscible systems.

APPENDIX: CRITICAL POINT WETTING EXPLAINED

The CPW theory is based on the behavior of the interfacial free energies as a function of temperature of the three interfaces involved (see Fig. A). As one approaches the critical temperature for L_1 and L_2, there is a rapid change in interfacial free energy for each interface as shown [1,7]. The plotted variation of interfacial free energy with temperature is based on the theoretical behavior for such interfaces.

One finds that at the transition temperature, T_w, the interfacial free energy for the L_1L_2 interphase interface drops more rapidly with temperature than the difference of the interfacial free energies between the liquid phases and the container (third phase). Therefore, at temperatures above T_w, one liquid phase will preferentially wet the container and cause the other phase to separate from the container wall. This is a direct consequence of the imbalance of the Young equation at temperatures above T_w and below T_c. The relative wetting characteristics between the three phases will therefore be sharply altered when the temperature is between T_w and T_c. In theory, the two fluid phases may be either those of an immiscible liquid system or of a single component, liquid-vapor system.

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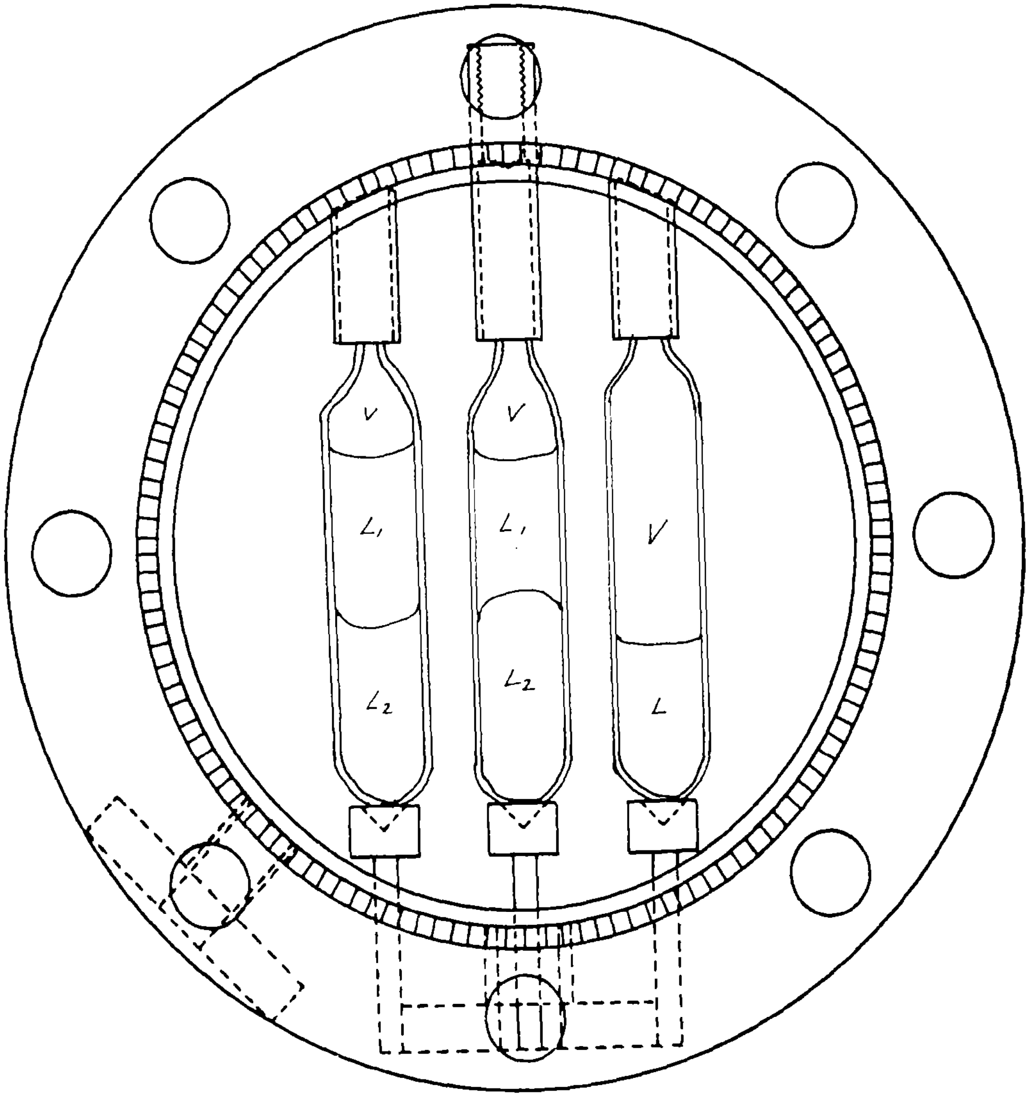


CAMERA VIEW OF CIRCULATING OIL BATH
FOR DROP TOWER EXPERIMENTS ON CPW

Figure 1.

