

A Test of Ideal Solution Laws for H₂, HD, and D₂. Vapor Pressures and Critical Constants of the Individual Components

Robert D. Arnold and Harold J. Hoge

Citation: *The Journal of Chemical Physics* **18**, 1295 (1950); doi: 10.1063/1.1747928

View online: <http://dx.doi.org/10.1063/1.1747928>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/18/9?ver=pdfcov>

Published by the AIP Publishing

Articles you may be interested in

A Critical Review of Aqueous Solubilities, Vapor Pressures, Henry's Law Constants, and Octanol–Water Partition Coefficients of the Polychlorinated Biphenyls

J. Phys. Chem. Ref. Data **15**, 911 (1986); 10.1063/1.555755

Extraction of Reaction Cross Section from Rate Constant Data: D+H₂→HD+H

J. Chem. Phys. **51**, 5449 (1969); 10.1063/1.1671971

Induced Rotation—Translation Spectra of Solutions of H₂, HD, and D₂ in Liquid Argon

J. Chem. Phys. **47**, 571 (1967); 10.1063/1.1711933

The Vapor Pressures and Critical Constants of Pure Ozone

J. Chem. Phys. **20**, 1158 (1952); 10.1063/1.1700683

The Vapor Pressure and Critical Constants of Neopentane

J. Chem. Phys. **19**, 948 (1951); 10.1063/1.1748412



Letters to the Editor

THIS section will accept reports of new work, provided these are terse and contain few figures, and especially few half-tone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge (\$8.00 per page) will not be made and no reprints will be furnished free.

A Test of Ideal Solution Laws for H₂, HD, and D₂. Vapor Pressures and Critical Constants of the Individual Components*

ROBERT D. ARNOLD AND HAROLD J. HOGE
National Bureau of Standards, Washington, D. C.
July 10, 1950

IN order to determine the approximate magnitude of the deviations from the law of ideal solutions in mixtures of H₂, HD, and D₂, dew-point pressures of several mixtures were observed at various temperatures. In these measurements a two-component gaseous mixture of known composition was forced in measured increments into an adiabatic calorimeter operated as a thermostatted container. The pressure in the container was then plotted as a function of the quantity of material admitted. These plots took the form of two straight lines of different slope, one in the gas-phase region and one in the gas-liquid region of the isotherm, joined by a rounded segment. The dew-point pressure of the mixture is taken to be the pressure at the junction of the two straight-line segments extrapolated to intersect. Table I contains the results.

The ortho-para-compositions were assumed to correspond to equilibrium at high temperature since no catalyst was used. This assumption is supported by the single-component condensation pressures (runs *E* and *H*) observed with this apparatus. Compositions shown in Table I were determined by measuring the pressure in the mixing vessel after the first gas was admitted and then again after the second. Mass spectrometric determinations of composition differed slightly from the values in Table I but were within the deviations shown. Traces of a third component in the binary mixtures were present as impurities (D₂ in HD and HD in D₂) and their amounts were determined by mass spectrometric analysis of the appropriate component before mixing.

Calculated pressures are based on the equation for the dew-point pressure of a mixture forming ideal solution, $1/P_d = Z_1/P_1 + Z_2/P_2 + Z_3/P_3$, which follows directly from the basic assumption that for a given component the mole fraction Z_i in the saturated vapor is proportional to $x_i P_i$, the product of the mole fraction in the liquid phase and the vapor pressure of the pure component, provided that the total pressure of saturated vapor is $\sum x_i P_i$. Vapor pressures of the pure components are from the report by

TABLE I. Dew-point pressures of mixtures of H₂, HD, and D₂

Run	E	F	G	H	J	K	L
T(°K)	20.04	19.00	20.00	18.01	18.005	17.03	18.00
Z ₁ (H ₂)	0	0.499	0.440	1.00	0.503	0.503	0.752
Z ₂ (HD)	0.008	0.004	0.004	0	0.496	0.496	0.248
Z ₃ (D ₂)	0.992	0.497	0.556	0	0.001	0.001	0
P _{calc} (mm Hg)	224.3	224±2	313±2	347.2	234±2	154±2	279±2
P _{obs} (mm Hg)	223.5	234±2	322±2	348.2	240±1	158±1	286±1
ΔP (mm Hg)	-0.8	10±4	9±4	1.0	6±3	4±3	7±3
100ΔP/P	-0.35	4.4	2.8	0.3	2.5	2.6	2.5

TABLE II. Vapor pressures and critical constants of ϵ -H₂, HD, and ϵ -D₂.

