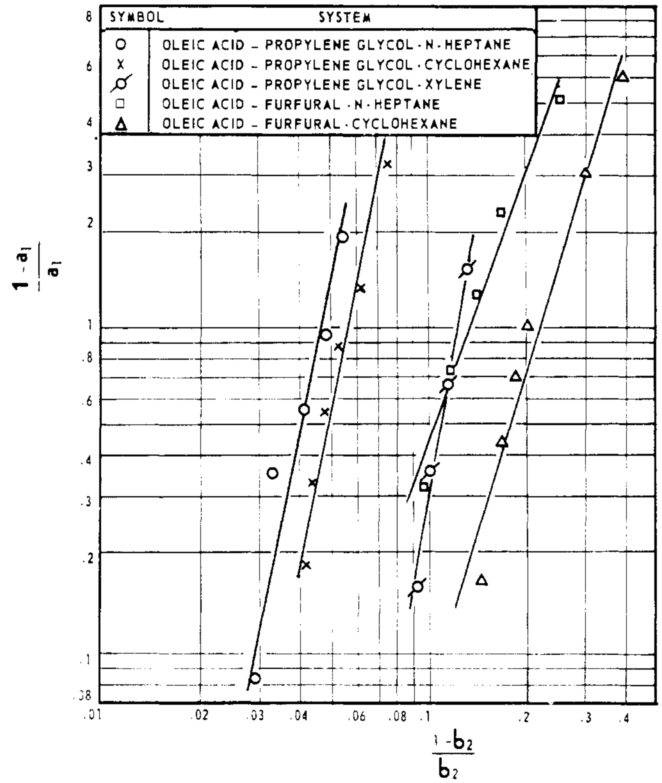

Figure 6. Othmer and Tobias tie-line correlation plot

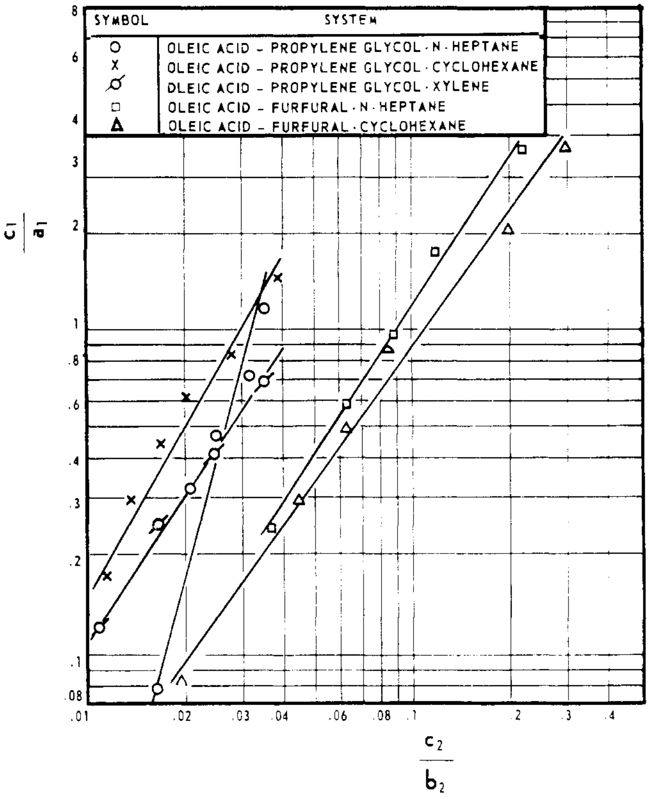

Figure 7. Treybal tie-line correlation plot

(4) Dunlop, A. P., Stout, P. R., Swadesh, S., Ind. Eng. Chem. 38, 705 (1946).
(5) Durrans, T. H., "Solvents," Chapman and Hall, London, 1944.
(6) Emery Industries, Inc., Cincinnati, Ohio, Circular, 1950.
(7) Gloyer, S. W., Ind. Eng. Chem. 40, 228 (1948).
(8) Gloyer, S. W., Am. Oil Chem. Soc. 27, 462 (1950).
(9) Goss, W. H., Ibid., 26, 584 (1949).
(10) Markley, K. S., "Fatty Acids," Interscience, New York, 1947.
(11) Maxwell, J. B., "Data Book on Hydrocarbons," Van Nostrand, New York, 1950.
(12) Mellan, I., "Industrial Solvents," Reinhold, New York, 1947.
(13) Othmer, D. F., Tobias, P. E., Ind. Eng. Chem. 34, 693 (1942).
(14) Passino, H. J., Ibid., 51, 280 (1949).
(15) Prescott, J. M., private communications, 1950.
(16) Sample, N. L., Ph.D. thesis, Purdue University, West Lafayette, Ind., 1951.
(17) Smith, J. C., Ind. Eng. Chem. 34, 234 (1942).
(18) Treybal, R. E., Ibid., 36, 875 (1944).
(19) Wittekindt, R. H., private communication, 1950.

