Densities of the Hydrazine-Methylhydrazine System

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Density data for methylhydrazine and binary solutions of hydrazine and methylhydrazine are reported. Temperatures from 30° to 90° C. are the range of interest. Densities of binary solutions can be predicted by mass average of pure component data, with error of less than 0.25%.

HYDRAZINE and its alkyl homologs have considerable importance as propellants and commercial reducing agents. The density of hydrazine has been determined over a wide temperature range (*1*). Some density data for the homologs and for various binary systems are reported, but original sources are very limited (*2, 3*). New density data for high purity methylhydrazine, from 30° to 70° C., and for hydrazine-methylhydrazine solutions, from 30° to 90° C., have been determined experimentally and are summarized below.

EXPERIMENTAL

Hydrazine and methylhydrazine were obtained as research samples from a commercial laboratory; initial purity was guaranteed better than 99.5 wt. %. A later check by gas chromatographic analysis verified this value as a realistic minimum. Samples were degassed by vacuum reflux and were stored in contact with their vapor in stoppered flasks. Pycnometers were provided with stopcocks to permit experimental observations under saturation conditions, without weight loss, also.

Samples were transferred by borosilicate glass syringes equipped with 20-gage, stainless steel needles on metal-to-glass seals. For measurements on pure methylhydrazine, samples were placed directly into 5-ml. pycnometers, degassed, and sealed. Solutions were prepared in a 6-ml. mixing pycnometer. Degassing of solutions was required primarily to remove ullage air; therefore, samples were chilled prior to degassing to reduce vapor pressure, composition changes, and weight corrections. Checks were run to detect weight loss during degassing of solutions, but no weight loss was observed. Solution compositions were evaluated on the basis of weight increments for the mixing pycnometer. Buoyancy corrections were applied in all weight determinations.

Pycnometers were calibrated with degassed, deionized, double distilled water at temperatures over the range of study. Several initial filling levels were employed to provide corrections for differential expansion of the glass container. The uniformity of pycnometer capillaries was checked, also, to ensure validity of interpolation between observations. Bath temperature was maintained constant within 0.02° C.; measurements were made with A.S.T.M. calibrated thermometers certified to ±0.01° C. Liquid levels were read with a universal cathetometer to an accuracy of ±0.01 mm. Detailed analysis of all errors in observations, techniques, and reference data led to a predicted total error in measured density of one part in ten thousand. This value refers to experimental manipulation only and relates to the accuracy of densities determined for whatever fluid is contained within the pycnometer. It includes weighing uncertainties in the preparation of solutions of two fluids but does not include any contribution owing to the finite impurity levels of the ingredients.

RESULTS AND DISCUSSION

Table I presents the density data of this study for methylhydrazine. By least-squares method, data were fitted to the following linear equation:

$$\rho = 0.89226 - 9.6782 \times 10^{-4}T \qquad (1)$$

where ρ is density in grams per milliliter and T is temperature in ° C.

The standard deviation of this linear equation was calculated to be 8.1×10^{-5} gram per ml. The standard deviation of a quadratic form was 7.8×10^{-5} gram per ml. Thus, over the temperature range, the linear relation is as good a predictor as a quadratic. In addition, this value for the standard deviation was in excellent agreement with the probable total error noted above.

Other density determinations for methylhydrazine have been performed. Ohm (*3*) reported a value of 0.8743 at 25° C. The experimental accuracy of this value was not cited, therefore, accuracy was assumed to be consistent with the significant figures reported—i.e., one to five parts in ten thousand. Barger (*2*) presented a linear variation of density with temperature, over a range of −50° to 85° C. In this case, also, there was no direct evidence from which to assess the probable error. Equation 1 yields densities that are 0.5 to 0.7% less than the equivalent data (*2*).

Propellant grade methylhydrazine was employed in these earlier measurements. This material was described as 99% methylhydrazine minimum. The remainder was largely water. Quantitative differences in composition were considered a probable source of differences in measured densities. Reduced water concentration in the present material could have produced the relatively uniform reduction in observed density.

Table II presents density data for three binary solutions of methylhydrazine and hydrazine. Temperatures of 30° to 90° C. were included. The table summarizes data for hydrazine mass fractions of 0.3024, 0.5615, and 0.7804.

Experimental determinations on the three binary systems were compared with densities predicted by a combination of Equation 1 and the quadratic expression for hydrazine reported by Ahlert, Bauerle, and Lecce (*1*). A check of

Table I. Density of Methylhydrazine

Temperature, ° C.	Density, G./Ml.
30.00	0.8632
35.00	0.8584
40.00	0.8535
45.00	0.8487
55.00	0.8391
60.00	0.8343
70.00	0.8245

Table II. Density Data for Three Binary Solutions

Temperature, °C.	Density, G./Ml., for Hydrazine, Mass Fraction 0.3024	0.5615	0.7804
30.00	0.9064	0.9419	0.9679
35.00	0.9016	0.9371	0.9634
40.00	0.8969	0.9322	0.9589
45.00	0.8921	0.9274	0.9544
55.00	0.8827	0.9179	0.9455
60.00	0.8779	0.9131	0.9411
70.00	0.8682	0.9036	0.9322
80.00	0.8584	0.8936	0.9231
90.00	0.8480	0.8838	0.9135

the validity of this expression for the hydrazine used in these measurements exhibited agreement within the reported experimental error. Calculated values were based on the mass fraction of pure components. The average absolute deviation between observed and predicted values was 0.18% of the observed density. The largest deviation, among 27 experimental points, was −0.25%. The authors concluded that calculated, mass average densities are acceptable predictors exhibiting a uniform low deviation from measured data over the entire composition range and a range of temperatures from 30° to 90° C.

SAFETY

Hydrazine and methylhydrazine are highly toxic materials. They can be absorbed through the skin and can cause blindness on very short contact with the eye. Every effort should be made to avoid oral ingestion, breathing, or skin contact. In this work, good ventilation, safety glasses, and rubber gloves were mandatory.

Compounds of the hydrazine family undergo violent autodecomposition at high temperatures. They also decompose readily in the presence of inorganic catalysts and common laboratory residues. Clean glassware and stainless steel equipment are necessary safety precautions. Excessive heating—i.e., above 200° C.—is to be avoided. Unnecessary confinement under pressure and/or in metal containers is hazardous.

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Mass Spectral Data of Substituted Acetylenes

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The Time-of-Flight mass spectra of 12 alkynes were obtained at a bombardment energy of 30 electron volts. All of the alkynes studies were unbranched disubstituted acetylenes ranging in length from four to 10 carbon atoms. The fragmentation patterns were normalized to a total ionization of 100 units and analyzed in terms of the relative occurrence of α, β, and γ carbon-carbon scissions. In the 2-alkyne series, β scission predominated in the C_4 to C_8 compounds. As the chain length increases, the γ scission products increase until they eventually predominate at C_9 and C_{10}. β Scission products were the most abundant in all of the 3-alkynes studied. In the 4-alkynes, α bond rupture prevailed with only a slight tendency toward α bond scission.

ALTHOUGH several acetylenic compounds have been studied through electron impact phenomena (*2*), no systematic study has every been done on the fragmentation patterns of disubstituted acetylenes. Because of a separate study (*5*) on the radiation chemistry of acetylenic compounds, the authors have undertaken this mass spectrometric study of alkynes to aid in the interpretation of the degradation of these compounds. This approach is based on the assumption that the mass spectrum of a particular compound gives a distribution of ionic species which reasonably resembles that created when the compound is exposed to a highly energetic radiation field (*3*).

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