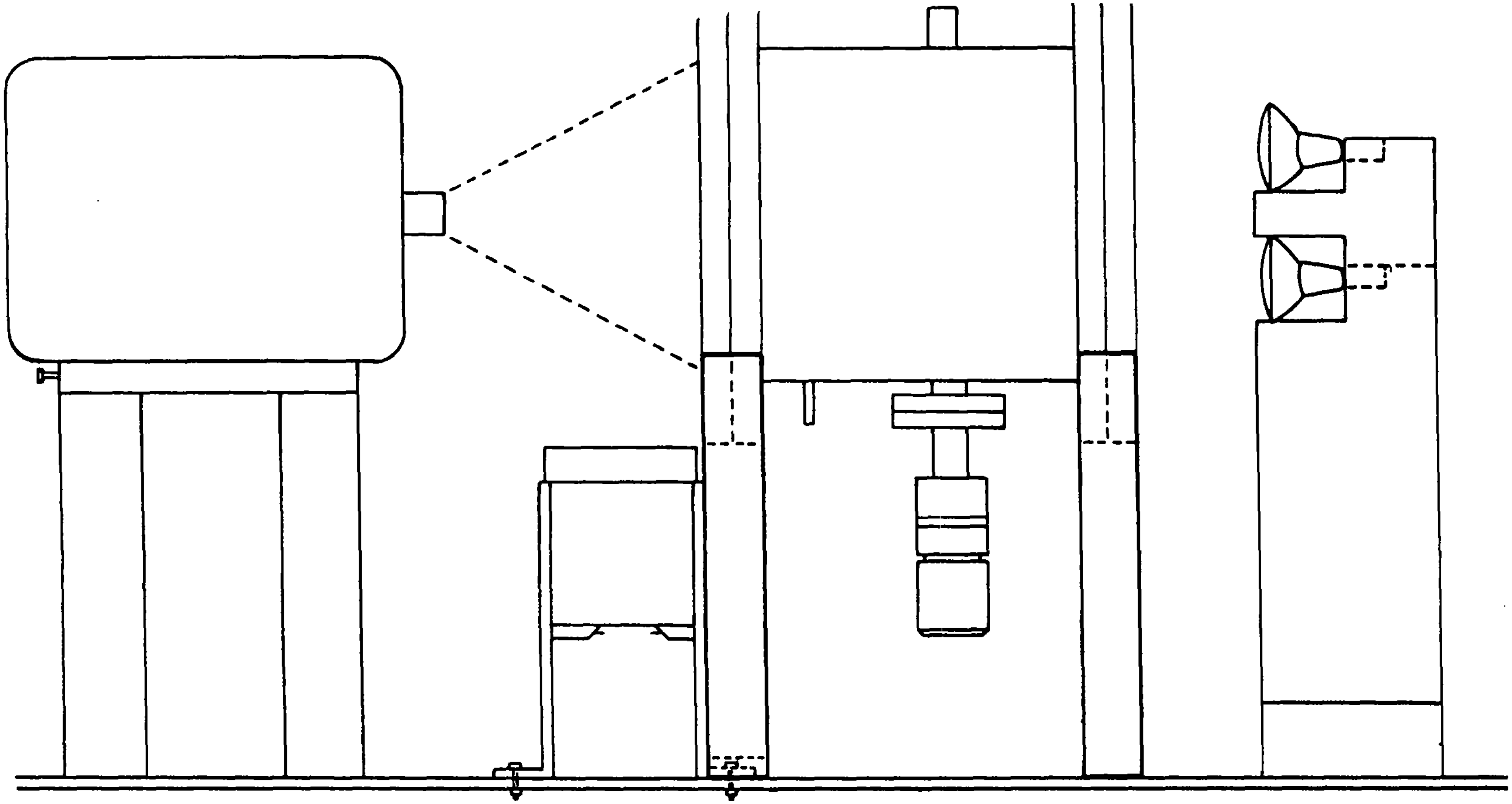


Figure 2. PROFILE VIEW OF EXPERIMENT PACKAGE SHOWING LIGHTS, OIL BATH, CAMERA AND TEMPERATURE CONTROLLER.