Received for review July 6, 1955. Accepted April 30, 1956

Phase Equilibria in Dimethylhydrazine-Water System

LEE T. CARLETON
Aerojet-General Corp., Azusa, Calif.

The design of a distillation process for separating pure asymmetrical dimethylhydrazine from aqueous solution requires vapor-liquid equilibrium data for the binary system dimethylhydrazine-water.

A series of equilibrium vapor and liquid compositions and temperatures at atmospheric pressure were determined experimentally. Plotting these values in the usual ways gave smooth, plausible curves. These data are unusual in that the activity coefficients calculated from them deviate widely from conformity with the Gibbs-Duhem equation. A few additional determinations at 102 mm. of mercury showed the occurrence of a high-boiling azeotrope at reduced pressures.

INTRODUCTION

In one process for the preparation of asymmetrical dimethylhydrazine (DMH), the reaction product consists of the desired dimethylhydrazine in dilute aqueous solution, together with various impurities. If dimethylhydrazine is to be isolated by distillation, the principal problem is separation from water.

Several trial distillations in efficient columns under various operating conditions showed that dimethylhydrazine of satisfactory purity could be taken off as distillate, but with only partial recovery. Evidently, design of an efficient distillation process requires a basic analysis of the separation; for this purpose, a study was undertaken of the phase equilibria between vapor and liquid in the simple binary system.

APPARATUS

The apparatus used is all glass, of a form evolved at the Shell Development Co. It is described in the literature as an apparatus "of the Othmer type, with internal agitation supplied by a Cottrell vapor pump" (3). Actually, although this apparatus recirculates condensate in the same manner as an Othmer still, it differs from it in the following ways:

A cylindrical boiler has a recessed bottom for the insertion of a heating element. Within the boiler a bell covers the recess in such a manner that all boiling takes place under the bell, and the boiling mixture of liquid and vapor rises continuously to the top of the bell. The top of the bell is constricted, then branches into two prongs of a Cottrell pump, which throw the boiling liquid onto a central thermometer well. (Use of the Cottrell pump ensures an accurate determination of equilibrium temperature and is superior to arrangements in which the thermometer is suspended either in the body of boiling liquid or in the vapor space.) A hood attached to the thermometer well covers the pump and deflects spray downward into the liquid. The entire vapor space is slightly superheated by a metal sheath, electrically heated and insulated, covering the outside of the boiler. This arrangement prevents enrichment of the vapor in rising up and out through the boiler. Splashing of liquid into the vapor space and subsequent evaporation is prevented by the hood.

TABLE I.

PHASE EQUILIBRIA OF DIMETHYLHYDRAZINE-WATER

Fraction	DMH, Wt. %	DMH, Mole %	Temp., ° C., 760 mm.	γ_1	γ_2
Liquid	1.10	0.33	99.9	0.395	0.999
Vapor	1.52	0.46			
Liquid	3.8	1.2	99.8	0.372	0.990
Vapor	5.0	1.6			
Liquid	6.5	2.0	99.6	0.421	0.978
Vapor	9.3	3.0			
Liquid	10.3	3.4	99.4	0.448	1.000
Vapor	16.0	5.4			
Liquid	11.75	3.9	99.25	0.422	0.968
Vapor	16.9	5.8			
Liquid	25.6	9.3	98.1	0.522	0.985
Vapor	39.8	16.5			
Liquid	36.8	14.9	95.8	0.619	0.967
Vapor	58.0	29.3			
Liquid	55.2	27.0	87.8	0.829	0.968
Vapor	80.4	55.1			
Liquid	70.4	41.6	79.4	0.929	1.054
Vapor	89.5	71.9			
Liquid	89.5	71.9	68.3	0.994	1.143
Vapor	96.6	89.5			
Liquid	92.0	77.6	66.7	1.016	1.192
Vapor	97.8	92.9			
Liquid	95.0	85.0	64.5	1.014	1.629[a]
Vapor	98.1(twice)	94.0			
Dimethylhydrazine			62.2	1.000	

[a] Accuracy questionable because of difficulties of analysis at this concentration.

The vapor emerges from a lateral tube joined to the boiler near its top. As in the Othmer still, it is condensed and the condensate is accumulated in a small tube, up to a constant volume fixed by an overflow line. The overflowing condensate returns to the bottom of the boiler. The opening of the line is enlarged, so that the condensate is premixed with the boiler contents before it enters the boiler proper. Boiler and condensate accumulator are provided with stopcocks for sampling.