Property	ϵ -H ₂	HD	ϵ -D ₂
P at 25°K (atmos.)	3 242	2 124	1 457
P at 30°K (atmos.)	8.108	5.883	4 441
P at 35°K (atmos.)	—	—	10 286
P _c (atmos.)	12.77	14.64	16.28
T _c (°K)	33.00	35.91	38.26
V _c (cm ³ mole ⁻¹)	65.5	62.8	60.3
P _c V _c /RT _c	0.309	0.312	0.312

Woolley *et al.*¹ Principal sources of error are (1) in P_{calc} the uncertainty in the composition and (2) in P_{obs} the uncertainty in extrapolating the two straight lines to their intersection. Observed pressures are about three percent above those calculated from the equation. The estimated error in these deviations is about ± 50 percent. Significant deviations from the law of ideal solutions in mixtures of ortho- and para-H₂ have been reported by Woolley *et al.*²

Vapor pressures and critical constants of H₂, HD, and D₂ (single-component systems only) were observed in a different apparatus capable of withstanding higher pressures. This apparatus and the methods of using it are described in a recent publication.³ All measurements made thus far with this apparatus have been on material catalyzed to ortho-para-equilibrium at 20.4°K (except for HD, which has no ortho- and para-varieties). The prefixed symbol ϵ is used to indicate material in equilibrium at this particular temperature. The catalyst was Nd₂O₃, a pale blue powder furnished by Dr. Raleigh Gilchrist and Mr. Ernest Weise of this Bureau. Complete conversion to ortho-para-equilibrium at 20.4°K appeared to take place in less than the time required to condense a sample on the catalyst and pump it off again. Table II contains the critical constants derived from the measurements, and also a few selected vapor pressures obtained from smooth curves representing the data. The critical pressures, temperatures, and volumes of HD and ϵ -D₂ are thought to be the first experimental values to be reported. It is planned to make measurements on normal hydrogen (n -H₂) such as have now been made on ϵ -H₂, HD, and ϵ -D₂, after which complete reports covering all our work on dew points of mixtures, vapor pressures, and critical constants will be submitted for publication in *J. Research NBS*. The critical constants in Table II were derived after plotting isotherms of $\log P$ vs. $\log V$ for the critical region of each modification. The three sets of curves were superposed in such a way as to form one single family of isotherms, after which a single reduced critical point was determined simultaneously for the entire family. Accepting the law of corresponding states $\log(P/P_c)$ should, for any given value of T/T_c , be a universal function of $\log(V/V_c)$. The relative displacements of the three sets of curves take into account the differences in the values of $\log P_c$ and $\log V_c$ for the various modifications. It is thought that the use of this procedure substantially improved the accuracy of the critical constants in Table II. Correlation with isotherms of n -H₂ may subsequently lead to minor changes in the values now being reported; also the data in Table II have not been corrected for the presence of the small amounts of isotopic impurities detected by the mass spectrometer. Effects of such corrections will probably be no more than a few units in the last decimal place. In the V_c values the last decimal place is significant only on a relative basis.

The HD was prepared, and the HD and D₂ purified, by A. Fookson, P. Pomerantz, and E. H. Rich of this Bureau by methods to be described in *Science* and in *J. Research NBS*. Mass spectrometer analyses were made by the Mass Spectrometry Section of this Bureau.

* Supported in part by the AEC

¹ Woolley, Scott, and Brickwedde, *J. Research Nat. Bur. Stand.* **41**, 379 (1948), RP1932

² See reference 1, p. 454.

³ Harold J. Hoge, *J. Research Nat. Bur. Stand.* **44**, 321-45 (1950), RP2081.