cell at bath liquid level was calibrated and found to be 1.17 cc. In the later phases of the experimental work this volume was reduced to 0.55 cc.

The deadweight gage was calibrated by comparison of its reading, when subjected to the vapor pressure of carbon dioxide at the ice-point of water, with the value 505.56 $\pm$0.02 psia given for this point in the International Critical Tables. The relative masses of the weights used with this gage were determined by comparison with one of the weights used as a standard. It was found that the maximum deviation of any weight from the standard weight corresponded to a pressure of less than 0.05 psi. After all corrections, a reading of 505.6 psia was obtained with this gage, so it was considered quite reliable.

B. Experimental Procedures

1. Preparation of Mixtures. Two procedures for preparing mixtures were used. In Method No. 1, valves 2, 5, 7 and 8 (Fig. 7) were closed and all other valves opened. Then the spaces above the mercury level in Jerguson gage D_1, and in the manifold and equilibrium cell, were evacuated by means of a vacuum pump connected by heavy rubber tubing to valve 1. Nitrogen was introduced into Jerguson gage D_1 through valve 2 after valve 1 was closed. The level of mercury in the Jerguson gage, and the pressure and temperature, were recorded; the amount of nitrogen admitted was calculated with the aid of a compressibility factor chart prepared from the data of Bloomer and Rao.[7] Valves 2 and 4 were then closed, valve 1 opened, and the manifold and cell evacuated.

Ethane was then admitted into the manifold and cell through valve 2 after closing of valve 1. The amount of ethane required to give the desired composition was calculated, and approximately this amount was added through valve 4 into Jerguson gage D_1 by control of the pressure drop in the manifold and cell. The piston gage was used in all cases to measure the manifold pressure. The amount of ethane admitted was calculated with the aid of a compressibility factor chart, prepared from the data of Sage and Lacey,[21] from the known volume of the manifold, the pressures in the manifold system, and the temperature.

After evacuation of the manifold, cell and Jerguson gage D_2, valve 1 was closed and the contents of Jerguson gage D_1 were thoroughly mixed by repeated forcing of the gas back and forth between the two Jerguson gages and the equilibrium cell, by means of the mercury in reservoir C. The accuracy of this method was such that the quantity of ethane added to the nitrogen could be calculated to $\pm$0.2%.

In Method No. 2, nitrogen was introduced into Jerguson gage D_1 as described above. Ethane was then introduced into Jerguson gage D_2 in the same manner. The mercury level and pressure in D_2 were adjusted to give the desired amount of ethane. The manifold was then evacuated after closing of valve 5, and the contents were mixed as described above. The accuracy of this method is such that the quantity of each component measured in the Jerguson gages can be determined to an estimated accuracy of $\pm$0.2%. The accuracy with which a mixture can be prepared is dependent on its composition; for example, assuming a mixture containing 30% ethane is to be prepared, the calculation is:

$$\text{Percent ethane} = \frac{(0.3000 \pm 0.0006)\ 100}{(0.3000 \pm 0.0006) + (0.7000 \pm 0.0014)} = 30.00 \pm 0.08\%$$

In these calculations it is assumed that the ethane and nitrogen are pure, or that the impurities are known to be less than 0.01%. The maximum error would be $\pm$0.1%. Method No. 1 was used to prepare mixtures containing 10% or less of one of the components, because such small quantities of a component could not be measured accurately in the Jerguson gages.

These calculated compositions were checked by mass spectrometer analyses, but the calculated values were slightly more precise because the proximity of the ethane and nitrogen peaks on the mass spectrometer record causes interference, preventing high resolution of the components.