In the particular apparatus used here, the volume of boiling liquid is about 60 ml. and the volume of condensate in the accumulator is about 5 ml.

In operation, the boiler is charged with a mixture of the desired composition, and boiling is begun and continued until the accumulator has been flushed several times with condensate and the thermometer-well temperature, which rises slowly at first, has leveled off at a constant value. Operation is continued for 10 to 15 minutes after the steady-state temperature is reached. Boiling is then stopped and samples of liquid and condensed vapor are withdrawn for analysis.

The equilibrium pressure may be maintained at any desired value by connecting the condenser vent to a manostat. For the study of the dimethylhydrazine-water system, the apparatus was filled with an atmosphere of nitrogen at ambient pressure.

It is of interest to compare the present method with other equilibrium still methods. A single separation was performed on the system ethylene dichloride-toluene, for which accurate data are available in the literature (5). Comparison of the measured results (analyses by refractive index) with those from the literature gives:

	Measured	Literature	
Equilibrium temp., ° C., 760 mm. Hg	91.3	92.2	90.2
Liquid compn., x, mole % E.D.	59.9	58.5	70.0
Vapor compn., y, mole % E.D.	78.2	76.5	84.4
Volatility ratio, $\gamma = \left[\frac{y/x}{(1-y)/(1-x)}\right]$	2.40	2.31	2.32

MATERIALS AND ANALYSIS

Because of the scarcity of pure dimethylhydrazine at the beginning of this study, it was necessary to use several different specimens. Each had been prepared by concentrating the reaction product from a pilot preparation—first, either by salting out or by a preliminary distillation, and then by carefully fractionating the concentrate and selecting a center cut. The degree of purity was established by titration with standard acid, with an independent check by potentiometric titration with potassium iodate. Thus, the following were used in preparing the mixtures charged to the equilibrium still:

Specimen	DMH, Wt. %		Other Properties
	By acid	By KIO_3	
a	99.9	99.3	$n_D^{20} = 1.4074$; $d_4^{25} = 0.786$
b	98.4	99.6	
c	99.0	101.4	

Because of difficulties in standardizing the procedure for analysis with potassium iodate, samples from the equilibrium runs were all analyzed by titration with standard acid.

Decomposition of dimethylhydrazine is believed to be negligible under the conditions of the experiment, from all present knowledge. Thus on determination of vapor pressure in a closed system, no trace of volatile decomposition products had been detectable up to the highest temperature, 50° C. On prolonged boiling under an atmospheric pressure of nitrogen, no change in boiling temperature and little change in other physical properties had been noted. However, to minimize possible decomposition effects, no material was re-used more than once. That is, charges of wholly fresh material were made after every run or after every other run.

EXPERIMENTAL RESULTS

The results of the phase equilibrium study are a series of corresponding values of vapor composition, liquid composition, and temperature. The experimental temperatures were taken at 748 ± 3 mm. pressure for all runs for presentation, and these values were all corrected to 760 mm. of mercury by adding 0.4° C. (Table I). When temperature was plotted against liquid and vapor composition, and vapor composition against liquid composition, the series of points shown in Figures 1 and 2 was obtained.

CORRELATION OF RESULTS

These results were examined further for consistency by application of the Gibbs-Duhem equation. For this purpose, activity coefficients of the two components were calculated as

$$\text{(DMH)}\ \gamma_1 = \frac{760 y_1}{p_1^0 x_1} \qquad \text{(Water)}\ \gamma_2 = \frac{760 y_2}{p_2^0 x_2}$$

where

p_1^0 is pressure (mm. of mercury) of pure dimethylhydrazine at the equilibrium temperature.

p_2^0 is pressure (mm. of mercury) of pure water at the equilibrium temperature.

x and y are, respectively, liquid and vapor compositions (mole fractions).

Values of p_1^0 were not available from existing vapor pressure equations, because these do not extend into a sufficiently high range of temperatures. Accordingly it was necessary to derive an estimated relationship. This was taken as the equation of the straight line relating log p and the reciprocal of the absolute temperature passing through the atmospheric boiling point determined here and the accurate value of 122.44/293.095° K. from Aston, Wood, and Zolki (2). The relation is

$$\log p(\text{mm.}) = 8.3791 - \frac{1843.9}{T}$$

where T is absolute temperature, ° K. Use of this equation, particularly for extrapolation, may result in some error, but this is small in comparison with the effects of other factors on the activity coefficients. The calculated activity coefficients are shown in Table I.