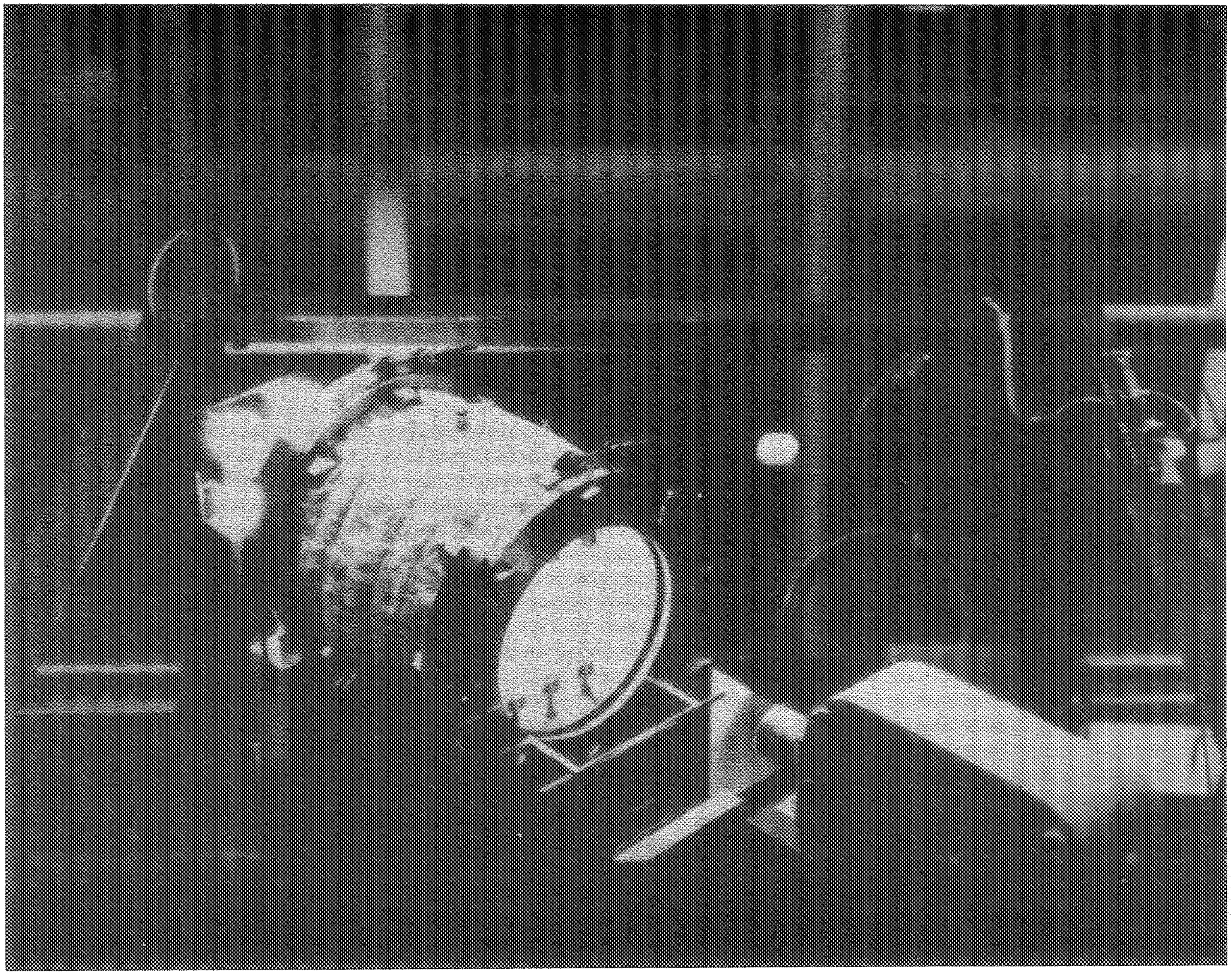


Figure 3

