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The Fugacities of Ethyl Alcohol and Water in their Gaseous Mixtures. Deviations from Perfect Solutions[1]

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Introduction

The purpose of this paper is to show how gaseous mixtures of ethyl alcohol and water deviate from perfection under isothermal changes in pressure.

The imperfections of twelve gaseous solutions of these two components, ranging in composition from pure water to very nearly pure alcohol, were determined by pressure–volume measurements at three elevated temperatures.

Experimental

Materials.—Commercial ethyl alcohol was purified by repeated fractional distillation with lime. The product used boiled completely within 0.1° and had a density of 0.78997 g./cc. at 20° (99.8% alcohol). This product was not used for the experiments on pure alcohol but the various solutions of different concentration used in this investigation were made by precalculated dilution of this alcohol and their resulting composition checked by density measurements. Colorimetric examination (Caro's reaction) indicated the absence of an appreciable amount of aldehydes. The material for the run on "pure alcohol" was obtained from a different source. "Absolute Ethyl Alcohol" (Scientific) a product of the U. S. Industrial Chemical Company, Inc. (Refined Chemicals Department) labelled 99.8–100% alcohol was redistilled. The distillate had a density of 0.78988 g./cc. at 20° (99.83% alcohol).

Twice distilled water was used. The mercury was chemically refined and redistilled.

Apparatus.—A diagram of the principal part of the apparatus is shown in Fig. 1. The bomb which contained the Pyrex piezometer "A" consisted of a steel pipe 91 cm. high, 5 cm. in internal diameter, and 6.4 mm. thick. The piezometer, held in place by fiber washer "B," stood, with its open end, in a well of mercury "I." Through its sides, at definite intervals, were sealed tungsten wires "H," each communicating, by insulated leads, with an outside battery circuit by way of side arm "G." Side arm "G" contained a gas-tight seal of litharge–glycerol cement. "E" indicates a capsule which contained the liquid charge and "F" the constriction in tube "D" upon which it rested. Tube "D" is simply the extension of the piezometer which was exposed when cap "C" was removed for glassblowing purposes. Side arm "J" connected the bomb to the source of nitrogen gas pressure. The pressure was measured by an open mercury manometer. A voltmeter placed in the above-mentioned battery circuit indicated the position of the mercury and the volume of the gaseous mixtures in the piezometer.

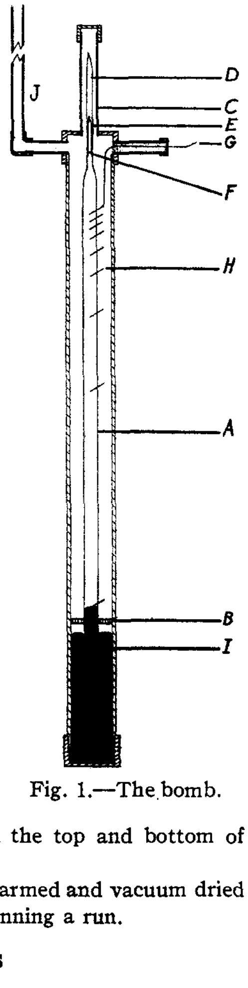

Fig. 1.—The bomb.

The constant temperature bath consisted of a 35 gallon upright cylindrical tank thermally insulated with magnesia brick. The high grade cylinder oil it contained was heated electrically and stirred by a rotary pump. The temperature was thermostatically controlled to 0.1° although a temperature differential of 0.2° existed between the top and bottom of the tank.

The bomb and contents were warmed and vacuum dried for several hours just before beginning a run.

TABLE I

AVERAGED α VALUES IN LITERS PER MOLE

Mole fraction of EtOH, N_2	1–5 Atm. 152.9°	1–6 Atm. 163.5°	1–8 Atm. 173.9°
0.000	0.284	0.278	0.254
.116	.312	.335	.300
.201	.370	.355	.318
.249	.374	.362	.326
.295	.378	.353	.329
.343	.370	.363	.327
.455	.384	.375	.343
.555	.392	.395	.343
.702	.432	.392	.350
.803	.444	.403	.363
.939	.492	.455	.413
.996	.498	.469	.424

Results

The number of moles of each of the samples used and subsequently the molar volumes of each of the mixtures at the three elevated temperatures and integral pressures were determined as the results of extrapolating to zero pressure the PV isothermal curves. Instead of the direct molal PV data the average differences between the observed molal volumes V and the molal volumes calculated from the gas law, $(RT/P) - V = \alpha$, are shown in Table I.