2. Operating Procedures. The complete P-T loop (dew and bubble point curve) for a given mixture was determined as follows: With the temperature of the cryostat held constant, gas was added slowly from Jerguson gage D_1 to the evacuated equilibrium cell until the pressure was about 10 psi below the expected dew point pressure. Time for attainment of equilibrium was allowed (five minutes was found to be ample). Addition of gas to the cell was then continued so that the rate of pressure rise in the equilibrium cell was about 1-2 psi per minute. In this stage of addition the gas was added from the manifold system only, with Jerguson gage valves 4 and 5 closed. The rate of addition could then be accurately judged by the

rate of pressure drop in the manifold system, as determined from the Bourdon gage A. This addition of gas was continued until the formation of minute drops of liquid could be detected on the cell wall. The cell was viewed by transmitted light, from a fluorescent tube, through 1-in.-wide windows in the Dewar vessel. Observation was facilitated by use of a 7-power magnifying glass. After liquid was first detected, a pressure increase of a few tenths of a pound resulted in the wall of the cell being covered by a film of liquid.

A deposit of iron oxide from the stirring ball on the inside of the cell wall aided the observation of the film. The minute particles impressed dimples into the film and caused refraction of the light, which made detection of the liquid film much easier. Condensation probably started on these minute particles, as the wall of the cell appeared to gradually fog up before the film formed. The dew point was taken as the pressure at which the minute drops were first detected, and could be duplicated to within at least 1 psi at lower pressures, and within 2 psi in the critical region.

After the first dew point was obtained, a series of dew points were determined at progressively higher temperatures up to the cricondentherm temperature. For temperatures above the cricondentherm, dew points were obtained by pressurizing the cell to a known pressure and then cooling the cell until liquid began to form. After liquid was detected, the cell was cooled or warmed slowly for determination of the exact dew point. For mixtures with large retrograde regions it was necessary to be certain that no liquid formed in the capillary. The foregoing procedure was followed up to the critical point.

When the mixture was cooled below the critical temperature, liquefaction occurred until only a small bubble of gas remained. The bubble point at each temperature was determined by adding gas to the cell until only a very small bubble of gas remained, and then agitating the contents until a constant pressure reading was attained. The bath was warmed until the gas bubble completely disappeared, and the bubble point taken as the pressure at which the gas bubble first appeared on cooling. Bubble points could be checked to within 1.0 psia or less. A series of bubble points were obtained at progressively lower temperatures.

Three-phase data points were obtained by use of two procedures. In the first, the liquid-liquid phase boundary pressure was obtained, by the standard bubble point method, for a given mixture as the point at which the homogeneous liquid separated into two phases. In the second procedure the bath was maintained at a constant temperature and a known amount of ethane condensed in the cell so that it was approximately one-third filled with liquid. Measured volumes of nitrogen were then added; after each addition the contents of the cell were stirred and the resulting equilibrium pressure was measured. Increments of nitrogen were added to the cell until both the low and high boundary pressures for the three-phase region for the particular bath temperature had been determined (Fig. 1). The data for the three-phase region obtained by the two procedures checked within one psi and 0.1°F.

The mass of gas in the equilibrium cell at the bubble point was determined by noting the initial and final mercury levels in the Jerguson gage, and the air bath temperature. Before making the final readings the mercury level was adjusted so the initial and final pressures in the Jerguson gage were the same. The moles of gas added to the cell were then calculated from these readings, with use of the compressibility factor data of Reamer *et al.*[18] for nitrogen-ethane mixtures. Correction was applied for the gas in the piping system connected to the cell, to obtain the moles of gas in the equilibrium cell at the bubble point. Density data for the saturated liquid phase obtained in this manner have an estimated accuracy of $\pm 1\%$ except in the critical region, where the error may be larger.

Due to the small difference between the mercury level initially in the Jerguson gage, and that at the dew point, the values of the saturated vapor densities calculated from the gage readings would contain a large degree of uncertainty. Therefore the saturated vapor densities were not obtained.

III. Gas Phase P-V-T Apparatus

A. Description of Apparatus

The pressure-volume-temperature apparatus, presented schematically in Fig. 11 and pictured in Fig. 12, is a constant volume apparatus consisting of high- and low-pressure systems. It is similar in design and operation to the Bean apparatus used extensively in the natural gas industry to measure "supercompressibility factors."[1]

The low-pressure system was used to determine the mass of gas charged to and expanded from the high-pressure system. It consisted of a water-jacketed glass buret A of accurately known volume, and a glass manifold connected to the manometer B and to the high-pressure system. Gases were charged to the high-pressure system by placing the