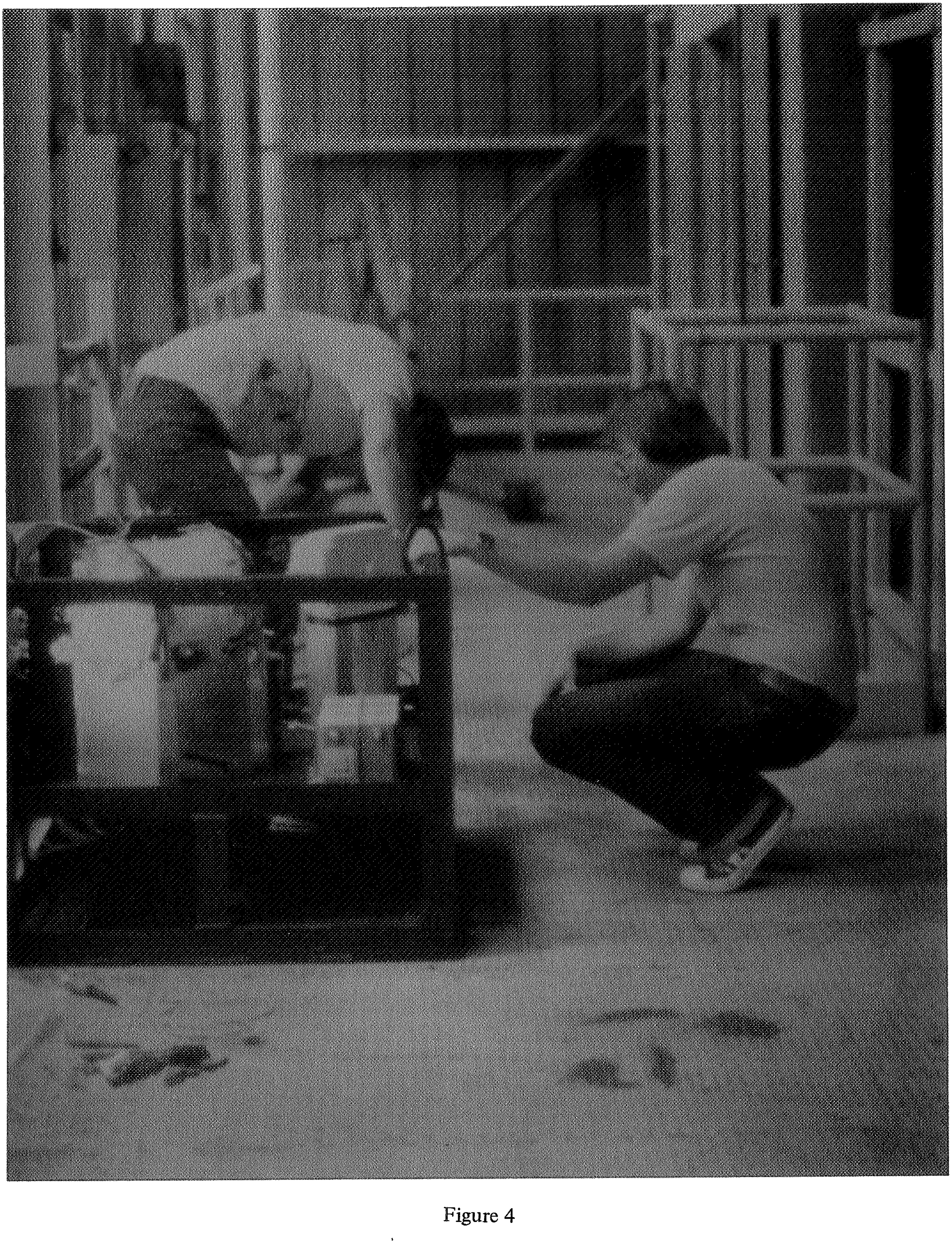
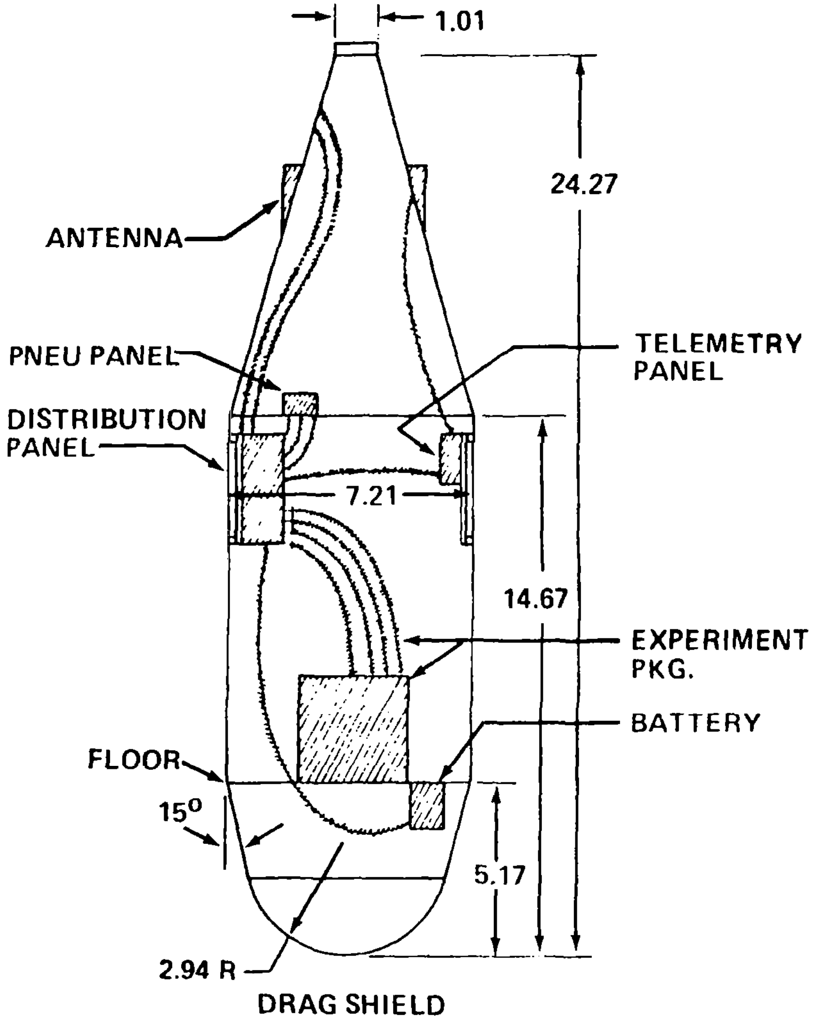


