steric factors permitting. (See the discussion of n:1 complexes at the end of Section II.) Dispersion-force attractions tend to be largest in orientations bringing maximum polarizabilities into play, while the orientational properties of charge-transfer forces, as shown in Sections II and III, are governed by considerations of quantum-mechanical symmetry of molecular wave functions. The two kinds of forces are thus different in this respect, and probably the sharpness of the orientational effect is stronger for the charge-transfer forces.

From what has preceded, it appears likely that charge-transfer forces may often be of the same order of magnitude as dispersion forces. Perhaps dispersion forces usually predominate for interactions between like molecules, but charge-transfer forces often in solutions and other systems in which molecules of different kinds are present together. Charge-transfer forces may well also be important in heterogeneous systems and in adsorption phenomena, and may afford new possibilities for understanding intermolecular interactions in biological systems. Definite conclusions about these points must, however, wait upon further investigations.

Even if it should turn out that charge-transfer forces are relatively unimportant for one-component liquids and crystals not under strong internal or external pressure, the theory indicates that if in any way a substance is sufficiently compressed, the charge-transfer forces should increase rather rapidly. (See here also the discussion of "hard' and "soft" molecules in Section IV.) Such compression might perhaps be effected by internal ionic forces in the case of a partially ionic crystal, by unusually strong dispersion or dipole forces, or by strong external pressure. The existence of charge-transfer forces should in general contribute considerably—in an anisotropic manner because of their strong orientational properties—to compressibilities. Here it is relevant to recall the studies of Gibson and Loeffler[61] who found marked shifts in the locations of the absorption spectra of aniline-polynitrobenzene and similar solutions under pressures of 1000 atmospheres; these are spectra which are attributable to the presence of very loose charge-transfer complexes.[62]

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[62] R. E. Gibson and O. H. Loeffler, THIS JOURNAL, **61**, 2877 (1939); **62**, 1324 (1940).

CHICAGO 37, ILLINOIS RECEIVED JUNE 11, 1951

[CONTRIBUTION FROM THE LOS ALAMOS SCIENTIFIC LABORATORY]

Molar Volumes of Liquid Deuterium and of a 1:1 Mixture of Tritium and Deuterium, 19.5 to 24.5°K.[1]

BY EUGENE C. KERR

The molar volumes of liquid deuterium and of a 1:1 mixture of tritium and deuterium have been measured over a temperature range 19.5 to 24.5°K. The results deviate from fitted equations by about 0.2%.

The only previous determination of the molar volume of deuterium is that by Clusius and Bartholemé[2] who made eight measurements between 18.8 and 20.5°K. This report presents the results of molar volume measurements in the range 19.5 to 24.5°K. for pure deuterium and for a 50:50 atom per cent. mixture of deuterium and tritium.

Apparatus and Procedure.—The apparatus used consisted essentially of (1) a calibrated gas pipet and constant volume manometer to measure the amount of gas added to the condensing system, (2) a mercury "pusher" to compress the gas into the condensing system, (3) a small volume line leading to the pycnometer and including a Wallace and Tiernan differential pressure gage for measuring the system pressure, and (4) the pycnometer proper.

The pycnometer was connected to the filling line by a small glass capillary tube on which a fine mark was etched to define the liquid volume. The pycnometer volume to this mark was 0.06417 cm.^{3} and the capillary volume in the vicinity of the mark was 0.000360 cm.^{3}/mm.

A double compartmented dewar vessel containing liquid nitrogen and liquid hydrogen served as a cryostat for the apparatus. It was attached by means of a sliding seal so that the liquid hydrogen bath level could be maintained at a constant level with respect to the fiduciary mark on the pycnometer. Various temperatures were attained by varying the bath pressure up to 30 lb. gage pressure by an auxiliary pressure regulating device. Temperatures were measured by a strain-free platinum resistance thermometer which had been calibrated at the Bureau of Standards. Occasional temperature checks were made by comparing the resistance thermometer temperature with that obtained from the vapor pressure of the liquid hydrogen bath.

Molar volume measurements were made by adding successive small amounts of gas (measured in the gas pipet) to the condensing system until liquid was condensed in the pycnometer up to the vicinity of the calibration mark. The system was allowed to equilibrate for about 30 minutes and then the meniscus level with respect to the mark was noted by means of a cathetometer, the resistance thermometer current and potential were measured on a White double potentiometer, and the bath and system pressures were observed. A plot of the condensing system pressure as a function of the volume (NTP) of gas added gave the usual sharp break at the "dew point." The *difference* between the amount of gas required to fill the pycnometer with liquid to the calibration mark and that required to fill it with "dew-point" gas was taken as the true amount of gas required to fill the liquid density bulb.

The pycnometer volume was determined in the same manner except that pure hydrogen was used as a calibrating liquid, the data of Scott and Brickwedde[3] being used to establish the volume. The "noxious volume" of the gas in the connecting lines was determined by independent measurements as a function of the bath temperature in order to compensate for the uncertain part of the volume just above the bath level which was in a severe temperature gradient region.

The deuterium used contained 0.4 atom per cent. of protium as the only impurity determinable by the mass spectrograph. The tritium was originally 99.7% pure, but, once the 50:50 mixture was made up, a gradual increase in

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[1] This paper is based on work performed under University of California contract with the Atomic Energy Commission.

[2] K. Clusius and E. Bartholemé, *Z. physik. Chem.*, **B30**, 237 (1935).