The Gibbs-Duhem equation gives

$$x_1 \frac{d \ln \gamma_1}{dx_1} + x_2 \frac{d \ln \gamma_2}{dx_1} = 0 \qquad (1)$$

This is conveniently transformed (6) to

$$\int_0^1 \ln \left(\frac{\gamma_1}{\gamma_2}\right) dx_1 = 0 \qquad (2)$$

When Equation 2 is applied to the tabulated activity coefficients, it appears at a glance that they do not satisfy the equation. The discrepancy is very large. The actual value of γ_1 in dilute solution is far smaller than the equation would predict. The low activity of dimethylhydrazine in dilute solution explains the difficulties in obtaining good recoveries by simple distillation of dilute feeds. (It also indicates a tendency toward azeotrope formation, and a few additional measurements at 102-mm. of mercury pressure showed that a high-boiling azeotrope containing about 6 mole % dimethylhydrazine does indeed occur.)

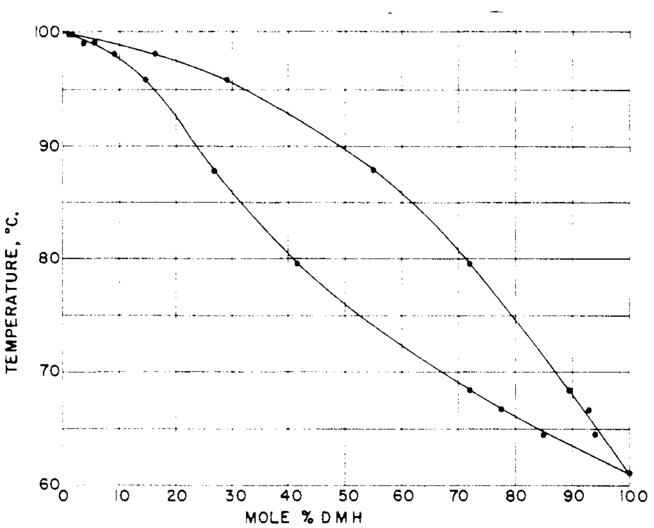

Figure 1. Vapor-liquid equilibrium for asymmetrical dimethylhydrazine and water at 760 mm. of mercury

This behavior marks the system as unusual, and merits discussion. Because so many binary systems follow Equation 1 with fair accuracy, there is a tendency to forget that this equation and its various integrated forms (the Margules and van Laar equations, as well as Equation 2) apply rigorously only under conditions of constant pressure and temperature. In actual measurements either the temperature or pressure is held constant, and the other quantity must vary with the composition. The consequence, as pointed out by Ibl and Dodge (4), is that under isobaric

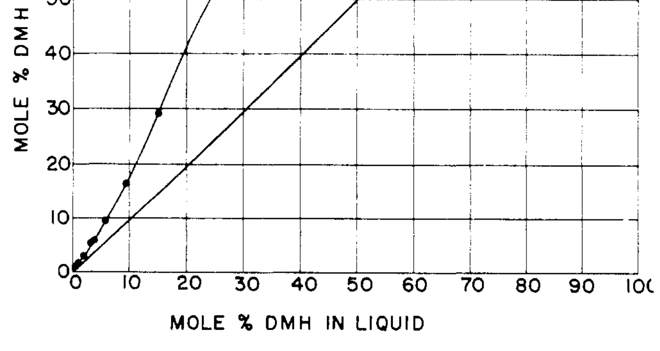

Figure 2. Relationship between vapor and liquid compositions at equilibrium for asymmetrical dimethylhydrazine and water at 760 mm. of mercury

conditions the left-hand side of Equation 1 is not equal to zero; instead, the true equality is

$$x_1 \frac{d \ln \gamma_1}{dx_1} + x_2 \frac{d \ln \gamma_2}{dx_1} = \frac{-\Delta H}{RT^2} \frac{dT}{dx_1} \qquad (3)$$

where ΔH is the integral molal heat of mixing at the composition defined by x_1 and x_2. While in many binary systems ΔH and dT/dx are sufficiently small to make Equation 1 a good approximation for Equation 3, one cannot overlook the cases in which the right-hand side of Equation 3 is not negligible—e.g., the case of acetic acid and water (1), although this is complicated by the occurrence of association in the vapor. Thus, the behavior of γ_1 and γ_2 in the present system may be accounted for by assigning appropriate values to ΔH.

ACKNOWLEDGMENT

The many helpful suggestions of Paul Blatz, Albert O. Dekker, and Otto Redlich are acknowledged with thanks.

