



Fig. L.—SATURATED VAPOR-LIQUID DENSITIES FOR ETHANE, NITROGEN, AND SOME OF THEIR MIXTURES

## VI. Saturated Liquid and Vapor Density Data

Saturated liquid and vapor densities of some of the mixtures investigated are presented in Table F and plotted versus temperature in Fig. L. The liquid density values were obtained in the dew and bubble point apparatus as described in **Experimental Procedures**. The saturated vapor density values for three mixtures were obtained by extrapolation of gas phase P-V-T data along the isometric until the dew point curve was intersected. This procedure gave the dew point temperature and pressure corresponding to a known density.

The required extrapolation was very slight in all cases, since isometric data were obtained at temperatures almost down to the dew point curve. Errors in interpolating data obtained with the dew point apparatus to the compositions of the mixtures investigated in the P-V-T apparatus were minimized, since the compositions of those mixtures investigated in each apparatus were almost identical. The saturated vapor density values for two other mixtures were obtained by interpolation, from the intersections of the two-phase and single-phase region isometrics. Saturated vapor densities at low pressures were also calculated by use of the equation of state.

## DISCUSSION

### I. Estimated Accuracy of the Data

#### A. Dew and Bubble Point Data

The principal sources of error in the dew and bubble point method can be attributed to:

- 1) Inaccuracies in the pressure and temperature measurements;
- 2) Fractionation and diffusion phenomena between the liquid in the cell and the warmer gas in the piping system;
- 3) Errors in measuring the dew point due to non-equilibrium conditions and overshooting the dew point; and
- 4) Errors in the composition of the gas mixture as prepared.

Temperature fluctuations of the cryostat were controlled to  $\pm 0.01^\circ\text{F}$  when readings were taken, and the pressure was measured to  $\pm 0.1$  psi. The thermocouple used to measure temperature was estimated to be accurate to  $\pm 0.2^\circ\text{F}$ .

Diffusion between the condensed liquid in the cell and vapor in the inlet tubing system could cause an error in the bubble point by changing the composition of the liquid in the cell from the bulk composition of the gas mixture as originally prepared. The concentration of ethane in the condensed liquid in the cell would tend to increase, which would lower the bubble point pressure. When the volume of the piping system and cross-sectional area of the connecting tube were reduced, this source of error was minimized. For the equipment used in this work it was found that after a continuous 8 hour run, the maximum change in composition due to fractionation was 0.3 mole percent. The maximum fractionation occurred for mixtures containing 25 and 31.7 mole percent nitrogen between the temperatures of  $-80$  and  $-150^\circ\text{F}$ . In all other mixtures, composition change due to fractionation was very small, and error in bubble point pressure due to this change did not exceed 2 psi.

Errors in dew point pressure measurement, due to the nonequilibrium condition existing when liquid first formed on the cell wall, were minimized by the following procedure. The pressure in the cell was very gradually increased by addition of a small quantity of gas, until liquid droplets were detected on the walls of the cell. The valve to the cell was then closed, and the bath warmed, about  $0.1^\circ\text{F}$ , until all liquid disappeared. The bath was

again cooled to the reappearance of liquid. This was taken as the dew point. Duplicate readings on the same mixtures and in some cases on duplicate mixtures were obtained and agreed within less than  $\pm 1$  psi or  $\pm 0.1^\circ\text{F}$ .

The error in the calculated composition of the gas mixture was estimated to be  $\pm 0.1\%$ .

All sources of error considered, the dew and bubble points for each mixture investigated, assuming that composition of the mixtures as calculated was correct, should be accurate to  $\pm 2$  psi or  $\pm 0.3^\circ\text{F}$ , whichever is larger.

#### B. P-V-T Data

The important sources of error are the calibration of the volume of the high-pressure bomb ( $\pm 0.02\%$ ), the calibration of the piston gage used to measure the pressure in the high-pressure bomb ( $\pm 0.05\%$ ), and the measurement of mass in the high-pressure bomb. The measurement of mass is subject to these sources of error: volumetric calibration of buret ( $\pm 0.01\%$ ), measurement of pressure in buret ( $\pm 0.03\%$ ), measurement of temperature in buret ( $\pm 0.01\%$ ), and the compressibility factor of gas in buret ( $\pm 0.05$ ).

Estimation of the maximum probable error in the data is difficult, since most of the errors are calibration errors rather than random experimental errors. The composition of the mixtures is probably accurate to  $\pm 0.03$  mole percent. The error in the reported values of the compressibility factors is probably within the range of 0.2 to 0.3%.

#### C. Internal Consistency of the Data

A quadruple-junction and two sets of triple-junction thermocouples were calibrated with a standard platinum resistance thermometer and were used to measure and check the temperature. The thermocouples were calibrated at the temperatures of liquid nitrogen, subliming  $\text{CO}_2$ , an ice-water mixture, and at intermediate temperatures by maintenance of a constant temperature with the low-temperature bath. All the calibrations were made against a standard platinum resistance thermometer that had been calibrated by the U. S. Bureau of Standards. Two deadweight gages were used to measure pressures. Volume calibration of the system was made from time to time and found to be constant.