[3] R. B. Scott and F. G. Brickwedde, *J. Research Natl. Bur. Standards*, **19**, 237 (1937).

He^3 due to disintegration and an increase in protium content due to exchange with stopcock grease was evident. These impurities interfered with condensation of the T-D mixture when attempts were made to make measurements in the temperature region above 24.5°K. Only results from freshly prepared mixtures are reported here. Earlier experiments on material in which the impurity buildup had been excessive were discarded. A correction for the small amount of impurities present in the original deuterium and tritium was applied on the assumption of a linear relationship between the mole fraction and the molar volume. For this purpose, the molar volume of HT was assumed to be the same as that of deuterium.

Results

A. Deuterium.—The molar volumes of deuterium in the temperature range 19.5 to 24.2°K. are shown in Table I. The five experimental values of this research were combined with the eight measurements of Clusius and Bartholemé by the least squares method to obtain the equation

$$V_M(\text{cm.}^3/\text{mole}) = 20.188 + 0.03587T + 0.006565T^2$$

The maximum deviation of the experimental points from this equation is 0.025 cm.^{3}/mole (or 0.1%) and the standard deviation is 0.01 cm.^{3}/mole (or 0.04%)

B. Deuterium–Tritium Mixture.—A mixture containing 49.7 mole per cent. tritium and 50.3 mole per cent. deuterium was used in these measurements. Since T_2 and D_2 equilibrate rapidly even at room temperatures, the mixture was actually a three component one containing approximately 50% TD as shown by mass spectrometric analysis.

The ten experimental points are shown in Table II and can be represented by the equation

$$V_M(\text{cm.}^3/\text{mole}) = 18.555 + 0.1294T + 0.004203T^2$$

with a maximum deviation of 0.08 cm.^{3}/mole (or 0.35%) and a standard deviation of 0.05 cm.^{3}/mole (or 0.2%)

A comparison of these results with similar data on pure tritium[4] shows a small positive deviation in the molar volume of the mixture over the mean molar volumes of the components. This volume increase on mixing is a linear function of temperature, varying from 0.7% at 21°K. to 0.2% at 26°K.

TABLE I

MOLAR VOLUME OF DEUTERIUM

T, °K.	V_M (cm.^{3}/mole)	Dev. (calcd. − obsd.)
24.20$_5$	24.905	−0.003
23.41	24.620	+ .006
22.37$_5$	24.281	− .004
21.14	23.889	− .009
19.51	23.411	+ .025

TABLE II

MOLAR VOLUME OF A 50:50 ATOM PER CENT. TRITIUM–DEUTERIUM MIXTURE

T, °K.	V_M (cm.^{3}/mole)	Dev. (calcd. − obsd.)
24.06	24.11	−0.01
23.28	23.79	+ .06
22.64	23.68	− .04
22.56	23.69$_5$	− .08
22.46	23.53	+ .05
21.75	23.39	− .03
21.12	23.09	+ .07
20.73	23.05	− .01
19.56	22.66	+ .04
19.55	22.74	− .05

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[4] E. R. Grilly, THIS JOURNAL, **73**, 5307 (1951).

LOS ALAMOS, NEW MEXICO RECEIVED AUGUST 20, 1951

[CONTRIBUTION NO. 167 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMICAL ENGINEERING, IOWA STATE COLLEGE]

Production of a Hafnium Concentrate by Adsorption[1,2]

BY GERHARD H. BEYER, ALFRED JACOBS AND RICHARD D. MASTELLER

A process has been developed for concentrating hafnium from a naturally-occurring feed material containing 2 wt. % hafnium oxide (based on hafnium and zirconium content) to an approximately 90 wt. % hafnium oxide in two cycles, involving adsorption and differential stripping with mineral acids at room temperature. Each cycle consists of the adsorption of hafnium and zirconium tetrachlorides in methanol solution on activated silica gel, and the subsequent stripping of the gel using a methanol-hydrogen chloride strip solution and, finally, a sulfuric acid strip solution. Approximately 70% of the original hafnium adsorbed can be recovered as high-hafnium concentrate.

Introduction

The quantity of hafnium occurring with zirconium in common American ore varies from about 0.020 to 0.025 hafnium to zirconium weight ratio. Because of their chemical similarity, hafnium and zirconium are difficult to separate, most of the proposed separation methods being quite laborious and expensive. The limited industrial use of hafnium in the preparation of certain lamp filaments and photoelectric cells,[3] reflects its high cost. Experimentally, it has been used in the making of X-ray photographs, in special glasses, and in television tubes. There is reason to believe that the development of efficient processes for removing hafnium from zirconium may make hafnium available as a by-product at greatly reduced cost.

An adsorption method for the separation of hafnium from zirconium was recently reported.[4] Separation was effected by preferential adsorption of hafnium on activated silica gel from a methanol solution of hafnium and zirconium tetrachlorides. Later results[5] indicated further concentration of the

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(1) From the M.S. Thesis of Alfred Jacobs, Iowa State College 1951.

(2) This work was performed in the Ames Laboratory of the Atomic Energy Commission.

(3) A. G. Arend, *Chem. Products*, **11**, 30 (1948).

(4) R. S. Hansen and K. Gunnar, THIS JOURNAL, **71**, 4158 (1949).

(5) R. S. Hansen, K. Gunnar, A. Jacobs and C. R. Simmons, *ibid.*, **72**, 5043 (1950).