

cury column in the sight glass was balanced at a fixed reference mark. The gas in the bomb was assumed to have reached the bath temperature when a constant pressure reading was obtained at a constant bath temperature.

3. Expansion of Gas to the Low-Pressure System. The expansion of gas from the high-pressure bomb to the low-pressure buret was performed in essentially the reverse of the charging operation. The mercury level was brought to the top etch mark of the buret and the manifold brought to atmospheric pressure by opening of the three-way stopcock to the atmosphere. The stopcock was then closed, and the needle valve connecting the high- and low-pressure systems was opened carefully to throttle gas into the buret. The buret leveling bulb was lowered at a rate sufficient to maintain atmospheric pressure in the low-pressure system. The needle valve was closed when the mercury level in the measuring buret reached the bottom etch mark. The system was then allowed to come to equilibrium and the barometric pressure, the temperature of the buret, and the pressure in the buret above or below atmospheric as read on the manometer, were noted.

C. Calculation of Results

Since the pressure and temperature of the high-pressure system were measured directly, the only calculation required was the determination of the moles of gas in the high-pressure bomb. This was done by a straightforward application of the ideal gas law to the measurements obtained on the low-pressure buret, using a correction for the deviation of the gas from the ideal gas law as noted before. It was also necessary to apply a small correction for that part of the high-pressure system which was not at the temperature of the low-temperature bath. This was accomplished by calculating the moles of gas, n , in this part of the system, with the equation:

$$n = Pv/zRT$$

P = absolute pressure of the bomb
 v = volume of the high-pressure system not in the low-temperature bath = 0.26 cc
 R = universal gas law constant
 T = absolute temperature
 z = compressibility factor

Since this system was at room temperature, values of z for the various mixtures could be interpolated from the data of Reamer *et al.*¹⁸

The number of moles in this part of the system was then subtracted from the total moles, to obtain the moles of gas in the high-pressure system at the temperature of the low-temperature bath.

Since the volume of the high-pressure bomb was not constant, but varied with temperature, the pressure-temperature data obtained for a given number of moles in the high-pressure system were not true isometric data. True isometric data were calculated from the experimental data by plotting the experimental pressures against the corresponding density along a constant temperature line for each temperature investigated. By graphically determining the slope of this line, the rate of change of the pressure with density at constant temperature was determined for each experimental point. Then the pressures that would have existed along a true isometric were calculated:

$$P = P_E + (\delta P/\delta d)_T (d_T - d_E)$$

P = pressure that would have been obtained at the true isometric density
 P_E = experimental pressure at actual density in bomb
 $(\delta P/\delta d)_T$ = slope of the pressure versus density curve at constant temperature
 d_T = density of desired true isometric
 d_E = actual density in bomb

The density of the desired true isometric was always taken as the density at an intermediate value of the series of temperature points. The pressure correction was always less than 0.5% of the observed pressure, and it is believed that no significant error was added, by this procedure, to the pressure values reported for the true isometrics.

