Table I. Experimental Data for Naphthalene Vapor Pressure

Liquid		Solid	
t, °C.	P, torr	t, °C.	P, torr
80.33_4	7.51_9	40.33_7	0.35_4
82.88_8	8.55_7	49.45_1	0.74_1
83.35_6	8.80_0	54.17_0	1.11_4
85.69_7	9.71_8	60.22_7	1.83_6
88.85_2	11.30_2	61.20_0	1.90_8
92.74_6	13.58_1	65.05_8	2.54_1
93.28_2	13.85_8	66.35_8	2.88_6
94.31_9	14.64_7	70.18_7	3.75_9
98.66_5	17.67_5	70.98_1	3.91_4
102.93_7	21.25_7	75.61_4	5.44_8
106.19_6	24.33_5	76.70_6	5.92_0
109.23_0	27.73_1	79.34_4	6.99_5
109.49_4	27.88_0		
109.80_9	28.28_6		
115.55_9	35.63_9		
115.57_1	35.67_3		
119.22_2	41.03_1		
124.44_9	50.05_6		
124.91_8	50.98_7		
125.91_2	52.95_2		
133.28_1	69.06_8		
133.69_4	69.97_0		
138.48_3	82.63_4		
139.61_0	86.08_3		
140.83_8	89.64_3		
149.64_8	120.0_1		
150.38_0	122.8_6		
158.01_2	155.7_0		
159.08_8	161.3_1		
159.54_0	163.6_2		
168.70_4	214.8_0		
179.51_5	290.9_5		

At the triple point, 80.27° C. (*4*), Equations 1 and 4 give values of 7.47_7 and 7.49_4 torr, respectively. These values agree within the calculated precision. The use of a nonlinear regression and minimization of the deviation of P rather than of log P is feasible only with the aid of the computer. This method was chosen because it fits the experimental condition of a relatively constant error in the measurement of P, rather than the constant percentage error in P implied in the minimization of the deviation of log P. Trial calculations showed that the two methods do not lead to large differences in calculated values of the constants or of P. However, the authors believe there is a real gain in obtaining the value of the deviation in P directly from the calculation of the interpolating equation.

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Liquid Phase Density in the System Helium-Nitrogen

W. B. STREETT[1]
Inorganic Chemistry Laboratory, University of Oxford, Oxford, England

Densities have been measured at 25 points in the compressed liquid region of the helium-nitrogen system at 77.38°, 100.61°, and 117.30° K. at pressures up to 544 atm. Density *vs.* pressure curves have been extrapolated to the saturation curves to obtain densities for the saturated liquid.

EXPERIMENTAL studies of liquid-vapor phase equilibria have been published for many low temperature binary systems; however, few of these include data on the densities of the coexisting phases. Such data are required for performing meaningful thermodynamic analyses and correlations of the phase data, but they are difficult to obtain because of the low temperature and sometimes high pressure at which these systems exist. Often the vapor phase density can be estimated from an equation of state, but estimates of the liquid density are far less reliable, especially when one of the pure components is a supercritical gas. In this paper, experimental measurements of densities in the compressed liquid region of the helium-nitrogen system are presented at temperatures of 77.38°, 100.61°, and 117.30° K. and at pressures from just above saturation to 544 atm. Density *vs.* pressure curves have been extrapolated to the saturation line to obtain saturated liquid densities.

EXPERIMENTAL

Liquid densities reported here have been measured by the method of gas expansion. In this method a small quantity of the fluid under study is confined in a cell of known volume at fixed pressure and temperature, and expanded into a large volume, thermostatically controlled at room temperature. The mass of gas is determined from known low pressure PVT relations in the large volume, and used to calculate the density under conditions in the cell. A detailed description of the experimental equipment and its

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[1] Present address: Department of Chemistry, U. S. Military Academy, West Point, N. Y. 10996

use in measuring densities of pure liquids has been given (2). A brief discussion of the procedure used in measuring mixture densities is reported here.