Because α isothermally varies so slowly under these limited pressures, it is possible to estimate,

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by the method of least squares, that the experimental average deviation is 0.09%. The PV values obtained in this work on pure water, $N_2 = 0$, are greater by an average of 0.12, 0.09 and 0.32%, respectively, than those calculated from the data of Knoblauch, Linde and Klebe[2] for the three temperatures, 152.9, 163.5 and 173.9°. In a comparison between the data of Knoblauch, Linde and Klebe and the M. I. T. provisional equation of state based on the M. I. T. volume data for steam made by Keyes, Smith and Gerry,[3] the observed volumes of the former are greater than those of the latter by 0.08, 0.13, and 0.20% at round temperatures roughly corresponding to those used in this work, *i. e.*, 150, 160 and 170°, respectively. At and above 4 atmospheres, where only a comparison is possible, the PV values obtained in this work on very nearly pure alcohol, $N_2 = 0.996$, are consistently less than those calculated from the data of Ramsay and Young[4] by an average of 3.6%.

The data of this experiment were all obtained under the same conditions. The values shown are thus a measure of the behavior of these solutions as the concentration is varied.

Mathematical

Calculations.—The method used for calculating the deviations of these gaseous solutions from perfection is similar to that used by Gibson and Sosnick,[5] and B. Sosnick.[6]

Conclusions.—1. At one atmosphere and in this temperature range these gaseous mixtures are substantially perfect solutions—a conclusion which lends, indirectly, support to the assumption made by Essex and Clark[7] in substituting mole fractions for the activities of ethyl alcohol and water in their gaseous mixtures.

2. Those solutions for which the mole fraction of the considered component (alcohol in water, $N_2 = X$ or water in alcohol, $N_1 = X$) is greater than 0.2, deviate less than 2% even at the maximum pressures recorded for each of the three temperatures.

3. The greatest deviations occur in the values of each component at zero concentration. For alcohol in pure water ($N_2 = 0$) the fugacity of alcohol at 152.9° and 5 atmospheres is 5.3% less than that calculated on the basis of a perfect solution. At 163.5° and 6 atmospheres, it is 8.6% and at 173.9° and 8 atmospheres, 11.2%. For water in pure alcohol ($N_1 = 0$), at 152.9° and 5 atmospheres the fugacity of water is 1.1% greater than that calculated on the basis of a perfect solution; similarly, at 163.5° and 6 atmospheres, 3.6%; and at 173.9° and 8 atmospheres, 3.4%. It is apparent that with these gaseous solutions, as with fluid solutions in general, the greatest deviations from perfection (*i. e.*, from the relation $f = f°N$), and the greater graphical errors, are shown by the considered component which is present at zero concentration.

Summary

1. The molal volumes of twelve gaseous mixtures of ethyl alcohol and water, ranging in composition from zero to 99.83% alcohol, have been experimentally determined at three elevated temperatures over a pressure range from one atmosphere to near the condensation pressure of water.

2. From the smooth PV mole fraction curves, the deviations from the perfect solution have been calculated.

3. At one atmosphere and in this temperature range, the solutions are substantially perfect.

4. Those solutions for which the mole fraction of the considered component (alcohol in water $N_2 = X$ or water in alcohol $N_1 = X$ solutions) is greater than 0.2, deviate less than 2% even at the maximum pressures recorded for each of the three temperatures.

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(2) Knoblauch, Linde and Klebe, *Mitt. u. Forsch. Geb. Ing. hrsg. deut. Ing.*, **21**, 33 (1905).

(3) Keyes, Smith and Gerry, *Mech. Eng.*, **56**, 87 (1934).

(4) Ramsay and Young, *Phil. Trans. Roy. Soc.*, **177**, 123 (1886).

(5) Gibson and Sosnick, THIS JOURNAL, **49**, 2172 (1927).

(6) Sosnick, *ibid.*, **49**, 2255 (1927).

(7) Essex and Clark, *ibid.*, **54**, 1299 (1932).