Figure 4



TOTAL DROP HEIGHT	333.8 FT
FREE FALL HEIGHT	293.8 FT
DRAG SHIELD FREE FALL TIME	4.275 SEC
DRAG SHIELD DECELERATION	25 G

DRAG SHIELD DIMENSIONS:

LENGTH	24′ 3¼″
DIA.	7′ 2½″
WT.	3620 POUNDS
TEST AREA	6′ X 8′

PACKAGE SIZE:

HEIGHT	3 FT
WIDTH	3 FT
LENGTH	3 FT

MAX TEST PACKAGE WT 450 LBS, MUST BE BALANCED

LOW GRAVITY RANGE:

MAX	4×10^{-2} G
MIN	1×10^{-5} G

AUX DRAG SHIELD THRUST 75 LBS.

Figure 5.

CALCULATED INTERFACE PROFILE FOR VARIOUS BOND NUMBERS. A REPRESENTS THE SUCCINONITRLE AND WATER INTERFACE; B REPRESENTS THE CYCLOHEXANE-METHANOL INTERFACE; C REPRESENTS THE INTERFACE BETWEEN DIETHYLENE GLYCOL AND ETHYL SALICYLATE; ALL AT ROOM TEMPERATURE. D IS FOR COMPARISON

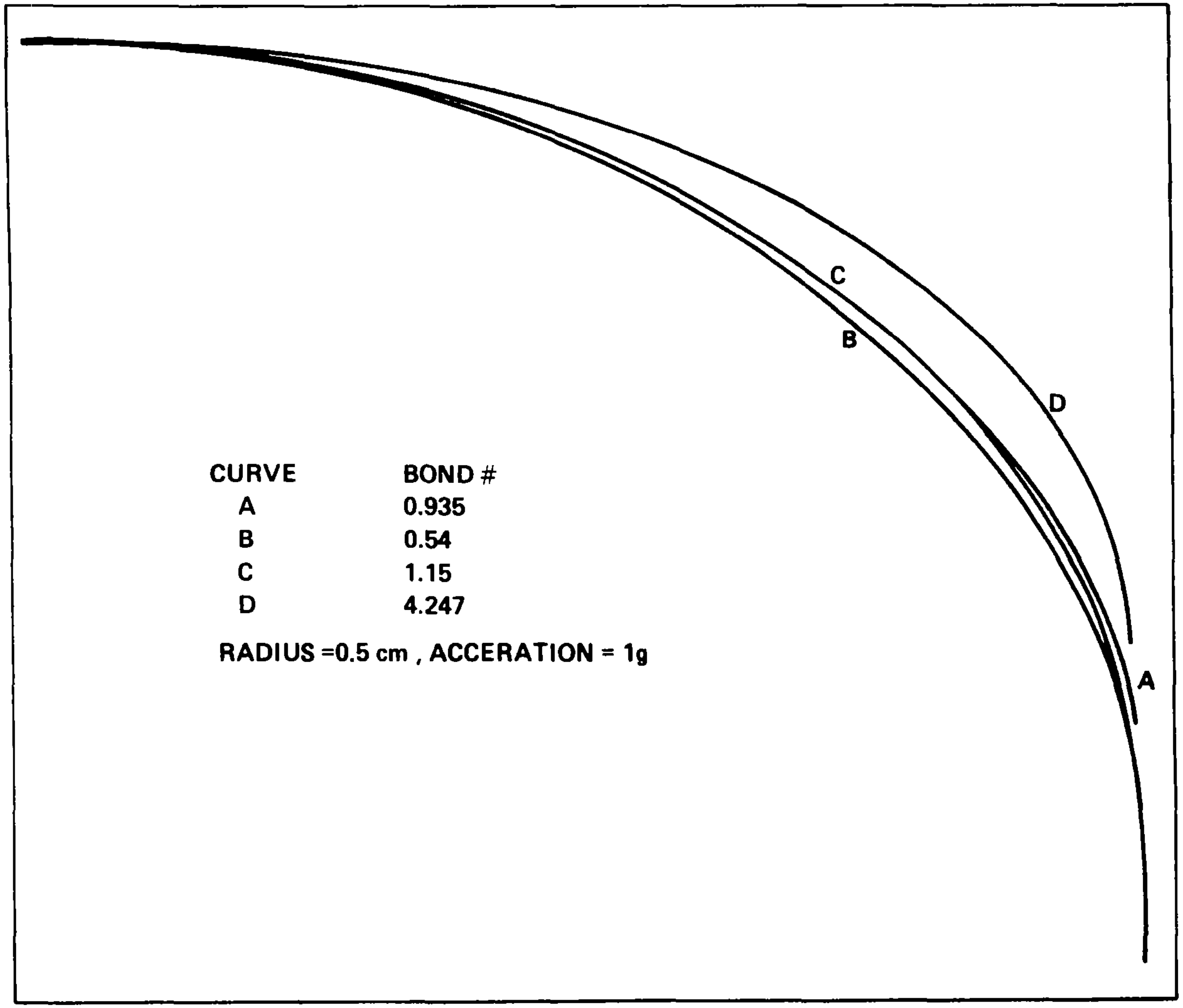
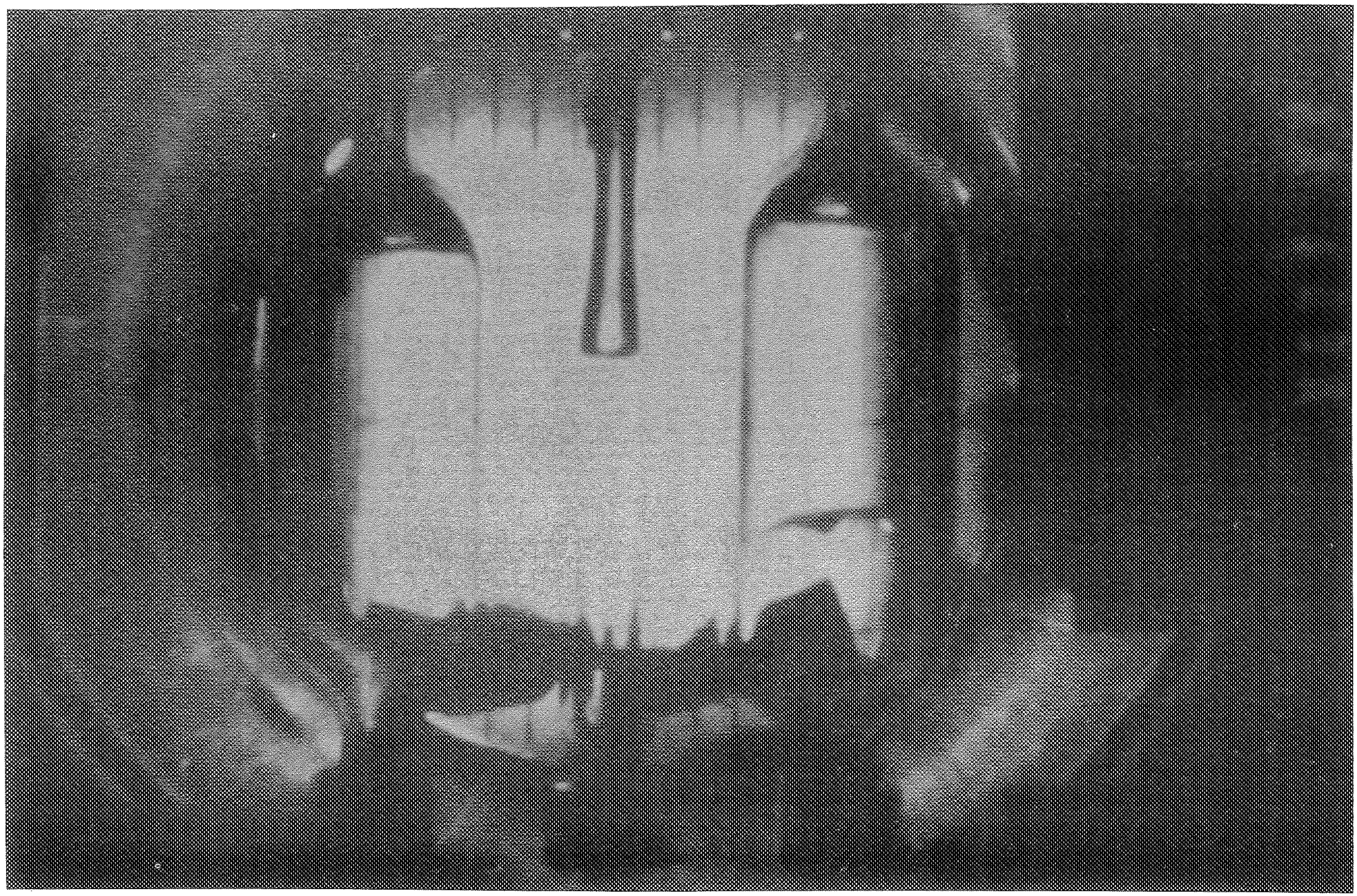