The experimental method is explained by Figure 1. Curve *a-b* is the saturated liquid line for the helium-nitrogen system at temperature T_1. [The saturated liquid lines for the three temperatures of interest were determined earlier, and have been reported (*1*).] After this phase boundary curve has been determined, a series of gas mixtures of known compositions ($X_1 - X_3$) are prepared. A mixture such as X_1 is then pumped into the high pressure cell of known volume, at temperature T_1, to a pressure well above the saturation pressure, such as point *c*. The high pressure cell is fitted with a soft iron stirring bar, actuated by an electromagnet wound on the outside of the cell, which is used to stir the mixture and ensure complete mixing. After the cell and its contents reach pressure and temperature equilibrium, the pressure is lowered, in steps of 50 to 100 atm., by expanding the contents into the low pressure expansion volume, thermostatically controlled

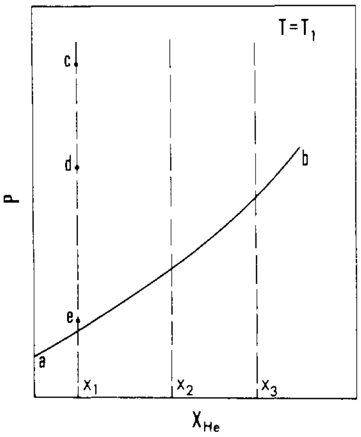

Figure 1. Method of density determination for mixtures

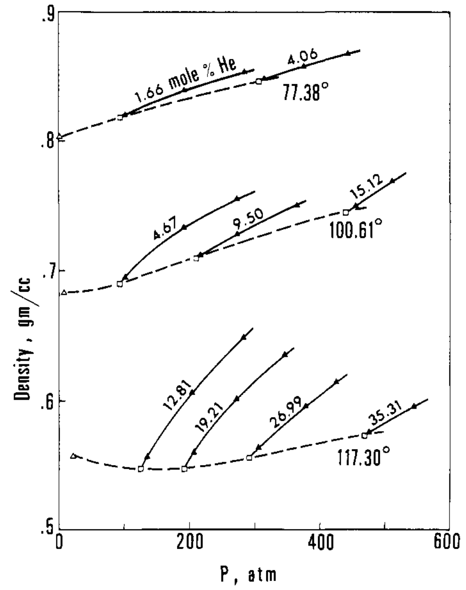

Figure 2. Density-pressure diagram

▲, experimental curves
☐, saturated liquid
△, pure nitrogen density

Table I. Density and Molar Volume of Helium-Nitrogen Liquid Mixtures

$T = 77.38°$ K.

1.66 Mole % He

P, atm.	ρ, g./cc.	V, cc./mole
282.3	0.853	32.38
190.5	0.839	32.94
102.0	0.821	33.66
95.2[a]	0.819	33.72

4.06 Mole % He

P, atm.	ρ, g./cc.	V, cc./mole
442.2	0.868	31.18
374.1	0.858	31.52
312.9	0.848	31.89
306.1[a]	0.847	31.94

$T = 100.61°$ K.

4.67 Mole % He

P, atm.	ρ, g./cc.	V, cc./mole
272.2	0.756	35.58
190.5	0.733	36.70
102.0	0.696	38.67
91.8[a]	0.689	39.03

9.50 Mole % He

P, atm.	ρ, g./cc.	V, cc./mole
363.9	0.751	34.26
272.2	0.728	35.33
217.7	0.712	36.15
210.9[a]	0.710	36.25

15.12 Mole % He

P, atm.	ρ, g./cc.	V, cc./mole
510.2	0.768	31.74
455.8	0.751	32.46
438.8[a]	0.745	32.73

$T = 117.30°$ K.

12.81 Mole % He

P, atm.	ρ, g./cc.	V, cc./mole
282.3	0.649	38.45
204.1	0.607	41.11
136.1	0.556	44.83
125.9[a]	0.548	45.51

19.21 Mole % He

P, atm.	ρ, g./cc.	V, cc./mole
346.9	0.636	36.81
272.2	0.602	38.86
204.1	0.560	41.81
190.5[a]	0.547	42.78

26.99 Mole % He

P, atm.	ρ, g./cc.	V, cc./mole
425.2	0.614	35.06
373.5	0.595	36.19
306.1	0.564	38.19
292.5[a]	0.557	38.66

35.31 Mole % He

P, atm.	ρ, g./cc.	V, cc./mole
544.2	0.596	32.81
476.2	0.575	33.96
469.4[a]	0.574	34.03

[a] Saturation pressure.

