PHYSICAL-CHEMICAL PROPERTIES OF ETHANE-NITROGEN MIXTURES



high-pressure bomb in liquid nitrogen and then displacing measured increments of the gases, with mercury, from the buret into the bomb at a pressure near atmospheric. When ethane-nitrogen mixtures were prepared, ethane was condensed in the bomb first and the nitrogen added subsequently. The vapor pressures of the mixtures were sufficiently low that they were completely condensed in the bomb at atmospheric pressure and liquid nitrogen temperature.

With this procedure, mixtures of any desired composition could be charged and liquefied in the high-pressure bomb. Sufficient quantities of the mixtures were liquefied in the bomb so any desired pressure up to 4000 psia could be obtained on warming the bomb and its contents to the desired minimum operating temperature. This system of charging permitted precise measurement of the volume and composition of the gases charged to any desired density.

The high-pressure system consisted of a bomb C of accurately known volume immersed in a constant-temperature bath, a combined value and tee



Fig. 12.—IGT Pressure-Volume-Temperature Apparatus

D of the "Aminco" high-pressure type, and a system for measuring the bomb pressure. The latter consisted of manifolded piston gages, E having a maximum range of 4000 psi, and F a maximum of 1000 psi. A mercury filled sight-tube, G, was used for detecting balance between the weights on the piston and the pressure in the cell.

The apparatus was operated so that isometric data were obtained. In this method the mass of gas in the bomb is held constant and the temperature is varied. At each of several temperatures the resulting pressure is measured. After securing data along one isometric, part of the gas is expanded back into the glass buret, where the mass expanded can be accurately measured. Pressure-temperature data are then taken along the second isometric. This procedure is continued, with data taken along several more isometrics, until the gas in the highpressure bomb has been expanded to atmospheric pressure. The total mass expanded from the bomb, and remaining in the bomb at atmospheric pressure, are then summed to verify the total mass initially charged to the system.

The taking of isometric rather than isothermal data offers the following advantages:

- 1) A comparable range of conditions can be covered by the isometric method with fewer gas expansions required than for isotherms, giving less opportunity for volume measurement error.
- 2) The complete range of data desired can be obtained with one sample of gas and one charging of the high-pressure bomb, whereas the isothermal method requires a recharging of the bomb for each isotherm.
- 3) The form of the data is more convenient for testing and adjusting the constants of an equation of state.

B. Experimental Procedures

1. Preparation of Mixtures. The entire PVT system was first evacuated with the high-vacuum pump. After the system was checked for leaks, the high-pressure valve was closed and the bomb placed in a small Dewar vessel containing liquid nitrogen. The needle valve on the high-pressure sample cylinder was then slowly opened, and gas added to the buret at about atmospheric pressure, gradually displacing mercury from the buret to the leveling bulb. When the mercury in the buret reached the lower etch mark and a pressure slightly above atmospheric, the valve to the sample cylinder, and the stopcock connecting the buret to the leveling bulb, were closed. About 5 minutes was allowed for the gas in the buret to come to equilibrium; meanwhile the temperature of the circulating water in the buret was determined and the barometric pressure read. The vacuum pump was disconnected from the three-way valve, and the excess pressure in the buret was relieved by very slow opening of the three-way stopcock to bleed excess gas to the atmosphere. A long piece of rubber tubing was connected to the bleed stopcock outlet to prevent any air diffusing back into the buret. After one minute the three-way stopcock was closed.

Next, the high-pressure valve to the bomb was cracked, and the gas slowly charged into the bomb. During the charging the pressure in the buret was kept at approximately atmospheric by raising the leveling bulb. Near the end of the operation the rate of charging was slowed considerably, and the gas in the buret was kept under a pressure slightly above atmospheric. When the mercury level reached the top etch mark of the buret, the stopcock at the top of the buret was closed. The highpressure valve was closed at the moment the manifold pressure became equal to atmospheric pressure as observed on the manometer. This procedure was followed so the volume of gas in the manifold and manometer would not enter into the charging calculations, since it would be under atmospheric pressure before and after the charging of the gas to the high-pressure bomb. In the event there was a small residual plus or minus pressure in the manifold from one charging cycle, an attempt was made to cancel it out in the following cycle. The above procedure constituted one charging cycle, which was repeated until the desired amount of each component gas had been charged.

2. Determination of Pressure-Volume-Temperature Relationships. This involved only the determination of the pressure at a fixed temperature, since the volume of the bomb was known and the number of moles in the bomb was calculated from the volumetric measurements made in the buret.

A series of temperatures and the corresponding gas pressures were determined for each density of gas. The density of gas was then changed by expanding part of the gas back into the low-pressure system, as discussed in Section 3 below.

To determine the pressure in the bomb, the valve connecting the mercury sight glass and the deadweight gages was carefully opened, and weight added to or removed from the gage until the mer-