LITERATURE CITED

(1) Altsheler, W. B., Unger, E. D., Kolachov, P., Ind. Eng. Chem. 43, 2559-64 (1951).
(2) Aston, J. G., Wood, J. L., Zolki, T. P., J. Am. Chem. Soc. 75, 6202-4 (1953).
(3) Dunn, C. L., Millar, R. W., Pierotti, G. J., Shiras, R. N., Sounders, M., Jr., Trans. Am. Inst. Chem. Engrs. 41, 631-44 (1945).
(4) Ibl, N. V., Dodge, B. F., Chem. Eng. Sci. 2, 120-6 (1953).
(5) Jones, C. A., Schoenborn, E. M., Colburn, A. P., Ind. Eng. Chem. 35, 666-72 (1943).
(6) Redlich, O., Kister, A. T., Ibid. 40, 345-8 (1948).

Received for review February 2, 1956 Accepted May 8, 1956

Volumetric and Phase Behavior in the Nitric Acid–Nitrogen Dioxide–Water System

H. H. REAMER, W. H. CORCORAN, AND B. H. SAGE
California Institute of Technology, Pasadena, Calif.

Pressure-volume-temperature measurements on three mixtures of nitric acid, nitrogen dioxide, and water at physical and chemical equilibrium were made at temperatures between 190° and 340° F. and at pressures up to 5000 pounds/square inch absolute. The ratio of the weight fraction of water to the sum of the weight fractions of water and nitric acid was kept essentially constant.

This restricted ternary system showed a decrease in bubble-point pressure at physicochemical equilibrium with increasing concentration of nitrogen dioxide. The bubble-point pressure reached a minimum at 0.10 weight fraction nitrogen dioxide and gradually became greater at higher weight fractions. At the lower concentrations of nitrogen dioxide, chemical equilibrium at 190° F. was achieved only after several hours elapsed. As the concentration of nitrogen dioxide was increased, the approach to equilibrium was more rapid.

Experimental information is available concerning the volumetric and phase behavior at physical equilibrium of nitric acid and its mixtures with water and nitrogen dioxide. Klemenc and Rupp (6) contributed materially to the knowledge of the volumetric behavior of the liquid phase at atmospheric pressure. Taylor compiled information concerning the bubble-point pressure of mixtures of nitric acid and water (19). The freezing points of the nitric acid-water system were investigated, and at least two hydrates of nitric acid were reported (8). Forsythe and Giauque (4) added greatly to the knowledge of the thermodynamic properties of nitric acid and its mixtures with water. Sprague (17) proposed several analytical expressions for variations in specific weight with composition for the nitric acid-nitrogen dioxide-water system. All of the above studies were made at physical equilibrium only, without regard for the gradual chemical rearrangement which takes place in these systems even at ambient temperature.

Information obtained at both physical and chemical equilibrium for pure nitric acid (11, 15,20), the nitric acid-nitrogen dioxide system (2), the nitric acid-water system (3), and for samples of commercial red and white fuming nitric acid (12) is available. Additional information concerning mixtures of nitric acid, water, and nitrogen dioxide during their approach to physical and chemical equilibrium was obtained (20).

Insufficient experimental information is available to predict the volumetric and phase behavior of ternary mixtures of nitric acid, water, and nitrogen dioxide in the composition interval normally encountered in industrial practice. For this reason an investigation of the specific volume and the bubble-point pressure of three mixtures of nitric acid, water, and nitrogen dioxide was made. All three of the mixtures were selected so as to yield a ratio of the weight fraction of water to the combined weight fractions of nitric acid and water of approximately 0.090. The investigation was carried out at pressures up to 5000 pounds/square inch absolute in the temperature interval between 190° and 340° F. The time required for the attainment of chemical equilibrium at temperatures below 190° F. was great enough to render investigation unprofitable at lower temperatures. All measurements were made at both chemical and physical equilibrium except that limited information is included concerning the approach to chemical equilibrium.

EQUIPMENT AND METHODS

The methods and equipment employed in this investigation were the same as those used (11) for the study of the behavior of pure nitric acid at physical and chemical equilibrium. The sample was confined within a glass piston-cylinder combination (11) which was surrounded by a fluorinated hydrocarbon confined within a stainless steel pressure vessel. Introduction and withdrawal of the fluorinated hydrocarbon accomplished the change in volume of the sample within the glass piston-cylinder combination. Clearances between the piston and cylinder were sufficiently small so that there was very little tendency for loss of the sample into the fluorinated hydrocarbon. Experience with this equipment indicates that the relative probable error in the measurement of specific volume was 0.6% after calibration as a function of pressure and temperature.

The quantity of nitrogen dioxide employed was deter-