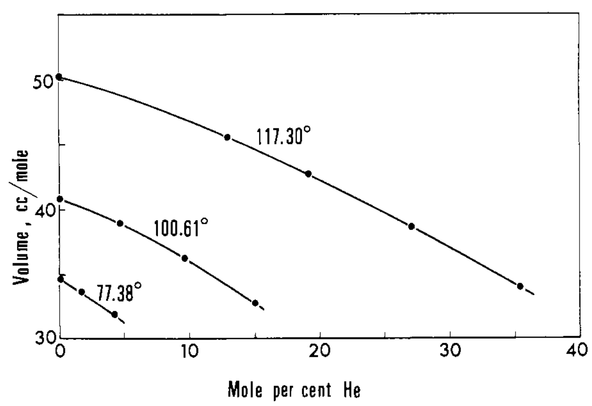

Figure 3. Saturated liquid lines plotted as molar volume vs. composition

at room temperature, from which the quantity of gas removed in each pressure step is determined. When a pressure just above saturation is reached (point *e*), the entire cell contents are expanded, to give the density at that pressure. The densities at higher pressures (points *c*,*d*) are then obtained by adding the increments for each pressure step. This procedure is repeated for other mixtures (X_2, X_3), resulting in a network of P-ρ-X points in the compressed liquid region at temperature T_1. Temperatures have been measured by a platinum resistance thermometer calibrated by the National Bureau of Standards, and are accurate to within ±0.02° K. Pressures have been measured by a calibrated Heise bourdon gage, with an accuracy of ±0.5 atm. The unit of pressure is the international atmosphere.

RESULTS AND DISCUSSION

The experimental density measurements are shown in Table I with the equivalent molar volumes. Experimental density *vs.* pressure curves have been plotted in Figure 2 and extrapolated to the saturation pressure to give the saturation density for each mixture composition. Pure nitrogen density points in Figure 2 have been taken from reported data (*2*) and are estimated to be accurate to within ±0.1%. The expansion of each mixture in steps, as outlined above, reduces the accuracy of the mixture densities, as compared with those for pure liquid nitrogen, for which the entire cell contents were expanded from each P-T point. The mixture densities are estimated to be accurate to within ±1.0%.

A smooth curve has been drawn through the saturated liquid density points at each temperature. These curves for the 100.61° and 117.30° K. isotherms have an inflection point at pressures around 300 to 400 atm., but it is not clear whether this is a feature of the system or whether it is a result of scatter in the data. These curves might reasonably be expected to be complicated, since increasing pressure is accompanied by increasing helium content, and these two factors produce opposite effects on the density of the mixture. A plot of molar volume *vs.* composition for the saturated liquid is better behaved (Figure 3).

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Heat of Formation of Hydroxylammonium Perchlorate by Combustion Calorimetry

M. F. ZIMMER, E. E. BAROODY, G. A. CARPENTER, and R. A. ROBB
Research and Development Department, Naval Ordnance Station, Indian Head, Md. 20604

The energy of combustion of solid hydroxylammonium perchlorate with diethyl oxalate as fuel was determined in a rotating bomb calorimeter. The standard heat of formation of hydroxylammonium perchlorate at 25° C. and 1 atm. is −66.16 ± 0.65 kcal. per mole (±0.65 is estimated standard deviation of the mean) and was calculated using a computer program which was developed for compounds containing carbon, hydrogen, nitrogen, oxygen, and chlorine.

COMBUSTION REACTION of hydroxylammonium perchlorate was carried out in an oxygen atmosphere using diethyl oxalate as the fuel. The idealized reaction equation from which the heat of formation is determined is:

$$H_4O_5N_1Cl_1(c) + C_6H_{10}O_4(l) + 4.75\ O_2(g) + 143.5\ H_2O(l) \rightarrow$$

$$6\ CO_2(g) + HCl \cdot 150\ H_2O(l) + 0.5\ N_2(g) \qquad (1)$$

The chlorine gas liberated in the reaction was converted to the chloride ion by adding arsenious acid solution to the bomb (*5*). The heats of formation of perchlorates or other highly oxygenated compounds are usually obtained from heat of solution experiments. For such reactions, however, the heats of formation of the other reactants and reaction products must be known. The reactants and products will vary for each different compound of the general formula $C_aH_bO_cN_dCl_e$ and so will their thermal data that must be obtained either from literature or experiments that subjects the final results to other possible sources of errors. The combustion of hydroxylammonium perchlorate with diethyl oxalate according to Equation 1 is equivalent to burning a compound of the general formula $C_aH_bO_cN_dCl_e$ in the presence of oxygen and water. The reaction products, CO_2, H_2O, HCl, and N_2 are always the same and no auxiliary data besides the heat of formation for diethyloxalate are necessary. Thus with a slight modification for chlorine compounds, the "Washburn corrections" used for $C_aH_bO_cN_d$ compounds can be applied. Since the final combustion products for all compounds are the same, a computer program has been set up for data reduction (*5*).

EXPERIMENTAL

Material. Hydroxylammonium perchlorate was synthesized at this laboratory. After synthesis, the material was dissolved in ethyl ether, filtered, and precipitated by the rapid addition of benzene, yielding fine needles. The very fine needles were desirable to provide the most intimate contact between the oxidizer and fuel to obtain good combustion. The precipitate was filtered and dried at 50° C.