Figure 6.



ONE 'G'

Figure 7

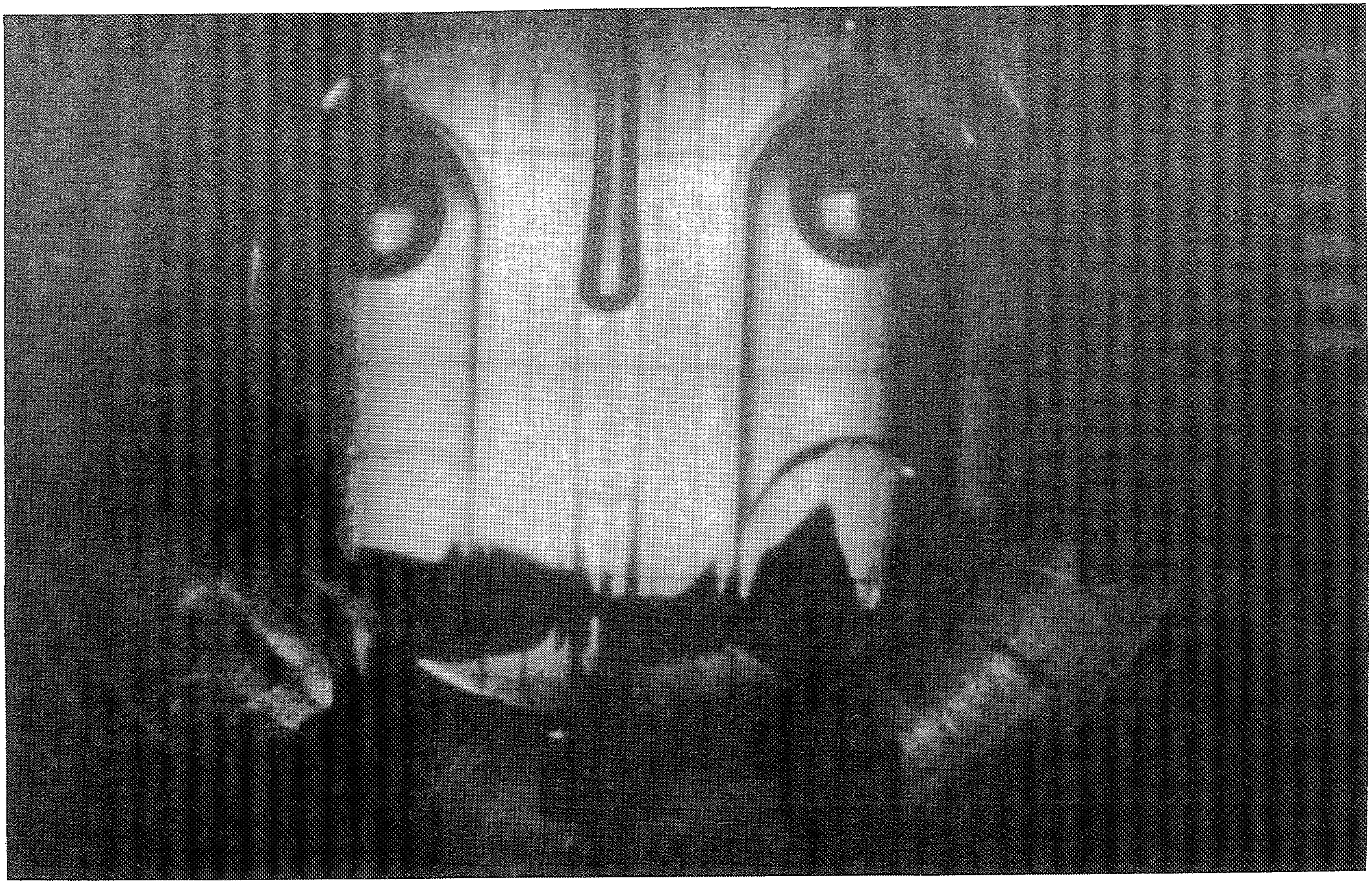
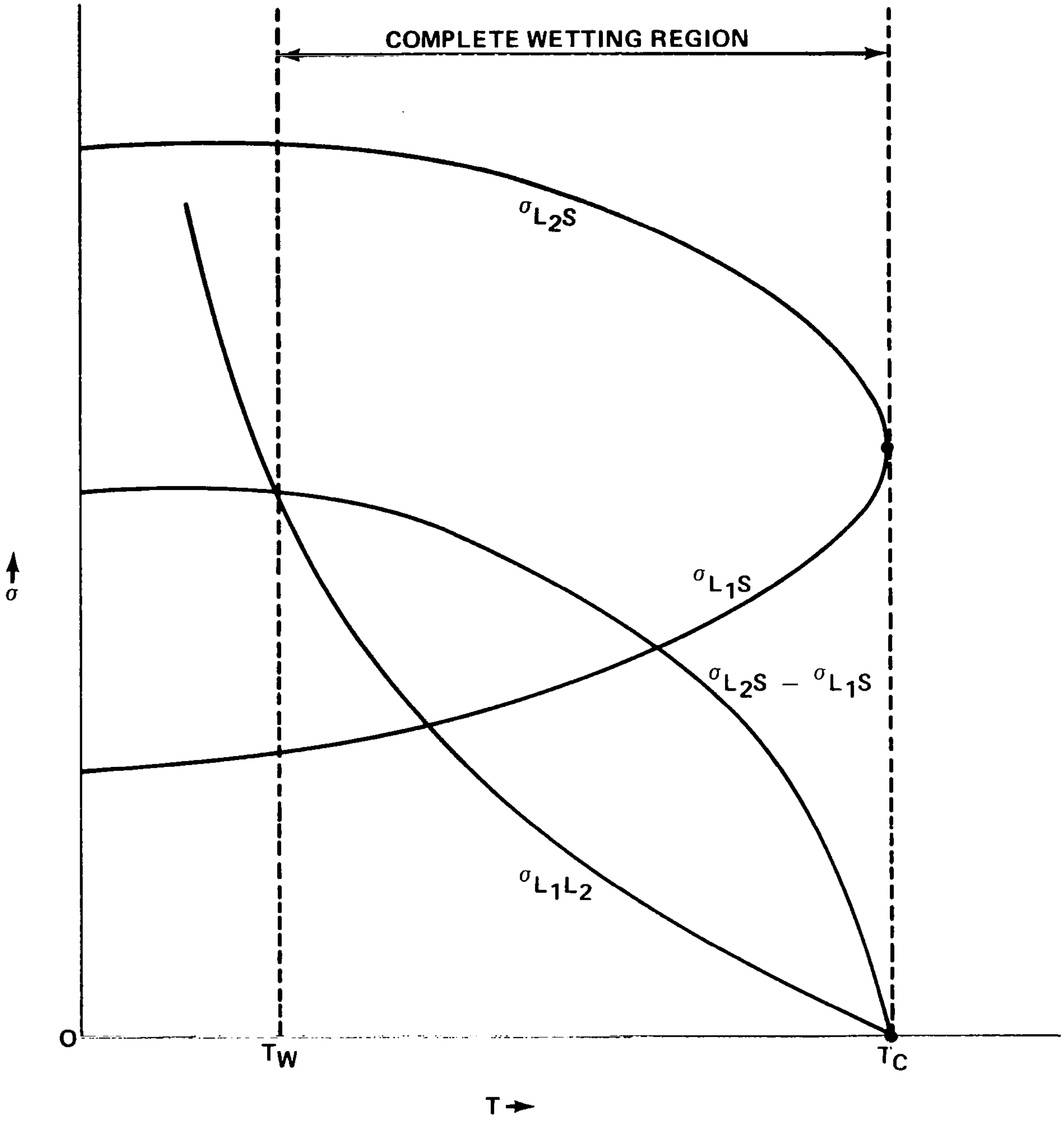


Figure 8



VARIATION OF INTERFACIAL ENERGIES WITH TEMPERATURE

Figure A.